Self-Assembly of pODMA-b-pBA-b-pODMA Triblock Copolymers in Bulk and on Surfaces. A Quantitative SAXS/AFM Comparison

Wei Wu, Jinyu Huang, Shijun Jia, Tomasz Kowalewski, and Krzysztof Matyjaszewski

Center for Macromolecules Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

T. Pakula†

Max-Planck Institut für Polymerforschung, Postfach 3148, 55128 Mainz, Germany

A. Gitsas and G. Floudas*

Department of Physics and Foundation for Research and Technology-Hellas, Biomedical Research Institute (FORTH-BRI), University of Ioannina, P.O. Box 1186, 451 10 Ioannina, Greece

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The phase state of a series of poly(n-octadecyl methacrylate)-b-poly(tert-butyl acrylate)-b-poly(n-octadecyl methacrylate) (pODMA-b-pBA-b-pODMA) triblock copolymers, synthesized through atom transfer radical polymerization, has been investigated in bulk and on surfaces using small-angle X-ray scattering and atomic force microscopy, respectively. The mean-field theory was employed to construct the bulk phase diagram. Excellent agreement was found between the bulk and surface morphologies as well as for the domain spacing (domain spacing scaled as $d \approx N^{0.64}$), suggesting that the strong polymer−polymer interactions in bulk are also the dominant interactions on surfaces.

I. Introduction

Block copolymers self-assemble into well-controlled nanoscale structures ranging from spheres, cylinders, and lamellae to the more complex bicontinuous cubic phase, with a $Ia3d$ symmetry group, known as a double gyroid. The self-assembly of block copolymers in bulk depends on several factors: (1) the product of the Flory−Huggins interaction parameter $\chi$ with the total degree of polymerization $N$, (2) the volume fraction $f$, (3) the copolymer architecture,5-9 (4) the conformational asymmetry,10,12 and (5) the fluctuation effects.12 According to the mean-field theory (MFT),13,14 the phase state was discussed only in terms of the first two parameters ($\chi N$ and $f$), but it soon became apparent that the remaining three factors have a crucial role in the phase behavior.

The established techniques that have been employed in obtaining these phase diagrams are small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). In some cases, the different viscoelastic contrast of the various nanostructures assisted in the construction of these phase diagrams.

Recently, atomic force microscopy (AFM), with its nanometer spatial resolution and ability to distinguish different materials without staining, emerged as an attractive method for surface structure characterization. Because AFM relies on the mechanical interrogation of the sample surface by the ultrasharp tip, interpretation of AFM images is not always as straightforward as it might initially appear, and it may necessitate taking into account artifacts related to the tip geometry and the mechanical response of the sample, which could, for example, lead to complex contrast-reversal phenomena.15,16 The presence of external surfaces and the confinement effects in ultrathin films may alter the morphology of materials,17-21 or even, as described below, lead to the stabilization of unusual, nonbulk structures. For example, a bounding

1 Deceased June 7, 2005.
(3) Leibler, L. Macromolecules 1980, 13, 1602.
(4) de la Cruz, M. O.; Sanchez, I. C. Macromolecules 1986, 19, 2501.
surface with a preference for one of the two blocks can induce order in diblock copolymer melts, as found experimentally.\textsuperscript{22} The order-to-disorder transition temperature (\(T_{\text{ODT}}\)) in films of polystyrene-b-poly(methyl methacrylate) (PS-b-PMMA) was found to increase as the film thickness was reduced.\textsuperscript{23} More recently, for a lamellar-forming triblock copolymer of polystyrene-b-polybutadiene-b-poly(methyl methacrylate) (SBM), the near-surface morphology was found to deviate from the bulk lamellar morphology;\textsuperscript{24} isolated microdomains of the backfolding species embedded in a perforated lamellar of the respective other end block were identified by AFM. For cylinder-forming block copolymers, the deviations from the bulk structure include a wetting layer,\textsuperscript{25} spherical microdomains,\textsuperscript{26} perforated lamellae,\textsuperscript{26} and cylinders with terraces (as with the lamellar orientation).\textsuperscript{27,28,29}

For a polystyrene-perforated layers. The cylindrical orientation was found forming diblock copolymer, a helical morphology is found radical polymerization (ATRP).\textsuperscript{32}

The system investigated is the poly(tert-butyl acrylate)-poly(styrene-b-poly(methyl methacrylate)) (pODMA-b-pBA-b-pODMA) triblock copolymer with a cylindrical microdomain structure in bulk, several different structures were found on the Si substrate, after being annealed from chloroform vapor, as a function of film thickness: from a disordered phase in the thinner part of the film to cylinders with parallel (C\(_{\parallel}\)) and perpendicular (C\(_{\perp}\)) orientations and perforated lamellae.\textsuperscript{30} The cylindrical orientation was found to change in sequence as C\(_{\parallel}\) \(\rightarrow\) C\(_{\perp}\) \(\rightarrow\) C\(_{\parallel}\) at steps between terraces (as with the lamellar orientation).\textsuperscript{28,29}

The above systems are some examples of surface reorganization revealing a strong interplay between the strength of the surface field and the deformation of the structure. This interplay can either cause the orientation of the bulk structure or lead to surface reconstruction. In addition, the film thickness modulates the stability regions of the different phases via interference and confinement effects. With respect to the latter, recent studies revealed that the severe confinement of a symmetric diblock folding species embedded in a perforated lamellar of the surface structure alone.\textsuperscript{24} It is evident that one cannot infer the bulk morphology from the surface structure alone.

In this study, we make a detailed comparison between the phase behavior of a triblock copolymer system in bulk and on the surface using SAXS and AFM, respectively. The system investigated is the poly(n-octadecyl methacrylate)-b-poly(tert-butyl acrylate)-b-poly(n-octadecyl methacrylate) (pODMA-b-pBA-b-pODMA) triblock copolymer, which is synthesized through atom transfer radical polymerization (ATRP).\textsuperscript{30,31} pODMA undergoes side-chain crystallization\textsuperscript{35} below \(\sim 285\) K (with a melting temperature at 300 K), whereas pBA is an amorphous polymer with a glass transition temperature (\(T_{g}\)) at 320 K (i.e., above the crystallization and melting temperatures of the pODMA). AFM and SANS studies reported here were made above the pODMA melting temperature using the samples prepared in a way intended to ensure the formation of equilibrated morphologies. Remarkably, both methods were found to be in excellent agreement, suggesting that the surface morphologies did not deviate significantly from the bulk microdomain structures. In particular, domain spacings obtained from SANS and AFM for the nearly symmetric block copolymers agreed very well with each other, suggesting strongly segregated blocks that were in agreement with their phase state. Moreover, some additional AFM studies, described in Supporting Information, pointed to the relative insensitivity of the salient features of the surface morphologies of studied copolymers to sample preparation conditions, lending further support to their strong segregation behavior.

### II. Experimental Section

**Materials and Characterizations.** \(n\)-Octadecyl methacrylate (ODMA) (Polysciences Inc.; 99%) was purified by being dissolved in hexane and extracted four times with 5% aqueous NaOH. After the organic phase was dried over magnesium sulfate, the solution was passed through neutral alumina, and solvent was removed under reduced pressure. tert-Butyl acrylate (tBA) (Aldrich; 98%) was dried over calcium hydride and then distilled in a vacuum. Cu(II)Br (Acros; 98%) and Cu(II)Cl (Acros; 99%) were purified by being washed with glacial acetic acid, followed by absolute ethanol and acetone, and then dried under vacuum.

The monomer conversion of tBA was determined using a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector (FID) using a J&W Scientific 30-m DB WAX Megabore column. Injector and detector temperatures were kept constant at 250 °C with a heating rate of 20 °C/min. The monomer conversion of nODMA and the copolymer composition were analyzed by \(^1\)H NMR in CDC\(_12\) on a Bruker 300 MHz instrument.

Copolymer molecular weights were determined using a gel permeation chromatography (GPC) equipped with a Waters WISP 712 autosampler, Polymer Standards Service guard columns (10^\(^{\circ}\), 10^\(^{\circ}\), and 10^\(^{5}\) Å), and a Waters 410 RI detector for linear polystyrene or poly(methyl methacrylate) standards in tetrahydrofuran (THF; 1 mL/min) at 35 °C, and toluene was used as the internal standard.

**Synthesis of the Difunctional pBA Macroinitiator.** In a 25-mL degassed Schlenk flask, deoxygenated tBA (16 g, 0.12 mol), PMDETA (52 μL, 0.25 mmol), and anisole (4 mL) were added; the reaction mixture was degassed by three freeze—pump—thaw cycles. After the mixture was stirred for 20 min at room temperature, Cu(II)Br (36 mg, 0.25 mmol) was added under N\(_2\), and the flask was placed in a thermostated oil bath at 65 °C. After 10 min, DMDHB (21.7 μL, 0.1 mmol) was injected, and an initial kinetic sample was taken. During the polymerization, samples were removed to analyze conversion by gas chromatography (GC) using anisole as the internal standard and molecular weight by GPC. We stopped the reaction cooling the mixture to ambient temperature and opening the flask to the air. The mixture was then diluted with 100 mL of THF, passed through a neutral alumina column, concentrated by rotary evaporation, and precipitated into 800 mL of a MeOH/H\(_2\)O (80/20 vol ratio) solution. The isolated polymer was precipitated.
from THF into MeOH/H2O (80/20 vol ratio) three times to remove the remaining monomer and dried under a vacuum at 40 °C.

**Synthesis of the pODMA-b-pBA-b-pODMA Triblock Copolymer.** In a 25-mL Schlenk flask, Cu(II)Cl2 (1.22 mg, 0.009 mmol), the pBA difunctional macroinitiator (1.91 g, 0.045 mmol), and dNbpy (81.5 mg, 0.2 mmol) were added. After the flask was vacuumed and back-filled with nitrogen three times, deoxygenated ODMA (6.5 g, 20 mmol) in 10 mL of toluene were added. After the solution was stirred for 1 h at ambient temperature, Cu(II)Cl (8.9 mg, 0.09 mmol) was added, and the flask was placed in a thermostated oil bath at 90 °C. An initial kinetic sample was taken, and samples were removed to analyze conversion by NMR and molecular weight by GPC during the polymerization. We stopped the reaction by cooling the mixture to ambient temperature and opening the flask to the air. The kinetic sample was taken, and samples were removed to analyze conversion by NMR and molecular weight by GPC during the polymerization. We stopped the reaction by cooling the mixture to ambient temperature and opening the flask to the air. The mixture was then diluted with 30 mL of THF, passed through a neutral alumina column, concentrated by rotary evaporation, and precipitated into 600 mL of hexane. The isolated polymer was precipitated from THF into hexane five times to remove the remaining ODMA monomer and dried under a vacuum at 25 °C. The molecular characteristics of the triblock copolymers are shown in Table 1.

### Table 1. Molecular Characteristics of the pODMA-b-pBA-b-pODMA Triblock Copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mₐ (g/mol)</th>
<th>Mₐ (g/mol)</th>
<th>Mₐ (g/mol)</th>
<th>wt %</th>
<th>f_{pODMA}</th>
<th>Mₐ/Mₘ</th>
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<tbody>
<tr>
<td>S14</td>
<td>94900</td>
<td>11400</td>
<td>83500</td>
<td>0.12</td>
<td>0.14</td>
<td>1.18</td>
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<tr>
<td>S39</td>
<td>112600</td>
<td>39400</td>
<td>73200</td>
<td>0.35</td>
<td>0.39</td>
<td>1.11</td>
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<tr>
<td>S45</td>
<td>94900</td>
<td>38900</td>
<td>56000</td>
<td>0.41</td>
<td>0.45</td>
<td>1.18</td>
</tr>
<tr>
<td>S47</td>
<td>28100</td>
<td>12100</td>
<td>16000</td>
<td>0.43</td>
<td>0.47</td>
<td>1.18</td>
</tr>
<tr>
<td>S52</td>
<td>105200</td>
<td>50500</td>
<td>54700</td>
<td>0.48</td>
<td>0.52</td>
<td>1.17</td>
</tr>
<tr>
<td>S58</td>
<td>16000</td>
<td>8000</td>
<td>7400</td>
<td>0.54</td>
<td>0.58</td>
<td>1.25</td>
</tr>
<tr>
<td>S65</td>
<td>71000</td>
<td>43000</td>
<td>27700</td>
<td>0.61</td>
<td>0.65</td>
<td>1.29</td>
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<tr>
<td>S81</td>
<td>108800</td>
<td>84900</td>
<td>23950</td>
<td>0.78</td>
<td>0.81</td>
<td>1.15</td>
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<tr>
<td>S90</td>
<td>94900</td>
<td>84500</td>
<td>10400</td>
<td>0.89</td>
<td>0.90</td>
<td>1.22</td>
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<tr>
<td>S94</td>
<td>124200</td>
<td>115500</td>
<td>8700</td>
<td>0.90</td>
<td>0.94</td>
<td>1.35</td>
</tr>
</tbody>
</table>

a NMR, b ρ_{pODMA} = 0.8556 g/cm³; f_{pODMA} = 1 g/cm³.

#### III. Results and Discussion

**Bulk Morphology.** Before we proceed with the bulk and surface morphologies, we would like to briefly comment on the mechanical properties of the copolymers. The surface morphology, as explored by TMAFM, is sensitive to the inherent differences in the mechanical loss of the two blocks as well as that of the particular phases formed. The mechanical loss, in particular, can best be studied by probing the shear modulus as a function of temperature and frequency. The shear moduli of the triblock copolymers S94 (f = 0.94) and S14 (f = 0.14), which have nearly antisymmetric compositions, display some common features as well as some differences (Figure 1). For S14, the degree of side-chain crystallinity is very low, and the high modulus of the glassy pBA block precludes the identification of the corresponding Tₘ in the DSC trace, however, the pODMA side-chain melting temperature can be identified by the small endothermic peak around 303 K. Upon an increase in temperature, the loss modulus goes through a maximum and crosses with the storage modulus at 320 K, identifying the pBA glass temperature. At even higher temperatures, the moduli develop a plateau at T ≈ 400 K, suggesting the existence of an entangled transient network. Notice the parallel behavior of the moduli at T > 400 K and that the system does not flow even up to the highest temperature investigated (T ≈ 423 K), which further suggests the existence of a microphase-separated structure. For S94, rich in the crystallizable block, the features are similar; however, there are two exceptions: (1) the discontinuous decrease of the moduli at the apparent melting temperature (that is in agreement with the position of the endothermic peak in DSC) and (2) the lower plateau modulus (at ~3 × 10⁸ Pa) reflecting an ordered melt in a “super soft” state. The detailed rheological investigation will be the subject of a separate investigation.

For this study it suffices to mention that (1) there is a significant contrast between the glassy pBA and the pODMA melt, (2) there is no flow up to 400 K, and...
The dynamic shear storage ($G'$; open symbols) and loss ($G''$; filled symbols) moduli for two copolymers: S94 (squares) and S14 (circles). The vertical lines indicate the pODMA melting temperature (red) and the pBA glass temperature (blue). (Bottom) The corresponding DSC traces (rate: 10 K/min) during the second heating run for S94 (red) and S14 (blue).

Figure 2. SAXS curves from four copolymers: S14 ($f = 0.14$, $T = 303$ K): arrows indicate peaks at positions 3$^{1/2}$, 4$^{1/2}$ relative to the main peak; S39 ($f = 0.39$, $T = 313$ K): arrows indicate peaks at positions 2:3:4:5 relative to the main peak; S47 ($f = 0.47$, $T = 313$ K): arrows indicate peaks at positions 2:3 relative to the main peak; and S81 ($f = 0.81$, $T = 313$ K): arrows indicate peaks at positions 4$^{1/2}$, 7$^{1/2}$ relative to the main peak.

(3) no order-to-disorder transition exists for the two copolymers investigated.

Next we investigate the phase state of the copolymers in bulk using $T$-dependent SAXS. Figure 2, provides representative scattering curves for some triblock copolymers. The scattering contrast (see below) of the two blocks is rather low; nevertheless, it is still possible to identify the microdomain morphology. The arrows indicate the positions of the higher-order reflections with respect to the primary peak at $q^*$; for S14 ($f = 0.14$), some broad peaks with relative (approximate) positions at 1:3$^{1/2}$, 4$^{1/2}$ suggest distorted hexagonally packed cylinders (on the basis of nearest neighbors correlations) as the microdomain morphology. For S39 ($f = 0.39$), the peaks are at relative positions with ratios 1:2:3:4:5, revealing lamellar microdomain morphology. A similar morphology is obtained for the S47 ($f = 0.47$) triblock copolymer (peaks with relative positions at 1:2:3). Notice the large shift in $q^*$, which reflects the lower molecular weight of the sample. For S81 ($f = 0.81$), peaks with relative positions at 1:4$^{1/2}$, 7$^{1/2}$ are observed, suggesting hexagonally packed cylinders. The domain spacings from SAXS are summarized in Table 2.

The SAXS investigation can provide not only the microdomain morphology and the relevant spacings but it also aids in the construction of the complete phase diagram by employing the scattering curves from the disordered phase (correlation hole scattering). In a SAXS experiment, the scattered intensity due to concentration fluctuations, $I_s$, is related to the static structure factor $S(q)$, through: $I_s = \Delta n^2 V S(q)$, in which $\Delta n = n_A - n_B$ and is the difference in the electron density of the two blocks, and $V$ is the volume of the chain. In the context of the MPT, the structure factor of homogeneous block copolymers arising from composition fluctuations has the general form

$$\frac{N}{S(q)} = F(x,f) - 2\chi N$$

in which $F(x,f)$ is given by the general expression

$$F(x,f) = \frac{g_{AA} + g_{BB} + 2g_{AB}}{g_{AA}g_{BB} - g_{AB}^2}$$

For an A-B-$\Lambda$ triblock copolymer with corresponding block fractions of $f_1$, $f_2$, and $f_3$ these functions take the form

$$g_{AA} = g_D(f_1 - x) + g_D(f_2 - x) + g_D(3x) + g_D(1 - x)$$
$$g_{BB} = g_D(f_2 - x)$$
$$g_{AB} = \frac{1}{2}[g_D(1 - f_1 - x) + g_D(1 - f_3 - x) - g_D(f_1 - x) - g_D(f_3 - x) - 2g_D(f_2 - x)]$$

in which $g_D$ is the Debye function:

$$g_D(x) = \frac{2}{x^2}[\sin x - x e^{-x} - 1]$$

![Table 2. Types of Nanostructure and Characteristic Spacings from SAXS and AFM](image)
and \( x = q^2 R_g^2 \) (\( R_g \) is the unperturbed radius of gyration).

In the present case (symmetric copolymer, i.e., \( f_1 = f_2 \)), the mean-field phase diagram predicts a first-order transition to body-centered cubic (bcc) spheres for all compositions \( f = 0.5 \) and order-to-order transitions from bcc to hexagonal (hex) to lamellar (lam) with increasing \( \chi N \). However, in contrast to A–B diblock copolymers, the mean-field phase diagram of A–B–A triblock copolymers is highly asymmetric as a result of the higher entropic penalty in deforming the central B blocks to accommodate the two outer blocks into the A domains.

We have used the above mean-field structure factor to describe the scattered intensity of the S88 (\( f = 0.58 \), \( M_w = 16000 \) g/mol) in the disordered state. The resulting fits to the disordered \( I(q) \) are shown in Figure 3, together with the \( \chi N(T) \) dependence. Notice that the theory satisfactorily describes the experimental points, except in the low-\( q \) range, in which the theory predicts \( S(q \rightarrow 0) = 0 \) (incompressible system). The thus extracted interaction parameter displays a strong \( T \) dependence as \( \chi = 0.12 + 38/T \) (obtained from a linear fit to the highest temperatures that are least prone to fluctuations\(^{12,36} \)), resulting in \( \chi N = 18.2 \) at the transition, which is in agreement with the MFT predictions (\( f = 0.58 \)). On the basis of this \( \chi (T) \), a mean-field phase diagram was constructed and is shown in Figure 4. The phase diagram is dominated by the lamellar phase, with smaller regions of hexagonally packed cylindrical and cubic phases (i.e., the classical phases). We mention here that the introduction of fluctuation corrections\(^{34} \) using the angle-dependent Hartree approximation, gives rise in asymmetric phase diagrams with only a small region of bcc for symmetric triblock copolymers. For symmetric triblock copolymers with \( N = 10^6 \), the bcc phase is completely absent, and the corrected phase diagram allows for direct transitions from the disordered to the lam and hex phases. In addition, order-to-order transitions are also predicted for weak/intermediate segregation. For the triblock copolymer investigated herein, no order-to-order transitions were found, which is in agreement with the strong segregation picture. In addition, the double gyroid phase was not observed because of the limited systems existing in weak segregation and within the lam/hex phase boundaries. With the exception of S58 and S47, which are within the weak segregation regime, the high molecular weights and the strong \( \chi (T) \) render the remaining copolymers strongly segregated. In this regard, it is of interest to compare the bulk with the surface morphology of both the strongly and the weakly segregated triblock copolymers and to compare the corresponding microdomain spacings.

**Surface Morphology.** The surface morphologies of all of the copolymers were investigated using TMAFM. In this work, we took advantage of the well-known ability of TMAFM to differentiate regions of materials exhibiting different levels of energy dissipation during intermittent tip–sample contacts. This is accomplished by mapping (along with topography) the phase of cantilever oscillation, which is sensitive to energy flow in the tip–sample system. These maps are then displayed in false color scales in which areas of more pronounced phase shift (energy dissipation) appear darker\(^{29,37} \). Because of this ability, AFM became a particularly popular tool in visualizing the phase structure in phase-separated block copolymers. One of the challenges of AFM in the characterization of block copolymer morphologies is the extent to which the boundary conditions present in thin/ultrathin films “skew” the surface morphology in comparison to that of the bulk. Providing at least a partial answer to this question was one of the goals of this study.

Interestingly, despite the above concerns about the sensitivity of morphology to boundary conditions, in all cases the morphologies observed in TMAFM images were in good agreement with the morphologies determined by SAXS. For example, for the triblock copolymer S14, which possesses the lowest volume fraction \( f_{\text{ODMA}} = 0.14 \), the AFM phase images shown in Figure 5a revealed the nearly hexagonal pattern of darker (higher mechanical loss) round features dispersed in a brighter (lower mechanical loss) matrix. On the basis of the results of our previous work\(^{37} \), these features were identified as phase-separated domains of pODMA surrounded by the pBA matrix. Their round appearance and hexagonal packing symmetry point to either spherical or cylindrical morphologies (with cylinders normal to the surface). Annealing at 353 K for 1 h helped to identify the exact microdomain morphology (Supporting Information); under these conditions, a fraction of short cylinders appeared parallel to the surface, revealing that the surface morphology is the one suggested by SAXS. Samples with ODMA content of \( f = 0.39–0.65 \) (Figure 5b–g) all showed characteristic striped patterns.
of alternating bright and dark areas, which is in excellent agreement with the bulk lamellar structures found in SAXS. These lamellar patterns were highly regular and exhibited little branching, with the exception of S58 (f = 0.58), for which the stripes were much finer and highly curved. In the copolymers with f > 0.8 (Figure 5h–j), there was a phase inversion, and pBA became the minority dispersed phase, as manifested in the AFM images showing round bright domains surrounded by a dark matrix. The AFM morphology for the S81 copolymer (f = 0.81; Figure 5h) revealed hexagonally packed cylinders (annealing results in some cylinders lying parallel to the surface), which is in agreement with the SAXS morphology. The more asymmetric copolymers S90 (f = 0.90; Figure 5i and S94 (f = 0.94; Figure 5j), exhibited, according to SAXS, a cubic morphology. Apparent hexagonal order in the AFM images of these copolymers could indicate that the spherical domains underwent surface reconstruction into hexagonal packing, which is expected for 2D spherical systems.

The AFM surface morphologies exhibited enough periodicity to be analyzed with the aid of a 2D Fourier transform (FT). Subsequently, the 2D FT maps were radially averaged to produce magnitude plots analogous to the scattering patterns. After the spatial frequency scale was recalculated to scattering vector units (2πd), these curves could be overlaid with the corresponding SAXS data (Figure 6), and the corresponding domain spacings are given in Table 2. As shown in Figure 6 and in Table 2, there is good agreement between the domain spacings.

One marked exception here was sample S65, for which the spacing determined by AFM was 25% larger than that obtained from SAXS. One possible explanation of this discrepancy could involve the tilting of the lamellae with respect to the sample surface or the frustration effects outlined in the introduction.

Theories in the strong segregation limit1,2 (SSL, χN ≫ 10) predict extended block conformations, as opposed to the unperturbed (Gaussian) limit, which has a scaling of the domain spacing as d ≈ N^0, with δ ≈ 1/2. Chain extension results from the combined effects of the localization of the block junction points at a narrow interface and the requirement for an overall uniform density within the domains. Helfand and Wasserman (HW)38,39 and subsequently Semenov (S),40 treated the chain extension in strongly segregated block copolymers through different approaches and predicted that the domain period in the limit χN → ∞ should scale as

\[
d ≈ N^\delta \chi^\nu
\]  

(5)
in which $\delta \approx 9/14$ and $\nu = 1/7$ (HW), and $\delta \approx 2/3$ and $\nu = 1/6$ (S). In the latter approach, the stretched chains were envisioned as the chains in grafted polymer brushes. The high incompatibility of the blocks ($\gamma N \approx 100$) makes the comparison of the SAXS (and AFM) domain spacing with the above scaling predictions feasible. The molecular weight dependence of the domain spacing is shown in Figure 7 for the symmetric (S47, S52) and the nearly symmetric (S45, S58) block copolymers in a double logarithmic representation. Notice the good agreement of the surface and bulk spacings, with the exception of S58 in which the AFM value is higher than the SAXS. This difference could originate from (1) the highly curved lamellae in AFM and (2) the lower molecular weight of the block copolymer (weak segregation limit), suggesting the influence of surface effects. Nevertheless, the SAXS domain spacing scales as $\delta \approx 0.64$, which is in accord with the predictions of the SSL theories (AFM alone results in a somewhat lower value, $\delta \approx 0.56$). In addition, we have calculated the effective domain size for each of the phases from the AFM images. The discussion of the size of the effective domains can be found in Supporting Information.

Having established the microdomain morphology, in a future study we will report on the dynamics of the same triblock copolymers as a function of temperature and pressure. More specifically, we will report on the effect of pressure on increasing the crystallization (pODMA) and glass (pBA) temperatures of the two blocks, along with the consequences of this effect on their thermoplastic behavior.

IV. Conclusions

ATRP was used to synthesize a series of $A-B-A$ triblock copolymers containing pODMA as the side-chain crystalline segments and pBA as the amorphous segments. The bulk and surface morphologies were studied using SAXS and AFM, respectively, aiding (1) in the comparison of the surface and bulk morphologies and in constructing the relevant phase diagram and (2) in the comparison of the corresponding domain spacings.

In the SAXS study, the MFT was employed to obtain the segment–segment interaction parameter and to construct the bulk phase diagram that is composed from the classical structures: cubic, cylindrical, and lamellar. For the majority of the investigated block copolymers, $\gamma N \approx 100$, suggesting strong segregation, which is in accord with the absence of any order-to-order transitions and the absence of nonclassical phases.

The difference in the mechanical elasticity of the different blocks gave rise to well-resolved microdomain structures in TMAFM images. The surface morphologies of the samples that were prepared by drop casting and visualized with TMAFM were in very good agreement with the SAXS results. Quantitative agreement was found between SAXS and AFM, not only for the phase state, but also with respect to the domain spacing (scaling with a molecular weight as $d \approx N^{0.64}$), indicating strong segregation and extended chains. Such good agreement suggests that, for the studied copolymers, substrate and boundary effects did not result in the formation of “nonbulk” morphologies, and the drop casting method produced well-equilibrated samples. The latter assertion was supported by the observation that samples prepared by drop casting showed little change upon annealing. In contrast, samples prepared by spin coating (i.e., under conditions much less favorable for reaching equilibrium) were observed to produce less sharply defined morphologies, which, upon annealing, tended to evolve toward those observed in the case of drop casting. All this suggests that strongly segregating systems, like the ones under study here, are likely to be less prone to be skewed by the boundary conditions and to be more sensitive to kinetic factors mediated by solidification conditions.

From a methodological perspective, the results presented here demonstrate the benefits of SAXS (reciprocal space) and AFM (real space) combination in the studies of the phase structure of block copolymers, especially those exhibiting strong segregation behavior. The SAXS–AFM “tandem” appears to be particularly promising in view of recent developments in grazing incidence techniques (GISAXS), especially those utilizing bright synchrotron sources.

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Supporting Information Available: Material synthesis and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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