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Thermoreversible Gelation of Isotropic and Liquid Crystalline Solutions of a “Sticky” Rodlike Polymer

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ABSTRACT: Thermoreversible gelation of rodlike poly(γ-stearyl-α-L-glutamate) in *n*-dodecane has been studied by differential scanning calorimetry, polarized light microscopy, visual observations, and temperature ramped fluorescence photobleaching recovery. Solutions spanning a wide range of concentrations can produce gels. In solutions that are initially liquid crystalline, long-range features such as cholesteric twist appear to be frozen by gelation. Although gelation is rapid, some of the polymer molecules retain significant mobility, allowing the gels to “cure” slowly.

Introduction

Thermoreversible gelation of rodlike polymers is a vexing problem. Rods lack the flexibility to form the extended intermolecular crystallites that often act as the cross-links of thermoreversible gels of crystallizable or partially crystallizable random coil polymers. Yet most rodlike polymers do gel under appropriate conditions.[1−6] The most frequently studied example is poly(γ-benzyl-α-L-glutamate), PBLG, which gels in many solvents.[2,3,6−21] In the absence of any obvious mechanism by which rodlike polymers could form extensive crystallites, Miller and co-workers[2,7,22] proposed that phase separation is an important factor in the formation of PBLG gels. This is consistent with observations by electron and optical microscopy, which sometimes show the existence of phase-separated domains, possibly “pinned” or “frustrated” from progressing toward macroscopic phase separation by entanglement effects or by specific interactions. A dynamic treatment of the phase separation of rods is a complex problem because there is one conserved order parameter (concentration) and one nonconserved order parameter (orientation).[19,23−25] Phase separation surely plays a role in the gelation of some rod-bearing systems, but it does not completely describe all such systems.

The interesting case of PBLG/toluene gels has been reopened recently.[17,18,21] It seems likely that phase separation is *not* the only factor in that system, which can display remarkably clear or somewhat turbid gels depending on sample history. Self-diffusion studies of PBLG in a good solvent, pyridine, suggested that equilibrium entanglement effects would not suffice to “pin” any nascent polymer-rich zones.[26] Weak thermal signals were correlated with the melting of the gels, suggesting that specific polymer−polymer or polymer−solvent interactions stabilize the PBLG/toluene gels. The nature of the interaction is not precisely known, but the importance of specific polymer−solvent interactions in gelation is increasingly accepted.[27,27] Compelling calorimetric and small-angle X-ray evidence supporting solvent-mediated interactions has been presented by Izumi et al. for the case of PBLG/benzene gels.[28]

With solid evidence for specific interactions, one may contemplate simple connectivity transitions without phase separation. In the limit of a pure connectivity transition, polymers above the overlap condition simply “stick” to each other to form a network, and the large concentration gradients associated with gelation by phase separation are not present. Reversible gelation of random coil polymers with “stickers” has been treated thermodynamically.[29−31] In the more recent results,[30,31] the transition from sol to gel appears not to be a thermodynamic transition; however, gelation is accompanied by a tendency for phase separation in Θ solvents. The possibility of a simple connectivity transition was considered at length for PBLG/toluene gels, and such a transition was tentatively overlaid on the traditional Flory phase boundary for rods (see Figure 1 of ref 21). The problem with PBLG/toluene gels is that frustrated phase separation and specific interactions are close competitors. There is no single, dominant reason why that system gels.

Poly(γ-stearyl-α-L-glutamate), PSLG, shares the same α-helical backbone as PBLG, along with other desirable properties such as modest polydispersity, electrical neutrality, rigidity, and good solubility in several solvents. In place of the benzyl substituent is a long, waxy $C_{18}H_{37}$ side chain; see Figure 1. PSLG forms lyotropic liquid crystals,[32] as does PBLG,[33] but at slightly elevated temperatures it also “dissolves” in its own side chains to give a thermotropic liquid crystal.[34,35] PSLG and related polymers[36,37] appear to be the largest, most flexurally rigid polymers with this ability. PSLG dissolves in warm linear alkanes but gels on cooling. Unlike PBLG, there is an obvious mechanism: interchain associations among the C18 side chains. These interactions are likely to be much stronger than they are for PBLG, which presents appealing and important technical opportunities. The formation of side chain

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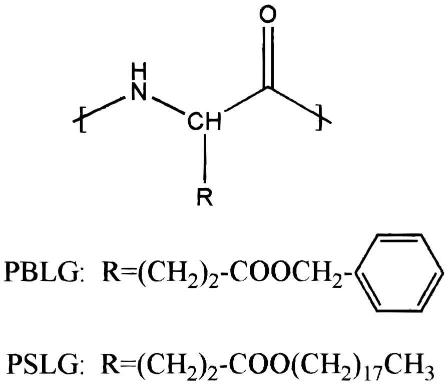

Figure 1. PBLG and PSLG.

crystallites could be used to freeze the alignment provided in the liquid crystalline state without the covalent bonding steps that have been used for PBLG.[32,38] Isotropic gels of PSLG are possibly the simplest gelling system, since the molecules cannot undergo the intrachain looping that confounds understanding of random coil gels. In this study, visual and microscopic observations, differential scanning calorimetry (DSC), and temperature-ramped fluorescence photobleaching recovery (TRFPR) are used to investigate a rodlike polymer system that really *should* gel, PSLG in dodecane.

The TRFPR method deserves some introductory comments. Methods for studying gels can be characterized as “direct” or “indirect” according to whether they do or do not detect molecular mobility or flow.[39] Differential scanning calorimetry, light scattering, and turbidity are indirect. Changes in the signal may herald the appearance or disappearance of the gel, but neither mobility nor flow is directly measured. Rheological measurement is the classic direct method. TRFPR was introduced[40] as a more molecular type of direct gelation assay, reliant on large changes in molecular diffusion rather than flow. The method requires fluorescently labeled polymers. A striped pattern is “written” into the gel. In the absence of diffusion—in a perfect gel—the pattern would remain indefinitely. In real gels, the pattern often fades a little bit, due to the sol fraction mobility. After this reduction in contrast, a temperature ramp is started. The remaining contrast disappears when the gel melts. The method can determine the diffusion coefficient of the sol fraction, the percent sol fraction, and the transition temperature. The present experiments use a modulation detection scheme to follow the pattern contrast. This eliminates most limitations of the original method[40] and makes TRFPR a strong competitor of other optical tracer diffusion techniques that have been combined with temperature ramping for the study of gels.[41]

Materials and Methods

The PSLG polymers, described in Table 1, were synthesized by polymerization of the corresponding *N*-carboxy anhydride (NCA) as described below. All reagents were purchased from Aldrich, if not otherwise stated.

Synthesis of NCA. The starting ester, i.e., γ-stearyl-α-L-glutamate (SLG), was obtained by esterification of L-glutamic acid with stearyl alcohol (1-octadecanol) in *tert*-butyl alcohol at reflux using sulfuric acid as catalyst.[42] The corresponding carboxy anhydride, γ-stearyl-α-L-glutamate *N*-carboxy anhydride (SLG-NCA), was synthesized by reacting SLG with triphosgene (i.e., hexachlorodimethyl carbonate) in tetrahydrofuran (THF)[43] ^{1}H NMR: 0.8 ppm (t), 1.3 ppm (s), 2.2 ppm (m), 2.6 ppm (t), 4.1 ppm (t), 4.4 ppm (t), 6.8 ppm (s).

Table 1. Polymers Used

code	M_w (uncertainty)	M_w/ M_n^{a}	fluorescent label?
PSLG-28	28 000^a (15%)	1.7	no
PSLG-129	129 000^b (est 10%)	1.2	no
PSLG-214	213 700^a (6%) 239 000^b (est 10%)	1.4	no
LPSLG-46	46 440^a (5%)	2.9	yes
LPSLG-205	205 000^a (13%)	1.14	yes

^{a} From GPC/LS (stated error represents three or more repeat determinations). ^{b} From Zimm plot (error estimates represent combined systematic effects).

Synthesis of PSLG. All PSLG samples were prepared by anionic polymerization of SLG-NCA in THF (approximately 10% monomer concentration) initiated by amines (*N*,*N*-diethyltrimethylsilylamine was obtained from Huls America, Inc). The reaction took 3−4 days at room temperature depending on the initiator used. The molecular weight was controlled by the ratio between the NCA and the initiator used.

Synthesis of Fluorescently Labeled Polymers. SLG-NCA monomer (1.5 g) was dissolved in THF (30−50 mL) at room temperature, and the polymerization was initiated with benzylamine (3.9 μL, monomer-to-initiator ratio of 100). After the reaction was completed (about 4 days), fluorescein isothiocyanate, isomer I, was added (27 mg, dye-to-initiator ratio of 2). The mixture was allowed to react for an additional 2 days and then precipitated in methanol. The excess free dye in the labeled PSLG was extracted with methanol using a Soxhlet apparatus until the extracting methanol was colorless. The polymer was dried, redissolved in THF, reprecipitated in methanol, and submitted to a new methanol extraction. The extraction and reprecipitation operations were repeated until the precipitating methanol was free of dye as tested by UV−vis spectroscopy.

Differential Scanning Calorimetry. DSC measurements were made using a Seiko heat-flux DSC6200 EXSTAR system with a heating ratio of 2 °C/min (1 °C/min for cooling). Fifty microliter aluminum pans (Seiko P/N SSC000E031), sealed to withstand a pressure of 30 atm, were used as sample holders. An empty pan served as the reference. The DSC pans were filled with pieces of PSLG/dodecane gel and weighed. Samples were run in the DSC not more than once in any 24 h period and were refrigerated while not in use. For all DSC experiments, gels were first heated to 50 °C at 2 °C/min and cooled to 8 °C at 1 °C/min. This enabled the gel to melt and re-form in good thermal contact with the sample pans. In the annealing time experiments, the gels were then allowed to anneal for a given time at 8 °C and then reheated to 80 °C at 2 °C/min. For determination of concentration and molecular weight effects, each sample was allowed to anneal for 1 h at 8 °C. Then each gel was heated to 80 °C at 2 °C/min and cooled to 8 °C at 1 °C/min. All measurements were repeated at least thrice. In addition, a blank heating and cooling run was performed on the dodecane solvent.

Gel Permeation Chromatography/Light Scattering. The polymers were characterized by gel permeation chromatography/light scattering (GPC/LS) in tetrahydrofuran using a Wyatt DAWN DSP multiangle light scattering spectrometer, a Waters 590 pump, and a Waters model 410 differential refractive index detector. Two or three Phenogel 10 μm columns (Phenomenex #10H-0201-KO, #10H-0646-KO, and #00H-641-KO) were connected in series. The value 0.080 mL/g[44] was used for the differential refractive index increment.

Visual Observations. To determine the gelation time, a stopwatch was started when molten samples (ca. 1 mL) containing small (ca. 1 × 1 × 3 mm) magnetic stirring bars were immersed into a water bath at the desired temperature. When a magnetized rod held 0.5 cm from the cells could no longer move the stirring bars perceptibly, the stopwatch was turned off. Each sample was measured three times.

Fluorescence Photobleaching Recovery. The only change to our previously described[45] FPR apparatus was the substitution of a Mettler FP80 programmable hot stage. Gel samples adhering to a coverslip were placed in the middle of a ring of uncured epoxy glue drawn on a microscope slide. Measurements were made after the epoxy had cured, and no significant loss of dodecane was detected. The striped patterns were written by illuminating a 100 lines/in. Ronchi ruling placed in the rear image plane of a 10× microscope objective with a 488 nm argon ion laser operating at 50−100 mW for 1−5 s. These photobleaching pulses, which were longer and less intense than used for the study of isothermal diffusion in normal solutions, destroyed 5−10% of the dye groups. Even longer bleaches (30 min) at even lower intensities (1 mW) produced essentially the same results, suggesting that gel “melting” during the bleach cycle is not a factor. The period of the striped pattern in the sample was $L = 80.8\ \mu$m, corresponding to a spatial frequency of $K = 2\pi/L = 778$ cm^{-1}. The fading of the pattern was followed at greatly reduced beam intensity, using a modulation detector similar in concept to that developed by Lanni and Ware.[46] By translating the Ronchi ruling in the direction perpendicular to its stripes and to the laser beam, a weak modulation was produced as the illumination pattern came in to and out of phase with the pattern written in the sample. The voltage envelope of this ac signal was recorded with a tuned amplifier/peak detection circuit. The dc signal was also followed, representing the total intensity. As the measurements sometimes lasted more than 1 h, some parasitic photobleaching occurred even at the reduced laser power used during the read portion of the measurements. The true contrast of the pattern was obtained by dividing the ac signal by the dc signal. The temperature ramp rate was 0.3 °C/min.

Results and Discussion

Visual Observations and Microscopy. Fluid PSLG/dodecane solutions are clear. When cooled, they turn cloudy and then gel. When contained in a cell of 1 cm thickness, the appearance of the gels ranges from translucent but turbid to nearly opaque. They lack the complete opacity of PBLG/DMF/H_2O gels[9,47] but generally are cloudier than PBLG/toluene gels.[8,17,18,21] The turbidity immediately precludes any thought that a connectivity transition occurs absent formation of aggregates or incipient phase separation.

The gels often exude some degree of free solvent (syneresis), but the main PSLG/dodecane phase is a *true* gel[48] in the sense that dilute, macroscopically large samples (say, 1 mL) do not flow perceptibly during any practical span of time. A gel made in a tilted sample vial will retain its shape indefinitely when the container is uprighted. Well-formed gels at high concentration can be broken by mechanical shock (e.g., rapping the vial on a lab bench). The sharp, irregular shape of the fragments does not change perceptibly over periods of several weeks. More dilute gels distort to smooth shapes when shocked; however, they again retain that shape and show no sign of flow for at least several weeks. These dilute preparations might actually be slurries of aggregates. At still lower concentrations, clumps form and sink to the bottom of the container. In a smaller vessel, one might conclude that such clumps qualify as a space-filling, self-supporting gel. In standard 1 cm diameter machine vials, using 1 min as the flow time criterion, the critical gel weight fraction for gels of several milliliters volume was $w_c = 0.02 \pm 0.005$ for $M = 28\,000$ and $w_c = 0.0045 \pm 0.0005$ for $M = 214\,000$ at 20 °C. Although the polymers may aggregate prior to gelation, it is still interesting to compare these concentrations to the Doi−Edwards semidilute regime, which begins near a number density of one rod per volume L^3, where L is the rod length. The corresponding weight fraction is

$$w^* = \frac{M}{N_a L^3 \rho} \tag{1}$$

where M is the molar mass, N_a is Avogadro's number, and ρ is the solution density. We may compute L as

$$L\ (\text{in Å}) = 1.5M/M_0 \tag{2}$$

where M_0 is the monomer molar mass (381.5 g) and 1.5 Å represents the translation of a monomer unit along the α-helix axis. The semidilute regime ends approximately when the rod number density exceeds $1/dL^2$, where d is the diameter. This marks the beginning of interactions serious enough to align the rods, and the corresponding weight fraction is

$$w^{**} = \frac{M}{N_a d L^2 \rho} \tag{3}$$

We seek only approximate values, so using the solvent density (0.75 g/mL) instead of the actual solution density will suffice. For 28 000 and 214 000 molecular weight PSLG, this yields $w^* = 0.05$ and 0.0009, respectively. Using $d = 36$ Å, one finds that $w^{**} = 0.14$ and 0.021 for 28 000 and 214 000 molecular weight PSLG, respectively. For the shorter sample, gelation takes place below w^*, perhaps indicating some end-to-end aggregation. For the longer sample, the onset of gelation lies well above w^* but well below w^{**}. These results suggest that alignment is not required for gelation. More detailed studies of the molecular weight dependence of the onset of gelation would be desirable, as would a better understanding of the aggregation state of PSLG in dodecane at temperatures above the gel transition.

PSLG/dodecane gelation can be remarkably fast. Figure 2a shows that gelation is hastened by increasing concentration or reducing temperature. Higher molecular weight samples require significantly more time to gel than lower-M samples, as shown in Figure 2b.

Figure 3 is a polarized light microphotograph taken from a particular sample that contains both isotropic and liquid crystalline phases when heated. The sample had been annealed 2 weeks at 100 °C so that the thumbprint pattern characteristic of polypeptide cholesteric liquid crystals is distinctly visible. The thumbprint patterns remain on cooling, despite loss of colors and a dramatic decrease in the light intensity due to clouding. Heating the gel restores the brightness and the colors, but the sample becomes slightly more opaque just prior to conversion of the gel to a fluid, suggesting that some previously trapped polymers experience melt crystallization, or aggregation, to increase the turbidity. The cholesteric thumbprint pattern is unchanged after a cooling−“melting” cycle, suggesting that it is possible to freeze the liquid crystal. Fluorescent patterns written in cooled liquid crystals reveal that these, like the isotropic systems, are gels.

Calorimetry. Figure 4a shows the DSC transition temperatures on heating and cooling for PSLG-129 as a function of concentration. The error bars represent three repeat runs. The melting and cooling transitions are separated by 13−16 °C, indicating significant hysteresis. In a narrow concentration regime, 25%−30%, two endotherms were discerned. By polarized light

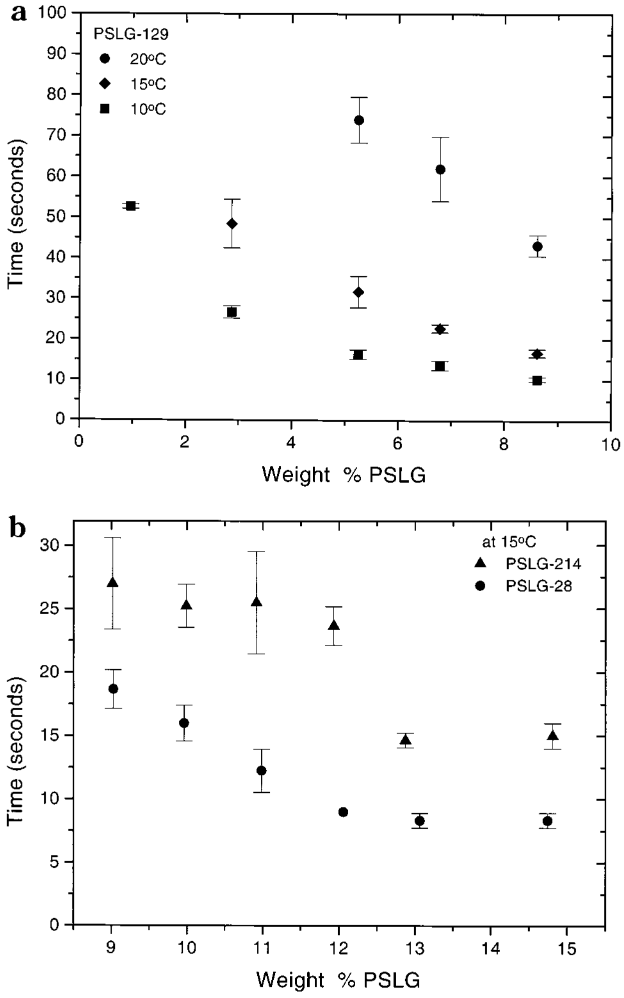

Figure 2. (a) Time required for gelation for PSLG-129/dodecane at three different temperatures, indicated. (b) Time required for gelation for $T = 15$ °C at two different molecular weights, indicated.

Figure 3. PSLG/dodecane solution containing liquid crystalline spherulites with cholesteric banding bathed in dark, isotropic phase. Image spans ~2 mm in the horizontal dimension.

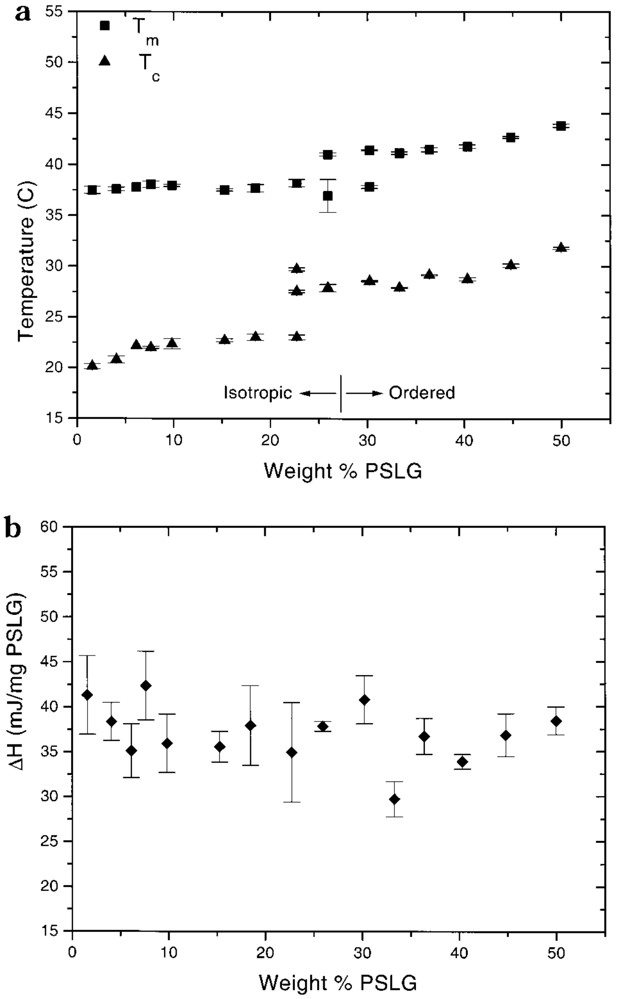

Figure 4. PSLG-129/dodecane gels at various concentrations: (a) transition temperatures T_m and T_c for melting and cooling, respectively; (b) melting enthalpy.

microscopy, these concentrations correspond to the transition from an isotropic phase to liquid crystal. Melting occurs 3−4 °C higher in the LC phase than in the ISO. The melting transition trends higher with concentration in the LC phase, while it is essentially constant in the ISO phase. Figure 4b shows that the enthalpy of melting per gram of polymer, ΔH_m, is independent of concentration within uncertainty. Since the Kelvin melting temperature, T_m, is the quotient of enthalpy and entropy, i.e., since $T_m = \Delta H_m/\Delta S_m$, it seems that ΔS_m is somewhat smaller for the LC phase than it is for the ISO phase. An isotropic system gains more entropy, per unit mass polymer, on melting than does a LC system. The observation of two endotherms on melting in a limited range of compositions for PSLG/dodecane does not seem to be related to the two peaks observed in isotropic PBLG/benzene.[28]

The melting temperatures of 15 wt % gels were identical for PSLG-28 and PSLG-214, but the higher-*M* sample had about a 15% lower enthalpy of melting. This may indicate that the higher-*M* sample might be impeded, i.e., not fully cured. The effect of curing time was investigated by cooling a 5 wt % gel to 8 °C and then melting it in the DSC after a certain time, which was varied on repeat experiments. Figure 5 shows the results. The transition temperature did not vary with curing time (Figure 5a). The interactions continued to strengthen for up to 1 h (Figure 5b), even though gelation takes place quickly.

Temperature-Ramped Fluorescence Photobleaching Recovery. A typical TRFPR trace appears in Figure 6. Following the photobleach, but before the temperature ramp is started, a considerable amount of contrast decay does take place, corresponding to a sol

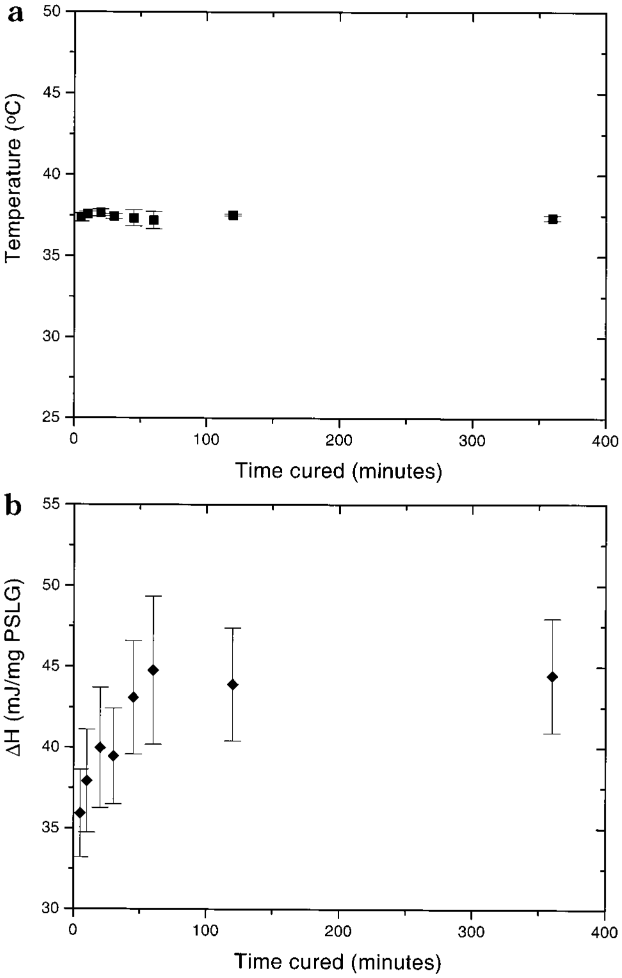

Figure 5. Melting temperature (a) and enthalpy (b) for 5% PSLG-129/dodecane gel plotted against time allowed to cure after cooling.

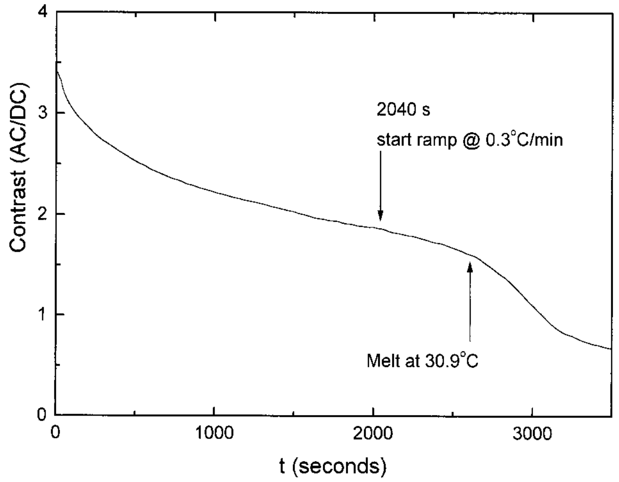

Figure 6. TRFPR trace for 10% LPSLG-46/dodecane gel.

diffusion coefficient of about 10^{-8} cm^2 s^{-1}. (This comes from the approximate rate of decay and the known spatial frequency of the grating.) About 30% of the molecules in the post-bleach gel are mobile. If enough time were allowed, it might be found that essentially all the molecules are mobile, albeit at some lower rate of diffusion. Instead, a temperature ramp is initiated after the contrast begins to level off. The sudden decline corresponds well with the DSC-determined melting temperatures, as shown in the overlay plot (Figure 7).

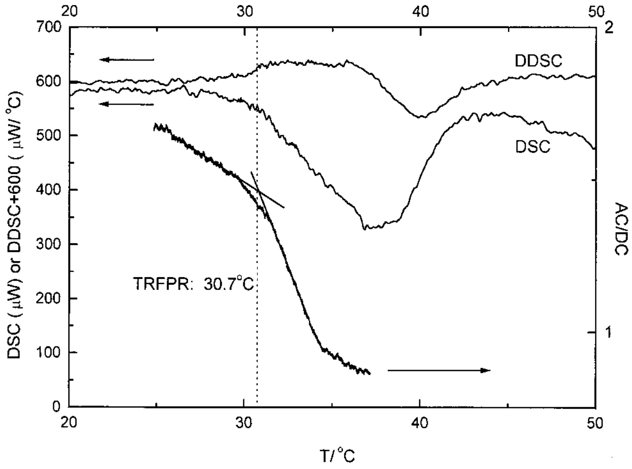

Figure 7. Overlay of TRFPR and DSC melting curves for 5.2% LPSLG-205/dodecane gel.

Indeed, the gel melting point can be determined with a consistency similar to or perhaps somewhat better than that afforded by DSC. The difference is that TRFPR provides direct evidence that the network has disappeared, whereas DSC tracks the underlying cause, the disappearance of the interactions that stabilize the gel.

Other authors have combined temperature ramping and a related optical tracer technique, holographic relaxation spectroscopy, also known as forced Rayleigh scattering. The main application has been gelatin gels.[41] Prior to the gelatin melting point, unusually strong scattering behavior is seen. We note in passing that such pretransitions are not evident in TRFPR measurements on gelatin gels; they melt with simple patterns similar to the one shown in Figure 6.

Conclusion

PSLG/dodecane is a convenient system for the study of thermoreversible gelation. Formation of large structures prior to gelation is indicated by the cloudy character of the gels, yet the completely opaque appearance of some other rodlike polymer gels is absent. Alignment seems not to be a requirement for gelation. DSC melting endotherms taken at various stages of annealing demonstrate that, although gelation is rapid, curing continues beyond the gel point. Together with the observation that high-M gels are slower to gel, this suggests that gelation is partly impeded in PSLG/dodecane, possibly by entanglements. The TRFPR measurements show that many chains are mobile in PSLG/dodecane gels. Indeed, it is not clear that any of the polymer molecules are completely immobilized, since there is evidence for a slow diffusion process. This does not preclude gelation; a rod may leave its position in the network and diffuse to another site without the network collapsing. The vacancy it leaves behind can be filled by other mobile rods. At a temperature very similar to the DSC transitions, all chains become *rapidly* mobile, confirming that DSC is following the gel melting and not some other thermal process. Thermoreversible gelation of liquid crystalline samples preserves long-range spatial features, such as cholesteric twist alignment.

The present observations merely introduce the PSLG/dodecane system. Much remains to be learned, including details of the gel structure, the role of dodecane in establishing the stabilizing junctions, and the molecular state of PSLG in dodecane prior to and after gelation. Rheological studies of the sol−gel transition have reached a high state of development (see ref 49 and references therein). The viscoelastic behavior of a model rodlike polymer network, one with highly rigid elements, reasonably good molecular weight uniformity, and not requiring aggressive or unstable solvents, may prove illuminating.

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