

CONCLUSIONS

To summarize, we have shown that the use of phase detection imaging in Tapping Mode AFM of block copolymers significantly improves the quality of the data. This leads to a much better characterization of the surface morphology as obtained on thick layers of MBM triblocks compounds. By mapping the phase difference of the cantilever oscillation during the Tapping Mode scan, we obtained information concerning the viscoelastic properties of those block copolymers. Depending of the value of Φ_{PMMA} , these preliminary PDI-TMAFM data indicate that the hard segments of PMMA form lamellar structure ($\Phi_{PMMA} = 0.50$), cylindrical ($\Phi_{PMMA} = 0.33$) and spherical ($\Phi_{PMMA} = 0.11$) microdomains dispersed in the elastomeric matrix of PBD.

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MOLECULAR AND TEXTURAL ORDERING OF THERMOTROPIC POLYMERS IN SHEAR FLOW

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ABSTRACT

The texture and microstructural order present in mesomorphic polymers and their relation to their macroscopic behavior has been investigated using rheological, optical and dynamic scattering (WAXS and SALS) experiments. Shear orientation is observed under constant rate-of-deformation conditions where this orientation is always parallel to the flow direction. However, the high degree of orientation suggested by optical and SALS measurements is not reflected in the degree of molecular order observed in WAXS experiments. After cessation of flow, a rapid relaxation of stress is observed, while only little microstructural relaxation is found, *i.e.*, the state of orientation is very stable.

INTRODUCTION

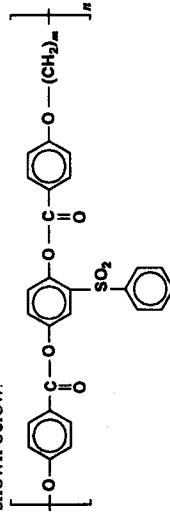
The mechanical properties of polymeric materials (flexible chain and mesomorphic) are closely related to their morphological structure and molecular orientation.^{1,2} The need for specific data regarding their mechanical behavior has led to a great deal of interest in a better understanding of the molecular, director, and interfacial orientation phenomena. The goal is to establish more detailed relationships between flow kinematics, microstructure, and mechanical properties. Microstructural studies of polymeric fluids carried out under conditions mimicking a processing operation (*in-situ*) are of particular interest since they provide unique information on the mechanisms involved in polymer deformation.³⁻⁷

We have designed and built an apparatus that combines simultaneous stress measurements with optical microscopy, as well as light and x-ray scattering techniques. Additionally, the instrument can reach temperatures at least as high as 345°C, making it unique for the study of polymeric melts, both isotropic and anisotropic.

Here, we present some results of the application of *in-situ* microscopic probes to the monitoring of orientation/disorientation processes in thermotropic liquid crystalline polymers in the nematic phase. Our results derived from optical microscopy, small-angle light scattering, and wide-angle X-ray scattering reveal the inter-relationship of molecular and textural orientation.

EXPERIMENT

Materials For this study, semiflexible aromatic polyesters based on a triad ester mesogenic unit were synthesized. The mesogen contains an arylsulfonyl-substituted hydroquinone and has either six methylene groups as the flexible spacers (hereafter referred to as PSHQ6) or ten methylene groups as the flexible spacers (hereafter referred to as PSHQ10).⁷ The polymers have the chemical formula shown below.



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Details of polymerization and characterization experiments are given elsewhere.⁷ PSHQ6 was characterized by a weight average molecular weight, M_w , of 30,000, a glass transition temperature, T_g , of 100 °C, a melting point, T_m , of 130 °C, and a nematic-isotropic transition temperature, T_{ni} , of 228 °C. The PSHQ10 sample featured $M_w = 45,000$, $T_g = 92$, $T_m = 110$, and $T_{ni} = 175$ °C. As-cast specimens for *in-situ* microstructural characterization were dried in a vacuum oven at room temperature for at least three weeks and, prior to measurements, at 90 °C for 48 hours to remove any residual solvent and moisture.

Shearing Cell *In-situ* rheo-microscopy measurements were performed in transmission mode using a custom built parallel-plates shear cell which has been described elsewhere.⁸ This device produces shear flow by sliding one plate with respect to the other (simple shear mode) using a stepper motor, and enables microscopic measurements from room temperature to about 345 °C, with temperature control better ± 0.5 °C. The gap separation can be set accurately by micrometers, and the minimum gap achievable is 20 μm (± 5 μm). The instrument is computer controlled, making possible the programming of different shear protocols under well controlled conditions (steady shear, oscillatory shear, etc.). For rheo-optical experiments optical-grade glass plates were utilized, and a separation gap of 20 μm was chosen. For rheo-X-ray scattering measurements we utilized copper plates covered with a 50 μm thick polyimide (Kapton™) film. The film limits the upper working temperature to 340 °C and does not leave a detectable diffraction imprint within the scattering range of interest for the polymers studied. Channel ports were drilled into the copper plates to enable the transmission of incident and scattered beam. In this case a gap separation of 600 μm was chosen.

Optical Microscopy *In-situ* rheo-optical measurements were performed by viewing the sample between crossed polarizers. The optical axis is oriented along the velocity gradient direction, therefore the plane imaged is that containing the velocity (horizontal) and vorticity (vertical) axes. Crossed polarizers are oriented at 45°-135° to the flow direction. A long working-distance lens with x25 magnification was used. Micrographs were recorded photographically.

Small-Angle Light Scattering The apparatus utilized for the *in-situ* SALS measurements is shown schematically in Figure 1. Components a-e were mounted to an optical breadboard. Components f-k were attached to a rail mounted vertically on the breadboard. This allowed the shear cell (g) to be positioned with the sample plane horizontal, a distinct advantage for samples of low viscosity. The polarized light source (a) used for all measurements was a 15 mW HeNe laser ($\lambda=632.8$ nm). The incident intensity was collimated and attenuated by apertures (b,d) and neutral density filters (c) respectively. The polarization direction of the vertically deflected beam was set by the $\lambda/2$ plate (f). The scattered light, after passing through a 80 mm diameter analyzer (h) and collected by the ground glass (i), was recorded by the color video CCD camera (k) (Panasonic KR222, 768 x 494 pixel density), equipped with a close focus lens (j). The scattering patterns were displayed on color monitor (l) and recorded to videotape. Frame grabbing and image analysis were performed using Global Lab Image™ software. For a typical arrangement of optical elements, the observable range of scattering angles is $0.12 < |\mathbf{q}| < 1.96$ μm^{-1} .

Wide-Angle X-ray Scattering *In-situ* X-ray scattering measurements were performed at Beamline X18-A, National Synchrotron Light Source, Brookhaven National. Symmetric

transmission diffraction patterns were recorded on image plates and digitized for further analysis. A constant exposure time of 3 seconds and radiation of $\lambda=1.127$ Å were used throughout.

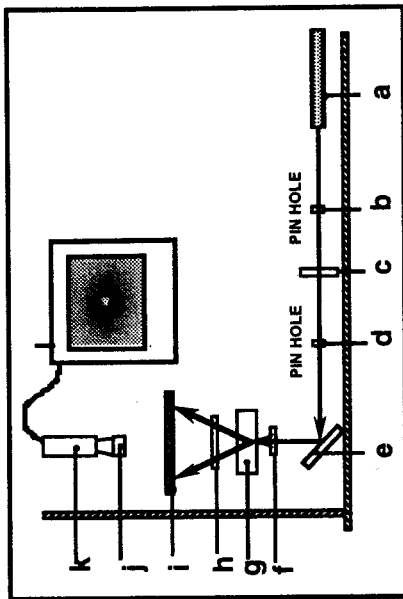


Figure 1. Schematic of Laser light scattering apparatus: a) 15 mW HeNe (632.8 nm) laser; b) and d) pin-hole apertures; c) Neutral Density Filters; e) Mirror; f) $\lambda/2$ plate; g) Shear Cell; h) Analyzer; i) Ground Glass Plate; j) Close Focus Lens; k) Color Video CCD Camera; l) Color Video Monitor.

RESULTS

The rheological characterization of PSHQ10 has been reported elsewhere,⁹ whereas that of PSHQ6 is part of a future publication. It was found that, under steady shear, PSHQ10 displays a Newtonian plateau (Region II in the Onogi and Asada model¹⁰) at low shear rates (0.01 to 1.0 s^{-1}), whereas PSHQ6 is shear-thinning over this same range of shear rates. The typical rheo-SALS response of PSHQ10 in the nematic state, at a shear rate of 1.0 s^{-1} , is shown in Figure 2. It is seen that the stress-trace presents a large overshoot occurring at a strain near 2, and reaches a steady-state plateau after 20 strain units. This overshoot in stress is only observed during the first shear start-up experiment following cooling from the isotropic to nematic phase.⁹ The V_v SALS pattern does not change significantly during the first several strain units (Figure 2a-b), while the shear stress rises dramatically to an overshoot. During this time, the sample is quite turbid and the intensity of scattered light is small due to multiple scattering. That the SALS pattern remains unchanged during such a large rise in shear stress suggests the possibility that the overshoot arises from distortional elasticity⁵ of the nematic director between disclination lines of the initially fine texture. We further postulate that the stress incurred by this elastic-"distortional" - modulus ultimately achieves a yield value such that beyond the overshoot (Figure 2c-e), the V_v pattern evolves to show decreased turbidity while the shear stress drops precipitously by approximately a factor of three.

The sequence of SALS patterns show a slightly anisotropic pattern associated with the defect-populated texture of this material. Application of steady shearing flow produces textures yielding anisotropic patterns, with streaks oriented orthogonal to the flow direction, indicative of the texture evolution under flow. The textural evolution was further examined by studying the influence of shear rate on the SALS patterns of both thermotropic LCPs. In both cases it was found that, under steady-state conditions, the streaks shorten as the shear rate increases. The

shrinkage of the SALS patterns indicate growing uniformity of the sample orientation over a length scale comparable to the laser wavelength. Figure 3(a) shows the optical micrograph corresponding to the steady state condition at 1 s^{-1} , with the crossed polarizers oriented at 45° to the velocity direction. The uniformity of texture orientation was further substantiated by rotating the crossed polarizers at 0° - 90° to the velocity direction where nearly total extinction was found.

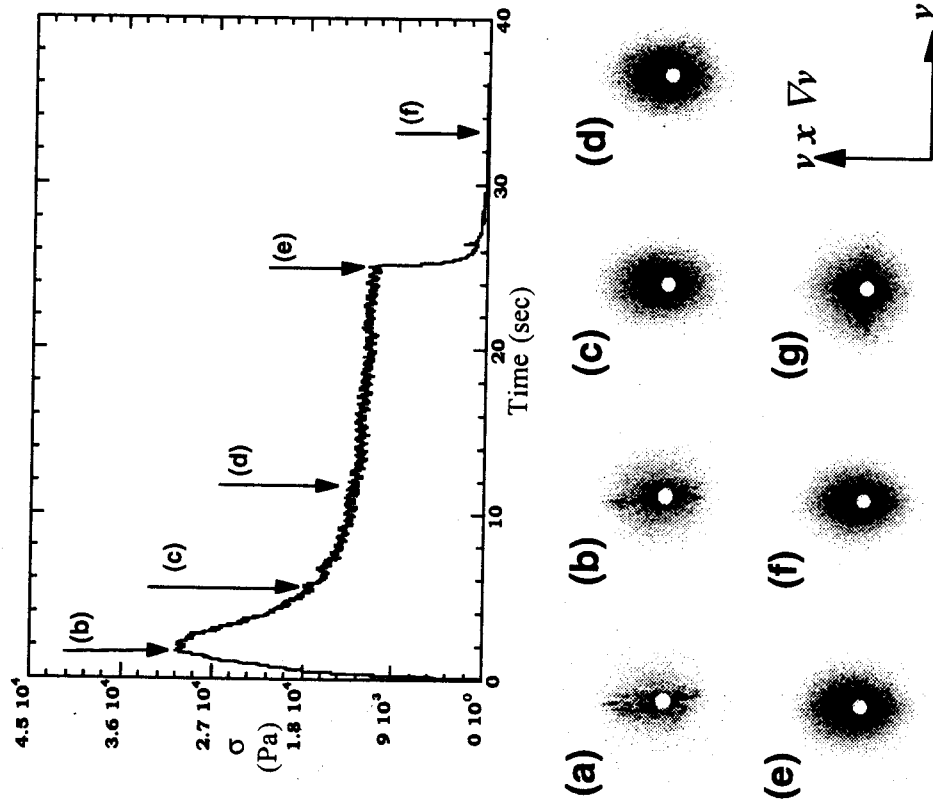


Figure 2. Stress growth trace of PSHQ10, taken at 160°C and 1.0 s^{-1} . Arrows indicate the corresponding SALS diffraction patterns taken after: (a) 0.0; (b) 1.52; (c) 5.32; (d) 11.52 and (e) 24.77 seconds continuous shear. Relaxation was followed (f) 8.5, and (g) 215 seconds after cessation of shear. Vv polarization (polarizer and analyzer each oriented in the flow direction) was used.

Figure 2 also shows that the stress relaxation after cessation of shear takes place over only several seconds, whereas the texture shows only small relaxation within the same period of time, Figures 2e-f. However, after annealing the sample for several minutes, optical diffraction peaks begin to grow on the velocity axis, Figure 2(g), indicating that a banded texture, akin to that observed in other high molecular weight LCPs¹¹, has formed. Figure 3(b) shows the corresponding micrograph of this banded texture, observed after following an identical thermo-mechanical history.

The degree of molecular order was investigated by using wide-angle X-ray scattering measurements. Figure 4 shows diffraction patterns taken (a) in the quiescent condition, before shear was applied, and (b) during steady shearing flow at 1.0 s^{-1} . The angular range observed covers $0.42 < |q| < 3.1\text{ \AA}^{-1}$. Initially the diffraction pattern looks slightly anisotropic, indicative of the mechanical history associated with the loading of the sample between the shear plates. The amorphous nature of the equatorial reflection (at about 1.4 \AA^{-1}) indicates that the material is indeed molten. Application of shearing flow produces a concentration of intensity on the vorticity axis, indicating that the polymer chains are, on average, aligned in the flow direction. The azimuthal spread of the reflections, however, show that the degree of alignment is rather modest. Calculation of the orientation parameters¹² gives $\langle P_2 \rangle = 0.61$ and $\langle P_4 \rangle = 0.21$. We note that increasing the shear rate does not produce a significant increase in the degree of molecular alignment, whereas the texture does coarsen further. In other words, molecular orientation appears to saturate at a lower shear rate than does textural coarsening. Experiments on PSHQ6 showed that the degree of molecular alignment is practically the same as found in PSHQ10, and in both cases the same limit of orientation ($\langle P_2 \rangle \sim 0.6$) was found. Studies on orientation relaxation after cessation of steady shear in PSHQ6 or PSHQ10 showed that this modest level of molecular chain ordering remains relatively unchanged even after five minutes has elapsed.

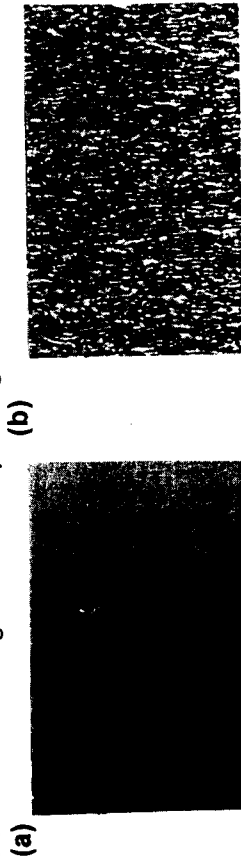


Figure 3. Optical micrographs of thermotropic PSHQ10 taken at 160°C . Crossed polarizers oriented at 45° - 135° to flow (horizontal) direction. (a) Steady state shear at 1 s^{-1} . (b) Micrograph taken 215 seconds after cessation of shear.

CONCLUSIONS

We have begun to examine the microstructural response of two semiflexible thermotropic LCPs using several probes: small-angle light scattering, polarizing optical microscopy, and wide-angle x-ray diffraction. It has been shown in this preliminary study that such observations reveal, qualitatively, a high degree of orientation in sheared PSHQ10 (and PSHQ6) samples when examined with small-angle light scattering and polarizing optical microscopy, provided the shear rate is sufficiently high. Surprisingly, however, quantitative examination of wide-angle x-ray scattering data of samples sheared under identical conditions indicates a limiting orientation parameter, $\langle P_2 \rangle$, of only ~ 0.6 . A possible explanation for this is that for PSHQ polymers the local nematic director (between defects) is characterized by a relatively low order parameter (at the temperatures studied) so that shear-induced coarsening of the defect texture can only raise the

macroscopic orientation parameter to values approaching this modest local nematic order parameter. Infrared dichroism measurements yielding the orientation parameter of various groups within the polymer chains would be enlightening in this regard. Of additional interest is the relationship of the stress-growth trace to the evolution of the V_V SALS patterns (Figure 2) which for low strain values suggests the possibility that the large stress overshoot results from "distortional elasticity." We are currently examining this possibility in greater detail by investigating the relationship between the textural length scale prior to shear start-up and the magnitude of the stress overshoot.

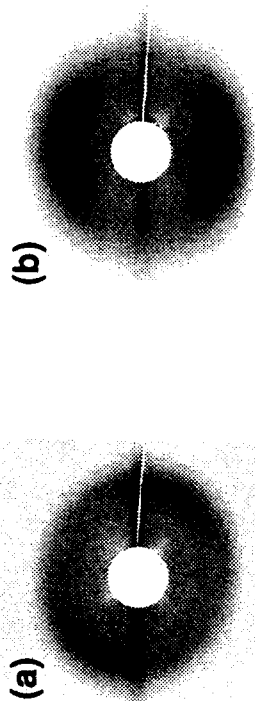


Figure 4. In-situ wide-angle X-ray scattering patterns of PSHQ10, at 160 °C. (a) Quiescent conditions, before any shear was applied. (b) Steady state at 1 s^{-1} . Synchrotron X-ray radiation of $\lambda = 1.127 \text{ \AA}$ was used.

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PHASE BEHAVIOR OF TRIBLOCK COPOLYMERS UPON INCORPORATION OF NON-PARENT, MIDBLOCK-ASSOCIATING ADDITIVES

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ABSTRACT

Addition of a block-selective homopolymer to a microphase-ordered block copolymer is known to result in preferential swelling of the chemically compatible microdomain. In this work, we examine the miscibility between a triblock copolymer and a relatively low-molecular-weight, chemically dissimilar, midblock-associating homopolymer and demonstrate that the homopolymer molecules residing in the swollen midblock matrix self-assemble to avoid repulsive interactions with neighboring microdomains. We extend this investigation to include systems composed of a very low-molecular-weight, midblock-associating additive (an oil). At high oil concentrations, the glassy copolymer endblocks micellize, resulting in the formation of a thermoplastic elastomer gel.

INTRODUCTION

As an attractive alternative to tailored *chemical* synthesis, the morphological characteristics and corresponding properties of ordered block copolymers can be controllably modified through the *physical* incorporation of either a miscible (i) parent or block-selective homopolymer [1-3] or (ii) a second copolymer of differing composition [4-6] or molecular weight [7,8]. Previous experimental efforts exploring blends with an added parent homopolymer have focused primarily on determining the dependence of blend morphology on factors such as homopolymer molecular weight (M_h), copolymer molecular weight and volume-fraction concentration (ϕ_h) [1,2,9-11]. The presence of an added homopolymer impacts the effective thermodynamic repulsion (characterized by the Flory-Huggins interaction parameter, χ) of the blend [12], as well as the efficiency of interfacial chain packing [13]. It has been shown that the incompatibility between the homopolymer and non-host block decreases as M_h is reduced. Thus, if M_h is significantly less than that of the host block, the added homopolymer behaves as a preferential solvent. At sufficiently high concentrations of a low- M_h homopolymer (i.e., within the disordered copolymer regime), the compatible (host or parent) blocks are highly swollen, whereas the incompatible (non-host) blocks typically organize into various microstructural elements to reduce the propensity of energetically unfavorable contacts. Spheroidal [14] micelles, as well as complex bilayered membranes [15,16], have been observed in numerous binary copolymer/homopolymer blends varying in M_h .

In the events that (i) M_h is much smaller than the molecular weight of the host copolymer block and (ii) the copolymer is a triblock composed of glassy endblocks and elastomeric midblocks (e.g., styrene-diene-styrene copolymers), micellization of the glassy endblocks induced by extensive midblock swelling results in the formation of a thermoplastic elastomer gel (TPEG). The characteristic features of TPEGs are schematically depicted in Fig. 1. A fraction of the swollen midblocks forms bridges between endblock-rich micelles; these bridges serve as physical crosslinks and are responsible for stabilizing the gel network. Within a reasonable composition range, the low- M_h additive is completely bound within the midblock matrix, which consists of biconformational midblocks that are either bridged or looped. Reynaers and co-workers [17,18] have examined copolymer gels via small-angle neutron scattering (SANS), and provide evidence that is consistent with the illustration displayed in Fig. 1. Their results have been recently verified by transmission electron microscopy (TEM) [19] of comparable gels (see Fig. 2). The thermomechanical properties of TPEGs are expected *a priori* to be particularly sensitive to processing due to variation in the fraction of network-forming bridged (or viscosity-enhancing looped) midblocks.