Start-up Shear Flow and Nanoscale Structure of a Thermotropic Liquid Crystal Polymer

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Liquid crystalline polymers (LCP) exhibit complex response to flow due to a combination of the features of low molecular weight liquid crystals and high molecular weight polymers. While aspects of the steady flow behavior remain to be elucidated, understanding of their transient flow characteristics lags far behind. Although certain of the start-up flow characteristics exhibit some similarity to those of flexible polymer melts, there are also significant differences. For instance, under fast start-up shear, flexible polymer melts exhibit a stress overshoot at a shear strain (γ) in the range $1 < \gamma < 10$, followed by a steady state. Thermotropic liquid crystalline polymers (TLCP) also exhibit a stress overshoot at a similar γ. In addition, before the steady state is reached, a second stress overshoot at $\gamma \approx 100$ has been observed in some TLCP [1] but not in others [2]. The reasons for the difference, the molecular origin of the phenomenon and its relation to changes in the underlying morphology remain unclear. To address these questions, we began our investigations with the start-up shear flow of the liquid crystalline state of p-hydroxybenzoate/2-hydroxy-6-naphthoic acid (HBA/HNA), a widely used random copolyester with a chemical structure different to the one used in [1].

Fig.1 exhibits the γ dependence of the shear stress, normalized using the height of the first maximum, for several shear rates, $\dot{\gamma}$. It is clear that two stress maxima can be observed. For the investigated $\dot{\gamma}$, the first stress maximum occurs at $\gamma \approx 3$, independent of $\dot{\gamma}$. For entangled flexible polymer melts and at $\dot{\gamma}$ less than the inverse of the chain Rouse time, a similar superposition is observed but for $\gamma \approx 2$. However, as the TLCP exhibits a domain morphology in the quiescent state, it is unclear if the underlying physics is similar in both cases. Fig. 1 also indicates that a second stress maximum can be observed at a larger γ. Upon increasing $\dot{\gamma}$, this maximum progressively shifted to larger γ and appeared to saturate at $\gamma \approx 200$. In order to investigate the effect of the shear flow on the nanoscale structure, samples rapidly quenched at several strains were examined using small angle x-ray scattering. As can be seen from Fig. 2, the orientation seen in the two dimensional scattering patterns exhibit a 90° rotation upon traversing the second maximum. Interestingly, sector averages of the two dimensional scattering patterns indicated that the nanostructure was not otherwise affected. This suggests that, at the nanoscale, the flow results in a 90° rotation of the underlying structure but does not otherwise perturb it not unlike observations in low molecular weight liquid crystals.
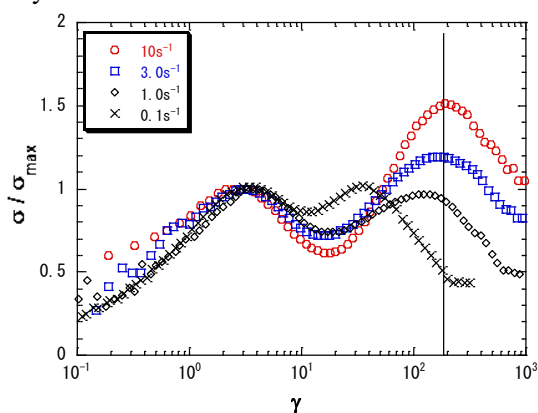

Fig. 1 Dependence of shear stress, normalized with the height of the first peak, on γ for several $\dot{\gamma}$ under start-up shear flow at 310 ℃.
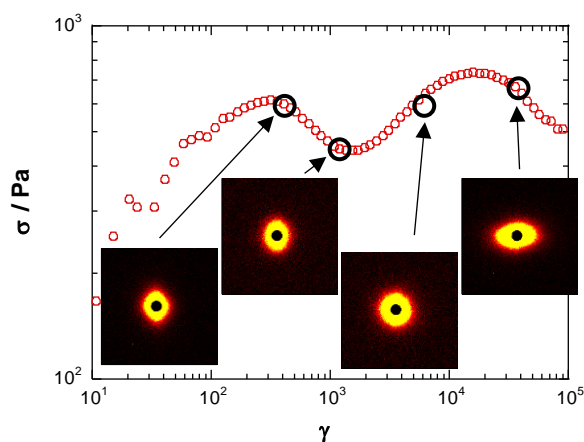

Fig. 2 SAXS results under start-up flow at a shear rate of 3.0 s^{-1} and a temperature of 310 ℃.

References

[1] Guo, et al. Polym. Eng. sci. 45, 187 (2005).

[2] I. Pilar, M.E. Munoz, J.J. Pena, and A. Santamaria, Polym. Eng. Sci., 36, 721 (1996).