Origins of Region I Shear Thinning in Model Lyotropic Liquid Crystalline Polymers

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Introduction. As first described by Onogi and Asada,[1] the steady shear viscosity behavior of liquid crystalline polymers (LCPs) is often interpreted in terms of three distinct regions: shear thinning at high rates (region III), a plateau of approximately constant viscosity at intermediate rates (region II), and an additional regime of shear thinning at low shear rates (region I). regions II and III, observed in a variety of LCPs,[2−4] are analogous to the Newtonian plateau and shear thinning observed in flexible polymer melts and solutions and may be explained by molecular models of rigid rod dynamics.[5] Region I, on the other hand, is more uniquely characteristic of the ordered character of LCPs. It is believed to reflect a *piled polydomain* texture, composed of nematic domains possessing little or no macroscopic flow-induced orientation. Distortional elasticity associated with spatial variations in the director field is believed to contribute *directly* to the measured viscosity;[6] in this respect region I shares similarities with low-frequency viscoelasticity arising in other ordered fluids such as block copolymers and smectics.[7] Since LCPs usually have a high defect density, it is speculated that region I should be a universal consequence of distortional elasticity and texture.

Although many LPCs show some indications of three-region behavior,[2] two lyotropic LCPs have emerged as model systems exhibiting all three viscosity regimes at conveniently accessible shear rates. Concentrated solutions of hydroxypropylcellulose [HPC] in water[8] and poly(γ-benzyl L-glutamate) [PBLG] in *m*-cresol[9] have been the focus of a recent detailed characterization of region I behavior. These studies have shown extensive similarities in rheology between the two systems. One difference is that while all anisotropic solutions of HPC in water show region I,[4,8] PBLG solutions only exhibit region I beyond a threshold concentration, well above the critical concentration for formation of a nematic phase.[3,9] Here we employ *in situ* X-ray scattering during steady shearing to study the structural origins of region I behavior in these model LCPs.

Experimental Section. We have studied the same two polymer solutions used in previous rheological studies of region I behavior: a 60 wt % solution of HPC (Klucel E) in water[8] and a 40 wt % solution PBLG, molecular weight = 238 000 (238k) in *m*-cresol.[9] In addition, a separate series of PBLG solutions of higher molecular weight (280k) was used to study the effects of solution concentration on fluid structure and rheology, at concentrations of 30, 35, 38, and 40 wt %. *In situ* X-ray scattering has been identified in recent years as a powerful tool for studying sheared LCPs.[10] Here we adopt experimental methods described in a recent paper,[11] employing a rotating disk shear cell with a sample thickness of 1 mm and mica windows to allow X-ray transmission. X-ray experiments were conducted on beam line X-18A at the National Synchrotron Light Source, using focused bending magnet radiation with a wavelength of 1.77 Å. Using published rheological data as a guide,[8,9] preshearing ≥200 strain units ensured that samples had reached steady state. Viscosity measurements were conducted using a cone and plate rheometer.

Results and Discussion. Figure 1 shows representative X-ray scattering patterns and radial intensity scans from 60 wt % HPC in water and 40 wt % PBLG (238k) in *m*-cresol. For HPC, the scattering pattern begins as a diffuse ring at low shear rates, subsequently sharpening into two equatorial intensity lobes at high shear rates. A quantitative measure of the degree of molecular orientation may be obtained by computing an orientation parameter, S, as an average of the second Legendre polynomial, P_2, weighted by an azimuthal intensity scan $I(q,\alpha)$,

$$S \equiv \langle P_2(\cos \alpha)\rangle = -2\left[\frac{\int_0^{\pi/2} I(q,\alpha)\, P_2(\cos \alpha) \sin \alpha \, d\alpha}{\int_0^{\pi/2} I(q,\alpha) \sin \alpha \, d\alpha}\right]$$

where the azimuthal angle α is measured from the flow direction. Here we take azimuthal scans at the scattering vector q corresponding to the peak associated with lateral packing of rods in the nematic state (Figure 1d). Figure 2 shows that HPC has a nearly random orientation (low S) at low shear rates but becomes increasingly aligned in the flow direction with increasing shear rate. Rheological data on this solution[8] show that the low-orientation regime at low rates corresponds precisely to region I. HPC is thus consistent with the proposition that piled polydomain texture in nematic LCPs is the cause of region I shear thinning.

Turning to the 40 wt % solution of PBLG (238k), the X-ray scattering patterns at low rates (Figure 1b) are strikingly different from those in HPC. A sharp reflection is superimposed on the diffuse nematic peak. With increasing shear rate, the sharp peak is reduced at the expense of the diffuse peak, until at high rates the pattern for PBLG is similar to that for HPC (Figure 1c). Radial intensity scans from the PBLG solution show that the sharp peak in the scattering pattern occurs at a slightly larger q than the diffuse peak, corresponding to a smaller lateral packing distance between rods. In addition, this sharp peak is accompanied by two faint higher order peaks that may be indexed to a hexagonal lattice (see Figure 4 below). Although NMR characterization of this solution showed no evidence of multiphase behavior,[9] these X-ray results strongly suggest a coexistence between hexagonal and nematic phases, driven by the same excluded volume interactions that induce liquid crystallinity at much lower concentrations (~12 wt %). Several studies have previously documented hexagonal ordering in highly concentrated PBLG solutions;[12] Figure 1c demonstrates that application of shear at high rates is able to transform the system back to a wholly nematic phase. This differs from other classes of polymers in which shear enhances the formation of ordered phases.[13]

A measure of the fraction of the hexagonal phase may be computed directly from the X-ray scattering pattern by separating it into the diffuse peak characteristic of the nematic phase, and the sharp peak associated with the ordered phase. After appropriate q-dependent polarization and geometrical weighting factors are ap-

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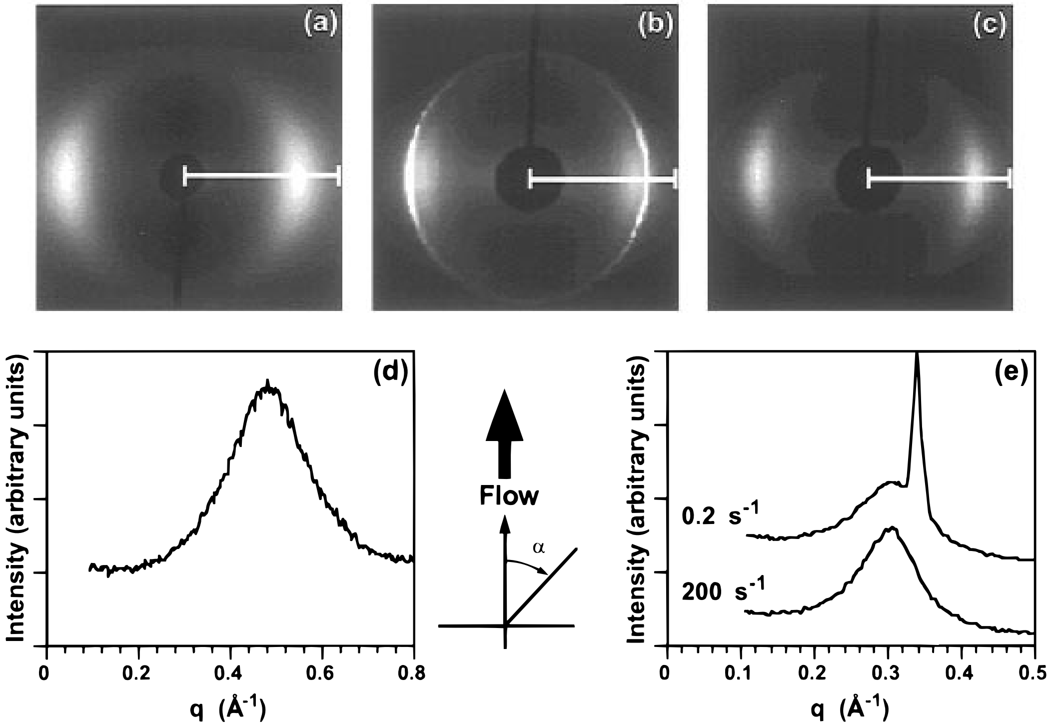

Figure 1. Representative X-ray scattering patterns under shear for (a) 60 wt % HPC in water at 5 s^{-1}, 40 wt % PBLG (238k) in cresol at (b) 0.2 and (c) 200 s^{-1}, and associated equitorial radial intensity scans for (d) HPC and (e) PBLG.

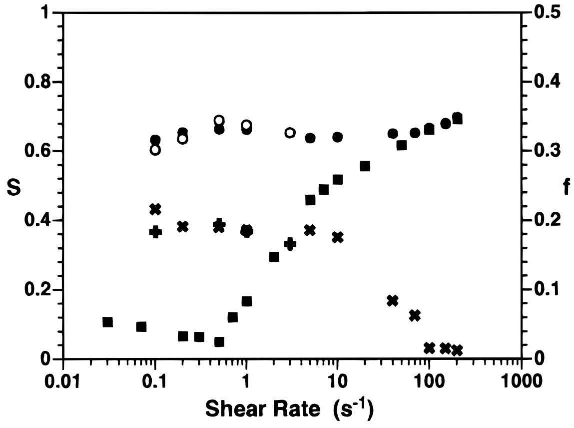

Figure 2. Evolution of steady shear orientation parameters for 60 wt % HPC in water (■) and 40 wt % PBLG (238k) in cresol (●), and the fraction of the hexagonal phase as a function of *increasing* shear rate for PBLG (×). Also plotted are orientation parameters (○) and the fraction of hexagonal phase (+) as a function of *decreasing* shear rate for the PBLG solution.

plied,[14] the areas under these peaks are computed and summed over all azimuthal angles to yield the relative *volumes* under the entire 2-D scattering pattern. The ratio of the volume under the hexagonal peak to the total volume, *f*, is then used as a measure of the fraction of the additional ordered phase in the sample. As seen in Figure 2, the fraction of hexagonal phase present in this PBLG solution remains relatively constant at low shear rates. This plateau is followed by a steady decrease in *f* toward zero at high shear rates, illustrating the destruction of the hexagonal phase by applied shear.

It is apparent from the scattering pattern in Figure 1b that there is substantial flow-induced orientation in the PBLG solution, even at low rates. Orientation parameters were computed using azimuthal intensity scans at the radial location corresponding to the diffuse nematic scattering peak (*S* values based on the hexagonal peak show qualitatively similar behavior). Unlike the HPC solution, *S* increases only slightly with shear rate and is significantly nonzero at the lowest rates studied, well within region I.[9] Although rheologically similar to HPC, it is clear that region I shear thinning in PBLG does not fit the prevailing explanation, which requires only (i) nematic ordering and (ii) negligible flow-induced orientation of the polydomain texture. Neither of these conditions is satisfied in the PBLG solution. Instead, since previous X-ray scattering studies on lower concentration PBLG solutions showed no evidence of a hexagonal phase,[11] and since lower concentration PBLG solutions do not exhibit region I,[3,9] it seems likely that the additional contributions to low shear rate viscosity are *caused* by the presence of the hexagonal phase.[15]

To test this hypothesis, we have studied both steady shear viscosity and X-ray scattering in a series of concentrated PBLG (280k) solutions in *m*-cresol. Figure 3 demonstrates that while a 30 wt % solution shows neither ordering nor region I shear thinning, the more concentrated solutions show both the hexagonal peak and the characteristic enhancement in viscosity at low rates. The fraction of the hexagonal phase, *f*, and the magnitude of region I viscosity both increase substantially with increasing concentration in the range from 35 to 40 wt %, consistent with the picture that the solutions are biphasic in this concentration range. A sufficiently high fraction of the ordered phase could render the solutions solidlike, perhaps explaining other observations at higher concentrations.[9] These combined rheological and X-ray data prove that the presence of an ordered hexagonal phase is intimately related to the onset of region I shear thinning in concentrated PBLG solutions. For experiments on the 280k PBLG solutions, 2-D scattering patterns were collected over a sufficiently wide angular range to see a total of four reflections which may be indexed to a hexagonal lattice (see Figure

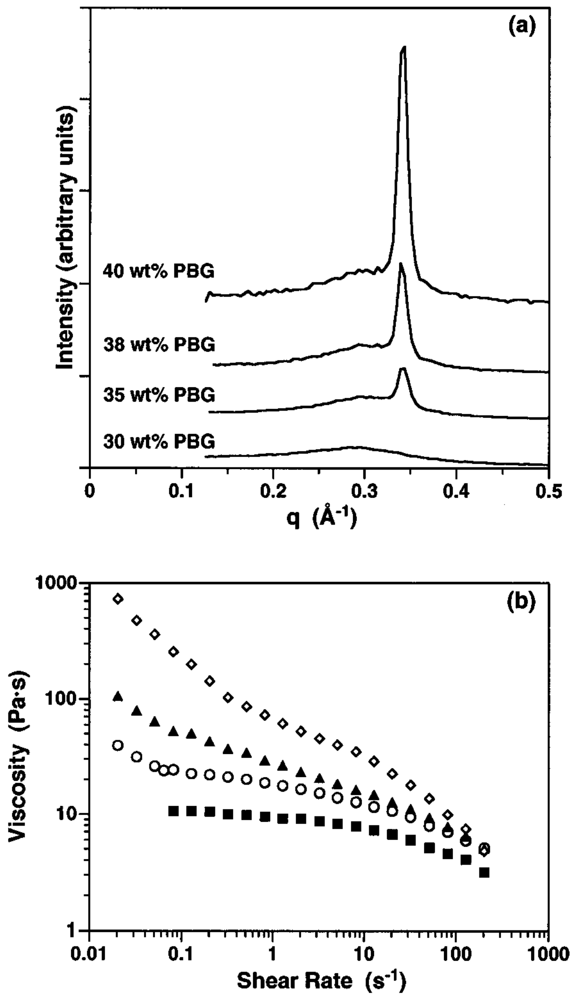

Figure 3. Effect of concentration in PBLG (280k) solutions in cresol. (a) Radial scans of X-ray patterns measured at a shear rate of 1 s^{-1} for 30, 35, 38, and 40 wt % solutions. (b) Steady shear viscosity as a function of shear rate for 30 (■), 35 (○), 38 (▲), and 40 wt % (◇) solutions.

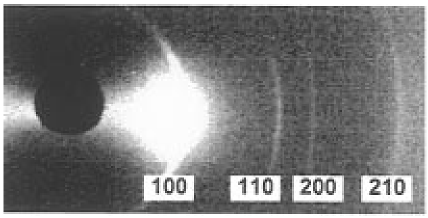

Figure 4. Expanded 2-D X-ray scattering pattern for 40 wt % solution of PBLG (280k) at a steady shear rate of 1 s^{-1}, showing indexing of higher order reflections to a hexagonal phase. Gray scale intensities were adjusted to enhance the contrast of the higher order reflections.

4), confirming our assignment of the sharp peak to a hexagonal phase.

Rheological studies conducted by Walker *et al.* on concentrated PBLG (238k) solutions showed an abrupt jump in low shear rate viscosity at concentrations between 37 and 38 wt % PBLG,[9] somewhat higher than transitions seen in Figure 3. One possible source of the discrepancy is the different molecular weight distributions of the two polymer samples: a sample with higher molecular weight might be expected to order at lower concentrations. This outlook is supported by comparing radial scans for the 40 wt % solutions of the 238k and 280k PBLG samples in Figures 1 and 3. At the same concentration, the hexagonal phase is more dominant in the higher molecular weight sample, consistent with the lower transition concentration for this solution.

Walker *et al.* report an additional complication in the region I rheology of PBLG due to the presence of upper and lower "branches" in the viscosity *vs* shear rate curve.[9,16] A freshly loaded sample follows the lower branch until a critical shear rate is reached [3 s^{-1} for 40 wt % PBLG (238k) in cresol]. If shear rate is decreased from this point, the viscosity follows the upper branch. We followed similar protocols in our X-ray experiments on this solution. Figure 2 demonstrates that in the shear rate range below 3 s^{-1} there is no significant difference observed in either orientation parameter or hexagonal phase fraction during ascending or descending shear rates, so that there is no obvious explanation for the dual branch behavior at the level of molecular ordering. It may not be possible to draw definitive conclusions from this, however, since the X-ray flow cell is loaded by injecting the sample through a syringe, which may generate a sufficiently severe deformation history to condition the sample into the upper branch.

To summarize, region I shear thinning appears to have radically different origins in the HPC and PBLG model systems. While the structure of HPC under flow is consistent with the established picture, region I arising through nematic distortional elasticity in a piled polydomain, this study conclusively demonstrates that region I behavior in PBLG results from the formation of a hexagonal phase at high concentrations. This result suggests that region I may not be universally expected in all nematic liquid crystalline polymers. We have further found that applied shear directly influences the transition between nematic and hexagonal phases in PBLG, motivating further inquiry into this phenomenon.

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(15) It has been previously suggested that gel-like quasi-solids of PBLG in *m*-cresol at concentrations above 40 wt % result from columnar ordering: Larson, R. G.; Promislow, J.; Baek, S.-G.; Magda, J. J. *Proceedings of an Osak University Symposium on Odering in Macromoleculear Systems*; Springer: Berlin, 1993.

(16) The concentration solutions of PBLG (280k) studied in Figure 3 also showed upper and lower branches of the viscosity curve. All data in Figure 3b were collected under conditions that yield upper branch behavior.

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