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Gel/Sol and Liquid-Crystalline Transitions in Solution of a Rigid-Rod Polyimide

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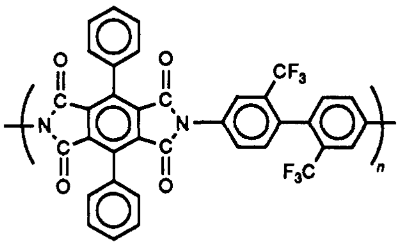
ABSTRACT: A soluble, rigid-rod polyimide has been synthesized from 3,6-diphenylpyromellitic dianhydride (DPPMDA) and 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB). Hot, isotropic solutions of the polymer in *m*-cresol undergo two major transitions during cooling for concentrations greater than 1%. A mechanical sol/gel transition occurs first possibly through a nucleation-free, liquid–liquid phase separation. This is followed by the development of lyotropic, liquid-crystalline spherulites through a nucleation and growth mechanism. Both processes are thermally reversible. On heating however, the gel/sol transition and the liquid crystal/isotropic solution transition appear to occur almost simultaneously. The latter process is endothermic, typical of an order/disorder transition. Isothermal annealing studies show that although the rate of spherulite formation is faster at lower temperatures, the structures formed are less ordered than those formed at higher temperatures. An increase in polymer concentration increases the rate of spherulitic growth at a given temperature but does not affect the structure developed. Scanning electron microscopy observations of gels from which the solvent had been extracted reveal that the rigid-rod chains pack in a microfibrillar network.

Introduction

Many years ago, Ferry defined a gel as a substantially diluted system that exhibits no steady-state flow.[1] This phenomenological definition is independent of the gelation mechanism. Thus, the term is satisfactory and sufficient to describe the thermally reversible gel phenomenon that occurs in many solutions of polymers in poor solvents. In these cases, gels form when the solvation power of the solvent in a homogeneous, free-flowing solution is suddenly reduced, usually through a decrease in the temperature. Polymers with widely varying degrees of chain flexibility and morphology have been found to participate in gel formation. For example, noncrystallizable, flexible macromolecules such as atactic polystyrene[2-7] and weakly crystallizable systems such as poly(vinyl chloride)[8-14] and various random copolymers[15,16] form thermally reversible gels. The cross-links responsible for gelation in these systems arise from molecular associations that vary from system to system. Crystallizable, flexible macromolecules such as isotactic polystyrene[17-23] can also form gels. In these cases, cross-linking appears to arise through the formation of crystalline domains.

Solutions of rigid-rod polymers have also been found to undergo gelation. In these systems, extreme chain rigidity is attained through chemical structure, intramolecular interactions, and/or interactions between the chain and the solvent. Above the critical concentrations, the lyotropic liquid-crystal state may form when the rigid-rod polymers dissolve in good solvents, as described by Flory.[24,25] However, the behavior of rigid-rod polymers in poor solvents is different. Most of the work on this subject has been reported for poly(γ-benzyl α,L-glutamate) (PBLG).[26-32] Another rigid-rod polymer system that can form gels is poly(p-phenylenebenzobisthiazole) (PBZT) in concentrated sulfuric acid (H_2SO_4).[33-35] The gels predominantly show a permanent space-filling lattice texture with microfibrillar network. People have speculated that a spinodal decomposition mechanism is involved for liquid–liquid phase separation during gelation. This process may occur relatively quickly. Any slow coagulation which may lead to cocrystals of PBZT and solvent is induced by gradual absorption of moisture.[34,35] At this time however, no concrete conclusion about the gelation formation mechanism for rigid-rod polymers can be made.

In this paper, we report our recent results on a system consisting of one rigid-rod polyimide and *m*-cresol as solvent. This polyimide was synthesized through 3,6-diphenylpyromellitic dianhydride (DPPMDA) with 2,2′-(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB). Its chemical structure is



DPPMDA–PFMB

with a molecular mass of 649 g/mol of repeat units. On the basis of computer modeling, the planes of two phenyl side groups in DPPMDA are almost perpendicular to that of the backbone imide group. In PFMB, two phenylene groups are twisted toward each other with two trifluoromethyl groups locked in. This leads to an extended rigid-rod chain conformation.[36] At high temperatures, isotropic solutions are formed for concentrations $\leq 17\%$ (w/w). Gel formation occurs with decreasing temperature. Changes in the gel/sol transition temperatures, gel textures, and the different structure formation kinetics are discussed as functions of concentration.

Experimental Section

Materials. The polymer was synthesized by following published procedures.[37] In brief, the route to the 3,6-diphenylpyromellitic dianhydride (DPPMDA) was initiated with the Diels–Alder addition of 2,5-diphenyl-3,4-bis(4-methoxyphenyl)-cyclopentadien-1-one to dimethylacetylendicarboxylate in refluxing *o*-dichlorobenzene. The reaction afforded an 85% yield of dimethyl 3,6-diphenyl-4,5-bis(4-methoxyphenyl)phthalate.

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The intermediate was oxidized with chromium trioxide in acetic acid to dimethyl 4,5-dicarboxy-3,6-diphenylphthalate, which was hydroxyzed to 1,2,4,5-tetracarboxy-3,6-diphenylbenzene. The tetraacid was dehydrated by heating at 220 °C under reduced pressure. The yellow DPPMDA was purified by recrystallization from toluene.

DPPMDA was polymerized with 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB) in *m*-cresol at high temperatures. The polymer solution with the highest monomer concentration (17% w/w) remained completely in solution when the polymerization was carried out until allowed to cool to below 110 °C. The mixture then formed a gel. The intrinsic viscosity of the DPPMDA-PFMB in *m*-cresol at 30 °C is 2.6 dL/g. Solutions with different concentrations were obtained by diluting the solution as-polymerized to predetermined concentration by using hot *m*-cresol.

Equipment and Experiments. Differential scanning calorimetry (DSC) measurements were conducted on a Perkin-Elmer DSC2. The temperature and heat flow scales were calibrated by using standard materials. The samples as-polymerized exhibited the gel state; these were tightly sealed in liquid DSC pans. A temperature range from 0 to 170 °C was scanned at a heating rate of 10 °C/min.

Isothermal experiments were performed by first heating the samples to 170 °C and then quenching to the predetermined isothermal temperature for different time periods. The heating traces were recorded at a heating rate of 10 °C/min without prior cooling.

Polarized light microscopy (PLM) was carried out with a Nikon Labophot-Pol. After polymerization the hot polyimide solution droplets were placed between two glass slides. The samples were then sealed under nitrogen atmosphere to avoid moisture contamination and stored in vacuum prior to observation. A hot stage (Mettler FP52) was coupled to the PLM for observations of texture change with temperature. A heating rate of 10 °C/min was used.

Two techniques were used to determine the gelation and gel/sol transition temperatures: the test tube "tilting" and the ball-drop methods. In the first method, the gelation time in the isothermal experiments was determined by tilting the test tube containing the solution. The time at which the solution no longer flowed was taken as the time of gelation. In the second method, a steel ball with a weight of 50 ± 0.5 mg and a diameter of 2.37 ± 0.005 mm was placed on the top of the gel. The temperature was increased at a rate of about 0.05 °C/min, and the depth of the steel ball was recorded as a function of temperature. The vertical resolution of the measurements was 1.0 mm. The point at which the depth–temperature curve deviated from horizontal was taken as the gel/sol transition temperature.

Small-angle light scattering (SALS) H_v patterns were obtained with a photogoniodiffusometer. The samples were quenched from 170 °C to a predetermined annealing temperature and irradiated by a helium–neon (He–Ne) laser beam ($\lambda = 632.8$ nm) for different annealing times. X-type SALS patterns are related to a spherulitic-like texture, and circularly symmetric patterns are representative of rodlike morphology. For more detailed descriptions, see ref 38.

Scanning electron microscopy (SEM) studies were conducted using a JSM-U3 with an accelerating voltage of 25 kV. The solvent (*m*-cresol) in the gel samples was extracted by putting the samples into a methanol bath at 25 °C for 5 days. The bath solvent was replaced with fresh methanol every 12 h. The samples were freeze-dried from methanol in a vacuum. Then, air was admitted slowly to prevent collapse of the sample texture. The dried samples were then coated with Au/Pt metal alloy.

Results and Discussion

Figure 1 shows the DSC heating traces of the as-polymerized samples of DPPMDA–PFMB at different concentrations. It is evident that there is a rather sharp endothermic transition peak detected for each trace. The peak temperature increased from 70 to about 110 °C and the heat of transition from 0.44 to 5.0 J/g as the concentration was increased from 1.0% to 12% DPPMDA–PFMB solid content. This kind of endothermic process usually indicates a first-order transition, which is characteristic of an order/disorder transition.

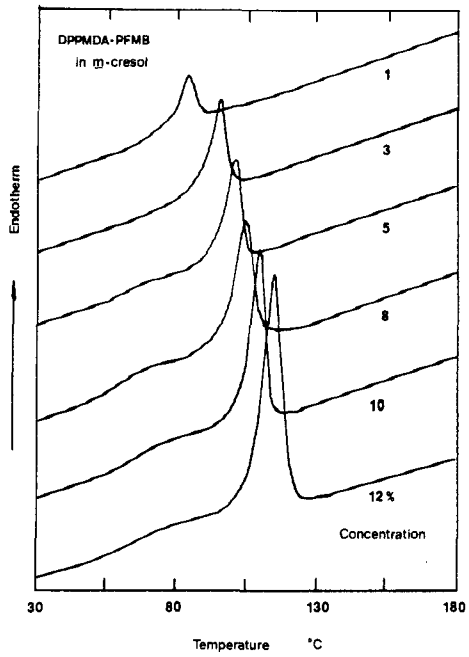

Figure 1. DSC heating traces of the as-polymerized DPPMDA–PFMB samples at different concentration. The heating rate is 10 °C/min.

Such an order/disorder transition can be directly proven from the PLM observations. At low temperatures, the samples are in the gel state. Under PLM, spherulitic-like textures with high birefringence are seen as shown in Figure 2. Figure 2a shows the texture observed in the gel containing 8.5% concentration, and Figure 2b shows more dense and tilted textures in the gel of 12% concentration. The extinction cross patterns are clear. To distinguish this texture from crystal spherulites, one can simply rotate the sample and see the direction change of the extinction cross pattern. If the extinction cross pattern remains unchanged, the texture indicates crystalline spherulites since crystallization with radial growth is three-dimensionally isotropic. On the other hand, if the extinction cross pattern rotates in the same direction as does the sample, a lyotropic liquid-crystal texture with positive birefringence is indicated. If it rotates in the opposite direction, negative birefringence is indicated. This is because of special orientations of the rigid-rod polymer chains.[39] In our observations, the textures as shown in Figure 2 are classified to be lyotropic liquid crystals with negative birefringence. With changing DPPMDA–PFMB concentration, the density of this texture changes. However, the texture pattern is essentially unchanged. When one heats a sample displaying this texture in the hot stage at 10 °C/min, the texture disappears at the temperature that corresponds to our DSC measurements (see Figure 1). This confirms that the endothermic process observed through DSC is indeed characteristic of an order/disorder transition. In our case, it is a transition from a lyotropic liquid-crystal state to an isotropic solution state.

A direct observation of the gel/sol transition based on Ferry's definition is available from thermal mechanical measurements. We adopted the ball-drop experiment since it is sensitive to the liquification change of the system. Figure 3 illustrates the phase boundaries observed in both DSC and ball-drop experiments. It is interesting that the temperatures at which the order/disorder transition occurs are close to the temperatures where the liquification

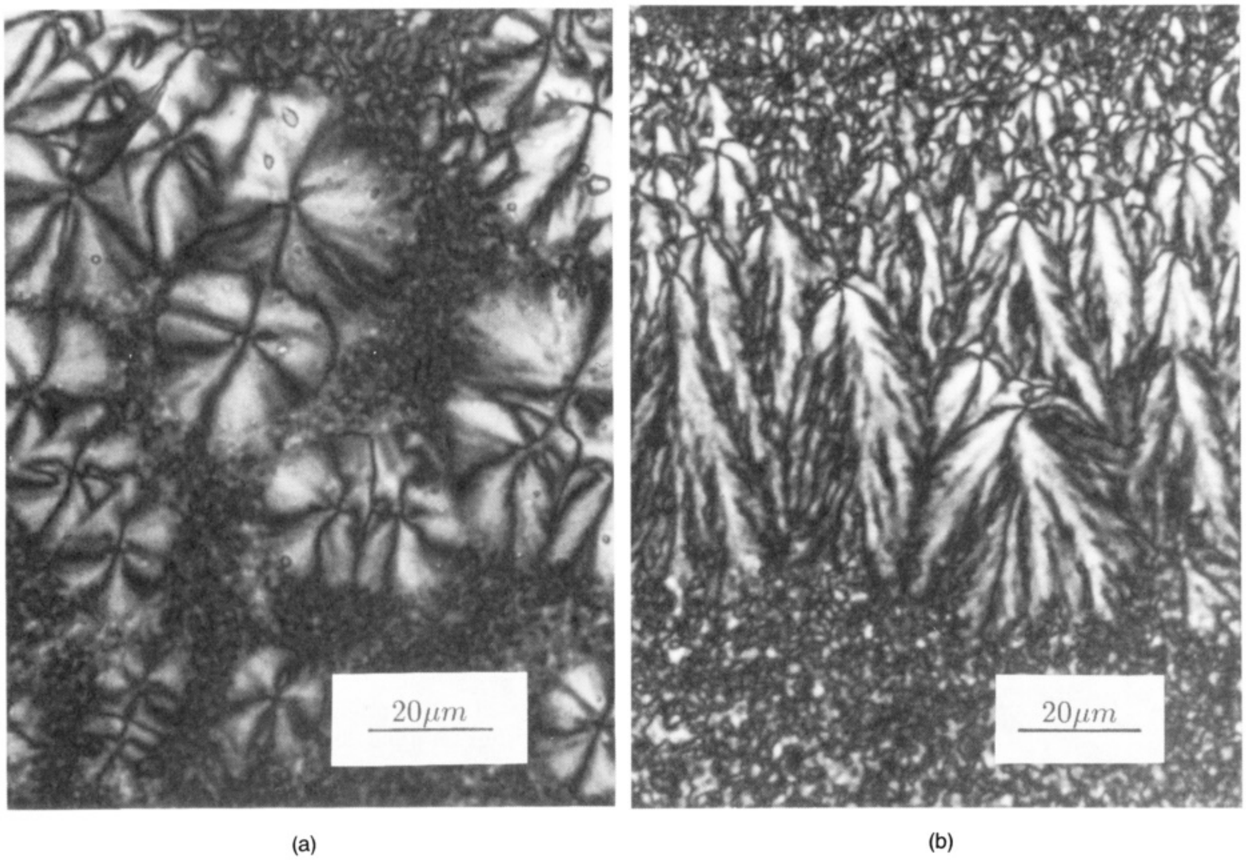

Figure 2. Spherulitic-like lyotropic liquid-crystal texture in the gel state (30 °C) at two different concentrations (w/w): (a) 8.5%; (b) 12%.

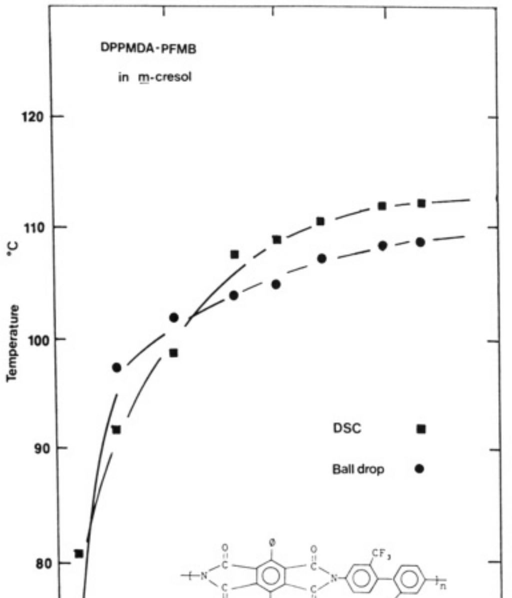

Figure 3. Phase boundaries of the DPPMDA–PFMB samples measured through DSC and ball-drop experiments at different concentrations.

changes, despite the fact that they could in principle be independent of each other. Therefore, our results indicate that accompanying the order/disorder transition, a gel/sol transition simultaneously occurs during heating in the as-polymerized DPPMDA–PFMB samples.

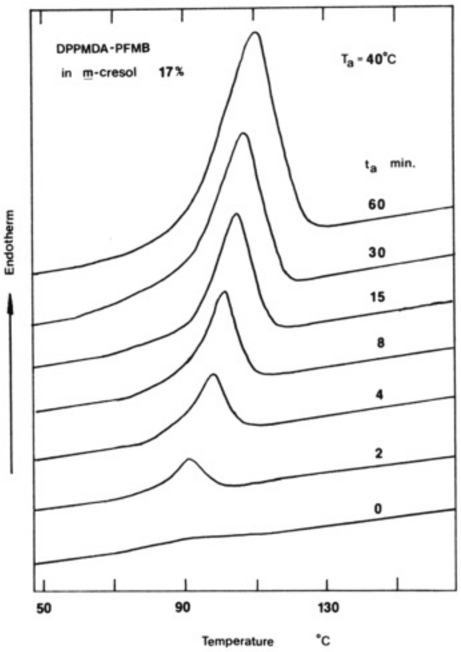

Figure 4. DSC heating traces of the samples after isothermal experiments at 40 °C for different annealing times.

The next step is to investigate structure formation kinetics in DPPMDA–PFMB. Basically, two kinetics should be studied: the kinetics of forming the lyotropic liquid-crystal state, and the kinetics of forming the mechanical gel. Figure 4 shows DSC heating traces of the DPPMDA–PFMB samples with 17% concentration after the samples were quenched from 170 to 40 °C and held for different annealing times. It is evident from the reheating trace after immediate quenching (annealing time t_a = 0) that little to no endothermic order/disorder

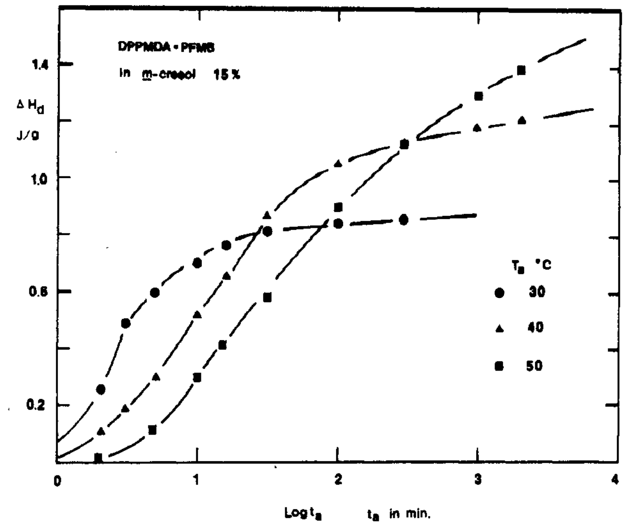

Figure 5. Relationships between heats of transition (ΔH_d) and logarithm of annealing time ($\log t_a$) for DPPMDA–PFMB samples with constant concentration (15%) at different annealing temperatures (T_a).

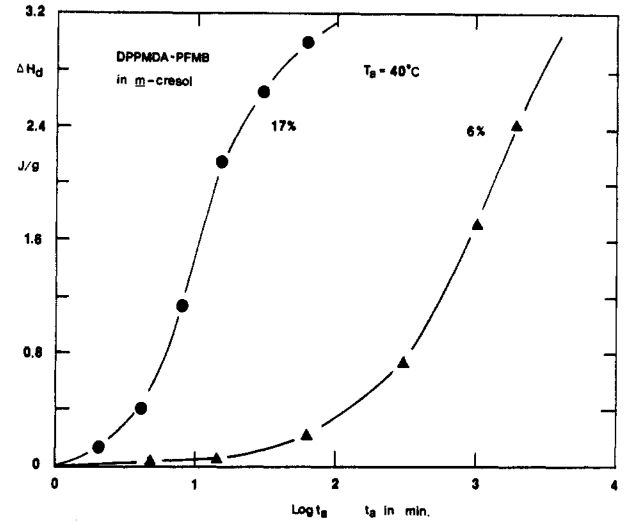

Figure 6. Relationships between ΔH_d and $\log t_a$ for the samples with two different concentrations (6% and 17%) at constant annealing temperature (40 °C).

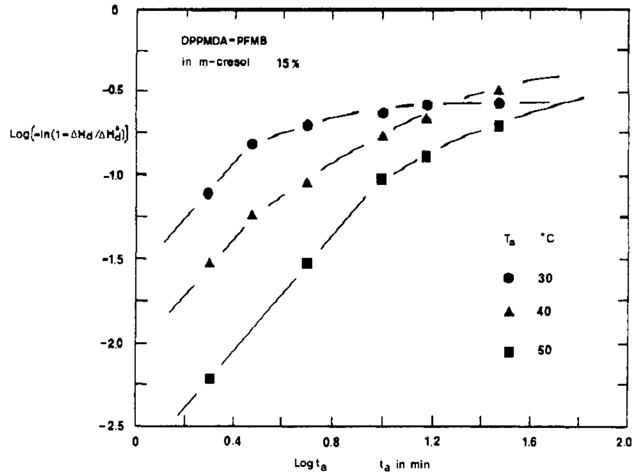

Figure 7. Relationships between $\log\,[-\ln\,(1 - \Delta H_d/\Delta H_d°)]$ and $\log t_a$ for the order/disorder transition at different isothermal temperatures for DPPMDA–PFMB samples with constant concentration (15%).

transition occurs. With increasing annealing time, an endothermic peak gradually develops; its peak shifts to higher temperatures (T_d), and its heat of transition (ΔH_d) also increases.

Figure 5 shows relationships between the heat of transition (ΔH_d) versus logarithm of annealing time ($\log t_a$) at different annealing temperatures for DPPMDA–PFMB samples with constant concentration (15%). It is interesting that with decreasing annealing temperature the structure formation process accelerates, but results in a lower heat of transition. For example, at T_a = 30 °C, the structure developed nears completion at about 30 min, and it contributes 0.8 J/g to the heat of transition. Longer annealing time leads to only a very minor increase in the heat of transition, indicating a perfection process. However, at T_a = 50 °C, even with an annealing time longer than 1 month, the structure development is still not complete but exhibits a higher heat of transition (almost double the value compared with that at T_a = 30 °C). Furthermore, the structure formation kinetics is also concentration dependent, as shown in Figure 6. At the same annealing temperature (40 °C), the structure development in the samples with 17% concentration occurs about 2 orders of magnitude faster than for that with 6% concentration.

If we plot relationships between $\log\,[-\ln\,(1 - \Delta H_d/\Delta H_d°)]$ and logarithm of annealing time, as shown in Figure 7, at three different annealing temperatures (using data from Figure 5), linear relationships can be found in the initial stage of structure development. The value of ΔH_d is the maximum ΔH_d experimentally observed. The slopes of these linear relationships range between 1.7 and 2.0. They seem invariant with annealing temperature at constant concentration. After the initial structure development, a perfection process with very low slope values seems to appear as shown in Figure 7. The data treatment in Figure 7 is, in fact, a type of Avrami equation.[40] An Avrami exponent of 1.7–2.0 typically indicates a two-dimensional growth mechanism.[41] When one uses the Avrami equation to treat data shown in Figure 6, the Avrami exponent is essentially unchanged with varying DPPMDA–PFMB concentration. This reveals that the structure formation mechanism for this lyotropic liquid crystal differs little with concentration change. However, with lower concentrations, the development of this structure becomes increasingly prolonged, as indicated in Figure 6.

We ask ourselves whether this lyotropic liquid-crystal structure is responsible for gelation. Figure 8 shows the results of SALS experiments for samples of two different concentrations (0.5% and 12%), quenched from 170 to 25 °C and annealed at different times. The lower concentration (0.5%) sample does not form gel at 25 °C even at prolonged annealing times. After quenching, the immediate SALS pattern does not show any scattering, as shown in Figure 8a. This reveals that there is no texture formed in the solution. During long annealing times the sample shows the X-type H_v SALS pattern, indicating developments of a spherulitic type of texture (Figure 8b). For the high-concentration sample, there is also no scattering pattern seen at t_a = 0 (Figure 8c). However, with 2 h of annealing time, in addition to the X-type H_v pattern attributed to the spherulitic type of texture, one can find in Figure 8d a strong scattering in the small-angle region near the incident beam. Such a pattern corresponds to rodlike morphology, and it is not found in the 0.5% concentration sample. As a consequence, this rodlike texture must develop in the high-concentration sample, which should be associated with the gelation process. Therefore, we must further study the kinetics of mechanical gelation. In Figure 9, the time of gelation, t_g, refers

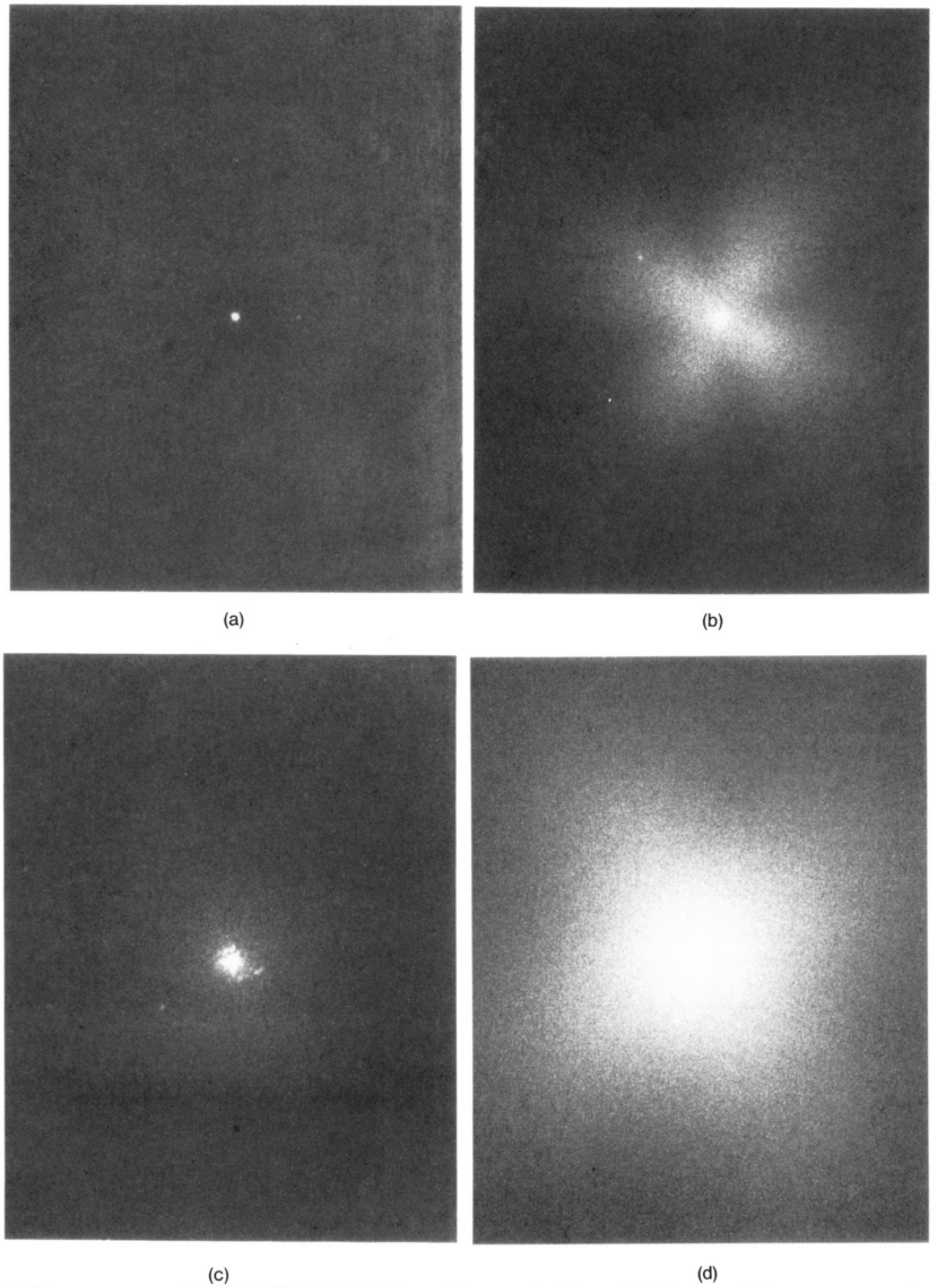

Figure 8. SALS measurements for the DPPMDA–PFMB samples quenched from 170 °C at two different concentrations: (a) 0.5% w/w at T_a = 25 °C, t_a = 0 h; (b) 0.5% w/w at T_a = 25 °C, t_a = 160 h, where the system is not in gel state; (c) 12% w/w at T_a = 25 °C, t_a = 0 h; (d) 12% w/w at T_a = 25 °C, t_a = 2 h, where the system is in gel state. A scale bar of 0.25 cm corresponds to 1° scattering angle.

to when there is no steady-state flow. It is obvious that with increasing DPPMDA–PFMB concentration, this time decreases logarithmically at the same supercooling ($\Delta T_a = T_{gel} - T_a$). On the other hand, the time of gelation increases with temperature (or decreasing supercooling) at a constant concentration. Basically, Figure 9 serves as a map of the mechanical gelation kinetics.

In comparing this kinetic map of mechanical gelation with the lyotropic liquid-crystal formation, it is evident that the kinetics are quite different. This indicates that, indeed, a development of the lyotropic liquid crystal is not responsible for the mechanical gelation. Instead, two different processes coexist. A relatively fast mechanical gelation is followed by slow development of the lyotropic liquid crystal in the gel state.

A question of particular importance: what is the mechanical gel formation mechanism? Miller et al.[26,27] hypothesized that gelation of nonionic PBLG in poor solvents was the result of liquid–liquid phase separation by a spinodal decomposition.[42] This speculation was based

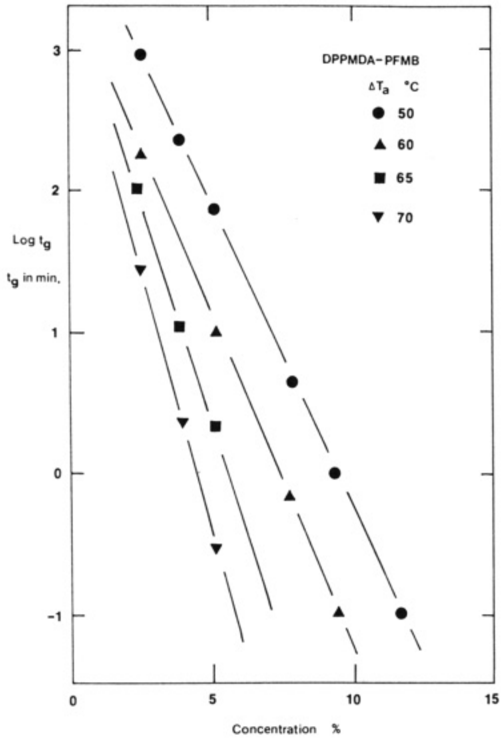

Figure 9. Relationships between the times of gelation and supercooling for the quenched DPPMDA-PFMB samples at different concentrations.

on freeze fracture electron microscopy observations,[27] where a distinctly bicontinuous structure can be found, and a relatively flat phase boundary, which suggests a narrow metastability gap. However, kinetic structure investigations by light scattering do not show a classical spinodal mechanism in dilute PBLG gels.[29,30] On the basis of the observations of Russo and other workers, the scattering power (or turbidity) has dramatic changes with gel temperature. This indicates that development of concentration inhomogeneities is primarily through expansion of the concentration gradient and not physical size considerations. It was proposed that those observations could be explained in terms of the polymer mobility present during the highly entangled state through which an isotropic solution must pass en route to equilibrium phase separation.[30,43,44]

A system closer to our case is that of the PBZT/H_2SO_4 (97%) gels. There is circumstantial evidence for microphase separation by a nonequilibrium, nucleation-free mechanism from the decidedly porous, bicontinuous texture. Microfibrillar networks in this system have been reported.[34,35] By using video epillumination microscopy, Russo et al. have followed "real-time" visualization of the gelation process and observed that initially large inhomogeneities give way to a smaller porous structure.[33] In our systems, we have found from SEM that similar microfibrillar networks exist, as shown in Figure 10. Figure 10a is representative of the texture in a concentration of 7.8% DPPMDA-PFMB sample, and Figure 10b shows texture observed in a concentration of 15%. The microfibrillar texture in Figure 10a displays relatively open networks. Changing the concentration leads to compact aggregates of the microfibrillar texture. Therefore, the mechanical gel formation process also seems to follow a nonequilibrium nucleation-free mechanism with rapid liquid-liquid phase separation. Nevertheless, it should be noted that the sample preparation in this SEM study was by solvent extraction as described in the Experimental Section. Although extra care was taken, a variation of the textures observed with that present in the fresh gels might be possible.

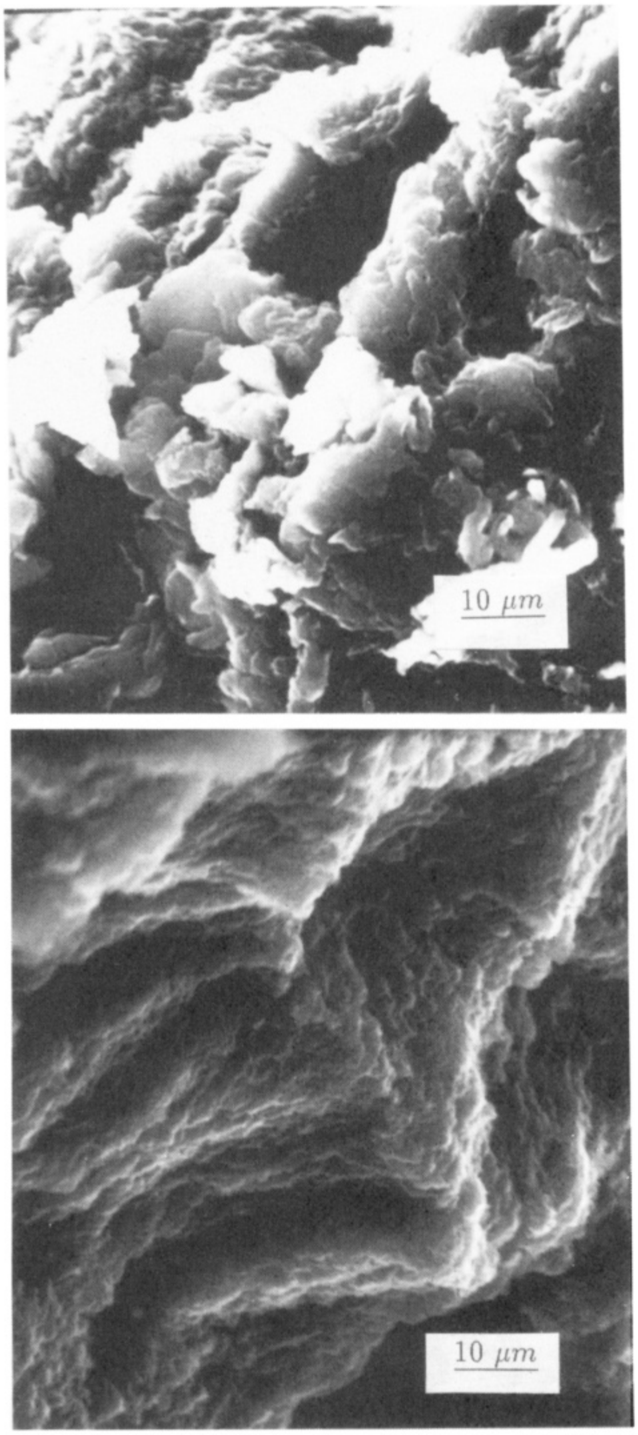

Figure 10. Microfibrillar textures observed through SEM at two different concentrations: (a) 7.8% w/w at T_a = 25 °C, t_a = 150 h; (b) 15% w/w at T_c = 25 °C, t_a = 150 h.

Finally, it is interesting to ask, how does the lyotropic liquid crystal develop in the gel state? The answer is largely speculative. However, it must be associated with two processes. First, the liquid-liquid phase separation creates a bicontinuous phase where certain locations are rich in polymer. When the DPPMDA-PFMB concentration reaches its critical concentration, an anisotropic phase may form. Second, these anisotropic domains grow further into the textures that were observed under PLM. This indicates that a large-scale molecular motion must be involved. Since the molecular motion is temperature dependent, the structure cannot be fully developed at low temperatures, even though the initial stage of the development is rather fast (see Figure 5). If this is true, we expect that the second process should also be molecular mass dependent. This idea of a two-step gelation processes has also been recently reported in another rigid-rod polymer (PBLG), in which the liquid-crystalline state was observed to form after a very long time in gels that were initially amorphous. The dynamic light-scattering data obtained by Russo's group indicated that molecular motion of polymers within the gel enable slow structural reorganizations to occur.[30] On the other hand, in synthetic random coil polymers and in some biological systems, similar two-step gelations have also been observed.[45–47]

Conclusion

DPPMDA-PFMB solutions in *m*-cresol are perhaps one of the few examples for which rigid-rod polymers have solubility in an organic solvent. With decreasing temperature, the solution may undergo a liquid–liquid phase separation to form a mechanical gel. A parallel structural development is lyotropic liquid-crystal formation from the gel state. The kinetics of this state seem to involve nucleation and growth mechanisms. This process must be related to the local concentration and orientation of the polymer and to the polymer mobility in the gel state. The lyotropic liquid-crystal formation is not responsible for the mechanical gelation. However, the liquid–liquid phase separation may serve as a precursor to this state.

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