Molecular Orientation in Slit-Channel Flows of Main-Chain Thermotropic Liquid Crystalline Polymers

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Introduction

Liquid crystalline polymers offer considerable potential as high-strength/lightweight materials.[1] Their mechanical properties are directly dependent on the average orientation state of the constituent rigid macromolecules; this in turn is strongly affected by flow fields encountered during processing. We have developed *in situ* experimental protocols to measure molecular orientation during steady-state channel flow extrusion of polymer melts; this allows us to perform quantitative measurements of molecular orientation under actual flow conditions.

Methods and Materials

In situ measurements have been performed on two main-chain thermotropic liquid-crystalline polymers available in commercial quantities: Xydar® resin obtained from Amoco,[2] and hydroxypropylcellulose (Klucel E®) obtained from Aqualon.[3] These experiments utilized an x-ray-capable extrusion die described in detail elsewhere.[2],[3] These experiments rely on access to high-energy x-rays (25 keV) to reduce absorption in the two 1-mm-thick aluminum windows that confine the polymer melt in the extrusion die. Here we make comparisons of these data to more recent experiments on a custom synthesized polymer, denoted as DHMS-7,9, which consists of rigid mesogenic units separated by flexible spacers. Details on the synthesis and characterization of this polymer are available elsewhere.[4] Due to limited quantities of DHMS-7,9, these experiments were performed on solid samples, quenched steady slit-channel flow that had been applied long enough to reach steady-state conditions. The flow cell was designed to be geometrically similar to the extrusion die used in the earlier experiments, so that the overall kinematics are identical. The virtue of comparing prior results to DHMS-7,9 is that this latter polymer has been definitively classified as "shear aligning,"[5] and thus provides a reference point of comparison against which to compare the behavior of Xydar® and HPC, whose alignment characteristics are unknown.

Results and Discussion

Figure 1 presents axial distributions of molecular orientation measured along the centerline in 4:1 slit-contraction and 1:4 slit-expansion flows of the three materials under consideration. In the case of DHMS-7,9, known to be flow aligning, the contraction has a negligible effect on the average molecular orientation. This is consistent with expectations for shear-aligning nematics, since the shear flow upstream of the contraction should have already promoted a high degree of orientation; the extension associated with the contraction would then be expected to have a negligible effect on the overall orientation. Conversely, the other two materials (HPC and Xydar®) both show a substantial increase in orientation in slit-contraction flow. This behavior is similar to prior *in situ* measurements of orientation in channel flows of a lyotropic liquid-crystalline polymer solution, which is known to exhibit director tumbling dynamics.[6] In the case of tumbling, shear upstream of the contraction is expected to degrade the overall orientation to some extent. Then, stretching along the flow direction can lead to significant enhancement in orientation as extension suppresses director tumbling. These results strongly suggest that both thermotropic HPC, as well Xydar,® are of the tumbling type.

In slit expansion flow, HPC and Xydar® both exhibit a dramatic drop in orientation, as stretching transverse to the flow direction partially flips the orientation in a portion of the sample towards the vorticity direction. DHMS-7,9 shows some loss of orientation, but its response to the expansion is not nearly as dramatic as that of HPC and Xydar®. This is again consistent with the fact that DHMS-7,9 is shear aligning and that HPC and Xydar® are tumbling, since model calculations suggest that tumbling materials are more susceptible to the effects of transverse extension in expansion flows.[7]

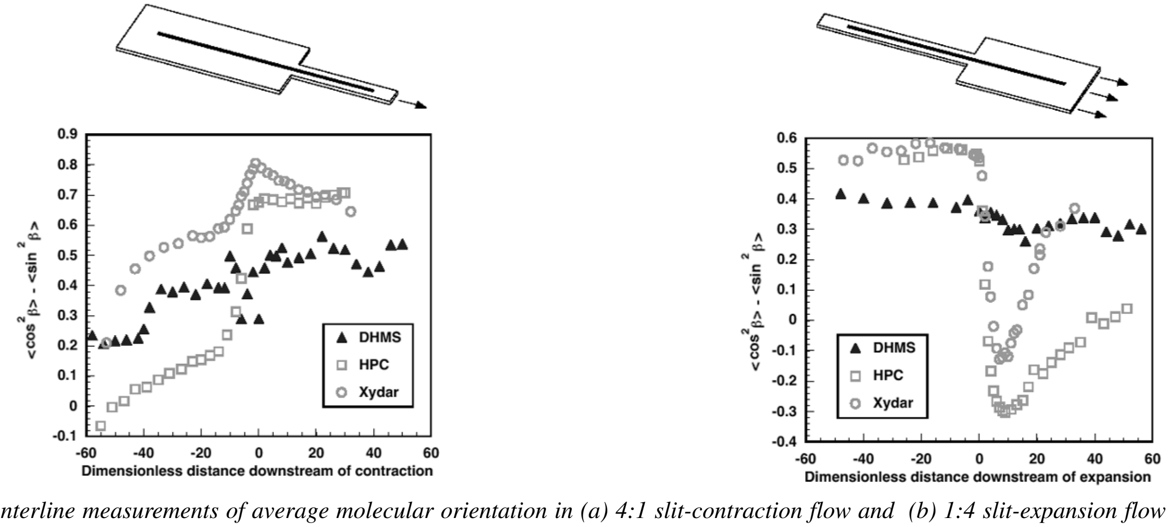

FIG. 1. Centerline measurements of average molecular orientation in (a) 4:1 slit-contraction flow and (b) 1:4 slit-expansion flow of thermotropic HPC (squares), Xydar® (circles), and DHMS-7,9 (triangles).

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