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Effect of Defects on the Response of a Layered Block Copolymer to Perpendicular Deformation: One-Dimensional Necking

Yachin Cohen*,† **and Edwin L. Thomas**‡

Department of Chemical Engineering, Technion-Israel Institute of Technology, Haifa, Israel 32000, and Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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ABSTRACT: The morphology of oriented lamellar stacks in roll-cast triblock copolymer films exhibits a nonuniform distribution of defects. The lamellae predominantly orient parallel to the plane defined by the velocity and velocity-gradient directions of the flow field between the counterrotating cylinders. However, the orientation effect along the flow direction in as-cast films is much stronger. Annealing at elevated temperature results in uniaxial symmetry about the main orientation axis of the lamellar normals. The response of a triblock copolymer structure, composed of alternating glassy and rubbery lamellae, to deformation along the lamellar normal direction is evaluated by comparing as-cast and annealed films. The defect distribution governs the macroscopic and microstructural behavior. Annealed samples deform uniformly without necking, and lamellar tilting and folding into the "chevron" morphology occurs about any axis perpendicular to the stretching direction with equal probability. In as-cast samples, a unique "one-dimensional" necking is observed macroscopically. The cross section is reduced only along one spatial dimension (the velocity gradient direction of the flow field), and lamellar tilt is observed only about a single axis (the velocity direction of the flow field). These observations highlight the dominant role of defects in perpendicular deformation of block copolymer structures composed of alternating glassy and rubbery layers.

Introduction

The microstructural response of ordered block copolymer mesophases to mechanical deformation underlies their unique macroscopic properties ranging from thermoplastic elastomers to toughened thermoplastics.[1,2] The lamellar structure is the simplest of the block copolymer morphologies. By choice of its chemical constitution, the layers can be controlled to exhibit alternating glassy and rubbery character. Strong interlayer adhesion is due to localization of junctions between the constituent blocks at the interface. The response of such a structure to deformation in the direction of the lamellar normal ("perpendicular deformation") shows rigid−elastic initial behavior followed by yielding at relatively low strain. From the microstructural point of view, perpendicular deformation results in transition of the layered structure to the "chevron" morphology of tilted layers, as shown in several studies.[3−7] Mechanical analysis and finite-element simulation presented recently by Read et al.[8] showed that the yielding of the layered structure subjected to perpendicular deformation is due to sinusoidal buckling, similar to the undulation instability in other systems such as smectic liquid crystals.[9]

In a previous publication,[10] we reported a detailed morphological study on deformation of highly ordered lamellar styrene−butadiene−styrene (S−B−S) films. In particular, perpendicular deformation was shown to cause folding of the layers to form the "chevron" morphology, exhibiting symmetric tilt boundaries parallel to the deformation axis. With increasing strain the lamellar normal tilts away from the stretching direction, whereas the lamellar layer repeat spacing remains constant. In a subsequent publication, the low-strain behavior of alternating glassy/rubbery layers under perpendicular deformation was evaluated.[11] Synchrotron small-angle X-ray scattering (SAXS) measurements, at 0.5% strain resolution, showed negligible layer dilation in the elastic region prior to the mechanical yield point, whereas the breadth of the orientation distribution of the lamellar normals increased continuously. Observations by scanning probe microscopy (SPM) at relatively low strain suggested that tilt grain boundaries nucleate in the vicinity of defects such as edge dislocations. These observations suggested an alternative mechanism to the undulation instability model, namely, nucleation and propagation of tilt boundaries due to defects in the lamellar structure.[11]

Here we investigate further the effect of defects on the perpendicular deformation behavior of the lamellar block copolymer structure. Defects in the lamellar structure are inherent to any processing technique, even those resulting in a highly ordered nearly single-crystal-like morphology. Therefore, careful annealing procedures were undertaken in our previous studies,[10,11] so as to minimize the defect concentration. These samples exhibited uniaxial symmetry about the lamellar normal direction, and indeed their perpendicular deformation behavior reflected that symmetry. Tilting of the layers and folding into the "chevron" morphology was observed with equal probability about any axis perpendicular to the deformation axis. The behavior of annealed lamellar structures is compared with that of the unannealed ones, which do not exhibit uniaxial symmetry due to the distribution of defects in the as-processed morphology.

Experimental Section

Details of the material used and most experimental procedures were reported previously.[10] The triblock copolymer, Vector 4461-D, having S−B−S block molecular weights of 18.5,

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† Technion-Israel Institute of Technology.

‡ Massachusetts Institute of Technology.

* Corresponding author: e-mail yachinc@tx.technion.ac.il.

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45, and 18.5 kDa, respectively (PS content of 45% w/w), was obtained from Dexco Polymers. Oriented films were prepared from solutions containing 40% (w/w) polymer in cumene, using the roll-casting technique.[12,13] After drying in a vacuum oven for 48 h at 50 °C and subsequent short heating (about 5 min) to 80 °C, the material is termed an *as-cast* film. The short heat treatment of as-cast samples was needed to relax residual chain stretching along the flow direction which results in reduced lamellar periodicity relative to the equilibrium state.[13] *Annealed* films were obtained after further heat treatment of 48 h at 120 °C under vacuum. The equilibrium lamellar spacing is thus 27 nm, which remains constant throughout this study. The coordinate axes of the sample, in relation to the roll-casting process, are denoted as follows. The x axis is parallel to the velocity direction (tangential to the rolling cylinder), the y axis is parallel to the velocity-gradient direction (radial to the rolling cylinder), and the z axis is parallel to the neutral direction (parallel to the rolling cylinder axis). The lamellae in the roll-cast samples are predominantly oriented in the $x-y$ plane (lamellar normal along the z axis, which was also the deformation axis). Test specimens having dimensions of $1.35 \times 1.2 \times 13.5$ mm (x, y, z axes, respectively) were cut from the roll-cast films. Tensile stress−strain characteristics were obtained using an Instron 4201 apparatus at crosshead speed of 2.6 mm/min (an average of data from five test samples is reported). SAXS measurements were performed at the Advanced Polymers Beamline, X27C, National Synchrotron Light Source, Brookhaven National Laboratory. The wavelength used was 0.1307 nm, the beam size was about 0.4 mm in diameter at the sample position and the sample-to-detector distance was 145 cm. Samples were stretched in a custom-built tensile stage with an attached load cell, at a crosshead speed of 2.6 mm/min to given strains, at which 30 s exposures were recorded on Fuji imaging plates.

Results and Discussion

A striking difference between the behavior of the lamellar block copolymer samples under perpendicular deformation before and after thermal annealing can be easily seen by visual inspection. As-cast samples exhibit a unique "one-dimensional" necking phenomenon, in which the cross-section dimension of the sample decreases abruptly at the necking front only along the y direction, as demonstrated by the photographs shown in Figure 1. Typically, necking was initiated at both grips and advanced upon further deformation toward the center of the sample. This differs markedly from the behavior of annealed samples under perpendicular deformation, which do *not* show macroscopic necking. Rather, the cross-section dimensions of annealed samples decrease continuously in both x and y directions as the material extends uniformly throughout the perpendicular deformation process, up to strains larger than 600%, as reported previously.[10]

The mechanical response of as-cast and annealed samples, subjected to perpendicular deformation, is presented by the nominal engineering stress−strain curves in Figure 2. The initial modulus of the annealed samples is somewhat higher than the as-cast ones, 64 vs 44 MPa, respectively. Both samples exhibit yielding at a relatively low strain. The distinct necking of the as-cast samples is consistent with the drop in load observed in the stress−strain curve at the yield point (Figure 2). It is a consequence of the material having a relatively high yield stress and low strain hardening beyond the yield point. In terms of the nominal stress (σ_n) and strain (ϵ_n), the stability criterion is $d\sigma_n/d\epsilon_n > 0$.[14] The absence of macroscopic necking in the annealed samples is consistent with the positive slope of the nominal stress−strain curve, as shown in Figure 2, and reported in a previous publication up to higher strains.[10]

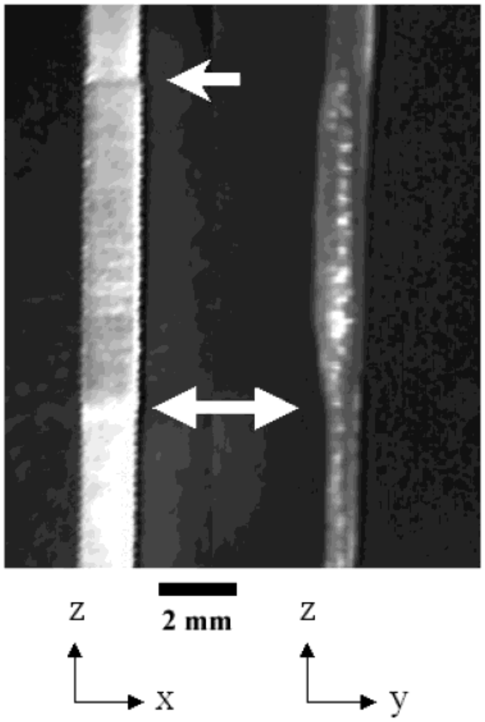

Figure 1. Photographs of an as-cast sample under perpendicular deformation showing "one-dimensional" necking. Arrows indicate the necking front. Reduction of the cross-section dimension in the neck occurs only in one direction, the y axis.

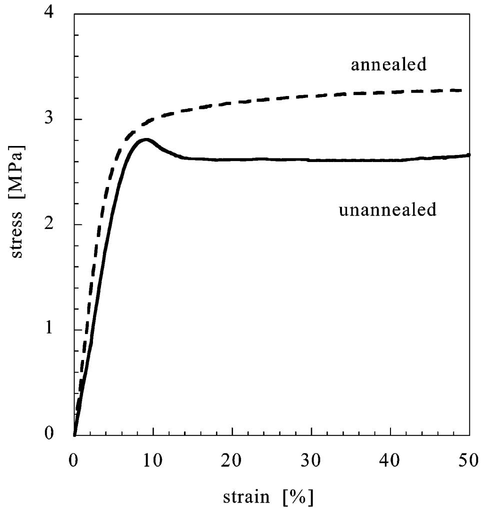

Figure 2. Stress−strain curves (engineering units) of oriented lamellar samples undergoing perpendicular deformation at relatively low strain: solid line, as-cast films; dashed line, annealed films.

The unique "one-dimensional" necking phenomenon observed in as-cast lamellar samples and its elimination upon annealing will be related below to the uniquely asymmetric distribution of defects in the initial state.

The roll-casting process provides an initial morphology of highly aligned layers, predominantly parallel to the $x-y$ plane.[12] The crystallographic directions of the lamellar structure can be thus defined in relation to the sample coordinates as $\hat{x} = [100]$, $\hat{y} = [010]$, $\hat{z} = [001]$, as shown in Figures 3 and 4. There are, however, significant differences between as-cast and annealed samples. This is evident in the SAXS patterns, obtained with the incident beam oriented along the x and y axes, shown for the as-cast and annealed films in Figure 3, a and b,

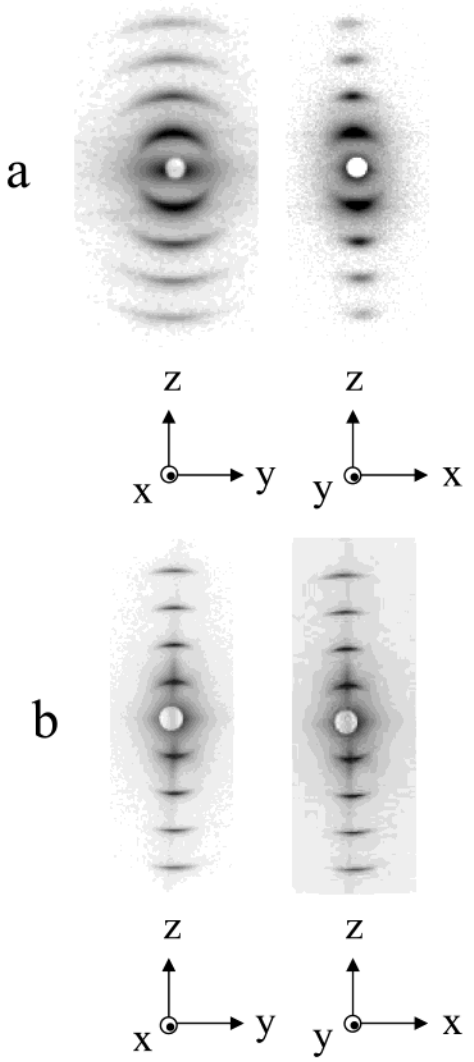

Figure 3. SAXS patterns obtained with the incident beam along the *x* and *y* axes from (a) as-cast and (b) annealed films, showing the orientation distribution of the lamellar normals in the undeformed state. Intensities are presented on a logarithmic scale. The lamellar spacings of the lamellar structure is 27 nm.

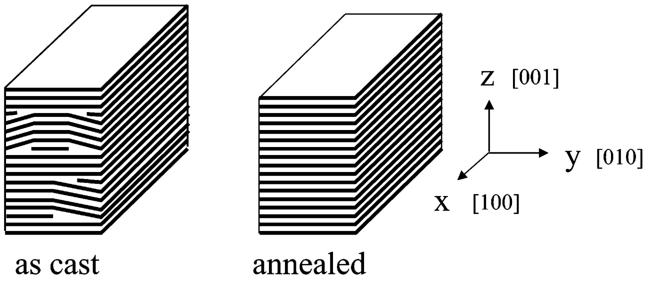

Figure 4. Schematic representation of the morphology in as-cast and annealed film, highlighting the nonuniform distribution of defects in the as-cast film.

respectively. Significant arcing of the reflections from the as-cast films is observed when the incident beam is along the *x* axis compared to those obtained with the incident beam along the *y* axis. The azimuthal breadth of the reflections, as judged from the full width at half-maximum (fwhm) of the (001) peaks, is about 45° in the former case and 20° in the latter. Azimuthal broadening of the reflections in the $y-z$ plane is due to the presence of numerous grains in the diffracting volume, with a distribution of orientations of the lamellar normals about the *z* axis. Evidently, this distribution is broader in the $y-z$ plane (viewed with the incident beam along the *x* axis) than in the $x-z$ plane (viewed with the incident beam along the *y* axis).

Further heat treatment results in several changes in the SAXS pattern, as shown in Figure 3b. The azimuthal breadth of the reflections is reduced to 10° (fwhm) in both the $y-z$ and $x-z$ planes. In fact, it was verified that the annealed samples exhibit uniaxial symmetry about the *z* axis. The axial width of the reflections is also reduced significantly (from 1.7 to 0.7 mrad fwhm), and the higher-order (00*l*) reflections become more prominent. The effects of thermal annealing on the lamellar morphology in roll-cast block copolymer films of the same polymer as in this study were previously reported.[13] In particular, the morphology in sections normal to the *x* axis visualized by transmission electron microscopy (TEM) is shown in Figure 9 of ref 13. The microstructure in the $y-z$ plane of as-cast samples was shown to be composed of many small grains with numerous helicoid surface twist boundaries[13] as well as isolated edge dislocations. Helicoid surface twist grain boundaries form in lamellar block copolymers at low twist angles up to 15°.[15,16] Annealing significantly reduces the number of grains and twist boundaries.[13] The annealed structure can be described as approaching that of a "single crystal" with edge dislocations, some isolated and some forming low-angle tilt grain boundaries.[10,11] The edge dislocations are defined by the Burger's vector $\vec{b} = d_0[001]$, where $d_0 = 23$ nm is the lamellar spacing, and the line vector of the core axis $\vec{t} = [100]$. A schematic representation of the lamellar microstructure in the as-cast and annealed states is presented in Figure 4.

The way in which a flow field interacts with a microphase-separated block copolymer melt or solution has been a subject of intense investigations as a means for achieving single domain morphologies of controlled orientations.[17] The effect of processing conditions on lamellar orientation in shear flow, and the formation of nearly "single-crystal" textures, is quite well described in the literature.[18] Much less is known about the orientation effects in the roll-casting process. Kinematic analysis of fluid flow between counterrotating cylinders shows two major fields in the nip region between the cylinders, shear flow and extensional flow, both with the velocity direction tangential to the cylinders (*x* axis).[19,20] In the relatively high-speed roll-casting process of our experiment, the strongest driving force for alignment of the lamellae is the tangential extensional flow at the nip of the rolling cylinders. The secondary alignment direction is along the *y* axis, radial to the rollers, most likely due to extensional flow in the vicinity of the meniscus, downstream of the nip (radial direction, *y* axis).[21] The morphological observations demonstrate that the orienting fields are not equivalent. Much better alignment is achieved along the *x* axis due to the extensional flow in the nip. The rate of elongation ($\dot{\epsilon}$) can be estimated by[22]

$$\dot{\epsilon} \approx 0.75\omega(D/G)^{1/2} \tag{1}$$

where ω is the angular velocity, D is the cylinder diameter, and G is the gap at the nip. At the conditions of our experiment the elongation rate is approximately 100 s^{-1}. The extensional flow causes chain stretching in the *x* direction, which is trapped during roll casting

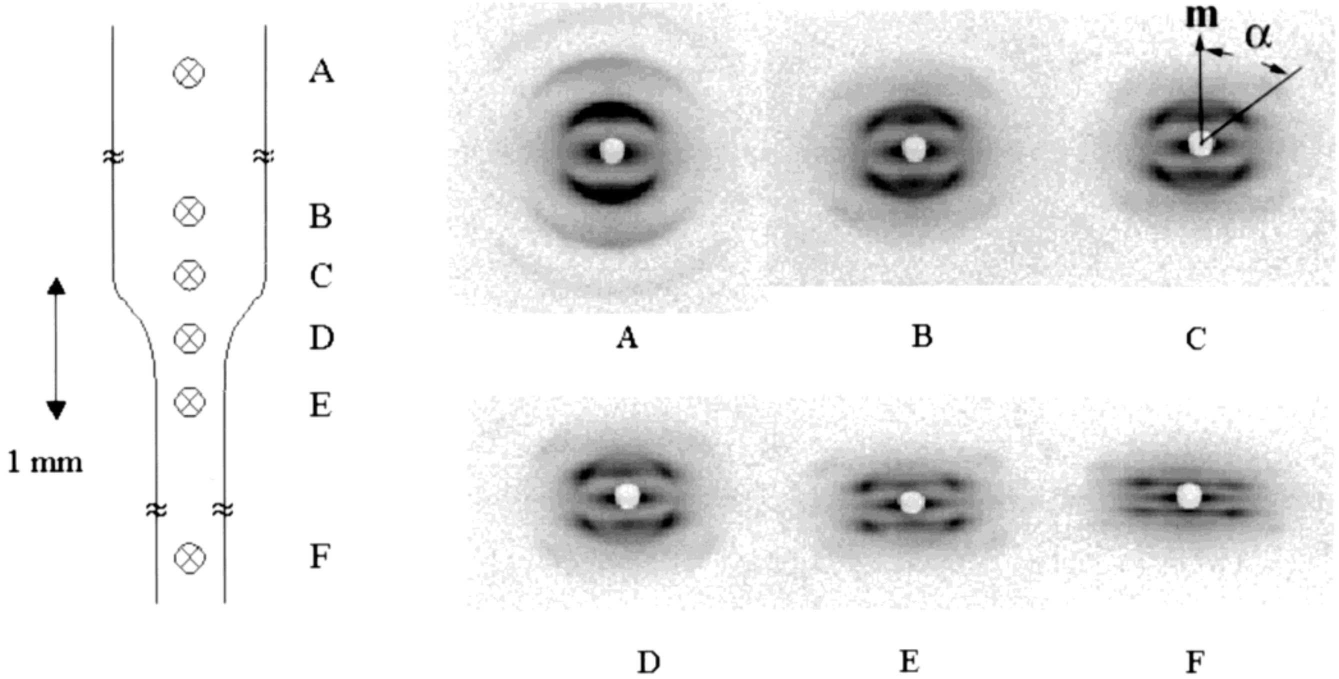

Figure 5. SAXS patterns from the region of the necking front, at different positions along an as-cast film stretched to 100% strain along the *z* axis (perpendicular), obtained with the incident beam along the *x* axis. A−F denote different positions as indicated in the scheme at left. The lamellar spacing (27 nm) remains unchanged.

when the PS domains vitrify during solvent evaporation. It was shown previously that the first heating above 80 °C results in 25% contraction of sample dimensions along the *x* axis, whereas the dimensions in the *y* and *z* directions increase by 18% and 7%, respectively.[13] This is accompanied by an increase in the lamellar repeat *d* spacing to its equilibrium value, 27 nm in this case. The short heating of as-cast samples in the current experiments is sufficient to relax chain stretching to its equilibrium value but is not enough to anneal away the morphological defects. This is achieved by the longer heat treatment at the higher temperature.

It is well established that a structure of oriented block copolymer lamellae, in which the alternating layers are glassy and rubbery, folds to the "chevron" morphology, at large strains perpendicular to the layers.[2−7,10] At low strain, sinusoidal undulations were demonstrated by simulation[8] and SPM imaging.[11] The "chevron" morphology is characterized by a four-point pattern in SAXS and in optical transforms of microscopy images,[10] whereas undulations cause arcing of the SAXS pattern or the optical transform of images.[11] The transition from undulation to "chevron" morphologies with increasing strain has been analyzed for liquid-crystal systems.[23]

As mentioned above, well-annealed lamellar samples deform uniformly without necking. Tilting of the layers during perpendicular deformation, observed by SAXS measurements, occurs about any axis perpendicular to the stretching direction with equal probability.[10] For the as-cast samples reported here, tilting of the layers in response to perpendicular strain is observed only about the *x* axis. This is clearly evident in SAXS measurements. When the incident beam is oriented along the *y* axis, the lamellar reflections are lost even at low strain. The reflections are, however, clearly observed with the incident beam along the *x* axis. Figure 5 shows the SAXS patterns taken from different positions in a sample stretched to a total nominal strain of 100% perpendicular to the layers, in particular in the vicinity of the necking front. As the incident beam is moved along the tensile axis of the sample, within a region less than 1 mm in length on either side of the necking front, an entire gallery of SAXS patterns can be observed. These are similar to the patterns described previously during homogeneous deformation of annealed samples as a function of strain.[10] These range from arcing at low strain, splitting of the meridional arc into a four-point pattern at intermediate strain, and finally formation of a well-defined sharp four-point pattern on meridional streaks at very high strain. The morphological changes of the lamellar structure during necking are shown schematically in Figure 6, highlighting the observation that the transition from undulations to "chevron" folding occurs at the necking front.

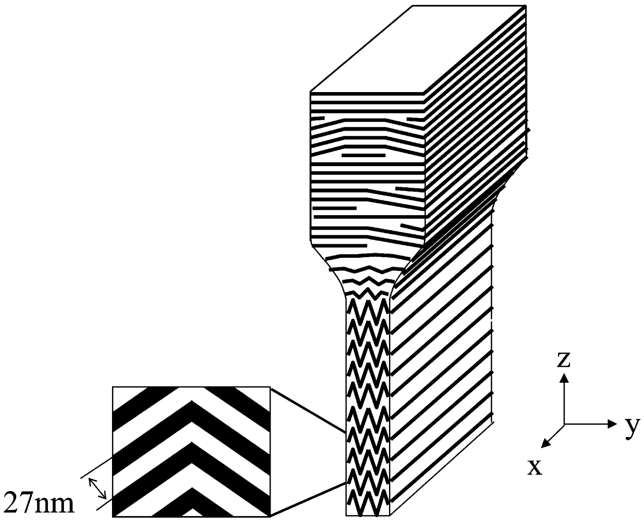

Figure 6. Schematic representation of the morphology in the region of the necking front, highlighting the "one-dimensional" nature of the neck. The cross section is reduced in thickness only in the *y* direction. The transition from undulations to "chevron" morphologies occurs at the necking front.

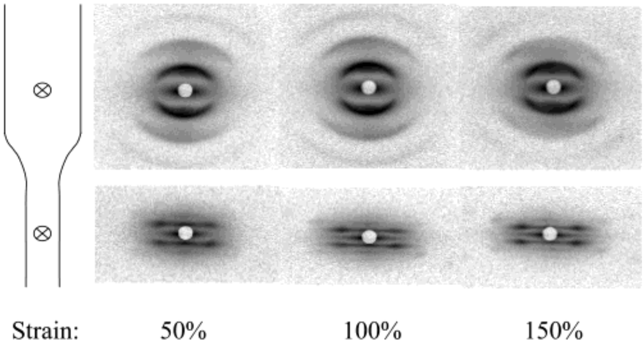

Figure 7. SAXS patterns taken from within the necked and unnecked regions of as-cast samples at 50%, 100%, and 150% macroscopic strain. The incident beam was directed along the *x* axis, and the stretching direction is vertical. Intensities are presented on a logarithmic scale. The lamellar spacing (27 nm) remains unchanged.

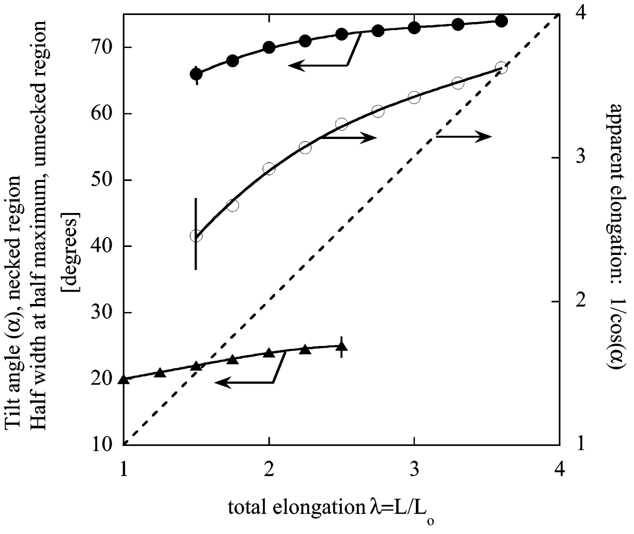

Figure 8. Relationship of the total sample elongation $\lambda = L/L_0$ to the characteristics of the SAXS patterns of as-cast samples: (▲) the half-width at half-maximum (hwhm) of the arced reflections from the unnecked regions; (●) the lamellar tilt angle (α) of the four-point SAXS patterns from the necked regions. The apparent elongation in the neck, 1/cos(α), is also shown (○). The dashed line represents equality of the apparent and nominal elongations.

The strain in the neck region can be evaluated from the tilt angle (α) of the four-point SAXS reflections away from the meridional axis (*m*), as shown in Figure 5c. It was shown for perpendicular deformation of annealed samples that the lamellar tilt angle is related to the nominal elongation ($\lambda = L/L_0$, where L_0 and L are the initial and final sample lengths, respectively) as[10]

$$1/\cos(\alpha) = \lambda \qquad (2)$$

Figure 7 shows SAXS patterns taken from within the necked and unnecked regions at 50%, 100%, and 150% strain. Patterns from the unnecked regions exhibit arcs that broaden somewhat with increasing strain, whereas those from the necked regions exhibit fully developed four-point patterns situated on meridional streaks. In the necked region, the tilt angle increases only slightly with increasing strain. Figure 8 shows the tilt angle α, evaluated from the four-point patterns of the necked regions, and the azimuthal breadth of the arcs of the unnecked regions, as a function of the total elongation. For the latter, the half-width at half-maximum (hwhm) is used as a measure of lamellar tilt. The apparent elongation in the neck, calculated using eq 2, increases from about 2.5 to 3.6, as the necking front proceeds through the sample. At the latter elongation, complete necking is observed throughout the sample, and the apparent elongation equals the macroscopic one, as shown in Figure 8. The high level of elongation in the neck, and the four-point SAXS patterns, indicate the fully developed “chevron” morphology in that region. Our previous analysis of perpendicular deformation of the annealed lamellar structure showed that the mechanical behavior of the material at this level of elongation is rubber-elastic.[10,11] This is due to breakage of the glassy PS layers at the tilt grain boundaries that form during high deformation.

The present observations demonstrate that the distribution of defects in the lamellar block copolymer structure directly governs the microstructural and macroscopic behavior of the material composed of alternating glassy and rubbery layers under perpendicular strain. In the as-cast lamellar samples, the distribution of defects is not symmetric about the orientation axis of the lamellar normals. For example, there are more edge dislocations with their cores oriented along the velocity axis of the roll casting process [100] than along the velocity gradient direction [010], as illustrated in Figure 4. Therefore, tilting of the lamellae due to deformation along the lamellar normal direction occurs about the [100] axis—the predominant direction of dislocation cores. This supports the hypothesis that defects nucleate tilt grain boundaries[10,11] and also explains the unique “one-dimensional necking” observed macroscopically. The important role of defects in structural transformations of block copolymer melts has already been identified.[24] Nucleation of kink bands from preexisting defects was deduced from studies on shear deformation of a lamellar diblock copolymer melt.[24,25]

These observations are also relevant to the question of the three-dimensional nature of the deformed structure in annealed samples. In smectic liquid crystals it has been shown that buckling occurs in the form of a “square lattice” or “egg-box” morphology, where the layers fold simultaneously along perpendicular in-plane directions. This buckling mode has a lower free energy relative to folding along just one in-plane direction.[26] In the case of the as-cast block copolymer structure composed of alternating glassy and rubbery lamellae, layer folding occurs about a single in-plane axis due to the asymmetric distribution of defects. We thus conceive that during perpendicular deformation of annealed samples individual domains or correlated lamellar stacks also fold about a single axis, characteristic of the defect distribution of that specific grain. Uniform macroscopic deformation with uniaxial symmetry of the microscopic tilting of lamellae is due to uniaxial symmetry in the distribution of defects in the annealed state. A full three-dimensional description of the microstructure in the deformed state of uniaxial samples is still lacking.

Conclusion

The results presented in this work support the hypothesis that the mechanical response, observed in perpendicular deformation of block copolymer structures composed of alternating glassy and rubbery layers, is defect-mediated nucleation and propagation of tilt grain boundaries.[10,11] The dominant role of defects is readily manifested in this study due to their strong anisotropic distribution. The morphology of oriented lamellar stacks, developed in the roll-casting process, does not exhibit uniaxial symmetry about the main orientation axis of the lamellar normals (z axis); rather, the defects in the lamellar stacking in the as-cast films are distributed nonuniformly. Edge dislocations are predominantly oriented with their cores aligned along the x axis, and twist grain boundaries are predominantly parallel to the $y-z$ plane. Thus, the orientation distribution of the lamellar normals is significantly broader in the $y-z$ plane than in the $x-z$ plane. The defect distribution governs the macroscopic and microstructural behavior, such that necking occurs only along one spatial dimension (reduction in cross-section dimension along the y axis) and the lamellae tilt only about the x axis. Concerning the yielding mechanism, it is conceivable that a defect-free lamellar structure would exhibit the undulation instability, as demonstrated by simulation.[8] However, even in the most aligned and annealed samples we have processed, defects still dominate the deformation behavior, as tilting of the layers occurs first in their vicinity.[11] The observations reported in this study highlight the role of defects in perpendicular deformation of block copolymer structures composed of alternating glassy and rubbery layers.

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