Critical Behavior of Shear-Induced Transient Periodic Structures in a Lyotropic Liquid Crystalline Polymer as a Function of Molecular Weight

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ABSTRACT: The threshold shear rate ($\dot{\gamma}_{c1}$) for producing a transient periodic structure in a film of the lyotropic liquid crystalline polymer poly(γ-benzyl L-glutamate) in dioxane/nitrobenzene decreases with increasing molecular weight (MW). $\dot{\gamma}_{c1} \propto \mathrm{MW}^{-a}$, where a is larger than 3. A high molecular weight and the consequent high anisotropy of the polymer favor the appearance of the transient periodic structure from both an energetic and dynamic point of view. The critical shear strain (γ_c) is an increasing function of and proportional to the MW. The scaling rule for the appearance of the periodic structure, as well as the damped oscillation of viscosity in transient flow, can be attributed to the liquid crystal polymer tumbling behavior.

Introduction

There have been many studies of the mechanical properties of liquid crystalline polymers (LCPs) as a consequence of their promising applications as high-strength materials. Because of their high molecular weight (MW) and consequent high anisotropy, LCPs display many striking and unique macroscopic phenomena. One of these is a transient periodic structure as a dynamic response to the application of external fields.[1–6] When a well-aligned nematic sample is suddenly rotated in a strong magnetic field, for example, a transient periodic structure appears. The origin of the effect has been explained as follows:[1] (1) a periodic distortion occurs preferentially yielding a uniform texture which has a lower effective viscosity; (2) because of inherent nonlinearities, that distortion mode having a faster initial growth rate suppresses all slower ones and becomes macroscopically observable. For LCPs consisting of very long molecules, there is not only a larger viscosity but also a high anisotropy in physical properties. Consequently, the periodic structure is very long-lived. The high anisotropy also results in a very broad range of conditions under which the periodic structure occurs. The transient periodic structure is a common dynamic phenomenon and is easily observed experimentally, providing a useful means of studying the mechanical properties of LCPs.[3,6]

In recent work, textures and textural evolution in LCPs have been studied by shearing a well-aligned thin nematic sample at very low shear rates.[4,5,7] A shear-induced transient periodic structure is observed when the shear rate $\dot{\gamma}$ is larger than a critical value $\dot{\gamma}_{c1}$, and the shear strain, γ (shear rate × shear time), is equal to a critical value γ_c. $\dot{\gamma}_{c1}$ is proportional to h^{-2}, where h is the sample thickness. The shear strain γ_c is independent of both h and $\dot{\gamma}$ when $\dot{\gamma} > \dot{\gamma}_{c2}$. In this work, values of $\dot{\gamma}_{c1}$ and γ_c are determined as a function of the MW of LCPs. The results are discussed in terms of a model of semiflexible but fully extended long rods.[8]

Experimental Section

Details of the sample preparation and shearing apparatus have already appeared.[4] Poly(γ-benzyl L-glutamate) (PBLG) of known MW was purchased from Sigma Chemical Co. It was dissolved in a mixture of dioxane/nitrobenzene = 42/58 (v/v). For each sample, the concentration of PBLG was 20% (w/v). The MW of PBLG varied from 187K to 435K. In this solvent, PBLG solutions are known to be in the nematic phase at room temperature.[9] The sample is sandwiched between two slides, which are coated with a thin film of a mixture of tin and indium oxides. A spacer supporting the sample between the two slides is created by masking the center area of the slide and spraying the remainder with a Teflon spray. In this manner, a sample can be kept in the shear cell for more than a week without appreciable loss of solvent and the spacer can be controlled to ±2 μm. After several hours, domains larger than 1 cm² are formed with good homeotropic alignment (director perpendicular to the surface of the slide).

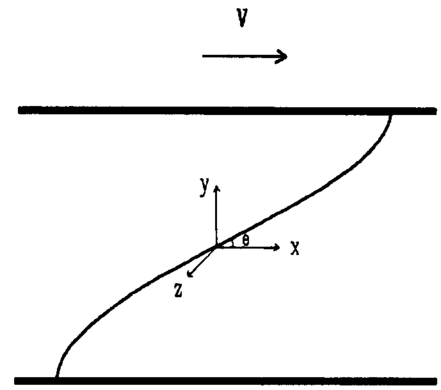

Figure 1. The director profile in the shear plane.

When shear is initiated with $\dot{\gamma} > \dot{\gamma}_{c1}$, the director is rotated toward the shear direction and confined within the shear plane x–y as is shown in Figure 1. When shear strain is equal to γ_c, the director tips out of the shear plane in a periodic manner along the shear direction.[4,5] The structure observed between crossed polars with the lower polar parallel to the shear direction consists of alternate white and black bands perpendicular to the shear direction, as shown in Figure 2. When the sample is further sheared, perpendicular bands are replaced by either parallel bands or disclinations. Variation of the spacing of the perpendicular band with shear rate is given in Figure 3, showing that the band spacing increases with decreasing shear rate.

Variations of the two critical quantities, $\dot{\gamma}_{c1}$ and γ_c are plotted as a function of MW of PBLG in Figure 4. γ_c is the shear strain when the shear rate $\dot{\gamma} > \dot{\gamma}_{c2}$. When $\dot{\gamma} < \dot{\gamma}_{c2}$, the bands appear very slowly and it is therefore difficult to measure the time frame. Since the shear rates used in these experiments are in the lower linear shearing regime and the

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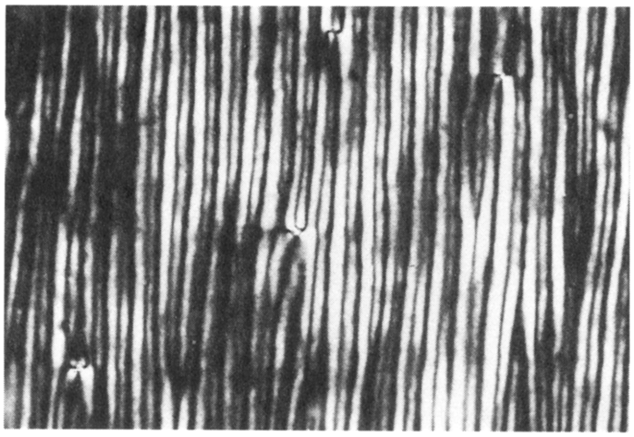

Figure 2. Photomicrograph of a PBLG(318K) 20 μm thick sample sheared at $\dot{\gamma} = 0.5\ s^{-1}$. The photo was taken 78 s after the initiation of shear flow under crossed polars with the lower polar parallel to the shear direction.

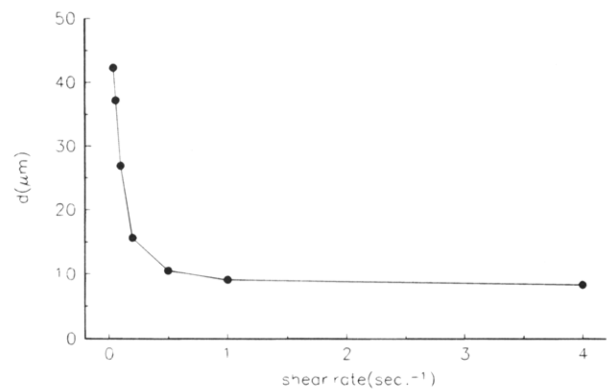

Figure 3. Band spacing, d, of the transient periodic structure as a function of shear rate for a 20 μm thick PBLG(318K) sample.

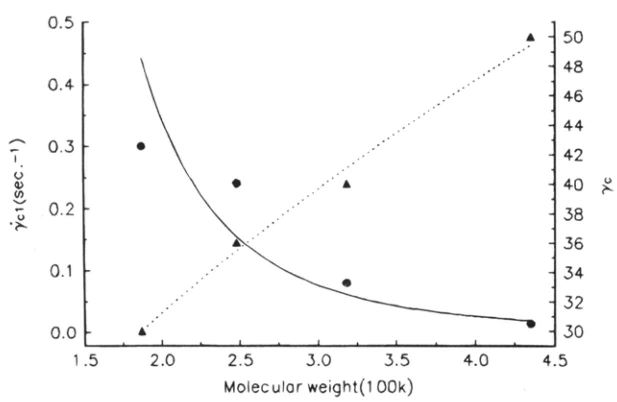

Figure 4. Threshold shear rate, $\dot{\gamma}_{c1}$, and shear strain, γ_c vs MW of PBLG. h, the sample thickness, is 10 μm. (●) = $\dot{\gamma}_{c1}$; (▲) = γ_c.

area of the monodomain is much larger than the molecular dimensions, the linear continuum theory of Leslie and Ericksen can be applied.[4,10] Concentrations of all samples are 20% (w/v), so the volume fraction of the polymer in the solution is almost constant at 16%. As can be seen in Figure 4, $\dot{\gamma}_{c1}$ decreases while γ_c increases with increasing MW.

Discussion

Lyotropic nematic LCPs, unlike small-molecule nematics, show tumbling behavior at low shear rates characterized by $\alpha_3/\alpha_2 < 0$,[11-14] where α_i are the Leslie viscosity coefficients. For tumbling nematics, there is an instability in which the director can tip out of the shear plane when the shear rate is larger than a threshold value.[4,5,7,15-17] Furthermore, LCPs consisting of long rodlike molecules usually have a high anisotropy in their mechanical properties. The high anisotropy is reflected in the large differences among their elastic constants K_i and Leslie viscosity coefficients α_i.[8] The high anisotropy of the LCP energetically favors this instability. After initiation of shear, the director with initially homeotropic alignment tends to tip toward the shear direction under the viscous torque.[4,5] If the director is still confined within the shear plane (the $x-y$ plane), its profile in the plane is shown in Figure 1, a purely splay–bend distortion. When the director tips out of the shear plane, the splay–bend distortion will mix with a twist distortion. Since K_1 and K_3 are much larger than K_2 and also increase with MW,[8] more energy is needed for further rotation of the director in the shear plane than for its tipping out of the shear plane. From elastic energy considerations, the larger the MW of the LCP, the higher is the anisotropy and the easier it becomes for the director to deviate out of the shear plane.

Zúñiga and Leslie[15] have theoretically studied the instability involved when the director deviates out of the shear plane. They assume that the director tips out of the shear plane in a uniform way rather than in the periodic way shown in Figure 2. As mentioned in the last section, the band spacing increases as the shear rate approaches $\dot{\gamma}_{c1}$. Here it is assumed that the band spacing is to be infinite at $\dot{\gamma}_{c1}$, and the theory of Zúñiga and Leslie will then be applicable. The dimensionless velocity of the top slide corresponding to the instability, V_c, is equal to $v_c h\gamma_1/K_1$, where v_c is the actual velocity of the top slide and γ_1, the rotational viscosity, is equal to $\alpha_3 - \alpha_2$. By definition, $\dot{\gamma}_{c1} = v_c/h = V_cK_1/(\gamma_1 h^2)$, and therefore $\dot{\gamma}_{c1} \propto h^{-2}$, consistent with previous results.[4,7] Since $\gamma_1 \propto (L/d)^2$ and $K_1 \propto L/d$,[8] then $\dot{\gamma}_{c1} \propto V_cK_1/\gamma_1 \propto V_cd/L = V_c/\mathrm{MW}$. From Figure 4, $\dot{\gamma}_{c1}$ varies from 0.30 to 0.015 $\mu m{\cdot}s^{-1}$ as MW varies from 187K to 435K. $\dot{\gamma}_{c1}$ is proportional to MW^{-a}, where a is larger than 3. Therefore, V_c is a decreasing function of MW.

Since the configuration of the viscous field and the director field before the appearance of the transient periodic structure is symmetric with respect to the shear plane, as is also the case for magnetic field induced structures,[1] it is equivalent for the director to flip out of the shear plane in either the z or the $-z$ direction, rather than in a uniform way.[1,7,8] Long rods possess a strong coupling between their rotation and translation. Because of momentum conservation, the movement of molecules must be compensated by the opposite motion of molecules in nearby areas. The back-flow effect leads to this periodic deviation. The corresponding effective viscosity changes from a purely rotational γ_1 into a bend viscosity η_{bend}.[18,19] Usually long rods with large MW become more flexible. γ_1 increases with MW while η_{bend} is saturated and approaches η_b.[8] According to the measurements made by Lee and Meyer, η_b is only a few percent of γ_1 in the case of the MW used in the rheo-optical experiments.[8] Therefore, introduction of a periodic mode leads to a significant drop of the effective viscosity. The transient periodic structure appears more rapidly in long rodlike LCPs.[1]

It is well known that after shear initiates, the director with initially homeotropic alignment tips toward the shear direction and is confined within the shear plane before the appearance of transient periodic structures.[4,5] The angle of tip at the midplane (θ_0 in Figure 1) decreases with increase of shear rate or shear strain at

$\dot{\gamma} > \dot{\gamma}_{c1}$. The decrease in tipping does not saturate since there is no angle at which the viscous torque on the director vanishes. θ_0 eventually approaches 0°; that is, the director points in the shear direction. When this occurs, the flow becomes unstable with respect to the secondary flow that takes the director out of the shear plane.[7,15,16] The time taken for the director in the midplane to rotate from 90 to 0° is equal to one-quarter of the LCP tumbling period (P). It is therefore reasonable to assume that t_a, the time taken for the appearance of the transient periodic structure after initiation of shear, should be proportional to P. Marrucci[12] utilized viscoelastic coefficients provided in ref 20 and compared constrained tumbling with free tumbling. He found that the tumbling period is about the same in both cases, while severe distortion of the director orientation occurs in the free tumbling case. Assuming that this conclusion is valid for the current experiments, $P = 4\pi/[\dot{\gamma}(1 - \lambda^2)]$, where $\lambda = \gamma_2/\gamma_1 = -1 - 2\alpha_3/\gamma_1$.[4,5,7,17] Then t_a is proportional to $4\pi/[\dot{\gamma}(1 - \lambda^2)]$. The appearance of transient periodic structures scales to the total shear strain $\gamma_c = \dot{\gamma}t_a$ at $\dot{\gamma} > \dot{\gamma}_{c2}$. The scaling rule is independent of shear rate and the sample thickness.[4,5] $\gamma_c \propto (1 - \lambda^2)^{-1/2}$ and can be easily deduced to be proportional to $(\gamma_1/\alpha_3)^{1/2}$ since α_3/γ_1 is much smaller for LCPs.[8] Since α_3 is independent of L/d,[8] $\gamma_c \propto (\gamma_1/\alpha_3)^{1/2} \propto L/d \propto$ MW. The result shown in Figure 4 agrees with this conclusion. The appearance of the transient periodic structures, as well as the damped oscillation of the viscosity in transient flow, scales with shear strain. Obviously, both phenomena are consequences of the LCP tumbling behavior.[4,5]

Conclusions

The critical behavior of a transient periodic structure in LCPs has been studied. The threshold shear rate ($\dot{\gamma}_{c1}$) decreases with increasing MW and is roughly proportional to MW^{-a}, where a is larger than 3. The unique properties of LCPs, such as high anisotropy, provide circumstances for the preferred formation of a transient periodic structure energetically and dynamically. The shear strain, γ_c, at $\dot{\gamma} > \dot{\gamma}_{c2}$ increases with and is proportional to MW. The scaling rule for the appearance of the banded structure with shear strain results from LCP tumbling behavior as well as from damped oscillation of the viscosity in transient flow.

In this work, primary emphasis has been placed on shear-induced transient periodic structures in LCPs. In this discussion of the scaling rule for the appearance of the transient periodic structure with shear strain, it was assumed that (1) the director in the midplane is along the shear direction when it is deviating out of the shear plane, (2) formation time for the transient periodic structure after initiation of shear is one-quarter of the LCP tumbling period, and (3) the existence of an elastic force does not affect the LCP tumbling period. Even though these assumptions have been confirmed for several other systems,[12,15,20] their applicability to the current case needs further investigation. Zúñiga and Leslie's theory[14] considers the director to deviate out of the shear plane in a uniform way by an angle Φ which is independent of x. For LCPs, the director tips out of the shear plane in a periodic way, resulting in the banded structure seen in Figure 2, when the shear rate is greater than $\dot{\gamma}_{c1}$. A theory considering the dependence of Φ on x is necessary to account for the behavior shown in Figure 3. The measurement of the threshold shear strain has thus far only been performed at $\dot{\gamma} > \dot{\gamma}_{c2}$. Improvement of the experiment, investigation of the threshold shear strain at $\dot{\gamma} < \dot{\gamma}_{c2}$, and measurement of band spacing around $\dot{\gamma}_{c1}$ are clearly important to further understand the phenomenon of shear-induced transient periodic structures.

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