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Shear-Induced Lamellae Alignment in Matched Triblock and Pentablock Copolymers

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ABSTRACT: Lamellae forming CEC triblock and CECEC pentablock copolymers located near the order−disorder transition temperature were subjected to reciprocating shear as a function of strain amplitude and thermal history. Both variables strongly influence the mix of perpendicular vs parallel lamellae alignment in the triblock copolymer, while only the strain amplitude significantly affects the pentablock material. Dramatically different responses of CEC vs CECEC to shear are rationalized on the basis of viscoelastic contrast and nonlinear chain stretching, each operating differently on the initially disordered and ordered states.

Transformation of highly defective or polydomain ordered materials into macroscopic "single-crystal" monoliths represents a fundamental processing operation in materials science and engineering. With bulk block copolymer melts this is most efficiently accomplished using flow or mechanical deformation.[1−28] (Electric fields, which also can produce microdomain orientation,[29] are better employed in the thin film limit.[30]) Progress in this field has occurred in three distinct waves. Keller and co-workers[1,2] discovered macroscopic microdomain orientation in the early 1970s in extruded cylinder-forming SIS Kraton triblock copolymers. Late in the same decade Hadziioannou et al.[3] developed an innovative reciprocating shear device that was applied to lamellae and cylinder forming SIS triblocks, demonstrating the efficient formation of macroscopic sheets of "single-crystalline" material. In the early 1990s Koppi et al.[6−8] built a modified version of this shear apparatus, which could be operated while simultaneously conducting small-angle neutron scattering (SANS) experiments. The subsequent discovery of lamellae rotation,[6] also known as "flipping", from a parallel to perpendicular orientation induced by changes in shear rate helped catalyze a third, expansive wave of research in block copolymer melt dynamics that continues today. A host of research groups[1−28] have subjected all forms of ordered block copolymers (lamellae, cylinders, spheres, and even the gyroid) to extensional or shear deformation (or combinations of both) as a function of various processing variables. Notwithstanding the associated impressive literature, which includes a few theoretical papers,[31−34] the current state of understanding is largely phenomenological.

Four variables have emerged as critically important for controlling the orientation of lamellae when processing symmetric block copolymers with reciprocating shear: (i) shear rate, (ii) strain amplitude, (iii) temperature relative to the order−disorder temperature (T_{ODT}), and (iv) the initial morphological state of the specimen. The most comprehensive studies have focused on diblocks.[6−8,11−26,28] However, recent experiments with a CECEC pentablock copolymer[10] (C and E denote poly(cyclohexylethylene) (also known as PCHE) and poly(ethylene), respectively) have confirmed earlier speculation based on triblock data[9,27] that chain architecture also plays a crucial role in establishing lamellae orientation. Recognizing that essentially every bulk application of block copolymers relies on a triblock or multiblock architecture, we have expanded our research effort to include these higher-level structures.

This paper describes our preliminary findings from reciprocating shear experiments conducted on compositionally symmetric, lamellae forming, CEC triblock and CECEC pentablock copolymers. In addition to chain architecture, two processing parameters have been examined in this work: strain amplitude ($0.2 \leq \gamma \leq 6$) and thermal history (initiate shearing from the disordered vs the ordered state). The shear rate and the relative process temperature, $\Delta T = T - T_{\mathrm{ODT}}$, were fixed. Figure 1 illustrates the basic features of this study. Following a prescribed course of shearing, the specimens were cooled to room temperature (the glass transition and melting temperatures are $T_{\mathrm{g,C}} = 145$ °C and $T_{\mathrm{m,E}} = 108$ °C), sectioned into pieces, and interrogated by small-angle X-ray scattering (SAXS). These experiments have revealed remarkable differences in the susceptibility to flow alignment of triblocks vs pentablocks and provide fresh insights into the relative contributions of domain and single chain dynamics to the overall mechanisms responsible for producing parallel vs perpendicular alignment.

CEC and CECEC block copolymers were produced in relatively large batches (>80 kg) at the Dow Chemical Company by hydrogenating SBS and SBSBS precursor compounds using a heterogeneous porous silica supported platinum catalyst, where S and B refer to poly(styrene) and poly(butadiene), respectively. The B blocks contained 10% vinyl repeat units resulting in semicrystalline E domains (15−20% crystallinity) in the hydrogenated materials. Sequential anionic polymerization of styrene and butadiene was employed in the production of the precursor block copolymers. Greater than

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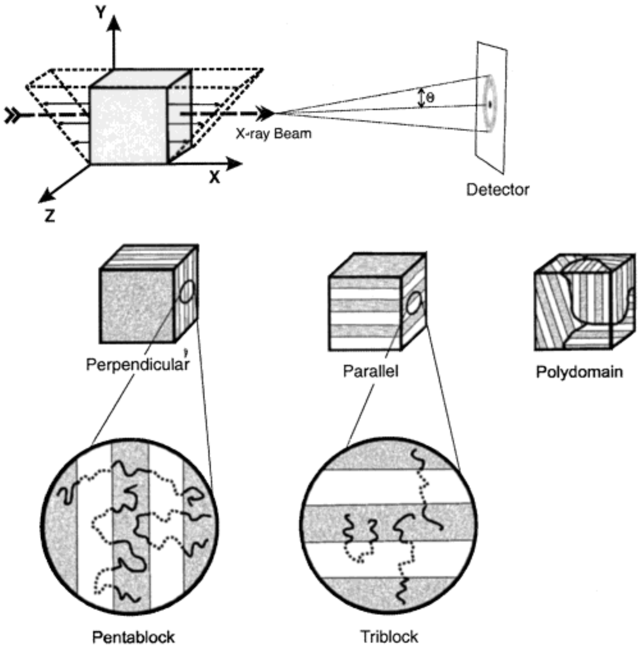

Figure 1. Illustration of reciprocating shear and SAXS arrangements. Representative triblock and pentablock chain configurations are shown within the perpendicular and parallel alignments. Bridging and looping configurations are implicated in this work in the selection of these lamellae orientations.

99% saturation and C block compositions (mass fraction) of 61% (CEC) and 56% (CECEC) were verified by ^{1}H NMR. SEC measurements conducted on the saturated materials revealed relatively narrow ($M_w/M_n \leq 1.05$) and monomodal molecular weight distributions; within experimental resolution both specimens were devoid of submolecular fragments, i.e., homopolymer, diblock, triblock, or tetrablock impurities. Weight-average molecular weights of 33 800 g/mol (CEC) and 51 900 g/mol (CECEC) were established from the synthesis stoichiometry and confirmed by light scattering measurements. SAXS measurements established a lamellae morphology for both specimens above $T_{g,C}$.

Linear viscoelastic properties were measured as a function of temperature using a Rheometrics Ares dynamic mechanical spectrometer. Representative time−temperature shifted dynamic elastic moduli, $G'(\omega)$, are shown in Figure 2 for the CEC and CECEC specimens; dynamic loss data, $G''(\omega)$, omitted for simplicity, also were used in determining the a_T shift factors. Although not rigorously justified, this method of presenting the dynamic moduli facilitates identification of the ordered and disordered regimes. Both sets of data are characterized by a distinct transition from terminal ($G' \sim \omega^2$) to nonterminal behavior at a well-defined temperature that we associate with T_{ODT}. Low-frequency isochronal temperature ramp measurements (not shown) corroborate ODT temperatures of 243 and 231 °C for the CEC and CECEC block copolymers, respectively. To maintain a nearly constant ΔT, shearing experiments were conducted at 200 and 190 °C, respectively (see below); these were used as the reference temperatures in constructing the master plots shown in Figure 2. The corresponding shear rate used during nonlinear processing corresponds to $\dot{\gamma} \cong \omega_c$ (arrows in Figure 2), where the crossover frequency ω_c separates domain-dominated ($\omega \ll \omega_c$) and entanglement-dominated ($\omega \gg \omega_c$) dynamics. This choice was not accidental. Because we are interested in exploring the influence of strain amplitude on alignment behavior without varying the shear rate, we chose a deformation rate that would access both limiting dynamics, at least in the linear regime.

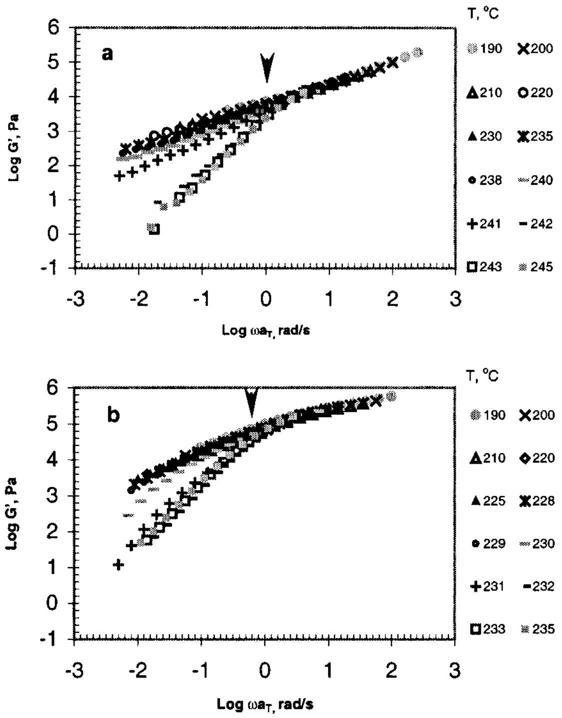

Figure 2. Linear dynamic elastic shear moduli for the (a) CEC and (b) CECEC block copolymers. These data have been time−temperature superimposed using the high-frequency branches of the G' and G'' (not shown) spectra. The arrows identify the shear rate, $\dot{\gamma} \cong \omega_c^{-1}$, used during nonlinear high strain processing.

The block copolymers were processed while under nitrogen using a modified version of the sliding plate reciprocating shearing device described by Koppi et al.[8] Specimens were held between 2.54 cm by 1.91 cm aluminum plates at a thickness of 1.2 mm. A single shear rate of $\dot{\gamma} = 0.16$ s^{-1} was employed for all experiments while strain amplitude was varied between 0.2 and 6 strain units. All experiments were initiated by heating the polymer to $T_{ODT} + 7$ °C and holding the specimen at that temperature for 10 min. Then one of the following two procedures was followed. In *shear from disorder* the shear device was turned on while still above T_{ODT}.[7,9,10] Then the temperature was reduced at about 5 °C/min down to the target value (i.e., 200 °C for CEC or 190 °C for CECEC) where shearing continued isothermally. For the second protocol, referred to as *shear from order,* the specimen was cooled at 5 °C/min from above T_{ODT} without deformation, followed by isothermal shearing at the target temperature. Prior studies have shown that the disordered state can be supercooled a maximum of approximately 20 °C below T_{ODT}.[7,9,10,35] Therefore, the two processing treatments provide application of shear from two distinctly different initial states: the disordered liquid and an ordered but polydomain state.[10] Isothermal shearing was applied to the CEC and CECEC polymers for 60 and 30 min, respectively. (Selected 3 h shearing experiments did not produce measurably different results. However, we cannot exclude the possibility of a long time dependence, particularly for the triblock copolymer.)

Upon completing a processing sequence, the shear device was stopped and the specimen was cooled to room

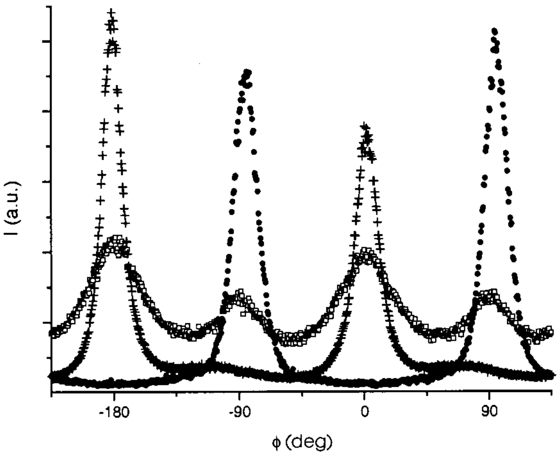

Figure 3. Representative SAXS patterns taken as a function of azimuthal angle ϕ at the scattering wave vector q^* corresponding to the peak intensity with the X-ray beam directed along the axis of shear (see Figure 1). Parallel (+) and perpendicular (●) orientations produce two sharp peaks while a mixed alignment (□) results in a combination of four peaks. The fraction of parallel (or perpendicular) alignment was determined on the basis of a linear combination of these peak intensities.

temperature over the course of about 1 h. Representative pieces of the processed material were probed by SAXS at room temperature with the X-ray beam directed along each of the three Cartesian coordinates. (Because the C blocks vitrify prior to E block crystallization, the morphology is preserved in these materials when cooled to room temperature.[10]) Here we report only data from the shear direction (x-axis in Figure 1) since this view provides simultaneous information about the perpendicular and parallel orientations. Details about the SAXS instrument, which is fitted with an area detector, can be found elsewhere.[36] Three representative SAXS results are presented in Figure 3. These data were obtained by averaging the intensity over a narrow band of scattering wavevectors, $q = 4\pi\lambda^{-1}\sin(\theta/2)$, centered on the principal peak value $q^* = 2\pi/d^*$, as a function of the azimuthal angle ϕ, where d^* is the lamellae periodicity; $d^*_{\mathrm{CEC}} = 180$ Å and $d^*_{\mathrm{CECEC}} = 175$ Å. In the limits of complete perpendicular or complete parallel alignment two sharp reflections are obtained rotated from each other by 90°. Mixed levels of alignment produce four peaks. We have quantified the degree of orientation on the basis of a linear weighting of the respective peak intensities.[37]

The results of this study are summarized in Figure 4. Orientation, identified as the fraction of parallel vs perpendicular SAXS intensity, is plotted against strain amplitude for the triblock (Figure 4a) and pentablock (Figure 4b) materials, each processed by *shear from disorder* and *shear from order*. Each data point represents the average of two to six separate experiments with a representative variability in alignment shown by the error bar. These materials exhibit remarkably diverse responses to shear deformation. We first consider the CECEC pentablock behavior.

At relatively large strain amplitudes, $\gamma \geq 2$, the CECEC compound forms essentially perfect perpendicular lamellae (see Figure 1), independent of the initial state of order, consistent with an earlier report.[10] In the small strain limit, $\gamma \leq 0.1$, a nearly perfect parallel arrangement is obtained. The transition between these behaviors is somewhat dependent on the sample history. When sheared from the disordered state, the transition to perpendicular lamellae begins and ends at lower strain amplitudes than with the initially ordered material. We ignore this minor difference in this report. Overall, the pentablock copolymer is characterized by just two limiting dynamical responses.

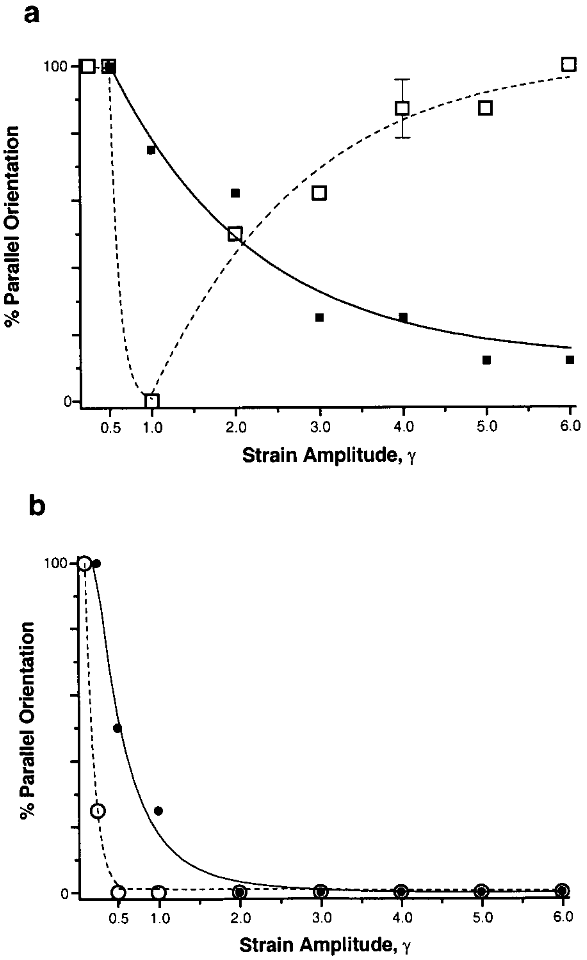

Figure 4. Fraction of perpendicular alignment as a function of strain amplitude. (a) CEC triblock copolymer with *shear from disorder* (□) and *shear from order* (■) processing histories. (b) CECEC pentablock copolymer with *shear from disorder* (○) and *shear from order* (●) processing histories.

We propose that the small strain behavior reflects a mechanism dominated by viscoelastic (or mechanical) contrast.[11,32,38,39] The C and E blocks exhibit very different melt dynamics, evidenced by strikingly different homopolymer entanglement molecular weights, $M_{\mathrm{e,C}} \cong 40M_{\mathrm{e,E}}$.[40] A parallel lamellae orientation, which can support an inhomogeneous strain, minimizes the associated stress during deformation. However, the pentablock architecture, which places some amount of C and E bridging blocks in every domain, creates a severe penalty as the strain amplitude is increased. Nonlinear chain stretching soon dominates the total stress as γ is increased, resulting in a transition to the perpendicular arrangement and a homogeneous distribution of strain throughout the material. We suspect this change is accompanied by a conformational transition that favors an all-bridging arrangement (i.e., the block copolymers extend along the vorticity direction, or z axis, in Figure 1), which would minimize chain stretching in the shear direction. A cooperative molecular alignment of this type, also suggested in an earlier report,[10] could have a profound influence on the mechanical properties of the material, an issue we are currently investigating. Thus, for the CECEC pentablock viscoelastic contrast dominates at small strains, and chain stretching is the controlling factor at large strains.

The alignment characteristics of the CEC triblock copolymer are more complicated. In the limit of small strain amplitudes, $\gamma \leq 0.5$, a purely parallel morphology is again obtained, independent of processing history. This behavior also can be explained on the basis of viscoelastic contrast. Taken together, all four sets of small strain experiments provide strong support for the viscoelastic (mechanical) contrast theory,[32] which does not discriminate among molecular architectures or processing history. Certain reports dealing with diblock copolymers reinforce this conclusion. Notably, Leist et al.[16] conclude that the parallel-to-perpendicular transition (which is followed by a perpendicular-to-parallel transition) occurs at $\gamma\omega$ = constant in PS−PI diblocks, i.e., increasing γ at constant ω (or $\dot{\gamma}$) induces the shift in orientation.

For $\gamma > 0.5$ the CEC response becomes strongly dependent on process history. When sheared from the "polycrystalline" state (i.e., the *shear from order* protocol), the CEC material acquires an increasing degree of perpendicular order as the strain amplitude is increased. By $\gamma = 6$ the material achieves roughly 90% perpendicularity. Entirely different results were obtained with the *shear from disorder* procedure. Increasing the strain amplitude from $\gamma = 0.5$ to 1 produced an abrupt transition from purely parallel to purely perpendicular lamellae, but remarkably, as γ is raised from 1 to 6, the parallel alignment is reestablished. Clearly, the processing history is pivotal in determining the final state of lamellae orientation with triblocks in marked contrast with the pentablock.

Our interpretation of the large strain ($\gamma > 0.5$) triblock results is more speculative than those presented in the previous paragraphs. Apparently, both the parallel and perpendicular orientations are relatively stable to reciprocating shear at $\dot{\gamma} \cong \omega$ and $\gamma = 6$. Otherwise, one or the other would dominate, e.g., as occurs with the pentablock. We cannot be certain of the factors that give rise to this near degeneracy. However, based on the CECEC results, the absence of any bridging C blocks is clearly implicated (see Figure 1). The dangling C blocks in the CEC polymer make sliding within the C domains feasible, thereby supporting an inhomogeneous strain profile, something we already ruled out with the pentablock architecture. In this respect triblocks bear a much closer resemblance to diblocks than to pentablocks (see below).

The strain dependence evident in Figure 4a represents a manifestation of distinctly different responses to large-amplitude shearing of the (initially) polydomain and disordered states. The starting condition for the *shear from order* experiments is an isotropic distribution of lamellae. Shearing produces a complex mixture of micromechanical events. The final state of alignment reflects the response of individual packets of lamellae, initially distributed over all orientations within the specimen, each coupling differently to the stress field. Below a threshold strain viscoelastic contrast sweeps all the lamellae into the parallel form. Above this threshold strain the perpendicular arrangement is increasingly favored, which, by analogy with the pentablock behavior, likely minimizes chain stretching by conformational extension along the vorticity direction.

With the *shear from disorder* protocol a qualitatively different set of results is obtained. We assume that cooling the disordered melt through the ordering transition under the influence of small reciprocating strains favors the perpendicular orientation.[41] Once ordered, subsequent small strain shearing transforms the perpendicular lamellae to the parallel form owing to viscoelastic contrast, as discussed earlier. Apparently, between $\gamma = 0.5$ and 1 the viscoelastic contrast mechanism fails to compete with the initially formed perpendicular orientation; on the basis of the pentablock findings, we attribute this to nonlinear chain stretching.

According to our principal assumption, the formation of more and more parallel lamellae when γ is increased from 0.5 to 6 reflects the state of alignment created as the disordered melt passes through the ordering transition. Why would this result in parallel lamellae? We hypothesize that the disordered chains become elongated and aligned under the combined influence of a large strain and a critical shear rate. Upon ordering, such an extended macromolecular state could enhance the population of looping molecular configurations (see Figure 1), thereby facilitating slip in both microdomains. Related conclusions have been drawn from SANS data acquired from triblock[9] and pentablock[10] copolymers induced to disorder at relatively high rates and strain amplitudes while 30−40 °C below the quiescent T_{ODT}. Parallel and transverse orientations were produced by abruptly stopping the flow from the (shear-induced) disordered state. The PEP−PEE−PEP triblock result,[9] in particular, supports this conjecture. While we cannot be certain about the detailed molecular events responsible for the "reentrant" parallel lamellae behavior, a confluence of shear-induced chain stretching in the disordered state at large strain amplitudes and $\dot{\gamma} \cong \omega$ and near degeneracy in the susceptibility of parallel and perpendicular lamellae at the same conditions seems plausible.

The CEC triblock copolymer results in Figure 4a bear striking similarities to oscillatory shear data acquired from SI diblock copolymer melts[16−20] and solutions.[25] In a series of illuminating articles, Weisner et al. established the importance of strain amplitude[16] and sample history[17] (e.g., annealing time after cooling from the disordered vs strongly segregated state) for producing a prescribed state of orientation. The qualitative similarities between the SI diblocks and CEC triblocks are remarkable, notwithstanding certain quantitative experimental differences. For example, Wiesner et al.[16−20] worked with smaller strain amplitudes ($\gamma < 1$) and never applied shear while cooling from the disordered state. Elegant in-situ SANS experiments by Wang and co-workers[25] on concentrated solutions provide additional insight into the role of sample history and processing conditions on diblock lamellae alignment. Overall, triblocks and diblocks appear to respond to shear in a similar manner in sharp contrast to pentablocks.

This investigation sheds new light on the evolving field of nonlinear block copolymer dynamics. We hope these preliminary findings and tentative interpretations stimulate new ideas, particularly theoretical ones. Ultimately, this knowledge should enhance the properties of block copolymers produced by extrusion, fiber spinning, and molding operations.

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