Variable Shear-Induced Orientation of a Diblock Copolymer Hexagonal Phase

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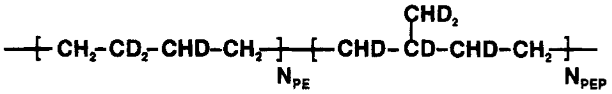
Deformation and flow are known to influence the orientation and state of order of nanostructured soft materials. Thermotropic[1] and lyotropic[2] liquid crystals, colloidal suspensions,[3] and block copolymers[4] have been investigated extensively over the past 2 decades, and all of these materials exhibit certain common thermodynamic and dynamic features. For example, just above the nematic−smectic transition temperature, steady shear can induce smectic order in some thermotropic compounds,[5] where the layer normals are found to be perpendicular to both the shear direction and gradient. Symmetric diblock copolymer melts behave similarly when sheared just above the order−disorder transition (ODT) temperature,[6] and both results can be explained based on fluctuation effects.[7] Asymmetric diblock copolymers that microphase separate into spherical domains, packed on a body-centered-cubic lattice, recently have been shown[8] to respond to a dynamic shear field in a complicated manner that mimics the behavior of certain colloids.[9,10] Moreover, near the cylinder-to-sphere transition, shearing a block copolymer cubic phase can drive a cubic-to-hexagonal phase transition.[8]

These and numerous other results can be intuitively rationalized as responses that minimize flow stress by orienting microstructures in ways that reduce interference between self-assembled molecules. In the case of lamellae (or smectic layers) this can be accomplished by either a "parallel" or "perpendicular" stacking[11] (i.e., the layer normals parallel to the shear gradient or perpendicular to the shear gradient and shear direction, respectively). However, this simple explanation cannot anticipate which of these two orientations will occur as a function of temperature, shear rate, or other material factors, such as entanglement density. For diblock copolymer lamellae, there is now considerable experimental[11−13] and theoretical[7,15] evidence that the selection of a particular mode of ordering depends on both thermodynamic (e.g., fluctuation) and dynamic (e.g., functional) properties of the material.

At intermediate compositions, between those associated with spheres and lamellae, a hexagonally ordered cylindrical microstructure occurs. (Recent experiments have also documented hexagonally modulated and perforated layered phases and a bicontinuous cubic phase with $Ia\bar{3}d$ space symmetry.[16−18] The deformation of these microstructures is treated separately.[15−17]) Keller et al.[19] first documented flow-induced orientation of cylinders in extruded plugs of SBS triblock copolymer. Subsequently, Hadziioannou et al.[20] investigated the influence of dynamic shearing on similar materials, demonstrating a high susceptability for cylinder alignment along the direction of shear. (SAXS) Small-angle X-ray scattering measurements also revealed that the (11) and (10) planes were arranged parallel and perpendicular, respectively, to the shear plane; i.e., the [11] direction was coincident with the shear gradient. However, this result seems to conflict with other experiments on diblocks[21] and triblocks.[22−26] SAXS and small-angle neutron scattering (SANS) experiments demonstrate shear-induced alignment of hexagonally packed cylinders that place the (10) plane parallel to the plane of shear, as first noted by Skoulios.[23] Other *in-situ* steady-shear SANS experiments with triblock copolymer have produced puzzling results that were explained based on the coexistence of two sets of hexagonally packed cylinders, with different unit cell dimensions.[27,28] Motivated by our results with lamellae[6,11] and spheres,[8] we have reexamined the issue of cylinder orientation in diblock copolymer melts using a reciprocating steady-shear device. Our initial findings are reported in this paper.



$$-\!\!\left[\mathrm{CH_2{-}CD_2{-}CHD{-}CH_2}\right]_{N_{PE}}\!\!-\!\!\left[\mathrm{CHD{-}\overset{CHD_2}{\overset{|}{C}}D{-}CHD{-}CH_2}\right]_{N_{PEP}}\!\!-$$

Figure 1. Predominant microstructure of the polyethylene−poly(ethylenepropylene) (PE−PEP) polymer used in this work. Catalytic deuteration of the polydiene precursor leads to isotope exchange and a modest degree of neutron contrast. The distribution of hydrogen and deuterium shown here is only one of many possible configurations. The PE and PEP blocks also contain approximately 6% ethylethylene and isopropylethylene repeat units, respectively.

The experiments described here were conducted with a polyethylene−poly(ethylenepropylene) (PE−PEP) diblock copolymer that contains 37% by volume PE. This polymer was prepared by sequential anionic polymerization of butadiene and isoprene in cyclohexane at 40 °C using a lithium counterion. These reaction conditions lead to approximately 94% 1,4- and 6% 1,2-butadiene addition and 94% 1,4- and 6% 3,4-isoprene addition. Saturation (>99%) of the polydiene precursor over a Pd/$CaCO_3$ heterogeneous catalyst yields the PE−PEP product. Deuterium gas was used in the saturation reaction. Preferential isotope exchange imparts a modest degree of neutron contrast to PE−PEP as described elsewhere.[29] A sketch of this compound is given in Figure 1. The molecular weight and polydispersity were determined by light scattering and size-exclusion chromatography (both performed on the polydiene precursor) to be $M_n = 170\ 000$ and $M_w/M_n = 1.05$. Rheological and small-angle neutron scattering measurements established that this PE−PEP specimen is characterized by a hexagonally packed cylindrical microstructure that disorders at $T_{ODT} = 189 \pm 1$ °C. Below 108 ± 1 °C the PE block is semicrystalline.

SANS experiments were conducted at the Risø National Laboratory on the 12 m instrument using $\lambda = 8.0$ Å wavelength neutrons with $\Delta\lambda/\lambda = 0.09$. An *in-situ* shearing device, described in a separate publication,[8] was operated while performing some of the measurements reported here. This machine allows us to shear a specimen while simultaneously recording SANS patterns. Polymer is held between 1 in. by 1 in. channel-cut aluminum plates. Anodized rails provide hardened surfaces that facilitate sliding the opposing plates, which imposes a reciprocating steady-shear deformation on the material. A sketch of the channel-cut plate

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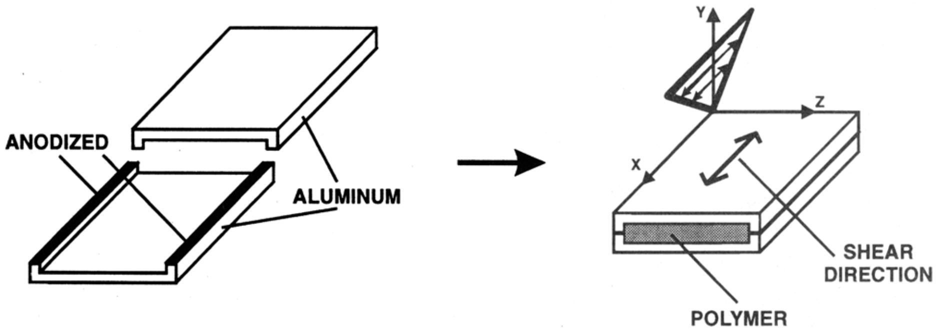


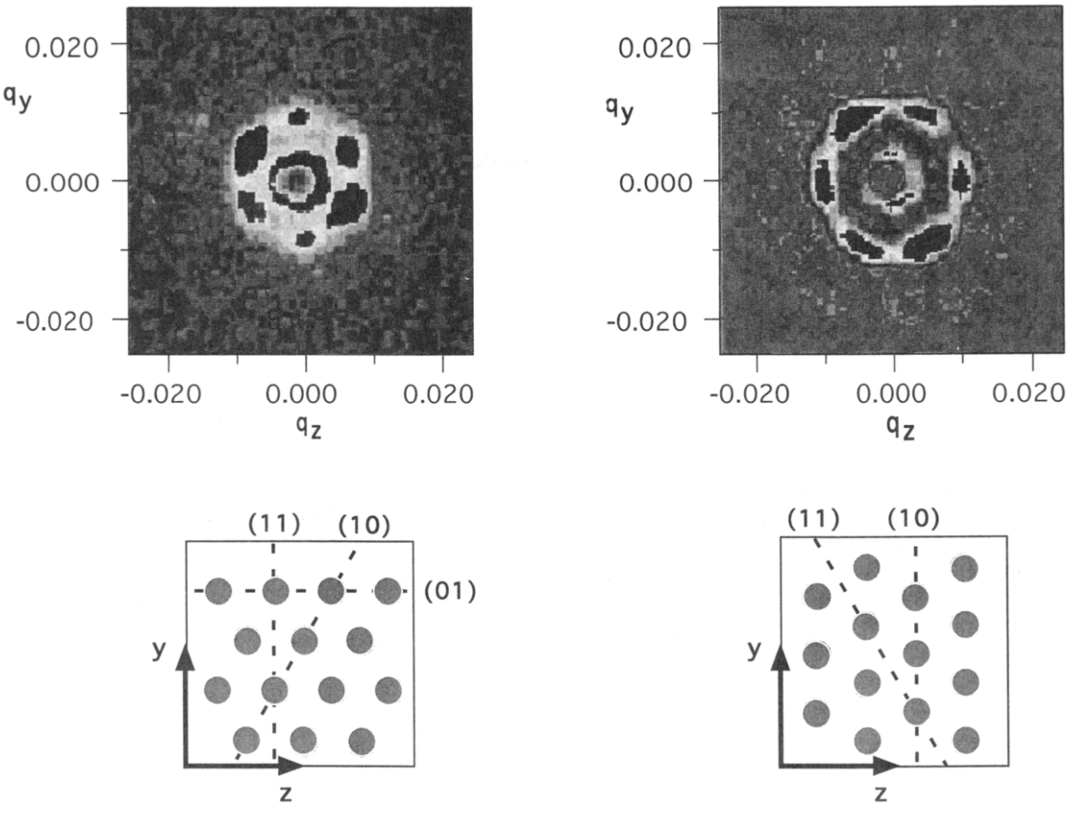
Figure 2. Shear cell assembly and coordinate system for a dynamic SANS shearing device. The anodized surfaces facilitate sliding.

assembly is given in Figure 2. The experiments reported here were executed using a 1.2 mm gap and a shear strain amplitude of $\gamma = 1$ (100%). After loading the polymer, the shear cell is inserted between two brass holders and the entire assembly is mounted into the temperature-controlled shearing device (see ref 8 for a sketch). An important design feature of this instrument is the method of loading and removing the aluminum plate/brass holder assembly. This is accomplished by a simple horizontal sliding motion; as a consequence, the assembly can be removed in several seconds, even at elevated temperatures. We have found that crystallization of PE in diblock copolymers can distort or disrupt the microstructure present above 108 °C. However, quenching a melt specimen into liquid nitrogen seems to minimize microstructural damage, presumably by suppressing coherent crystallization. In this work we have made use of this quenching technique, which is facilitated by the sample holder design.

Two different shear experiments were conducted with the PE−PEP specimen. In the first, the polymer was loaded in the shearing device, heated to 130 °C, and subjected to a reciprocating shear deformation at a shear rate of $\dot{\gamma} = 0.35\ \mathrm{s}^{-1}$ for 30 min; the shearing and scattering coordinate system is identified in Figure 2. SANS patterns obtained in 5-min increments during this period revealed a rapid development of orientational order; the initially isotropic ring of scattering evolved into two reflections along $\mathbf{q}_z$, where $|\mathbf{q}| = 4\pi\lambda^{-1} \sin(\theta/2)$ is the scattering wavevector. Upon cessation of shearing this pattern persisted, indicating a stable oriented morphology. Unfortunately, the scattering geometry afforded by the *in-situ* shearing device (neutron beam parallel to the y axis in Figure 2) does not allow us to directly confirm a hexagonal symmetry or establish the unit cell orientation around the cylinder axis (x axis in Figure 2). Therefore, the sheared specimen was removed from the device and quenched in liquid nitrogen. At cryogenic temperatures the aluminum cell opens easily, and the oriented material can be removed as a coherent sheet. After warming to room temperature, the specimen was sliced into 1-mm strips that exposed the x (shear axis) and z directions to SANS analysis. A neutron scattering pattern obtained with the beam directed along the shear direction is presented in Figure 3a. The hexagonal scattering pattern clearly indicates a cylinder orientation that places the (10) plane parallel to the shear plane (x−z in Figure 2). This is the same orientation obtained by us,[21] and others,[22−26] in separate studies of different block copolymer systems. (In this, and previous studies that include other diblock systems,[8,16,21] we have consistently observed this orientation, regardless of whether the sample was sheared as-loaded or disordered and cooled into the ordered state before shearing. Provided the sample was sheared well below T_{ODT}, the (10) plane is found to lie parallel to the shear plane.)

In the second experiment the PE−PEP specimen was first disordered by heating to 195 °C and then cooling to 185 °C while shearing at $\dot{\gamma} = 0.45\ \mathrm{s}^{-1}$. Cooling took about 5 min and was followed by an additional 12 min of shearing at 185 °C. As with the previous experiment, orientation was evidenced by the development of two reflections along $\mathbf{q}_z$; in this case the diffraction developed abruptly as the sample cooled. Cessation of shear left the SANS pattern unaffected. The sample holder assembly was removed and rapidly immersed in liquid nitrogen, and the polymer sheet was extracted from the shear plates. The material was cut as before, and SANS patterns were taken with the neutron beam directed along the x and z axes. Figure 3b depicts the result obtained with the neutrons directed along the shear axis. Again, a hexagonal pattern is observed, but rotated 30° relative to the previous case. Obviously, this preparative history has produced a qualitatively different result. Sketches of the associated real-space projections along the cylinder axis are also provided in Figure 3.

There is a striking similarity between the conditions leading to the two hexagonal cylinder orientations described here and our previous discovery of parallel and perpendicular orientations in dynamically sheared lamellae.[11] In fact, our choice of shearing histories was guided by the earlier work. Experiments with lyotropic liquid crystals[2] and block copolymers[30] suggest a correspondence between the layer plane (i.e., (001)) in lamellae and the (10) plane in the hexagonal phase (see Figure 43 in ref 2 for an illustration of this relationship). Here we note that an analogous dynamic correspondence appears to be operative in diblock melts. Well below T_{ODT} shear produces parallel lamellae,[11] and here we have demonstrated the analogous state with cylinders (Figure 3a); a 30° rotation of the (10) plane places an equivalent plane parallel to the shear plane. Shearing symmetric diblocks near (above or below) T_{ODT} induces a perpendicular lamellar state[6,11] which also seems to be duplicated with the asymmetric polymer (Figure 3b). In a separate publication[31] we have shown that T_{ODT} increases with increasing shear rate in a cylinder-forming diblock copolymer, similar to the situation with the lamellar−disorder transition.[6] In both cases there seems to be a clear connection to fluctuation effects[6,21] which have also been implicated in the occurrence of perpendicular lamellae.[32] However, we are not aware of any theoretical treatments that deal with cylinder orientation. Moreover, separate experiments



(a) (b)

Figure 3. SANS patterns (logarithmic intensity contour levels) obtained with the neutron beam directed along the shear (x) axis (upper panels) and the associated orientation of the aligned and hexagonally packed cylinders (lower panels). These SANS images were collected from specimens that were quenched in liquid nitrogen after being sheared at (a) 130 and (b) 185 °C. The asymmetric intensity distribution in these hexagonal SANS patterns derives from slight misalignment of the specimen, which consists of several 1 mm strips that were cut from the quenched sample, stacked, and epoxied onto a quartz disk. The 30° rotation of the hexagonal diffraction patterns indicates two distinct unit cell orientations relative to the plane of shear (see Figure 2). The dashed lines identify crystallographic planes in the hexagonal lattice.

with an asymmetric PEP−PEE polymer[33] suggest that the unusual perpendicular cylinder orientation may not always be the most stable state under steady-state shearing. Formation of the perpendicular form may be followed by a rearrangement into the parallel geometry. Obviously the activation barriers to reorientation will be considerably smaller in a cylindrical microstructure than with lamellae, where domain disruption or long-range correlated rotation is required. However, this interesting behavior may also depend on parameters other than just temperature and shear rate. For example, we suspect that the ratio of block relaxation times may play an important role in determining the nonlinear rheological behavior of these materials.[14] In this regard, the triblock copolymers studied by Hadziioannou et al.[20] represent an extreme case, which might explain the discrepancy between the cylinder orientation they measured versus that reported by others.[22,29]

In summary, we have shown that varying the shearing conditions of an asymmetric PE−PEP diblock copolymer leads to two distinct cylinder orientations. Near the order−disorder transition (ODT) dynamic shear places the (10) plane of the hexagonal microstructure perpendicular to the plane of shear. Shearing the ordered material well below T_{ODT} leads to a parallel alignment of (10) planes with respect to the shear plane. This finding is strikingly similar to the dynamic behavior of block copolymer lamellae and should provide an important link in our efforts to understand the evolution of structure and properties in soft materials in response to deformation and flow.

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