Coexistence of Liquid Crystalline Phases in Poly(γ-benzyl α,L-glutamate)–Dimethylformamide

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ABSTRACT: A region of coexistence of two liquid crystalline (LC) phases in the poly(benzyl glutamate) (PBLG)–dimethylformamide (DMF) system, as predicted by theory, was investigated by determining the temperature dependence of the periodicity spacing of the cholesteric screw axis in the liquid crystalline phase. The periodicity spacing decreases with decreasing temperature in PBLG–DMF but increases with decreasing PBLG concentration. Crossing a LC–LC phase boundary would reverse the observed temperature coefficient. The reversal was observed, making firm the existence of the LC–LC region, in agreement with prior, less secure results. By contrast, poly(ϵ-carbobenzoxy-α,L-lysine) (PCBL), which has no phase boundaries in the temperature region investigated, had a periodicity spacing which varied smoothly and linearly with temperature. The pitch of the cholesteric screw axis was found to be left handed in *PBLG*–DMF as determined by small-angle light scattering. The time evolution of the periodicity spacing in samples quenched from the isotropic phase was followed. In some cases, it took weeks for the periodicity spacing to reach a constant, but not always equilibrium, value.

Introduction

The phase behavior of binary solutions of stiff-chain polymers is quite different from the behavior of random coil polymers in that ordered or liquid crystalline phases are possible. In his original lattice theory of hard, rigid rods, Flory[1] tentatively predicted the coexistence of two liquid crystalline phases of different composition within a small region of the phase diagram (LC–LC, Figure 1), so long as the rod axial ratio was greater[2] than ~50. Further considerations have strengthened the prediction.[3,4] The critical χ for LC–LC coexistence depends on axial ratio but in all cases is very small ($0 < \chi_c < 0.12$). Many aspects of the phase behavior of the binary system poly(γ-benzyl α,L-glutamate) (PBLG)–dimethylformamide (DMF) have been determined,[5-7] particularly the location of the narrow and wide liquid crystalline–isotropic biphasic regions (Figure 2). These correspond rather well to the lattice model predictions with deviations understandable in terms of rod flexibility and flexible side chain–solvent mixing.[6,8] The only feature of the lattice model which has not been assessed reliably is the existence of the LC–LC biphasic region. The temperature dependence of the second virial coefficient[9] suggested that if this region exsisted, it should be in the vicinity of room temperature or slightly below, as the second virial coefficient turned negative below 23 °C. Using proton NMR data, Wee and Miller[5] tentatively identified a phase boundary which implied such a region (Figure 2, line A), although the method used has no underlying foundation as a means of determining phase boundaries. Isopiestic measurements[6] implied a LC–LC region in that the isopiestically determined phase boundary (Figure 2, line B) extends to a higher temperature than the lowest temperature at which the narrow biphasic region is reliably observed (Figure 2, point C).

In this paper the tentatively identified phase boundary is further investigated by exploiting the temperature and concentration dependence of the cholesteric pitch in the region of the suspected phase boundary. In all helical polypeptide–diluent systems which have been studied, the cholesteric pitch decreases rapidly with increasing concentration at constant temperature. A theoretical basis for the concentration and solvent dependence has been given.[10] At constant composition the cholesteric pitch has been observed to vary weakly but monotonically with temperature. *Whether the temperature coefficient* is positive or negative depends on the polymer–diluent system. Empirically it has been correlated with the handedness of the cholesteric twist.[11] With PBLG–DMF the pitch becomes smaller with decreasing temperature. If a phase boundary is encountered upon lowering the temperature at fixed composition, the resulting change in pitch will depend on the nature of the phase boundary, as depicted in Figure 3.

Experimental Section

PBLG of molecular weight 310 000 was obtained from New England Nuclear. Poly(ϵ-carbobenzoxy-α,L-lysine) (PCBL) of molecular weight 275 000 was from Pilot Chemicals. Aldrich Gold Label DMF was dried over 4-Å molecular sieves and then distilled under reduced pressure at about 50 °C just prior to use. The solutions were prepared by weight. For conversion to volume fraction we took the specific volume of PBLG as 0.791 mL/g,[12] that of PCBL as 0.845 mL/g,[8] and the density of DMF as 0.944 g/mL. The solutions were capped and stirred magnetically for several days at room temperature. For temperature-dependent studies, 12.87 vol % PBLG and 14.2 vol % PCBL solutions were prepared. The solutions were transferred under a dry nitrogen atmosphere saturated in DMF to 3 cm × 1 cm × 0.1 cm path length cells from Markson. These cells were modified by fusing a length of tubing to the open end to facilitate sealing. Nevertheless, a small loss of solvent may accompany sealing.

To ensure the independence of periodicity measurements at different temperatures, the samples were always raised briefly (1–3 minutes) to about 100 °C (isotropic region), typically centrifuged back and forth in the cell, reheated, checked for blackness (isotropic behavior), and plunged into a well-regulated bath (±0.002 °C over a period of weeks at the desired temperature). Additionally, temperature was varied in a nonsystematic fashion; thus measurement at 18 °C was followed by measurement at 40 °C, etc. Given this scheme, the consistent trends observed imply that no degradation of the sample occurred.

At intervals, the samples were withdrawn from the bath to take photomicrographs of several regions within the cell. Generally, the samples were returned to the bath within 5–10 min, so that microscope measurements did not perturb these slowly responding systems. The periodicity spacing between bright fringes was measured using a Leitz polarizing microscope. Magnification in the photographic plane was obtained directly by photographing a micrometer scale. Several measurements are often possible in the same photomicrograph. These provide values clustered about an average. The distribution of spacings within the sample, typically ±5 μm, exceeds the error in measurement, typically ±1 μm. We continued the process until no further evolution in the

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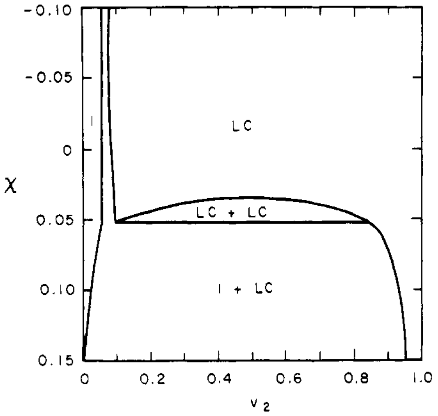

Figure 1. Binary phase diagram calculated for rigid, hard rods of axial ratio 150 by Flory lattice model. Phases are isotropic (I) and liquid crystalline (LC).

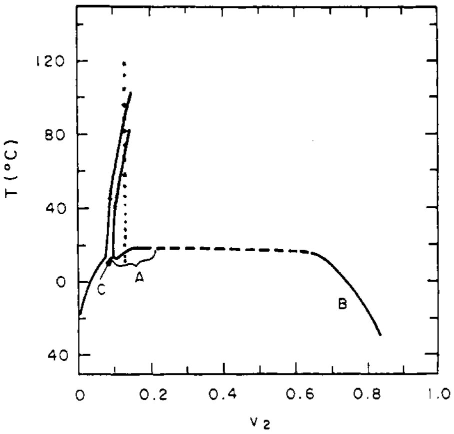

Figure 2. Temperature–composition phase diagram for PBLG in DMF.[5-7] The dashed vertical line is the composition investigated in this paper. See text for meaning of A, B, and C.

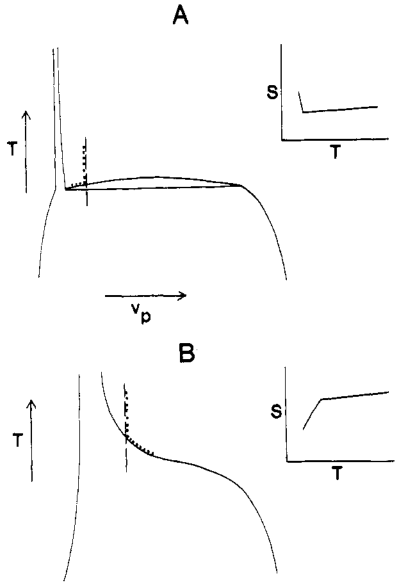

Figure 3. Schematic representation of the expected temperature dependence of the periodicity spacing (*S*) if a PBLG–DMF solution of fixed composition (---) is cooled from the liquid crystalline phase through a phase boundary. The composition (···) of the observable LC phase will depend on the nature of the phase boundary (A or B).

average periodicity spacings was observed with time.

The periodicity spacing also gives rise to diffraction of visible light at small angles, as noted previously.[13,15] We sometimes

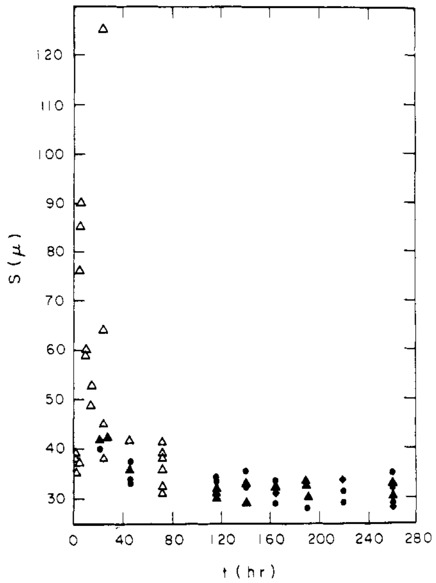

Figure 4. Time evolution of periodicity spacing in 12.87 vol % PBLG in DMF at 15 °C, quenched from 100 °C at time $t = 0$. The spacings were determined from optical microscopy (△,▲) and from light diffraction (○,●); diamonds indicate overlapping results from the two methods. Filled points, run 1; open points, run 2.

determined periodicities from the Bragg diffraction angles produced when thick (0.1 cm) samples were placed in the path of a He–Ne laser ($\lambda = 6328$ Å). The periodicity *S* was determined from Bragg's law

$$m\lambda = 2S \sin(\theta/2), \qquad m = 1, 2, 3, ...$$

where θ is the scattering angle external to the cell. Higher order diffractions, when observed, can only be explained by nonlinear or inhomogeneous twisting.[16a] At low angles the solution refractive index factors out to a good approximation.

The sense of the cholesteric twist was determined by the method of Hashimoto, Ebisu, and Kawai[16b] using photographic small-angle light scattering.[17]

X-ray diffraction patterns were obtained by using a thermostated cell in a Warhus pinhole-collimated flat-plate camera and nickle-filtered Cu Kα radiation.

Results

The periodicity lines which appeared after an initially isotropic solution was plunged to lower temperature were found to be time dependent. An example is shown in Figure 4. The results from optical microscopy and from small-angle light diffraction agreed well. The PCBL sample generally stabilized within 1 day, while the PBLG sample typically required 15 days and as much as 6 weeks at 50 °C. Typically the spacings within a sample at early times varied widely, with some being very large. Ultimately, the large spacings were seen no more and the variance in values measured from different locations in the cell decreased. The results in Figure 4 are typical; however, on some occasions the time dependence was slight, and on rare occasions an equilibrium spacing was approached from below. Equilibrium spacings were taken to be the time-independent values. At the lowest temperatures studied (~14 °C) the periodicity spacings ultimately disappear and the sample gels.

The temperature dependence of the periodicity spacing in both the PBLG and PCBL samples is shown in Figure 5. The error bars, centered on the average of spacings observed at long times, indicate the mean deviation from that average. The inset is the expanded-scale, low-temperature PBLG data showing only the average spacing at each temperature.

The PCBL data vary linearly from 50 to 5 °C, showing no anomalies. Previous studies indicate that no phase

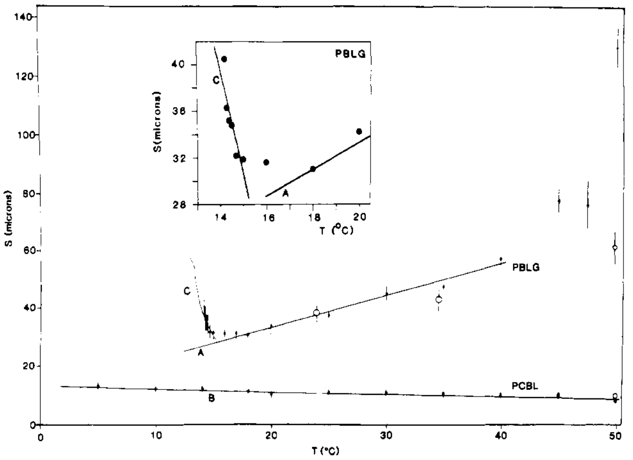

Figure 5. Temperature dependence of the time-independent periodicity spacing (one-half the cholesteric pitch) in 12.87 vol % PBLG and 14.2 vol % PCBL in DMF. Line A is the least-squares fit to PBLG from 18 to 40 °C, line B is the least-squares fit over all PCBL data points, and line C is predicted spacing if previously determined phase boundary is correct (see text). All values shown were obtained by quenching from the isotropic phase (~100 °C), except for the open points, which were obtained by raising the temperature from 22 °C to the indicated value.

boundaries exist at this concentration over the temperature range studied.[7] The PBLG spacings behave differently, showing a linear temperature dependence only from 18 to 40 °C. At lower temperatures, starting about 15 °C, there is a sudden and rapid increase of spacing in response to a small decrease in temperature.

A brief attempt was made to observe by X-ray diffraction the coexistent high-concentration PBLG–DMF liquid crystalline phase. This phase contains ~70% by volume PBLG (see Figure 2). Judging from the extrapolated concentration dependence for PBLG of this molecular weight in DMF,[18] the periodicity spacings of this phase will be too small to observe by microscopy. The high-concentration phase was not detected by X-ray diffraction in the 12.87 vol % sample below 15 °C. This is not surprising, since less than 1 vol % of this sample would be in the high-concentration phase at 14 °C. The high-concentration phase has, however, been observed by X-ray diffraction under other conditions.[17]

The periodicity spacing in the single-phase region was found (Figure 5) to have a positive temperature coefficient in PBLG–DMF and a negative coefficient in PCBL–DMF, an effect which may be due to the handedness of the cholesteric pitch.[11] The sense of pitch was determined by the small-angle light scattering technique for PBLG–DMF, PCBL–DMF, and PBLG-1,2-dichloroethane (DCE). Patterns similar to those of Hashimoto et al.[16] were observed. The PCBL–DMF and the PBLG–DCE samples had the same handedness, which was opposite to the PBLG–DMF handedness.

Discussion

Coexistence of Liquid Crystalline Phases. The main thrust of this investigation was to substantiate the suspected phase boundary enclosing coexistent ordered phases in the PBLG–DMF system. The periodicities shown in Figure 5 result from competition between temperature and concentration effects. Various temperature dependences of the pitch have been reported.[11,21,22] However, in all cases where there is no inversion of the sign of the cholesteric twist, the pitch varies monotonically with temperature. Increased concentration always produces a strong decrease in the cholesteric pitch.[13,14,17a,18] We thus expected for PBLG in DMF that upon lowering the temperature in the liquid crystalline phase, the periodicity should at first vary smoothly. However, if the suspected phase boundary is crossed, most of the solution in our fairly dilute sample will assume a new, lower concentration, *with a considerably larger periodicity.* The smaller portion of the sample assuming a higher concentration (ca. 70 vol % from Figure 2) will not produce any periodicities visible in the optical microscope because *S* decreases rather strongly with concentration, especially in PBLG–DMF.[17a,18] We therefore expected that if the liquid crystal–liquid crystal phase equilibrium did exist, the slope of a plot of the observed periodicity vs. temperature would change sharply in the region of the phase boundary.

The adherence of the measured temperature dependence of *S* for PBLG–DMF to the above hypothetical scheme leaves little doubt that a true thermodynamic equilibrium does exist. We note that the sudden upturn in the periodicity occurs near 15 °C, in agreement with the empirical NMR observations for a 12.87 vol % solution. Moreover, the line C in Figure 5, which was calculated from the measured concentration dependence[18] and the NMR-determined phase boundary A of Figure 2, is in good agreement with our present measurements of *S*. This greatly amplifies the reliability of the semiempirical boundary A of Figure 2.

The coexistence of ordered phases in PBLG–DMF is thus established on three counts: (1) the sudden upturn in the *S* vs. *T* behavior, (2) the semiempirical NMR results, reinforced by their ability to predict the *S* vs. *T* behavior, and (3) the isopiestic measurements, line B of Figure 2, which lie above the point C of Figure 2.

Theoretical consideration based on hard rods[1] or on rods with soft anisotropic interactions[3,4] have lead to prediction of the existence of this region over a narrow range of χ or reduced temperature, respectively. Although theory predicts coexistence, it gives little aid in knowing over what range of a laboratory variable, such as temperature, the coexistence may be stable. If the temperature range is very shallow, it would be difficult to find. In addition, the viscosity of high-concentration, high molecular weight polymer solution makes attainment of equilibrium difficult. Reducing the rod length will lower the viscosity and shorten the time effects but may be disappointing as it may eliminate the liquid crystalline biphasic region.[1,2,4] Thus, although it would be of much interest to investigate critical scaling around the liquid crystalline critical point and compare it to critical scaling around the isotropic critical point observed in random coil polymers, the PBLG–DMF system does not seem to be the most appropriate one to use.

The coexistence of two ordered phases of poly(methyl glutamate) in pyridine has been reported.[19] Unfortunately, little is known concerning the phase boundaries. The phase behavior of numerous surfactant systems has been investigated.[20] On thermodynamic grounds some should contain coexisting liquid crystalline phases. None appear to have been reported, though it is not clear that they have been carefully examined on this point.

Time Dependence of Liquid Crystalline Morphology. We have observed some very long time dependences in the development of the periodicity spacings. We have not found this reported in the literature, and it may well be that some literature values are nonequilibrium ones. For example, in the PBLG–dioxane system, Duke and DuPrê[21] found *S* was linear with temperature, while in the same system *S* has been reported to be linear with reciprocal temperature.[11] We found *S* to be linear with temperature over the entire temperature range in PCBL–

DMF. In PBLG–DMF it was linear from 18 to 40 °C, but at higher temperatures S increased much more rapidly, resembling the behavior for PBLG–benzene seen by Patel and DuPré.[23] In the high-temperature range of nonlinear behavior the time span to reach a stable periodicity increased to 6 weeks. However, further investigation indicated that these stable values may not be equilibrium values. If, for example, the sample with equilibrium periodicity spacing at 22 °C is jumped to 50 °C, rather than quenched to 50 °C from the isotropic state, a much lower stable spacing is observed (Figure 5), which is achieved in 1 week and does not change over 4 additional weeks of observation. The very large increase in spacing above 40 °C observed when the sample is quenched must not represent equilibrium values.

In a previous study on the kinetics of phase formation[22] it was observed that a quenched solution was completely converted to the liquid crystalline form long before periodicity lines appeared. Upon initial conversion to the ordered state, the domains must not be of sufficient size or order to observe the periodicity spacing. Eventually domains are of sufficient size that parallel periodicity lines extending over hundreds of microns are observed and their time course followed (Figure 4). At the higher temperatures, particularly as one approaches the isotropic–liquid crystalline phase boundary, the driving force to rearrange may become exceedingly small ($<kT$), with further changes unlikely. Only by approaching the temperature of observation from below, as well as from above, can equilibrium spacings be determined with confidence.

Structure of the Liquid Crystalline Phase. We found that the temperature coefficient of the periodicity spacing had the opposite sign in PBLG–DMF compared to PCBL–DMF. The sense of twist, as determined from small-angle light scattering, was also opposite in the two systems.[24] This is in accord with the correlation found by Toriumi et al.[11] In light of the negative temperature dependence for PCBL in DMF, it seems pertinent to comment on the positive temperature dependence predicted theoretically by Samulski and Samulski,[10] based on a reduction in the electrodynamic forces acting between chiral rods due to rotational averaging about the long axis. Rotational averaging would be expected to increase linearly with temperature, since the energy for such motion is proportional to kT. However, since the exchange of electrodynamic forces between rodlike molecules spaced, for example, at 30 Å requires only $\sim 10^{-17}$ s, we would not expect rotational averaging from the comparatively slowly moving rods to be important. Additionally, if rotational averaging did occur, one would expect to find smaller periodicity spacing for higher molecular weights, since the rotational diffusion coefficient for motion about the long axis of a rodlike molecule is directly proportional to its molecular weight. However, S has been reported to increase[25] or remain essentially constant[13] with increasing molecular weight. A theoretical interpretation of the former observation has recently appeared.[26] We conclude that rotational averaging of electrodynamic forces is insignificant in determining the cholesteric pitch. We hasten to emphasize that in matters not related to the temperature dependence of the cholesteric pitch, the theory of Samulski and Samulski is quite satisfactory, yielding good agreement with empirical results in mixed-solvent systems when reasonable assumptions regarding the electric permittivity are made.[10] Unfortunately, short-range phenomena, such as interaction of side-chain dipoles with solvent, considerably complicate the application of the theory in general.

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