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A Neutron Scattering Study of the Orientation of a Liquid Crystalline Polymer by Shear Flow

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ABSTRACT: The orientational response of a liquid crystalline polymer (LCP) solution, specifically poly(benzyl L-glutamate) (PBLG) in deuterated benzyl alcohol, to the application of a shear field has been determined by *in-situ* neutron scattering. By analyzing the anisotropic two-dimensional scattering pattern, the orientation of the LCP at different shear rates, $\dot{\gamma}$, in the flow−vorticity plane was determined. It was found that the LCP response has three regimes. At low shear rates, $\dot{\gamma} < \dot{\gamma}_1$, the orientation of the LCP molecule increases with $\dot{\gamma}$, at intermediate flow rates, $\dot{\gamma}_1 < \dot{\gamma} < \dot{\gamma}_2$, there is not much change in the orientation of the PBLG molecule with $\dot{\gamma}$, and at high $\dot{\gamma}$, $\dot{\gamma} > \dot{\gamma}_2$, there is again an increase in the orientation of the LCP with shear rate. The crossover shear rates, $\dot{\gamma}_1$, and $\dot{\gamma}_2$, have been shown to correlate well to the first two relaxation times of a rodlike polymer in concentrated solution. The results are also compared and contrasted to some recent studies of the rheology of LCP in solution.

Introduction

Liquid crystalline polymers (LCPs) exhibited great promise of opening a new era of lightweight, high-strength materials when they were first introduced commercially. Unfortunately, these hopes and predictions have not come to fruition due to difficulties in processing and their complicated physics in solutions and blends. Yet, despite these problems, the demand for LCPs has grown and is predicted to continue growing in the future. In order to optimize the ability of industry to utilize LCPs in commercial products, a better understanding of the rheology, processing−structure−property relationship, and fundamental physics of LCPs is necessary.

Many polymer structures exhibit liquid crystalline behavior, and these are all termed liquid crystalline polymers. All LCPs incorporate an anisotropic element, a mesogen, into their architecture. The alignment of this anisotropic structure results in the unusual ultimate properties and unique physics of LCPs. For commercial products that are manufactured from liquid crystalline polymers, this alignment of the mesogenic structure usually occurs during processing; *i.e.*, shear-induced alignment is responsible for the molecular orientation. Given the importance of this process on the ultimate properties of the final product, there is, surprisingly, a glaring absence in the understanding and theoretical explanation of the interaction of a shear field with an LCP that accounts for the observed responses of an LCP to shear flow. Anomalies among these responses include low die swell,[1] a negative first normal stress difference,[2,3] strong dependence of transient rheological behavior and structure on shear and thermal history,[4,5] banded structures upon cessation of shear,[6,7] and extremely long relaxation times.[8]

Recently, there has been a great deal of progress in understanding the coupling of the orientation of a liquid crystalline polymer to a shear field. Marruci[9] has shown that, at certain shear rates, the shear field causes a spread in the distribution of the alignment of the rod in solution about the equilibrium orientation. The solution attempts to retract to the equilibrium state, and this response results, in this regime, in a negative first normal stress difference (N_1). The transition from positive to negative N_1 occurs near the shear rate at which rotation or tumbling of the LCP is overcome by the shear field. Larson[10] extended these calculations to three dimensions and mapped the orientation distribution of an LCP in shear flow. Larson[11] *et al.* also studied the effect of initial director orientation (in or out of the shearing plane) on the response of an LCP to a shear field. Experimentally, many studies have been completed using rheo-optical techniques.[12−17] These techniques look at large (*ca.* 100−1000 Å) length scales and can be complicated by the polydomain structure of the LCP sample. By contrast, there have been fewer studies on the length scale of neutron and X-ray scattering.[18−20]

Interest in the rheology of LCPs was sparked by the observation by Kiss and Porter[2,3] of the existence of negative first normal stress differences at intermediate shear rates in solutions of α-helical polypeptides. Since then, some of the studies of the rheology and rheo-optics of LCPs have examined the following unique aspects to LCP rheology: the presence of three regimes in the shear rate dependence of the viscosity,[24] the appearance of banded structures after cessation of shear,[6,7] transient behavior in shear flow,[29,30] orientation of the LCP by shear flow,[13] the role of director tumbling on the rheology of LCPs,[31,32] and the physical explanation for the existence of a negative normal stress difference.[9]

Theoretically, Onogi and Asada[24] have put forward a domain-based model that accounts for the shear rate dependence of the viscosity by correlating the response of the well-known polydomain nature of a liquid crystalline polymer in solution to shear flow. They define three regimes, as depicted in Figure 1, to explain the viscosity dependence of an LCP solution on shear rate.

The viscosity dependence is explained with respect to the response of the domain structure to the shear flow. In regime I the domain structure is not altered, but the domains flow over each other, resulting in a shear-thinning regime. Regime II describes the system as the domains are starting to break up due to the shear flow. Simultaneously, domains are flowing within an incipient monodomain. Regime III begins where the shear rate becomes strong enough to break up all the

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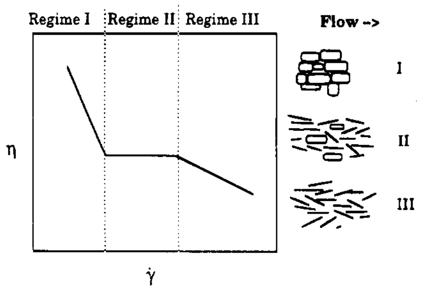


Figure 1. Diagram depicting three regimes of an LCP under shear flow as defined by Onogi and Asada.[24]

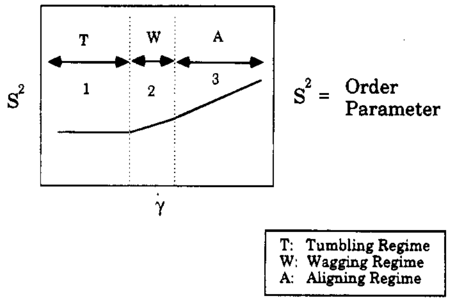


Figure 2. Diagram depicting response of an LCP to shear flow as calculated by Larson.[10]

domains and create a single monodomain.

Larson[10] has solved the Doi equation in three dimensions to determine the orientation distribution of an LCP in solution under shear flow. By accounting for excluded volume and the flow field, the order of the system can be determined at varying shear rates. In the projection of our experiments (the flow–vorticity plane), this leads to the existence of three regimes with respect to the order of the system with changing shear rate. At low shear rates, the shear flow is not flow aligning and the director tumbles under flow. In this regime there is no change in the order of the system with shear rate. As the shear rate increases, the flow dampens the tumbling of the director, but as the director still wants to rotate, a wagging motion ensues. Though the overall order of the system decreases dramatically in this regime, the molecular order of the solution in the flow–vorticity plane is predicted to initially exhibit a barely perceptible decrease and then increase with shear rate in this regime. Finally, at further increased shear rate, the flow becomes shear aligning, with an increase in the order with increased shear rate. This dependence of the response of the director and the order of the system in the flow–vorticity plane on the shear rate for this model is depicted in Figure 2.

Recent experimental results include studies utilizing shear small-angle light scattering[16] (shear SALS), optical birefringence,[13,29,31] and shear X-ray scattering[18–20] in hopes of understanding the effect of shear rate on the structure of a liquid crystalline polymer in solution. Ernst *et al.*[16] observed a fundamental change in the small-angle light scattering pattern of an LCP solution under shear flow at a critical shear rate via shear SALS. This was attributed to the coalescence of disclination points and the formation of a continuous monodomain as the shear rate increases. Burghardt *et al.*[13] have used optical birefringence to map the order in a liquid crystalline polymer solution under shear flow and correlated their results with the theoretical work of Larson. Specifically, they find a shear rate dependence of the order parameter of a solution of PBLG in *m*-cresol that is similar to that described in Figure 2. A significant divergence from theoretical predictions occurs in the absolute magnitude of the order present as found from optical birefringence. Picken and co-workers[18,19] used synchrotron X-ray scattering to determine the effect of shear rate on the order parameter in polyaramid solutions. These studies found no substantial change in the order of the system with shear rate in the shear-thinning regime. Keates *et al*[20] have also used X-ray scattering to determine the change in the order of an LCP solution with shear rate, but the system they studied was (hydroxypropyl)cellulose in water, a semiflexible liquid crystalline polymer. Their results differ from those of Picken to show an increase in the order of the system with increasing shear rate as the system enters and remains in the shear-thinning regime.

Aggregation and gelation are two processes that play an important role in the processing of liquid crystalline polymers[21,22] and yet are usually avoided in model systems when studying the physics and rheology of LCPs in solution. We have purposely chosen a system that has demonstrated aggregation of the solute and conditions near its gel point to observe the role of these conditions on the response of an LCP to shear flow.

Experiments to determine the molecular response of a liquid crystalline polymer to the application of a flow field have been completed by examining an LCP in solution *in situ* under shear flow with small-angle neutron scattering. With this technique, the change in orientation of an LCP at different shear rates and temperatures have been ascertained as well as simultaneous measurement of the viscosity of the solution. The results will be discussed in the context of previous experiments and theoretical predictions as well as our own interpretations.

Experimental Section

Disclaimer: Certain equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental detail. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best for the purpose.

Sample. The sample used is a 21 wt % solution of poly(γ-benzyl L-glutamate) (Sigma Lot 109F5501) in deuterated benzyl alcohol (DBA) (Cambridge Isotope Laboratories). The molecular weight of the PBLG is 236 000. The scattering experiments were completed on the NG5 8 m small-angle scattering instrument in the Cold Neutron Research Facility at the National Institute of Standards and Technology (NIST) in Gaithersburg, MD. The shear cell that was used is an in-house design which allows the *in-situ* scattering of a polymer solution, melt, or blend while under shear flow in a Couette geometry as well as the simultaneous measurement of the viscosity. Its particulars are described in detail elsewhere.[23] In this geometry the incident radiation enters parallel to the shear gradient and the collected scattering pattern is in the flow and vorticity directions. Shear rate and temperature were varied to determine the effect of these two parameters on the response of the LCP to shear flow. Shear rates that were studied range from 0.07 to 1081 s^{-1}, while the temperatures that were studied were 55, 65, and 75 °C. All scattering patterns were taken under steady-state conditions. In other words, data were only collected after at least the first 100 strain units, $\dot{\gamma}t > 100$, so that the transient did not contribute to the scattering pattern.

The collected scattering data were corrected for empty cell scattering, detector nonlinearity, electronic noise and stray scattering, sample transmission, and incoherent scattering. These corrected data were radially averaged over defined azimuthal sectors and then reduced to absolute units using a silica gel as a secondary standard to obtain scattering curves of $I(q)$ (cm^{-1}) vs q ($Å^{-1}$). q is the scattering wavevector ($q =$

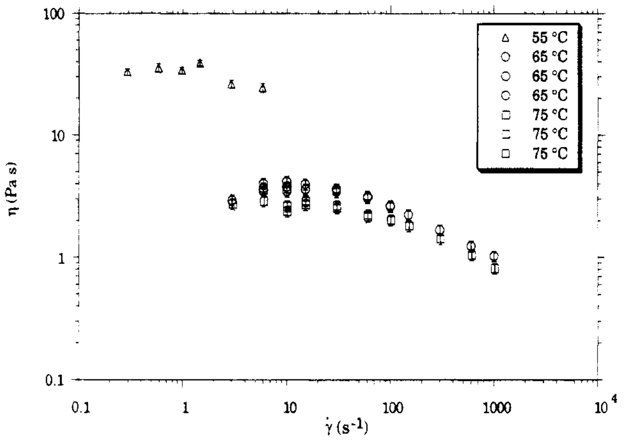


Figure 3. Viscosity of PBLG in deuterated benzyl alcohol (DBA) for the conditions of the scattering experiments.

$(4\pi/\lambda)\ \sin(\theta/2)$, where λ is the wavelength of the incident radiation and θ is the scattering angle).

In order to analyze the scattering pattern along separate axes, it is possible to complete the radial averaging over an azimuthal sector. For all of the following results the radial averaging has been completed over 10° sectors that are centered parallel and perpendicular to the shear flow direction.

Results

Figure 3 is a plot of viscosity of the PBLG/DBA solution vs shear rate as determined simultaneously with the scattering experiments. This plot clearly shows that, for 65 and 75 °C, the shear rates studied include the plateau and the shear-thinning regions of the viscosity curve (regimes II and III of the Onogi and Asada scheme).[24] For these two temperatures, the force transducer in the shear cell used to ascertain the viscosity was not sensitive enough to determine the viscosity at lower shear rates. The viscosity at 55 °C displays anomalous behavior, exhibiting a viscosity that is almost an order of magnitude higher than that of the 65 and 75 °C samples. This can be explained by the fact that this temperature is near the gelation temperature of this sample (≈50–60 °C)[21,25] and the observed viscosity is the consequence of the onset of large-scale aggregation or gelation.

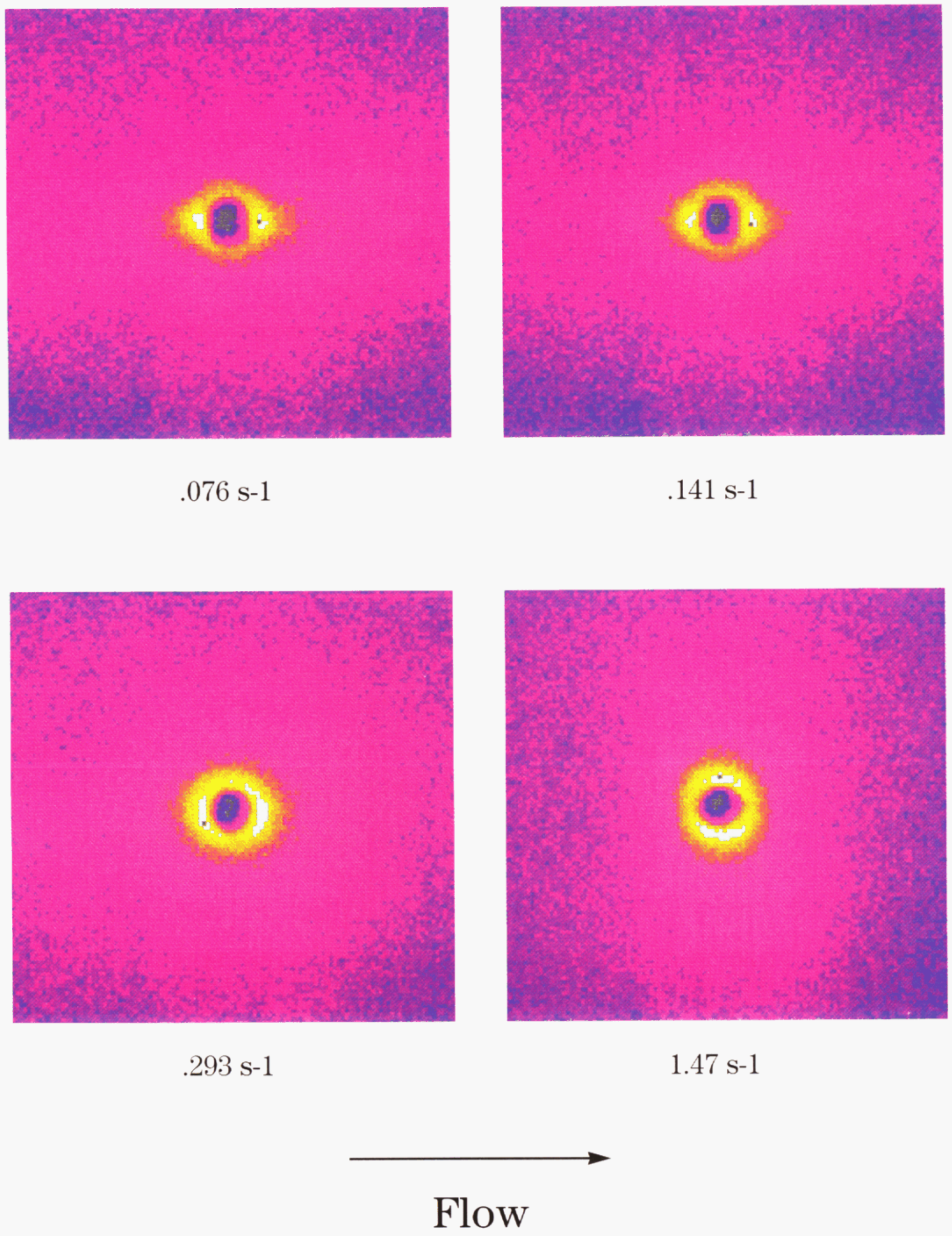
Figure 4 shows the scattering patterns at 55 °C with $\lambda = 9$ Å for four different shear rates. The direction of flow is denoted in the figure. At the lowest shear rate, $\dot{\gamma} = 0.076\ \mathrm{s}^{-1}$, there is an increased correlation *perpendicular* to the flow direction, characterized by an increase in scattering intensity along the flow direction. As the shear rate is increased, the anisotropy of the scattering becomes smaller, until when $\dot{\gamma} = 1.47\ \mathrm{s}^{-1}$ there is an increased correlation parallel to the shear flow which is characterized by an increase in the scattering intensity normal to the flow direction. To our knowledge, this behavior, the alignment of the LCP perpendicular to the flow direction as a stable flow mechanism, has not been previously observed experimentally and yet may be explained by theoretical predictions.[11] This will be considered further in the Discussion.

Figure 5 shows representative two-dimensional scattering patterns of PBLG in DBA at 65 °C under shear flow at different shear rates: (a) 0.6067, (b) 6.11, (c) 61.09, and (d) 611 s^{-1}. The flow direction is as shown in this figure. Even at the lowest shear rate (0.6067 s^{-1}), there is an anisotropy to the scattering patterns demonstrating the alignment of the PBLG by the shear field. As the shear rate is increased, the anisotropy becomes better defined, until at the highest shear rate the scattering pattern is a pair of well-defined lobes. It should be noted here that due to the nature of the neutron scattering experiment, the collected scattering pattern describes the *average* state of the LCP solution for the given parameter conditions. This is due to the fairly long sample times (~2 h) and large scattering windows (12 mm diameter). The only weakness in this method is that the scattering does not give the evolution of—or the separate contributions to—this average state. Therefore, direct observation of such transient behavior as disclination production or annihilation or director tumbling cannot be verified with this method. Consequently, the calculated quantities from the collected scattering patterns should be viewed as time- or ensemble-average quantities.

Due to its polydomain structure, an LCP solution that is quiescent in the anisotropic phase will give an isotropic scattering pattern. This is because the concentration fluctuations that scatter the radiation are isotropic in the scattering window. However, on the application of the shear flow the structure of the solution and the resultant scattering pattern become anisotropic. Simplistically, the director and the LCP molecules begin to align with the shear flow. As this happens the concentration fluctuations become anisotropic, with an increase in fluctuations normal to the molecular axis and a decrease parallel to it. The resultant scattering pattern then has an increase in intensity perpendicular to the flow direction and a suppression along the shear flow. In the quiescent state an analysis that is completed in two orthogonal directions will give identical results due to this isotropy in the scattering pattern. As the solution and scattering pattern become anisotropic, the reduction and analysis will give different results in the parallel and perpendicular directions. This is exemplified in Figure 6, which shows intensity vs q scattering patterns at three shear rates in the directions parallel and perpendicular to the shear flow. In Figure 6a, at a shear rate of 0.15 s^{-1}, there is a small, but finite, difference between the scattering in the two orthogonal directions. As the shear rate increases, so does this difference signifying the effect, at the molecular level, of the shear flow on the LCP orientation.

The molecular response or alignment of the PBLG molecule to the application of shear flow is of interest. Due to the geometry of this experimental setup, the orientation or alignment that is measured is in the flow–vorticity plane. A common method of determining the extent of the alignment of the LCP from scattering experiments is to calculate the order parameter, S, from the breadth of the meridional peaks in the diffraction pattern that appear due to the nematic ordering of the LCP.[18-20] The order parameter, S, is defined as $S = (3\langle\cos^2\theta\rangle - 1)/2$, where θ is the angle between the director and the molecular axis and is a measure of the amount of orientational order present in the solution. Unfortunately, the meridional peaks for these conditions cannot be obtained for the accessible scattering dimensions of these experiments. Consequently, the data have been analyzed such that the change in the molecular alignment with shear rate can be understood using the measured data.

To do this, the fact that neutron scattering gives information of the solution on a molecular length scale is utilized. As previously discussed, a polydomain quiescent solution results in a two-dimensional isotropic scattering pattern because the fluctuations that occur



.076 s-1 .141 s-1

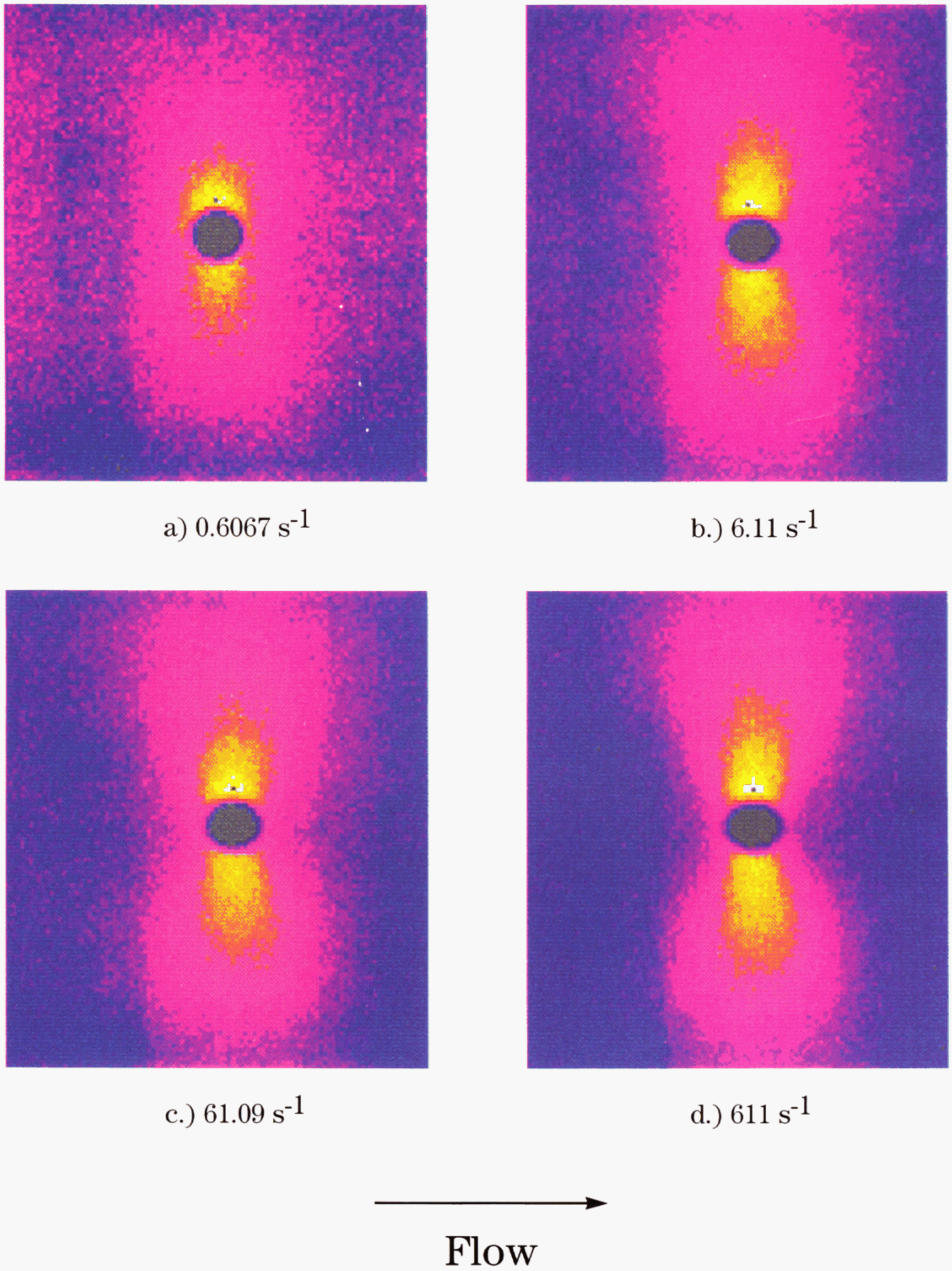
.293 s-1 1.47 s-1

Figure 4. Scattering patterns of PBLG in DBA at low shear rates near the gel point.

are isotropic in nature. However, as the flow field interacts with the LCP, the fluctuations become anisotropic. This can be seen with the help of Figure 7. The lines in this figure represent example trajectories of molecules in each domain, and the free space in between the molecules represents the fluctuations as determined by neutron scattering. Figure 7a shows the polydomain structure of an LCP solution at rest, while Figure 7b shows the same solution that has been partially oriented by a flow field. Due to the polydomain structure of the LCP solution, at rest the fluctuations that occur are isotropic. As the LCP molecule is aligned along the flow direction, there is an increase in the concentration fluctuations along the vorticity direction and a decrease along the flow direction. This results in a decreased correlation length, *i.e.*, average fluctuation size, normal to the flow direction and an increase in the correlation length parallel to the flow. It follows that the two-dimensional scattering pattern of an LCP solution under shear that is aligned by the flow field will have an increased intensity perpendicular to flow and a suppression parallel to flow.

Furthermore, the extent of the alignment of the LCP by the flow field can be characterized by the scattering intensity at low angles, which is proportional to the number of fluctuations present, in the flow and vorticity directions and their change with shear rate as well as a measure of the correlation length along the two orthogonal directions.

It is well known that the static susceptibility, $I(q=0)$, can demonstrate a crossover from mean field to Ising behavior near a critical point.[27] Thus, the susceptibility is composed of a mean field contribution and an Ising contribution, with one dominating over the other under certain conditions. Away from the critical point, which we are for these experiments, $S(q=0)$ is dominated by the mean field component. By completing an Ornstein–Zernike (OZ) style analysis, *i.e.*, fitting the scattering


a) 0.6067 s^{-1} b.) 6.11 s^{-1}

c.) 61.09 s^{-1} d.) 611 s^{-1}

Figure 5. Representative two-dimensional scattering patterns of PBLG in DBA at various shear rates.

profile to

$$I(q) = \frac{I(0)}{1 + q^2\xi^2}$$

in the q-range of this experiment, we can determine $I(q{=}0)$ and the correlation length, ξ, for the mean field contribution to the structure factor. Due to the anisotropic nature of the fluctuations, completing this analysis in the vorticity and the flow direction allows the determination of a correlation length, ξ, and the intensity at $q = 0$, $I(0)$, in both directions from the scattering patterns. This equation can be rewritten as $1/I(q) = 1/I(0)(1 + q^2\xi^2)$. It is this form of the equation that is fit to the data. Figure 8 is an example of this fit, $1/I(q)$ vs q^2, for 65 °C and $\dot{\gamma}$ = 60.1 s^{-1} in the parallel and perpendicular directions.

Figure 9 shows the dependence on shear rate of $I(0)$ in the same two directions for 65 and 75 °C as calculated from the OZ fit. The values for 75 °C have been shifted up for viewing. Figure 10 displays the dependence on different shear rates of $\Delta I(0) = I(0)_v - I(0)_f$, where $I(0)_v$ is $I(0)$ in the vorticity direction and $I(0)_f$ is $I(0)$ in the flow direction. From the previous discussion on the effect of flow on fluctuations in an LCP solution, it can be seen that this parameter correlates very well to the overall orientation of the LCP solution. Inspection of this plot shows that, at the lowest shear rate, $\dot{\gamma}$ = 0.15 s^{-1}, and 65 °C, there is a small, but definite difference between $I(0)_v$ and $I(0)f$. For 65 °C, as the shear rate is

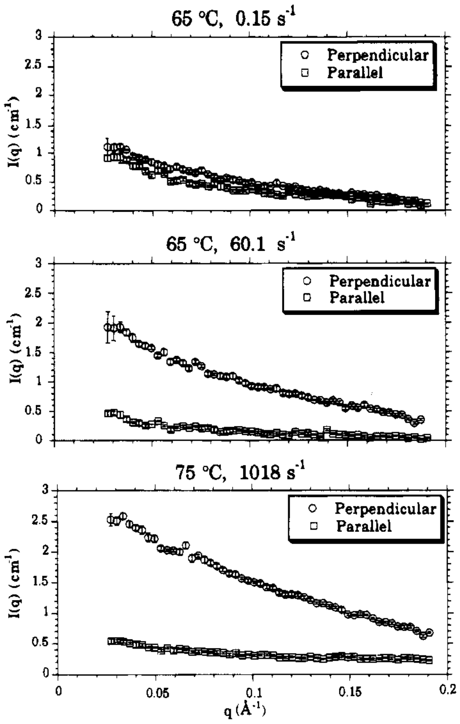


Figure 6. q dependence of the scattering intensity at different shear rates in the directions parallel and perpendicular to the flow direction.

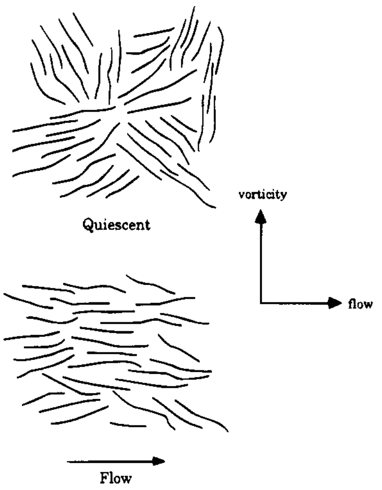


Figure 7. Diagram of an LCP solution in the quiescent state (a) and partially aligned by shear (b).

increased, the difference between the two continues to increase until a first critical shear rate is reached, $2 < \dot{\gamma}_1 < 5\ \mathrm{s}^{-1}$. This indicates that in this regime there is an increase in the molecular alignment with shear rate. As the shear rate increases further, there is a slight change in the difference between the two, signifying little change in the molecular orientation in this regime, until a second critical shear rate is reached, $20 < \dot{\gamma}_2 < 50\ \mathrm{s}^{-1}$. Above this second critical shear rate, $\dot{\gamma}_2$, the two orthogonal scattering intensities begin the diverge again, connoting a more dramatic increased alignment of the LCP with shear rate in this regime. The same variation of orientation of the LCP with shear rate is seen at 75 °C.

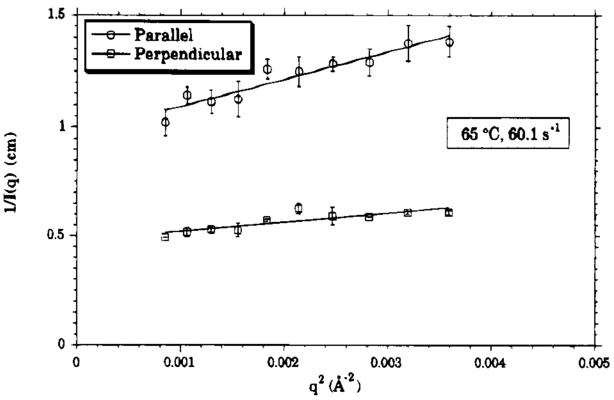


Figure 8. A plot of $1/I(q)$ vs q^2 for the sample at 65 °C and $\dot{\gamma} = 60.1\ \mathrm{s}^{-1}$ demonstrating the Ornstein–Zernike fit. Note the dramatic difference between the two orthogonal directions.

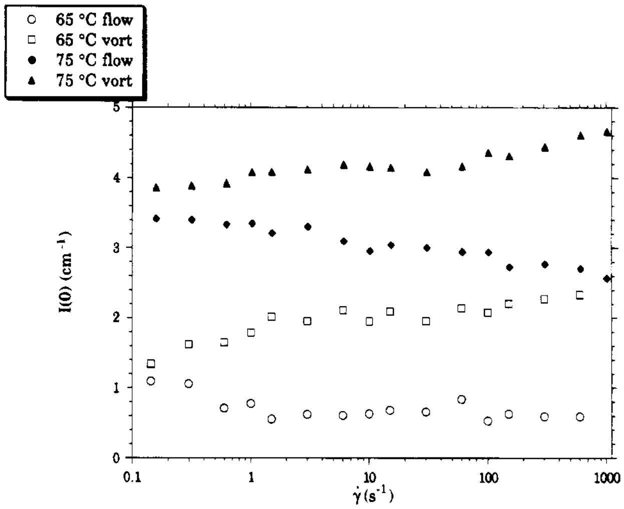


Figure 9. Change with shear rate in the scattering intensity at $q = 0$ of the polymer solution parallel, $I(0)_f$, and perpendicular, $I(0)_v$, to the flow direction. Note that the 75 °C data have been shifted up for clarity.

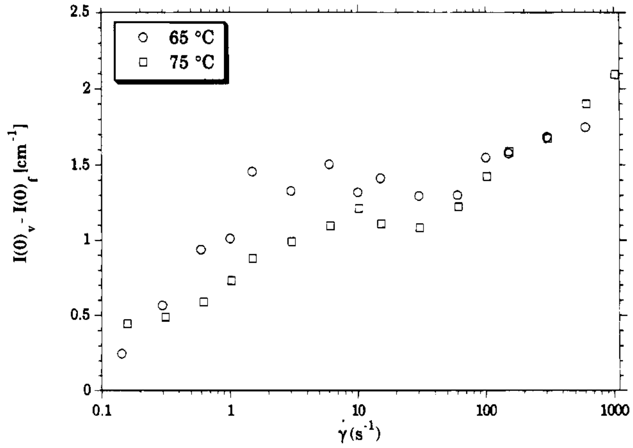


Figure 10. Shear rate dependence of the difference $I(0)_v - I(0)_f$.

The determination of the change with shear rate of the orthogonal correlation lengths in the vorticity and flow directions does not show the same dependence on shear rate, as is expected. It seems that ξ is becoming too large to be measured in this q range and any changes with shear rate are not seen due to measurement difficulties. It is clear that the calculation of ξ from this experimental setup is not a valid parameter to map the change in the alignment of the solution with shear rate, and only the $I(0)$ calculation will be used for further discussion.

The lobe or anisotropy of the scattering pattern is also a result of the anisotropy of the sample. Therefore, by quantifying the anisotropy of the two-dimensional scattering pattern, an independent measure of the orientation of the LCP can be garnered. An azimuthal trace

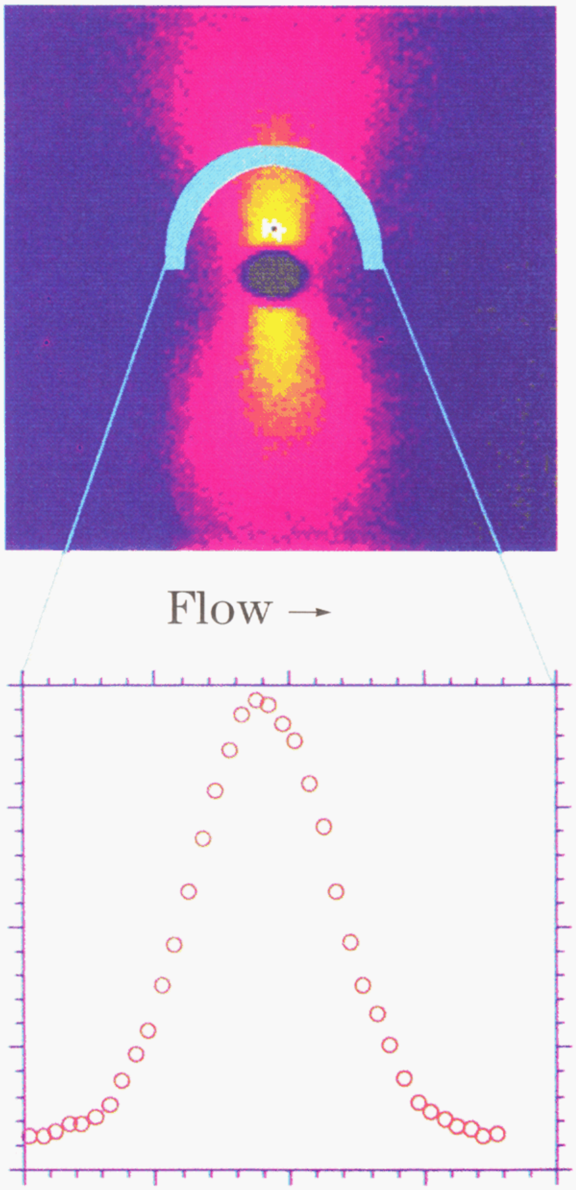


Figure 11. Diagram outlining the azimuthal trace of the two-dimensional scattering pattern.

of the scattering pattern can be obtained as shown in Figure 11. From this trace, the breadth of the lobe and peak height can be ascertained. The breadth of the lobe is a direct measure of the distribution of the LCP about the flow direction, and the peak height is proportional to the average number of molecular segments that are aligned parallel to the flow. Both of these parameters are a measure of the LCP orientation by the shear flow and can track the effect of shear rate on the molecular alignment.

An azimuthal trace was calculated by averaging the intensity over a 10 pixel annulus centered at $q = 0.045$ Å^{-1}. The azimuthal trace was fitted to a Lorentzian to determine the peak height and half-width at half-maximum. This analysis was attempted at various q values. There was no discernible difference between q values, and $q = 0.045$ Å^{-1} was chosen arbitrarily.

Figure 12 plots the change in the azimuthal peak height vs shear rate for 65 and 75 °C. Figure 13 shows the change in the azimuthal peak width with shear rate for the same conditions. Both of these plots show the same variation with shear rate as the $I(0)$ analysis: that is, a regime at low shear rate, $\dot{\gamma} < \dot{\gamma}_1$, where there is an increase of alignment with shear rate, a second regime, $\dot{\gamma}_1 < \dot{\gamma} < \dot{\gamma}_2$, where there is only a small change in the alignment with shear rate, and a third regime, $\dot{\gamma} > \dot{\gamma}_2$, where there is larger increase in alignment with shear rate.

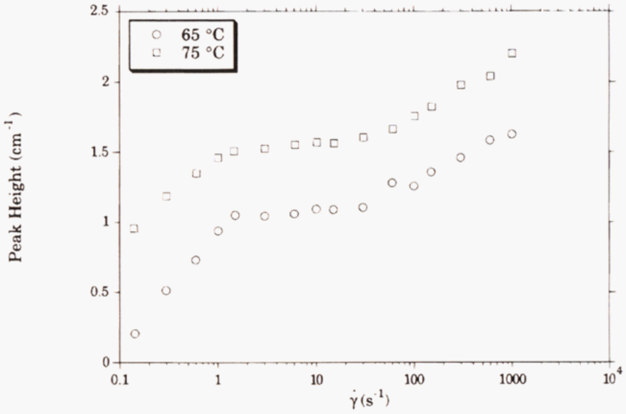


Figure 12. Dependence of the peak width of the averaged azimuthal intensity on the shear rate. This value is a measure of the distribution of the molecular segments about the shear direction.

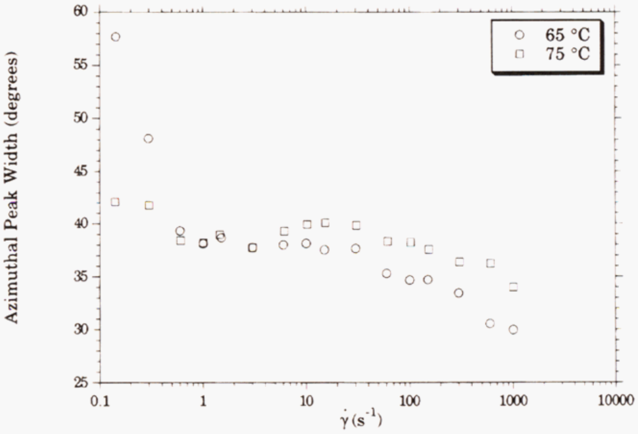


Figure 13. Same as Figure 9; 65 °C, except with delimiters, $\dot{\gamma}_1 = 1/\tau_0$ and $\dot{\gamma}_2 = 1/\tau_1$ as calculated from molecular quantities, marking the crossover between separate regimes.

Discussion

55 °C Results. Unique results have been reported for the scattering patterns of a liquid crystalline polymer near the gel point under shear flow. At low shear rates, the scattering exhibits an increased correlation perpendicular to the shear flow. Upon increasing the shear rate, this anisotropy becomes weaker, presumably promoting an increased correlation parallel to the shear flow. A log rolling mechanism where the rodlike polymer rolls along its long axis in the shear field, parallel to the vorticity axis, accounts for the observed scattering pattern. Moreover, log rolling has been predicted to possibly occur[11] at low to moderate shear rates. The existence of log rolling as a stable mechanism depends on the nematic potential and the initial director configuration. As a generalization, the director must be initially aligned closer to the vorticity axis to have log rolling be a stable state as the nematic potential becomes stronger.

The nematic potential of this solution is very large (U from ref 11 $\approx$ 50). Consequently, log rolling would only be expected to be observed if most of the sample is initially aligned near the vorticity axis. This seems highly unlikely. However, as the viscosity at this temperature shows, there are large-scale aggregates of rodlike polymers at this temperature. This in turn will alter the nematic potential of the solution, and therefore, the calculated nematic potential is not valid; the actual value will be much lower than the theoretical value. This raises the interesting question of the temperature dependence of the nematic potential. Regardless, the actual nematic potential is probably less than calculated, and therefore, it seems feasible that the limits of the initial director alignment for which log rolling is a stable flow mechanism are larger than predicted from theory. Theoretically, the required out of shearing plane initial director alignment, where the shearing plane is defined as parallel to the shear and gradient directions, is the only criterion that must be met for the sample to exhibit log rolling. Unfortunately, there is no direct evidence that an out-of-plane orientation exists. However, it is possible that the initial alignment could be out of plane due to the thermal history of the sample. The shear and thermal histories of the sample prior to collecting the initial scattering patterns are as follows. The sample was loaded and was then sheared at 14 s^{-1} for 10 min at 50 °C. The temperature was then raised to 70 °C, and the sample was sheared for 15 min at a rate of 100 s^{-1}. This protocol was followed to erase the loading history of the sample. Consequently, the temperature was lowered to 55 °C and the observed scattering patterns were obtained. With hindsight, it seems possible that, upon cooling from 70 to 55 °C, there would be a contraction of the solution into the cell. This in turn would cause a flow of the sample into the cell that results in an alignment of the LCP that is perpendicular to the flow plane. Furthermore, the observed scattering patterns are shear and thermal history dependent, in that shearing of the parallel-aligned sample, *i.e.*, after $\dot{\gamma} = 1.47\ s^{-1}$, at a lower shear rate, *i.e.*, $\dot{\gamma} = 0.076\ s^{-1}$, does not reproduce the observed correlation perpendicular to the shear direction. This strongly suggests a preorientation of the sample for the initial scattering patterns that was not duplicated in further attempts to reproduce the results. Therefore, there is strong evidence that the theoretically predicted requirements for the mechanism of "log rolling" to be stable, a low nematic potential and an initial out-of-plane alignment, have been met, giving credence to the explanation of these unique scattering results by invoking this mechanism. Further experiments are necessary to verify and examine this unusual response mechanism.

65 and 75 °C Results. The high-temperature experiments demonstrate the existence of three regimes for the response of this LCP to shear flow with respect to the molecular orientation. At low shear rates, $\dot{\gamma} < \dot{\gamma}_1$, there is a substantial increase in molecular alignment with shear rate; at intermediate shear rates, $\dot{\gamma}_1 < \dot{\gamma} < \dot{\gamma}_2$, there is a slight change in the average orientation of the LCP with shear rate; and at high shear rates, $\dot{\gamma} > \dot{\gamma}_2$, there is again a dramatic increase in molecular orientation with shear rate. This indicates that $1/\dot{\gamma}_1$ and $1/\dot{\gamma}_2$ denote some characteristic time scales of the polymer solution. As this sample is being examined on molecular length scales and this polymer is known to be stiff and rodlike, the molecular dynamics of a rodlike polymer in concentrated solution is a natural starting point in an attempt to determine the physical origin of these time scales.

The relaxation spectrum of a rod in solution is different from that of a coil, which models an amorphous polymer in solution. The Zimm spectrum, τ_i, can adequately describe the relaxation modes of a coillike polymer. However, a rodlike polymer has a first relaxation mode whose time scale is separate from the spectrum of the local dynamics of the polymer. Therefore, in this case the relaxation times are more readily described by $\tau_0 + \tau_i$. The relaxation mode attributed to the longest relaxation time τ_0 is the end-over-end rotation of the rod in solution. The first relaxation mode in the spectrum, τ_1, has been attributed to the response of a rodlike LCP to perturbations that cause the rod to flex perpendicular to the long axis of the molecular, *i.e.*, the flexural relaxation time. Using these times as the two longest characteristic time scales of an LCP in solution, we can define three regimes in the molecular response of a rodlike LCP to shear flow as follows:

Slow: Shear rate is not fast enough to affect the dynamics of the rod in solution

$$\dot{\gamma} < 1/\tau_0$$

Moderate: Shear rate becomes fast enough to overcome rotation of LCP but not fast enough to overcome local dynamics

$$1/\tau_0 < \dot{\gamma} < 1/\tau_1$$

Fast: Shear rate affects the local chain motion

$$\dot{\gamma} > 1/\tau_1$$

From Doi and Edwards,[26] τ_0 can be estimated from molecular parameters using the following relations:

$$\tau_0 = \frac{1}{6D_r} \tag{1}$$

$$D_r = D_r^*\left(\frac{\nu^*}{\nu}\right)^2(1 - S^2) \tag{2}$$

$$D_r^* = D_{ro}\beta(\nu^* L^3)^{-2} \tag{3}$$

$$D_{ro} = \frac{3\ \ln(L/a)kT}{\pi L^3 \eta_0} \tag{4}$$

where L is the length of the molecule (=1617 Å), a = the diameter of the molecule (=18 Å), η_0 = the solvent viscosity ($\approx 1.6 \times 10^{-3}$ Pa s), D_{ro} = the rotational diffusion coefficient in dilute solution, β = a numerical constant ($\approx 1.3 \times 10^3$), ν = the polymer concentration in the LC phase (5.43×10^{-7} Å^3), D_r^* = the rotational diffusion coefficient in the isotropic phase, ν^* = the relative polymer concentration in the isotropic phase (2.12×10^{-8} Å^3), S = the order parameter (≈ 0.7), and D_r = the rotational diffusion coefficient in concentrated solution. S is approximated from Burghardt's[13] optical birefringence measurements. From these known parameters, τ_0 is estimated to be $\cong 0.5$ s. Ferry and coworkers[27,28] have worked extensively on the relation of τ_1 to τ_0 for rodlike polymers in solution. They have determined that the τ_0/τ_1 ratio for a rodlike polymer in solution, and specifically PBLG, is approximately 8–15, depending on conditions such as solvent quality, the strength of the rodlike molecule, and the L/a ratio of the rod. For the following calculations, a value of 10 is used.

From these calculations it is logical to assign $\dot{\gamma}_1 = 1/\tau_0 = 2$ and $\dot{\gamma}_2 = 1/\tau_1 = 20$. Comparison to the observed results, as shown in Figures 14 and 15, shows that these

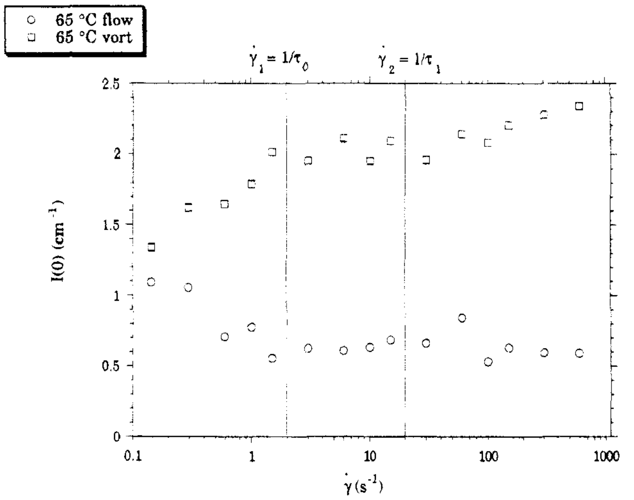


Figure 14. Same as Figure 12, except with crossover shear rates as determined from molecular parameters.

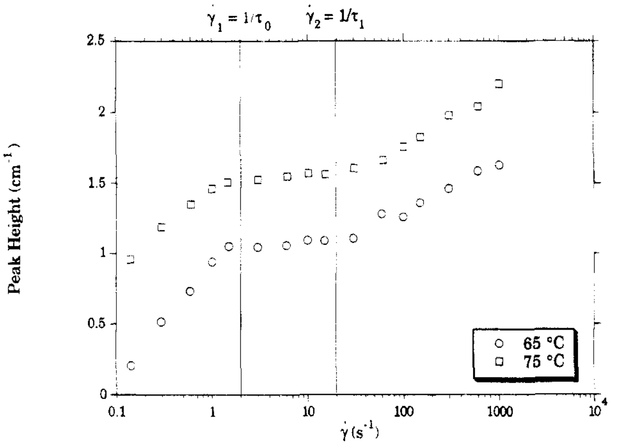


Figure 15. Change in viscosity and molecular orientation, as measured by the peak height of the azimuthal intensity, with shear. This plot exhibits ability to correlate the microresponse (molecular orientation) of a rod in solution to its macroresponse (viscosity).

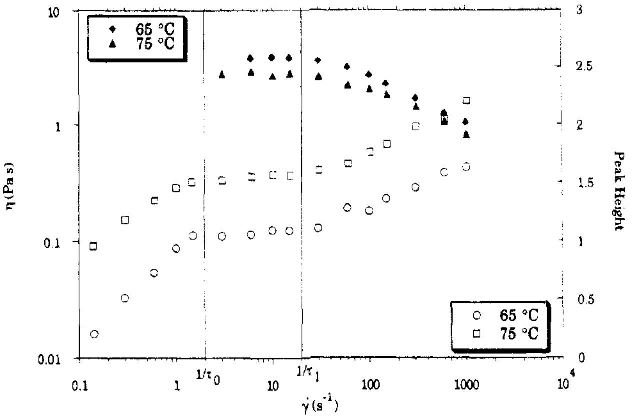


Figure 16. Change in viscosity and molecular orientation, as measured by the peak height of the azimuthal intensity, with shear. This plot exhibits ability to correlate the microresponse (molecular orientation) of a rod in solution to its macroresponse (viscosity).

values mark the crossover points of the experimentally defined regimes very well in terms of the $I(0)$ analysis and the peak height measurements, respectively.

Therefore three regimes of the molecular response of this LCP to a shear field can be defined as follows:

I. A slow regime, $\dot\gamma < 1/\tau_0$: In this region, the shear flow is not fast enough to overcome the molecular rotation but still affects the average alignment of the molecular.

II. An intermediate regime, $1/\tau_0 < \dot\gamma < 1/\tau_1$: For these shear rates, the flow field is fast enough to overcome rotation of the LCP but not fast enough to affect the local dynamics of the polymer chain. In this region, there is not much change in the molecular orientation with shear rate.

III. A fast regime, $\dot\gamma > 1/\tau_1$: The shear flow is fast enough that the local flexural motions are damped by the flow field. This results in a straightening of the molecule and a narrowing of the distribution of the orientation of the LCP about the flow direction.

The simultaneous measurement of scattering patterns and viscosity allows a method to correlate the microstructure of the polymer solution to its macroresponse. Figure 16 exemplifies this, showing the change with shear rate in the azimuthal peak height, which measures the orientation of the LCP in the flow field, and the viscosity of the PBLG/DBA solution at 65 °C. As was discussed earlier, the force transducer used is not sensitive enough to determine the viscosity below the reported values. This is unfortunate as this sensitivity limit occurs at *ca.* $\dot\gamma_1$, and therefore the viscosity of the solution cannot be correlated to the molecular alignment in the slow regime. Further experiments are planned to correct this shortcoming. However, the microstructural responses in the intermediate and fast regions correlate well with the viscosity. At moderate shear rates the solution displays Newtonian behavior while the alignment of the molecule also displays not much dependence on shear rate. As the solution enters the fast regime, however, the molecules become more oriented with increasing shear rate, and this manifests itself in the viscosity as shear-thinning behavior.

Comparison to Previous Studies

There have been numerous studies of the rheology of LCPs, many of them outlined in the Introduction. While by no means exhausting previous works, we would like to compare and contrast the reported results to complementary studies and their conclusions. There have been no experimental studies, to our knowledge, of the effect of aggregation on the molecular orientation under shear flow. Therefore, we hope that our unique results will stimulate interest in this important aspect of the rheology of LCPs in solution.

In terms of a comparison of our results to previous reports, our results most conspicuously disagree with those of Picken[18,19] in that an increase in the molecular orientation is found with increasing shear rate in the shear-thinning regime in our study. Our results, however, are in agreement in this regime with the results of Keates,[20] Burghardt,[13] Asada and Onogi,[24] and Larson[10] and even with Ernst's[16] interpretation of the shear SALS patterns. Our results clearly show that as a solution of PBLG in DBA enters into the shear-thinning regime, the distribution of the orientation of the polymer about the flow direction narrows. The universality of this observation is important for future studies.

In general, our observations are in agreement with other previous results. Ernst *et al.*[16] saw a fundamental change in the shear SALS pattern of PBLG in *m*-cresol above a critical shear rate. They attributed this change to the shear becoming fast enough to orient the molecules and affect the domain structure of the solution. Their critical shear rate is approximately equal to our $\dot\gamma_1$, showing good agreement between complementary techniques.

The specificity of our reported results, however, is not in total agreement with our peers' studies. At low shear rate, an increase in the orientation of the polymer is observed with increasing shear rate. This is opposite to Burghardt's[13] experimental and Larson's[10] theoretical results. They both found that at low shear rates there is no change in the order of the system with shear rate, though their absolute values of the amount of order present did not coincide.

At intermediate shear rates, however, our observed results in this projection agree with the works of Burghardt and Larson, except our results only display a slight increase in the orientation of the LCP with shear rate. Our description of this regime as where the shear has overcome rotation of the LCP but is not fast enough to affect the local dynamics of the molecule seems to correlate well with the "wagging" regime as defined by Larson. Larson[11] has correlated the crossover between regimes with the change of sign of the first normal stress difference (N_1). Future experiments will concentrate on correlating the sign of N_1 with our observed orientation transitions to correlate more closely our results to theoretical predictions.

There are two possible explanations for the difference between our results and that of Larson and Burghardt in the low-shear region. First, the difference may merely lie in the fact that the observations are being completed using different techniques and assumptions. The calculation of Larson assumes a uniform initial orientation parallel to the shear gradient. The polydomain nature of the experimental sample and initial molecular orientation must influence the response of the system, especially in the tumbling regime where there is not expected to be a steady state. Larson's[11] later work demonstrates how the initial director orientation dramatically influences the response of an LCP to shear flow. Further calculations by Larson and Doi,[33] in an attempt to account for the polydomain nature of LCP solutions, utilize an approximation of shear rate dependent texture refinement that yields a shear rate independent order in the tumbling regime. Therefore, in this calculation, this result of shear rate independent order is not as much a prediction as an assumption. Clearly, the initial director orientation will affect the response of the LCP to solution, especially in the tumbling regime, and this may account for the discrepancy between theory and experiment.

Our observation of an increase in the orientation of the LCP with shear rate in the predicted tumbling regime may be a consequence of the nature of the experiment as well as the nature of the rotation of the director. As was previously described, due to the large scattering window (12 mm) and long scattering time (2 h), the experimentally determined scattering pattern, and therefore the molecular orientation, is a time- or ensemble-averaged quantity. This is not true for optical measurements, where the scattering window and time are both small. The nature of the director rotation is important as it is not a symmetrical, continuous orbit, but rather a rotation that is slower near the flow direction and faster orthogonal to it. Due to the nature of this orbit, even while tumbling, the molecule is oriented most of the time (70–80%) close to the flow direction. If the increased shear rate speeds the rotation of molecules orthogonal to the shear direction and slows it while near the shear direction, as seems feasible, this would result in an increase in the amount of time spent close to the flow direction. This in turn would manifest itself in these scattering experiments as an increase in the average molecular orientation, and may not be other techniques.

A second possible explanation for the difference between our results and previous results may lie in the nature of the solution. Though *m*-cresol is known to show slight aggregation of PBLG in solution, aggregation of PBLG in DBA is profound[21] and has been seen at very low concentrations (<1%) as well as high temperatures (*ca.* 70 °C). The response of any aggregates that may exist, as opposed to individual rods, could account for the observed results. Further experiments are planned to examine this possibility.

A final point worth mentioning is the role of τ_0 and τ_1 in determining the transition between molecular orientation responses. Previous schemes, including that of Asada and Onogi,[24] have attributed the onset of shear thinning to the ability of the shear flow to overcome rotation of the LCP, *i.e.*, $\dot{\gamma}_2 = 1/\tau_0$. In their predictions, the first transition (regime I to regime II in the scheme of Onogi and Asada) is attributed to the breakup of the domain structure by the shear flow. It is our speculation that the first transition is due to the ability of the shear flow to overcome rotation, *i.e.*, $\dot{\gamma}_1 = 1/\tau_0$, which in turn may allow the shear flow to break up the domain structure. Only when the shear rate becomes fast enough to overcome the local dynamics, $\dot{\gamma}_2 = 1/\tau_1$, does the shear actually narrow the distribution of the orientation of the LCP about the shear direction, which manifests itself as shear-thinning viscosity.

Conclusions

By measuring the scattering patterns of a liquid crystalline polymer solution while subjected to shear flow, the response of the LCP solution to the shear flow, in terms of the orientation of the rodlike molecule, was determined. As the shear rate was increased, the existence of three regimes in the flow of this LCP in solution with respect to its molecular response to shear was found. With τ_0 and τ_1 being the first two relaxation modes of an LCP in solution, the regimes are defined as follows:

Slow regime, $\dot{\gamma} < 1/\tau_0$: In this regime there is an increased average alignment of the LCP in solution with shear rate. This may correlate to an increase in speed of the tumbling of the director with shear rate.

Intermediate regime, $1/\tau_0 < \dot{\gamma} < 1/\tau_1$: In this regime there is a slight change in the average alignment of the LCP with shear rate. This is due to the inhibition of the rotation of the LCP by the shear flow.

Fast regime, $\dot{\gamma} > 1/\tau_1$: The distribution of the alignment of the LCP about the shear direction narrows in this regime. This occurs as the flow field overcomes the local dynamics of the LCP. This manifests itself in the viscosity as shear-thinning behavior.

It was also seen that the response of this LCP to shear flow near the gel threshold exhibits an unusual correlation perpendicular to the shear direction at low shear rates. This seems to be accounted for by the theoretically predicted mechanism of log rolling. To our knowledge this is the first experimental evidence of log rolling as a stable flow mechanism. This unusual mechanism for the flow of LCP is of interest and deserves further study. In addition, it is seen that the alignment of the LCP molecules as measured by neutron scattering under shear flow correlates well to the macroresponse (*i.e.*, viscosity). This is of importance as the completion of *in-situ* neutron scattering experiments is not trivial.

Therefore, the correlation of these results to a more common laboratory technique, such as rheological measurements, is useful. However, the universality of this correlation must be verified with future experiments before it can be generally accepted.

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References and Notes

(1) Jerman, R. E.; Baird, D. G. *J. Rheol.* **1981**, *25*, 275.
(2) Kiss, G.; Porter, R. S. *J. Polym. Sci., Polym. Symp.* **1978**, *65*, 193.
(3) Kiss, G.; Porter, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 361.
(4) Mewis, J.; Moldenaers, P. *Mol. Cryst. Liq. Cryst.* **1987**, *153*, 291.
(5) Grizzuti, N.; Cavella, S.; Cicarelli, P. *J. Rheol.* **1990**, *34*, 1293.
(6) Navard, P. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 435.
(7) Peuvrel, E.; Navard, P. *Macromolecules* **1991**, *24*, 5683.
(8) Moldenaers, P.; Mewis, J. *J. Non-Newtonian Fluid Mech.* **1990**, *34*, 359.
(9) Marruci, G.; Maffettone, P. L. *Macromolecules* **1989**, *22*, 4076.
(10) Larson, R. *Macromolecules* **1990**, *23*, 3983.
(11) Larson, R.; Öttinger, H. C. *Macromolecules* **1991**, *24*, 6270.
(12) Kiss, G.; Porter, R. S. *Mol. Cryst. Liq. Cryst.* **1980**, *60*, 267.
(13) Hongladarom, K.; Burghardt, W. R.; Baek, S. G.; Cementwala, S.; Magda, J. J. *Macromolecules* **1993**, *26*, 772.
(14) Fuller, G. G.; Smith, K.; Burghardt, W. R. *J. Stat. Phys.* **1991**, *62*, 1025.
(15) Hsiao, B. S.; Stein, R. S.; Deutscher, K.; Winter, H. H. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 1571.
(16) Ernst, B.; Navard, P.; Hashimoto, T.; Takebe, T. *Macromolecules* **1990**, *23*, 1370.
(17) Berry, G. C.; Srinivasarao, M. *J. Stat. Phys.* **1991**, *62*, 1041.
(18) Picken, S. J.; Aerts, J.; Visser, R.; Northolt, M. G. *Macromolecules* **1990**, *23*, 3849.
(19) Picken, S. J.; Aerts, J.; Doppert, H. L.; Reuvers, A. J.; Northolt, M. G. *Macromolecules* **1991**, *24*, 1366.
(20) Keates, P.; Mitchell, G. R.; Peuvrel-Disdier, E.; Navard, P. *Polymer* **1993**, *34*, 1316.
(21) Dadmun, M. D.; Muthukumar, M.; Han, C. C.; Hempelmann, R.; Schwahn, D.; Springer, T. Submitted to *Macromolecules*.
(22) Van der Schoot, P. *J. Phys. Chem.* **1992**, *96*, 6083 and references therein.
(23) Nakatani, A. I.; Kim, H.; Han, CC. *J. Res. Natl. Inst. Stand. Technol.* **1990**, *95*, 7.
(24) Onogi, S.; Asada, T. *In Rheology*; Astarita, G., Marruci, G., Nicolais, L., Eds.; Plenum: New York, 1980; Vol. 3.
(25) Horton, J. C.; Donald, A. M. *Polymer* **1991**, *32*, 2418.
(26) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: New York, 1986.
(27) Warrent, T. C.; Schrag, J. L.; Ferry, J. D. *Biopolymers* **1973**, *12*, 1905.
(28) Rosser, R. W.; Schrag, J. L.; Ferry, J. D.; Greaser, M. *Macromolecules* **1977**, *10*, 978.
(29) Hongladarom, K.; Burghardt, W. R. *Macromolecules* **1993**, *26*, 785.
(30) Moldanaers, P.; Fuller, G. G.; Mewis, J. *Macromolecules* **1989**, *22*, 960.
(31) Burghardt, W. R.; Fuller, G. G. *Macromolecules* **1991**, *24*, 2546.
(32) Srinivasarao, M.; Berry, G. C. *J. Rheol.* **1991**, *35*, 379.
(33) Larson, R.; Doi, M. *J. Rheol.* **1991**, *35*, 539.