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Notes

Role of Strain in Controlling Lamellar Orientation during Flow Alignment of Diblock Copolymers

V. K. Gupta, R. Krishnamoorti, and J. A. Kornfield*

Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

S. D. Smith

Procter & Gamble, Cincinnati, Ohio 45239

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Introduction

One means to affect molecular and mesostructural alignment in complex biological and synthetic materials is by using flow fields.[1,2] However, achieving this in a rational and optimal manner necessitates understanding the nature of the strong coupling between applied deformation and the local microstructure. Theoretical explorations of this relation have been restricted to modeling uniformly aligned microstructures.[3,4] The complex dynamics resulting from a distribution of orientations are conspicuously absent from these descriptions. Experimentally, the importance of these dynamics is emphasized by our intriguing results during flow-induced alignment in microphase-separated diblock copolymers.[5,6] In this paper we focus on polymers with lamellar morphology, since certain features of their shear orientation and viscoelastic behavior are common to the broad class of layered systems that spans smectic liquid crystals, surfactant membranes, and layered polymer composites.[1,2,7]

In most block copolymers above an order−disorder transition temperature (T_{ODT}) the material exists in a disordered, homogeneous state. Moving through T_{ODT} in the absence of an applied field leads to local segregation into periodic microstructures (ordered, microphase-separated state) that are randomly oriented. Symmetry-breaking fields such as electric fields and flow fields can induce "single-crystal"-like order on global length scales in these microphase-separated block copolymers.[4,7−9]

When a shear field is applied to diblock copolymers that exhibit a lamellar morphology, three states of global alignment can be envisaged (Figure 1). Only two, with layer normals along the shear gradient direction (parallel) and with layer normals along the vorticity direction (perpendicular), are stable and can be induced using large-amplitude oscillatory shear flows.[9] Intriguingly, these two distinct microstructural arrangements can be achieved by a mere change in shear frequency at the same temperature and strain amplitude.[9,10] The underlying causes and mechanisms of alignment and the selection of one alignment over the other remain largely speculative in spite of more than two decades of theoretical and experimental work.[3,4,7−12]

Much of the previous experimental work on block copolymers has focused on two classes of systems: well-entangled diblock copolymers of polyolefins;[9,10] and diblock copolymers of polystyrene−polydiene (where the diene may be either butadiene or isoprene).[7,8,11,12] It has been shown that in both classes either perpendicular or parallel alignment can be produced by large-amplitude oscillatory shear.[7,9,11,12] To date, only frequency and temperature have been cited as controlling the selection of orientation. It has been found that perpendicular alignment is induced at temperatures near T_{ODT} and below a critical frequency (ω_c') that coincides with the crossover from the dynamic region dominated by the macromolecular response to one controlled by the lamellar mesostructure. In contrast, the frequency regime where parallel alignment is induced is very different for the two systems. In polyolefin diblocks, parallel alignment is found at temperatures and frequencies lower than that for perpendicular alignment, while for polystyrene−polyisoprene (PS−PI) this alignment is induced at correspondingly higher frequencies than those where perpendicular alignment is found.[13]

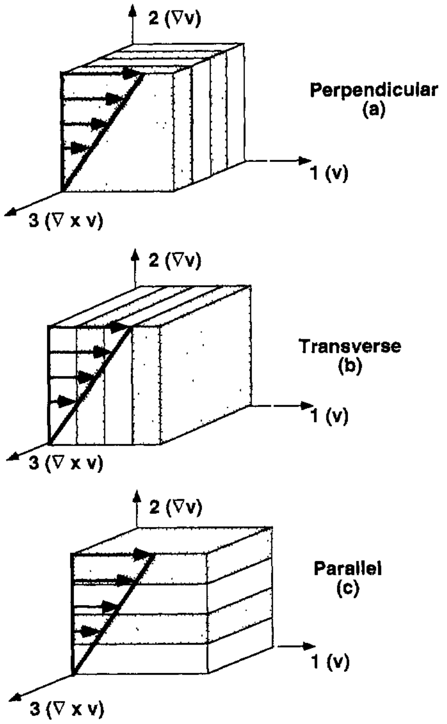

Figure 1. Schematics of the possible lamellar orientations for macroscopically ordered lamellar diblocks. In liquid crystal and surfactant literature these have been generally indicated as (a) perpendicular, (b) transverse, and (c) parallel.

To probe the physics that controls the crossover from parallel to perpendicular alignment, we focus here on frequencies at the boundary between the two regimes.

Experimental Section

In our present study we used a nearly symmetric PS−PI diblock copolymer with $M_{\mathrm{w}} \simeq 20$ kg/mol and $M_{\mathrm{w}}/M_{\mathrm{n}} \leq 1.06$ prepared by anionic synthesis. Rheological determination[5] of the order−disorder transition temperature showed $T_{\mathrm{ODT}} \simeq 164$ °C. All experiments were performed under a nitrogen atmosphere. The mechanical and stress-optical properties of this

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block copolymer were characterized using a rheo-optical apparatus uniquely suited for simultaneous, quantitative measurements of dynamic stress and birefringence.[15]

The anisotropic refractive index tensor $\Delta \mathbf{n}$ of PS–PI is directly related to the orientation distribution of the lamellae, since the form birefringence ($\Delta \mathbf{n}_f$) contribution from the block copolymer microstructure dominates over the intrinsic or "molecular" contribution ($\Delta \mathbf{n}_i$).[16] Rheo-optical experiments are performed using the "shear-sandwich" geometry, with the light propagation along the velocity gradient direction (axis 2), probing the projection of $\Delta \mathbf{n}_f$ on the 1,3-plane, $\Delta \mathbf{n}_{13}$. Due to the flow symmetry, the principal axes of $\Delta \mathbf{n}_{13}$ are along axes 1 and 3, so its anisotropy is completely described by $\Delta n_{13} = n_{11} - n_{33}$. The evolution of the nonoscillatory component of Δn_{13}, *i.e.*, $\Delta n_{13}^{(d)}$, is sensitive to the development of alignment, since it is directly related to the orientation distribution of the lamellar normal ($\hat{\mathbf{u}}$) in the 1,3-plane.

We previously established the distinct trajectories for $\Delta n_{13}^{(d)}$ that correspond to the development of either perpendicular or parallel alignment.[5,6] In PS–PI, the lamellar normal ($\hat{\mathbf{u}}$) of a grain coincides with its optical "fast" axis, *i.e.*, axis of lower refractive index. Therefore, evolution of $\Delta n_{13}^{(d)}$ from a small, near-zero value (from unaligned grains) to a large and positive value indicates perpendicular alignment ($\hat{\mathbf{u}} \parallel 3$). In contrast, $\Delta n_{13}^{(d)}$ moves from a near-zero initial value, through large values, and back to nearly zero when the system evolves from an unaligned condition to the parallel aligned state ($\hat{\mathbf{u}} \parallel 2$).[17]

To establish a reproducible initial condition, the sample was heated well into the disordered phase (180 °C),[19] allowed to equilibrate for 15–20 min, then cooled to the desired temperature in the microphase-separated state, and equilibrated for 15 min. Thus, the initial state was locally ordered into lamellar regions, with the lamellae randomly oriented on macroscopic-length scales. The linear viscoelastic behavior in both the disordered and ordered (but unaligned) states was characterized by storage (G') and loss (G'') moduli measured using small strains. These moduli, along with the frequency shift factors (a_T), were reported earlier, where we also estimated the value $\omega_c' \approx 3-7$ rad/s (at 120 °C) by extrapolating the disordered state data.[5]

Flow alignment experiments were carried out using oscillatory shear ($\gamma = \gamma_o \sin \omega t$) over a range of shear frequencies (ω) and strain amplitudes (γ_o) for temperatures ranging from 100 ($T/T_{\mathrm{ODT}} \approx 0.85$) to 150 °C ($T/T_{\mathrm{ODT}} \approx 0.97$).[5,6] The final state of alignment was characterized by the birefringence (Δn_{13}) and the small-strain dynamic moduli.

Results and Discussion

In agreement with earlier work,[7,11] we found that there were two distinct frequency regimes of alignment: parallel alignment was achieved at high reduced frequencies relative to the critical frequency (*i.e.*, $a_T\omega \geq 10$ rad/s and $\gamma_o \geq 0.6$, $T_o = 120$ °C), while perpendicular alignment was found at lower frequencies ($a_T\omega \leq 1$ rad/s and $\gamma_o \geq 0.45$, $T_o = 120$ °C).[5,6]

Quite surprisingly, we discovered that the *direction* of alignment was very sensitive to strain amplitude for a shear frequency lying in the crossover region between the two regimes. Here we illustrate this phenomenon with results at 120 °C and $\omega = 4$ rad/s. Oscillatory shear at $\gamma_o = 0.4$ resulted in buildup of a large positive birefringence ($\Delta n_{13}^{(d)}$) typical of perpendicular alignment (Figure 2a). The final value of birefringence was $\sim 7.5 \times 10^{-4}$, indicating a high degree of alignment, like that achieved for perpendicular alignment at 1 rad/s.[5,6,20] In contrast, shearing with $\gamma_o = 1.1$ induced parallel alignment, as indicated by the shape of the birefringence trajectory, a near-zero final $\Delta n_{13}^{(d)}$ (Figure 2a), and the dynamic moduli of the aligned material.

Small-strain dynamic moduli G' and G'' of the final aligned states were significantly lower than those of the initial unaligned state (Figure 2b). Furthermore, as expected, the aligned material exhibited a high degree of mechanical anisotropy: the moduli for the perpendicularly aligned sample were greater than those for the parallel aligned sample throughout the measured frequency range. These observations agreed with earlier studies[5,7,11] and supported our assignment of the orientation of distinct aligned states.

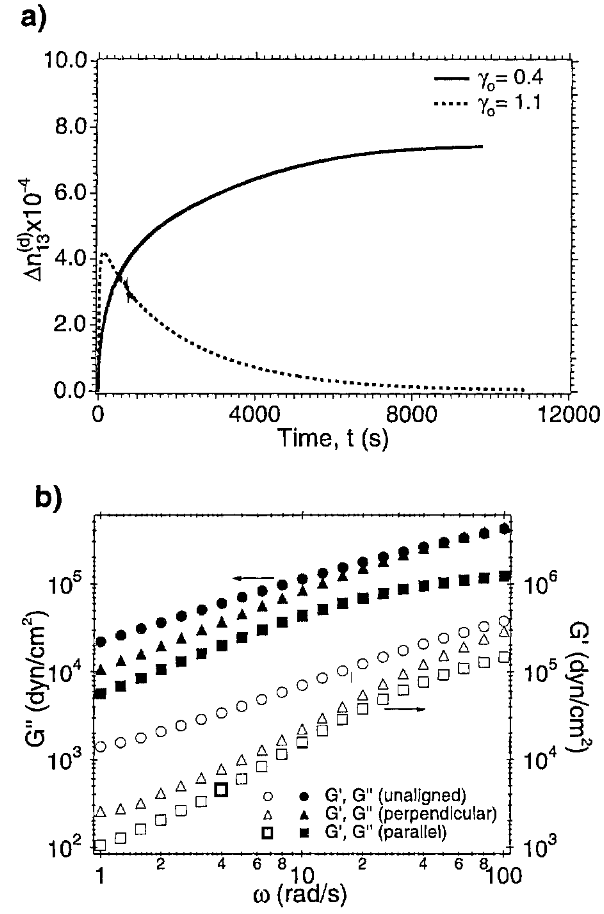

Figure 2. (a) Evolution of the steady offset in 1,3-birefringence during large-amplitude shear alignment at 4 rad/s to parallel aligned state when $\gamma_o = 1.1$ and perpendicular aligned state when $\gamma_o = 0.4$. (b) Dynamic moduli obtained using small-strain oscillatory shear measurement before and after large-amplitude shear at 4 rad/s, $\gamma_o = 1.1$, and $\gamma_o = 0.4$ to characterize effect of macroscopic alignment on relaxation behavior.

From the *in situ* measurements of $\Delta n_{13}^{(d)}$, we can infer changes in the orientational distribution of the sample and, thereby, the microstructure. The initial state prior to large-amplitude shear consists of randomly oriented grains, resulting in a near-zero 1,3-birefringence. We schematically illustrate this by the isotropic sphere (Figure 3a). In our experiments we see the projection of the orientational distribution in the 1,3-plane. Upon application of oscillatory shear at 4 rad/s, the initial rise in $\Delta n_{13}^{(d)}$ for both alignments (Figure 2a) can be explained by a rapid change of the orientational distribution, depleting the projection along the transverse direction ($\hat{\mathbf{u}} \parallel 1$), illustrated[22] by a flattening into the 2,3 plane (Figures 3b,c and f,g).

This initial "fast" process is followed by dramatically different "slower" processes for $\gamma_o = 0.4$ and $\gamma_o = 1.1$ that lead to the different final aligned states (Figure 2a). Shear alignment at $\gamma_o = 0.4$ results in a slow reduction in the projection along the parallel direction

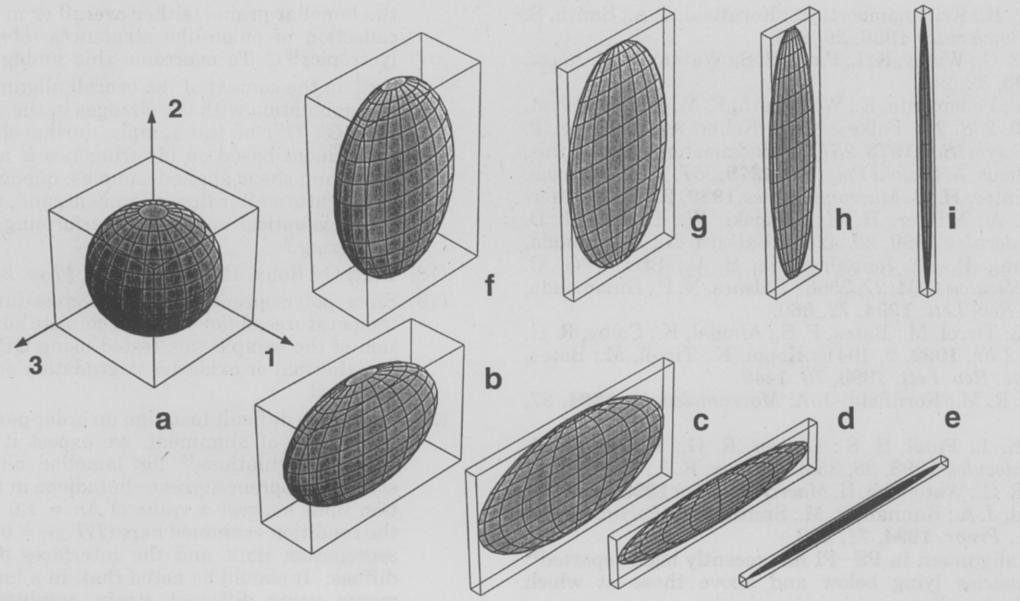

Figure 3. Schematic depiction of the evolution of orientational distribution during parallel and perpendicular alignments. In our experiments, we observe the projection in the 1,3-plane. See text for discussion.

$(\hat{\mathbf{u}} \parallel 2)$ (Figure 3d,e). At this strain amplitude, both the fast and slow processes are accompanied by continuous enhancement in the perpendicular direction, visualized as collapse of the ellipsoids of orientation onto axis 3 (Figure 3e), consistent with a large positive value of the final birefringence.

In contrast, based on the observed evolution of $\Delta n_{13}^{(d)}$ at $\gamma_o = 1.1$ (Figure 2a), the later, slower process results in a decrease in the projection of the orientational distribution along the perpendicular direction ($\hat{\mathbf{u}} \parallel 3$) (Figure 3h,i). The enhancement of the grains biased along the parallel direction is visualized as a collapse of the ellipsoid onto axis 2 (Figure 3i). This results in a final value of the birefringence $\Delta n_{13}^{(d)} \approx 0$, which along with the dramatically lower small-strain moduli for the aligned state, suggests parallel alignment.[5,6,17]

Thus, we find that strain amplitude plays a critical role during flow alignment, not merely influencing the rate or degree of alignment,[6] but even selecting the *direction* of alignment.

The effects of strain amplitude are extremely valuable in discriminating between the simple concepts put forth in the literature to explain alignment. For example, perpendicular alignment has been attributed to lamellar fluctuations, which lead to selective layer melting.[3,9] However, at a fixed ω and T, obtaining perpendicular alignment at low γ_o and parallel alignment at high γ_o shows that the former orientation cannot be attributed solely to selective layer melting, since the propensity to disorder is greater at higher strain amplitudes. For parallel alignment there is no proposed mechanism in the high-frequency regime, only the vague notion that it results from viscoelastic contrast between the lamellae.[10,21] In addition to proposing mechanisms of alignment, several investigators have hypothesized about parameters that control the selection between parallel and perpendicular orientations. Our results[5,6] demonstrate that minimization of modulus is not a necessary criterion:[21] *e.g.*, parallel alignment has a lower modulus at $T = 120$ °C and 4 rad/s during shear and after alignment. Alignment in block copolymers is also not simply controlled by either the shear rate, the cumulative strain, or the flow energy,[5,6]

We believe that the complex kinematics occurring in a polydomain microstructure must be understood in order to capture the crossover between orientations: more specific models of the dynamics of alignment must be proposed in order to determine how one mechanism (*e.g.*, one that may depend on viscoelastic contrast) might overtake another one (*e.g.*, one that may depend on lamellar fluctuations) with a modest increase of strain. The control of the final state of alignment by strain, apart from providing another valuable means to manipulate structure to induce coherent macroscopic order, forces us to reexamine the role of dynamical processes in affecting the direction of alignment. The dynamics of alignment can be clarified only by monitoring the trajectory of alignment, and therefore, it is imperative to perform *in situ* and *real-time* experiments to guide and verify future models.

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(13) Parallel alignment in PS−PI has recently been reported[14] at frequencies lying below and above those at which perpendicular alignment is induced.

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(17) A near-zero birefringence can correspond to many possible states: *e.g.*, parallel alignment, an isotropic distribution of the lamellar grains (either overall or in the 1,3-plane) or a collection of onion-like structures (observed in lamellar lyotropics[18]). To overcome this ambiguity, we interpret $\Delta n_{13}^{(d)}$ in the context of the overall alignment trajectory and in combination with the changes in the mechanical properties (G', G'') of the sample during shear. In addition, assignment based on birefringence is also corrobrated by preparing shear aligned samples, quenching them to room temperature after flow alignment, and, upon removal from the rheo-optical apparatus, performing small-angle X-ray scattering.[6]

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(19) Since polyisoprene is prone to cross-linking at such high temperatures, following our complete suite of experimentation of the sample was tested using GPC. No evidence of any thermal or oxidative degradation or cross-linking was observed.

(20) While it is difficult to assign an order parameter to describe the degree of alignment, we expect it to be quite high. Recent calculations[16] for lamellar block copolymers of styrene−isoprene/styrene−butadiene in the strong-segregation limit suggest a value of $\Delta n \simeq 1.6 \times 10^{-3}$. However, the condition examined here ($T/T_{\mathrm{ODT}} \simeq 0.89$) is in the weak-segregation limit and the interfaces are expected to be diffuse. It should be noted that, in a large suite of experiments using different strain amplitudes[5] and reduced frequencies, the largest final birefringence we have observed for the perpendicular state is 1.0×10^{-3}.

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(22) These ellipsoids are schematic and are not intended to advocate a particular shape of the orientation distribution; rather, they illustrate which projections disappear at which relative rates.

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