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Polymer 42 (2001) 10147–10153

polymer

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Molecular orientation in quenched channel flow of a flow aligning main chain thermotropic liquid crystalline polymer

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Received 25 June 2001; received in revised form 6 August 2001; accepted 7 August 2001

Abstract

We report measurements of molecular orientation in solid specimens of a main-chain thermotropic liquid crystalline polymer (LCP) that were quenched from mixed shear-extensional channel flows. The polymer under investigation is a random copolyether with mesogens separated by flexible hydrocarbon spacers. This polymer is known to exhibit ‘flow aligning’ dynamics under slow shear flow. Experiments were designed to preserve the molecular orientation state, representative of steady, isothermal channel flow in the solid samples, so that comparisons could be made against in situ channel flow measurements on other main chain thermotropes without flexible spacers, including a commercial fully aromatic copolyster. In the flow aligning material, little change in orientation was found in slit-contraction flows, and only modest drops in orientation were found in slit-expansion flow. This contrasts strongly with data on commercial LCPs, suggesting that these materials may be of the ‘tumbling’ type. © 2001 Published by Elsevier Science Ltd.

Keywords: Liquid crystalline polymer; Director tumbling; Injection molding

1. Introduction

The physical properties of liquid crystalline polymers (LCPs) depend critically on their molecular orientation state [1]. High degrees of molecular orientation lead to strength and stiffness along the alignment direction, but also result in highly anisotropic properties that may be detrimental when multidimensional strength and stability are required. Since flow fields during processing significantly influence the molecular orientation state in LCPs, it is desirable to develop both fundamental understanding of, and the ability to model, those factors that influence the orientation state in LCPs under flow. In the case of lyotropic solutions of rodlike polymers, considerable progress has been made in elucidating the fundamental mechanisms of flow-orientation interactions [2], which sets the stage for attempts at detailed simulation of LCP structure in simple and complex flows [3,4]. The situation is not nearly as advanced for the case of thermotropic LCPs, in part because certain attributes that contribute to their commercial viability (e.g. high melting point) also make fundamental rheological or in situ structural studies quite difficult [1,2].

The most basic question surrounding the relationships among flow, molecular orientation and rheology of LCPs concerns classification of a material’s fundamental response to shear flow. In the limit of low shear rates, a nematic LCP may be classified as either *flow aligning*, in which case shear promotes alignment of the nematic director at a particular angle relative to the flow direction, or *tumbling*, in which case shear promotes continuous rotation of the director in a shear flow field [2]. Lyotropic LCPs are generally known to exhibit director tumbling at low shear rates, which leads to reductions in average orientation [5] and a proliferation of orientational defects [6]. Thermotropic side chain LCPs have been shown to be either tumbling or shear aligning depending on the details of the molecular structure [7,8]. Much less is known about the definitive classification of thermotropic main chain LCPs. Despite the central importance of this question for development of orientation in extrusion and molding processes, there have been no definitive experiments to determine the aligning properties of any commercial thermotropic LCP. Only two main chain thermotropes have been subjected to monodomain shear experiments that provide the most direct test of this question; both of these are main chain polymers in which rigid mesogenic units alternate with flexible spacers. In one case, shear aligning behavior was found near the nematic–isotropic transition with tumbling behavior at lower temperatures near a transition to a smectic phase [9]. In the other, more

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0032-3861/01/$ - see front matter © 2001 Published by Elsevier Science Ltd.
PII: S0032-3861(01)00575-4

recent example, shear aligning behavior was found throughout the nematic phase [10]. The polymer studied in this latter case was a polyether based on the mesogen dihydroxy-α-methylstilbene, which was randomly copolymerized with hydrocarbon spacers of length 7 and 9 carbon atoms. This polymer, denoted as DHMS-7,9, is also the focus of the present study.

Commercial thermotropes present considerable challenges to direct determination of the shear flow alignment characteristics. Even conventional rheological experiments that might provide clues about their alignment properties are complicated by uncertainties associated with the effects of prior thermal and flow history [11]. It is our thesis in this work that careful studies of molecular orientation in more complex mixed shear-extensional flows might, paradoxically, provide indirect evidence as to whether commercial LCPs are aligning or tumbling in shear. For several years we have pursued quantitative measurements of orientation in both lyotropic [12,13] and thermotropic [14–16] LCPs in complex channel flows. Our prototypical geometries are slit-contraction and slit-expansion flows, in which extensional velocity gradients are superimposed on the shear deformations present in slit flows. Elementary rheological models for nematic materials leads to some simple heuristic predictions about how LCP orientation should respond in these slit-channel flows [13,17]. In slit-contraction flows, the superimposed extension acts parallel to the prevailing shear flow. In the case of flow aligning materials, shear gradients upstream of the contraction should have already led to a high orientation state, so that added extension should have a minimal effect. Conversely, director tumbling would suppress the average orientation upstream of the contraction, so that superimposed extension should lead to a significant enhancement in the degree of molecular orientation, followed by a subsequent decay downstream of contraction when tumbling once again degrades the orientation. In slit-expansion flows, extension acts orthogonal to the prevailing flow direction. Here, both tumbling and shear aligning LCPs are expected to suffer a loss in macroscopic molecular orientation, although tumbling materials are expected to be more susceptible to the effects of the transverse extension [17].

Measurements of orientation in a lyotropic solution of hydroxypropylcellulose (HPC), which is known to be tumbling, are in accord with these expectations. Contractions lead to large temporary enhancements in the degree of molecular orientation, which subsequently decay downstream [12,13], while an expansion leads to a temporary loss in orientation which subsequently recovers [13]. More recently, we have used an X-ray capable extrusion die to make in situ measurements of molecular orientation in two thermotropic LCPs. The first was a commercial thermotropic copolyester, Xydar® [14,15], while the second was thermotropic HPC melt [16]. In both cases, slit-contraction flows led to significant enhancements in molecular orientation, consistent with the hypothesis that these polymers exhibit tumbling dynamics. This hypothesis would be further bolstered if the observed behavior could be contrasted with similar measurements on a known shear aligning LCP. Our objective in this work is to exploit the known shear aligning character of the semiflexible LCP DHMS-7,9 to explore how superimposed extension in slit-channel flows influences the average orientation state.

2. Experimental section

2.1. Material

The DHMS-7,9 polymer used in this study was synthesized according to standard procedures; details are available elsewhere [18]. The weight average molecular weight, measured using gel permeation chromatography relative to polystyrene standards, is 28,000 (28k). The prior direct confirmation of shear aligning dynamics in DHMS-7,9 utilized a lower molecular weight sample; however, steady state [18] and transient [19] rheological and rheo-X-ray orientation measurements on the 28k sample (as well as a sample with still higher molecular weight, 65k) exhibit behavior that is fully consistent with shear aligning dynamics. The 28k sample exhibits a nematic to isotropic clearing temperature of 191°C. Below a temperature of 121°C, the sample exhibits an intermediate, high viscosity phase whose detailed character has not been determined, but whose dynamics is reminiscent of smectic layered fluids. The crystal melting point of this sample is 91°C.

2.2. Quenched channel flow die

In our prior studies of molecular orientation in channel flows we developed experimental methods that allow in situ testing under isothermal, steady state flow conditions. This contrasts with many prior ex situ measurements of molecular orientation in injection molded test specimens [20–23], in that we have been able to consider the effects that the mixed shear-extensional flows have on the orientation state, free from complications due to the transient and nonisothermal characteristics of molding. In the case of thermotropic LCPs, these measurements were performed in an extrusion-fed X-ray capable channel flow die. The large quantities of material required by this experiment do not pose a significant problem for studying commercially available thermotropic LCPs, but render this experiment impractical for studying a custom synthesized polymer such as DHMS-7,9 which is available only in gram quantities. For this reason, in the present work, we study orientation in solid DHMS-7,9 samples that have been quenched in a channel flow die.

In the present apparatus, the channel flow geometry is defined by a spacer sandwiched between two aluminum blocks (Fig. 1). These spacers are designed to mimic those used in our earlier extrusion experiments [14–16]; here, we consider 4:1 slit-contraction and 1:4 slit-expansion

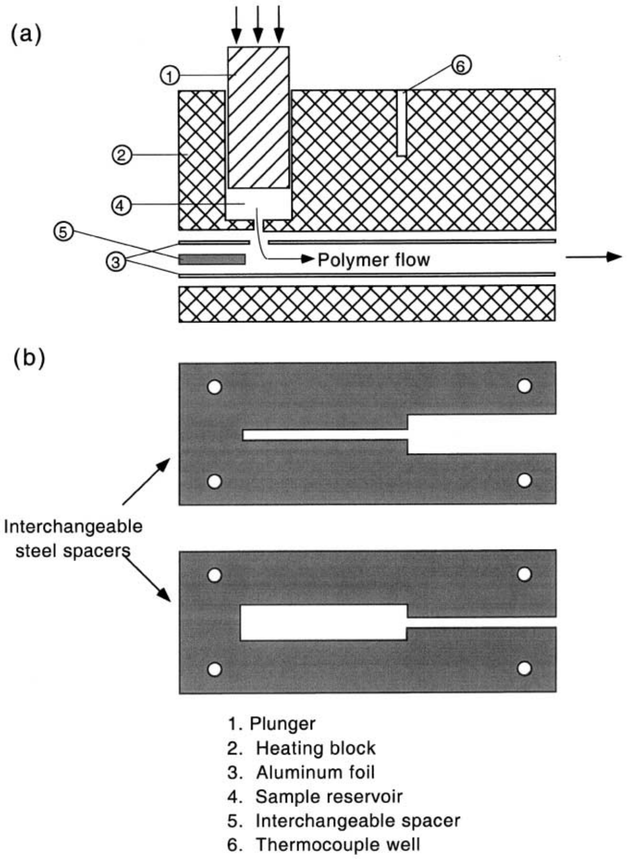

Fig. 1. Schematic illustration of batch channel flow die.

geometries. The spacer thickness is 0.5 mm, while the width of the narrow and wide channels is 2.5 and 10 mm, respectively. These geometries are geometrically similar to those used in the extrusion die, but scaled down by a factor of 2 in all linear dimensions to reduce the quantity of sample required. Thin aluminum foil was inserted on either side of the spacer to allow the quenched solid sample to be removed from the apparatus free from any adhesion to the heating blocks.

After assembly of the flow cell, a charge of the DHMS-7,9 polymer was loaded into the cylindrical reservoir in the larger aluminum block. A flexible tape heater wrapped around the entire assembly was used to heat the flow cell to 150°C (within the nematic phase of DHMS-7,9). After thermal equilibration, the polymer melt was forced into the channel using a piston driven at constant velocity by a microstepping motor. A small quantity of polymer leaked back between the piston and the cylindrical reservoir; this leakage was accounted for in determining the mass flow rate of polymer through the channel. In these experiments, a mass flow rate of 0.5 g/min was used, corresponding to characteristic shear rates of around 3.3 and 13 l/s in the upstream and downstream sections, respectively. This flow condition was selected to mimic as closely as possible typical conditions used in our earlier steady state extrusion studies. Flow was stopped at the point when the reservoir emptied, and the entire assembly was cooled using dry ice. Approximately 20 min were required for the temperature to drop below the melting point of DHMS-7,9, at which point solidification locked in the structure present in the melt.

While the limited available quantities of DHMS-7,9 prevented in situ studies under true steady state conditions, our goal is to achieve conditions under which the quenched solid samples reflect as faithfully as possible the orientation state present under steady isothermal flow. This first requires that the flow continue long enough so that the initial transients associated with filling the channel have been ‘washed out’ as the polymer continues to flow through it. In these experiments, the total amount of sample flowed through the channel was seven times the amount required to fill the channel completely, which should insure that the orientation state very nearly achieves steady flow conditions. Given the finite time required to cool the flow cell below the polymer freezing point, a second requirement is that the orientation state should not significantly relax during this period. Previous in situ, isothermal measurements of molecular orientation in nematic DHMS-7,9 have in fact shown that shear-induced molecular orientation relaxes only very slowly upon cessation of shear flow [19], so this condition is also satisfied. Finally, one must consider the possibility that the crystallization process itself might perturb the orientation state present in the melt prior to solidification. To assess this, we have also performed measurements on solid disk samples that had been sheared to varying degrees in a rotational rheometer, and then subjected to a thermal quench. Results of this test will be discussed in detail below.

2.3. X-ray experiments

After solidification, the samples were removed from the aluminum heating blocks, still sandwiched between the aluminum foils and contained within the steel spacer. One of the foils was removed to visually inspect the sample and verify that the channel was completely filled during the flow experiments with no gaps or voids. In subsequent testing, the sample was left in the spacer with the other foil intact to help maintain the integrity of the thin quenched sample. X-ray scattering measurements were performed on beam line 5BM-D of the Advanced Photon Source at Argonne National Lab. 2-D wide angle X-ray scattering patterns were collected on a CCD detector. The sample was placed on a translation stage so that images could be collected as a function of position on the solid samples.

2.4. Data analysis procedures

Fig. 2 presents representative scattering patterns collected in the sample quenched from 1:4 slit-expansion flow. Rather than the anisotropic diffuse peaks that characterize oriented nematics, these quenched samples show several crystal diffraction lines. However, the flow-induced anisotropy is readily apparent in the patterns.

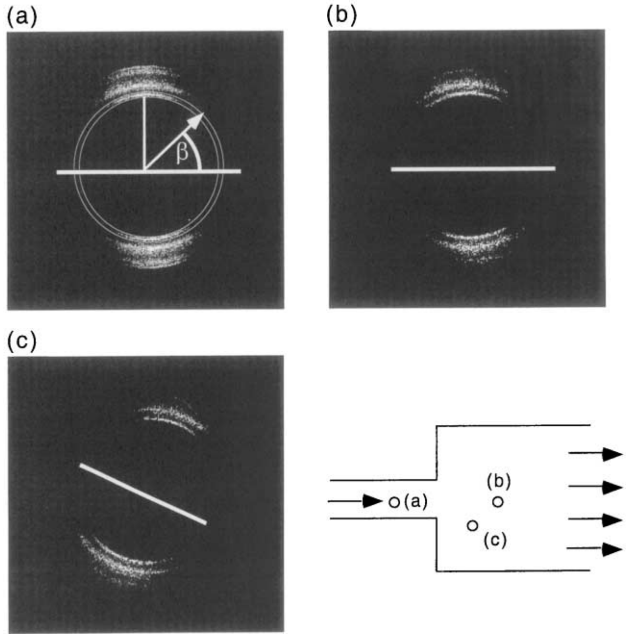

Fig. 2. Three representative X-ray scattering patterns from DHMS-7,9 sample quenched from 1:4 slit-expansion flow. Anisotropy analyses were performed using azimuthal intensity scans taken over indicated q-range.

Such anisotropic X-ray scattering patterns are often analyzed to determine an orientation parameter. However, standard methods of analysis assume a uniaxial distribution of orientation about a pre-determined symmetry axis. Our prior in situ studies of LCP melts in channel flows have frequently shown complex orientation states for which such assumptions are unjustifiable [14–16]. Following these previous studies, we instead use a simple method to directly characterize anisotropy in the X-ray scattering pattern. A point on an azimuthal intensity scan is represented by a unit vector, **u**. Anisotropy in the X-ray scattering pattern is then characterized by computing the second moment tensor

$$\langle \mathbf{uu} \rangle = \begin{bmatrix} \langle u_1u_1 \rangle & \langle u_1u_2 \rangle \\ \langle u_1u_2 \rangle & \langle u_2u_2 \rangle \end{bmatrix} = \begin{bmatrix} \langle \cos^2 \beta \rangle & \langle \sin \beta \cos \beta \rangle \\ \langle \sin \beta \cos \beta \rangle & \langle \sin^2 \beta \rangle \end{bmatrix} \tag{1}$$

where $\langle \cdots \rangle$ represents an average weighted by the azimuthal intensity distribution $I(\beta)$, where β is measured from the flow direction (see Fig. 2). For instance, the 11-component is given by

$$\langle \cos^2 \beta \rangle = \frac{\int_0^{2\pi} \cos^2 \beta I(\beta) \mathrm{d}\beta}{\int_0^{2\pi} I(\beta) \mathrm{d}\beta} \tag{2}$$

We report an 'anisotropy factor', taken to be the difference in the principal values of the second moment tensor, $\sqrt{(\langle u_1u_1 \rangle - \langle u_2u_2 \rangle)^2 + 4\langle u_1u_2 \rangle^2}$, while the average orientation direction is computed from the principal directions of the second moment tensor. Noting that diffraction from rodlike molecules is concentrated perpendicular to their axes, the average orientation direction is given by the eigenvector associated with the smaller of the two principal values. We have compared anisotropy factors computed using the various diffraction peaks present in the 2-D patterns, and found that they give essentially the same results. Results presented here are based on the innermost sharp reflection, as indicated in Fig. 2.

3. Results and discussion

3.1. Quenched samples from torsional shear flow

As discussed above, interpretation of the quenched channel flow experiment requires that the molecular orientation measured in quenched solid samples retains a high degree of fidelity to the orientation state that had been present in the melt prior to quenching. To test this, we have performed measurements of molecular orientation, using similar procedures, on solid disk samples that had been subjected to torsional flow in a rotational rheometer with parallel plate fixtures. In these trial experiments, a DHMS-7,9 sample was loaded into the rheometer and then heated into its isotropic phase. Subsequent cooling into the nematic phase caused the material to order, but with a globally random 'polydomain' orientation state. The samples were then subjected to torsional shear for varying amounts of time, flow was stopped, and the samples were quenched into the solid state. Previous in situ X-ray studies of DHMS-7,9 in homogeneous shear flow have demonstrated that orientation develops monotonically as a function of applied shear strain [19]. Since strain increases linearly with radial position in torsional shear, there should be an increase in average orientation with radius for any given sample, and those samples that were subjected to larger edge strain $\gamma(R)$ should have higher orientation overall.

Vector plots of orientation measured in radial scans in these disk samples are generally in accord with these expectations (Fig. 3). Data on a control sample subjected to no shear flow shows weak anisotropy oriented radially (Fig. 3(a)). We attribute this to squeeze flow effects due to thermal contraction of the fixtures during temperature changes in the nematic melt prior to solidification. Application of nine shear strain units is sufficient to induce orientation predominantly along the expected tangential direction, although the overall degree of orientation is still weak (Fig. 3(b)). Further increases in strain lead to significant molecular orientation along the tangential direction, and

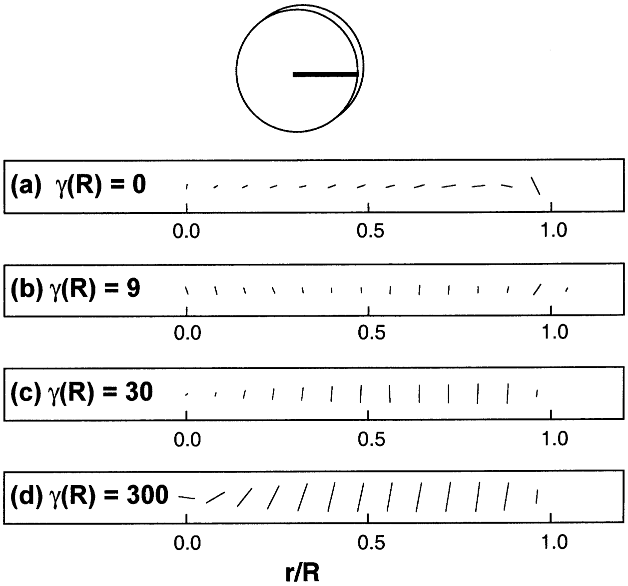

Fig. 3. Test of the fidelity with which quenched solid samples reflect prior orientation state in melt. The vector diagrams represent the degree and direction of anisotropy measured in solid DHMS-7,9 disks that had been loaded in a parallel plate rheometer, and sheared to edge strains of (a) 0, (b) 9, (c) 30 and (d) 300 strain units prior to quenching into the solid state.

the expected increase in the degree of orientation with radial position. Thus, we see that, despite some complications due to changes in sample thickness during quenching, the quenched solid samples reflect with reasonable fidelity the orientation state that would have been anticipated in the melt prior to quenching. Further, it is important to note that parasitic effects should be much more severe in this trial experiment than in the channel flow experiments below. This is because changes in sample thickness are due to the thermal expansion/contraction of the *full* heated length of the rheometer fixtures. Conversely, in our channel flow die, Fig. 1, there will be minimal changes in sample thickness during the cooling process, with the anticipated result that the orientation state measured in quenched samples should provide an even more accurate representation of the melt-phase structure.

3.2. Orientation in slit-contraction flow

Measurements of anisotropy factor along the centerline on the solid DHMS-7,9 sample quenched from 4:1 slit-contraction flow show no particular effects of the contraction (Fig. 4). Instead, starting from a relatively low orientation state induced by entrance effects in the wide upstream section [15,16], the anisotropy factor increases gradually and more or less monotonically towards a 'fully developed' value of around 0.45. This behavior contrasts strongly with prior in situ measurements in two thermotropic LCPs in similar 4:1 slit-contraction geometries, for which data are reproduced in Fig. 4 for comparison. In both thermotropic hydroxypropylcellulose (HPC) and a commercial aromatic LCP copolyester (Xydar®), the orientation shows a significant increase in the contraction region, where extensional gradients act parallel to the prevailing flow direction.

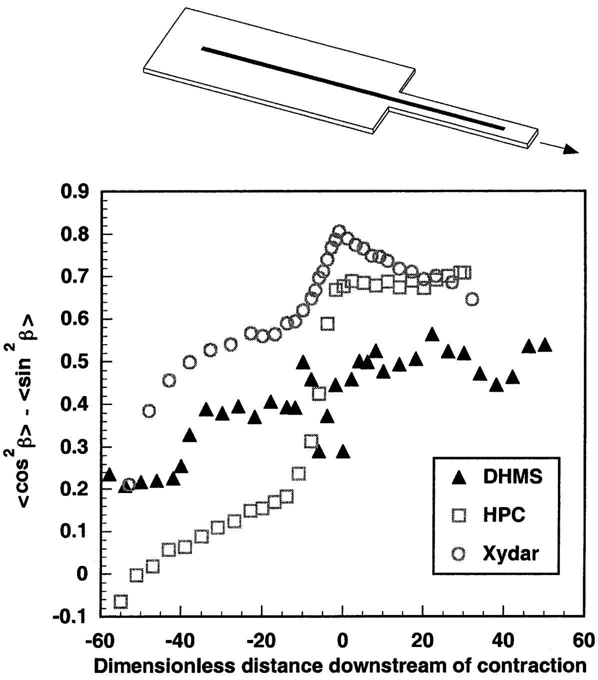

Fig. 4. Centerline anisotropy as a function of dimensionless axial distance in DHMS-7,9 sample quenched from 4:1 slit-contraction flow (▲). Shown for comparison are similar data collected during in situ measurements on Xydar (○) and thermotropic HPC (□) melt samples.

3.3. Orientation in slit-expansion flow

Centerline measurements of anisotropy factor on the solid DHMS-7,9 sample quenched from 1:4 slit-expansion flow similarly show a very strong contrast in behavior relative to prior in situ measurements on thermotropic HPC and Xydar® (Fig. 5). Here, the narrower upstream channel leads to a higher initial average orientation [15,16]. In this case, it does appear that the orientation is degraded in the expansion region due to the extension acting transverse to the prevailing flow direction. This is qualitatively similar to the behavior previously observed in HPC and Xydar®, but much less dramatic in terms of the magnitude of orientation loss. A 2-D vector plot depicting the degree and direction of average orientation downstream of the expansion in the DHMS-7,9 sample reinforces the point that the orientation state is only subtly affected by the competition between shear and extension in the downstream region (Fig. 6). Similar plots constructed from in situ measurements on HPC and Xydar® show dramatic effects on the average orientation state, including the development of bimodal orientation states in the expansion region [15,16]. In DHMS-7,9 we found no evidence of bimodal orientation states, and instead the average orientation seems more or

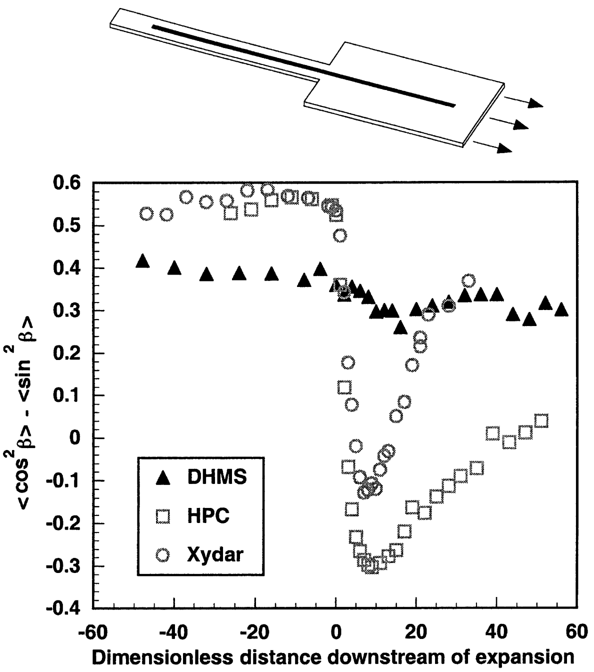

Fig. 5. Centerline anisotropy as a function of dimensionless axial distance in DHMS-7,9 sample quenched from 1:4 slit-expansion flow (▲). Shown for comparison are similar data collected during in situ measurements on Xydar (○) and thermotropic HPC (□) melt samples.

less to simply track the expected streamline patterns in the expansion region.

4. Discussion

Independent measurements have (i) directly confirmed that DHMS-7,9 is a shear-aligning nematic [10], and (ii) that its orientation behavior in homogenous shear flows is quite unremarkable as a result [18,19]. The data presented in Figs. 4–6 are also consistent with expectations for the behavior of a shear aligning nematic in these more complex channel flows. Specifically, a contraction in cross sectional area in slit flow is seen to have no measurable effect on the orientation. An expansion in cross sectional area does lead to reductions in average orientation, but these are much less pronounced than those observed in other thermotropes. Prior measurements on a known tumbling lyotropic LCP yielded rather different behavior [12,13]. Taken together, these results now provide two firm reference points against which the data on thermotropic HPC and Xydar (for which nothing conclusive is known about tumbling or aligning characteristics) may be compared. The most compelling comparison concerns the behavior in slit-contraction flows. Both Xydar and HPC show a significant enhancement in orientation, followed in the case of Xydar® by a subsequent decay. The fact that no such large enhancement in orientation is expected in shear aligning materials, and that no such enhancement is observed in shear aligning DHMS-7,9, provides strong circumstantial evidence that both HPC and Xydar® are tumbling nematics. The behavior in slit-expansion flows is less definitive, since both aligning and tumbling materials are expected to suffer a loss in orientation. Still, the fact that HPC and Xydar® experience much more significant drops in orientation than DHMS-7,9 is consistent with model predictions that tumbling nematics should be more susceptible to the effects of superimposed transverse extension than shear aligning nematics [17].

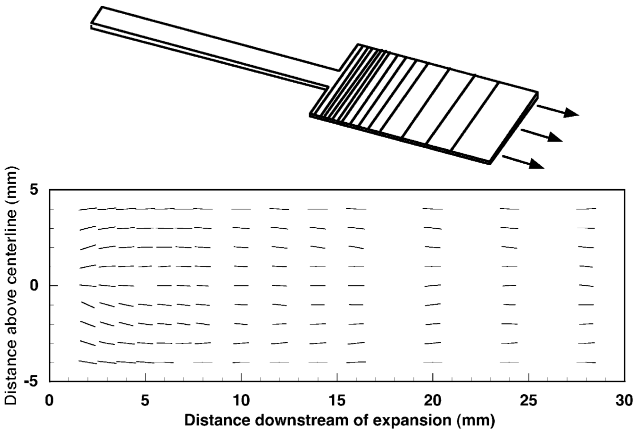

Fig. 6. Vector plot depicting 2-D average orientation state in DHMS-7,9 sample quenched from 1:4 slit-expansion flow.

It is important to emphasize that the arguments advanced here are not definitive: there is no substitute for a direct experiment capable of quantitative classification of a nematic as either shear aligning or tumbling (for instance, optical conoscopy on a sheared monodomain sample [9,10]). However, the high melting temperature and limited thermal stability of most commercial LCPs present serious barriers to the formation of stable, defect free nematic monodomains from these materials. In the absence of such definitive experiments, these indirect inferences may provide the simplest way to make an informed hypothesis. It is interesting to note that those main chain thermotropes for which flow aligning dynamics have been confirmed all have flexible hydrocarbon spacers along the chain; this appears to be a major factor leading to their aligning character [10]. Conversely, most commercial thermotropes have greater backbone rigidity, and hence might more reasonably be expected to show tumbling, drawing upon accumulated knowledge in lyotropic LCPs [2]. The results of this study seem to be consistent with this overall picture.

5. Summary

Molecular orientation of a known shear aligning nematic thermotropic LCP (DHMS-7,9) has been studied in solid samples quenched from slit-contraction and slit-expansion flows. As anticipated for an aligning material, the superimposed extension has minimal effects on the average orientation state. This contrasts strongly with prior measurements on two other main chain thermotropes, and bolsters the hypothesis that these other materials are of the tumbling type. Chain flexibility appears to be the critical variable in determining whether a given thermotropic LCP is aligning or tumbling.

Acknowledgements

We acknowledge financial support from an AFOSR MURI on Liquid Crystals, Grant F49620-97. X-ray experiments were conducted at the DuPont-Northwestern-Dow Collaborative Access Team (DND-CAT) Synchrotron Research Center located at Sector 5 of the Advanced Photon Source. DND-CAT is supported by the E.I. DuPont de Nemours and Co., the Dow Chemical Company, and the National Science Foundation through Grant DMR-9304725 and the State of Illinois through the Department of Commerce and the Board of Higher Education Grant IBHE HECA NWU 96. Use of the Advanced Photon Source was supported by the US Department of Energy, Basic Energy Sciences, Office of Energy Research under Contract no. W-31-102-Eng-38.

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