Shear Stress Overshoots in Flow Inception of Semiflexible Thermotropic Liquid Crystalline Polymers: Experimental Test of a Parameter-Free Model Prediction

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ABSTRACT: We explore the origins of shear stress overshoots upon flow inception of main-chain thermotropic liquid crystalline polymers from a random polydomain initial condition. A simple polydomain simulation strategy, based on Ericksen's transversely isotropic fluid model, is capable of predicting a shear stress overshoot arising from the reorientation dynamics of domains toward a steady state flow aligned state. When model parameters are estimated using elementary molecular theories for semiflexible main-chain thermotropes, both the relative magnitude of the shear stress overshoot and the steady state ratio of first normal stress difference to shear stress are determined solely by the "tumbling" parameter, λ. This implies a universal correlation between these two variables. We test this prediction against an extensive data set on semiflexible polyesters and find good qualitative agreement between model and experiment.

Introduction

Shear stress overshoots upon shear flow inception are a common feature of flexible polymer solution and melt rheology at high shear rates.[1] Molecular theories suggest that these overshoots reflect strong transient stretching of the flexible molecules.[2] Liquid crystalline polymers (LCPs), too, frequently exhibit large shear stress overshoots upon flow inception,[3−6] but in this case there is no widely held explanation of their origin. Contributing factors could possibly include flow induced chain stretching (analogous to flexible polymers), flow induced changes in the molecular order parameter of the LCP, distortion of the "polydomain" texture typically seen in quiescent LCP samples, and flow induced development of macroscopic alignment.

Careful consideration of this topic is thwarted by the fact that many flow inception data in the literature on LCPs are compromised by poorly defined experimental initial conditions. This is particularly true in the case of commercial aromatic copolyesters, in which the nematic−isotropic temperature is inaccessible. For this reason, the entire flow history of a sample (including loading samples in a rheometer, molding of sample disks, or potentially even the original processing of polymer pellets during manufacture) influences the orientation distribution and polydomain texture (e.g., domain size) present at the start of an experiment. Persistent flow history effects associated with sample loading have caused considerable confusion about the magnitude of the first normal stress difference in some commercial LCPs, illustrating the difficulties posed by these materials.[7,8] Starting in the early 1990s, Han and co-workers have systematically studied the rheology of main-chain LCPs by employing custom synthesized and well-characterized semiflexible LCPs with high thermal stability and accessible clearing temperatures. Heating a sample into the isotropic phase provides a way to "erase" the effects of prior thermal and shear history and establish a well-defined and reproducible initial condition for rheological study. A prototypical experiment employs a fresh sample that has been thermally cleared so that it starts in an ordered but poldyomain state, with a globally random orientation distribution.[9] The first studies featured a liquid crystalline polyester poly[(phenylsulfonyl)-*p*-phenylene 1,10-decamethylene-bis(4-oxybenzoate)] (PSHQ10); side-by-side comparisons of experiments on PSHQ10 and commercial copolyesters convincingly illustrate the virtues of this approach.[10] Continuing research has led to an extensive collection of data on the rheological effects of molecular weight,[11] spacer length,[12,13] and pendant side group[14] for a class of polymers denoted P*x*HQ*n*, where *x* identifies the pendant side group and *n* denotes the length of flexible hydrocarbon spacers in the backbone.

Ugaz and Burghardt[15] used in-situ X-ray scattering to study the development of macroscopic orientation upon flow inception from a random initial condition in a PSHQ6-12 polymer that had been synthesized by Chang and Han.[13] The monotonic development of molecular orientation suggested that this polymer may *shear align*, in contrast to lyotropic solutions of rodlike polymers in which *director tumbling* dynamics typically prevail.[16] They explored this possibility in the context of simple polydomain simulations of the development of orientation upon flow inception, based on Ericksen's transversely isotropic fluid model.[17] In addition to nearly quantitative predictions of orientation development, this simple model was also capable of self-consistent predictions of the magnitude of shear stress overshoots and the steady-state ratio of first normal stress difference to shear stress in PSHQ6-12. In this paper we report a more extensive and stringent test of this model against data on seven different polymers in the P*x*HQ*n* family.

Model Description

The simulation strategy of the polydomain Ericksen model makes several postulates and simplifying as-

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sumptions. In the present work, we assume that shear aligning dynamics prevail such that the tumbling parameter $\lambda > 1$.[16] To simulate development of macroscopic orientation upon flow inception, an ensemble of "domains" with random initial orientations is generated. Upon flow inception, each domain evolves toward the steady flow alignment angle according to the predictions of Ericksen's model, *independently of all other domains in the ensemble.* That is, the model ignores any interactions between neighboring domains mediated by distortional elasticity. Predictions of macroscopic orientation development are then made by performing averages over the ensemble of director trajectories. Here our interest is on stress behavior, which is also calculated by performing ensemble averages of the stress predictions of Erickesn's model. This leads to the following expressions for time-dependent shear stress (σ) and first normal stress difference (N_1):[15]

$$\sigma(t,\dot{\gamma}) = \left[\mu + 2\mu_1\langle n_1^2 n_2^2\rangle + \frac{\mu_2}{2}\langle n_1^2 + n_2^2\rangle\right]\dot{\gamma} \qquad (1)$$

$$N_1(t,\dot{\gamma}) = 2\mu_1[\langle n_1^3 n_2\rangle - \langle n_1 n_2^3\rangle]\dot{\gamma} \qquad (2)$$

where μ, μ_1, and μ_2 are the Ericksen viscosities, $\dot{\gamma}$ is shear rate, n_1 and n_2 are director components in the flow and velocity gradient directions, respectively, and the bracket $\langle\cdots\rangle$ denotes an ensemble average. Even though only components n_1 and n_2 appear in eqs 1 and 2, the initial random ensemble includes all possible director orientations in three dimensions.

While orientation predictions depend only on the assumed value of λ, it is also necessary to specify values for μ, μ_1, and μ_2 in order to make stress predictions. Since data on these parameters are unavailable, we seek guidance from molecular models for semiflexible LCPs. Specifically, the nematic dumbbell model of Maffettone and Marrucci[18] and the recent nematic Rouse model of Long and Morse[19] (in the "anisotropic Gaussian chain" limit and assuming isotropic friction) both predict shear aligning dynamics ($\lambda > 1$) and in fact make *identical* predictions for the relative values of the Ericksen viscosities:

$$\frac{\mu_1}{\mu} = \frac{2\lambda}{\lambda - 1} \qquad (3)$$

$$\frac{\mu_2}{\mu} = -2 \qquad (4)$$

Of these predictions, eq 4 is particularly important. At steady state, all domains eventually adopt the flow alignment condition, in which ${n_1}^2 + {n_2}^2 = 1$ and $n_3 = 0$, which, in combination with eq 4, means that the μ and μ_2 terms cancel in eq 1. Thus, at steady state these models predict that the ratio N_1/σ depends only on the steady alignment angle, and hence solely on λ, according to[15]

$$\frac{N_1}{\sigma} = \frac{2}{\sqrt{\lambda^2 - 1}} \qquad (5)$$

In transient flow inception simulations starting from a random polydomain initial condition, eq 1 (using predictions of eqs 3 and 4) predicts a shear stress overshoot,[15] whose magnitude relative to the steady-state shear stress is also determined by λ. Representative calculations presented in Figure 1 show that the magnitude of the predicted overshoot becomes progressively larger as λ approaches 1; a series of simulations with different λ values were performed to establish this dependence. (Since distortional elasticity is neglected in the modeling, values of λ less than 1 would lead to persistent oscillations in the average orientation state and hence also in the averaged shear and normal stresses.)

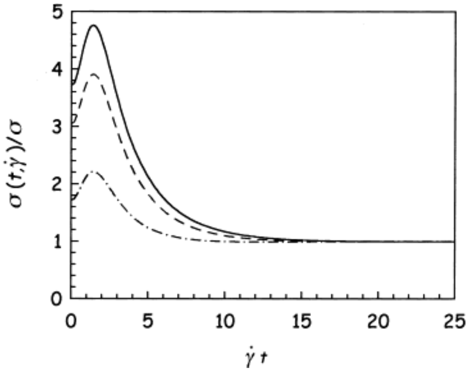


Figure 1. Polydomain Ericksen model prediction of shear stress as a function of shear strain after flow inception from a random polydomain initial condition. Stress is computed according to eq 1 using predictions of eqs 3 and 4 and normalized by its steady-state value. Calculations presented using $\lambda = 1.04$ (solid curve), 1.05 (dashed curve), and 1.1 (dot−dashed curve).

Table 1. Summary of Transition Temperatures of the LCPs Investigated in This Study

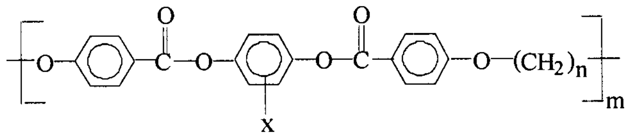
sample code	$[\eta]$ (dL/g)	T_g (°C)	T_{NI} (°C)
PSHQ5	0.547	104	167
PSHQ6	0.877	110	228
PSHQ10	0.667	92	181
PSHQ11	0.485	77	147
PSHQ6-12	0.765	93	194
PEHQ10[a]	1.393	51	239
PTHQ10	0.771	67	193

[a] PEHQ10 undergoes a smectic-to-nematic transition at 148 °C.

The fact that both the shear stress overshoot magnitude and steady state N_1/σ ratio are predicted to depend solely on λ implies a universal correlation between these two quantities, which may be represented in a cross plot in which the parameter λ is eliminated. Having adopted the polydomain simulation assumptions and the nematic dumbbell/Rouse model predictions, no remaining parameters may be adjusted to tune this model prediction. Comparisons of this prediction against experimental data thus provide a strenuous and simultaneous test of both the polydomain simulation strategy and the molecular model predictions of eqs 3 and 4.

Experimental Section

In this study we employed seven aromatic main-chain LCPs with chemical structure



where *x* denotes pendant side groups and *n* denotes the number of methylene groups as flexible spacers. Table 1 gives a summary of sample codes, glass transition temperature (T_g), and nematic-to-isotropic transition temperature (T_{NI}) of the polymers employed in this study. With reference to Table 1, P*x*HQ*n*s with $x = SO_2$-Ph and $n = 5, 6, 10$, and 11 are referred to as PSHQ5, PSHQ6, PSHQ10, and PSHQ11, respectively, and P*x*HQ*n* with $x = OC_2H_5$ and $n = 10$ is referred to as PEHQ10, and P*x*HQ*n* with $x = C(CH_3)_3$ and $n = 10$ is referred to as PTHQ10. PSHQ6-12 is a random copolymer of PSHQ6 and PSHQ12. The details of the synthesis procedures for PSHQ*n* (with $n = 5$, 6, 10, or 11) and PTHQ10 are given in refs 20 and 21, the details of the synthesis procedures for PSHQ6-12 are given in ref 22, and the synthesis procedures for PEHQ10 are given in ref 23.

For rheological measurements, specimens with a thickness of 0.5 mm were prepared by solvent casting from dichloromethane or tetrachloroethane in the presence of 0.1 wt % antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the majority of the solvent first at room temperature for 1 week and then at a temperature 10 °C *below* the glass transition temperature (T_g) for 3 days in a vacuum oven to remove any residual solvent. Specimens were dried further in a vacuum oven at a temperature 10 °C *above* the T_g of each polymer for 2 h. A Weissenberg rheometer (model R16) with a cone-and-plate (25 mm diameter plate, 4° cone angle) fixture, a Rheometrics mechanical spectrometer (RMS model 800) with a cone-and-plate (8 mm diameter plate, 0.1 rad cone angle) fixture, and a Rheometrics ARES with a cone-and-plate (8 mm diameter plate, 0.1 rad cone angle) fixture were used to measure in the transient shear mode shear stress growth ($\sigma^+(t,\dot\gamma)$) and first normal stress difference growth ($N_1^+(t,\dot\gamma)$) as functions of time (t) for various shear rates ($\dot\gamma$) and temperatures. Shear rates ranged from 0.1 to 2.7 s^{-1} depending on the sample and temperature; details on experimental conditions may be found in the original papers.[9-14] All samples were "cleared" by heating above the nematic–isotropic transition temperature and then cooled in the rheometer to the desired test temperature within the nematic phase to produce the random polydomain initial condition. The annealing time at the test temperature prior to flow inception was around 30 min. Each transient shear flow experiment lasted for a sufficiently long time to attain steady state. It turned out that shear stress reached a steady state in a relatively short time (say within 50 strain units), but the first normal stress difference sometimes did not attain a steady state even after 600–800 strain units. All experiments were conducted under a nitrogen atmosphere in order to preclude oxidative degradation of the specimen. The temperature control was satisfactory to within ±1 °C.

Results and Discussion

Experimental data collected on seven different P*x*HQ*n* polymers over a range of temperatures and shear rates are compared, in Figure 2, with the prediction by the polydomain model (the solid curve), where σ_{peak} is the shear stress overshoot. It is seen that the experimental data are in good agreement with the prediction by the polydomain model in conjunction with nematic dumbbell/Rouse viscosity predictions. Since there would be little reason, a priori, to anticipate the existence of such a correlation, much less the quantitative position of the correlation curve, these data suggest that these simple models are indeed capable of capturing some of the essential physics in flow inception of semiflexible thermotropes from a random polydomain initial condition. Several implications follow from this result.

The analysis and model assumptions leading to the predicted curve in Figure 2 only apply to the case of shear alignment. The success of this approach provides further, albeit indirect, evidence that shear aligning dynamics may be the norm in main-chain thermotropic LCPs containing aliphatic spacers in the main chain. This agrees with the inference drawn by Ugaz and Burghardt[15] from orientation development upon flow inception of PSHQ6-12 and with the limited body of direct evidence from monodomain shear experiments on similar polymers.[25,26]

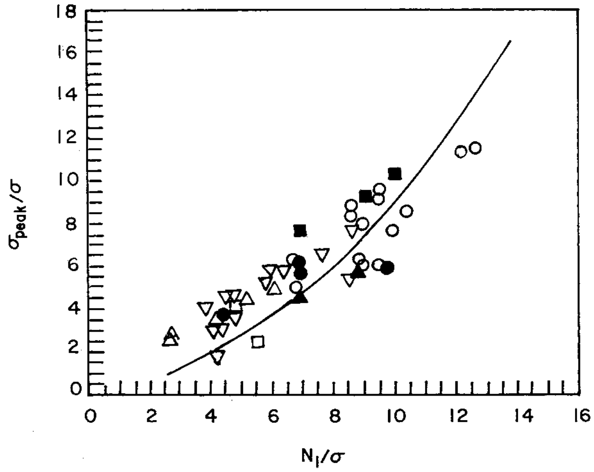


Figure 2. Plot of σ_{peak}/σ vs N_1/σ for P*x*HQ*n* at various temperatures: (○) PSHQ10 at 130, 140, 150, and 160 °C taken from refs 9, 11, and 14; (△) PSHQ5 at 148 and 150 °C taken from refs 12 and 24; (□) PSHQ6 at 210 °C taken from ref 12; (▽) PSHQ11 at 130 °C taken from refs 12 and 24; (●) PSHQ6-12 at 150, 160, 170, and 180 °C taken from ref 13; (▲) PEHQ10 at 160, 180, and 200 °C taken from ref 14; (■) PTHQ10 at 150 and 170 °C taken from ref 14. The solid curve is the prediction of the polydomain model.

The model assumptions provide for only one mechanism for shear stress overshoots: changes in instantaneous average viscosity of the polydomain sample as the ensemble of domain orientations evolves from the random initial condition toward the flow alignment angle, as described by eq 1. The results in Figure 2 suggest that this effect plays the major role in originating, and setting the magnitude of, shear stress overshoots in this flow inception protocol. This does not preclude other factors acting in parallel, such as direct stress contributions from distortional elasticity as the initially isotropic defect network is deformed. Indeed, such effects may contribute to the scatter of the data around the polydomain model prediction in Figure 2. Direct microscopic observations demonstrate that deformation of the initial polydomain texture is well correlated with shear stress overshoots in these materials.[27] However, domain reorientation from the random initial state to one of high alignment occurs over precisely the same range of strains.[15,28] Even in combination, such in-situ structural data cannot themselves resolve which factor dominates the stress overshoots. However, these simulations make clear that domain reorientation, by itself, goes a long way toward explaining the origin of shear stress overshoots. Note that the polydomain model automatically predicts strain scaling of the transient shear stress overshoot, in good agreement with experimental data.[8-14]

Since the Ericksen model is only valid for polymers in the slow-flow limit, the success of the polydomain model predictions in Figure 2 suggests that these experimental data were collected under conditions where nonlinear polymer viscoelastic effects (such as flow-induced chain stretching) do not play a significant role in the measured rheology.

Finally, despite the extreme simplicity of the molecular models used to predict the viscosity coefficients (for instance, their neglect of possible entanglement effects), these results suggest that the nematic Rouse and dumbbell models may provide a useful first step in the development of molecular descriptions of semiflexible LCP rheology, at least in their slow-flow limits for predicting the viscosities that appear in continuum models.

While the polydomain model's success in this test against experimental data is encouraging, it is also appropriate to highlight some failings of this modeling approach to provide a balanced perspective of its capabilities. Equations 1 and 2 predict that both shear stress and first normal stress difference depend linearly on shear rate at steady state, a prediction which is seldom borne out in thermotropic LCPs except perhaps over a limited shear rate range, and then only approximately. While the polydomain model is capable of predicting N_1 overshoots upon flow inception, their magnitude does not compare favorably with experiment, and the strain required for N_1 to reach steady state in experiments can be much larger than the polydomain model predicts.[15] Further, N_1 data upon flow inception can exhibit poor strain scaling,[8−14] while the polydomain model is only capable of predicting transient phenomena that scale with shear strain. P*x*HQ*n* polymers often exhibit multiple secondary stress maxima and minima in N_1 after the initial stress overshoot, and occasionally so does the shear stress. Having made the assumption of flow alignment, the polydomain model can predict only single stress overshoots upon inception from a random polydomain condition.

As noted by Ugaz and Burghardt,[15] it is likely that many of these deficiencies, particularly those involving the behavior of the first normal stress difference, arise from the neglect of interdomain interactions and direct contributions of distortional elasticity to the rheological response in polydomain LCPs. These are, in fact, radical simplifications, so it is not surprising that they may lead to unwelcome consequences. A realistic accounting of the detailed three-dimensional evolution of LCP defect texture under flow remains a daunting computational problem. The success of the polydomain model in Figure 2, however, suggests that even highly simplified model approaches can play a constructive role in helping to elucidate certain aspects of thermotropic LCP rheology.

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