X-ray Scattering Measurements of Flow-induced Molecular Orientation in a Commercial Thermotropic Liquid Crystalline Polymer

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Introduction

Liquid crystalline polymers [LCPs] exhibit much potential as high-strength, lightweight engineering materials [1]. Their intrinsically high degree of molecular orientation and the opportunity to further influence this orientation state through flow fields experienced during processing lead to exceptional strength and stiffness, in combination with a low melt viscosity that allows for fabrication of precision moldings. However, LCPs have not yet fulfilled this promise in the commercial arena, in part because of the difficulty in anticipating the orientation state that will result from any given processing operation. High molecular orientation, which leads to the exceptional properties of LCPs, can also be detrimental in that it results in highly anisotropic properties, in which strength transverse to the machine direction might be relatively poor. An improved fundamental understanding of how flow fields influence liquid crystalline polymer orientation could lead to improved processing strategies and more widespread application of these materials.

Recently, there has been significant progress toward understanding the flow properties of “model” main-chain liquid crystalline polymers that incorporate flexible spacers. It appears that, as a class, these polymers may routinely exhibit “shear aligning” dynamics, in which shear flow promotes high orientation along a particular direction [2, 3]. This contrasts with lyotropic LCPs, in which director tumbling is known to degrade the degree of macroscopic molecular orientation present in shear flow [4]. It is not clear to which category commercial LCPs belong. Experiments on commercial materials are much more challenging because of their high melting points, limited thermal stability, and the inaccessibility of the nematic/isotropic clearing point. However, there is a comprehensive rheological data set available for one commercial LCP, Vectra B [5], which suggests this polymer may be of the tumbling type. Here we report on *in situ* studies of molecular orientation under flow in an attempt to shed light on the fundamental flow/orientation characteristics of this polymer.

Methods and Materials

Experiments were performed on Vectra B950, a commercial thermotropic copolyester/amide. Its melting point is around 285°C; experiments were performed at a melt temperature of 300°C. To improve the stability of properties measured in homogeneous shear flow for extended periods, the sample was temporarily heated to 330°C when the sample was first loaded, and it was then cooled to the test temperature of 300°C, a procedure which ensures that all residual crystallites are melted.

X-ray scattering experiments were performed in a an x-ray-capable extrusion die that allows for investigations in a variety of complex slit-channel flows [6] and in a modified Linkam shear cell that allows for structural measurements in homogeneous shear flow [2]. Experiments were performed by using APS beamline 5-BM-D, with unfocused bending magnet radiation with an energy of 25 keV. Two-dimensional wide-angle x-ray scattering (WAXS) patterns were collected on a MarCCD (charge-coupled device) detector.

Results

Figures 1 and 2 present measurements of average molecular orientation measured along the centerline in slit contraction (4:1) and slit-expansion (1:4) of the Vectra B950. As discussed in our previous papers on similar measurements [6, 7], such data are useful not only for the direct information they provide about the orientation dynamics of LCPs in complex mixed shear/elongational flows but also because such experiments can provide insights into whether or not a particular material is shear aligning or tumbling. In this regard, data collected in slit-contraction flows (Fig. 1) are particularly important. If a material exhibits shear aligning dynamics, then the shear flow upstream of the contraction should already be sufficient to induce a high average degree of molecular orientation. Under these circumstances, superimposed extension should only have a moderate influence on the macroscopic degree of molecular alignment. Conversely, it is known that in tumbling materials, shear tends to degrade overall orientation, so that superimposed extension has greater potential to induce significant and temporary enhancements in the degree of orientation. Figure 1 illustrates that Vectra B shows a large and temporary enhancement in molecular orientation in a slit-contraction flow. This is consistent with prior data on another commercial LCP [6] and suggests, indirectly, that

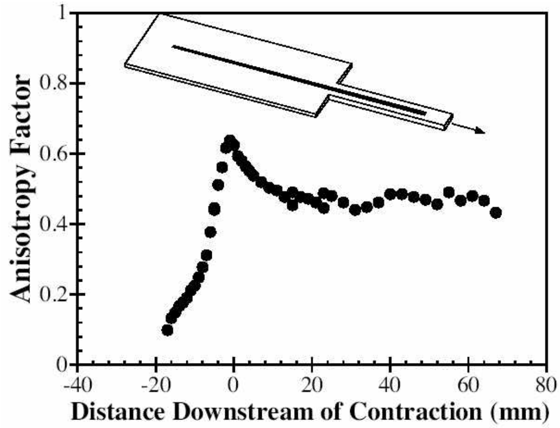

FIG. 1. Average molecular orientation in Vectro B950 as a function of axial position during slit-contraction flow at 300°C.

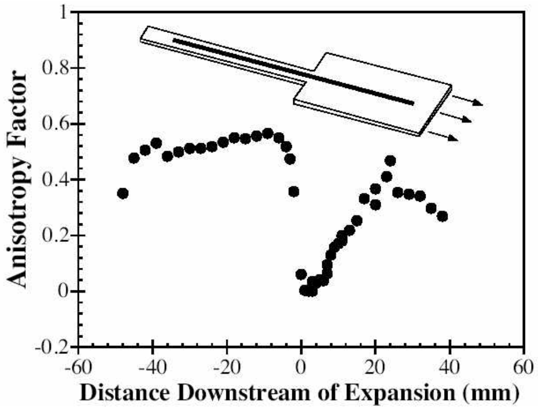

FIG. 2. Average molecular orientation in Vectro B950 as a function of axial position during slit-expansion flow at 300°C.

Vectra B (and perhaps all commercial LCPs more generally) might be of the tumbling type. The hypothesis of tumbling in Vectra B is consistent with certain transient rheological signatures documented by Beekmans and coworkers in rheological studies [5].

In slit-expansion flow, there is a significant loss of net orientation induced by extension transverse to the prevailing flow direction. This is also in line with prior observations in TLCP melts [6, 7].

Armed with a tentative assignment that Vectra B is tumbling, we may return to the supposedly simpler arena of homogeneous shear flow. A flow protocol that has been particularly useful in studying the rheology and structure of LCPs is that of a transient reversal in shear flow direction. Broadly speaking, tumbling materials exhibit oscillations in stress and structure because of the underlying tumbling dynamics of the nematic director [4]. Conversely, shear aligning materials appear to be characterized by a single, prolonged undershoot in molecular orientation upon flow reversal [8]. In either case, the structural rearrangements induced by a reversal in flow direction are usually rather pronounced.

Contrary to these expectations, in Vectra B we find only subtle changes in average molecular orientation upon reversal in shear flow direction (Fig. 3). The small magnitude of orientation change is consistent with the fairly subtle rheological signatures observed in similar flow protocols with this material [5] but contrasts strongly with the larger perturbations to structure normally associated with a shear flow reversal [4, 8].

Discussion

These results help make clear just how difficult it is to extract fundamental characteristics on commercial LCPs. Detailed monodomain conoscopy experiments [3] that can definitively classify a material as tumbling or aligning are out of the question because of the limited thermal stability in the melt. Even when indirect rheological signatures suggest the possibility of tumbling in a commercial material like Vectra B, the transient shear flow orientation response fails to exhibit any noteworthy behavior that can shed light on this issue. Instead, and somewhat paradoxically, it appears that the complex mixed shear/extensional flows, such as slit-contractions, may be the most promising for providing information from which educated guesses about the aligning or tumbling characteristics of commercial LCPs can be extracted. This helps to highlight the utility and significance of x-ray methods to probe complex fluid structure not just in homogeneous shear but also in more complex flow fields, such as the slit-contraction and expansion flows considered here.

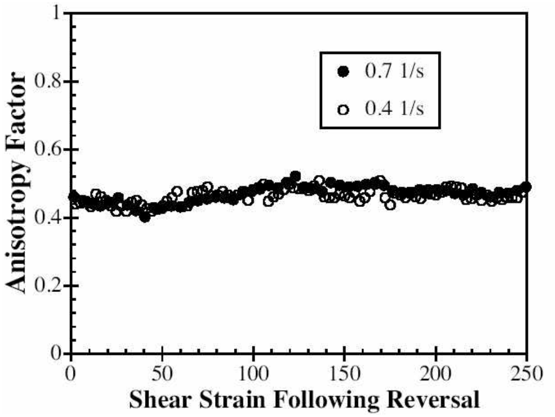

FIG. 3. Average molecular orientation in Vectro B950 as a function of applied shear strain following flow reversal at two shear rates at 300°C.

Acknowledgments

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References

[1] A. M. Donald and A. H. Windle, *Liquid Crystalline Polymers* (Cambridge University Press, Cambridge, United Kingdom, 1993).

[3] W. Zhou, J. A. Kornfield, and W. R. Burghardt, Macromolecules **34**, 3654-3660 (2001).

[4] W. R. Burghardt, Macromol. Chem. Phys. **199**, 471-488 (1998).

[5] F. Beekmans, A. D. Gotsis, and B. Norder, J. Rheol. **40**, 947-966 (1996).

[6] D. K. Cinader, Jr., and W. R. Burghardt, J. Polym. Sci. Part B: Polym. Phys. **37**, 3411-3428 (1999).

[7] D. K. Cinader, Jr., and W. R. Burghardt, Rheol. Acta **39**, 247-258 (2000).

[8] V. M. Ugaz, W. R. Burghardt, W. Zhou, and J. A. Kornfield, J. Rheol. **45**, 1029-1063 (2001).