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Moderately Concentrated Solutions of Polystyrene. 6. Gel Formation in Carbon Disulfide

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ABSTRACT: Gel formation of moderately concentrated solutions of anionically polymerized polystyrene in carbon disulfide is studied to conclude that association of the two sulfur atoms on CS_2 with phenyl rings on different polystyrene chains results in a few cross-link loci per polymer chain, creating an elastomeric gel. The equilibrium compliance J_e of a gel sample is evaluated from creep and recoverable strain measurements, and a light scattering method to analyze constrained oscillations in the gel is used to determine the storage modulus $G'(\omega)$ and the dynamic viscosity $\eta'(\omega)$ for ω small enough that $G'(\omega) \approx G_e = 1/J_e$. The sharp increase of the relative viscosity as T is reduced to within a few degrees of T_{gel} is modeled by the viscosity for a branched chain, with the number of cross-links per primary chain approaching unity as T goes to T_{gel}. The carbon disulfide/polystyrene interaction is supported by light scattering measurements on dilute solutions of polystyrene in a toluene–CS_2 mixed solvent, which show preferential solvation of polystyrene by CS_2 and the observation that the temperature T_{gel} required to form a gel with moderately concentrated solutions of polystyrene in a toluene–CS_2 mixed solvent is essentially independent of the toluene concentration. Further, the temperature dependence of the NMR spin–lattice relaxation time of the ^{13}C nucleus of CS_2 in solutions with polystyrene is about the same as that observed for J_e. It is noted that for high molecular weight polymer, T_{gel} scales with the condition for effective chain overlap, expressed by $c[\eta]_0\alpha_c{}^3$ with α_c the expansion factor at concentration c, and $[\eta]_0$ the intrinsic viscosity under Flory Θ conditions.

Introduction

Moderately concentrated solutions of polystyrene in CS_2 are unusual in that for appropriate ranges of concentration and molecular weight, they can transform to a thermoreversible gel at temperature T_{gel} well above the glass temperature T_g of the solution,[1–10] under conditions for which CS_2 appears to be a thermodynamically good solvent for polystyrene.[11–16] As a consequence, over a rather narrow temperature interval, the solution is transformed from a fluid with relatively low viscosity η to a solid with an equilibrium modulus G_e. Although gel formation under such conditions is not unknown for other polymers,[17–20] it is usually associated with polar materials, for which such behavior may be rationalized in terms of specific intermolecular interactions among repeat unit fragments, or crystallizable polymers, for which microcrystallites may serve as cross-link loci.[18–25] In a similar vein, it has been suggested that the formation of gels of polystyrene in CS_2 may be due to complexation of the sulfur of CS_2 with the phenyl of the repeat units of polystyrene, with gelation occurring when the two sulfurs of a CS_2 molecule interact with phenyls on two different polystyrene chains.[5,9,11,26] This study was undertaken to elucidate features of the solution thermodynamics, and the interactions of polystyrene with CS_2 in an attempt to better understand the gelation behavior. The study includes light scattering on dilute solutions of polystyrene in a CS_2–toluene mixed solvent and NMR relaxation time measurements on the ^{13}C nucleus of CS_2 in solutions of polystyrene in CS_2 to assess the tendency for preferential adsorption of CS_2. Measurements of creep and recoverable strain are used to determine the equilibrium compliance J_e, and constrained oscillations of the gel are used to determine the storage and loss moduli $G'(\omega)$ and $G''(\omega)$, respectively, for a frequency ω small enough that $G'(\omega) \approx G_e = 1/J_e$. Values of G_e are used to estimate the number of monomers per chain elements forming cross-link loci. Finally, T_{gel} is reported for solutions of polystyrene in a CS_2–toluene mixed solvent. The following sections describe the experimental procedures and give a presentation of the results, with minimal interpretation, a discussion of the results in terms of the gelation model, and some conclusions.

Experimental Section

The polymers used are listed in Table 1. Polystyrene and poly(α-methylstyrene) prepared by anionic polymerizations were obtained from Pressure Chemical Co., Pittsburgh, PA, and the poly(4-methylstyrene) and perdeuterated polystyrene were obtained from Scientific Polymer Products, Inc., Ontario, NY. Spectroscopic grade carbon disulfide (CS_2), Aldrich Chemical Co., Inc., was dried over CaH_2, distilled over CaH_2 under vacuum, and stored over CaH_2 in the dark until use. As discussed below, this stringent drying was found to be essential to avoid phase separation of extraneous water at low temperatures. Other solvents were reagent grade and used as received. Polymers were evacuated (10^{-3}–10^{-5} mmHg) for several days at 60 °C. Solutions were prepared by weighing the appropriate amount of polymer and about two-thirds of the desired solvent(s) into a centrifuge tube with a screw top cap (Teflon gasket), containing a Teflon-coated magnetic stirring bar. After several days, the solution was gently agitated by occasional swirling. After the solution was apparently uniform, the remainder of the desired solvent was added, and the solution was stirred slowly with the stirring bar for an additional 1–2 weeks at room temperature. The solution density ϱ was estimated from the gravimetrically determined weight fraction w of the polymer using the densities ϱ_1 and ϱ_2 of the solvent and polymer, respectively, on the assumption of additivity of volumes:

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Table 1. Compositions Studied for Gel Formation

polymer	$10^{-4}M_w$	M_w/M_n	weight fraction	T_{gel} (°C)
polystyrene	0.090	<1.1	0.519	−2
	5.10	<1.06	0.473	19
	11.5	<1.06	0.163	−11
	41.1	<1.06	0.079	−14
	86.0	<1.11	0.066	−14
	86.0		0.163	5
	180.	<1.2	0.061	−14
	180.		0.066	−14
	180.		0.080	−11
polystyrene-d_8	6.35	<1.10	0.379	−5
poly(α-methylstyrene)	142.6	<1.2		<−78[a]
poly(4-methylstyrene)	7.2	2.0		<−78[a]

[a] No gel formation in CS_2 observed for temperatures down to −78 °C.

$$1/\varrho = w/\varrho_2 + (1 - w)/\varrho_1 \tag{1}$$

where $\varrho_2 = 1.071$ g/mL for polystyrene and ϱ_1 is 1.266 and 0.866 g/mL for CS_2 and toluene at 25 °C, respectively. The concentration c and the volume fraction φ of the polymer were calculated as $c = w\varrho$ and $\varphi = c/\varrho_2$, respectively.

Static light scattering measurements were carried out using methods and apparatus described elsewhere.[27] The apparatus is equipped with a Dewar flask thermostat to facilitate measurements at low temperatures. The vertically polarized component of the light scattered by vertically polarized incident light was determined in all cases. Static light scattering data on the Rayleigh ratio $R(q,c)$ for dilute solutions as a function of c and the usual modulus $q = (4\pi n/\lambda)\sin(\vartheta/2)$ of the scattering wave vector (scattering angle ϑ, wavelength λ, and refractive index n) were analyzed using the usual relations[27,28]

$$[Kc/R(q,c)]_0 = M_{LS}{}^{-1}\{1 + R_{G,LS}{}^2q^2/3 + \ldots\} \tag{2}$$

$$[Kc/R(0,c)]^{1/2} = M_{LS}{}^{-1/2}\{1 + A_{2,LS}M_wc + \ldots\} \tag{3}$$

where K is an optical constant, proportional to the square of the refractive index increment $(\partial n/\partial c)_m$ at constant composition of the solvent, the subscript LS designates a light scattering average, e.g., see ref 28, the subscript zero indicates infinite dilution, M_{LS} is equal to the weight average molecular weight M_w for a binary system, but is equal to $M_w\{(\partial n/\partial c)_\mu/(\partial n/\partial c)_m\}^2$ for a solution in a mixed solvent, with $(\partial n/\partial c)_\mu$ the increment at osmotic equilibrium,[28-32] and R_G and A_2 are the root-mean-square radius of gyration and second virial coefficient, respectively. Solutions were prepared for light scattering by filtration into a light scattering cell, which was then flame-sealed under vacuum, and centrifuged in a swinging-bucket centrifuge prior to use. In the case of mixed solvents, the stock solution was dialyzed against the desired mixed solvent composition prior to use.

A data acquisition and autocorrelator described elsewhere (Science Research Systems, Troy, NY) was used to determine the (unnormalized) autocorrelation function $G^{(2)}(\tau)$ from the photon count rate $n(t)$:[28]

$$G^{(2)}(\tau) = \langle n(t)n(t + \tau)\rangle_t \tag{4}$$

In the apparatus used, the photon count is determined for each of a fixed number $T_p + 512$ $(=2^{12} + 512)$ intervals of preset duration $\Delta\tau = 3.2 \times 2^N\,\mu$s, where $N = 0, 1, \ldots, 17$. The results of M such experiments were used to compute an average estimator $G^{(2)}(k\Delta\tau)$ of $G^{(2)}(\tau)$ for integer k $(1 < k \le 512)$:

$$G^{(2)}(k\Delta\tau) = \frac{1}{MT_p}\sum_{j=1}^{M}(\sum_{i=1}^{T_p} n_in_{i+k})_j \tag{5}$$

The asymptotic value $G^{(2)}(\infty)$ of $G^{(2)}(\tau)$ for large τ, obtained from a statistical analysis of the photon counts, was used to calculate the normalized autocorrelation function $g^{(2)}(\tau) = G^{(2)}(\tau)/G^{(2)}(\infty)$.

A method developed by Nossal[33-36] to determine the storage and loss shear moduli $G'(\omega)$ and $G''(\omega)$, respectively, from data on $g^{(2)}(\tau)$ as torsional waves are applied to the cell was utilized here. Solutions (unfiltered) to be studied were sealed in a cylindrical cell (an NMR sample tube), over a small amount of CaH_2 present as a water scavenger; the cells had an inner diameter D of 0.907 cm and a height of solution of about 4.5 cm. The cells were mounted in the light scattering thermostat described above. In this method, the scattering from some extraneous matter (e.g., a dust particle, an air bubble, etc.) is monitored at a convenient scattering angle (see below) as the sample is subjected to a small torsion around the symmetry axis of the cell.[36] As implemented here, the base of the cell was held firmly, and arrangements were made to provide a small torque to a yoke attached to the top of the cylinder. The torque was developed by the action of periodic pulses from a solenoid (from a speaker core) on a lever attached to the yoke. As discussed in the next section, the pulse frequency may be varied over a wide range without effect on the results, provided it is different from the resonant frequency being studied. With this arrangement, under certain conditions elaborated below, the experiment is considered to operate in a heterodyne mode, so that $g^{(2)}(\tau)$ may be approximated in the form[33,34]

$$g^{(2)}(\tau) - 1 = \{g^{(2)}(0) - 1\}\sum r_\nu \cos(\omega_\nu\tau)\exp(-\gamma_\nu\tau) \tag{6}$$

where $g^{(2)}(0)$ is fixed by the optical arrangement employed. This corresponds to a set of Lorentzian peaks offset by frequency ω_ν from the origin in frequency space, with the νth peak having a half-width $(\Delta_{1/2})_\nu$ at half-height given by γ_ν.[28,37] As elaborated below, $G'(\omega_\nu)$ and $G''(\omega_\nu)$ are calculated from the values of ω_ν and $(\Delta_{1/2})_\nu = \gamma_\nu$.

In the arrangement described, several modes of motion may be activated if the sample is a solid (i.e., if $G'(0) = G_e > 0$), with frequencies $\omega_{\ell n}$ given by[36]

$$\omega_{\ell n} = k_{\ell n}[G'(\omega_{\ell n})/\varrho]^{1/2} \tag{7}$$

The modes are damped, with half-width at half-height of the resonance given by

$$\Delta_{1/2}(\omega_{\ell n}) \approx (3^{1/2}/2)k_{\ell n}{}^2[G''(\omega_{\ell n})/\omega_{\ell n}\varrho] \tag{8}$$

The wavenumbers $k_{\ell n}$ depend on the mode of motion and the diameter D and height h of the sample:

$$k_{\ell n} \approx \left\{\left(\frac{2\nu_\ell}{D}\right)^2 + \left(\frac{(2n - 1)\pi}{2h}\right)^2\right\}^{1/2} \tag{9}$$

where n and ℓ are integers and ν_ℓ is the ℓth zero of a first-order Bessel function of the first kind, i.e., $\nu_1 \approx 3.83$, $\nu_2 \approx 7.02$, etc. Thus, for the cells used here, $k_{\ell n} \approx 2\nu_\ell/D$ for the lower modes, so that $k_{1n} \approx 8.42$, $k_{2n} \approx 15.5$, etc. If only the lowest mode is excited ($\ell = n = 1$), then $\omega = \omega_{11}$ and the period P of the damped oscillation gives the frequency ω (i.e., $P = 2\pi/\omega$), and therefore the estimate $G'(\omega) = \varrho(\omega D/2\nu_1)^2$ and the logarithmic time decrement $\Delta_d = 2\pi\Delta_{1/2}/\omega$ is calculated from the successive maxima of $g^{(2)}(\tau_{max})$, each separated by time interval $2\pi/\omega$:

$$\Delta_d(\omega) = \ln\left\{\frac{[g^{(2)}(\tau_{max,i}) - 1]}{[g^{(2)}(\tau_{max,i+1}) - 1]}\right\} = 2\pi\gamma(\omega)/\omega \tag{10}$$

The equilibrium compliance J_e was determined using a rheometer with a concentric cylinder geometry ($R_{inner} = 0.50$ cm, $R_{outer} = 0.90$ cm, height = 2.50 cm), a magnetic eddy-current torque transducer and a magnetic-bearing suspension.[38,39] The platens and magnetically supported shaft were enclosed in a sealed glass housing to suppress loss of solvent. The rotation of the platen was monitored using a light lever and a linear displacement photocell to give a resolution of $\approx 10^{-1}$ radians. The strain was determined as a function of time in creep under a constant stress until equilibrium, and the subsequent recoverable strain was determined on removal of the stress. The stress was limited to values small enough for a linear viscoelastic response (<20 Pa). The strain imparted to the gel was less than 0.1 at temperatures near the gel temperature, and smaller than 0.0002 at the lowest temperature used.

Solution viscosities were determined for the moderately concentrated solutions using flame-sealed suspended-level capillary viscometers of a design reported elsewhere.[40] A suspended-level Ubbelhode viscometer of standard design was used for dilute solutions. The viscometers were immersed in a bath to provide temperature control to ±0.05 deg. Since kinetic energy corrections were negligible, the viscosity was calculated from the time t_{flow} for a fixed volume to flow through the capillary in the usual way: $\eta = \varrho K_{\text{cap}} t_{\text{flow}}$, with ϱ the solution density and K_{cap} a known calibration constant.

Measurements of the spin–lattice and spin–spin relaxation times T_1 and T_2, respectively, were carried out on moderately concentrated solutions over a range of temperatures using ^{13}C NMR spectra recorded with an NMR spectrometer operating at a Larmor frequency ν_o of 75.5 MHz, equipped with a variable temperature probe (an IBM NR/300 FT spectrometer). Additional data were obtained for $\nu_o = 50.3$ MHz through the courtesy of Dr. A. A. Jones, including nuclear Overhauser effect (NOE) data. All samples were prepared in 5 mm diameter NMR tubes, with 10% by weight of a locking solvent (methylcyclohexane-*d* or cyclohexane-*d*) and flame-sealed under vacuum following a freeze–thaw cycle to remove oxygen. An inversion-recovery method with a pulse sequence of $\{\pi - t - \pi/2 - T_d\}_n$ was used to determine T_1, where t and T_d are the evolution period and the delay time between successive measurements, respectively. Following the usual procedure, the peak height $A(t)$ in the inversion-recovery method is related to T_1:[41,42]

$$A(t) = A(\infty)\{1 - 2\exp(-t/T_1)\} \tag{11}$$

Values of T_2 were determined from the half-width $\Delta\nu_{1/2}$ of the resonant peak at half-height as $T_2 = 1/2\pi\Delta\nu_{1/2}$. In one case, the Hahn spin-echo method with a pulse sequence of $\{\pi/2 - t - \pi - t_{\text{echo}} - T_d\}_n$ was used in one case to determine T_2, where t and T_d are as above and $t_{\text{echo}} = 2t$ is the echo time. The amplitude $A_{\text{echo}}(2t)$ of the echo at time $2t$ is related to T_2[41,43]

$$A_{\text{echo}}(2t) \propto \exp[-(2t/T_2) - O(t^3)] \tag{12}$$

where the term in t^3 arises from certain diffusion effects.

Results

Dilute Solution Characterization. Data on the relative viscosity $\eta_{\text{rel}} = \eta/\eta_s$ of dilute solutions of polystyrene ($M_w = 4.11 \times 10^5$) in CS_2 at 12.9 °C were analyzed by standard methods with plots of $(\eta_{\text{rel}} - 1)/c$ and $(\ln \eta_{\text{rel}})/c$ vs c to yield a common intrinsic viscosity $[\eta] = 127$ mL/g, and a common Huggins constant $k' = 0.30$. By comparison, for this polymer, $[\eta]$ is 123, 71, and 53 mL/g in solutions in toluene (30 °C), 2-butanone (30 °C), and cyclohexane (35 °C, the Flory Θ temperature), respectively. Thus, CS_2 is a "good solvent" for polystyrene at 12.9 °C, far removed from the Flory Θ temperature. This is consistent with a report that $\partial \ln [\eta]/\partial \ln M \approx 0.8$ at 20 °C and that $[\eta]$ is essentially independent of temperature in the range −51 to +20 °C for solutions of polystyrene in CS_2.[16]

Light scattering measurements were not carried out on dilute solutions of polystyrene in CS_2 owing to the small refractive index increment of that system (≈0.025 mL/g). Static light scattering experiments were carried out at −3 and +27.8 °C with dilute solutions of polystyrene ($M_w = 8.6 \times 10^5$) in a mixed solvent of toluene and CS_2 (0.208 weight fraction CS_2; $(\partial n/\partial c)_m = 0.0933$ mL/g). As may be seen in Figure 1, the data were essentially the same at these temperatures. As shown below, moderately concentrated solutions of polystyrene in the mixed solvent will form thermoreversible gels. The static light scattering results, summarized in Figure 1 gave $M_{LS} = 10.4 \times 10^5$ compared with $M_W = 8.6 \times 10^5$ for this polymer, or $(\partial n/\partial c)_\mu/(\partial n/\partial c)_m = (M_{LS}/M_w)^{1/2} \approx 1.10$. This may be used to estimate the "preferential solvation" parameter λ from[27–32,44]

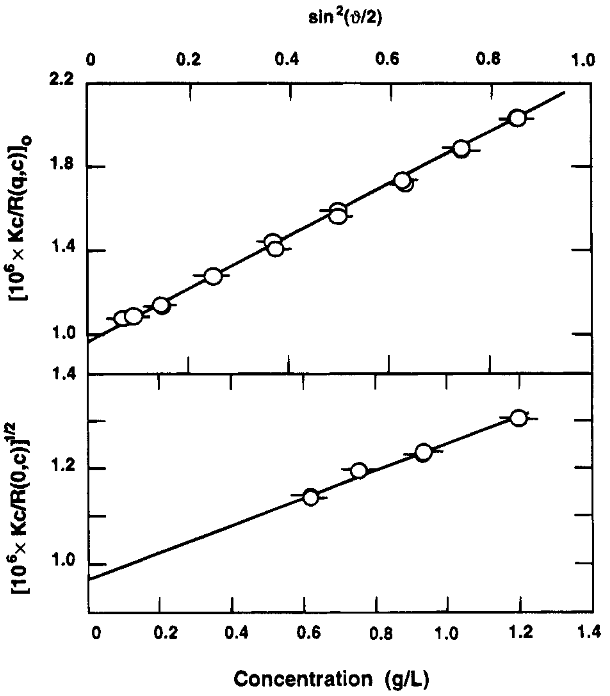

Figure 1. Light scattering data on dilute solutions of polystyrene in a mixture of toluene and CS_2 (0.208 weight fraction of CS_2) at two temperatures: pip left, 27 °C; pip right, −3 °C. Upper: Angular dependence, extrapolated to infinite dilution. Lower: Concentration dependence, extrapolated to zero scattering angle.

$$(\partial n/\partial c)_\mu = (\partial n/\partial c)_m + \lambda(\partial n/\partial \varphi_3)_c \tag{13}$$

with $\lambda = (\partial \varphi_3/\partial c)_\mu$, where φ_1 and φ_3 are the volume fractions of toluene and CS_2, respectively ($\varphi_1 + \varphi_3 \approx 1$ for dilute solutions). Measurements of the refractive index of mixtures of toluene and CS_2 gave $(\partial n/\partial \varphi_3)_c = 0.1037$ (with CS_2 being component 3), or $\lambda = 0.090$ mL/g, indicating a higher concentration of CS_2 in volume elements near a polymer chain than in the bulk solution, as elaborated below. The light scattering data give $(A_2)_{LS}M_{LS} \approx 280$ mL/g and $(R_G)_{LS} \approx 46$ nm, similar to data reported in the literature for solutions of polystyrene in toluene.[45,46]

Gelation Temperature. As discussed below, for moderately concentrated solutions of polystyrene in CS_2, η_{rel} is observed to be relatively independent of temperature, until increasing sharply with decreasing temperature over a narrow range of temperature until the solution forms a gel ($G'(0) > 0$ and $1/\eta = 0$, see below) at a certain temperature T_{gel}. This behavior is distinctly different from that of moderately concentrated solutions in toluene, for which η_{rel} is observed to increase smoothly over a wide temperature interval, without any certain indication that a gel has formed; i.e., η remains finite, though very large at low temperatures as the temperature approaches the glass temperature T_g of the solution.[47] The behavior of solutions of polystyrene in CS_2 facilitates determination of T_{gel} by simple observation of a solution in a flame-sealed tube. The temperature T_f for which the solution does not appear to flow (i.e., no flow for at least an hour) on tilting the tube was

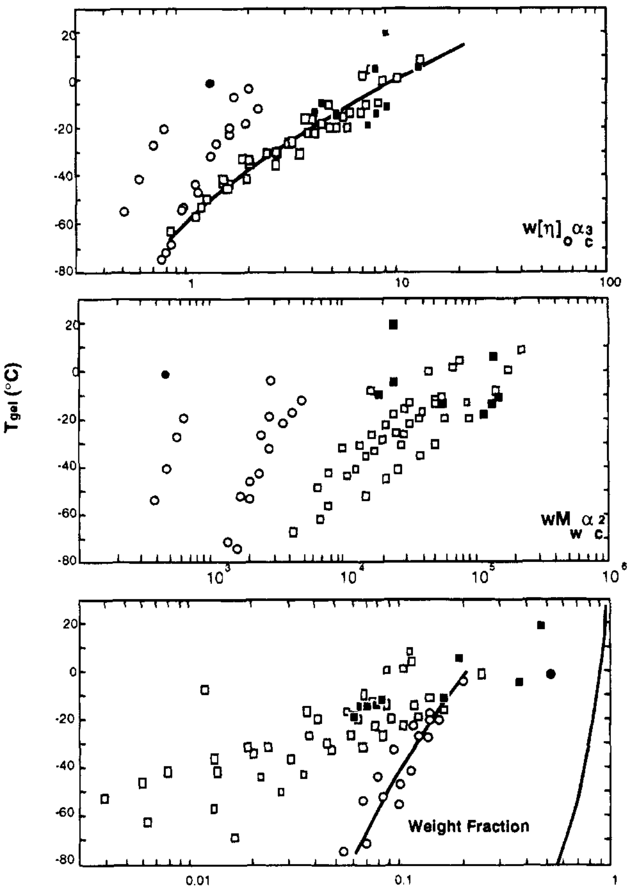

Figure 2. Gel temperature for solutions of polystyrene in CS_2. The filled and unfilled symbols are data from this study and from the literature,[2-7] respectively. The squares and circles give data with M_w greater and less than 30 000, respectively. The right-most solid curve in the lower panel gives T_g for high molecular weight polymer (M > 10 000); see text. The remaining curves are added to aid the reader in identifying behavior discussed in the text.

determined as the solution was slowly cooled, and the temperature T_m for which flow is observed on slow warming could be readily and reproducibly determined (±2 deg). These were equal within experimental error, and their mean was taken as T_{gel}. Results are presented in Figure 2 as a function of three parameters: the weight fraction w of the polymer; $wM\alpha_c^2$; and $w[\eta]_o\alpha_c^3$, where α_c is the chain expansion factor at weight fraction w (see below for the calculation of α_c) and $[\eta]_o$ is the intrinsic viscosity under Flory Θ conditions ($A_2 = 0$). The significance of these various representations is addressed in the Discussion. Data from the literature on T_{gel} for solutions of polystyrene in CS_2 are included for convenience.[2-7] Finally, the glass temperature T_g for solutions of high molecular weight polystyrene in CS_2 is also given in Figure 2. The published dependence[5,19b,48] of the glass temperature T_g on w and M for solutions of polystyrene in CS_2 may be fitted by the expression

$$1/T_g(w,M) \approx (1/T_g^\infty)\{1 + k_M/M\}\{1 + k_w(1 - w)\} \quad (14)$$

where T_g^∞ is the limiting value for undiluted high molecular weight polymer and $k_M \approx 300$ for polystyrene.[49,50] Since the value of k_w is among the largest known for solutions of polystyrene in CS_2 (e.g., see ref 19b), T_g is much suppressed for solutions in CS_2 compared with behavior in other solvents. For example, $k_w \approx 1.84$ for solutions of polystyrene in CS_2, whereas $k_w \approx 1.4$ for solutions in toluene with $w > 0.5$.[19b]

Table 2. Gelation Temperature for Moderately Concentrated Solutions of Polystyrene in Toluene/Carbon Disulfide Mixed Solvent ($M_w = 1.8 \times 10^6$)

weight fraction				
toluene	carbon disulfide	polystyrene	T_{gel} (°C)	T_{gel}^a (°C)
0	0.920	0.080	−11	
0.151	0.781	0.068	−16	−15
0.312	0.633	0.055	−20	−18
0.480	0.478	0.042	−30	−25
0.569	0.396	0.035	−35	−28
0.672	0.302	0.026	−42	−35
0.748	0.232	0.020	−51	−40
0.796	0.188	0.016	−57	−45

[a] T_{gel} for a solution in polystyrene in pure CS_2 at the weight fraction of polymer studied for the mixed solvent.[1]

Rheological studies[51] have shown that a number of the systems cited as gels in the initial study[1] of gel formation in solutions of polystyrene remained fluid to temperatures as much as 50 K below the reported T_{gel}. Several of the solutions exhibited $\eta \approx 10^4$ Pa·s at the temperature identified as T_{gel}, suggesting that a suppressed flow rate accompanying the usual increase in the viscosity with decreased T was mistaken for gel formation. Similarly, gelation of solutions of polystyrene in toluene is doubtful since the reported T_{gel} are so close to T_g, making it difficult to distinguish between the effects of gelation and a high viscosity without detailed viscoelastic studies. It was found that solutions of polystyrene in the mixed solvent toluene and CS_2 would form gels up to a substantial amount of toluene, with T_{gel} not too different from that observed for solutions of polystyrene in CS_2, as shown by the data in Table 2.

Solutions of poly(α-methylstyrene) and poly(4-methylstyrene) in CS_2 were examined for gel formation. No gel formation was observed for solutions of poly(α-methylstyrene) ($M_w = 1.42 \times 10^6$) with $w = 0.14$ or poly(4-methylstyrene) ($M_w = 7.2 \times 10^4$) with $w = 0.27$ for temperatures down to −78 °C. Finally, solutions of polystyrene in a number of sulfur and halogenated solvents were examined for gel formation, with negative results for temperatures down to the freezing temperature (in parentheses, °C): carbon tetrachloride (−23), chloroform (−63.5), 1,2-dichloroethane (−35), 1,3-dibromopropane (−34.2), hexafluorobenzene (5.3), dimethyl disulfide (−98), and dimethyl sulfide (−83).

Rheology of Moderately Concentrated Solutions. The dependence of η_{rel} on temperature for CS_2 solutions of polystyrene ($M_w = 1.8 \times 10^6$; $w = 0.061$) and poly(α-methylstyrene) ($M_w = 1.42 \times 10^6$; $w = 0.059$) is given in Figure 3 along with the viscosity η_s of CS_2 over the same temperature interval, including data on the latter from the literature[52,53] (for CS_2, $\partial \ln \eta_s/\partial T^{-1} = 796$ K, and $\eta_s = 0.352$ mP·s for $T = 25$ °C). A marked difference may be noted in the behavior, with η_{rel} for the polystyrene solution revealing a rapid increase over a narrow range of temperature as T nears T_{gel} on cooling, in contrast to the smooth, gradual change in η_{rel} for the poly(α-methylstyrene) solution.

Dynamic scattering was used to evaluate the rheological behavior of the gel and to provide an additional measure of T_{gel}. An example of $g^{(2)}(\tau)$ obtained for $T < T_{gel}$ is given in Figure 4, revealing the anticipated damped sinusoid oscillation. The oscillation in $g^{(2)}(\tau)$ disappears abrupty as T exceeds T_{gel}. It was found that $g^{(2)}(\tau)$ was independent of q, as expected, and also independent of the frequency f_{tap} of the torsional excitation over a wide range of frequencies. In practice, f_{tap} was adjusted so that $G^{(2)}(k\Delta\tau)$ did not depend on f_{tap}.

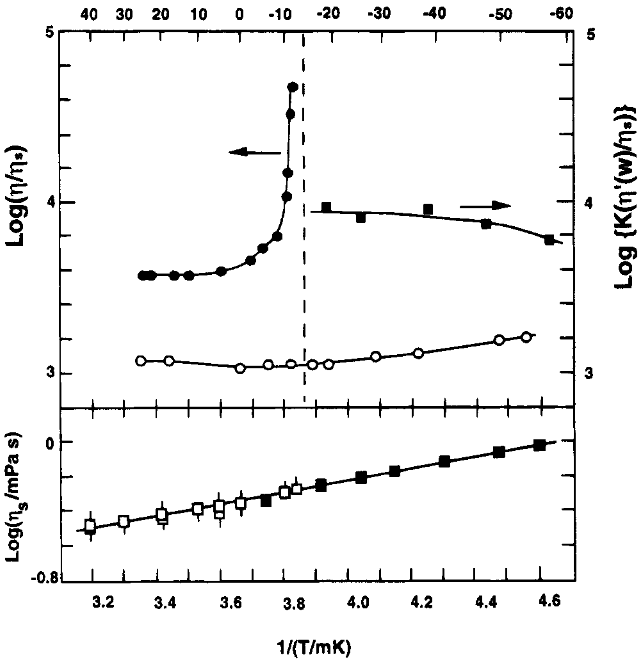

Figure 3. Viscosity of moderately concentrated solutions in CS$_2$ as a function of inverse temperature. Upper: The circles give the relative viscosity η/η_s. Filled circles are for a polystyrene ($M_w = 1.8 \times 10^6$, $wM_w = 11 \times 10^4$, $T_{gel} = -14$ °C) and the unfilled circles are for a poly(α-methylstyrene) ($M_w = 1.42 \times 10^6$, $wM_w = 8.4 \times 10^4$). The squares give the reduced dynamic viscosity $K(\eta'(\omega)/\eta_s)$, with $\omega/2\pi \approx 40-300$ Hz, for a polystyrene ($M_w = 4.11 \times 10^5$, $wM_w = 3.2 \times 10^4$, $T_{gel} = -14$ °C), where $K = (11/3.2)^{3.4}$. Lower: Viscosity of CS$_2$. Key: filled squares, this study; unfilled squares, pip down and pip up, refs 47 and 48, respectively.

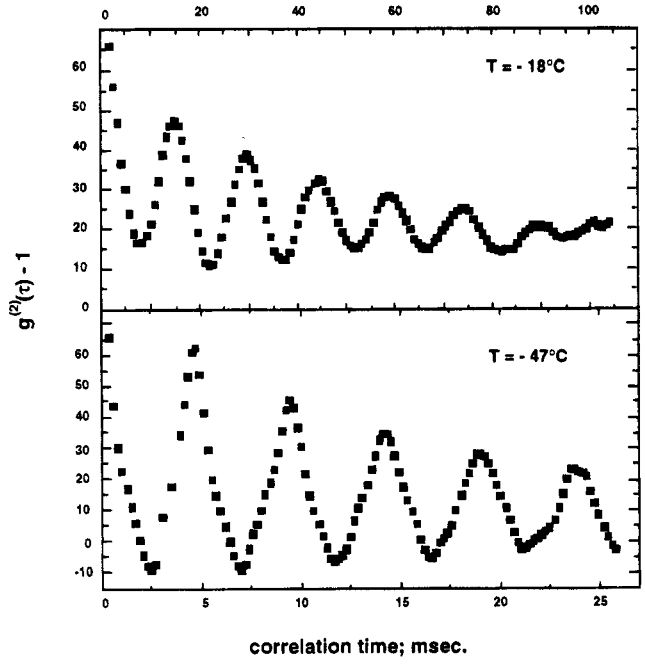

Figure 4. Examples of $g^{(2)}(\tau) - 1$ for gels of polystyrene in CS$_2$ at the indicated temperatures. Upper: $M_w = 115\,000$, $w = 0.163$, $T_{gel} = -11$ °C; tapping frequency of 10 Hz; $G'(\omega) = 230$ Pa, $\eta'(\omega) = 0.015$ Pa·s, $\omega/2\pi \approx 67.8$ Hz. Lower: $M_w = 411\,000$, $w = 0.079$, $T_{gel} = -14$ °C; tapping frequency of 20 Hz; $G'(\omega) = 3100$ Pa, $\eta'(\omega) = 0.090$ Pa·s, $\omega/2\pi \approx 210$ Hz.

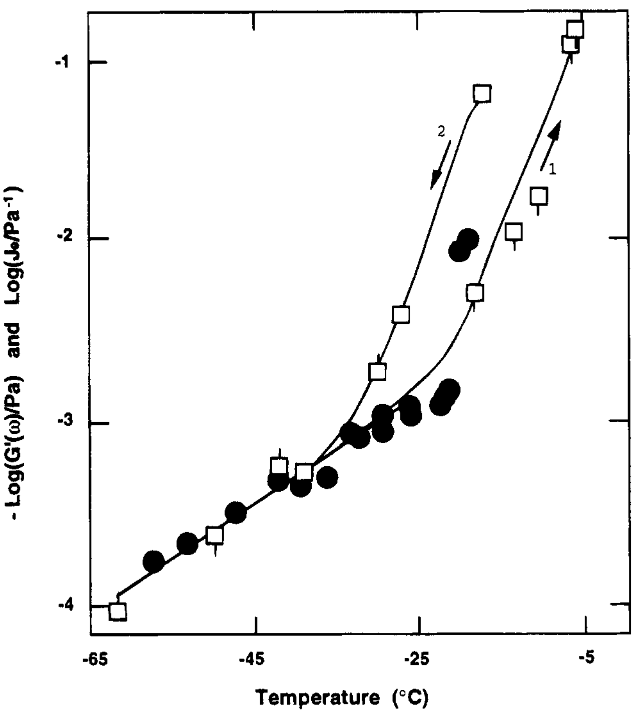

Figure 5. $1/G'(\omega)$ and J_e vs temperature for a solution of polystyrene in CS$_2$ ($M_w = 411\,000$, $w = 0.079$, $T_{gel} = -14$ °C. The frequencies range from 40 to 300 Hz. The circles and squares designate $1/G'(\omega)$ obtained by the light scattering and J_e determined in creep, respectively. Values of J_e determined during the first cooling, first warming (curve 1), and second cooling (curve 2) are designated by pip up, pip down, and no pip, respectively. The curves serve to guide the eye.

The resultant $g^{(2)}(\tau)$ never admitted more than a single component, taken to be from the excitation at $\omega = \omega_{11}$; owing to the weak dependence of $k_{/n}$ on n for the geometry used, modes with $n > 1$ could not have been distinguished. The arrangement was tested by determination of $G'(\omega)$ for gels of aqueous gelatin, with results in good accord with published data on G_e.[54] Values of $G'(\omega)$ computed on this basis are given in Figure 5 for one sample ($M_w = 4.11 \times 10^5$; $w = 0.079$; $T_{gel} = -14$ °C), where $\omega \approx \omega_{11} \approx (7.66/D)[G'(\omega)/\varrho]^{1/2}$, with $D = 0.907$ cm; e.g., for the data shown, $\omega \approx 2000$ s^{-1} at the lowest temperature studied. Values of $\eta'(\omega)$ for the same solution determined from the damping of $g^{(2)}(\tau)$ are given in Figure 3 as $K\eta'(\omega)/\eta_s$, where K is $(wM_w)^{3.4}$ for the solution divided into a reference value, taken to be $(wM_w)^{3.4}$ for the polystyrene solution for which η/η_s is given in Figure 3 (i.e., $K = (11.4/3.24)^{3.4}$ in Figure 3); the factor K reduces the data on $\eta'(\omega)/\eta_s$ to a basis of concentration and molecular weight comparable to that for the data on η/η_s.[19c,50,55-57] The data show that the reduced dynamic viscosity is about 2-fold larger than the relative viscosity η/η_s at temperatures well above T_{gel}; alternatively, $\eta'(\omega)/\eta_s$ is about 2-fold larger than η/η_s for a solution of the same M_w and concentration in benzene.[55]

Values of the equilibrium compliance J_e determined from the creep and recoverable strain are included in Figure 5 for comparison with $1/G'(\omega)$ determined on the same sample by the light scattering method. In the measurement of J_e, the solution was first quenched to -29.6 °C, where it formed a gel with J_e given in Figure 5. The sample was then further cooled, with measurements of J_e at -41.6 and -60.5 °C (points with pips up in Figure 5); the creep compliance $J(t)$ reached J_e within a few seconds, or less, for temperatures above -50 °C, but about 2 h was required for $J(t)$ to increase from its value at 1 s ($\approx J_0$) to its equilibrium value J_e at -60.5 °C. It may be noted that at a comparable temperature, $G'(\omega) \approx 1/J_e$, with $\omega = 2000$ s^{-1}, despite the retarded response for $J(t)$ on a time scale much longer than 0.5 ms. This behavior reflects the difference between relaxation and retardation times. A linear viscoelastic solid (e.g., a gel) will have equal numbers of retardation and relaxation times, and a terminal retardation time λ_m larger than the longest relaxation time τ_m (unless both are zero and the material exhibits a linear elastic response). For example, if there is only a single relaxation time τ, and therefore a single retardation time λ, then $\lambda = (G_o/G_e)\tau$, where G_o and G_e are the instantaneous and equilibrium moduli, respectively, and

$$J(t) = J_e - (J_e - J_o)\exp(-t/\lambda) \tag{15}$$

$$G'(\omega) = G_e + (G_o - G_e)(\omega\tau)^2/[1 + (\omega\tau)^2] \tag{16}$$

$$\eta'(\omega) = (G_o - G_e)\tau/[1 + (\omega\tau)^2] \tag{17}$$

with $G_eJ_e = G_oJ_o = 1$. Of course, the actual response may involve a broader distribution of relaxation (retardation) times, in which case $1 < \lambda_m < G_o/G_e$, but the observed behavior is still qualitatively that expected. On warming (points with pips down), J_e increased with increasing temperature, with the dependence markedly increasing for T larger than -10 °C and the material becoming a fluid for $T \approx -4.7$ °C. Finally, on recooling to the reported gel temperature of -14 °C, the sample did not appear to form a gel immediately. A weak gel was formed after standing for 12 h at -17.2 °C, i.e., J_e about 10-fold larger than that for the gel obtained on warming from -60.5 °C. On further cooling (points with no pips), the values of J_e reduced to the level seen on warming the sample from -60.5 °C. On the basis of the general correspondence of $G'(\omega)$ and $G_e = 1/J_e$, it is concluded that $G'(\omega) \approx G_e$ for the range of ω in the light scattering experiment. The increase of G_e with decreasing temperature is not unusual for thermally-reversible gels and reflects an increasing fraction of chain segments engaged in cross-link loci; see below.

Light Scattering on Moderately Concentrated Solutions. Preliminary static light results on solutions of polystyrene in CS_2 ($M_w = 8.6 \times 10^5$; $w = 0.066$) and on distilled CS_2 revealed a strongly enhanced scattering intensity for the solution, and a smaller enhancement for the solvent itself, at temperatures below about -5 °C, even at a 90° scattering angle. This was traced to the effects of residual moisture by comparison with the behavior of the same solutions containing a small amount of CaH_2 as a drying agent, for which the enhanced scattering was effectively suppressed. All data reported below are for materials containing a small amount of CaH_2. The angular dependence of a solution of polystyrene ($M_w = 8.6 \times 10^5$; $w = 0.066$) and poly(α-methylstyren) ($M_w = 1.42 \times 10^6$; $w = 0.052$) in CS_2 is shown in Figure 6 as a function of temperature. The scattering envelopes $1/R(q,c)$ versus $\sin^2(\vartheta/2)$ are similar at +9 and -16 °C for the polystyrene solution, for which $T_{gel} = -14$ °C, being approximately linear over the experimental range of scattering angle; the apparent extrapolation to negative values indicates curvature at small ϑ to a positive (unknown) small intercept $1/R(0,c)$, indicating a very high molecular weight. The scattering envelope for the poly(α-methylstyrene) solution at -38 and -17 °C are also approximately linear, again apparently extrapolating to negative $1/R(0,c)$; the scattering was much reduced at 22 °C, with enhanced scattering at small ϑ.

^{13}C NMR Relaxation Times. The ^{13}C NMR spectra of polystyrene and CS_2 are well-known,[58,59] and the expected features were observed. The peak due to the ^{13}C nucleus of CS_2 is well separated from any of the peaks due to the ^{13}C nuclei of polystyrene, making it easy to restrict the relaxation measurements to the ^{13}C nucleus of CS_2. Data were limited to $T \leq 42$ °C, as reliable results were not obtained as the temperature was increased to near the boiling temperature of CS_2 (46 °C at 1 atm), owing to difficulty in locking the signal. In the evaluation of T_1, the free induction decay (FID) following an evolution time t was subtracted from the FID determined for $t = 250$ s, and the results were transformed to frequency space to determine the difference amplitude $\Delta A(t) = A(\infty) - A(t)$ needed to determine T_1 with eq 11. Plots of $\ln[\Delta A(t)]$ vs t were found to be linear in all cases, and were analyzed to give $1/T_1 = -\partial\ln[\Delta A(t)]/\partial t$. Data on T_1 and T_2 are given in Figure 7. As may be noted, for the single solution studied here, T_2 is appreciably smaller than T_1, indicating a heterogeneous magnetic environment for CS_2 if it assumed that the extreme narrowing condition holds;[41] see below.

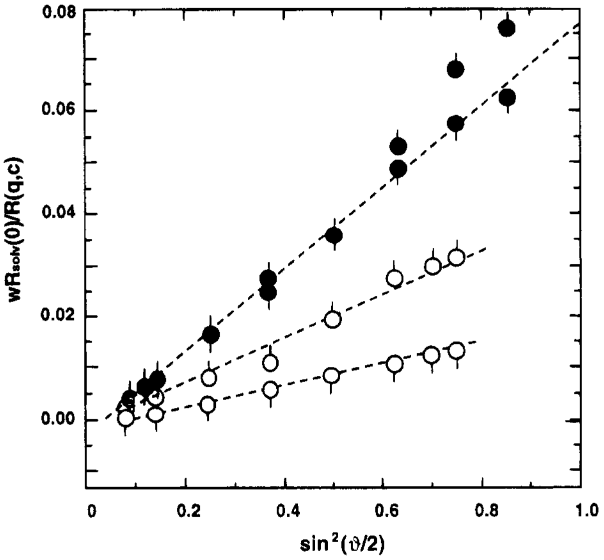

Figure 6. Light scattering for moderately concentrated solutions in CS_2. w is the weight fraction of polymer, $R_{solv}(0)$ is the Rayleigh ratio for the solvent scattering at zero angle, and $R(q,c)$ is the excess Rayleigh ratio for the solutions. Filled circles: polystyrene ($M_w = 8.6 \times 10^5$; $w = 0.066$; $T_{gel} = -14$ °C); pip up, 9 °C; pip down, -16 °C. Unfilled circles: poly(α-methylstyrene) ($M_w = 1.42 \times 10^6$; $w = 0.052$); pip up, -17 °C; pip down, -38 °C.

Data on T_1 obtained here for the ^{13}C nucleus in pure CS_2 ($\nu_o = 75.5$ MHz) are consistent with published data for $\nu_o = 14.0$, 30.1, and 61.9 MHz.[58] Following the treatment in ref 58, the data on T_1 for CS_2 may be analyzed using the relation[41,58]

$$1/T_1 = 1/T_1^{(dd)} + 1/T_1^{(csa)} + 1/T_1^{(sr)} \tag{18}$$

to obtain the contributions $1/T_1^{(csa)}$ and $1/T_1^{(sr)}$ to the overall relaxation rate $1/T_1$ from chemical shift anisotropy and spin–rotation, respectively, with the contribution $1/T_1^{(dd)}$ from dipole–dipole relaxation equal to zero for pure CS_2. In the extreme narrowing limit ($\omega_o\tau \ll 1$), for a linear molecule such as CS_2[41,58,60–62]

$$1/T_1^{(csa)} \approx \frac{2}{15}(\omega_o\Delta\sigma)^2\tau^{(csa)} \tag{19}$$

$$1/T_1^{(sr)} \approx \frac{4}{3}\frac{kT}{\hbar^2}IC_{sr}{}^2\tau^{(sr)} = \frac{2}{9}\left(\frac{IC_{sr}}{\hbar}\right)^2\frac{Hb}{\tau^{(csa)}} \tag{20}$$

where $\omega_o = 2\pi\nu_o$, $Hb = 6kT\,\tau^{(csa)}\tau^{(sr)}/I$ is the Hubbard number,[63] $\Delta\sigma$ is the chemical shift anisotropy, I is the molecular moment of inertia, and C_{sr} is the spin–

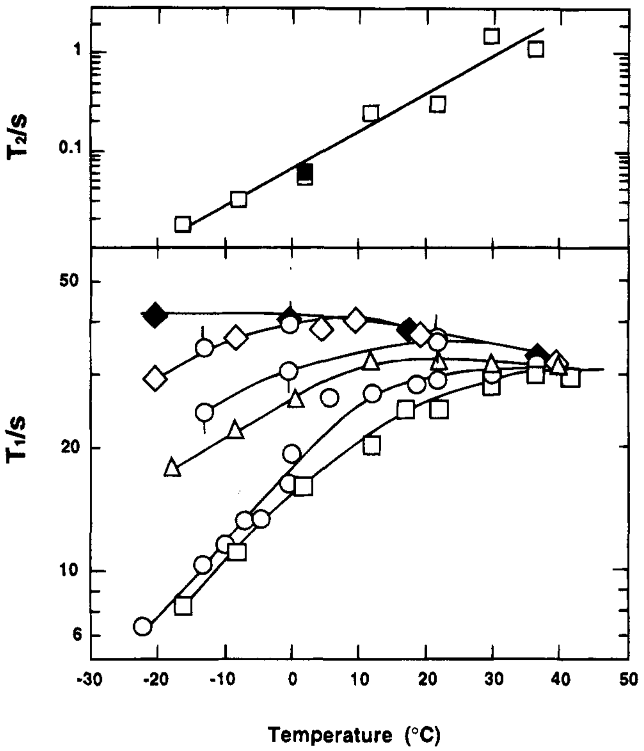

Figure 7. NMR relaxation times for $^{13}CS_2$. Lower: T_1 data for a solution of polystyrene in CS$_2$. Key: (square) M_w = 51 000, w = 0.473, T_{gel} = 19 °C; (triangle) M_w = 63 500 (perdeuterated), w = 0.379, T_{gel} = −5 °C; (circle) M_n = 900, (no pip) w = 0.519 and T_{gel} = −2 °C, (pip down) w = 0.312, (pip up) w = 0.135; (filled diamond) pure CS$_2$; (unfilled diamond) CS$_2$/toluene, w = 0.445 toluene. The curves serve to aid identification of the several data sets. Upper: T_2 data for solutions of polystyrene in CS$_2$ (M_w = 51 000, w = 0.473, T_{gel} = 19 °C). Unfilled squares are for T_2 calculated from the half-width $\Delta\nu_{1/2}$ of the resonant peak at half-height as $T_2 = {}^1\!/_2\pi\Delta\nu_{1/2}$, and the filled square is for T_2 determined by the Hahn spin-echo method.

rotation coupling constant. For the ^{13}C nucleus in CS$_2$: $\Delta\sigma = 438 \pm 44$ ppm, $I = 2.579 \times 10^{-38}$ g cm^2, and $C_{sr} = -13.8 \pm 1.4$ kHz (or $2(IC_{sr}/3\hbar)^2 \approx 0.24 \times 10^{-12}$).[58] Plots of $(1/T_1)$ vs ω_o^2 at each temperature were found to be linear, with an extrapolated value for $\omega_o = 0$ equal to $1/T_1^{(sr)}$, and a tangent $\partial(1/T_1)/\partial\omega_o^2 = (2/15)\Delta\sigma^2\tau^{(csa)}$. The results for $\tau_s^{(csa)}$ and $\tau_s^{(sr)}$ for pure CS$_2$ gave $\tau_s^{(csa)}RT/\eta_s \approx 8.3$ and $Hb \approx 1$ over the temperature range −20 to +40 °C, consistent with prior results.[58] Values of $1/T_1$, $1/T_1^{(csa)}$, and $1/T_1^{(sr)}$ entered in Table 3 for pure CS$_2$ were computed using these relations.

Data kindly provided by A. A. Jones for T_1 and the nuclear Overhauser effect, NOE, for ν_o = 50.3 MHz on a sample prepared in our laboratory permit an assessment of the contributions of $1/T_1^{(dd)}$, $1/T_1^{(csa)}$, and $1/T_1^{(sr)}$ to the overall relaxation rate $1/T_1$; the data on T_1 are included in Table 3. The NOE data were used to compute the dipole relaxation contribution $T_1^{(dd)}$ to T_1 given in Table 3 for a solution of polystyrene in CS$_2$ by use of the relation[41,64-66]

$$\mathrm{NOE} = 1 + 1.98(T_1/T_1^{(dd)}) \tag{21}$$

Although $1/T_1^{(dd)}$ is zero for pure CS$_2$, heteromolecular interactions can make $1/T_1^{(dd)} > 0$ for mixtures of CS$_2$ with a proton-containing solute.[41,66] It may be noted that an NOE involving heteromolecular relaxation is not commonly studied;[66] the lack of protons on CS$_2$ facilitates observation of the effect here. The NOE results (NOE = 1.22, 1.22, and 1.16 at −16, +2 and +42 °C, respectively) show that $1/T_1^{(dd)}$ is approximately 10% of the $1/T_1$ for the polystyrene solution studied; see Table 3. Accordingly, T_1 for the perdeuterated polystyrene, for which $1/T_1^{(dd)}$ is zero, is not expected to differ much from T_1 for the normal polymer, consistent with the data in Figure 7. The dependence of $(1/T_1) - (1/T_1^{(dd)})$ on ω_o was used to estimate the relative contributions from $1/T_1^{(csa)}$ ($\propto\omega_o^2$) and $1/T_1^{(sr)}$ ($\propto\omega_o^0$), with the results given in Table 3. As may be seen, $1/T_1^{(csa)}$ dominates $1/T_1$ at low temperature; the results give $Hb > 1$ for the polystyrene solution. For the data in Table 3, $\partial\ln(1/T_1^{(csa)})/\partial T^{-1} \approx$ 3000 K.

Values of T_1 were determined for the ^{13}C nucleus of CS$_2$ in mixtures of CS$_2$ with both toluene (0.55 weight fraction of CS$_2$) and methylcyclohexane (0.51 weight fraction of CS$_2$) over the temperature range −20 to +40 °C. No substantial difference was found between T_1 in the mixed solvents. The data on mixtures with toluene are given in Figure 7, where T_1 is seen to be similar to data for solutions of low molecular weight polystyrene in CS$_2$ (M_n = 900, w = 0.135).

Discussion

As reviewed above, it has been suggested that the formation of gels of polystyrene in CS$_2$ may be due to complexation of the sulfur of CS$_2$ with the phenyl of the repeat units of polystyrene. Gelation would involve complex formation of the two sulfurs of a CS$_2$ molecule with phenyls on two different polystyrene chains.[5,9,11,26] A gel is obtained when the number of cross-links per primary molecule exceeds approximately unity;[17-20,67] approximate equality of the time scales for the chain dynamics and the kinetics of the cross-link formation will result in observable chemorheological behavior.[68] Two of the most striking features of the gelation of solutions of polystyrene in CS$_2$ are that the gel is formed from a moderately concentrated solution at temperatures well above the glass temperature T_g of the solution (e.g., see Figure 2) and that CS$_2$ appears to be a thermodynamically good solvent for polystyrene at all temperatures of interest. As a consequence, the solution is transformed from a fluid with relatively low viscosity η and small rheological time constant $\tau_c = \eta J_e^0$, with J_e^0 the steady-state recoverable compliance, to a solid with an equilibrium compliance J_e. Furthermore, the gelation conditions are not appreciably altered on replacement of a large fraction of CS$_2$, by toluene, indicating that only a minor fraction of the CS$_2$ molecules are involved in the complex formation leading to gelation. The several pieces of data obtained in this study to assess the view that complex formation between a CS$_2$ molecule and repeat units on two different polystyrene chains is the source of the formation of an elastomeric gel are presented in the following paragraphs.

The light scattering data obtained here on dilute solutions of polystyrene in the mixed solvent (toluene + CS$_2$) show that the polymer is preferentially solvated by CS$_2$. A simplified model for the preferential solvation of a polymer (component 2) by component 3 of a mixed solvent (solvents 1 and 3) may be expressed by the excess number X_3 of molecules of component 3 in the vicinity of a repeat unit of the polymer with molar weight m_o, where X_3 is to be computed from λ:[44]

$$X_3 = \lambda m_o/\bar{V}_3 \tag{22}$$

with $\bar{V}_3$ the partial molar volume of component 3. With

Table 3. Nuclear Magnetic Resonance Relaxation Times for the ^{13}C Nucleus of CS$_2$ for Pure CS$_2$ and a Polystyrene Solution in CS$_2$ (T_{gel} = 292 K) (M_w = 5.1 × 10^4; w = 0.473)

	polystyrene/CS$_2$[a]				CS$_2$		
T (K)	1/(T_1 (ms))	1/($T_1^{(dd)}$ (ms))	1/($T_1^{(csa)}$ (ms))	1/($T_1^{(sr)}$ (ms))	1/(T_1 (ms))	1/($T_1^{(csa)}$ (ms))	1/($T_1^{(sr)}$ (ms))
257	112 (53.9)	5.1	105 (46.5)	2.3	23.4	10.1	13.3
265	90.9 (44.6)	4.7	83.3 (37.0)	2.9	23.8	9.8	14.0
275	64.5 (34.3)	3.8	54.3 (24.1)	6.4	25.0	8.8	16.2
285	49.5 (30.0)	3.8	35.1 (15.6)	10.6	25.6	7.0	18.6
303	34.2 (27.2)	4.5	12.7 (5.7)	17.0	30.0	6.8	23.2
315	33.9 (26.3)	2.0	13.7 (6.1)	18.2	33.0	6.1	26.9

[a] Data are for ν_o = 75.5 MHz, except for values in parentheses, which are for ν_o = 50.3 MHz by courtesy of A. A. Jones (Clark University), including NOE data used to estimate $T_1^{(dd)}$.

the definitions given above, component 3 is CS$_2$. With $\bar{V}_3$ approximated by the molar volume (95.4 mL/mol), $X_3 \approx 1$ excess CS$_2$ molecule per 10 repeat units of the polymer in the mixture studied (0.208 weight fraction of CS$_2$). The near independence of T_{gel} from the solvent composition in solutions of polystyrene in mixtures of toluene and CS$_2$ demonstrated in Table 2 is consistent with the preferential solvation by CS$_2$ if the gelation mechanism specifically involves an attractive interaction between CS$_2$ and the polymer.

The data on η/η_s in Figure 3 for solutions of polystyrene in CS$_2$ are interpreted to indicate that intermolecular association precedes gelation as the temperature is decreased. For a moderately concentrated solution, the viscosity may be expressed as[50,55,57]

$$\eta \approx \eta^{(R)}\{1 + (c/\varrho_2)(X/X_c)^{4.8}\}^{1/2} \qquad (23a)$$

$$\eta^{(R)} = N_A X \zeta/6 \qquad (23b)$$

where the Fox parameter $X = \alpha_c^2 c M_w g_w C/6M_L^2$ and $X_c = \varrho_2 M_c C/6M_L^2$ is found to be a constant for many polymers (400 × 10^{-17} in cgs units), g_w is the weight average ratio of the mean-square radii of branched and linear chains of common M_w, ϱ_2 is the density of the polymer, ζ is the friction factor for a segment of the chain of length ℓ, $M_L = M/L$ is the mass M per unit length L, $C = 6R_G^2/L\ell$, M_c is the molecular weight for the crossover from $\eta \approx \eta^{(R)}$ to $\eta \approx \eta^{(R)}(M_w/M_c)^{2.4}$ for undiluted polymer, and the expansion factor α_c reduces to unity with increasing $c[\eta]$:[28,57,69]

$$\alpha_c \approx \mathrm{MAX}\{1, \alpha_o[1 + (c[\eta])^2]^{-\sigma/4}\} \qquad (24)$$

Here, MAX(...) denotes the maximum of its two arguments, $\sigma = (2\mu - 1)/3\mu$, with $\mu = \partial \ln [\eta]/\partial \ln M$, and α_o is the expansion factor at infinite dilution. The effects of chain entanglements are expressed in the dependence on X/X_c.[55,57] For moderately concentrated solutions, $\zeta = \eta_s \Omega \exp(b_T w)$, where Ω and b_T are parameters expected to increase markedly as T approaches T_g, but to be weakly dependent on T otherwise, so that $\zeta \propto \eta_s$ for the range of w of interest here.[55,57] Thus, for a given polymer in solutions characterized by similar values of μ, η/η_s is expected to be essentially a universal function of $cM_w\alpha_c^2$ if T is well above T_g, as is the case for the compositions of interest here. As anticipated, for the solution of polystyrene in CS$_2$ reported here η/η_s for 25 °C is close to values for solutions in benzene,[55] indicating that there is negligible interchain association at that temperature. A similar result is obtained for data in ref 7, but surprisingly, results in ref 8 give a much larger (>1000-fold) η/η_s than would be expected on the basis of the behavior of polystyrene in benzene; the reason for this difference in behavior is unknown to us. The weak dependence of η/η_s on T seen for the solution of poly(α-methylstyrene) in Figure 3 is also consistent with $\zeta \propto \eta_s$. The marked increase in η/η_s with decreasing T near T_{gel} is taken to indicate the formation of branched moieties through intermolecular association. Small degrees of intermolecular association yielding a pseudorandom branched supramolecular structure have been treated by the approximation $g_w \approx \{\ln(1 + \nu_w)\}/\nu_w$.[40,70] Use of these relations (assuming α_c does not depend on T) gives the estimates for ν_w shown in Figure 8. These are related to the branching index γ_c, equal to the number of cross-links per primary chain, by the expression[17,71]

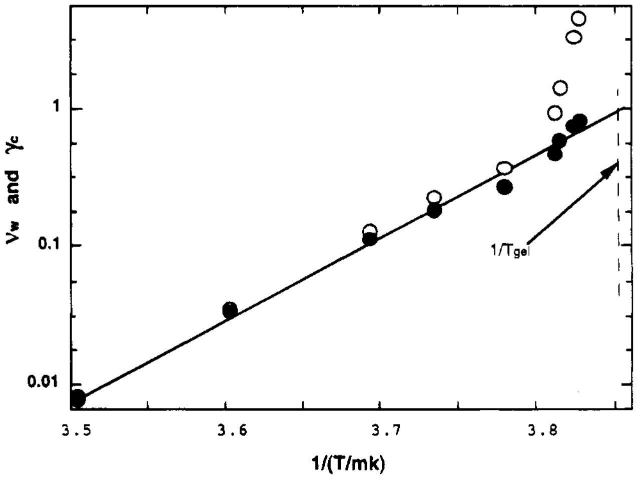

Figure 8. Degree of association ν_w (unfilled circles) and the cross-link index γ_c (filled circles) versus reciprocal temperature from analysis of the viscometric data in Figure 3 on a solution of polystyrene in CS$_2$. The gel temperature is shown for reference.

$$\nu_w = \frac{\gamma_c(1 - m_o/M_w)}{1 - \gamma_c(M_w/M_n)} \approx \frac{\gamma_c}{1 - \gamma_c} \qquad (25)$$

with M_w and M_n molecular weight averages for the dissociated chains, and the approximation is valid for a high molecular weight polymer with $M_w/M_n \approx 1$. Values of γ_c shown in Figure 8 are seen to extrapolate to $\gamma_c \approx 1$ for $T = T_{gel}$, as expected, and to increase exponentially with $1/T$, with $\partial \ln \gamma_c/\partial T^{-1} \approx$ 14 000 K. The latter value is unexpectedly large, but as discussed below, it is similar to $\partial \ln \gamma_c/\partial T^{-1}$ for the gel for T slightly below T_{gel}. The model comprising random association of the initially linear chains to form heterodisperse branched chains appears to capture the basic features of the viscometric behavior. Similar association has been reported for dilute solutions of polystyrene in CS$_2$ from the analysis of neutron scattering, which suggests the thermally reversible formation of a branched chain structure at very low temperatures.[10]

For the solution with $\eta'(\omega)$ given in Figure 3, T_g is at least 80 K below the experimental range, with the consequence that to a good approximation, $\zeta \propto \eta_s$, and $\eta'(\omega)/\eta_s$ is expected to be nearly independent of T, even at the lowest temperatures studied (excluding the effects of interchain association). For these gels, $\eta'(\omega)/\eta_s$ is about 2-fold larger than η/η_s for the comparable solution at temperatures well above T_{gel} and as may be seen in Figure 3, does not vary much with temperature over a range of temperatures for which G_e for the gel increases more than 10-fold (see Figure 5). Since the frequency ω in the experiment used to determine $\eta'(\omega)$ varies from 240 to 1800 s^{-1} as the temperature decreases from -19 to -57 °C, the weak dependence of $\eta'(\omega)/\eta_s$ on temperature, and therefore ω, suggests that $\eta'(\omega)$ may be near its limiting value $\eta'(0)$ at low ω, where

$$\eta'(0) = \int_0^\infty du\ \varphi(u) \tag{26}$$

with $\varphi(t) = G(t) - G_e$; of course, $\eta'(\omega)$ would be expected to decrease as ω increases, and $\eta'(0) = \eta$ for a fluid.[19d] Typically, random cross-linking of a flexible chain has a marked effect on $\varphi(t)$ near the gel point, usually giving $\eta'(0)$ for the lightly cross-linked polymer somewhat larger than the viscosity η_{eff} for the comparable un-cross-linked composition, with $\eta'(0)$ decreasing with increasing cross-linking, becomes less than η_{eff} ($\eta'(0)$ may be undefined at the point of incipient gelation[72,73]). Thus, the observed $\eta'(\omega)/\eta_s$ about 2-fold larger than η/η_s is not unusual and implies that segmental dynamics are not appreciably altered by gel formation in the range of the cross-link density encountered. This is consistent with experiments on the diffusion of a dye in solutions of polystyrene in CS_2.[74] This behavior is consistent with the proposed cross-link motif, and the relatively small number of intermolecular cross-link loci deduced in the range studied.

The light scattering data given in Figure 6 exhibit similar scattering for $T = T_{gel} + 15$ and $T \approx T_{gel}$, with the scattering envelope being approximately linear in both cases for scattering angles larger than 30° (with curvature indicated at smaller ϑ to maintain $1/R(q,c) > 0$). This scattering profile is similar to that noted previously for gel-forming solutions[75] and is characteristic of the scattering function for a randomly branched polyerm.[76] Similar behavior has been reported for neutron scattering from gels of polystyrene in CS_2.[11] The formation of a gel would be facilitated by a relatively loose, open supramolecular structure consistent with this scattering envelope and suppressed by the formation of tight, densely formed aggregates that would typically result in a strongly curved scattering envelope, with enhanced scattering at low scattering angle.[75] The polarized scattering $R_{Vv}(q,c)$ studied here for the moderately concentrated solution of polystyrene in CS_2 gave $R_{Vv}(q,c)$ essentially the same for $T = T_{gel} + 15$ °C and $T = T_{gel} - 2$ °C. By contrast, an abrupt increase in both the polarized scattering $R_{Vv}(q,c)$ and the depolarized scattering $R_{Hv}(q,c)$ have been reported for several compositions with a polystyrene with $M_w = 1.5 \times 10^6$.[77] The data on $R_{Vv}(q,c)$ in ref 77 are similar to those reported here for a comparable concentration, with $1/R_{Vv}(q,c)$ exhibiting increased curvature at low q for a larger concentration (the authors in ref 77 discount the curvature at lower q). In general, the excess scattering may be expressed as[28]

$$R_{Vv}(q,c) = R_{Iso}(q,c) + (4/3)R_{Aniso}(q,c) + R_{Cross}(q,c) \tag{27}$$

$$R_{Hv}(q,c) = R_{Aniso}(q,c) \tag{28}$$

Since the data in ref 77 gave $R_{Vv}(q,c) - (4/3)R_{Hv}(q,c) \approx R_{Iso}(q,c)$ invariant with T through the gelation event, whereas $R_{Hv}(q,c)$ was found to increase markedly, all of the enhanced scattering was attributed to $R_{Aniso}(q,c)$ (with neglect of any contribution from the cross term $R_{Aniso}(q,c)$, which reduces to zero for $q = 0$). This led to the suggestion that the gelation event corresponds to an increased persistence length for sections of the chain involved in the cross-link loci, with resultant enhanced order and orientational scattering seen in $R_{Aniso}(q,c)$. Since the depolarized scattering from CS_2 is strong, any tendency for enhanced solvent clustering in the vicinity of the polymer could also increase the depolarized scattering from the solution, providing an alternative explanation to the reported behavior unrelated to a change in the chain conformation. There is no evidence for such behavior in the scattering reported here, with essentially no change in $R_{Vv}(q,c)$ through the gelation event. One possible difference could be in a more dominant role for $R_{Iso}(q,c)$ for the solutions studied here, which were of lower concentration than most of those used in ref 77. The ratio $R_{Aniso}(q,c)/R_{Iso}(q,c)$ would be expected to increase with increasing c;[28] e.g., the data in ref 77 give $R_{Aniso}(0,c)/R_{Iso}(0,c) \propto c^{0.74}$ for moderately concentrated solutions of polystyrene in CS_2. The scattering at 22 °C for a solution of poly(α-methylstyrene) in CS_2 was very weak, with a scattering envelope characteristic of non-gel-forming aggregated solutions, with enhanced scattering at small ϑ indicating the presence of discrete supramolecular structures, perhaps few in number (or extraneous matter). The scattering at -17 and -38 °C was much stronger, and similar to that observed with solutions of polystyrene in CS_2, despite the absence of a gel, or effects on the relative viscosity indicating association. That may indicate that some degree of association took place, but that the aggregates tended to be more compact, and less able to span space to form a gel. In addition, the association loci may be more tenuous and/or short-lived, reducing the effects on the viscosity and eliminating gel formation.

The data on $G_e = 1/J_e$ provide a quantitative measure of the extent of the supramolecular structure. Since J_e is relatively large, and the response is viscoelastic with a relatively rapid response for T near T_{gel}, it is assumed that the theory of rubber elasticity may be used to estimate the number γ_c of elements per chain participating in cross-link loci:[67,75]

$$G_e = 1/J_e \approx kT\nu_o\gamma_c\{1 - \gamma_c^{-1} - 2\gamma_c^{-2}\} \tag{29}$$

where $\nu_o = cN_A/M$ is the number of primary molecules per unit volume prior to cross-linking. The values of γ_c vary from 2 to 14, increasing with decreasing temperature. Thus, as expected, only a minor fraction of the repeat units are involved in the cross-link loci, and a small shift in the equilibrium involving the associated sites can drastically modify the rheological behavior. For example, since a thermoreversible gel represents a balance between the formation of cross-link loci and their continual dissociation, hysteresis may be exhibited under some conditions. Thus, as shown in Figure 5, J_e for a solution recently cooled to a temperature just low enough to form a gel is observed to be larger than the value obtained at the same temperature after the same has been annealed at a lower temperature. The increasing G_e (or, equivalently, γ_c) with decreasing temperature is attributed to the temperature dependence of the equilibrium constant for the association of CS_2 with repeat units of polystyrene. For the data in Figure

5, $\partial \ln \gamma_c/\partial T^{-1} \approx 2780$ K over the temperature range −19 to −57 °C, similar to the estimate for $\partial \ln(1/T_1^{(csa)})/\partial T^{-1}$ quoted in the preceding, suggesting that the temperature dependence of $T_1^{(csa)}$ (and therefore, approximately that of T_1) is related to the association/dissociation equilibrium between CS_2 and polystyrene. As may be seen in Figure 5, $\partial \ln \gamma_c/\partial T^{-1}$ increases as T approaches T_{gel}, becoming closer to the value deduced for $T > T_{gel}$ from the temperature dependence of the viscosity. This behavior is strikingly different from that reported in ref 8 for G_e for gels studied by warming the temperature from a low temperature to $T \approx T_{gel}$, which gave G_e independent of T over a range from near T_{gel} to about 40 deg below T_{gel} for a composition with $c = 0.27$ g/mL and $M_w = 1.9 \times 10^6$, with the reported G_e giving $\gamma_c \approx 45$. The entanglement density $E = X/X_c$ is appreciably larger for the latter sample than for the solution studied here ($E \approx 16$, where $E \approx 1.3$ here). The authors report that G_e for the gel is nearly proportional to the entangelement pseudonetwork modulus G_N for the solution prior to gelation for the range of compositions they studied, with the suggestion that the entanglement pseudonetwork is essentially transformed to a "permanent" network at low temperatures; similar conclusions are reported for gels formed of star-shaped branched polystyrene in solutions in CS_2.[78] This behavior suggests that the association for compositions with large E studied may not be at equilibrium, being trapped at some degree of cross-linking for T not too far below T_{gel} as the temperature is rapidly decreased. For example, even for compositions with large E, a temperature dependence of G_e might be observed on slow cooling to temperatures below T_{gel}, where the approach to equilibrium might be facilitated.

The NMR data provide additional insight to the interaction of CS_2 with polystyrene on the NMR time scale (e.g., $1/\omega_o \approx 2$ ns for $\nu_o = 75.5$ MHz). As the extreme narrowing regime appears to be valid for CS_2[58] the substantial difference between T_1 and T_2 indicates multiple environments for the ^{13}C nucleus of CS_2 in solutions with polystyrene.[41] Similar behavior has been reported for selected ^{13}C nuclei of toluene in solutions of polystyrene in toluene.[79] Inspection of the data in Figure 7 for the mixtures at, e.g., −15 °C reveals several features to be reconciled: (i) T_1 is essentially the same for polymers with M_w equal to 900 and 51 000 for $w \approx 0.5$; (ii) T_1 increases with decreasing w for the polymer with $M_w = 900$; and (iii) T_1 for a polystyrene solution ($M_w = 900$, $w = 0.14$) is about equal to T_1 for a mixture of CS_2 and toluene (0.445 weight fraction toluene). In addition, as discussed above, the marked increase in $1/T_1^{(csa)}$ is responsible for the increase in $1/T_1$ for the gel for which a detailed examination was performed (see Table 3). The increase in $1/T_1^{(csa)}$ is associated with suppression of the rotational dynamics of CS_2 in the presence of the less mobile polymeric component. Thus, the behavior in Figure 7 may be explained as the effects of a complexed fraction of the CS_2 with relatively more slowly moving polystyrene repeat units, with T_1 decreasing as the fraction of complexed CS_2 molecules increases with increasing polymer concentration. The insensitivity to polystyrene chain length from a molecular weight of 900 up indicates that the association/dissociation time constant is short in comparison with the time scale for chain dynamics for chain lengths shorter than nine monomer units. By contrast, the relative insensitivity of T_1 to the addition of toluene indicates either no complex formation, or no appreciable effect on rotational dynamics of CS_2 in any complex. As noted above, the similarity of $\partial \ln \gamma_c/\partial T^{-1}$ and $\partial \ln(1/T_1^{(csa)})/\partial T^{-1}$ for temperatures well above T_g suggests that the formation of a transient complex of CS_2 with a moiety on those chains is related to the formation of the gel. The correlation is indirect, however, as effects of the polymer concentration on T_1 are observed at temperatures well above T_{gel}, with no noticeable discontinuity in the dependence of T_1 on T at T_{gel}; T_1 does not depend on the polymer concentration at higher temperatures, where the rate of interchange is rapid and, for example, the association/dissociation time is too short to permit formation of a gel or even affect the viscosity. Since the relative contributions of $1/T_1^{(dd)}$, $1/T_1^{(csa)}$, and $1/T_1^{(sr)}$ to the overall relaxation rate $1/T_1$ vary with temperature, an accurate description of the temperature dependence of T_1 is complex. Nevertheless, as may be seen in Table 3, over a reasonable temperature range at low temperatures, $1/T_1$ is dominated by $1/T_1^{(csa)}$, motivating representation by the simple form

$$T_1(T,w) \approx T_1(T,0) \exp(-\sigma_T w) \tag{30}$$

which approximates the behavior observed with the solutions of polystyrene in CS_2. Here $\sigma_T \propto \exp(-W/T)$, with W a constant reflecting the association/dissociation process; the data in Figure 7 give $W \approx 4000$ K. This behavior is consistent with a model in which an ever present temperature dependent association of CS_2 with polystyrene repeat units results in a gel under conditions for which the number of loci involving one CS_2 molecule and two different polystyrene chains becomes both about equal to one per polystyrene chain, and the loci exhibit a lifetime longer than the rheological time scale.

In accordance with the preceding, the dependence of T_{gel} on the weight fraction w and the molecular weight of the polymer marks the temperature for which $\gamma_c \approx 1$. The data in the upper panel in Figure 2 show that for $M > 60\,000$, T_{gel} scales with the parameter $c[\eta]_o\alpha_c^3$, which represents the condition required for effective intermolecular overlap.[28,57,69] That scaling does not apply for $M < 30\,000$ (the squares), with data for $M < 4000$ (the circles) exhibiting T_{gel} appreciably larger than would be expected on the basis of the behavior at larger M. This suggests that for the higher molecular weights, nascent intermolecular contacts obtaining at the "overlap concentration" are transformed to thermally reversible cross-link loci in sufficient number to satisfy the condition $\gamma_c \approx 1$. The middle panel in Figure 2 is motivated by two considerations: (i) $wM_w\alpha_c^2$ is a measure of the entanglement density, and (ii) a simple equilibrium model for the formation of cross-link loci from a spatially homogeneous system would suggest that T_{gel} should scale with cM_w ($\approx cM_w\alpha_c^2$) based on the criterion $\gamma_c \approx 1$ at gelation. The lack of any such correlation for the higher molecular weight polymer supports the postulate that nascent intermolecular contacts at compositions with $c[\eta]_o\alpha_c^3$ large enough for intermolecular overlap control the gelation process, with the possible exception of compositions with $4000 < M_w < 30\,000$, for which T_{gel} appears to correlate well with wM_w. The deviant behavior for $M_w < 4000$ may reflect non-Gaussian chain statistics. Since $\varrho_1 wM_w/\varrho_2 M_c < 1$ for most of the compositions shown, chain entanglements seem to be of secondary importance in the control of T_{gel}. The lower panel showing T_{gel} versus w emphasizes that T_{gel} lies far above T_g for gels of polystyrene in CS_2. The approximate correlation of T_{gel} with w for the data in the lower panel is surprising, as it appears to emphasize simply the monomer concentration in the gel formation.

The correlation with the overlap parameter $c[\eta]_o\alpha_c^3$ is suggestive. In the overlap state, a constant interchange of CS_2 molecules between states of association with polystyrene repeat units and dissociation would not destroy the gel if the time scale of that interchange is fast in comparison with the time scale of chain dynamics. That condition is apparently satisfied for CS_2 solutions of polystyrene with $M_w > 60\,000$; the converse may hold for solutions of poly(α-methylstyrene). Thus, for higher M_w, it appears that the chain dynamics for polystyrene are sufficiently torpid in comparison with the kinetics of the association/dissociation between CS_2 and polystyrene that an effective cross-link per molecule occurs as soon as the conditions for chain overlap are satisfied. The finding that T_{gel} is not much altered by the substitution of toluene for CS_2 up to ≈80% toluene is consistent with this observation, as is the observed tendency for preferential solvation of polystyrene by CS_2 in CS_2/toluene mixtures. The observed dependence of G_e and η_{rel} on T for the gels studied here is taken to mean that the association/dissociation between CS_2 and polystyrene does depend on temperature, as would be expected. The temperature invariance of G_e reported for compositions with much larger E may suggest departure from equilibrium, with the system being trapped at some degree of cross-linking for T not too far below T_{gel} as T is rapidly decreased through T_{gel}.

For $M_w < 20\,000$, the observed T_{gel} are higher than would be predicted by the correlation of T_{gel} with $c[\eta]_o\alpha_c^3$ for the data with $cM_w\alpha_c^2 > \varrho M_c$; i.e., the gel is formed more readily than would be expected by the overlap criterion. In this range, the high concentration of the repeat units is apparently sufficient to form a gel, perhaps because the chain dynamics are rapid enough in comparison with the association/dissociation kinetics of the CS_2/repeat unit complex that the complex may be considered to be "permanent" on the time scale required for chain collisions required to establish the intermolecular network to form the gel. Although not examined in this study, gels of low molecular weight polystyrene might exhibit pronounced chemorheological behavior. Conversely, the report[78] that T_{gel} is increased for star-shaped polystyrenes in CS_2 in comparison with the linear homolog at a given w and M is consistent with the postulates made here.

Conclusions

The rheological data presented above show that the gels of polystyrene in CS_2 studied behave as weakly cross-linked networks, with gelation occurring as expected with about one cross-link per chain on average. The light scattering and NMR data support the postulate that this cross-linking occurs through interaction of the CS_2 and polystyrene, even though no specific "fingerprint" for this interaction was obtained. With the postulate that the cross-links represent loci of association of the two sulfur atoms of a CS_2 with the phenyl rings on two different polystyrene chains to produce a cross-link loci, the gelation temperature represents the temperature for which the population of the polymer repeat units and the chain dynamics coincide with the polymer/CS_2 association/dissociation kinetics to allow approximately one effective cross-link per molecule on the experimental time scale. The formation of a stable complex may depend on the stereochemistry of the repeat units if a sulfur interacts with two phenylenes on adjacent repeat units. In that case, gel formation could be dependent on the stereostructure of the chain. The possibility of a complex involving a sulfur atom on CS_2 and a repeating unit phenyl ring has precedence, both in complexes reported for small molecules and for proteins.[79,80] This model is distinctly different from gelation caused by phase separation into dilute and concentrated phases in a poor solvent, with subsequent immobilization by proximity of the sample temperature to T_g of the concentrated phase that may occur with some systems.[19a,20,24,81] It is also distinct from gel formation owing to phase segregation of polymer crystallites, as may occur, for example, with solutions of crystallizable polymers, including isotactic polystyrene.[22,82,83] The rheological data show that association begins at temperatures above T_{gel}. The gel has about one cross-link per primary chain for a temperature just below T_{gel}, with the number increasing with decreasing temperature. The NMR behavior shows that the CS_2 interchange between magnetic environments is rapid enough to give averaged spin–lattice relaxation behavior, but not rapid enough to effect equivalence between T_1 and T_2. The interchange rate may be a critical factor in the gelation process, limiting the process to a small number of polymer/solvent pairs. The failure to find gelation in solutions of poly(α-methylstyrene) or poly(4-methylstyrene) in CS_2 indicates that the association/dissociation process must be delicately balanced to form gels, as does the failure to form gels with solutions of polystyrene in the α,ω-dihalogen or sulfur-containing solvents examined, even though the terminal atoms on the former or the sulfurs in the latter might be expected to interact with the phenyl rings on polystyrene.

Finally, we comment that in a general sense the specific solvation studied here reflects behavior that is not unique to the polymer/solvent pair studied. The solvation is made manifest here by the formation of a gel, perhaps due to the presence of two sulfur nuclei on a single carbon nucleus, but similar interactions are implicit in the solvation of all polymers. The possibility that less persistent repeat unit/solvent complexes may influence viscoelastic behavior has proved to be an elusive subject. Such effects could cause deviation from the universal scaling behavior normally assumed for polymer solutions. They may, for example, be involved in specific-solvent effects on the persistence length determined under Flory Θ conditions ($A_2 = 0$) and may play a role in behavior for which the contributions of the solvent to the solution properties are not simply additive. Thus, as mentioned above, the excess depolarized scattering from solutions of polystyrene in carbon disulfide may not reflect solute properties. Similarly, it has been found that in some cases the contribution of the viscosity to the stress tensor cannot be accounted for by a term linear in the solvent viscosity.[84]

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