

Frequency Dependence of Orientation in Dynamically Sheared Diblock Copolymers

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Introduction. The investigation of pattern formation in soft-matter physics has become a subject of increasing research interest in recent years.¹⁻⁵ Among various other materials block copolymers have proven to be particularly interesting, showing a surprising variety of periodically ordered equilibrium structures that can be strongly influenced by external mechanical fields.^{6,7}

Keller et al.⁸ were probably the first to successfully use flow fields in order to change the structure and induce long-range order in block copolymers. Numerous studies of the effect of unidirectional or oscillatory shear on cylindrical and lamellar-ordered phases have since elucidated conditions for producing single crystal type morphologies.⁹⁻¹⁵ Moreover, Albalak et al. have recently discovered a novel casting method they termed "roll-casting" to produce oriented block copolymer samples using solutions subjected to hydrodynamic flow.¹⁶ Nevertheless, the underlying mechanisms for flow alignment are not yet fully understood. This hampers the control of the lamellae orientation in the experiments. Koppi et al. discovered that depending on temperature and shear frequency two distinct lamellae orientations could be produced for a symmetric block copolymer poly(ethylenepropylene)-poly(ethylene) which has been termed PEP-PEE-2 in their nomenclature.¹⁷ Above a specific frequency and near the order-disorder transition temperature (T_{ODT}), large-amplitude oscillatory shear resulted in a perpendicular orientation, with the unit normal of the lamellae perpendicular to both the flow and velocity gradient directions. At lower frequencies or $T \ll T_{ODT}$ they observed a parallel orientation, usually found in these systems with the unit normal parallel to the velocity gradient direction. In their paper the authors related the different orientational behavior to two different dynamical regimes obtained from shear viscosity measurements of their block copolymer.

More recently perpendicular alignment has also been observed in a polystyrene-polyisoprene block copolymer (termed PS-PI 12/9) at temperatures close to T_{ODT} .¹⁸ In contrast to PEP-PEE-2 a regime of parallel alignment for this polymer has been found at higher frequencies than those producing perpendicular alignment.¹⁹ However, no attempt has been made for this polymer system to relate the orientational behavior to the shear viscosity of the sample. As already pointed out by Kannan et al.,²⁰ all these results together suggest that, although never observed in a single block copolymer sample, at least three frequency regimes exist, leading to different orientation behavior under shear flow.

In the present work we have indeed identified three frequency regimes for the orientational behavior related to the dynamic shear viscosity of a lamellar PS-PI diblock copolymer of low molecular weight at temperatures close to T_{ODT} . Using two-dimensional SAXS measurements, we show that large-amplitude oscillatory

shear in these frequency regimes leads to parallel, perpendicular, and parallel orientation, respectively. These observations support the idea that the "double flipping" of the alignment direction is dictated by a change in the time scale of the flow with respect to the characteristic time scale of the block copolymer dynamics.^{17,20} The present results suggest that there exists a common behavior of lamellar diblock copolymers subjected to oscillatory shear flow, allowing control of the orientational behavior based on shear viscosity measurements.

Experimental Section. The lamellar poly(styrene-*b*-isoprene) diblock copolymer termed PS-PI-3 in our nomenclature has been synthesized by anionic polymerization using cyclohexane as solvent and *sec*-butyllithium as initiator. The PS and PI block molecular weights are 8600 and 11 500 respectively, as determined by GPC for the PS precursor and ¹³C NMR for the PI block. The dispersity M_w/M_n as determined by GPC for the block copolymer is 1.06. All GPC's were performed using polystyrene as standards. The uncertainties in the molecular weight determination are about 5% for both techniques. The T_g 's for the PS and PI blocks as determined by DSC with a heating rate of 10 K/min are 335 and 215 K, respectively. Comparing these values with those usually found for PS (378 K) and PI (213 K) homopolymers of sufficiently high molecular weight, it follows that for the block copolymer especially the PS blocks suffer from a depression of T_g as a result of the low molecular weight and a plasticizing effect by the PI chains. It is important to notice at this point that the thermodynamics and consequently the dynamics of PS-PI block copolymers are extremely sensitive to changes in the molecular weight as evidenced, e.g., by NMR measurements on this and related systems.²¹⁻²³ T_{ODT} as determined by the temperature dependence of the storage modulus $G'(T)$ ^{24,25} at $\omega = 10$ rad/s is 404 ± 1 K. In all samples 2,6-di-*tert*-butyl-4-methylphenol was used as an antioxidant. More details about the block copolymer synthesis and characterization will be given in a further publication.

Samples were pressed at room temperature into disks with diameters of 25 mm and thicknesses of 1 mm and then annealed at 358 K under vacuum for more than 1 day. A Rheometrics mechanical spectrometer Model 800 (RMS-800) was used in parallel-plate geometry for the large-amplitude (100% strain) oscillatory shear experiments on these sample disks at different frequencies and temperatures as well as for the dynamic mechanical measurements on the oriented samples.

SAXS experiments were performed on specimens cut from shear-oriented sheets. A Rigaku Rotaflex X-ray source at 0.154 nm (Cu K α) was employed. A three-pinhole collimator was used to generate a beam with a diameter of 1 mm. Scattering patterns were recorded on a two-dimensional Siemens X-1000 area detector with a sample-to-detector distance of 130 cm. Three scattering experiments were performed for each shearing condition, corresponding to three orthogonal directions with respect to the deformation geometry as illustrated in the Figures.

Results and Discussion. In order to obtain a dynamic fingerprint of the block copolymer PS-PI-3, we have investigated its rheological behavior using parallel-plate geometry. In Figure 1 the results of the frequency dependence of the dynamic shear viscosity η are shown measured at 383 and 393 K, respectively, which is close to T_{ODT} of the sample at 404 K. Prior to these experi-

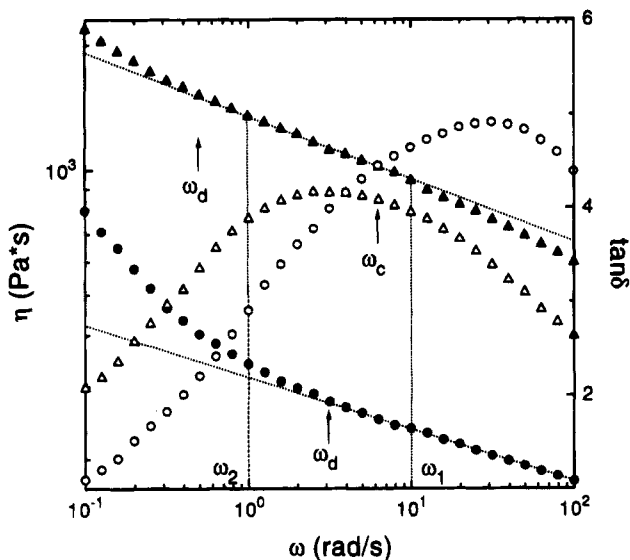


Figure 1. Dynamic shear viscosity $\eta = G''/\omega$ (filled symbols) and $\tan \delta = G''/G'$ (open symbols) of a parallel oriented sample PS-PI-3 for two different temperatures, 383 K ($\blacktriangle, \triangle$) and 393 K (\bullet, \circ), using dynamic mechanical measurements at 1 and 2% strain, respectively, in parallel-plate geometry. The frequencies used in the large oscillatory shear experiments to orient the different samples as discussed in the text are indicated as vertical, dotted lines.

ments revolutions were imposed on the material, producing parallel orientation which was confirmed by two-dimensional SAXS measurements as described below. In agreement with the results of Koppi et al.¹⁷ for PEP-PEE-2, the curve for 383 K indicates the existence of three distinct frequency regimes: a central regime of relatively moderate slope and two regimes of larger slopes at higher and lower frequencies, the onsets of which can be observed in our measurements. The curve corresponding to 393 K is dominated by the central and the onset of the lowest regime, due to the limited frequency range studied. According to the analysis of the above authors and Kannan et al.,²⁰ we identify two critical frequencies ω_d and ω_c as the lower and upper frequency bounds of the central regime, respectively (see Figure 1). The agreement between this method and the determination of ω_c using a master plot for the dynamic shear modulus has been checked, and results will be presented in a further publication. Above ω_c , relaxation processes intrinsic to the unstructured polymer melt dominate the rheological properties. The central regime ($\omega_d \leq \omega \leq \omega_c$) mainly reflects the mechanical responses due to the microphase-separated structure,^{24,26–29} while it was suggested that integrated motion of supermolecular lamellar structures dominates the rheological properties below ω_d .^{17,20} In addition to the dynamic shear viscosities, the corresponding results for $\tan \delta = G''/G'$ have also been included in Figure 1. For both temperatures these curves show maxima at frequencies within the central frequency regime of the shear viscosity described above.

On the basis of the frequency dependence of the dynamic shear viscosity, different conditions (more than 10 in total) were chosen within the three frequency regimes to orient the block copolymer PS-PI-3 using large-amplitude oscillatory shear. In the following three representative cases are discussed. The first two samples were sheared at 383 K which is about 20 K below T_{ODT} for 5 h at $\omega_1 = 10$ rad/s and 11.5 h at $\omega_2 = 1$ rad/s, respectively. These frequencies are indicated as vertical lines in Figure 1 and fall in the upper two regimes

observed for the shear viscosity at this temperature. The resulting morphologies as revealed by 2D SAXS measurements are shown in Figure 2. Two different orientations were obtained under these conditions. The sample sheared at higher frequency, $\omega_1 = 10$ rad/s, shows strong scattering peaks along q_{nor} both in the $q_{nor}-q_{tan}$ and $q_{nor}-q_{rad}$ plane, while the scattering in the $q_{rad}-q_{tan}$ plane is rather small (Figure 2a). This clearly indicates that the unit normal of the lamellar microstructure is preferentially oriented parallel to the velocity gradient direction (q_{nor}) of the flow, as schematically indicated on the right-hand side of Figure 2a. In analogy to earlier findings, we refer to this morphology as “parallel” orientation.^{17,18}

Shearing at lower frequency, $\omega_2 = 1$ rad/s, produced a distinctly different result as shown in Figure 2b. Here the SAXS peaks are along the q_{rad} direction in both the $q_{nor}-q_{rad}$ and $q_{rad}-q_{tan}$ planes, while the scattering in the $q_{nor}-q_{tan}$ plane is rather small. This shows that the normal unit of the lamellar microstructure is aligned preferentially in the radial direction (q_{rad}) of the sample disk as schematically indicated on the right-hand side of Figure 2b. This direction is perpendicular to both the flow and the velocity gradient directions. According to the literature we refer to this morphology as “perpendicular” orientation.^{17,19}

A third sample was sheared at a slightly higher temperature, 393 K, which is closer to T_{ODT} of the block copolymer for 7.5 h at $\omega_2 = 1$ rad/s. Because of the higher temperature, this corresponds to a lower effective frequency than in the above two cases falling in the lowest frequency regime below ω_d found for the shear viscosity at this temperature. The SAXS results in Figure 2c are similar to those found for the sample sheared at the highest effective frequency ω_1 at 383 K. Therefore, as indicated on the right-hand side of Figure 2c at the lowest effective frequency described in the present study again the parallel orientation of the lamellar microstructure was found.

As discussed in the beginning of this paragraph, the presented data are representative for the orientation behavior found for the three frequency regimes in various large oscillatory shear experiments. For instance, a sample sheared at 393 K at $\omega = 7$ rad/s which falls well into the central frequency regime of the dynamic shear viscosity at this temperature as shown in Figure 1 exhibits perpendicular orientation (not shown here). Furthermore, samples that were sheared at temperatures much lower than those discussed here (e.g., 358 K) at frequencies of typically 1–10 rad/s all showed parallel orientation behavior as expected for the upper frequency regime. A full account of these results in terms of a master plot for the dynamic shear modulus is presented in a subsequent publication.

Before turning to the discussion of these results, we would like to mention several additional features in the SAXS data that should be noted. First, in all cases the resulting orientation of the lamellae is substantial but not perfect as indicated by the residual peak intensities in the $q_{rad}-q_{tan}$ plane for the parallel alignment and in the $q_{nor}-q_{tan}$ plane for the perpendicular alignment. Second, the strong reflections depicted in Figure 2 are partly asymmetric and are unequal in peak width and integrated intensity. Inhomogeneities in the shearing field resulting from the parallel-plane geometry, and sample deformation during cutting and mounting along with slight misalignments in the X-ray beam, could be responsible for these differences. As pointed out by

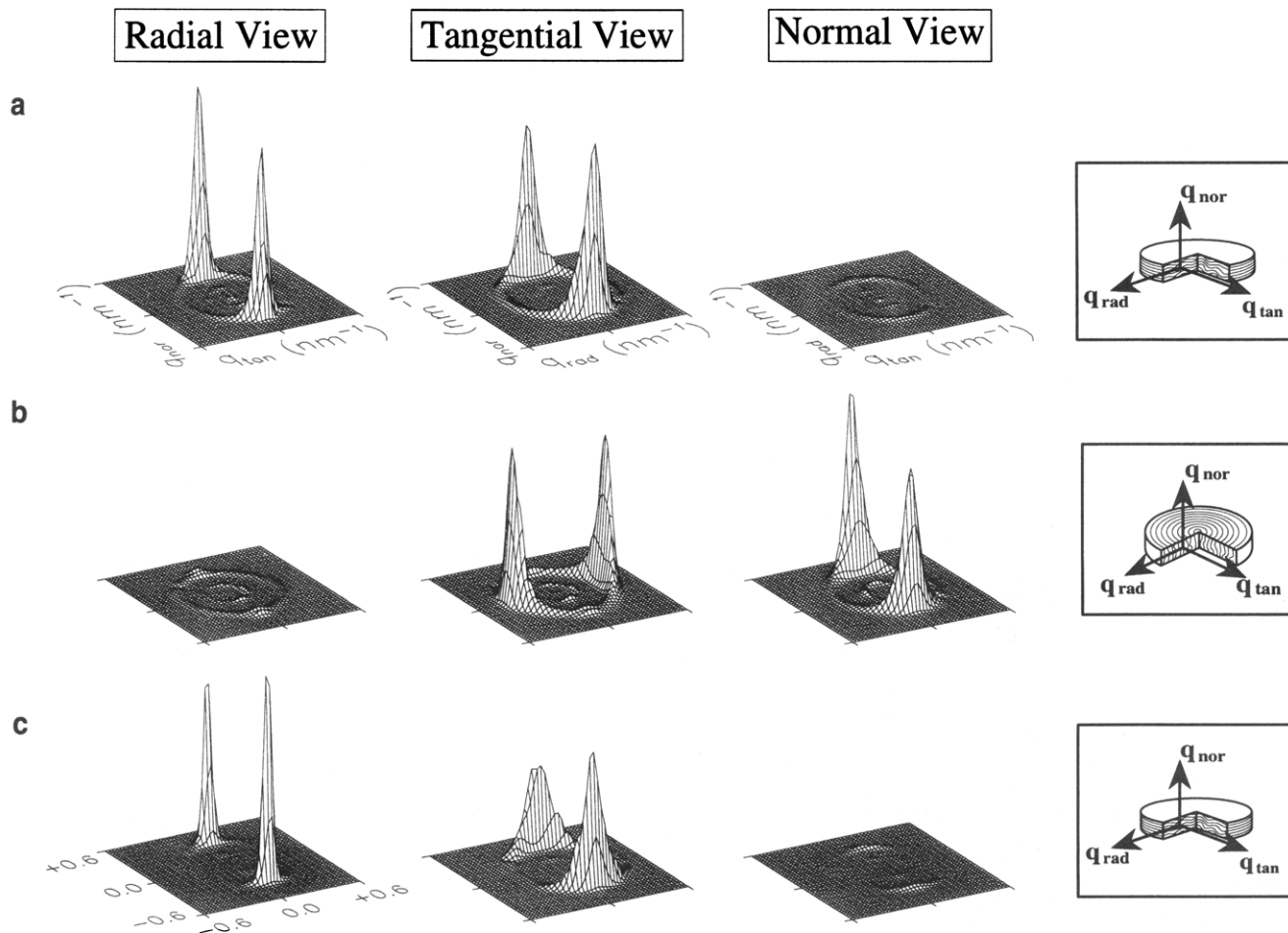


Figure 2. Two-dimensional SAXS results for PS-PI-3 following large oscillatory shearing (100% strain). Specimens were cut at half radius which corresponds to 50% strain. (a) $T = 383$ K and $\omega_1 = 10$ rad/s for 5 h; (b) $T = 383$ K and $\omega_2 = 1$ rad/s for 11.5 h; (c) $T = 393$ K and $\omega_2 = 1$ rad/s for 7.5 h. In the insets on the right-hand side, the resulting orientations are schematically depicted together with the used coordinate frame and including possible undulations in the lamellae as discussed in the text.

Almdal et al.¹⁵ an alternative cause may be small-amplitude undulations (ripples) in the lamellae. Such structural features are schematically indicated in the insets of Figure 2.

Our experiments show that the orientation of the lamellar microstructure of PS-PI-3 developing under large oscillatory shear strongly depends on frequency and temperature. Clearly for the three experiments described above the employed shear frequencies fall in different regimes of the dynamic shear viscosity. Thus we suggest that this change in the time scale of flow with respect to the characteristic time scale of the diblock copolymer dynamics provides the explanation for the different ordering behavior observed.

At 383 K the shear frequency ω_1 is higher than ω_c . At this frequency the dominating factor for orientation is the large viscoelastic contrast between the two blocks. The crucial point is the difference between the measurement temperature T and the T_g 's of the PS and PI blocks. Since T is only about 50 K above T_g of the PS blocks, residual density fluctuations within the glass transition region in the PS blocks restricting chain mobility will be present,^{30,31} while these fluctuations in the PI blocks are completely relaxed because T is about 170 K above their T_g . Under shear flow, the lamellar structure is expected to move as integrated plates due to these surplus density fluctuations in the PS blocks. Pictorially this behavior may be imagined as hard plates in a liquid. The parallel orientation is therefore naturally the most stable one for the lamellar structure

under oscillatory shear flow at frequency ω_1 .

At 393 K the shear frequency ω_2 is lower than ω_d (see Figure 1). In this frequency regime all local correlations of motion in both blocks have time to completely relax. Now the structural element that supports the stress is the interfacial region. Under shear flow, the lamellar structure again moves as integrated plates due to the motional correlations in this interface which exist due to the thermodynamic driving forces that restore the interface below T_{ODT} (χ driven phase separation or interface tension).^{17,18} Thus integrated motions of phase-separated structural elements under shear flow provide a reasonable explanation for the parallel orientation observed in the highest and lowest frequency regimes.

At 383 K the frequency ω_2 is in the central regime ($\omega_d \leq \omega_2 \leq \omega_c$) found for the dynamic shear viscosity (Figure 1). It is expected that in this regime the interface of the lamellar structure is still the main structural element supporting the shear stress. But the response of the block copolymer system to shear is dominated by viscous rather than elastic behavior, as revealed by the peak in $\tan \delta$ observed for this regime; see Figure 1. Therefore, in agreement with earlier work¹⁷ we suggest that large amplitude oscillatory shear flow leads to a destruction of the supermolecular structure rather than to integrated motions of phase-separated structural elements. Thus, as outlined by these authors, the original lamellar structure is probably destroyed and then reorganized into the most

stable structure under shear flow, the perpendicular orientation.

Conclusions. The frequency dependence of the dynamic shear viscosity together with the results of large amplitude oscillatory shear on a lamellar PS-PI diblock copolymer indicate three frequency regimes in which different mechanisms are suggested to dominate the orientational behavior of the phase-separated lamellar structure. In the high-frequency regime viscoelastic contrast between the PS and PI blocks is predominant. At intermediate frequencies lamellar interface destruction and reorganization occurs. At low frequencies the interface reorients as a whole. Thus, the orientational behavior can be controlled on the basis of the frequency dependence of the shear viscosity. These findings together with results published by other groups on different diblock copolymer systems suggest that there exists a common behavior of lamellar diblock copolymers subjected to oscillatory shear flow. Further theoretical and experimental studies are now in progress in our laboratory to confirm these ideas.

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