

Phase Transformations in Concentrated Solutions of Poly(γ -benzyl L-glutamate)

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ABSTRACT: The phenomenon of thermoreversible gelation is studied in solutions of poly(γ -benzyl L-glutamate) (PBLG) in benzyl alcohol at concentrations above the onset of liquid crystallinity. Phase transformations are determined by optical microscopy, differential scanning calorimetry (DSC), and small-angle X-ray scattering (SAXS) measurements. The gels obtained from these solutions exhibit two melting endotherms upon heating in the DSC. Strong diffuse scattering at small angles indicates a heterogeneous microstructure even in gels obtained from a single-phase liquid crystal solution. Analysis of the scattering patterns indicates a random two-phase structure having a characteristic length scale of 5–30 nm depending on sample history and concentration. The state of aggregation of the PBLG helices in the gel, determined from the low-angle diffraction, depends on the kinetic pathway for gelation. Disordered packing of adjacent helices is observed in a quenched gel. Two different crystalline phases are obtained either by slow gelation at a high temperature or by annealing a quenched gel. The observation of three states of aggregation in gels at the same concentration and temperature confirms the idea that concentrated PBLG gels may exist in a nonequilibrium state which depends strongly on sample history. We suggest that the two melting endotherms observed by DSC are also due to the heterogeneous microstructure. At a lower temperature aggregates melt to a surrounding isotropic solution whereas final disaggregation to a liquid crystal solution occurs at a somewhat higher temperature.

Introduction

Poly(γ -benzyl L-glutamate) (PBLG) is a synthetic polypeptide which is soluble in several organic solvents in which it assumes a helical conformation. Its solutions have been used for many years as a model system to study the phase behavior of rigid polymers. The typical equilibrium between isotropic and liquid crystalline phases, predicted theoretically by Flory,¹ is by now well established.² Other features pertaining to the phase behavior are less understood, in particular the phenomena of thermoreversible gelation and the multiplicity of crystalline forms.³

PBLG solutions in several solvents form self-supporting gels even at very dilute concentrations. Gelation can occur from the isotropic, biphasic, or liquid crystalline (LC) solutions and is induced by a reduction in temperature or addition of a nonsolvent.^{4–18} Gels formed from isotropic solutions remain isotropic, whereas gels formed from the biphasic or LC state retain features of the texture in the precursor phase. Despite many years of research, there is still much debate as to the mechanism of the gelation process and its relation to the equilibrium phase diagram.¹⁰ It has been suggested that the basis for gelation is phase separation to dilute isotropic and concentrated LC phases, induced by a reduction of temperature or the presence of moisture.^{4,5} Formation of crystalline phases has also been considered as the driving force for gelation,^{7–9,15} in particular in the PBLG/benzyl alcohol (BA) system. Nucleation and growth⁷ as well as diffusion-controlled cluster aggregation^{19,20} have been suggested as possible mechanisms for gelation. A classification of PBLG gels in relation to their precursor solution state was recently presented.¹⁰ The morphology of PBLG gels was shown to be a ramified network of interconnected microfibrils, ranging in width from under 10 nm to about 100 nm.^{19,21}

Larger inhomogeneities, on a micron scale, have also been observed in isotropic gels by light scattering and optical microscopy.^{13,22}

The solid state of PBLG is crystalline due to ordered packing of the helices. Five different crystalline forms have been reported. The realization of any particular form depends strongly on the solvent and method used for casting the solid film. The B form has a monoclinic unit cell containing two helices with opposite direction of main chain sequences, and it exhibits well-developed three-dimensional crystallinity.^{23,24} It is obtained from solutions in so-called "B-solvents" such as dimethylformamide (DMF) and benzyl alcohol by casting at high temperature. Very slow casting from a "B-solvent" at high temperature under vacuum resulted in ordered crystals with very large unit cells, containing 7 (form D) or 19 (form E) PBLG helices.²⁵ Casting PBLG films from solutions in DMF or pyridine ("B solvents") at low temperature resulted in a gel exhibiting a crystalline pattern termed the "complex phase",²⁶ which exists only in the presence of the solvent. Its structure was showed to be composed of three parallel PBLG helices with a unique quasi-helical packing scheme of the side chain benzyl groups.²⁷ Drying of such gels produced a disordered pseudohexagonal crystal containing four PBLG chains, termed the A form.²³ Casting solutions in chlorinated hydrocarbons produced the C form crystalline phase, described as a nearly hexagonal packing of chains in the plane perpendicular to the helical axis, with random placements of chains along this axis.²⁸

Two crystalline phases in gels of PBLG in benzyl alcohol (BA) were identified by Sasaki et al.,^{7,8} denoted complex A and B, and interpreted as crystalline complexes containing solvent molecules in the unit cell. Complex A is formed when the PBLG/BA solution is gelled above 48 °C, whereas repeated cycles of quenching and heating produced the complex B phase. The unit cell models presented for these phases suggested that the volume fraction of PBLG is 0.76 in complex A and 0.95 in complex B. The melting point of the

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complex B gel was a few degrees higher than the complex A gel; thus a single quench to low temperatures produced gels exhibiting two melting endotherms.⁷ The double melting transitions were observed only in concentrated PBLG/BA gels, above the critical concentration for liquid crystallinity in the solution.^{7,15} This behavior was associated with possible occurrence of different solid phases in the gel, such as a vitrified liquid crystal, a crystal solvate, and a pure polymer phase. Using infrared spectroscopy, Prystupa and Donald assigned three stages to the melting of PBLG/BA gels: the onset of side chain motion, fragmentation of polymer bundles into elementary fibrils, and finally fragmentation into individual chains.³⁰ Double-melting behavior was also observed in isotropic PBLG gels in solvent/nonsolvent mixtures,²⁹ whereby liquid-liquid phase separation was implied.

PBLG solutions can be oriented in a magnetic field due to the net magnetic dipole parallel to the helix direction.³¹⁻³⁴ As a result, the state of order in concentrated PBLG/BA solutions and gels could be followed by deuterium NMR experiments using a solvent probe (deuterated benzene).^{11,34} The degree of order of the solvent probe was shown to increase during cooling, with a discontinuity at the gelation temperature at which its mobility was reduced significantly.

In this study we evaluate the structural transformations in concentrated PBLG solutions undergoing gelation and gel melting. The objective is to understand the observed microstructures and crystalline phases in terms of an equilibrium phase diagram, which includes isotropic and LC solutions as well as crystal and crystal-solvate phases, and in consideration of kinetic processes of transformations between the equilibrium phases.

Experimental Section

PBLG was obtained from Sigma Chemical Co. Ltd., having a nominal molecular weight of 86 000. Spectroscopic grade benzyl alcohol (BA) was obtained from Merck GmbH and distilled before use. Solutions up to 30% (w/w) were prepared by dissolution at 80 °C with stirring. More concentrated solutions were prepared by dissolution in a mixed solvent composed of BA and chloroform, followed by evaporation of chloroform. The solutions were placed in thin-walled glass capillaries (Müller) for small-angle X-ray scattering (SAXS) measurements.

SAXS measurements were performed using Cu K α radiation with a compact Kratky camera having a temperature-controlled sample chamber (A. Paar Co.) and a linear position-sensitive detector system (Raytech). SAXS patterns are presented as a function of the scattering vector $h = 4\pi \sin \theta / \lambda$, 2θ being the scattering angle and λ the wavelength. Desmearing was performed using the procedure of Glatter³⁵ for indirect transformation in reciprocal space (ITR), using a stabilization function with low values in the peak regions (STAB). Differential scanning calorimetry (DSC) measurements were performed with a Mettler 2000 DSC instrument at a scan rate of 10 °C/min using high-pressure pans containing about 30 mg of sample. For observations by light microscopy, an Olympus microscope equipped with a Mettler hot stage and a CCD video camera (Sony) was used. Samples were sealed between a glass slide and a cover slip with epoxy glue and viewed between crossed polarizers.

Results and Discussion

The temperatures of gelation and gel melting were identified as enthalpic first-order transitions registered by DSC. The temperature range and the hysteresis between gelation and melting temperatures were in accord with previous studies.^{7,11,15} In general, the

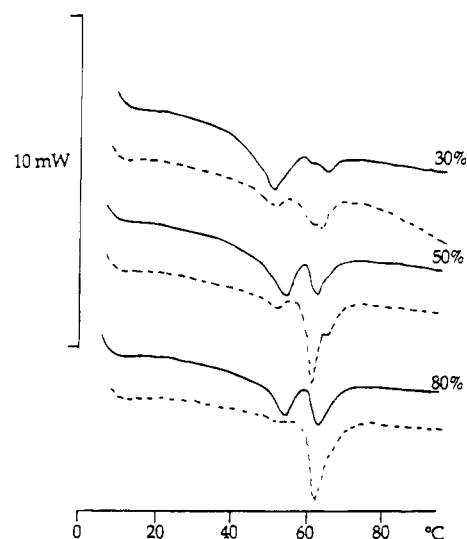


Figure 1. DSC traces of gels containing 30, 50, and 80% PBLG in benzyl alcohol: solid line, first heating run; dashed line, second heating run.

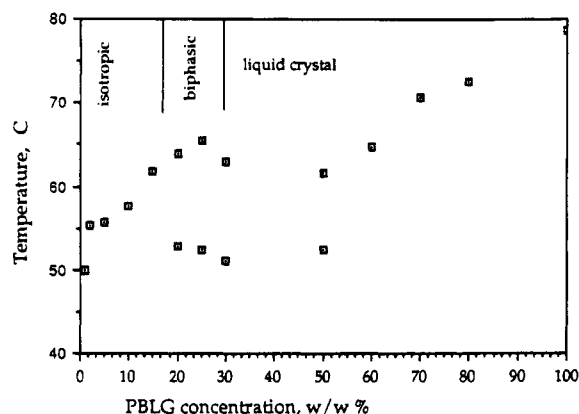


Figure 2. Temperatures of the endothermic peaks in the second heating runs of PBLG gels as a function of concentration. The state of the solution from which the gel was obtained is marked above the plot.

gelation temperature is significantly lower than the gel melting temperature, and its value is dependent to a large extent on the rate of cooling and thermal history of the solution. Endothermic transitions mark the melting of the gels. For isotropic gels obtained from isotropic solutions containing less than 20% PBLG, a single melting endotherm was observed. At higher PBLG concentrations two endotherms were observed during heating, as has already been reported.^{7,15} Traces of the first and second heating of gels containing 30, 50, and 80% (w/w) PBLG are plotted in Figure 1. Two peaks are observed in the first heating in the range of 50–65 °C. In subsequent heating cycles of gels containing 30–50% PBLG, the higher temperature peak becomes more prominent. Only one peak is observed in the second heating of gels containing 60% PBLG or more. The temperatures of the endothermic peaks in the second heating of gels are plotted in Figure 2 as a function of the gel concentration. The state of the solution from which the gel was obtained is noted in Figure 2 as either isotropic, biphasic, or liquid crystal. The origin of the two endothermic peaks is still being debated. Melting of two different crystal forms, which may contain both polymer and solvent in the unit cell, was suggested.^{7,15} Alternatively, a two-step melting process was proposed whereby polymer bundles break up first into elementary fibrils and subsequently into

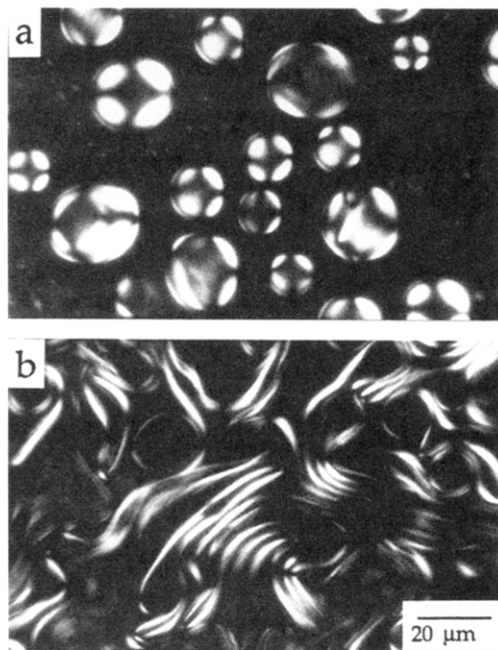


Figure 3. Optical micrographs (crossed polarizers) of PBLG/BA gels at 25 °C: (a) 20% PBLG; (b) 25% PBLG;

individual chains.³⁰ We will propose later another explanation related to the heterogeneous nonequilibrium microstructure of the gel.

The transition from the isotropic to the LC state is prominent when observed by optical microscopy under crossed polarizers. In Figure 3, an image of a gel containing 20% PBLG (MW = 86 000) in BA at 25 °C exhibits birefringent domains of the LC phase embedded in the isotropic phase. Gels containing 18% or less PBLG of MW = 86 000 appeared to be optically isotropic. At 25% PBLG the gel still appears biphasic, but now spherical isotropic domains appear to be embedded in a continuous LC phase, as shown in Figure 3b. Above 25% PBLG the gels appear in the optical microscope as a single LC phase. The onset of flow behavior in the images observed in the optical microscope marked the melting of the gels at all concentrations observed.

Both phases coexisting in the 20% PBLG sample are in the gel state at 25 °C. Its structure can be described as birefringent gel droplets embedded in an isotropic gel matrix. The transitions in this biphasic gel sample, when it was heated at a rate of 2 °C/min on a hot stage in the optical microscope, were recorded by a video camera. Melting of the isotropic gel matrix at about 58 °C was evident clearly from the onset of motion of the birefringent droplets. The temperature at which the LC gel within the birefringent droplets melted into the LC state could not be observed optically. However, there is indirect evidence that the birefringent regions become fluid at a higher temperature than that at which the isotropic gel matrix melts. Above 58 °C occasional impingement of two mobile birefringent droplets could be observed in the field of view. In the temperature range of 58–70 °C the impinged droplets remained as separate entities with well-defined boundaries for as long as they could be observed in the field of view, up to about 45 min. Above 70 °C coalescence of impinged droplets could be observed occasionally. Strikingly, in the temperature range of 75–85 °C coalescence of birefringent droplets could be observed in less than 1 min after impingement. Coalescence of a pair of droplets is shown in Figure 4 during a temperature scan at

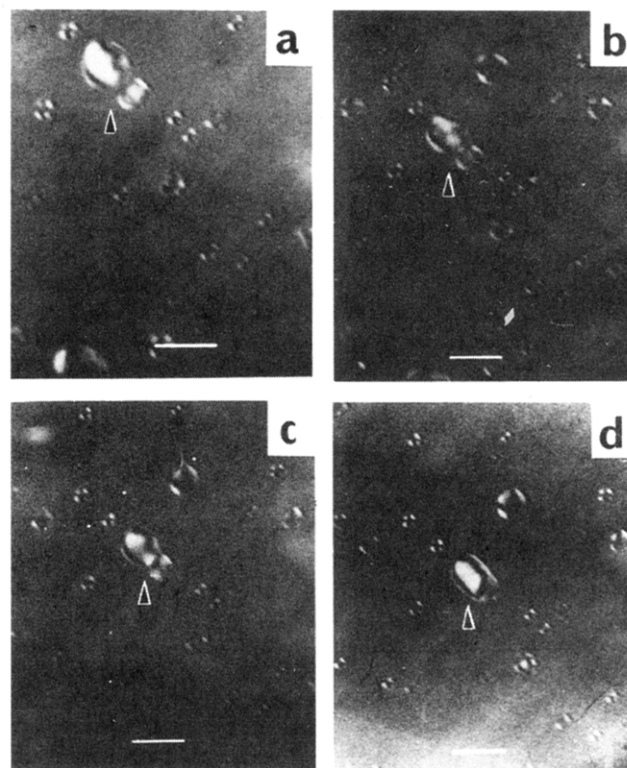


Figure 4. Video images of the 20% PBLG solution at temperatures above the melting of the isotropic gel matrix, at which the birefringent droplets become mobile. Note the coalescence of the droplets marked by the arrow. (a) 76 °C; (b) 82 °C; (c) 83 °C; (d) 84 °C; heating rate 2 °C/min.

2 °C/min. At even higher temperatures the LC phase melted into the isotropic phase, in which birefringence was not observed. Biphasic gels containing 25% PBLG, in which the birefringent regions formed the continuous phase, exhibited somewhat different behavior. At about 61 °C the boundaries of the isotropic domains were blurred. This was followed by observation of flow in the entire field of view above 65 °C.

These results suggest an alternative explanation for the double melting endotherms observed by DSC in biphasic gels: the first peak is due to melting of isotropic domains, and the second peak is due to melting of LC domains. Previous studies on isotropic gels have shown them to be composed of microfibrils in which the PBLG helices are packed. The microcrystalline nature of the microfibrils was suggested by an observation of a weak Bragg reflection at a spacing of 2 nm in gels containing just 1% PBLG.³⁶ It is plausible that the microcrystals in the isotropic gel matrix melt at a lower temperature than the crystallites within the birefringent gel regions. The melting of a polymer crystal to an isotropic solution is predicted to occur at a lower temperature than when it melts to a liquid crystal solution at the same concentration.^{37,38} This is due to the lower entropy difference between the two states in the latter case and to the smaller crystallite size in the former case. However, double melting endotherms are also observed in gels obtained from a single-phase LC solution and which appear optically as a single phase. Extension of our hypothesis to such gels will be discussed following analysis of their microstructure.

The state of aggregation of PBLG in the solutions and gels under study can be deduced from results of SAXS measurements, a preliminary account of which has been presented.²⁰ The sample containing 50% PBLG is in the liquid crystal state at 80 °C, as evident from the

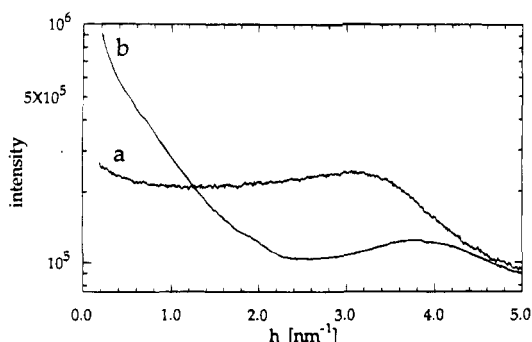


Figure 5. Small-angle X-ray scattering patterns from a 50% PBLG solution: (a) the liquid crystal solution at 80 °C; (b) the gel obtained by quenching to 20 °C.

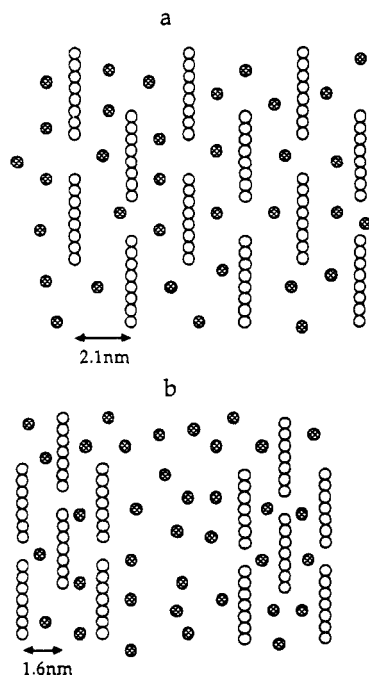


Figure 6. Schematic representation of the microstructural transition which occurs by quenching the liquid crystal solution, as deduced from the SAXS measurements in Figure 5: (a) the liquid crystal solution; (b) the quenched gel.

scattering pattern labeled a in Figure 5. The broad halo centered at 2.10 nm ($h = 3.00 \text{ nm}^{-1}$) indicates the interhelical separation in the LC state and is comparable to the observation of Luzzati for PBLG/pyridine of the same concentration.²⁶ When the sample is quenched to 20 °C, the scattering pattern labeled b shown in Figure 5 is observed. Two changes can be seen in the scattering pattern: a shift to higher angles of the LC halo, to a spacing of 1.64 nm ($h = 3.83 \text{ nm}^{-1}$), and a great increase in the excess scattering at small angles. The latter indicates that the quenched sample is inhomogeneous, containing regions with different polymer concentration. The former indicates that the polymer-rich region is a concentrated liquid crystal in which the interhelical spacing is close to the diameter of the PBLG "cylinder" (1.55 nm).⁷ A schematic representation of this transition is shown in Figure 6. These observations support the model by which quenching results in separation of the ordered solution to concentrated LC and dilute (isotropic) domains. It is possible that the temperature quench from 80 to 20 °C brings the LC solution to a thermodynamically unstable state within the spinodal. In such a case, as the concentration of the polymer-rich domains increases, it may undergo a

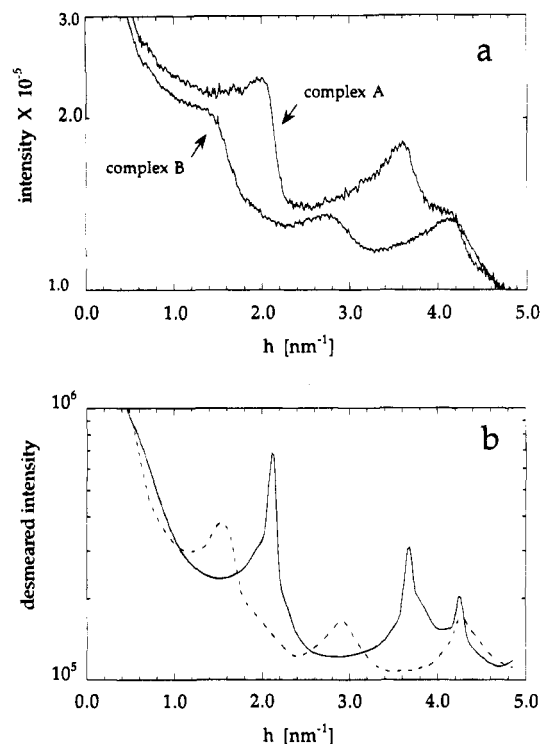


Figure 7. (a) SAXS patterns from gels containing 50% PBLG at 50 °C after the following thermal history: complex A obtained by cooling slowly to 50 °C, and complex B obtained by quenching to 20 °C and annealing at 50 °C. (b) The desmeared scattering patterns: solid line, complex A; dashed line, complex B.

glass transition producing a vitrified LC state, as reflected in its scattering pattern. Thermoreversible gelation of polymer solutions due to intersection of a liquid-liquid phase separation and a glass transition have already been discussed.^{39,40}

When the 50% PBLG solution is allowed to gel slowly from 80 to 50 °C, the pattern marked complex A in Figure 7a is observed. The peaks at 3.1, 1.75, and 1.5 nm ($h = 2.0, 3.6, \text{ and } 4.2 \text{ nm}^{-1}$, respectively) agree with the first three lines of the complex A pattern reported by Sasaki et al.⁷ Their model for this phase inferred that the unit cell contained both PBLG and BA in a stoichiometric ratio, with a polymer volume fraction of 0.76. The diffraction peaks of complex A disappear when the sample is heated above 65 °C. When the sample containing 50% PBLG is first quenched from 80 to 20 °C and then annealed at 50 °C, the pattern marked complex B in Figure 7a is observed. The peaks of this pattern at 4.4, 2.3, and 1.5 nm ($h = 1.4, 2.7, \text{ and } 4.2 \text{ nm}^{-1}$, respectively) agree with the first three lines reported by Uematsu and co-workers for complex B.⁸ The reflections from the complex B phase persisted upon further heating above 80 °C. The spacings of both complexes A and B show that they differ from the solid forms of PBLG. The spacings of the reflections shown in Figure 7a were verified by desmeared the experimentally measured patterns, taking into account the actual dimensions of the slit-collimated incident beam. The desmeared patterns are shown in Figure 7b.

The behavior of gels obtained from 30% PBLG solutions is similar to that of the 50% gels. The SAXS patterns from the 30% gels obtained by quenching to 20 °C and by gelation at 50 °C are shown as lines a and b in Figure 8, respectively. Again a disordered packing is indicated in the quenched gel and a complex A crystalline state appears in the slowly cooled gel. At a

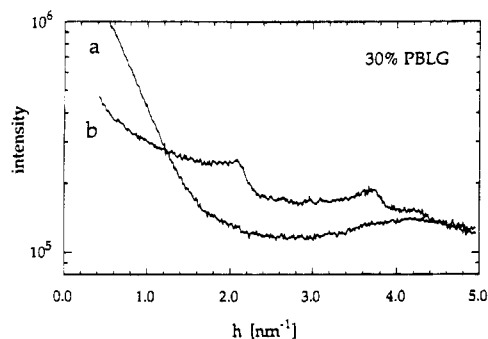


Figure 8. SAXS patterns from gels containing 30% PBLG: (a) obtained by quenching to 20 °C; (b) complex A obtained by cooling slowly to 50 °C.

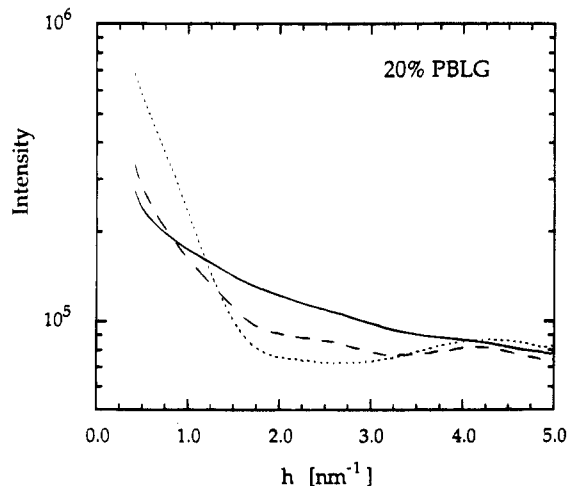


Figure 9. SAXS patterns from samples containing 20% PBLG: solid line, the solution at 70 °C; dashed line, the gel obtained by cooling slowly to 45 °C; dotted line, the gel obtained by quenching to 20 °C.

concentration of 30% PBLG the solution is near the high-concentration limit of the narrow biphasic region. Reducing the concentration to 20% brings the system close to the low-concentration limit of this biphasic region. The SAXS patterns from 20% PBLG gels are shown in Figure 9. At 70 °C, above the gel melting temperature, no diffraction maximum could be observed in the angular range where a broad peak was observed in the more concentrated liquid crystal solutions. This is probably due to the low amounts of material in the LC phase at this concentration and temperature. Upon quenching, a broad peak appears around a Bragg spacing of 1.6 nm ($h = 4 \text{ nm}^{-1}$), indicating a disordered aggregation of PBLG in a quenched LC state, as was the case for quenched gels containing 30 and 50% PBLG. Slow gelation at 45 °C, just below the melting temperature, resulted in a gel exhibiting weak reflections which could not be identified. Apparently, the small amount of LC phase present in the system prevented formation of crystals large enough for distinct diffraction, as in the more concentrated gels.

The small-angle X-ray diffraction patterns presented above are a clear indication that on the molecular level gelation is associated with aggregation of the PBLG helices, either in a disordered fashion during quenching or in a more ordered crystalline packing during gelation at low undercooling. The inhomogeneous gel microstructure due to the PBLG aggregates gives rise to the excess scattering observed at very low angles. The low-angle parts of the scattering patterns from the 50% PBLG solution at 80 °C and from the gels obtained by

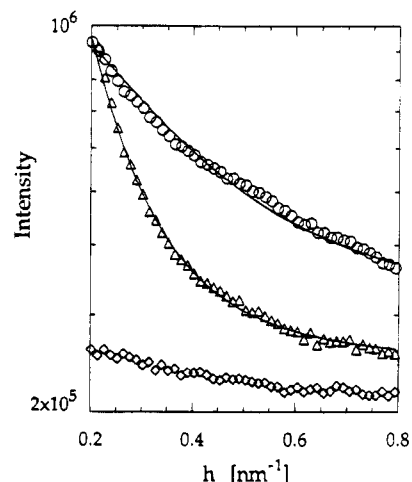


Figure 10. Low-angle parts of the SAXS patterns from samples containing 50% PBLG: (\diamond) the liquid crystal solution at 80 °C; (\triangle) the gel obtained by cooling slowly to 50 °C; (\circ) the gel obtained by quenching to 20 °C. Solid lines are fits of eq 1.

quenching to 20 °C and by gelation at 50 °C are shown in Figure 10. It is evident that the solution is a single homogeneous phase whereas the gels are heterogeneous. A characteristic dimension for PBLG aggregates can be obtained by fitting a structural model to the low-angle scattering patterns from the gels. We choose to use the model of Porod⁴¹ and Debye, Anderson and Brumberger⁴² for a random two-phase structure with sharp interfaces. It stands to reason that the molecular aggregates of PBLG are in the form of microfibrils, as observed in more dilute gels,^{5,19,21} and that the microfibrils exhibit locally some degree of orientational order. The local structure of the aggregates is therefore not strictly random. However, since the overall structure has a random distribution of local director orientations due to defects in the precursor LC state, we feel that this model can serve as a first approximation for estimating the aggregate size. The scattering pattern predicted for the random two-phase structure, when measured with slit-smeared X-ray optics, is⁴¹

$$I(h) = I(0)/(1 + \xi^2 h^2)^{3/2} + F_L \quad (1)$$

where $I(h)$ is the intensity at scattering vector h . $I(0)$ is the extrapolated intensity at zero angle, F_L is a constant describing the scattering from small-range fluctuations within the separated phases, and ξ is a characteristic length, related to the average cord length of the polymer-rich phase L_p :⁴²

$$L_p = \xi/(1 - \phi_p) \quad (2)$$

where ϕ_p is the volume fraction of the polymer-rich phase. The fits of eq 1 to the scattering patterns from the gels are shown as the solid lines through the data points in Figure 10. The characteristic lengths of the gels can be estimated as 2.4 and 9.4 nm for the gels obtained by quenching to 20 °C and by gelation at 50 °C, respectively. By assuming that the polymer volume fraction of the complex A phase is 0.76, that in the quenched phase it is 1.0, and that the densities of all phases involved are equal, the volume fraction of the polymer-rich phase can be roughly estimated. This allows evaluation of the dimensions of the PBLG aggregates as average cord lengths of 4.8 and 27.5 nm for

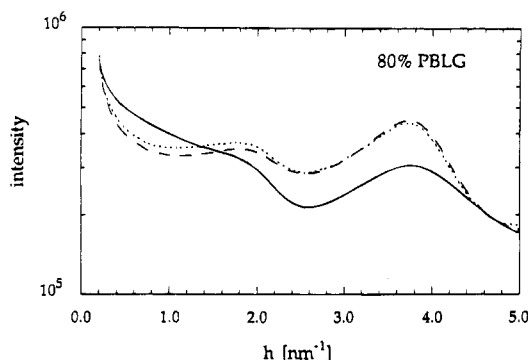


Figure 11. SAXS patterns from gels containing 80% PBLG: solid line, as prepared at 20 °C; dashed line, after heating to 60 °C; dotted line, after heating to 100 °C.

the gels obtained by quenching to 20 °C and by gelation at 50 °C, respectively.

The scattering measurements at low angles show that although the 50% PBLG gel appears as a uniform birefringent phase when observed by optical microscopy, the microstructure of the gel is inhomogeneous containing PBLG-rich aggregates and solvent-rich regions. Evidently, slow gelation yields a coarser structure with larger aggregates than rapid quenching. The nature of the polymer-poor regions cannot be determined by the present experiments. We suggest that they are composed predominantly of the solvent BA excluded from the polymer-rich aggregates. Preliminary NMR measurements using deuterated BA show it to exist in an isotropic liquid state in the concentrated gels.⁴³ We now return the observation of two melting endotherms by DSC. Two peaks were observed even in samples allowed to gel slowly at low undercooling and which exhibited only the complex A pattern. We therefore suggest that this phenomenon is related to the inhomogeneous microstructure and not to occurrence of different crystalline forms, in the following way: the PBLG aggregates are in contact with isotropic solvent-rich regions so that the first peak may be due to melting into an isotropic solution within the concentrated gel. As more aggregates melt, the concentration in the fluid regions reaches the LC state. The second melting peak may thus be attributed to melting of the remaining aggregates into the liquid crystal solution, at a somewhat higher temperature. It should be noted that although this explanation is consistent with experimental observations, so are other models³⁰ and this question remains open.

Gels were also made with PBLG content exceeding 50% by weight. Gels containing 60% PBLG and above exhibited two endothermic peaks in the first heating run in the DSC, but only a single peak in subsequent runs, as was shown in Figures 1 and 2. The SAXS patterns from an 80% PBLG gel, as prepared at 20 °C and heated to 60 °C and 100 °C, are shown in Figure 11. Two broad reflections, centered at about 3.3 and 1.65 nm ($h = 1.9$ and 3.8 nm^{-1} , respectively), are observed at all temperatures studied. These do not coincide with the known reflections of the A and B complex gel phases nor with the A, B, and C crystalline forms of pure PBLG. Some semblance may be found with the so-called "complex phase" observed in concentrated gels of PBLG in pyridine or DMF,^{26,27} where three equatorial reflections were observed at spacings of 3.3, 1.88, and 1.586 nm.²⁷ If so, it must be assumed that the second and third reflections are not resolved in the present experiment. Comparison of DSC and SAXS experiments of the 80%

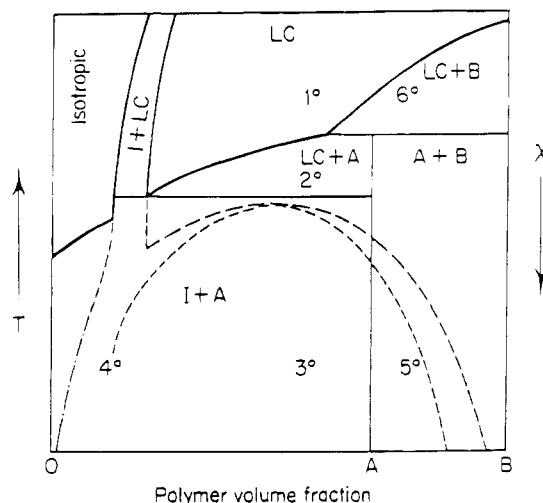


Figure 12. Schematic temperature-composition phase diagram for the PBLG/BA system. Solutions: I, isotropic; LC, liquid crystal. Crystalline solids: A, complex A; B, complex B. Dashed lines: the binodal and spinodal lines for liquid-liquid phase separation when crystallization is ignored. The numbered points are referred to in the text.

PBLG gels points to a discrepancy in the observed transition temperatures. Whereas endothermic peaks are observed by DSC around 60 °C, the broad crystalline reflections are barely changed up to 100 °C. Apparently, the main transition observed by DSC at 62 °C is not related to crystal melting, as seen from the SAXS measurements. It may be due to release of constraints on the mobility of the side chains, as occurs in the B-form of dry PBLG films at about 120 °C.⁴⁵ More experiments are required to elucidate the nature of the transitions in the very concentrated gels.

Finally, we propose to explain the transitions observed upon gelation of concentrated PBLG solutions using a schematic temperature-composition phase diagram. This does not imply that the gels are thermodynamic equilibrium states. On the contrary, the results indicate formation of an inhomogeneous non-equilibrium microstructure. However, we wish to explain the observation of three different states of aggregation of PBLG in the gels due to different thermal histories as metastable states using the equilibrium phase diagram. Using for example the 50% PBLG solution, it was shown in Figures 5 and 7 that a disordered packing resembling a concentrated LC state was obtained by quenching, whereas two different crystalline forms were obtained either by gelation at 50 °C or by annealing the quenched gel. A schematic phase diagram for PBLG/BA is shown in Figure 12. The two crystalline states shown are the complex A and complex B crystal solvates, for which the polymer volume fractions were estimated by Sasaki et al., to be 0.76⁷ and 0.95,⁸ respectively. We refrain from addressing the phase states at very high polymer concentration due to the multiplicity of PBLG crystalline forms and the lack of information on their transitions, especially in the presence of the solvent. Also shown in the schematic diagram are the isotropic solution and liquid crystal phases, separated by the narrow biphasic region at higher temperatures and a wide biphasic region at lower temperatures. Within the wide biphasic region the spinodal line is drawn schematically, as suggested by previous calculations.^{2,29} The liquidus lines are drawn schematically with a peritectic melting of complex A, without experimental proof. We also refrain from

addressing the issue of coexistence of two LC phases,^{12,44} which was not observed in our experiments and which is not relevant to the present discussion. For the sake of clarity, the liquidus is depicted above the binodal of the wide biphasic region. The observed transitions may be interpreted by means of the schematic phase diagram shown in Figure 12. Starting from a liquid crystal solution, such as 50% PBLG at 80 °C (point 1 in Figure 12), gelation within the biphasic LC-complex A region (point 2) results in crystallization of complex A. A temperature quench (to point 3) brings the system into the unstable region within the spinodal. Phase separation to dilute and concentrated domains occurs, leading to compositions which approach the spinodal line (points 4 and 5, respectively). Phase separation may be arrested at some intermediate concentration. This may be due to a percolative transition resulting from multiple interpolymer connections⁴⁶ or to a glass transition.^{39,40} The concentrated phase (point 5) can be viewed as a vitrified liquid crystal in which the PBLG helices are packed together more closely than in the initial LC state (Figure 6). Point 5 in Figure 12 is depicted at a higher polymer concentration than the complex A phase, so that annealing at an elevated temperatures (point 6) can result in transformation to the complex B.

Conclusion

The gelation and gel melting of concentrated PBLG/BA solutions exhibit complex behavior which is strongly dependent on the thermal history. The state of the solution from which the gel is obtained is of prime importance. In this study we report the behavior of gels obtained from solutions above the critical concentration for liquid crystallinity, i.e., solutions which are either biphasic or a single-phase liquid crystal. The gels obtained from these solutions exhibit two melting peaks. They show strong diffuse small-angle scattering indicating their heterogeneous microstructure, even when obtained from a single-phase liquid crystal solution. The state of aggregation of the PBLG helices in the gel, determined from the low-angle diffraction, depends on the kinetic pathway for gelation. Three states were identified: a disordered packing of adjacent helices as in a vitrified liquid crystal, is obtained by quenching the LC solution; two crystalline phases of PBLG were identified, one obtained by slow gelation at a rather high temperature and the other obtained by quenching followed by annealing. It is possible that the aggregated state is in the form of PBLG-rich microfibrils, as has been observed in dilute PBLG gels.

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