Shear Instability of a Gyroid Diblock Copolymer

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ABSTRACT: The stability of the gyroid phase of diblock copolymers has been studied using combined oscillatory shear and small-angle neutron scattering (SANS) techniques. It is shown that the gyroid phase of polystyrene−polyisoprene (PS−PI) is unstable when exposed to combined large-amplitude and high-frequency shear deformations. The bicontinuous cubic gyroid structure (G) transforms to the hexagonally cylinder phase (HEX). The transition is perfectly reversible, but with a significant difference in time constants. Upon application of shear the G → HEX transition is instantaneous within experimental resolution, while the HEX → G relaxation after cessation of shear takes hours. The texture of the shear-induced cylinder phase is shown to be a near ideal monodomain, while the relaxed gyroid phase constitutes a two-dimensional powder with the characteristic 10-spot scattering pattern. The shear-induced destabilization is discussed in relation to analogous observations on shear-induced order-to-order and disorder-to-order transitions observed in related block copolymer systems and in microemulsions. It is discussed whether these phenomena originate in shear-reduced fluctuations or shear-induced dislocations.

1. Introduction

It is well established that block copolymers form a variety of nanoscale ordered structures depending on temperature and copolymer composition. However, the stability of these phases upon exposure to external or internal fields like flow, thermal gradients, confinements, and chemical reactions is still a matter of debate and continued investigation. The stability issue is important in relation to materials design, fabrication, and applications.

Quite generally, soft materials show significant dependence on shear. Changes in morphologies and phase stability often occur as a consequence of the subtle balance between intermolecular forces resulting in low barrier for developing large amounts of dislocations and high sensitivity to thermal fluctuations.

In polymeric fluids flow fields can have a major influence on the degree of miscibility[1,2] by inducing phase transitions[3,4] via the formation of shear bands[5] or changes of texture.[5,6] In surfactant systems both shear-thinning and shear-thickening are phenomena with structural origin. For the ordered states of self-assembled block copolymer melts and micellar systems the effect of moderate shear is first of all to stabilize the ordered phase in a state with reduced texture. But also, shear-induced phase transitions are observed. Disordering as a result of flow mediated dislocations have been observed in both copolymer melts[4,7] and in colloidal and micellar systems.[8,9] Other studies have shown shear-induced ordering as a result of coupling to fluctuations.[3,10] For sufficiently high shear rates the polymer system becomes more mean-field-like, and the ODT temperature increases accordingly.[11,12]

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The equilibrium phase behavior of diblock copolymers is documented both experimentally and theoretically. Experimentally, the phase behavior has been determined using both imaging and scattering techniques.[13] Theoretically, self-consistent mean-field theory[14,15] has proven to be successful in determining the relative free energies and thereby accounting for the stability of the various morphologies observed experimentally. The equilibrium phases are the disordered mixed phase (DIS) and four ordered phases: body-centered-cubic arrangement of spheres (BCC), hexagonally ordered cylinders (HEX), bicontinuous gyroid phase with cubic $Ia\bar{3}d$ symmetry (G), and lamellae (LAM). Both experiments and theory have shown that the fifth ordered phase, the modulated lamellae phase (ML), is not a thermodynamic stable phase.[15−18]

The stability regime of the gyroid phase is sensitive to molecular parameters. Experimentally, it seems that this bicontinuous phase constitutes the largest regions in phase diagram for low-molar-mass copolymers.[19] This is in accordance with calculations where fluctuations are incorporated using the Landau−Brazovskii theory. Hamley and Podneks found that fluctuations markedly stabilize the gyroid phase.[20] However, model calculations with shear-induced dislocations conclude on destabilization of the gyroid phase with preference of either the lamellae or the hexagonal phases.[21] It is therefore tempting experimentally to probe the stability of the gyroid phase under the influence of external shear.

The present study concerns combined structural measurements and rheological studies during large-amplitude oscillatory shear (LAOS) on the gyroid phase of a PS−PI diblock copolymer using small-angle neutron

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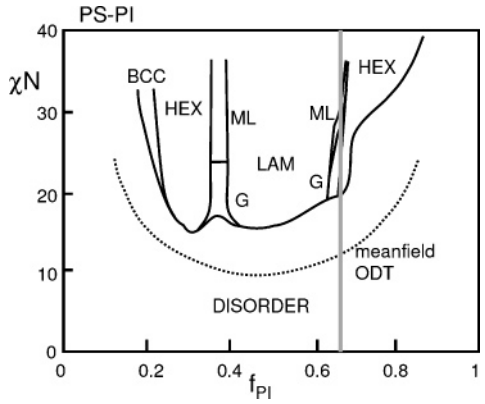

Figure 1. Phases of PS−PI diblock copolymers.[24] The $f = 0.67$ sample used for the present study is highlighted by the solid gray line.

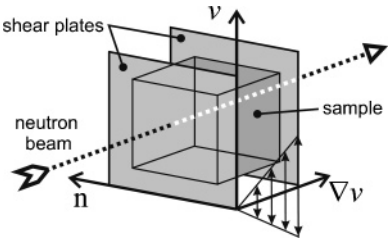

Figure 2. Schematic diagram of the flow geometry and the scattering setup used for in-situ rheology−SANS measurements.

scattering (SANS). A related study on flow-induced properties of (styrene−butadiene−styrene) triblock copolymers was recently reported by Sakurai et al.[22] Our studies support the speculations of Sakurai et al. with more conclusive and extended data.

2. Experimental Section

2.1. Sample. The polystyrene−polyisoprene (PS−PI) diblock copolymer (SI-29) was synthesized by high-vacuum anionic polymerization at University of California at Berkeley. The volume fraction of polyisoprene is $f_{PI} = 0.67$. The molecular weights of respectively the polyisoprene and the polystyrene blocks are $M_{w,PI} = 1.86 \times 10^4$ g/mol and $M_{w,PS} = 1.1 \times 10^4$ g/mol, with polydispersities less than 1.05. The sample used in this study is the PS−PI diblock copolymer mixed with the neutral 5% dioctyl teraphthalate (DOP) additive. The DOP was introduced to reduce the transition temperatures. With increasing temperature, this sample shows the following phase sequence: lamellae (LAM), (metastable) modulated lamellae (ML), gyroid (G), hexagonally arranged cylinders (HEX), and disorder (DIS) as verified by X-ray scattering and birefringence measurements.[23] The phase sequence is in perfect agreement with the previously reported diagram of PS−PI diblock copolymers,[24] which is redrawn in Figure 1 highlighting the sample composition used in the present study. By ML we refer to the metastable structure, which also is associated with other names: e.g., "hexagonally perforated lamellae" (HPL), "hexagonally modulated lamellae" (HML), or "perforated lamellae" (PL).

2.2. Rheo-SANS. The oscillatory shear experiments were performed using a Rheometrics RSA-II rheometer with a shear sandwich fixture and modified to accommodate in situ SANS measurements. The neutron experiments were performed at the SANS-II instrument located at SINQ, Paul Scherrer Institute, Villingen, Switzerland, using 6.0 Å neutrons with 9% wavelength resolution and 3 m sample-to-detector distance. The position of the shear cell with respect to the neutron beam is illustrated in Figure 2. The two-dimensional SANS patterns are correspondingly acquired in the (q_v,q_n) plane, q being the scattering vector and index v and n represent the flow (velocity) and neutral (vorticity) directions, respectively.

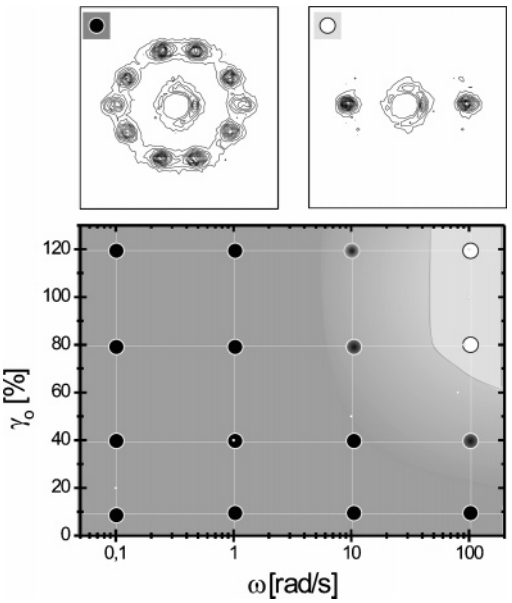

Figure 3. Shear diagram of PS−PI diblock copolymer, showing the stability of respectively gyroid cubic structure (10-spot pattern as given by the example in the upper left figure) and hexagonal cylinder phase (two-spot pattern as given by the example in the upper right figure). The 95% SI-29/DOP sample was in the fully oriented gyroid phase at 120 °C subjected to oscillatory shear at different settings of shear amplitude (γ_0) and frequency (ω). The dots indicate conditions where measurements were made. Typically either amplitude or frequency was kept constant, while the other was increased in a stepwise fashion. The solid circles outline shear settings, where the 10-spot (gyroid) scattering pattern is stable against shear. The open circles mark shear settings where the scattering transform into hexagonal structure with two equatorial peaks.

The experiments reported in this paper were performed at a constant sample temperature (120 °C), at which the sample is in the gyroid phase. Prior to the detailed experiments questioning the stability of the gyroid structure, the sample was subjected to oscillatory shear at an amplitude of $\gamma_o = 120\%$ and a frequency of $\omega = 100$ rad/s, followed by relaxation at quiescent conditions for at least 1 h. This procedure resulted in a highly resolved 10-spot SANS pattern, which is the well-established characteristic signature of a shear-aligned gyroid phase.[17] The data presented in this report were recorded using the same sample for all measurements. The high degree of reproducibility verified that degradation during the temperature and shear cycles play no significant role. The shear experiments were all performed with the same starting condition of a well-developed gyroid phase, which shows a clear 10-spot scattering pattern. At experiments involving continued shearing we interpret steady shear conditions to be obtained when we read constant values for the storage and loss moduli, as measured by the online rheometer.

Anisotropic scattering indicates high degrees of alignment of the sample. We used a custom-built goniometer to analyze the scattering of such a well-aligned sample. The goniometer—described elsewhere[25]—is made to hold the shear cells of the Rheometrics RSA-II rheometer. A similar goniometer, constructed for small-angle X-ray scattering, has recently been reported by others.[26]

3. Results

We have performed a series of well-controlled shear experiments on a prealigned polystyrene−polyisoprene diblock copolymer in its stable gyroid state. The general results of our study are pictured in the shear diagram in Figure 3, which illustrates the response of the sample

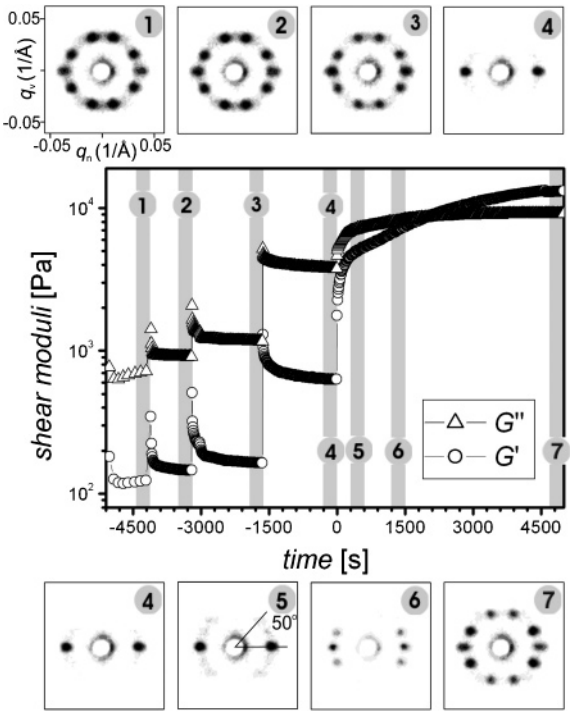

Figure 4. Simultaneous SANS and dynamic moduli (G' and G'') measurements of a PS−PI diblock copolymer, showing the characteristics of the G → HEX shear-induced transition and HEX → G relaxation after cessation of shear. The 95% SI-29/DOP sample is at $T = 120$ °C subjected to oscillatory shear with shear-amplitude $\gamma_0 = 120\%$ and with step increases in frequency: (1) $\omega = 0.1$ rad/s, (2) $\omega = 1$ rad/s, (3) $\omega = 10$ rad/s, (4) $\omega = 100$ rad/s. At time $t = 0$ s the shear conditions are changed to $\gamma_0 = 0.1\%$ and $\omega = 100$ rad/s, and the sample relaxes back to its original state.

as a function of the degree of shearing in terms of the applied shear frequency (ω) and the strain amplitude (γ_0). The mesh of points in the diagram indicates the systematic study of different shear frequencies and amplitudes subjected to the sample. At each experimental set of conditions the shearing was continued until achieving steady-state conditions.

The result of the shear analysis is very clear. All shear experiments were started with the sample in a prealigned gyroid state having a 10-spot scattering pattern.[17] For shear conditions where this 10-spot scattering pattern prevails, the shear diagram is marked by a solid circle. We see that the structure of the sample changes at high values of the maximum shear amplitude ($\gamma_0 = 80$ and 120%) and at the highest applicable shear frequency ($\omega = 100$ rad/s). These conditions are marked by open circles in the figure, and these strong shear fields transform the scattering from the sample into two equatorial spots.

Before we analyze the relaxation that follows an abrupt cessation of shear and the shear-controlled two-spot scattering itself, let us examine the details of one structural evolution en route to the sheared structure characterized by the two-spot scattering.

3.1. Shear-Controlled Structural Transition. Simultaneously acquired data from SANS and the dynamic moduli as measured by the on-line rheometer are illustrated in Figure 4. The data show the rheological response of the sample as it is subjected to oscillatory shear of increasing frequency over four steps from $\omega = 0.1$ rad/s to $\omega = 100$ rad/s while keeping the shear amplitude constant at $\gamma_0 = 120\%$. Two-dimensional

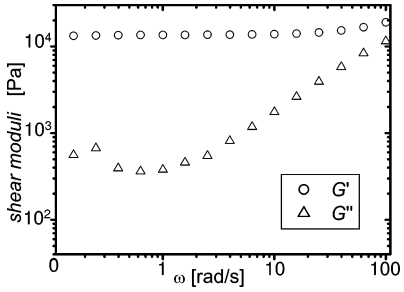

Figure 5. Dynamic moduli measurements of 95% SI-29/DOP with an oscillatory shear of 1% over the 0.1−100 rad/s frequency range at 120 °C. Storage modulus is almost constant and greater than the loss modulus ($G' > G''$) over the entire frequency range.

scattering patterns were collected every 300 s during the experiment. Gray bars on the figure show the sampling periods of the SANS data representing the steady-state scattering patterns for each step. Insets 1−3 in the figure show that the gyroid phase is intact in the frequency range $\omega = 0.1$−10 rad/s. However, the off-equatorial reflections in inset 3 are slightly reduced in intensity. A drastic change in the scattering signal is seen when the frequency was increased to $\omega = 100$ rad/s. Inset 4 shows the scattering, which has changed to a two-spot pattern. The transition is almost instantaneous and can be observed already in the first SANS data after the final increase of frequency within few seconds (not illustrated).

The loss modulus G'' is almost a decade greater in magnitude than the elastic shear modulus G' at all test conditions leading to the shear-induced two-spot scattering. The shear amplitude ($\gamma_0 = 120\%$) is far beyond the limit for linear viscoelastic behavior for this sample. The linear dynamic mechanical response ($\gamma_0 = 1\%$) of the sample at 120 °C is shown in Figure 5. The dynamic moduli exhibit a typical response from a solidlike sample ($G' > G''$), which is in agreement with the cubic gyroid phase. We conclude that the strong shear field deforms the gyroid structure and causes flow deformation, which results in the observed liquidlike response ($G'' > G'$).

3.2. Relaxation Following a Shear Quench. Following the deformation at maximum settings ($\gamma_0 = 120\%$, $\omega = 100$ rad/s) the shear was quenched to a minute level ($\gamma_0 = 0.1\%$ and $\omega = 100$ rad/s) at time $t = 0$ s in Figure 4. The relaxation of both the moduli and the scattering shows that the gyroid phase grows back during a 60−90 min time interval. Four transient peaks are observed within the early stages of the relaxation, as shown in inset 5 of the figure. The positions of these peaks are approximately 50° to the equator, which is why we attribute this scattering to be the metastable ML phase.[17,27,28]

Radially averaged SANS data from the relaxation process are displayed as a function of azimuthal angle in Figure 6 and show how the different peak members of the 10-spot gyroid pattern evolve. The data have been averaged within the 0.02−0.04 Å^{-1} q range. Each curve contains accumulated scattering for 300 s. The front curve shows the scattering from the last 300 s of shearing at maximum settings prior to the shear quench. The four scattering curves covering the time interval 0−1200 s are highlighted in light gray. Over this time interval we observe ML-type scattering come and go. The ML-type scattering is identified in the figure as the weak peaks A. The equatorial peaks (peaks B in the figure) of the shear-induced scattering overlap

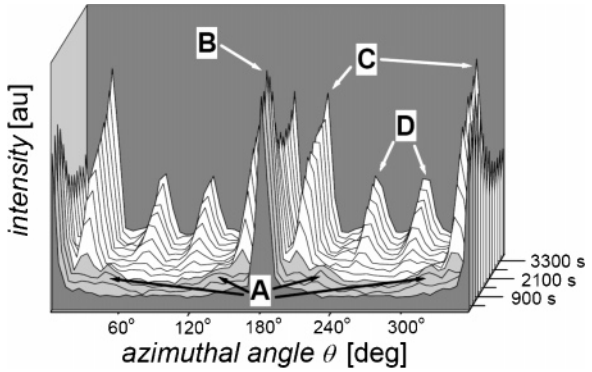

Figure 6. Azimuthal plots of scattering pattern averaged within the 0.02−0.04 Å^{-1} q range and acquired during relaxation from shear-induced hexagonal cylinder phase to cubic gyroid structure. (For explanation of indexes A−D, see text.)

epitaxially with the equatorial peaks of the final gyroid structure, and the relaxation can be followed by an overall decrease of the intensity of these peaks. In the last of the highlighted scattering curves (900−1200 s), we see coexisting ML and gyroid scattering profiles evidenced by the small buildup of peaks C from the gyroid structure. Peaks D also belong to the gyroid structure, but surprisingly these peaks are not growing simultaneously with peaks C. Peaks D are delayed approximately 600 s compared the growth of peaks C. This suggests a dependence of the growth rate on the rotational position of the morphology with respect to the shear geometry.

The formation of the ML phase is typically observed as a transient from the lamellar to the gyroid phase during heating. However, it has also been observed as a result of either a temperature cooling ramp[17] or a temperature quench[27] from the higher temperature hexagonal phase. The question here is: Does the observation of the transient ML state during relaxation give any indication of the nature of the shear-controlled two-spot pattern? Can we rule out a lamellar (LAM) or a hexagonal (HEX) origin? In earlier studies[17] we have shown that the ML phase is unstable to the gyroid phase. We also showed how a quenched hexagonal phase (supercooled 23 °C below its G → HEX transition) would transit directly into the gyroid phase without any ML scattering. However, cooling the same sample slowly from the hexagonal phase resulted in the formation of ML scattering at 48 °C below the G → HEX transition. Similar results were reported by Wang and Lodge.[27] They observed the transition from HEX to gyroid via a ML structure as a result of a "deep" temperature quench below the G → HEX transition, while a "shallow" temperature quench below the order−order transition (OOT) results in a direct transition with no intermediate morphology. Hence, it seems that transitions to the gyroid phase only take on intermediate morphologies at temperatures in the lower temperature part of the gyroid stability window. As suggested by Wang and Lodge,[29] there is a crossover temperature T_x in the gyroid stability window, which determines whether or not the transition mechanisms into the gyroid phase includes the formation of a transient ML structure. During the shear quench in Figure 6 the relaxation takes place at constant temperature. If the shear-controlled two-spot pattern has a hexagonal origin, the ML scattering shown in inset 5 of Figure 4 indicates that the sample is below such a crossover temperature.

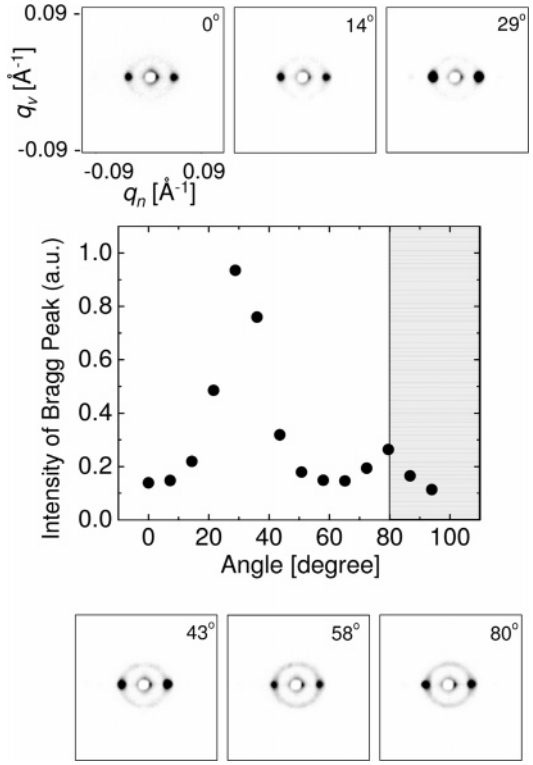

Figure 7. Crystallographic data of shear-induced hexagonal phase of PSPI diblock copolymer. The sample has been rotated around an axis parallel to shear flow q_v. Zero-angle rotation corresponds to the $q_v q_n$ shear plane obtained during shear experiments. For rotations above approximately 80°, the experimental setup causes limitation of exposed sample size, approaching zero at 90°.

This is reasonable considering the temperature stability window of the gyroid phase, which approximately spans the interval between 115 and 150 °C. From the evidence at hand we cannot here rule out the scenario that the shear-controlled two-spot pattern is lamellar and that the relaxation process correspondingly mimics a temperature increase from LAM to gyroid. Crystallographic studies presented below, on the other hand, clearly indicate that the shear-induced state is hexagonal rather than lamellae.

3.3. Crystallography of Shear-Controlled Structure. A detailed crystallographic study of the shear-controlled structure is presented in Figure 7. The sample was quenched to room temperature (which is below the glass transition temperature of polystyrene) during shearing and transferred to the custom-made goniometer. The sample in the goniometer allows for examination of the structure, as the SANS profiles are recorded while rotating the sample around the vertical direction—the direction of the previously applied shear. The sample was rotated a total of 90° in increments of 7.2°. The starting position was 0°, which is identical to the setup used during shearing, where the neutron beam is directed along the normal to the shear plates. At all rotation angles the SANS picture appears to be the same: two intense equatorial spots, as can be seen from the panels of 2D-SANS in Figure 7.

To examine this apparent rotational randomness, we mapped the peak intensity for each of the projections (rotation angles). The peak maxima of the equatorial spots are illustrated in Figure 7 with respect to the angle of rotation. The graph shows an apparent 5-fold variation of the primary peak intensities. The zero-angle

(0°) intensity represents a profound minimum, while a maximum is clearly measured at the rotation angle of 29°. A new minimum of similar intensity as that of the zero angle is observed at 58°. Because of the design of the goniometer and the shear plate fixture, there is unfortunately an instrumental limit to this quantitative comparison of peak intensities at approximately a rotation angle of 80°.

These data show a dominant alignment in the shear-controlled structure with maximum intensity at 30° rotation and with observed minima at approximately 0° and 60°. The data thereby strongly suggest that the shear-induced phase is the hexagonal cylinder structure, with near monodomain texture. A dominating shear-induced lamellae structure can clearly be rejected by these studies, while a minority fraction of lamellae phase is possible.

The morphology of single-crystal-like hexagonally aligned cylinders with (10)-planes parallel to the shear plates would result in a sharp Bragg peak exactly at a 30° rotation. The second sharp peak would be at exactly 90° rotation, but this cannot be monitored in the given setup due to the experimental cutoff mentioned above. At 0° and 60° rotations we would in the hexagonal cylinder phase expect dominating (11)-Bragg reflections at q values $\sqrt{3}$ times the $q(10)$ value. The two-dimensional insets (Figure 7) obtained at respectively 0° and 60° show some weak scattering at the expected Bragg position; however, the statistical significance is not reliable. The reason for the absence of strong (11)-reflections is due to the cylindrical form factor, which for the $f = 0.67$ copolymer composition has a minimum near the (11)-Bragg peak. Other higher order Bragg reflections are also observed only with questionable statistical significance. The two-dimensional inset obtained at 30° shows weak scattering at the expected (20)-Bragg position.

4. Discussion

Our combined structural and rheological studies clearly point to the fact that rather large shear amplitudes and frequencies are needed to destabilize the gyroid structure of a 30 kg/mol PS−PI diblock copolymer. Shear transforms the gyroid structure to a hexagonal cylinder structure.

The gyroid-to-lamellar transition was studied in detail previously by Förster et al., including shear behavior.[30] Within the temperature range of the thermodynamic stable gyroid phase, Förster et al. did not find any shear-induced transition like the one reported here. This is probably because they did not apply the sufficient combined values of shear rate and amplitude. On the other hand, Förster et al. clearly saw the effect of shear in the stabilization of the lamellar phase below the G-to-LAM transition temperature (T_{OOT}). Sakurai et al. reported recently a flow-induced gyroid-to-cylinder transition in elastomeric SBS polystyrene−polybutadiene−polystyrene triblock copolymers[22] and found results in good agreement with ours. The shear alignment procedure of Sakurai et al. did not allow real-time measurement of the rheological properties, and the shear mechanism applied also differs from the measurements reported here. Hence, direct comparison is difficult, but we would like to suggest that the results reported by Sakurai et al. are in perfect agreement with our conclusions.

The origin of the shear-induced order−order transition is not finally determined by our experiments. According to theories including fluctuation renormalization, shear generally increases the transition temperatures.[11,31,32] Cates et al. studied theoretically the effect of shear on the order−disorder transition (ODT) and suggested that the phase behavior of block copolymers is dominated by fluctuations in the proximity of the ODT.[11,12] Cates et al. also suggested that composition fluctuations parallel to the shear direction are suppressed and lose strength, provided that the shear rate is high relative to the characteristic fluctuation relaxation time. Thus, at sufficiently high shear rates the system becomes more mean-field-like, and the ODT temperature increases with shear rate. This is convincingly proven experimentally in studies on compositionally asymmetric poly(ethylpropylene)−poly(ethylethylene) (PEP−PEE) diblock copolymers, where a shear-induced transition from disorder to the hexagonally ordered structure was reported.[3,10,19,33] Corresponding results were obtained on a slightly asymmetric polystyrene−polyisoprene (PS−PI) diblock copolymer by Balsara et al., showing shear-induced lamellar phase formation above the quiescent ODT.[34,35] In $C_{12}E_5$ microemulsions, the cubic gyroid phase appeared unstable in steady shear, transforming to the disordered bicontinuous L_3 phase.[36] In other microemulsions Mahjoub et al. and Porcar et al. have found results that at first hand seems closely related to the results presented above.[37,38] Mahjoub et al. and Porcar et al. studied the stability of the isotropic bicontinuous phase L_3. Upon shear, they showed that the L_3 phase is unstable and transforms to the smectic L_α lamellar phase as expected from fluctuation theories.

With the observed LAM→ (ML) → G → HEX → DIS phase sequence of the present PS−PI block copolymer,[23] a coupling between shear flow and fluctuation would imply a shear-induced lamellae phase, in contradiction to our findings. This is equivalent with the interpretation that shearing of the sample effectively reduces the temperature. Experimentally we find the contrary. We therefore conclude that the effect of shear to effectively reduce thermal fluctuations is not the dominant effect in our studies.

In both colloidal and polymeric ordered systems flow-mediated dislocations have been shown to course phase changes and disordering. Ackerson et al.[8] and Gast et al.[9] have already at moderate shear rates observed continuous deformation of respectively colloidal and micellar lattices. At higher shear rates they found that the crystalline long-range order is lost, and an amorphous or liquidlike structure develops. Hajduk et al. and Register et al. observed similar behavior in block copolymer melts of diblock and triblock architecture.[4,7]

Theoretically, Zvelindovsky et al. studied the shear-induced destabilization of the gyroid phase of a triblock copolymer system using density functional calculations.[21] Zvelindovsky et al. found that the gyroid structure as a consequence of shear-induced dislocations may transform to hexagonally ordered cylinders as we find. However, their results seem rather more complex than our findings. Both lamellae and cylinder phases are induced by shear, and upon cessation of shear the density functional calculations do not reproduce the thermodynamic stable gyroid phase but lock in coexisting lamellae and cylinder phases.

5. Conclusion

In conclusion, we have shown that the gyroid phase of a diblock copolymer system is unstable when exposed

to shear. Combined structural (SANS) studies and applied oscillatory shear fields indicate that the gyroid phase transforms to hexagonally ordered cylinders when exposed to high shear rates and large strain amplitudes. This observation is in contrast to both the shear-induced shift in the order-to-disorder transition temperatures in related block copolymers and to the shear-induced L_3-to-L_α transition observed in microemulsions. The latter results were interpreted in terms of shear-reduced fluctuation renormalization, thus bringing the system into more mean-field-like conditions. The shear-induced gyroid → hexagonal cylinder phase is rather a result of shear-induced dislocations, possibly as a result of mechanical anisotropy between block domains. The results are to a large extent in agreement with recent theoretical calculations based on density functional methods.[21] It is highly likely that calculations with refined parameters may account for our results more quantitatively. Experimentally, it is clear that the shear-induced instability of the gyroid phase reported here is a general phenomenon for diblock copolymers. In preliminary studies of PEP−PDMS copolymers, we have found qualitative exact similar behavior. Under high shear the PEP−PDMS gyroid phase is suppressed within the whole temperature regime. Also, triblock copolymers of polystyrene−polybutadiene−polystyrene have recently been reported to show corresponding shear dependencies.[22]

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