583a In Situ Measurements of Molecular Orientation in Commercial Thermotropic Liquid Crystalline Polymers in Transient Shear Flows

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Despite significant advances in the understanding of dynamics of lyotropic liquid crystalline polymer (LCP) solutions, and 'model' thermotropic LCP melts characterized by flexible backbone spacers and lower transition temperatures, there is only limited fundamental understanding of commercial main-chain thermotropic LCPs. A major stumbling block is limited physical and chemical stability at the high melt temperatures of commercial LCPs which has to date rendered fundamental 'monodomain' studies impossible, and which creates well-documented complications even for conventional shear rheometry. As a result, it is not directly established whether commercial thermotropes are of the shear-tumbling or shear-aligning classification, the most basic information necessary to rationally anticipate how flow during processing might impact structure development. Instead, only indirect evidence is available, which tends to support the hypothesis of tumbling. In more idealized materials, direct measurements of molecular orientation in transient shear flows (reversals, step-changes and flow cessation) have often shed light on the underlying director dynamics. Here we report attempts to apply such methodology to two commercial thermotropic LCPs (Vectra A950 and B950). Synchrotron x-ray scattering in conjunction with a high speed area detector provides sufficient time resolution to limit the total time spent in the melt during testing, while further modifications to an x-ray capable shear cell provide a more robust platform for working with LCP melts at high temperatures. The transient orientation response to changes in flow condition do not yield definitive signatures of either tumbling or alignment. However, Vectra A shows clear responses to step-increase or step-decrease in shear rate, which contrasts with expectations and experience with shear-aligning nematics. Interestingly, these two polymers show opposite trends in orientation following flow cessation, which appears to correlate with evolution of dynamic modulus.