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# Reduced Domain Size and Interfacial Width in Fast Ordering Nanofilled Block Copolymer Films by Direct Immersion Annealing

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**Supporting Information** 

**ABSTRACT:** Block copolymers (BCPs) can function as nanoscale templates to organize nanoparticles within selective domains. Most functional applications of nanofilled BCPs generally require a high loading of nanoparticles, which is difficult to achieve due to particle aggregation, slow kinetics of ordering, and disruption of block copolymer order. A key parameter is the periodic domain spacing,  $L_0$ , which is important for tuning functional properties. We demonstrate direct immersion annealing (DIA) as a promising directed self-assembly (DSA) method to overcome these problems. DIA is shown to fully order highly filled (10.5 vol % Au-PSrPMMA nanoparticles) lamellar poly(styrene-*b*-methyl methacrylate) (PS–PMMA) BCP films, whose lamellar ordering is practically unimpeded by filler loading. Neutron reflection (NR) further confirms that DIA sharpens the interfacial width between PS–PMMA domains by ~20%. In situ NR studies further reveal that DIA predominantly induced film ordering in a



5 wt % anisotropic organoclay (C93A) filled PS–PMMA film in less than 30 s! In contrast, identical C93A nanofilled PS– PMMA films that were thermally annealed (19 h at 160 °C) only exhibit partial ordering near the free surface. DIA films also exhibit ~50% reduced  $L_0$ , resulting in twice the number of BCP domains, potentially useful to film functional properties such as gas barrier when filled with clay or plasmonics for gold nanoparticles. We further model this reduced  $L_0$  in DIA processed films with a scaling approach to correlate the final structure to degree of polymerization, *N*. Our results reveal that DIA, a roll-to-roll (R2R) compatible DSA method, can enable real-time manufacture of nanofilled block copolymers for functional applications.

# ■ INTRODUCTION

BCP self-assembly is a cost-effective patterning technique useful for many electronic<sup>1,2</sup> and nanolithographic<sup>3,4</sup> applications. BCPs are widely studied as an alternative to photolithographic methods for their ability to produce smaller, tunable nanofeatures at lower costs. Further, the addition of inorganic nanoparticles to BCPs has been shown to enhance mechanical,<sup>5-8</sup> electrical,<sup>9,10</sup> optical,<sup>11</sup> and other properties. Despite these advantages, the addition of high particle loadings to BCP microstructures can introduce challenges, important among which are decreased dynamics<sup>12–14</sup> and structural disruption.<sup>15</sup> In addition to this, the smallest feature size, which dictates the etchable line width, is generally limited by the lowest molecular weight for a given BCP where there is still a thermodynamic driving force for phase separation. For nanofilled BCPs, the ability to significantly reduce domain spacing would multiply the number of arrays where particles may locate without adding to the film dimensions. Such periodic, densely multilayered structures may be useful for applications such as dielectric capacitors or barrier films.

We examine a recently developed DSA technique,<sup>16,17</sup> DIA, as a method to process highly filled BCPs and overcome the obstacles associated with high loadings. Unlike solvent vapor annealing, DIA orders BCP films as they are directly submerged in bulk solvent. This eliminates any need for generating vapors or carefully controlling vapor pressures as is required in solvent vapor annealing (SVA), but it requires a fairly specific solvent quality for the BCP film that is tunable via a miscible solvent mixture. A large fraction of poor solvent for the BCP film prevents film dissolution, while a low fraction of good or mediocre solvent enables limited film swelling and molecular mobility for ordering. The presence of solvent during the ordering process introduces a tunable feature with potential for improving BCP structure, feature size, and kinetics while loaded with high volumes of filler.

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Figure 1. Schematic of direct immersion annealing (DIA) process.

Modi et al.<sup>16</sup> observed this technique using a nonfilled asymmetrical PS-PMMA system. An acetone/heptane mixture was used as the DIA solvent mixture, and swelling ratios (SR) were found to vary linearly with the composition of solvent. SR ranges for that system are defined for short- and long-range order as well as for dewetting and film dissolution. The study also determined the activation energy for the annealing process and found it to be considerably lower in comparison to thermal annealing techniques. In this paper we measure the effect of this reduced activation energy on ordering kinetics and demonstrate its advantage for offsetting the reduction in diffusion rate during the ordering of highly filled films. Specifically, we examine the capability of DIA rapid ordering of BCP structures at high particle loadings while also presenting a tunable path to enhance the interfacial sharpness between domains in lamellar forming PS-PMMA. We examine the synergistic effects of DIA and particle loading on film structure, determining their roles in reduced domain spacing and interfacial width. Neutron reflection is used to quantify the film's internal structure as well as the kinetics of ordering.

### RESULTS AND DISCUSSION

A ternary solvent mixture composition suitable for DIA induced ordering of PS-PMMA was determined. To this end, we first present solvent ratio mapping to establish film behavior regimes such as film dissolution, potential self-assembly, dewetting, and short-range or no order. We then present neutron reflectivity results on films with various loadings of AuNP, examining the film domain spacing, interfacial widths, and kinetics. This is followed by an analysis of the role of solvent and nanoparticles on the BCP film structures. AFM, TEM, and optical images are shown in Figure 2 for various solvent ratio DNA of films made from PS-PMMA with 10.5 vol % AuNP along with a ternary solvent diagram depicting the film behavior for different solvent mixtures. There are four main regions of the map that correspond to solvent combinations where film dissolution, dewetting, possible self-assembly, and no effect occur. Our measurements in this study were performed in the potential self-assembly map region.



**Figure 2.** (top) Ternary phase map of solvent annealing ratios for 33– 33 kg/mol PS–PMMA filled with 10.5 vol % AuNP. Left and right AFM images show the as-cast and solvent-processed films, respectively. The center optical image shows dewetting behavior of the film as a result of different annealing mixtures. (bottom) TEM images of 10.5 vol % AuNP films DIA processed with (a) 10:80:10, (b) 30:60:10, and (c) 25:75:5 acetone:heptane:toluene volume ratios.

Using the solvent self-assembly map region as an indication of optimal solvent combinations, PS-PMMA films with a deuterated styrene block (dPS-PMMA) were cast and DIA processed to study the internal structure of the postannealed dry films with isotropic particle loadings. This information was obtained using specular neutron reflection at the National Institute of Standards and Technology (NIST) for films at low and high limits of 0.0, 0.1, 0.4, and 10.5 vol % AuNP. It was observed that the solvent mixture composition not only determined the self-assembly of the BCP but also dictated the distribution of particles throughout the film. Transmission electron microscopy (TEM) images of several solvent mixtures are shown in Figure 2, and it was found that the DIA solvent mixture of the ratio 7.5 mL heptane:2.5 mL acetone:0.5 mL toluene gave the most favorable particle distribution (Figure 2c). This solvent composition is used for all DIA described in this paper unless otherwise stated. TEM was also used to confirm that particles were not lost into solution during DIA by comparing the quantity of particles present in the same film before and after DIA with image analysis. Oven annealed films were also prepared with the same particle loadings and thermally annealed at 185 °C for 12 h as a comparative control.

Figure 3 shows the scattering profiles of films annealed with DIA for various particle loadings. We note a strong preservation of the lower and higher order Bragg peaks (located at q = 0.043 and 0.086 Å<sup>-1</sup> where q is the scattering vector and is related to the angle of incidence,  $\theta$ , as  $q = 4\pi \sin(\theta)/\lambda$ , and  $\lambda$  is the wavelength of the neutron beam) as the loading of particles is increased, confirming that the layered structure is capable of holding a large volume of nanoparticles without disruption of the overall BCP lamellar structure.



**Figure 3.** Neutron reflectivity profiles of DIA processed 19.5–18.1 kg/ mol dPS–PMMA films with 0.0, 0.1, 0.4, and 10.5 vol % AuNP. (inset) SLD profiles of 0.0 and 10.5 vol % AuNP films.

It is observed that for low particle loadings (0.1%-0.4%) the domain spacing  $(L_0 = 2\pi/q^*)$  of each film remains consistent at 14.7 nm (see Table 1). At a much higher loading of 10.5%

 Table 1. Domain Spacing and Subdomain Spacing of DIA

 and Melt Processed Films

particle loading (vol %)	PMMA layer width (nm)	PS layer width (nm)	total domain spacing, $L_0$ (nm)		
DIA (2 h)					
0.0	$7.7 \pm 0.03$	$7.0 \pm 0.03$	$14.7 \pm 0.06$		
0.1	$8.0 \pm 0.04$	$6.7 \pm 0.05$	$14.7 \pm 0.09$		
0.4	8.1 ± 0.05	$6.6 \pm 0.05$	$14.7 \pm 0.10$		
10.5	$8.0 \pm 0.04$	$7.0 \pm 0.04$	$15.0 \pm 0.08$		
thermal annealing: 185 °C (12 h)					
0.0	$13.1 \pm 0.10$	$12.8 \pm 0.11$	$25.9 \pm 0.22$		
0.1	$13.1 \pm 0.06$	$13.1 \pm 0.07$	$26.2 \pm 0.13$		
0.4	$12.9 \pm 0.13$	$13.0 \pm 0.16$	$25.9 \pm 0.29$		
10.5	$13.6 \pm 0.24$	$12.1 \pm 0.33$	$25.7 \pm 0.57$		

AuNP, L<sub>0</sub> appears to increase slightly to 15.0 nm. At lower particle loadings, although the overall domain spacing does not change, the particles incorporated in the film affect the lengths of each subdomain. For a film with no particles, the PMMA layer is 7.7 nm and the PS layer is 7.0 nm. The addition of 0.1% AuNP increases the PMMA layer to 8.0 nm while decreasing the PS layer to 6.7 nm. At 0.4% AuNP, the PMMA layer increases to 8.1 nm and the PS layer decreases to 6.6 nm. At the highest loading of 10.5% AuNP, both PMMA and PS are swollen to 8.0 and 7.0 nm, respectively. Thus, the DIA ordered data match previous melt ordering studies<sup>18</sup> using these NPs that suggest the NPs mainly reside in the PMMA layer. The reduction of the PS layer at 0.1 and 0.4 vol % loadings is likely due to spreading of junction points as the PMMA layer is swollen by the particles (changes in layer thickness due to chain swelling is further discussed in future sections). As the solvent is removed and the chains collapse, the PMMA layer thickness is still increased due to the added volume of particles, but the PS layer is reduced as the junction points are less dense and it has no added volume of particles. We explain the swelling of both domains at the highest loading as a saturation point that is reached, forcing some of the particles into the polystyrene domains. This is not unreasonable considering that the PS-rPMMA outer shell grafted to the gold contains 20% PS. The presence of particles in both domains at higher loadings is also evidenced by and consistent with the changes in scattering length density (SLD) of each domain compared to the neat film (shown in the inset in Figure 3). The particles have a calculated SLD of  $2.7 \times 10^{-6}$  Å<sup>-2</sup>. As such, the SLD of PMMA will increase and that of dPS will decrease with the presence of nanoparticles in that domain. We assume that any reduction in the SLD of the dPS domain is caused by the presence of the nanoparticles and calculate the volume fraction of gold nanoparticles,  $\phi_{Au}$ , in the dPS domains using the following equation:

$$\phi_{Au} = \frac{SLD_{dPS,effective} - SLD_{dPS}}{SLD_{Au} - SLD_{dPS}}$$
(1)

Further, it is assumed that all AuNP not located in a dPS domain are located in a PMMA domain. The tabulated volume fractions of AuNP for each domain of films annealed with DIA are presented in Table 2. The volume fraction of AuNPs

Table 2. Effective SLD of DPS Domain and CalculatedVolume Fractions of AuNP in BCP Subdomains

Au loading (vol %)	$(10^{-6})^{\text{effective}}$	$\phi_{ m Au}$ in PS domain	$\phi_{\scriptscriptstyle m Au}$ in PMMA domain
0.0	$6.15 \pm 0.07$	0	0
0.1	$6.08 \pm 0.10$	0.02	0.98
0.4	$6.00 \pm 0.08$	0.04	0.96
10.5	$5.45 \pm 0.08$	0.20	0.80

calculated from the dPS SLD suggest that at the lowest loading of 0.1 vol %, 98% of the particles reside in the PMMA subdomain, but at the highest loading of 10.5 vol %, only 80% are present.

We next examine how DIA itself has impacted the BCP lamellar structure by comparison to melt annealed films. As can be seen from the neutron reflection of DIA and melt annealed films in Figure 4, DIA produces an ordered film that differs from that produced by melt annealing in several ways. First, we observe a dramatically shifted Bragg peak to a higher q value for DIA processed films. The Bragg peak location is a reflection of the lamellar domain spacing ( $L_0 = 2\pi/q^*$ ) and indicates a large reduction in  $L_0$  for DIA processed films without any reduction



Figure 4. Comparison of DIA (7.5 mL heptane:2.5 mL acetone:0.5 mL toluene solvent ratio) and thermal annealing (185  $^{\circ}$ C, 12 h) on 19.5-*b*-18.1 kg/mol dPS–PMMA films with 0.1% AuNP loading.

in molecular weight of the BCP. For 19.5-18.1 kg/mol dPS-PMMA films annealed using DIA,  $L_0$  is 14.7 nm. This is nearly half of the 25.9 nm  $L_0$  observed in melt annealed films. We attribute this structure to the difference in chain swelling during annealing in the melt compared to DIA. The presence of solvent swells the chains to a much greater extent than is observed in the melt from a gain in free volume (related to coefficient of thermal expansion, CTE) above  $T_{g}$ . The increase in volume is easily observed at the macro scale as the film thickness expands during DIA, previously observed<sup>16</sup> via in situ ellipsometry. For PS-PMMA melt ordered films, the estimated increase in volume based on a CTE of  $8.75 \times 10^{-5}$ /°C and an annealing temperature of 185 °C is a 4% volume increase in melt state compared to quenched state. By comparison, film swelling during DIA is 1.5 swelling ratio (50% volume increase). We first describe the scenario semiqualitatively. As depicted in Figure 5, chain swelling significantly reduces



Figure 5. Schematic of chain junction conformations during DIA and thermal annealing.

(spreads out) the chain junction point density along the interface of the BCP domains while ordering the cast BCP films from the disordered to in situ ordered state. Much of the film swelling occurs in the film normal direction in situ, since the film has restricted expansion in the lateral direction as it is adhered to the silicon substrate by the PMMA wetting layer. We note that if significant lateral film swelling had occurred, the film would have lost BCP resulting in a reduced dry film thickness, which is not observed. As seen when the film is ordering from the disordered state, about half of the number of chains are able to assemble next to each other in a given layer to accommodate the larger volume of the swollen chains. As a result, the remnant chains form more layers on top, resulting in approximately double the number of layers for DIA than what is observed for melt annealed films. Upon rapid solvent removal following DIA, the chains collapse back down, without altering significantly the lateral junction density, thereby creating thinner layers. The calculated chain junction densities utilizing the experimentally measured DIA processed dry film  $L_0$  and interfacial width w (see below) for the neat film annealed with DIA and oven are 1.5 and 2.6 junctions/nm<sup>2</sup>, respectively.

More quantitatively (for a full description, see Supporting Information), we can represent this reduced domain size as a function of the chain swelling in the swollen state using a scaling approach where the distance between chain junction points at the interface is equal to D, as shown in Figure 6. Assuming the block copolymer to be in the semidilute regime and looking at length scales smaller than the correlation length, D, the conformations of the *i*th block are those of self-avoiding chains of thermal blobs. The equilibrium size of the domain is



**Figure 6.** Schematic representation of an ordered block copolymer in the swollen state and the distance between junction points, *D*.

the result of a fine interplay between the surface energy of the interface with surface tension,  $\gamma_{AB}$ , between A and B domains and stretching of A and B blocks.

In the dry state after the solvent evaporates, the size of the domains can be estimated assuming that the spacing between grafting points of the chains localized at the interface between A- and B-rich domains does not change upon fast solvent removal. Under these conditions, it can be shown that the change in spacing depends on the chain degree of polymerization, N, and Flory exponent, v, as

$$L_{\rm dr}/L_{\rm sw} \propto N^{(1-3v)/(1+2v)} \propto N^{-4/11}$$
 (2)

where *v* is assumed to be that of a good solvent, equal to 3/5. We apply this scaling relationship to two different PS–PMMA molecular weights that were measured in both the dry and swollen ordered state with neutron reflection to determine  $L_{\rm dr}$  and  $L_{\rm sw}$ . 19.1–18.5 kg/mol dPS–PMMA (N<sub>355</sub>) and 33–33 kg/mol PS–PMMA (N<sub>647</sub>) were each measured. The *in situ* swollen measurement of N<sub>647</sub> was executed with a deuterated acetone component in the solvent mixture to enhance contrast. In the dried state it was found to have a sufficient SLD contrast between the hydrogenated layers to observe a small Bragg peak. N<sub>355</sub> films resulted in  $L_{\rm dr} = 14.7$  nm and  $L_{\rm sw} = 27.6$  nm, and N<sub>647</sub> resulted in  $L_{\rm dr} = 20.6$  nm and  $L_{\rm sw} = 38.8$  nm. Upon calculation of a prefactor, *K*, so that

$$L_{\rm dr}/L_{\rm sw} = KN^{-4/11}$$
(3)

we find that K = 4.5 and 5.6 for N<sub>355</sub> and N<sub>647</sub> films, respectively. Here we find that the prefactor K is constant within 10%, so the equation suggests that the scaling prediction for these molecular weights are within acceptable limits. Subsequent studies will perform a more robust test of this scaling relationship with solvent quality and molecular weight using the prefactor determined and various molecular weights.

In addition to the changes in domain spacing, we also observe DIA to reduce the interfacial widths between PS and PMMA domains. The sharpness of the interface between domains is an important parameter for technological applications such as line width and associated line edge roughness. The interfacial widths, *w*, shown in Table 3, were

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Figure 7. Depiction of interfacial width between domains.

Table 3. Interfacial Widths of DIA and Melt Processed Films

AuNP particle loading (%)	thermally annealed (185 °C) interfacial width (Å)	DIA interfacial width (Å)
0.0	51	44
0.1	51	44
0.4	54	46
10.5	66	60

calculated from volume fraction profiles as a function of film depth extracted from reflectivity data where

$$(d\phi_{dPS}/dz)_{\phi=0.5} = 1/w$$
 (4)

and  $\phi = 0.5$  refers to the location in the film where volume fraction of dPS is 0.5. For a neat film without particles, we observe a 15% reduction in interfacial width for a film processed with DIA as compared to melt annealing.

Theory derived by Helfand<sup>19</sup> predicts that the interfacial width is affected only by the statistical segment length and the Flory–Huggins interaction parameter,  $\chi$ , as follows:

$$w = 2a/\sqrt{6\chi} \tag{5}$$

As such, literature results have reported a consistent width of 50 Å for a PS–PMMA block copolymer<sup>20,21</sup> or blend.<sup>22</sup> The observed interfacial width of a melt annealed neat films (51 Å), shown in Table 3, agrees well with literature values. Because the statistical segment length is unchanged while using the same block copolymer for each annealing method, the decreased interfacial width from DIA can be assumed to be either a result of nonequilibrium solvated brush to dry state brush collapse transition or a contribution from an increase in the interaction parameter as discussed below.

The essential idea behind sharper interface formation in a solvated to dry state brush collapse process is that the lower chain junction density at the interface in the solvated state is transferred to the dry state film, resulting in reduced interchain interactions and thereby less chain stretching. On the other hand, if we assume the sharp interface results from a continuous quasi-equilibrated solvent annealing drying process, then we can assume the final dry state sharper interface is due to an increase in value of the interaction parameter. This increase of the interaction parameter can likely be a result of two factors: the reduced temperature at which annealing takes place during DIA (room temperature compared to 185 °C for thermal annealing) and the solvent selectivity for each copolymer block.

Zeman<sup>23</sup> has shown that for a polymer (1)-polymer (2)solvent (s) ternary system there is an increased phase separation when  $\chi_{1s} \neq \chi_{2s}$ . In addition to this reduced compatibility, Bank et al.<sup>24</sup> found that this effect remained between the polymer phases even after solvent removal, as evidenced by the glass transition temperatures and the dielectric loss factors of the solvent-cast films. Studies by Kern<sup>25</sup> of the critical concentration of PS-PMMA in different solvents show an increase in  $\chi_{12}$  up to 5 times the original value. The study by Zeman<sup>23</sup> predicts the effective value of  $\chi_{12}$  in a selective solvent is proportional to  $(\chi_{1s} - \chi_{2s})^2$  as shown here:

$$\chi_{12} = \frac{(\chi_{1s} - \chi_{2s})^2}{(\delta_1 + \delta_2 - 2\delta_s)^2} \frac{RT}{\nu}$$
(6)

where *R* is the universal gas constant, *T* is temperature,  $\nu$  is the molar volume, and  $\delta$  is the solubility parameter.

This increase of  $\chi_{PS-PMMA}$  from decreased temperature and individual block solvent selectivity explains the reduction in interfacial width between the blocks as acetone is highly preferential to the PMMA block. The values of  $\chi_{\text{PS-acetone}}$  and  $\chi_{\rm PMMA-acetone}$  are 0.9 and 0.48, respectively. This corresponds to a theoretical effective  $\chi_{\rm PS-PMMA}$  of 0.59 in the presence of pure acetone calculated from eq 6. We note here that the actual effective  $\chi_{PS-PMMA}$  is likely not increased by such a dramatic amount due to the presence of low concentrations of heptane and toluene that are also present in the film. While the solvent presence acts to reduce the interfacial width, it is also apparent that the addition of NPs acts to increase it. This result is easily explained by the same interaction parameter theory. The AuNP used in this study is grafted with both PS and PMMA components and, as such, exhibits a compatibilizing effect where the NPs reduce the interfacial tension between domains. This has the opposite effect of the selective solvent and can act to reduce the effective interaction parameter. The effect is not prevalent at low NP loadings but can easily be seen at a high loading with an increase in interfacial width of about 15 Å for both DIA and thermal annealing.

To determine whether the reduced interfacial width is the result of a melt brush collapse or of solvent quality, we altered the solvent mixture used for DIA to enhance the selectivity of the solvent. Toluene was completely eliminated from the DIA solvent mixture, as this is a good solvent for both blocks. Ignoring a small fraction of heptane that may be drawn into the film with the acetone, the composition of solvent in the swollen film during DIA should be almost 100% acetone. In this case, the BCP is exposed almost completely to a selective solvent. The solvent ratio that was used was 30:70 (acetone:heptane) volume ratio. For a film annealed with this solvent composition, the interfacial width was found to be even lower than films annealed with a DIA mixture containing toluene, as expected. The interfacial width of a neat dPS-PMMA was determined by neutron reflection to be 40 Å, which is a reduction of 22% from the thermally annealed film. This observation suggests that the cause of the interfacial width reduction in DIA is the variable effective interaction parameter. This result is not only significant in terms of enabling the formation of cleaner templates but shows that small variations of DIA mixture composition can provide a mechanism to tune the interfacial width by adjusting the solvent mixture selectivity.

We note that the differences observed in domain spacing as well as interfacial width are in fact reversible if the previously annealed (DIA) films are later exposed to thermal annealing. To show this result, we have taken a neat film that was previously annealed with DIA and further thermally annealed it at 185  $^{\circ}$ C for 12 h. The neutron reflection profile of this film is shown in Figure 8, where it can be seen that the Bragg peak has



**Figure 8.** Neutron reflection of 19.5–18.1 kg/mol dPS–PMMA annealed first with DIA for 2 h and then with thermal annealing at 185  $^{\circ}$ C for 12 h.

returned to 0.025 Å<sup>-1</sup> with the traditional domain spacing of 25.2 nm and interfacial width of 51 Å. It can be seen from the resulting SLD profile through the film that the structure is slightly imperfect when compared to a film that has been thermally annealed without any prior DIA ordering. We expect that longer annealing times may give a more regular structure.

In order to address diffusion concerns when ordering BCPs loaded with NPs, we studied the comparative kinetics of melt processed versus DIA ordered films using in situ neutron reflection. It is well-known that large anisotropic nanoparticles have low mobility and generally low miscibility with polymers leading to phase separation/aggregation unless enhanced by grafted polymers. Furthermore, the DIA almost independently interacts with the block copolymer swelling and ordering versus solvent-clay interactions, so that BCP/Clay interactions become relatively unimportant in DIA solution processing. To determine the efficacy of DIA, we load dPS-PMMA with a highly anisotropic cloisite clay particle, C93A, and first demonstrate how the clay loading adversely affects the normal melt ordering kinetics of PS-PMMA. With large lateral dimensions, these particles significantly slow the kinetics as well as lead to disruption to the long-range BCP layering order. The lateral dimensions and dispersion in the BCP are shown in Figure 9. Moderately well-dispersed clay was achieved with sonication and maintained during solvent annealing due to the presence of acetone.

The kinetics of a 5 wt % C93A in dPS–PMMA was measured with neutron reflection *in situ* during melt annealing. The film was annealed about 60° above the glass transition temperature of dPS–PMMA at 160 °C. The kinetics of this study are shown in Figure 10, where after 19 h of annealing at 160 °C, self-assembly has only propagated through about 20% of the film thickness, as observed in the SLD profile. Such a profile is driven by wetting of the PS block at the air surface. The bottom portion of the film remains in the disordered state with an average SLD in between that of dPS and PMMA, ~2.9  $\times 10^{-6}$  Å<sup>-2</sup>. To determine the contribution of the clay to the slow ordering, we compare these kinetics to that of an unfilled





**Figure 9.** Dispersion of C93A clay particles in 33–33 kg/mol PS– PMMA after annealing with 7.5 mL heptane:2.5 mL acetone:0.5 mL toluene as measured by top-down TEM.

film. In the absence of the clay, we find that an unfilled dPS– PMMA film is able to order noticeably faster. Figure 10b compares the neutron reflection profiles of an unfilled film annealed for 19 h *ex situ* at 160 °C to that of the filled film at times 7.7 and 19 h of annealing. The lack of clay enables the neat BCP film to propagate order within the film, initiated from the air surface, 3 times more than that of the clay-filled BCP system.

The dry, disordered film is first measured to confirm that all scattering contributing to the Bragg peak is a result of annealing. As shown in Figure 11, the reflectivity from this sample yields no Bragg peak.

The DIA solvent mixture is then injected into the chamber containing the film. After injection, a quick scan of the range 0  $\leq q \leq 0.06$  Å<sup>-1</sup> is performed to capture snapshots of the early time kinetics. Quite amazingly, within the first 30 s after solvent injection, a near fully formed Bragg peak is already present. The q range directly around the Bragg peak is thereby repeatedly scanned for several hours at 60 s intervals, observing only marginal changes. After equilibrium is reached, a scan of the full q range is performed revealing minimal change from the reflectivity taken within the first 30 s after solvent injection to the equilibrium reflectivity. The fitted profile to the equilibrium data in the inset of Figure 11 is consistent with a well-ordered lamellar dPS-PMMA film with nominal density variation of both dPS and PMMA subdomains that accounts for the clay volume fraction. As shown in prior work<sup>16,26</sup> on neat films of PS-PMMA with DIA, there is a greatly reduced activation energy when ordering BCPs with DIA as compared to thermal annealing. They report the activation energy for DIA as  $111 \pm$ 63 kJ/mol, and point out this is notably lower than the reported<sup>27</sup> 270 kJ/mol for thermal annealing of similar films. Apparently, the reduced activation energy is responsible for the ultrafast ordering kinetics reported here, even with the incorporation of a notable amount of highly asymmetric clay nanoparticles.

The fact that a thick BCP film can be ordered almost instantaneously in 30s with DIA, even in the presence of high aspect ratio platelets is remarkable given that standard melt ordering kinetics of the same clay-filled film takes almost a day to order only 60 nm of the film thickness at a temperature  $60^{\circ}$ 



**Figure 10.** *In situ* neutron reflection data of (a) 5 wt % C93A in 19.1–18.5 kg/mold PS–PMMA film thermally annealed at 160  $^{\circ}$ C at various times during annealing. (b) Neutron reflection of the clay-filled film at 7.7 and 19 h of thermal annealing and of the nonfilled film annealed *ex situ* for 19 h at 160  $^{\circ}$ C with (inset) corresponding SLD profiles. (c) Evolution of Bragg peak observed in 10a at various times. (d) Intensity of Bragg peak for clay-filled film as a function of time.



Figure 11. In situ neutron reflectivity data for DIA processed dPS–PMMA filled with 5 wt % C93A.

above  $T_{\rm g}$ . We can even estimate the ordering rate kinetics using a model free analysis method. As observed in Figure 10, the melt annealed clay-filled film shows that the intensity of the Bragg peak grows linearly with time. Since scattering intensity scales as the square of the amplitude, A(t)

$$I(t) \sim A(t)^2 \tag{7}$$

and it is observed from the melt ordering kinetics that  $I(t) \sim t^1$ , then the amplitude must scale as  $t^{0.5}$  as follows:

$$A(t) \sim t^{0.5} \tag{8}$$

The amplitude, A(t), is related to the average BCP domain composition fluctuation from its mean value,  $\Delta \langle \phi \rangle$ , so that the average composition at a given time, t, may be expressed as

$$\langle \phi \rangle_t - \langle \phi \rangle_{t=0} = k t^{0.5} \tag{9}$$

where k is the amplitude scaling constant. From this relation we express the scattering intensity as

$$I(t) = k^2 t \tag{10}$$

where the model-independent prefactor, k, is determined from the plot of I(t) in Figure 10d to have a value of 0.07 h<sup>-0.5</sup>. This is consistent with a diffusive mechanism for ordering within the film, where a low value of the prefactor k suppresses the melt ordering process due to the presence of clay. This slow Bragg peak evolution is in sharp contrast to the development of the fully formed Bragg peak observed *in situ* using DIA, which is formed almost instantaneously upon injection of the solvent mixture. Unfortunately, due to the ultrafast kinetics of DIA, a relationship between intensity and time could not be extracted to compare with the prefactor for DIA ordering process. This shows the substantial enhancement of DIA over thermal

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annealing processes especially when considering the loading of highly anisotropic nanoparticles in the film.

# CONCLUSIONS

A previous study<sup>16</sup> introduced DIA as an alternative ordering technique for producing excellent long-rang order and a reduced activation energy in BCP films. Here we have applied these advantageous features to highly filled BCPs and shown that DIA is a viable and scalable technique to overcome the prevalent challenges involved with these nanocomposites. The presence of solvent during self-assembly gives rise to unique BCP behavior such as reduced, and in general, tunable interfacial widths as well as highly reduced domain spacing that has thus far not been observed for conventional annealing techniques. The ability to control interfacial widths by tuning and selecting solvents that can alter the interaction parameter between two blocks of a BCP serves as a mechanism to produce self-assembled structures with sharp interfaces. Specifically, a reduction in interfacial width of 15% in both loaded and nonloaded films was observed for the ternary solvent mixture, and 22% for the two-solvent system of higher selectivity. This is a promising result for applications of neat BCP films in nanoelectronics as well as a cleaner templating route for organization of particles. The reduction in domain spacing serves as a pathway to create very small features that would otherwise require a greatly reduced BCP molecular weight that may not be able to self-assembly well because of the resulting reduction in  $\chi N$ . We accomplish a similarly small feature size with DIA with higher molecular weight BCP as a key advantage as also derived from theoretical predictions. We demonstrate that this technique is compatible with highly loaded nanofilled BCP systems and the increased number of domains that results from reduced domain spacing serves to add more templated layers in the matrix to partition the NPs into, a result that may be important for functional and film barrier properties. For low loadings, the addition of NPs to the film results in a conservation of domain spacing. The individual domain lengths adjust to accommodate the particles and maintain a domain spacing near that of the neat film. Furthermore, we demonstrate that these structures can be attained in less that 30 s, a tremendous improvement to traditional melt ordering that is orders of magnitude slower. The ability to quickly order loaded films while directly submerged in solvent shows the compatibility of DIA to nanofilled BCP systems, and the continuous nature of the process offers promise of easy scale up by roll-to-roll immersion processes. Finally, we note that the DIA annealed BCP structures are susceptible to change upon thermal annealing sufficiently above the  $T_{\rm g}$  of the block copolymer where diffusion becomes significant. This is however unlike patterning polymers by methods such as nanoimprint lithography (NIL) where the patterns decay or "slump" upon annealing just above the  $T_{\rm g}$  of the polymer due to built-in residual stress. The DIA ordered BCP films could be use as disposable thermal sensors for sustained overheating sensing applications for instance. A more robust route to preserving the smaller ordered feature, however, may be achieved by crosslinking these structures by radiation (gamma, electron), for instance. Notably, nanofilled BCP films ordered by DIA are expected to be more thermally stable well above  $T_{\rm g}$  in this regard due to their slow diffusion coefficient in the melt BCP phase.

#### EXPERIMENTAL SECTION

**Film Preparation.** PS–PMMA (MW = 33–33 kg/mol,  $M_w/M_n$  = 1.09, as reported by the supplier) and dPS–PMMA (MW = 19.5–18.1 kg/mol,  $M_w/M_n$  = 1.06, as reported by the supplier) were purchased from Polymer Source and used as received.<sup>*a*</sup> Heptane, acetone, and toluene were purchased from Sigma-Aldrich and mixed in ratios indicated in previous sections to form DIA solvent mixtures.

Two different nanoparticle/PS–PMMA BCP film systems were studied. An isotropic polymer grafted gold nanoparticle (AuNP) with a thermally stable (up to 200 °C), cross-linked shell was synthesized by Bang et al.<sup>28</sup> The AuNPs have an inner cross-linked PS shell and an outer shell of PS-*r*-PMMA (20:80 PS:PMMA mole ratio) ligands, as depicted in Figure 12. An anisotropic nanoparticle, Cloisite 93A



**Figure 12.** Depiction of AuNP structure synthesized by Bang et al.<sup>28</sup> The gold inner core is surrounded by a cross-linked shell of  $PSN_3$  (MW = 700 g/mol) and an outer brush of free ligands composed of a random copolymer of PS-*r*-PMMA (MW = 2500 g/mol) containing 20 mol % PS and 80 mol % PMMA, as specified by the supplier.

functionalized clay, was obtained from Southern Clay Products and used as received. Films were cast by flow coating 4-6 wt % toluene solutions of polymer and AuNPs at speeds about 8 mm/s. Films were cast on silicon wafers that were previously subjected to UV-ozone for 60 min. Cast (disordered) BCP film thicknesses were about 112 nm for all *ex situ* measurements and about 200 nm for *in situ* measurements. Solutions containing clay (*in situ* kinetic studies) were first sonicated before casting.

**Film Processing.** To anneal with DIA, cast films were placed in covered glass containers filled with various DIA solvent mixtures for a minimum of 30 min (up to 2 h). Upon removal from the solvent, the substrate-supported films were placed on a hot plate tilted about  $15^{\circ}$ – $20^{\circ}$  at a temperature of 70 °C for 60 s to enhance the drying process. For thermal annealing, films were placed in an oven under vacuum and held at 185 °C for 12 h.

Neutron Reflectivity. Neutron reflection measurements were performed at NIST on the NG7 beamline. A collimated neutron beam of 4.76 Å fixed wavelength and 0.18 Å wavelength divergence was used. A wave vector magnitude,  $q_z$ , range 0.008–0.14 was scanned for the films supported by a silicon substrate, where  $q_z = 4\pi \sin(\theta)/\lambda$  and  $\theta$  is the angle of incidence. The data were reduced and fit using Reflpak software (NIST CNR). Error intervals displayed in Tables 1 and 2 were calculated by adjusting the parameter of interest until the  $\chi^2$  indicator of good fit was changed by 5%. In situ solvent kinetics studies were achieved using an aluminum solvent chamber where DIA solvent mixture is injected into the chamber with the disordered BCP film on a silicon wafer. For in situ thermal kinetics, a thermal cell with three heating elements were used to control the temperature. The film was first measured in the disordered state at room temperature. The temperature was then heated to 90  $^{\circ}$ C (just below  $T_{\rm g}$ ) and realigned. The temperature is then increased to 160 °C and is measured. Each scan is 29 min and 13 s except for the final scan after 19 h, which is 50 min and 33 s. The temperature of the sample fluctuates during measurements between 55 and 60 °C.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.6b01690.

Figure S1 and eqs S1-S10 (PDF)

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#### Notes

The authors declare no competing financial interest.

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#### ABBREVIATIONS

BCP, block copolymer; DIA, direct immersion annealing; DSA, directed self-assembly; PS–PMMA, poly(styrene-*b*-methyl methacrylate); SVA, solvent vapor annealing; SR, swelling ratio; dPS–PMMA, deuterated poly(styrene-*b*-methyl methacrylate); TEM, transmission electron microscopy; SLD, scattering length density.

## ADDITIONAL NOTE

<sup>a</sup>Certain commercial equipment, instruments, or materials (or suppliers, or software, etc.) are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

# **REFERENCES**

(1) Samant, S. P.; Grabowski, C. A.; Kisslinger, K.; Yager, K. G.; Yuan, G.; Satija, S. K.; Durstock, M. F.; Raghavan, D.; Karim, A. Directed Self-Assembly of Block Copolymers for High Breakdown Strength Polymer Film Capacitors. *ACS Appl. Mater. Interfaces* **2016**, *8*, 7966–7976.

(2) Kim, H.-C.; Park, S.-M.; Hinsberg, W. D. Block Copolymer Based Nanostructures: Materials, Processes, and Applications to Electronics. *Chem. Rev.* **2010**, *110*, 146–177.

(3) Stoykovich, M. P.; Kang, H.; Daoulas, K. C.; Liu, G.; Liu, C.-C.; de Pablo, J. J.; Müller, M.; Nealey, P. F. Directed Self-Assembly of Block Copolymers for Nanolithography: Fabrication of Isolated Features and Essential Integrated Circuit Geometries. *ACS Nano* **2007**, *1*, 168–175.

(4) Ruiz, R.; Kang, H.; Detcheverry, F. Density Multiplication and Improved Lithography by Directed Block Copolymer Assembly, 2008.

(5) Tjong, S. C. Structural and Mechanical Properties of Polymer Nanocomposites. *Mater. Sci. Eng., R* **2006**, *53*, 73–197.

(6) Balazs, A. C.; Emrick, T.; Russell, T. P. Nanoparticle Polymer Composites: Where Two Small Worlds Meet. *Science* **2006**, *314*, 1107–1110.

(7) Mayes, A. M. Nanocomposites: Softer at the Boundary. *Nat. Mater.* 2005, 4, 651–652.

(8) Ahmed, S.; Jones, F. R. A Review of Particulate Reinforcement Theories for Polymer Composites. J. Mater. Sci. **1990**, 25, 4933–4942.

(9) Ma, P.-C.; Liu, M.-Y.; Zhang, H.; Wang, S.-Q.; Wang, R.; Wang, K.; Wong, Y.-K.; Tang, B.-Z.; Hong, S.-H.; Paik, K.-W.; et al. Enhanced Electrical Conductivity of Nanocomposites Containing Hybrid Fillers

of Carbon Nanotubes and Carbon Black. ACS Appl. Mater. Interfaces 2009, 1, 1090–1096.

(10) Leong, W. L.; Lee, P. S.; Lohani, A.; Lam, Y. M.; Chen, T.; Zhang, S.; Dodabalapur, A.; G. Mhaisalkar, S. Non-Volatile Organic Memory Applications Enabled by In Situ Synthesis of Gold Nanoparticles in a Self-Assembled Block Copolymer. *Adv. Mater.* **2008**, *20*, 2325–2331.

(11) Tsuchiya, K.; Nagayasu, S.; Okamoto, S.; Hayakawa, T.; Hihara, T.; Yamamoto, K.; Takumi, I.; Hara, S.; Hasegawa, H.; Akasaka, S.; et al. Nonlinear Optical Properties of Gold Nanoparticles Selectively Introduced into the Periodic Microdomains of Block Copolymers. *Opt. Express* **2008**, *16*, 5362.

(12) Wang, M.-J.; Lu, S. X.; Mahmud, K. Carbon-Silica Dual-Phase Filler, a New-Generation Reinforcing Agent for Rubber. Part VI. Time-Temperature Superposition of Dynamic Properties of Carbon-Silica-Dual-Phase-Filler-Filled Vulcanizates. *J. Polym. Sci., Part B: Polym. Phys.* **2000**, 38, 1240–1249.

(13) Liu, J.; Cao, D.; Zhang, L.; Wang, W. Time–Temperature and Time–Concentration Superposition of Nanofilled Elastomers: A Molecular Dynamics Study. *Macromolecules* **2009**, *42*, 2831–2842.

(14) Choi, J.; Hore, M. J. A.; Meth, J. S.; Clarke, N.; Winey, K. I.; Composto, R. J. Universal Scaling of Polymer Diffusion in Nanocomposites. *ACS Macro Lett.* **2013**, *2*, 485–490.

(15) Park, S. C.; Kim, B. J.; Hawker, C. J.; Kramer, E. J.; Bang, J.; Ha, J. S. Controlled Ordering of Block Copolymer Thin Films by the Addition of Hydrophilic Nanoparticles. *Macromolecules* **2007**, *40*, 8119–8124.

(16) Modi, A.; Bhaway, S. M.; Vogt, B. D.; Douglas, J. F.; Al-Enizi, A.; Elzatahry, A.; Sharma, A.; Karim, A. Direct Immersion Annealing of Thin Block Copolymer Films. *ACS Appl. Mater. Interfaces* **2015**, *7*, 21639–21645.

(17) Park, W. I.; Kim, J. M.; Jeong, J. W.; Jung, Y. S. Deep-Nanoscale Pattern Engineering by Immersion-Induced Self-Assembly. *ACS Nano* **2014**, *8*, 10009–10018.

(18) Yoo, M.; Kim, S.; Jang, S. G.; Choi, S.-H.; Yang, H.; Kramer, E. J.; Lee, W. B.; Kim, B. J.; Bang, J. Controlling the Orientation of Block Copolymer Thin Films Using Thermally-Stable Gold Nanoparticles with Tuned Surface Chemistry. *Macromolecules* **2011**, *44*, 9356–9365. (19) Helfand, E. Theory of the Interface between Immiscible Polymers. II. J. Chem. Phys. **1972**, *56*, 3592.

(20) Anastasiadis, S. H.; Russell, T. P.; Satija, S. K.; Majkrzak, C. F. The Morphology of Symmetric Diblock Copolymers as Revealed by Neutron Reflectivity. *J. Chem. Phys.* **1990**, *92*, 5677.

(21) Green, P. F.; Christensen, T. M.; Russell, T. P.; Jerome, R. Equilibrium Surface Composition of Diblock Copolymers. *J. Chem. Phys.* **1990**, *92*, 1478.

(22) Russell, T. P.; Menelle, A.; Hamilton, W. A.; Smith, G. S.; Satija, S. K.; Majkrzak, C. F. Width of Homopolymer Interfaces in the Presence of Symmetric Diblock Copolymers. *Macromolecules* **1991**, *24*, 5721–5726.

(23) Zeman, L.; Patterson, D. Effect of the Solvent on Polymer Incompatibility in Solution. *Macromolecules* **1972**, *5*, 513–516.

(24) Bank, M.; Leffingwell, J.; Thies, C. The Influence of Solvent upon the Compatibility of Polystyrene and Poly(vinyl Methyl Ether). *Macromolecules* **1971**, *4*, 43–46.

(25) Kern, R. J. Component Effects in Phase Separation of Polymer-Polymer-Solvent Systems. J. Polym. Sci. 1956, 21, 19–25.

(26) Berry, B. C.; Bosse, A. W.; Douglas, J. F.; Jones, R. L.; Karim, A. Orientational Order in Block Copolymer Films Zone Annealed below the Order–Disorder Transition Temperature. *Nano Lett.* **2007**, *7*, 2789–2794.

(27) Ruiz, R.; Bosworth, J. K.; Black, C. T. Effect of Structural Anisotropy on the Coarsening Kinetics of Diblock Copolymer Striped Patterns. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *77*, 054204.

(28) Yoo, M.; Kim, S.; Lim, J.; Kramer, E. J.; Hawker, C. J.; Kim, B. J.; Bang, J. Facile Synthesis of Thermally Stable Core-Shell Gold Nanoparticles via Photo-Cross-Linkable Polymeric Ligands. *Macromolecules* **2010**, *43*, 3570–3575.