Reinvestigation of the Block Copolymer Modulated Lamellar Structure

Kell Mortensen*,† **and Martin E. Vigild**‡

Biophysics, Department of Basic Sciences and Environment, University of Copenhagen, Frederiksberg, Denmark, and Department of Chemical and Biochemical Engineering, Technical University of Denmark, Kgs. Lyngby, Denmark

Received October 29, 2008; Revised Manuscript Received January 13, 2009

ABSTRACT: We report extended crystallographic studies on shear-aligned block copolymer systems within the metastable modulated lamellae (ML) state. With studies limited to the “classical” orientations parallel and perpendicular to shear plane, the apparent modulated state would likely have been assigned simple lamellar. Surprisingly, upon rotating the sample to intermediate angles additional scattering reflections appear, which reveal the apparent ML phase much beyond what was expected. The modulated structure is a slightly distorted fcc structure. With the sample sheared at relatively low temperature, presumably below the stable gyroid phase, we find a very well resolved ML texture corresponding to a simple twin structure of the distorted fcc structure. When shear-aligned within the hexagonal cylinder phase, and quenced to the gyroid phase or slightly below, we find ML alignment into a two-dimensional powder texture.

Introduction

Since the discovery in 1992 of intermediate modulated lamellar phases in the diblock copolymer systems,[1,2] this “phase” has been the subject of considerable study and debate.[3−17] Systematic studies have suggested the existence of the modulated lamellae as transient structures between the lamellar phase and either the hexagonal cylinder phase or the gyroid phase, depending on experimental route and specific sample. The structure is associated with a variety of abbreviations depending on exact observation: ML for modulated lamellae, PL for perforated lamellae, and HML or HPL for modulated or perforated lamellae with hexagonal symmetry, respectively. In the following, we will use the term *modulated* independent of whether the lamellae are perforated or just modulated.

The interest in especially the perforated structure arises from its topology: as in the ordinary unperforated lamellar phase, each component is continuous in the plane of its lamellae, but hexagonally packed perforations through the layer formed by the minority component impart three-dimensional continuity to the majority component. Selective removal of the minority component from the HPL structure would generate an array of slitlike nanopores held open by pillars of the 3D-continuous majority component.[18]

The experimental evidence of the modulated lamellar phase(s) comes from both scattering experiments and direct imaging by transmission electron microscopy. The energy differences between ordered states of block copolymers are often quite subtle, and with the slow dynamics characteristic for high molar mass polymers, it may be more or less impossible to prove the stability of a given phase experimentally. Transient metastable phases may therefore very well have been classified as stable phases. However, Hajduk et al. and Vigild et al. gave experimental indications that the modulated lamellar structures are only metastable with respect to either the gyroid or the hexagonal cylinder phases.[11,12] This conclusion is supported by a number of theoretical studies, which have convincingly argued that the modulated lamellar phase is not a thermodynamic stable phase in pure diblock copolymer systems.[7−10] Rather, the modulated phases reflect a transient stage between two ordered structures or fluctuations which in the shear oriented samples appear with rather well-defined scattering momentum transfer.

Using self-consistent-field calculations, Matsen et al. showed that the modulated structures are only metastable and clearly documented that the calculated free energy difference is quite small.[7,9] On the basis of a time-dependent Ginzburg−Landau approach, Qi and Wang suggested two possible origins of the modulated structures.[8,10] The structure may indeed be a kinetic, transient state within the transition from the lamellar morphology (LAM) to the hexagonal (HEX) or gyroid morphologies, but another possibility is that thermal fluctuation can lead to stabilization of a pseudo or metastable state.

With the subtle energy differences stabilizing the various phases, one may still speculate whether polydispersity or minor amounts of impurities in experimental polymer systems may stabilize more complex phases, like the modulated lamellae.

Previous experimental scattering studies reflecting the modulated lamellar state are mostly done either showing data within the shear plane or orthogonal to this, both cases showing additional reflections associated with the modulated structure. Experiments that show only the Bragg peaks associated with simple lamellae or hexagonal phase in these two scattering configurations were associated with the two pure states. Zhu et al. and Hamley et al. recently made a somewhat more elaborated crystallographic study showing some additional sample configurations with respect to the beam direction.[14,15] In the study presented below we observe that even deep into the phase which is associated with pure lamellar structure based on the usual scattering assignment, we find other scattering geometries that show additional well-resolved reflections which we associate with the modulated structure. We base our study on a reinvestigation of the very well characterized block copolymer system, polystyrene-*b*-polyisoprene (PS−PI), showing that the modulated lamellar structure remains much deeper into the lamellar state than previously anticipated. Preliminary studies of other block copolymer systems, poly(ethylenepropylene)-*b*-poly(dimethylsiloxane) (PEP−PDMS), prove this to be a general phenomena. The modulation has dominating fcc-like symmetry, but with the ratio of the axes in the plane of the lamellaes relative to that of the stacking direction equal 1.15, i.e., trigonal $R\bar{3}m$ symmetry.

---

* Corresponding author. E-mail: kell@life.ku.dk.
† University of Copenhagen.
‡ Technical University of Denmark.

10.1021/ma8024249 CCC: $40.75

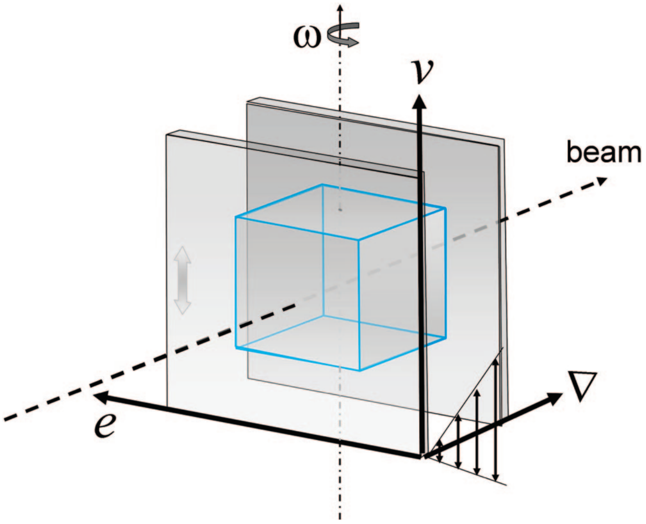

Figure 1. Schematic diagram of the flow geometry and the scattering setup used for in situ rheology−SANS measurements and for crystallographic measurements rotating the sample around the Ω-axis.

Previous Experimental Evidence of ML

While the experimental evidence of the modulated lamellar phase comes from both scattering experiments and direct imaging, we will in this report concentrate on observations based on scattering experiments.

In nonaligned copolymer samples the order of the perforations is generally too poor to reliably distinguish the modulated lamellar structure from the pure lamellae. Alignment of the structure by, for example, large-amplitude oscillatory shear (LAOS) often yields a regular pore arrangement, as evidenced by additional diffuse Bragg-like reflections in well-defined directions of shear oriented samples.[3,6,11−13,15,16,19,20]

Different routes have been followed to resolve the modulated stage in diblock copolymers. By shearing directly in the close region between the lamellar phase and either the hexagonal cylinder phase or the gyroid phase, the ML phase emerges as evidenced from four scattering peaks in the **ve**-shear plane, **v** being the flow direction and **e** being the neutral vorticity direction.[3,6,11,14,15,21,22] After release of shear, a 6-fold symmetric pattern of weak reflections evolves, reflecting the "hexagonal" abbreviations HML and HPL. When cooled, these six reflections disappear, taken as an indication that the pure lamellar state has evolved.[3]

Another route for creating the ML structure is by cooling from an aligned cylinder state into the gyroid phase.[11,13] In this case a perpendicular orientation of the ML phase evolve characterized by a 55° opening angle between the lamellar Bragg peaks and the ML characteristic peaks. The same scattering pattern is actually observed when the sheared parallel orientation is rotated 90° in the beam,[3,6] strongly indicating that the two routes result in the same metastable modulated state.

It has been discussed whether the shear itself may induce modulations. Zhu et al. argued that the stacking developed was controlled by the shear, rather than being an intrinsic feature of the structure. Register et al.,[23] on the other hand, described a diblock copolymer system which spontaneously and reproducibly adopts a highly regular HPL structure, without any perturbing applied fields. They also find coexistence between LAM and HPL over a substantial temperature range, with the relative fractions of the two structures depending uniquely on the temperature. Luo and Yang have approached the effect of shear theoretically, using a time-dependent Ginzburg−Landau approach.[24] Luo and Yang found thereby that the HML phase is a transient kinetic, intermediate state en route from LAM to HEX phases and that the shear flow cannot stabilize this intermediate state. Without steady shear flow the perforated lamellar phase stage actually survives for longer time, according to their calculations. Whether HML or HPL phases evolve depends on how deep the LAM phase is quenched into the HEX phase. The modulated phase emerges at first, but eventually it slowly transforms into the HEX cylinders. The simulation result also indicated that modulated phase has ABAB stacking sequence.

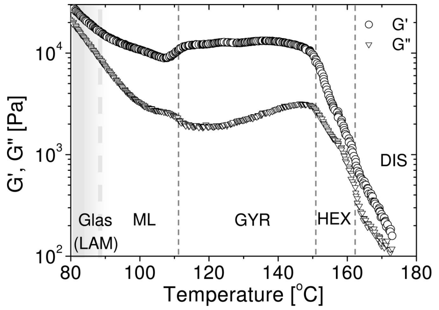

Figure 2. Rheological experiments, indicating the ML−GYR−HEX−DIS phase sequence of PS−PI.

Experimental Section

Sample. The present study is based on a diblock copolymer samples of relative high molar mass polystyrene-*b*-polyisoprene (PS−PI). Preliminary equivalent studies were in addition performed on a poly(ethylenepropylene)-*b*-poly(dimethylsiloxane) (PEP−PDMS) diblock copolymer with relative low molar mass. The equivalent findings of these two diblock polymer systems with quite different molecular characteristics strongly indicate that the results are general for diblock copolymers and not specific to a single system only.

The PS−PI diblock copolymer (SI-29) was synthesized by high-vacuum anionic polymerization at the University of California at Berkeley. The volume fraction of polyisoprene is $f_{PI} = 0.67$. The molecular weight of the PS−PI diblock copolymer is $M_w = 2.96 \times 10^4$ g/mol with polydispersities less than 1.05. In this study the PS−PI diblock copolymer was mixed with the neutral 5% dioctyl teraphthalate (DOP) additive, which 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).[16] The phase sequence is in perfect agreement with the previously reported diagram of PS−PI diblock copolymers.[25]

Previous experiments with the given samples have shown high degree of reproducibility, verifying that degradation during the temperature and shear cycles plays no significant role.[16]

Rheo-SANS: Rheology and Small-Angle Neutron Scattering. The diblock copolymer samples were mounted in a shear sandwich fixture within a Rheometrics RSA-2 instrument modified for the simultaneous measurements of both dynamic mechanical and structural properties and for studies of the structural response to large-amplitude oscillatory shear (LAOS).

The RSA-2 instrument was used for initial temperature-dependent rheological experiments, made in attempt to locate order−order phase transitions in the diblock copolymers melts. These studies were performed with a small-amplitude oscillatory shear of $\gamma = 1\%$ and an applied shear frequency of $\omega = 1$ rad/s.

The neutron experiments were performed at the SANS-II instrument at the Swiss Spallation Neutron Source (SINQ), the Paul Scherrer Institute (PSI), using 6 Å neutrons with a 9% wavelength resolution. The sample-to-detector distance and the collimation length were both 3 m.

The position of the shear cell with respect to the neutron beam is illustrated in Figure 1. The two-dimensional SANS patterns are correspondingly acquired in the ($\mathbf{q}_v$, $\mathbf{q}_e$)-plane, $\mathbf{q}$ being the scattering

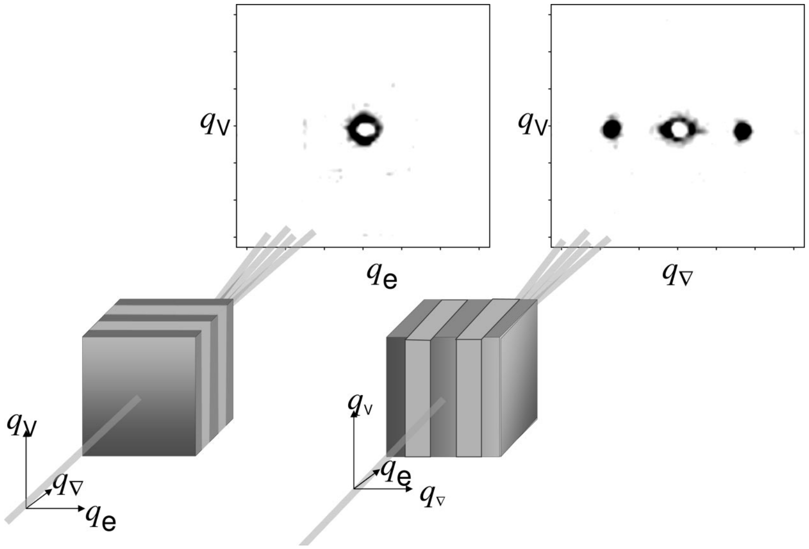

Figure 3. Small-angle neutron scattering pattern of a shear-aligned PS−PI sample, as measured in the shear fixture fixed to a goniometer. The two figures are the scattering pattern as obtained in the **ve**- and **v**∇-shear planes. These two sets of data are in perfect agreement with lamellar assignment.

momentum and the indices **v** and **e** reflecting the flow and the vorticity directions, respectively.

The large-amplitude oscillatory shear used for the shear alignment studies was carried out at a shear frequency (ω) up to 100 rad/s and oscillatory shear amplitudes (γ) up to 165%.

After the shear-induced alignment, the sample was quenched to ambient temperature, where the shear cell was fixed for crystallographic studies using a homemade goniometer.[26] The polymer sample was rotated stepwise around the axis parallel to the direction of the original shear flow (**v**), as illustrated in Figure 1. The crystallographic studies were made both at ambient temperature and at elevated temperatures.

The experimental observations were compared with the calculated scattering patterns from one or more crystalline domains.

Results

Rheological experiments were used to locate the order−order phase transitions in the diblock copolymers. The elastic G' and inelastic G'' moduli of the PS−PI diblock copolymer are shown versus temperature in Figure 2. With reference to equivalent studies in related block copolymers, we assign the different characteristics in the rheological data to the different phases: lamellar (LAM), modulated lamellar (ML), gyroid (GYR), hexagonal (HEX), and disorder (DIS).

The rheological measurements shown in Figure 2 were obtained during heating. The order−disorder transition temperature is $T_{\mathrm{HEX-DIS}} \approx 165$ °C, the gyroid-to-hexagonal order−order transition is at $T_{\mathrm{GYR-HEX}} \approx 150$ °C, and the apparent modulated lamellar-to-gyroid transition appear at $T_{\mathrm{ML-GYR}} \approx 120$ °C. The low-temperature lamellar phase seems not well resolved, if developed at all, since the polystyrene domains becomes glassy below approximately 80−90 °C. We observed the modulated lamellar structure at temperatures very near the glass transition. We assigned, in fact, originally the structure at 90 °C to be well-defined lamellar, as shear-alignment at this temperature led to a scattering pattern in the (**ve**)-shear plane that is unusually perfectly blank, while the pattern in the perpendicular (**v**∇)-plane shows well-resolved lamellar reflections, including higher orders (Figure 3). According to common procedures for assignment of block copolymer ordered phase, these findings would be associated with perfect lamellar structure. But by gradually rotating the sample in the beam, a number of additional Bragg reflections appear surprisingly in planes between the two principal orientations, disproving that the structure is simple lamellar. This is discussed in detail below.

Two routes of the scattering experiments and shear alignment are presented below. In the first study the PS−PI sample is shear-aligned at 160 °C within the hexagonal phase, while in the second route shear alignment is performed at 100 °C within the lamellar/modulated lamellar, presumably well below the gyroid state. The scattering experiments were in both cases performed by starting with a sample showing powderlike texture, as verified by rather homogeneous Debye−Scherrer rings in the scattering pattern (Figure 4).

Shear Align in Hexagonal Phase. Figure 4 shows the scattering pattern of PS−PI before and after application of large-amplitude (100%) oscillatory (100 rad/s) shear. Before applying the shear, we observe an isotropic Debye−Scherrer pattern reflecting the crystalline powder of hexagonally ordered polystyrene rods embedded in the polyisoprene matrix. During large-amplitude shear, the pattern evolves into two dominating Bragg peaks, reflecting the shear-aligned hexagonal texture. The two-spot pattern remain after cessation of shear. With the given geometry, we can only conclude that the cylinders are aligned with the shear field. We cannot judge whether the resulting texture is a two-dimensional powder or other higher ordered texture. At least some fraction of the {11} planes is preferentially oriented in parallel with both the shearing and scattering planes, leaving the {10} planes in Bragg condition, as observed. With reference to previous studies of shear-aligned copolymer systems within the hexagonal state, it is likely that the Bragg reflections observed actually represent a minority component of the aligned domain structure, while the majority component has the alignment 90° rotated around the shear axis.[11,27]

When the shear-aligned sample is cooled to 100 °C, additional reflections appear, reflecting the transition from hexagonally ordered cylinder structure to modulated lamellar phase, as observed previously by several groups.[11,13] The strong equatorial reflections are caused by the dominating layered structure, while the off-equatorial reflections at 55° with respect to the equator characterize the in-plane modulation. The pattern changed with time after quench, being fully developed after about 10 min.

With the sample fixed in the goniometer, we made more detailed crystallographic studies of the ML texture as evolved by cooling from the hexagonal structure. Five shows the results when the sample is rotated 0−90° in steps around the vertical

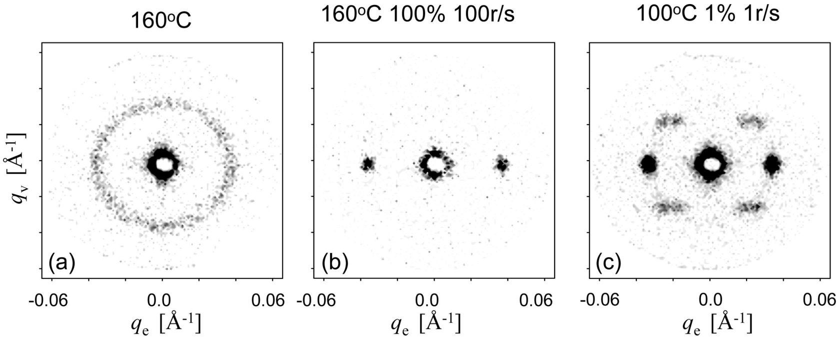

Figure 4. Small-angle neutron scattering pattern of the PS−PI sample as shear-aligned in the HEX phase and subsequently quenched to ML: (a) measured as mounted in the shear fixture (powder sample), (b) sheared within the HEX phase, and (c) after being quenched to the ML phase. The figures are the scattering pattern as obtained in the **ve**-shear planes.

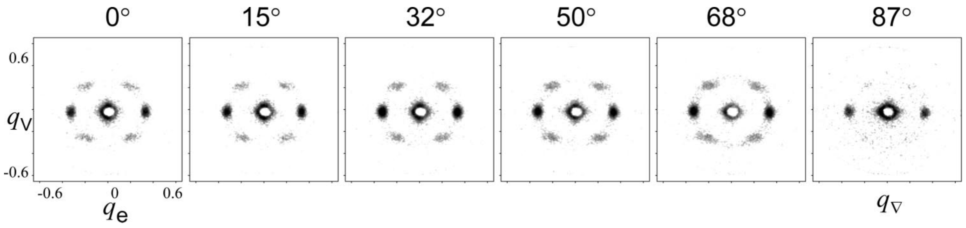

Figure 5. Crystallographic studies of the ML state as emerged by quenching from the shear aligned HEX state. The SANS pattern shows no dependence on rotation around the vertical axis parallel to original shear flow and original cylinder axis, proving a two-dimensional ML powder.

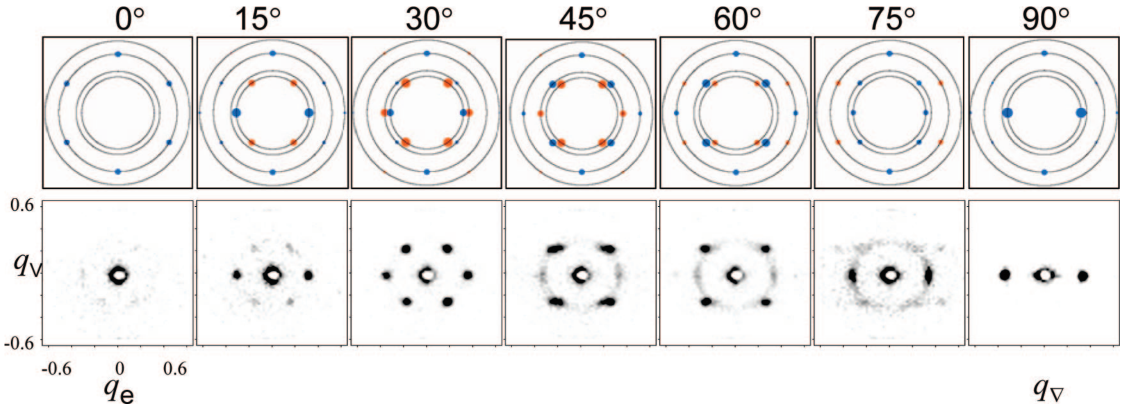

Figure 6. Small-angle neutron scattering pattern of PS−PI, as measured at different rotation angles Ω between the beam direction and the direction of the shear-gradient ∇ when rotated around the flow direction **v**. The bottom row are experiments. The top row are calculations, where the two colors represent scattering from the two twin domains.

shear velocity axis. All patterns appear very similar, independent of rotation angle, proving that the shear-aligned hexagonal structure evolve into a two-dimensional powder of (modulated) lamellar. Even without detailed knowledge about the texture in the hexagonal phase, such 2D powder is to be expected since only the cylinder axis is expected to remain as a characteristic domain axis during transformation to lamellar structure. Corresponding 2D powders are observed in the transformation from cylinder phase to gyroid structure.[28,29] One may notice that the off-equatorial reflections are split into two, resulting from respectively [111] and [200] type of reflections appearing simultaneously in the two-dimensional powder pattern. This is more clear referring to Figure 6: each powder pattern shown in Figure 5 corresponds to the sum of all twin patterns shown in Figure 6.

At 100 °C we did not observe changes in ML pattern within time frame of the order of hours. This is in opposition to corresponding studies made at 120 °C, where transformation to the gyroid structure was observed.[16]

Shear Align within the Modulated Lamellar Phase. In the second experimental route, we made shear alignment at 100 °C, which is believed to be well below the stable gyroid phase. In this case the isotropic Debye−Scherrer ring evolves into four, resolution-limited reflections. While the isotropic ring is believed to reflect the dominating lamellar structure, the four spot-pattern likely reflects the in-plane modulations. Quite similar results have previously been observed.[6] The q value of the four spots are 1.15 times the value of the lamellar Bragg peak, q^*.

In opposition to previous studies, on the other hand, we observe that the four-peak pattern almost completely disappear upon cessation of shear. Within experimental statistics the scattering pattern appear blank. There is no signature of single weak spots and only very little signature of a correlation ring, which may correspond to either a very small fraction of remaining crystalline powder or the block copolymer structure factor of a minor amount of disordered material. With additional measurements in the perpendicular (**v**∇)-plane, made with the sample mounted in the goniometer, we observe very well resolved lamellar reflections, including higher orders. According

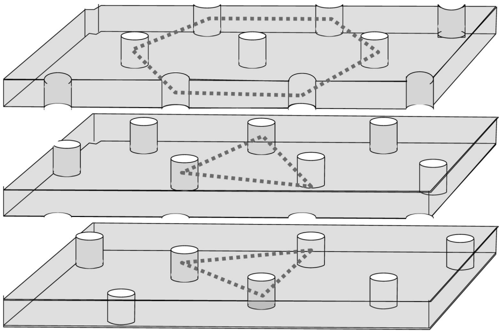

Figure 7. Schematic illustration of a modulated lamellar structure with distorted fcc symmetric, where the two phases are shown in gray and white, respectively.

to the common procedure for crystal assignment, these findings would be associated with relaxation to perfect lamellar structure, as illustrated in Figure 3.

With the more detailed crystallographic studies, measuring the scattering pattern in a variety of orientations with the temperature T fixed at 100 °C, a large number of additional Bragg-like reflections appeared, as shown in Figure 6.

These experimental observations were compared with the calculated scattering patterns from one or more crystalline domains. Because of the highly asymmetric planar sample geometry, with the sample situated inside the shear fixture, we were unfortunately not able to resolve the relative intensities, only the three-dimensional position in reverse **q**-space.

We found very good agreement with the result of a simple twin structure of a slightly distorted fcc structure, i.e., the trigonal $R\bar{3}m$ structure with ABC type of stacking. The calculations were made using a crystal mosaicity of 10°. The unit cell value within the plane of the lamellae is 1.15 times the value of the unit-cell parameter perpendicular to the plane of the lamellae. This is in perfect agreement with the results of Zhu et al. and Hamley et al.[14,15]

Figure 6 shows the experimental SANS data and corresponding calculated scattering patterns obtained on two fcc-crystal domains with the [011] axis parallel to the shear flow and with the [111] and $[11\bar{1}]$ axes parallel to **e**, respectively. The crystal planes parallel to the **ve**-plane is accordingly the $\{21\bar{1}\}$ and $\{2\bar{1}1\}$, respectively. In the figure the two twin domains are represented by blue and red color, respectively. Figure 7 illustrate the structure of one of the domains of the modulated lamellar structure.

The zero-angle data show the characteristic blank scattering pattern, reflecting that no reflections are in Bragg conditions. The pattern obtained at 30° rotation have near 6-fold symmetry, but while the equatorial reflections are dominated by (200)-type reflections, the off-equatorial peaks reflect (111)-type reflections. The patterns obtained at a 45° and 60° rotation shows four dominating reflections, but while the 60° pattern reflects dominance of only (200)-type reflections, the smeared looking peaks of the 45° pattern reflects near overlap of (111)- and (200)-type reflections. The 90° pattern reflects dominance of the lamellar Bragg peak which in the overall structure correspond to (111).

While the scattering pattern within the (**ve**)-shear plane appear completely blank after cessation of shear, we observed that the four spots to some extend reappear upon cooling to ambient temperature. The intensity is not as strong at originally, but they are easily resolved. This finding is to large extend reproducible, cycling the sample between ambient and 100 °C. The origin of this change in scattering pattern remains unclear to us. Quenching to ambient temperature will make the PS into the glassy state, and we should not expect any significant changes in structure or fluctuations. On the other hand, it seems not likely that the phenomenon is a consequence of changes in scattering contrast. With mass densities for PS and PI equal to respectively 0.969 and 0.830 g/cm^2,[30] giving the neutron scattering length densities $\rho_{PS} = 1.30 \times 10^{10}$ cm^{-2} and $\rho_{PI} = 0.243 \times 10^{10}$ cm^{-2} for PS and PI, respectively, we have a rather good scattering contrast. A minor change in mass density versus temperature will not significantly change the neutron contrast. Crystallographic studies do not reveal additional information. Except for the stronger initensity of the four reflections observed at 0 and at 15° rotation, the patterns appear the same. It is possible that quenching the sample to ambient temperature causes a slight stress that will cause a slight rotation of parts or of the whole sample.

Discussion

Zhu et al. recently made a detailed crystallographic analysis of the HPL structure, as based on SAXS and TEM experimental studies. They showed that the HPL phase had a mixed morphology with the majority of trigonal twins (80%) (ABC) but a minority hexagonal structure (20%) (AB).[14] Our experiments agree very well with the results of Zhu et al., except that in our experiments we see no indications of the hexagonal structure. We can explain all observed reflections within the simple trigonal twin structure. We must admit, however, that the neutron scattering technique often miss weak reflections that may be resolved using high-flux X-ray instruments. With the rather equal energy levels of the ABC and ABAB type of stacking, we will not exclude that small amounts of the hexagonal ABAB structure also exist in our samples.

Hamley et al. recently made a crystallographic study somewhat similar to ours, making shear-aligned PEP−PDMS diblock copolymers within the HML phase.[15] The sample was shear-aligned in the temperature regime where the HPL phase is metastable and subsequently cooled to ambient temperature where the shear plates were fixed and mounted onto a goniometer stage. The sample was rotated from $\Omega = 0$ to 60° at various angles. Hamley reported diffraction shear-plane patterns consisting of two strong equatorial reflections, in addition to broad rings at the same value of q^* and at $1.1q^*$. Inside the first ring are four weak reflections located at ±57° with respect to the equator that arise from perforations within the lamellae similar to our findings. Upon rotation to 60°, however, a pattern of 10 reflections at q^* were observed. Hamley et al. argue that these reflections correspond to various projections of the HPL structure. Clearly, this sample texture is much less well-defined, as compared to that we find. Hamley et al. actually also noticed that the pattern of the four weak peak reflections disappeared after some time, but they did not comment further on this.[15] One may speculate whether their sample actually will emerge into a texture equal to the one that we have reported.

Conclusions

We have made extended crystallographic studies showing that such studies are needed to resolve the structure and the stability of block copolymer modulated lamellar phase. With only the "classical" orientations parallel and perpendicular to shear plane, the modulated state would have been assigned simple lamellar. The modulated structure is a slightly distorted fcc structure: the trigonal $R\bar{3}m$ structure with ABC type of stacking. With the sample sheared at relative low temperature, presumably below the stable gyroid phase, we find a very well resolved ML texture corresponding to a simple twin structure of the distorted fcc structure. When shear-aligned within the hexagonal cylinder phase, and quenched to the gyroid phase or slightly below, we find ML alignment into a two-dimensional powder texture.

Acknowledgment. This study was financially supported by the Danish Natural Science Research Council through the support of Instrument Centre for Synchrotron X-ray and Neutron Scattering (DANSCATT). Neutron scattering was performed at the Paul Scherrer Institute in Switzerland. We thank Ruya Eskimergen and Nitash Balsara for illuminating discussions and synthesizing the PS−PI copolymer sample.

References and Notes

(1) Almdal, K.; Koppi, K. A.; Bates, F. S.; Mortensen, K. *Macromolecules* **1992**, *25*, 1743–1751.
(2) Hashimoto, T.; Koizumi, S.; Hasegawa, H.; Izumitani, T.; Hyde, S. T. *Macromolecules* **1992**, *25*, 1433–1439.
(3) Hamley, I. W.; Koppi, K. A.; Rosedale, J. H.; Bates, F. S.; Almdal, K.; Mortensen, K. *Macromolecules* **1993**, *26*, 5959–5970.
(4) Spontak, R. J.; Smith, S. D.; Ashraf, A. *Macromolecules* **1993**, *26*, 956–962.
(5) Disko, M.; Liang, K. S.; Behal, S. K.; Roe, R. J.; Jeon, K. J. *Macromolecules* **1993**, *26*, 2983–2986.
(6) Hamley, I. W.; Gehlsen, M. D.; Khandpur, A. K.; Koppi, K. A.; Rosedale, J. H.; Schulz, M. F.; Bates, F. S.; Almdal, K.; Mortensen, K. *J. Phys. II* **1994**, *4*, 2161–2186.
(7) Matsen, M. W.; Schick, M. *Phys. Rev. Lett.* **1994**, *72*, 2660–2663.
(8) Qi, S.; Wang, Z. G. *Phys. Rev. Lett.* **1996**, *76*, 1679–1782.
(9) Matsen, M. W.; Bates, F. S. *J. Chem. Phys.* **1997**, *106*, 2436–2448.
(10) Qi, S.; Wang, Z. G. *Phys. Rev. E* **1997**, *55*, 1682–1697.
(11) Vigild, M. E.; Almdal, K.; Mortensen, K.; Hamley, I. W.; Fairclough, J. P. A.; Ryan, A. J. *Macromolecules* **1998**, *31*, 5702–5716.
(12) Hajduk, D. A.; Ho, R. H.; Hillmyer, M. A.; Bates, F. S.; Almdal, K. *J. Phys. Chem. B* **1998**, *102*, 1356–1363.
(13) Wang, C. Y.; Lodge, T. P. *Macromolecules* **2002**, *35*, 6997–7006.
(14) Zhu, L.; Huang, P.; Chen, W. Y.; Weng, X.; Cheng, S. Z. D.; Ge, Q.; Quirk, R. P.; Senador, T.; Shaw, M. T.; Thomas, E. L.; Lotz, B.; Hsiao, B. S.; Yeh, F.; Liu, L. *Macromolecules* **2003**, *36*, 3180–3188.
(15) Hamley, I. W.; Castelletto, V.; Mykhaylyk, O. O.; Gleeson, A. J. *J. Appl. Crystallogr.* **2004**, *37*, 341–344.
(16) Eskimergen, R.; Mortensen, K.; Vigild, M. E. *Macromolecules* **2005**, *38*, 1286–1291.
(17) Mareau, V. H.; Akasaka, S.; Osaka, T.; Hasegawa, H. *Macromolecules* **2007**, *40*, 9032–9039.
(18) Lee, J. S.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 2602–2606.
(19) Ahn, J. H.; Zin, W. *Macromolecules* **2000**, *33*, 641–644.
(20) Zhu, L.; Huang, P.; Cheng, S. Z. D.; Ge, Q.; Quirk, R.; Thomas, E.; Lotz, B.; Wittman, J. C.; Hsiao, B. S.; Yeh, F.; Liu, L. *Phys. Rev. Lett.* **2001**, *86*, 6030–6033.
(21) Förster, S.; Khandpur, A. K.; Zhao, J.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W. *Macromolecules* **1994**, *27*, 6922–6935.
(22) Hamley, I. W.; Fairclough, J. P. A.; Ryan, A. J.; Mai, S. M.; Booth, C. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2097–2101.
(23) Loo, Y. L.; Register, R. A.; Adamson, D. H.; Ryan, A. J. *Macromolecules* **2005**, *38*, 4947–4949.
(24) Luo, K.; Yang, Y. *Polymer* **2004**, *45*, 6745–6751.
(25) Khandpur, A. K.; Förster, S.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W.; Almdal, K.; Mortensen, K. *Macromolecules* **1995**, *28*, 8796–8806.
(26) Vigild, M. E. Mesomorphic phase behavior of low molar mass PEP-PDMS diblock copolymers. Risø ISBN 87-550-2326-6, Denmark, **1997**.
(27) Mortensen, K. *J. Phys.: Condens. Matter* **1996**, *8*, A103−A124.
(28) Olsson, U.; Mortensen, K. *J. Phys. II* **1995**, *5*, 789–801.
(29) Vigild, M. E.; Mortensen, K.; Almdal, K., to be published.
(30) Rubinstein, M.; Colby, R. H. *Polymer Physics*; Oxford University Press: New York, 2003.

MA8024249