

## Estimating the Segregation Strength of Microphase-Separated Diblock Copolymers from the Interfacial Width

### Adam B. Burns<sup>1</sup>, Dane Christie<sup>2</sup>, William D. Mulhearn, Richard A. Register<sup>2</sup>

<sup>1</sup>Materials Science and Engineering Division, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899 <sup>2</sup>Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey, 08544 Correspondence to: A. B. Burns (E-mail: abburns0@gmail.com)

Received 30 January 2019; revised 19 May 2019; accepted 22 May 2019; published online 7 June 2019 DOI: 10.1002/polb.24848

**ABSTRACT**: The ever-growing catalog of monomers being incorporated into block polymers affords exceptional control over phase behavior and nanoscale structure. The segregation strength,  $\chi N$ , is the fundamental link between the molecular-level detail and the thermodynamics. However, predicting phase behavior mandates at least one experimental measurement of  $\chi N$  for each pair of blocks. This typically requires access to the disordered state. We describe a method for estimating  $\chi N$  from small-angle X-ray scattering measurements of the interfacial width between lamellar microdomains,  $t_{xr}$  in the microphase-separated melt. The segregation strength is determined by comparing  $t_x$  to self-consistent field theory calculations of the intrinsic interfacial width,  $t_{y}$  as a function

**INTRODUCTION** Block copolymers have garnered tremendous attention due to their inherent ability to self-assemble.<sup>1</sup> Selfassembly reflects the balance between the enthalpic penalty of interblock segmental contacts and the entropic penalty associated with chain stretching. Ordered nanostructures, the periodicity of which is commensurate with the size of the chain ( $\approx 10$  nm to  $\approx 100$  nm), result. The canonical parameters describing the phase behavior of A–B diblock copolymers<sup>2</sup> are the volume fraction of one of the blocks,  $\phi_A$ , and the segregation strength,  $\chi N$ . The total number of segments, N, is proportional to the number-average molecular mass,  $M_n$  ( $N = M_n/(\rho N_{Av} v_{ref})$ , where  $\rho$  is the mass density,  $N_{Av}$  is Avogadro's number, and  $v_{ref}$ is the volume of a segment). The temperature-dependent Flory-Huggins  $\chi$  parameter describes the energy penalty for pairwise contacts between A and B segments and is thus the fundamental connection between the chemistry and the phase behavior. Despite decades of experience,<sup>3–6</sup> a comprehensive theory for predicting  $\chi$  for a pair of blocks has proven elusive. Even when  $\chi$ values have been measured for the two blocks in question (A and B) against a common reference component, C,  $\chi_{A-B}$  cannot reliably be calculated from  $\chi_{A-C}$  and  $\chi_{B-C}$ .<sup>4-6</sup> We pause to emphasize that the numerical value of  $\chi$  depends on the arbitrary choice of  $v_{ref}$ , while the quantity  $\chi N$  does not. For this

of the mean-field  $\chi N$ . The method is validated using a series of independent experimental measurements of  $t_x$  and  $\chi N$ , measured via the order–disorder transition temperature,  $T_{ODT}$ . The average absolute relative difference between  $\chi N$  calculated from  $t_x$  and the value calculated from  $T_{ODT}$  is a modest 11%. Corrections for nonplanarity of the interfaces are investigated but do not improve the agreement between the experiments and theory. Published 2019. This article is a U.S. Government work and is in the public domain in the USA. J. Polym. Sci., Part B: Polym. Phys. **2019**, *57*, 932–940

**KEYWORDS:** block copolymers; microphase separation; polymer interfaces; self-consistent field theory; small-angle X-ray scattering

reason, the bulk of this work will refer to  $\chi N$ ; however,  $\chi N$  and  $\chi$  are functionally equivalent in this context.

At present, it remains necessary to experimentally measure  $\chi N$ (or equivalently  $\chi$ ) for each new pair of blocks. Two approaches, typically applied to compositionally symmetric ( $\phi_A \approx \frac{1}{2}$ ) diblocks, dominate the literature. The first is to locate an orderdisorder transition temperature (ODT) at which point the diblock transitions from the ordered, microphase-separated state to the disordered state. The value of  $\gamma N$  at the ODT,  $(\gamma N)_{ODT}$ , is taken from theory, for example, self-consistent field theory (SCFT). The  $T_{\text{ODT}}$  is readily identified via temperature-dependent small-angle X-ray $^{5-8}$  or neutron<sup>9</sup> scattering (SAXS or SANS, respectively), depolarized light scattering,<sup>8</sup> or rheological<sup>3,9,10</sup> measurements. The second approach is to extract  $\chi$  by fitting the disorderedstate structure factor (measured by SAXS or SANS) to a model, most commonly the random phase approximation (RPA) developed by Leibler.<sup>11</sup> Both SCFT and the RPA yield the mean-field  $\gamma N$ . Though the second method does not require direct access to the ODT, the intensity of the disordered-state structure factor peak is strongly attenuated far from the ODT. Thus, measuring  $\chi N$  for a new pair of blocks using either of these approaches requires the preparation of a diblock copolymer that has a thermally accessible ODT or permits access to the disordered state

Additional Supporting Information may be found in the online version of this article.

Published 2019. This article is a U.S. Government work and is in the public domain in the USA.

near the ODT. The synthesis of such a material can be challenging and often necessitates the iterative synthesis of a series of diblocks with varying  $M_n$ .

Few attempts have been made to measure  $\gamma N$  from diblocks in the ordered state,<sup>12-14</sup> Prior work made use of theoretical predictions for the domain spacing, d, and the width of the interfacial mixing region, *t*, in the lamellar phase as a function of  $\gamma N$ ; these predictions were made by SCFT or the earlier strong segregation theory (SST, valid for  $\chi N \gg (\chi N)_{ODT}$ ). Scherble et al.<sup>12</sup> estimated  $\gamma$  for a series of methacrylate-based diblocks from the interfacial width measured by neutron reflectivity (NR), after applying a correction for the effect of thermocapillary waves. A direct comparison between  $\gamma N$  determined from the interfacial width in the ordered state and  $\chi N$  determined by one of the aforementioned methods was not available; however, the authors noted that the capillary wave correction produced a large uncertainty in  $\chi$ (50–100%). Ren et al.,<sup>13</sup> and later Davidock et al.,<sup>14</sup> estimated  $\chi$ from SAXS measurements of the domain spacing for two series of diblocks, each derived from a single precursor via a mild postpolymerization fluorination route; the segregation strength was tuned by varying the fluorination level. Their analyses made use of the analytical SST result,  ${}^{15} d/(bN^{1/2}) \sim (\chi N)^{1/6}$ , where b is the average statistical segment length for the diblock. The challenge with this approach is that the dependence of *d* on  $\chi N$  is weak, so the estimate of  $\chi N$  is highly sensitive to the value of *b*; each 1% uncertainty in *b* produces a 6% uncertainty in  $\chi N$ . An accurate measure of b for a new polymer is not trivial, as it typically requires SANS measurement on partially deuterated samples. Ren et al.<sup>13</sup> executed such SANS measurements, yet still found that for the fully fluorinated polymer, the  $\chi$  value derived from *d* was 1.7× larger than the value measured via the  $T_{\text{ODT}}$  approach, even when the latter was corrected for the effect of fluctuations.

The present report builds on these previous efforts to determine  $\gamma N$  in the ordered state. We describe a method of estimating  $\gamma N$ from SAXS measurements of the width of the interfacial mixing region between ordered lamellae in the melt state,  $t_{x}$ , of (nearly) compositionally symmetric diblocks. The segregation strength is then calculated by comparing the experimental  $t_x$  to the SCFT prediction of the intrinsic interfacial thickness,  $t_i$ , as a function of the mean-field  $\chi N$ . Crucially, the procedure requires no additional measurements or input parameters. We advance previous work by (a) advocating the use of the integrated intensities of SAXS reflections as a robust technique for measuring  $t_{x_1}$  and (b) critically examining the validity of the approach by compiling independent measurements of  $t_x$  and  $\chi N$  for a number of diblock chemistries and molecular masses. This method provides a reliable estimate of  $\chi N$ , which agrees well with estimates from the  $T_{\text{ODT}}$  approach without requiring access to the disordered state. Several corrections for nonplanarity of the lamellar interfaces are investigated, but none of them improves the accuracy of the approach.

#### **EXPERIMENTAL**

SCFT calculations were conducted using the open-source polymer self-consistent field code.<sup>16</sup> Composition profiles for A–B diblock

copolymers were discretized into 128 points and expressed as the local volume fraction of A segments,  $\phi_A(\tilde{z})$ , where  $\tilde{z}$  is the coordinate normal to the lamellar interfaces normalized by the domain period. Profiles were calculated as a function of the mean-field segregation strength,  $\chi N$ , using a global volume fraction of  $\phi_A = \frac{1}{2}$  and equal statistical segment lengths,  $b_A = b_B$ . The statistical segment length is related to the radius of gyration by  $R_g^2 = b^2 N/6$ . The calculations were repeated for conformationally asymmetric diblocks with  $b_A/b_B = [(R_g^2/M_n)_A/(R_g^2/M_n)_B]^{1/2} = 1.3$  and 1.6 (Fig. S1), covering the experimentally relevant range of conformational asymmetries in the present work.

The domain-period-normalized interfacial widths,  $t_i/d$ , were calculated using eq (1) (where *t* represents either  $t_i$  or  $t_x$ ), which assumes nothing about the detailed shape of the composition profile and is thus applicable across the entire range of  $\chi N$ .

$$\frac{t}{d} \equiv \left(\frac{d\phi_A(\widetilde{z})}{d\widetilde{z}}\right)^{-1} \bigg|_{\phi_A(\widetilde{z}) = 1/2} \tag{1}$$

Experimental measurements of the domain-period-normalized interfacial widths,  $t_x/d_1$  (consistent with eq (1)) for a number of lamellar block copolymers have been compiled from the literature or measured in this work. The following interfacial widths were calculated using the melt-state SAXS structure factor peak analysis described herein: (a) diblocks containing a random copolymer block of hydrogenated medium-vinyl polyisoprene (hPI) with either polystyrene (PS) or polyvinylcyclohexane: hPI-P(SrhI), PE-P(SrhI), and PE-P(VCHrhI), where PE is linear low-density polyethylene from hydrogenated low-vinyl polybutadiene;<sup>17</sup> (b) hydrogenated ring-opened polynorbornene-based (hPN) diblocks hPPhN-LPE, hPPhN-hPHxN, and hPPhN-hPiPrN, where Ph, Hx, and iPr denote phenyl, n-hexyl, and isopropyl substituents in the 5-position, respectively, and LPE is linear PE from hydrogenated ring-opened polycyclopentene;<sup>6</sup> and (c) a poly(n-butyl methacrylate)-b-poly(methyl methacrylate) diblock (PBMA-PMMA).<sup>18</sup> In all cases, SAXS measurements were conducted in the melt.

Thin film measurements of the interfacial width of PBMA–PMMA,<sup>12</sup> PS–PMMA,<sup>19</sup> and PS-*b*-poly(2-vinylpyridine)<sup>20</sup> (PS–P2VP), made by NR, and PS-*b*-1,4-polyisoprene<sup>21</sup> (PS–P1), made by X-ray reflectivity (XRR), are also included, as is a measurement of the interfacial width of a PS–PMMA thin film by soft X-ray scattering (SoXS, which is functionally equivalent to the SAXS measurements reported herein).<sup>22</sup> All of the thin film measurements were reported at room temperature (below the glass transition temperature of at least one of the blocks) following extensive annealing in the melt and quenching to room temperature.

The interfacial widths of the polynorbornene-based series<sup>6</sup> have not been reported previously. SAXS patterns of hPPhN–LPE, hPPhN–hPHxN, and hPPhN–hPiPrN were collected using an Anton-Paar compact Kratky camera driven by a PANalytical PW3830 X-ray generator with a long-fine-focus Cu tube producing Cu K $\alpha$  radiation ( $\lambda$  = 0.15418 nm), and equipped with a



temperature-controlled sample stage, and an MBraun OED-50 M position sensitive detector. The raw data were corrected for detector linearity and sensitivity, empty beam scattering, sample thickness and transmittance, and desmeared for slit length.<sup>23</sup> The scattering patterns were placed on an absolute intensity scale using a PE standard.<sup>24</sup> Absolute intensities,  $I/I_eV$ , were plotted versus the magnitude of the momentum transfer vector,  $q = (4\pi/\lambda) \sin \theta$ , where  $\lambda$  is the wavelength of the incident radiation and the scattering angle is 2 $\theta$ .

The mean-field segregation strength for each diblock pair has been quantified independently using the  $T_{\text{ODT}}$  approach by invoking the SCFT prediction for  $\chi N$  at  $T_{ODT}$ ,  $(\chi N)_{ODT}$  = 10.5 for  $\phi_A$  =  $\frac{1}{2}$ . Multiple  $T_{\text{ODT}}$  values (for diblocks of different  $M_{\text{p}}$ ) have been reported for hPI-P(SrhI), PS-PMMA, PS-P2VP, and PS-PI; in these cases, the reported temperature dependence of  $\chi$  was used to calculate  $\chi N$  at the temperature corresponding to the  $t_x/d$  measurement,  $T_x$ . For the thin film measurements on PS-PMMA, PS-P2VP, and PS-PI,  $T_x$ was taken as the annealing temperature. For the remaining diblock pairs, a thermally accessible  $T_{\text{ODT}}$  has been reported for a single diblock with molecular mass  $M_{n,ODT}$ . In these cases, the segregation strength for a diblock of the same chemistry and arbitrary molecular mass,  $M_n$ , is given by  $\chi N = (\chi N)_{ODT} [M_n / M_{n,ODT}]$ . The difference between  $\chi(T_x)$  and  $\chi(T_{ODT})$  is necessarily neglected (except for hPPhN–LPE, for which  $T_x = T_{ODT}$ ). Further details are provided in the Supporting Information.

### **RESULTS AND DISCUSSION**

SST was first used to describe the interfacial mixing region between immiscible polymers.<sup>25–27</sup> Semenov later expanded the SST treatment to account for the effects of finite molecular mass and block connectivity on the intrinsic interfacial width between block copolymer microdomains (eq (2)).<sup>15</sup> Theoretical treatments commonly nondimensionalize by the unperturbed rootmean-square end-to-end distance,  $bN^{1/2}$ . This is inconvenient in practice since the chain statistics are not known for new materials. To alleviate this concern when comparing theory and experiments, we instead normalize  $t_i$  and  $t_x$  by the lamellar period, d, as d can be measured directly on the ordered block copolymer by SAXS or reflectivity, and its value similarly incorporates the effects of chain stiffness (see Fig. S1).

$$\left(\frac{t_i}{d}\right)_{\rm SST} = \left(\frac{\pi}{2\sqrt{6}\chi N}\right)^{2/3} \left[1 + \frac{4}{\pi} \left(\frac{3}{\pi^2 \chi N}\right)^{\frac{1}{3}}\right]$$
(2)

Though convenient, the analytical SST result is rigorous only in the strong segregation limit ( $\chi N \gg (\chi N)_{ODT}$ ), which is rarely achieved in practice. SCFT provides a more accurate description of the microphase-separated state spanning the weak, intermediate, and strong segregation regimes.<sup>2,16,28</sup> Here, we utilize SCFT to calculate the domain-spacing-normalized intrinsic interfacial width,  $t_i/d$ , across the experimentally relevant range of  $\chi N$ . Composition profiles,  $\phi_A(\tilde{z})$ , were computed as a function of  $\chi N$  using the software package developed by Arora et al.<sup>16</sup> Example profiles

are shown in Figure 1. The normalized interfacial widths,  $t_i/d$ , calculated using eq (1) (red lines in Fig. 1), are in excellent agreement with those originally reported by Matsen and Bates.<sup>2</sup> The results (solid line in Fig. 2(a)) show a marked increase in  $t_i/d$  near the ODT (SCFT predicts ( $\chi N$ )<sub>ODT</sub> = 10.5) as compared with the SST prediction (dashed line). Germane to the ensuing analysis is the difference between the SCFT  $\chi N$  and the SST  $\chi N$  at a given value of  $t_i/d$ , which can be large even in the intermediate segregation regime.

Although  $t_i/d$  was calculated for a single global composition,  $\phi_A = \frac{1}{2}$ , the following analysis is robust with respect to experimental variations in  $\phi_A$ . The SAXS analysis (vide infra) has been developed for the lamellar phase where the phase boundary,<sup>2</sup> ( $\chi N$ )<sub>ODT</sub>, is a weak function of  $\phi_A$ . For composition asymmetries of  $\phi_A = 0.5 \pm 0.05$ , ( $\chi N$ )<sub>ODT</sub> is increased by only 2%, which would in turn shift the theoretical  $t_i/d$  curves to higher  $\chi N$  by the same amount. Refer to the Supporting Information for additional discussion.

Reflectivity<sup>12,19–21</sup> and SAXS<sup>29–37</sup> measurements have long been used to experimentally probe interfacial widths in block copolymers. The interfacial width can be assessed from the decay of the reflected or scattered intensity with increasing wave vector magnitude, q. Broader interfaces cause the intensity to decay more rapidly. Reflectivity is well suited to systems with parallel planar interfaces, such as thin films of block copolymer lamellae oriented parallel to the film surfaces. NR provides excellent sensitivity, but requires access to a neutron source, and often the costly



**FIGURE 1** Half-domain composition profiles at  $\chi N = 12$  (a),  $\chi N = 25$  (b), and  $\chi N = 70$  (c) from SCFT calculations. Red tangent lines and dashed lines demarcate the interfacial mixing region defined by eq (1). [Color figure can be viewed at wileyonlinelibrary.com]



**FIGURE 2** Normalized interfacial width, t/d, versus segregation strength,  $\chi N$  (a) and comparison between  $\chi N$  from  $t_x/d$  and  $\chi N$  from  $T_{ODT}$  (b). Symbols denote experimental measurements; open symbols, the "\*", and the "×" denote values from NR, XRR, and SoXS respectively. All others were measured by SAXS using eq (3). In panel (a), curves represent values of the intrinsic t/d calculated by either SCFT (solid line) or SST (dashed line). In panel (b), the solid line represents perfect agreement between  $\chi N$  from  $t_x/d$  and  $\chi N$  from  $T_{ODT}$ . [Color figure can be viewed at wileyonlinelibrary.com]

preparation of deuterium-labeled samples.<sup>12,19,20</sup> Conversely, XRR does not require specialized samples or facilities, but suffers from relatively poor sensitivity to the internal interfaces due to limited interdomain contrast.

Like XRR, SAXS measurements can be performed on lab-scale equipment (or at a synchrotron) without the need for isotopic labeling. Prior efforts with SAXS focused on determining the interfacial width by analyzing deviations from Porod's Law in the high-q region where the structure factor contribution is negligible.<sup>29–35</sup> However, this analysis is fraught with potential pitfalls. The principal issue is that the scattered intensity in the high-q Porod region is dominated by background scattering (e.g., from thermal density fluctuations within the domains),

ADVANCED SCIENCE NEWS which must be empirically subtracted. The calculated interfacial width is highly sensitive to the details of the background subtraction (the shape of which is not precisely known) and statistical noise in this region.<sup>29,31</sup>

The structure factor peaks are subject to the same intensity decay due to the finite interfacial width but are much more intense, and therefore less sensitive to the background subtraction and counting statistics. Thus, for well-ordered block copolymers, directly analyzing the structure factor peaks provides a more robust approach for assessing the interfacial width. SAXS patterns of lamellar block copolymers are characterized by a series of structure factor peaks in integer *q*-ratios  $(q_n/q^* = 1, 2, 3, \text{ etc.}, \text{ where})$ *n* is the integer peak order and the domain period is  $d = 2\pi/q^*$ ). The interfacial width can be extracted by modeling the composition profile as a Heaviside step function convolved with a Gaussian to impart a finite interfacial width.<sup>30-36</sup> The result of the convolution is the error function composition profile, which, along with the nearly identical<sup>22,31</sup> hyperbolic tangent profile, has long been used to successfully describe polymer-polymer interfaces.<sup>15,25–27,31–34</sup> Moreover, this functional form adequately describes the SCFT profiles (Fig. 1) over a broad range of  $\chi N$ . Using this model, the integrated scattered intensity of the *n*thorder peak is given by:

$$I_n \sim \Delta \rho_e^2 n^{-4} \left[ \sin^2(n\pi \phi_A) \right] e^{-kn^2} \tag{3}$$

where  $\Delta \rho_e$  is the electron density difference between the domains and the damping parameter  $k = 2\pi (t_x/d)^2$ , where  $t_x$  is the experimentally measured interfacial width (see Supporting Information for derivation). The definition of  $t_x/d$  in eq (3) is consistent with the definition in eq (1).<sup>36</sup> The intensity of the even-order peaks is strongly attenuated near  $\phi_A = \frac{1}{2}$  and is thus a sensitive function of  $\phi_A$  near the symmetric condition. If three peaks (two intensity ratios,  $I_2/I_1$  and  $I_3/I_1$ ) can be resolved,  $t_x$  and  $\phi_A$  can be calculated simultaneously, and the resulting value of  $\phi_A$  can be compared against  $\phi_A$  measured by other techniques.<sup>17,38</sup> It is worth noting that eq (3) remains valid for specimens in which the lamellae are macroscopically aligned.<sup>35</sup>

Figure 3 shows example SAXS data from hPHxN-hPPhN in the melt; at least three structure factor peaks are clearly visible. Although the intensity in Figure 3 has been placed on an absolute scale, the present analysis does not require absolute intensity. The data in Figure 3 are acquired on a slit-collimated instrument and desmeared.<sup>23,39</sup> The desmearing procedure tends to amplify background noise, which can complicate the background subtraction, particularly if the peak intensity is weak. This issue can be avoided (at the expense of flux) by using point collimation. Regardless of the source and the type of collimation, the use of the integrated peak intensities in eq (3) minimizes the influence of instrumental factors on the result. The background subtraction was performed for each peak independently using the simple piecewise functional form:  $log(I_{bkg}) = c_1q + c_2$ . The blue dashed lines in Figure 3 represent the local background subtraction and the shaded areas represent the integration regions. To assess the sensitivity of the computed value of  $t_x$  to the functional form of



**FIGURE 3** SAXS pattern of hPHxN–hPPhN in the melt showing the empirical background subtraction [of the form  $\log(l_{bkg}) = c_1q + c_2$ , blue dashed lines] and peak integration regions (shaded) plotted on logarithmic (a) and linear (b) intensity scales. Red triangles denote the structure factor peak positions ( $q_r/q^* = 1, 2, 3, and 4$ ). [Color figure can be viewed at wileyonlinelibrary.com]

the background subtraction, calculations were also performed using the equally simple, but more crude, piecewise form:  $I_{bkg} = c_1'q + c_2'$  (see Fig. S2). The values of  $t_x$  determined using  $I_{bkg} = c_1'q + c_2'$  were systematically larger than those calculated using  $\log(I_{bkg}) = c_1q + c_2$ , but by only 4% on average. Similarly, we find that the sensitivity to the *q*-range employed for determining  $I_{bkg}$  and performing the integrations alters the value of  $t_x$  by only  $\pm 3\%$  on average (standard deviation of three calculations each from SAXS patterns of six diblocks), irrespective of the functional form of  $I_{bkg}$ . These findings confirm that the contribution of the background subtraction to the uncertainty in  $t_x$  is greatly reduced when analyzing the structure factor peaks as compared to the Porod region,<sup>29</sup> despite the lack of *a priori* knowledge of the true form of the underlying background scattering.

Numerous independent measurements of  $t_x/d$  (made by scattering or reflectivity) and the mean-field  $\chi N$  (computed from  $T_{\text{ODT}}$ measurements, as described above) have been compiled to vet our method. These experimental data, which span a variety of chemistries and chain lengths, are plotted with the SCFT and SST predictions in Figure 2(a). The agreement between experiment and theory is generally good. The value of  $\gamma N$  is estimated from the interfacial width by mapping  $t_x/d$  onto the SCFT prediction for  $t_i/d$ (referred to as  $\chi N$  from  $t_x/d$ ). The average of the absolute value of the fractional difference between  $\gamma N$  from  $t_x/d$  and  $\gamma N$  calculated from measured  $T_{\text{ODT}}$  values (for near-symmetric diblocks of the same chemistry but different  $M_{\rm p}$ , referred to as  $\chi N$  from  $T_{\rm ODT}$ ), is 11%. Instances where the experimental  $t_x/d$  values lie above the SCFT prediction for  $t_i/d$ , referred to as positive deviations, yield estimates for  $\chi N$  from  $t_x/d$  which are less than the values of  $\chi N$ from  $T_{\text{ODT}}$ . Both positive and negative (i.e.,  $t_x/d < t_i/d$  and  $\chi N$  from  $t_x/d$  greater than  $\chi N$  from  $T_{ODT}$ ) deviations are observed in Figure 2(a). Positive deviations from the SCFT line are of greater magnitude; the average and maximum discrepancies are 16% and 34%, respectively. Negative deviations have average and maximum discrepancies of 4% and 15%, respectively, and none of the points lies below the SST limit. Figure 2(b) recasts the same experimental data as  $\gamma N$  instead of t/d, and directly compares the values of  $\gamma N$  extracted from the interfacial thickness with values of  $\gamma N$ derived from  $T_{\text{ODT}}$  measurements. Note that the points which lie above the SCFT prediction in Figure 2(a), which we refer to as positive deviations, lie below the solid line in Figure 2(b).

There are several potential sources of the observed discrepancies between  $\chi N$  from  $t_x/d$  and  $\chi N$  from  $T_{ODT}$ . SCFT calculations indicate that conformational asymmetry (i.e.,  $b_A/b_B \neq 1$ ) is not a major contributor; the interfacial width is minimally affected up to at least  $b_A/b_B = [(R_g^2/M_n)_A/(R_g^2/M_n)_B]^{1/2} = 1.6$  (corresponding to the largest experimental asymmetry in this work, see Fig. S1). Some of the disparity between experiment and theory may be attributed to the lack of  $\chi(T)$  correlations for some of the polymers (see Fig. S3), which translates to uncertainty in the x-coordinate in both panels of Figure 2. It is worth pointing out that in principle, it is possible to estimate  $\chi(T)$  from temperature-dependent measurements of the microphase-separated state of a single polymer. Davidock et al.<sup>14</sup> used the theoretical scaling  $d \sim \chi^{1/6}$  to calculate  $\chi(T)$  from SAXS measurements of d as a function of T. Theoretically,  $t_x/d$  is more sensitive to  $\gamma$  than is d alone—SST predicts  $t_i/d \sim \gamma^{-2/3}$ . However, neither approach can be independently validated with the available experimental data.

Positive deviations  $(t_x/d > t_i/d)$  likely stem from the effect of lattice distortions, which cause the scattered (or reflected) intensity to decay more strongly with *q* than the effect of finite interfacial width alone, inflating the apparent  $t_x$  determined by SAXS (or reflectivity).<sup>35,37,40,41</sup> SAXS and reflectivity cannot distinguish local displacements of the lamellar interfaces about their mean positions (nonplanarity or interfacial roughness) caused by thermal motion from the intrinsic segmental mixing. Interfaces between block copolymer lamellae are commonly treated as liquid–liquid interfaces.<sup>12,15,42,43</sup> The mean-square displacement of a liquid–liquid interface due to thermocapillary waves has been modeled as:

$$\langle \zeta^2 \rangle = \frac{k_B T}{2\pi\gamma} \ln\left(\frac{\lambda_{\max}}{\lambda_{\min}}\right)$$
 (4)

where  $k_B$  is the Boltzmann constant,  $\gamma$  is the interfacial tension, and  $\lambda_{min}$  and  $\lambda_{max}$  are the minimum and maximum

The intrinsic (segmental mixing) and capillary contributions to the interfacial width are independent and are thus presumed to add in quadrature. To facilitate comparison between experiment and theory, we use eq (5) to subtract the calculated capillary wave contribution from the experimentally measured interfacial width (the factor of  $2\pi$  ensures consistency with eq (1)).<sup>12,15,42,43</sup>

$$t_{\rm cc} = \left[ t_x^2 - 2\pi \langle \zeta^2 \rangle \right]^{1/2} \tag{5}$$

WWW.POLYMERPHYSICS.ORG

 $t_{cc}^{t}/d$  (symbols) or  $t_{i}/d$  (curves)

0.1

(a)

The normalized, capillary-corrected interfacial width,  $t_{cc}/d$ , for each of the diblocks described above is plotted in Figure 4(a). Figure 4(b) again recasts the experimental data in  $\chi N$  instead of  $t_{cc}/d$ . This treatment of thermocapillary waves does not resolve the disagreement between the data and the SCFT calculations. A large portion of the data is overcorrected. The negative deviations are now 17% on average, and several points lie below the SST prediction. In the extreme case of PS–P2VP, the calculated capillary wave contribution is larger than the measured interfacial width.

One possible explanation is that the strong segregation limit scaling<sup>27</sup>  $\gamma \sim \chi^{1/2}$  is not appropriate. Using a modified form of SCFT for freely jointed chains, Matsen<sup>45</sup> found that the interfacial tension scaling increases from  $\gamma \sim \chi^{1/2}$  to  $\chi^1$  when the interfacial thickness is less than the statistical segment length  $(t_i/b < 1)$ . Though this regime is unlikely to be reached for any of the polymers considered here, this effect does produce an increase in  $\gamma$  (and a commensurate decrease in  $\langle \zeta^2 \rangle$ ) for  $t_i/b \approx 1$ : by a factor of approximately 1.2 for  $\chi = 0.2$ , corresponding to the order of magnitude of  $\chi$  for the polymers considered here. However, reducing  $\langle \zeta^2 \rangle$  by a factor of 1.2 does not significantly reduce the disagreement between the data and the theory in Figure 4.

Another possibility is that the interfaces between lamellae cannot be treated as simple liquid-liquid interfaces. Smectic-A liquid crystals, lamellar assemblies of rod-like molecules, provide an alternative model.<sup>46</sup> In smectic layers, the restoring forces that damp thermal displacements of the interface are the layer compressibility, B, and the splay constant, K, rather than the surface tension.<sup>47,48</sup> Expressions for the mean-square displacement of smectic-A layer interfaces (eqs S13a and S13b) are analogous to eq (4), where  $2\pi\gamma$  is replaced by  $8\pi$ (KB)<sup>1/2</sup> and the cutoff distances  $\lambda_{min}$  and  $\lambda_{max}$  depend on the geometry (thin film vs. isotropic bulk specimen). Amundson and Helfand developed expressions for K and B for diblock copolymers in the weak segregation limit  $(\chi N \gtrsim (\chi N)_{ODT}, eqs$ S14 and S15).<sup>46</sup> Treating the diblock lamellae as smectic-A layers and repeating the preceding analysis produces similar results to the capillary wave treatment (Fig. S4). Disregarding PS-P2VP, which is still severely overcorrected, the average segregation strength,  $\chi N$  (a) and comparison between  $\chi N$  from  $t_{cc}/d$  and  $\chi N$  from  $T_{ODT}$  (b). Symbols and curves are as in Figure 2. [Color figure can be viewed at wileyonlinelibrary.com]

disagreement is 14%, somewhat better than the capillarycorrected result, but still worse than the uncorrected data.

Clearly, the corrections corresponding to these two limiting cases do not improve the agreement between experiment and theory. The fact that the dimensionless ratio  $4(\text{KB})^{1/2}/\gamma$  is order unity strongly suggests that an accurate description of the interfaces requires contributions from both models. Rather than attempt to develop a combined model (which would suffer from the approximations and uncertainties in both), we have instead formulated an empirical correction using the results of a recent<sup>49</sup> simulation study on diblock melts.

Medapuram et al. investigated composition fluctuations (distinct from the thermal undulations discussed to this point) in symmetric diblock copolymer melts using coarse-grained simulations.<sup>49</sup> As part of the study, the apparent interfacial width was quantified through the ratio of the third and first Fourier

JOURNAL OF POLYMER SCIENCE, PART B: POLYMER PHYSICS 2019, 57, 932-940



SST

SCFT

hPI-P(Srhl) PE-P(Srhl)

PE-P(VCHmI)

hPPhN-hPiPrN PBMA-PMMA

hPPhN-LPE

**PS-PMMA** 

PS-P2VP PS-PI

937



# JOURNAL OF POLYMER SCIENCE POLYMER

amplitudes  $(A_3/A_1)$  of the ordered-state composition profiles. This ratio is directly related to our structure factor peak analysis:  $I_n \sim |A_n|^2$ . The apparent interfacial width from the simulations was substantially larger than the SCFT prediction at a given value of  $\chi N$ , with shorter chains deviating more strongly. This apparent interfacial broadening reflects the combined contributions of thermal undulations, mediated by layer compressibility and splay as well as surface tension, and composition fluctuations. We find that normalizing the segregation strength by the appropriate value at the ODT approximately collapses the simulations onto the SCFT prediction except in the immediate vicinity of the ODT (Fig. S5), as discussed below. This empirical normalization is a straightforward way of mapping between the simulations, experiments, and theory.

Until now, we have dealt exclusively with the mean-field segregation strength,  $\chi N$ . However, the simulations were fully fluctuating, which increases the segregation strength at the ODT. For comparison, the experimental fluctuation-corrected segregation strength,  $(\chi N)^{\rm fluc}_{\rm ODT}$  was calculated<sup>6</sup> using the same  $T_{\rm ODT}$  method described above by replacing the mean-field value of  $(\chi N)_{\rm ODT}$  = 10.5 with the fluctuation-corrected value,  $(\chi N)^{\rm fluc}_{\rm ODT}$ . The value of  $(\chi N)^{\rm fluc}_{\rm ODT}$  is a function of chain length and is calculated using the correlation developed by Glaser et al.<sup>50</sup> Details are provided in the Supporting Information.

Composition fluctuations are strongest in a narrow range of  $(\chi N)^{\text{fluc}}$  on either side of the ODT and are rapidly attenuated in the ordered state as  $(\chi N)^{\text{fluc}}$  increases.<sup>49–51</sup> Consequently, measurements of  $(\gamma N)^{\text{fluc}}$  near the ODT (e.g., via  $T_{\text{ODT}}$  or by fitting the disordered state structure factor) are highly sensitive to composition fluctuations. Conversely, SCFT provides an accurate description of the ordered state, and composition fluctuations are not expected to strongly affect the interfacial width.<sup>49</sup> This is borne out by the collapse of the simulation data with  $\left(\chi N\right)^{\rm fluc}/(\chi N)^{\rm fluc}_{\rm ODT}$  , which breaks down only in the immediate vicinity of the ODT, that is,  $(\chi N)^{\rm fluc}/(\chi N)^{\rm fluc}_{\rm ODT} \lesssim 1.5$  [Fig. S5(b)]. The success of this simple normalization for  $(\chi N)^{\text{fluc}}/(\chi N)^{\text{fluc}}_{\text{ODT}} > 1.5$  implies that, to first order, the contribution of thermal undulations to the apparent interfacial width is adequately captured by the proximity to the ODT. This simple approach simultaneously accounts for the block incompatibility and chain length dependences of the apparent interfacial width.

Complicating this analysis is the finding that *d* is insensitive to composition fluctuations.<sup>49</sup> Thus, the appropriate segregation strength normalization is different for  $t_x$  and *d*: the former is  $(\chi N)_{\rm ODT}^{\rm fluc}$ , while the latter is the mean-field value, 10.5. To account for this disparity, we normalize the experimental segregation strength,  $(\chi N)_{\rm fluc}^{\rm fluc}$ , by  $(\chi N)_{\rm ODT}^{\rm fluc}$  and adjust *d* using the strong-segregation limit scaling<sup>2</sup>  $d \sim \chi^{1/6}$ . The resulting normalized interfacial width is given by  $(t_x/d) \left[ (\chi N)_{\rm ODT}^{\rm fluc} / 10.5 \right]^{1/6}$ . The *d*-spacing correction,  $\left[ (\chi N)_{\rm ODT}^{\rm fluc} / 10.5 \right]^{1/6}$ , is a modest 1.09 on average, and ranges from 1.05 for PE-P(VCH*r*hI) to 1.12 for



**FIGURE 5** Normalized interfacial width,  $(t_x/d) \left[ (\chi N)_{ODT}^{fluc} / 10.5 \right]^{1/6}$ , (symbols) versus the normalized fluctuation-corrected segregation strength,  $(\chi N)^{fluc} / (\chi N)_{ODT}^{fluc}$ . Theoretical predictions (curves) are plotted as t/d versus  $\chi N/10.5$ . Comparison between  $(\chi N)^{fluc}$  from  $(t_x/d) \left[ (\chi N)_{ODT}^{fluc} / 10.5 \right]^{1/6}$  and  $(\chi N)^{fluc}$  from  $T_{ODT}$  (b). Symbols and curves are as in Figure 2. [Color figure can be viewed at wileyonlinelibrary.com]

PBMA–PMMA. The results of this analysis are shown in Figure 5. For the SST and SCFT predictions, the abscissa is given by  $\chi N/10.5$  and the ordinate is  $t_i/d$ , as before. The average disagreement between experiment and theory is 14%. Importantly, all of the negative deviations are eliminated for  $(\chi N)^{fluc}/(\chi N)^{fluc}_{ODT} > 1.5$ , including the massive overcorrection of the PS–P2VP data, which is an improvement over the analytical treatments. This result further demonstrates the need to simultaneously account for surface tension and layer compressibility and splay and highlights the effect of finite chain length. However, the uncorrected data (Fig. 2) still provide the best agreement between experiment and theory.

Given the scatter in the data, it is unlikely that any universal correction, no matter how sophisticated, could substantively improve the agreement. The large positive discrepancies between  $t_x/d$  and  $t_i/d$  that persist in Figure 5 likely stem from other sources of lattice distortions (paracrystallinity), caused by, for example, incomplete equilibration, chain length or architectural dispersity, or a nonuniform distribution of terminated first-block homopolymer. Though paracrystallinity necessarily produces positive deviations  $(t_x/d > t_i/d)$ , a model analogous to eq (3) which accounts for the quantitative effect of paracrystallinity cannot be formulated *a priori*. In practice, the empirical deconvolution of the effects of paracrystallinity from the effect of finite  $t_i$  would require many orders of reflection to be resolved in the SAXS pattern.<sup>22,32,35</sup> Even if this analysis can be successfully carried out for a given sample, it is not easily transferrable to other samples because the nature of the paracrystalline distortions cannot be assumed constant. It is preferable to attempt to mitigate sources of paracrystallinity prior to the measurement by, for example, minimizing polydispersity during synthesis or through fractionation and annealing samples in the melt for an extended period.52

Consequently, none of the universal corrections explored can account for the observed deviations between  $t_x/d$  and  $t_i/d$ . In some sense, this finding is convenient, since all three of these corrections require some *a priori* knowledge of  $\chi$  and/or the chain statistics, which would diminish the utility of the present approach. Returning to the original objective of calculating the mean-field  $\chi N$  from the interfacial width, the simplest method—and with no loss of accuracy—is to compare the uncorrected  $t_x/d$  directly with the SCFT prediction for  $t_i/d$ , as in Figure 2. Increased precision can be obtained by simultaneously fitting measurements of  $t_x/d$  for multiple polymers of different  $M_n$  with the same pair of blocks using a common value of  $\chi N/M_n$ .<sup>38</sup>

### CONCLUSIONS

The segregation strength of diblock copolymers has been estimated from measurements of the interfacial width between lamellar microdomains in the ordered state by making use of SCFT calculations of the intrinsic interfacial width as a function of  $\chi N$ . A method for calculating the interfacial width from the integrated intensities of the structure factor peaks measured by SAXS is presented and proven to be largely insensitive to the empirical baseline subtraction. Normalizing the interfacial width by the domain period ensures that this method is free from uncertainties associated with the chain statistics, making it well suited to new diblock chemistries. The resulting values of  $\chi N$  are in good agreement with independent measurements of  $\chi N$  from the  $T_{ODT}$  method, illustrating that this is a robust approach for estimating  $\chi N$  for microphase-separated diblock copolymers for which the disordered state has not been or cannot be accessed. Three different treatments of thermal undulations are considered but do not improve the accuracy of the analysis. Since the magnitudes of the experimental deviations are greater in the positive direction  $(t_x/d > t_i/d)$ , likely due to paracrystallinity, the

value of  $\chi N$  obtained from  $t_x/d$  generally provides a lower bound estimate.

### ACKNOWLEDGMENTS

A. B. Burns acknowledges support from the National Research Council Research Associateship Program. This work was partially supported by the National Science Foundation, through the Polymers Program (DMR-1402180 to R. A. Register) and the Materials Research Science and Engineering Center Program through the Princeton Center for Complex Materials (DMR-1420541). A. B. Burns would like to thank August W. Bosse (ExxonMobil) for insightful discussions.

### **REFERENCES AND NOTES**

- 1 C. M. Bates, F. S. Bates, Macromolecules 2017, 50, 3.
- 2 M. W. Matsen, F. S. Bates, *Macromolecules* 1996, 29, 1091.

3 W. W. Maurer, F. S. Bates, T. P. Lodge, K. Almdal, K. Mortensen, G. H. Fredrickson, *J. Chem. Phys.* **1998**, *108*, 2989.

- **4** R. Krishnamoorti, W. W. Graessley, G. T. Dee, D. J. Walsh, L. J. Fetters, D. J. Lohse, *Macromolecules* **1996**, *29*, 367.
- 5 B. S. Beckingham, A. B. Burns, R. A. Register, *Macromolecules* 2013, *46*, 2760.
- 6 W. D. Mulhearn, R. A. Register, *Macromolecules* 2017, 50, 5830.

7 R.-J. Roe, M. Fishkis, J. C. Chang, *Macromolecules* **1981**, *14*, 1091.

8 H. Ahn, D. Y. Ryu, Y. Kim, K. W. Kwon, J. Lee, J. Cho, *Macro-molecules* 2009, *42*, 7897.

9 F. S. Bates, J. H. Rosedale, G. H. Fredrickson, *J. Chem. Phys.* 1990, *92*, 6255.

10 M. F. Schulz, A. K. Khandpur, F. S. Bates, K. Almdal, K. Mortensen, D. A. Hajduk, S. M. Gruner, *Macromolecules* 1996, *29*, 2857.

11 L. Leibler, Macromolecules 1980, 13, 1602.

12 J. Scherble, B. Stark, B. Stühn, J. Kressler, H. Budde, S. Höring, D. W. Schubert, P. Simon, M. Stamm, *Macromolecules* 1999, *32*, 1859.

**13** Y. Ren, T. P. Lodge, M. A. Hillmyer, *Macromolecules* **2000**, *33*, 866.

14 D. A. Davidock, M. A. Hillmyer, T. P. Lodge, *Macromolecules* 2004, *37*, 397.

15 A. N. Semenov, *Macromolecules* 1993, 26, 6617.

**16** A. Arora, J. Qin, D. C. Morse, K. T. Delaney, G. H. Fredrickson, F. S. Bates, K. D. Dorfman, *Macromolecules* **2016**, *49*, 4675.

17 B. S. Beckingham, R. A. Register, *Macromolecules* 2013, 46, 3486.

**18** D. Christie, R. A. Register, R. D. Priestley, *ACS Cent. Sci.* **2018**, *4*, 504.

**19** S. H. Anastasiadis, T. P. Russell, S. K. Satija, C. F. Majkrzak, *J. Chem. Phys.* **1990**, *92*, 5677.

20 N. Torikai, I. Noda, A. Karim, S. K. Satija, C. C. Han, Y. Matsushita, T. Kawakatsu, *Macromolecules* **1997**, *30*, 2907.

**21** M. Luo, J. R. Brown, R. A. Remy, D. M. Scott, M. E. Mackay, L. M. Hall, T. H. Epps III, *Macromolecules* **2016**, *49*, 5213.

22 G. E. Stein, J. A. Liddle, A. L. Aquila, E. M. Gullikson, *Macro-molecules* 2010, *43*, 433.

23 J. A. Lake, Acta Crystallogr. 1967, 23, 191.

24 R. A. Register, T. R. Bell, *J. Polym. Sci. Part B: Polym. Phys.* 1992, *30*, 569.

25 E. Helfand, Y. Tagami, Polym. Lett. 1971, 9, 741.



26 E. Helfand, Y. Tagami, J. Chem. Phys. 1972, 56, 3592.

27 E. Helfand, A. M. Sapse, J. Chem. Phys. 1975, 62, 1327.

28 M. W. Matsen, F. S. Bates, J. Chem. Phys. 1997, 106, 2436.

29 R.-J. Roe, J. Appl. Crystallogr. 1982, 15, 182.

**30** W. Ruland, J. Appl. Crystallogr. **1971**, 4, 70.

**31** J. T. Koberstein, B. Morra, R. S. Stein, *J. Appl. Crystallogr.* **1980**, *13*, 34.

32 T. Hashimoto, M. Shibayama, H. Kawai, *Macromolecules* 1980, *13*, 1237.

33 T. Hashimoto, M. Fujimura, H. Kawai, *Macromolecules* 1980, *13*, 1660.

34 F. S. Bates, C. V. Berney, R. E. Cohen, *Macromolecules* 1983, *16*, 1101.

35 M. Shibayama, T. Hashimoto, Macromolecules 1986, 19, 740.

**36** R.-J. Roe, *Methods of X-ray and Neutron Scattering in Polymer Science*; Oxford University Press: New York, **2000**, p. 155.

37 A. N. Semenov, Macromolecules 1994, 27, 2732.

38 A. B. Burns, R. A. Register, Macromolecules 2017, 50, 8106.

39 B. R. Pauw, J. Phys. Condens. Matter 2013, 25, 383201.

40 T. Hashimoto, M. Shibayama, H. Kawai, *Macromolecules* 1983, *16*, 1093.

**41** T. Hashimoto, K. Nagatoshi, A. Todo, H. Hasegawa, H. Kawai, *Macromolecules* **1974**, *7*, 364.

42 K. R. Shull, A. M. Mayes, T. P. Russell, *Macromolecules* 1993, 26, 3929.

**43** M. Sferrazza, C. Xiao, R. A. L. Jones, D. G. Bucknall, J. Webster, J. Penfold, *Phys. Rev. Lett.* **1997**, *78*, 3693.

44 A. W. Bosse, J. Vac. Sci. Technol. B 2011, 29, 06F202.

45 M. W. Matsen, *Macromolecules* 2012, 45, 8502.

46 K. Amundson, E. Helfand, Macromolecules 1993, 26, 1324.

47 R. Hołyst, Phys. Rev. A 1991, 44, 3692.

48 I. Sikharulidze, W. H. de Jeu, Phys. Rev. E 2005, 72, 011704.

49 P. Medapuram, J. Glaser, D. C. Morse, *Macromolecules* 2015, 48,819.

50 J. Glaser, P. Medapuram, T. M. Beardsley, M. W. Matsen, D. C. Morse, *Phys. Rev. Lett.* 2014, *113*, 068302.

51 G. H. Fredrickson, E. Helfand, J. Chem. Phys. 1987, 87, 697.

52 S. Li, R. A. Register, B. G. Landes, P. D. Hustad, J. D. Weinhold, *Macromolecules* 2010, 43, 4761.