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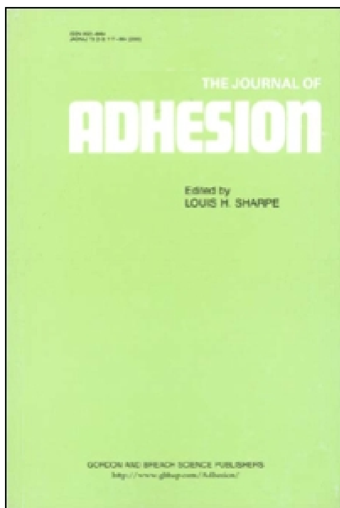

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Dewetting and Adsorption in Homopolymer Films Containing Triblock Copolymers: Role of Chain Architecture and Anchoring Block Molar Fraction

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Dewetting and Adsorption in Homopolymer Films Containing Triblock Copolymers: Role of Chain Architecture and Anchoring Block Molar Fraction

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Triblock copolymer additives are found to stabilize thin-film dewetting of B-type homopolymers with degree of polymerization (DOP) P deposited on silicon oxide. The triblock copolymers' architectures are ABA and BAB, where A and B represent anchoring and nonadsorbing blocks with DOP's N_A and N_B, respectively. Upon adding 1 vol.% of the ABA additive, dewetting is only observed for anchoring block molar fractions, f_A, below 4%. Dewetting is arrested in films containing 1 vol.% ABA, BAB, or AB that have similar values of $f_A \sim 8\%$, showing that chain architecture is not the only indicator of a successful additive. Compared with films containing diblock copolymers, the interfacial excess, z^*, of triblock copolymers at the melt/substrate interface is relatively small as measured by low-energy forward-recoil spectrometry. Because adsorbed copolymers can reduce the capillary driving force for dewetting and participate in entanglements with matrix chains, the higher coverage and grafting density observed for diblock copolymers suggests that diblocks are more effective than triblocks in improving thin-film stability.

Keywords: Adhesion; Dewetting; Forward recoil spectrometry; Polymer film; Triblock copolymers

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1. INTRODUCTION

Triblock copolymers are attractive additives used as stabilizers and flocculating agents that can be tuned by controlling the block–surface interaction [1–3]. Moreover, polymer-film stability on hard substrates has direct relevance to polymer-based displays, transistors, adhesives, and coatings [4, 5]. In many cases, dewetting of one-component films containing diblock copolymers [6–9], triblock copolymers [8], or homopolymers [9–12] have been investigated on hard and soft substrates. Most of these studies aim to understand the mechanism of dewetting, such as nucleation and growth. In contrast, few workers have investigated the effectiveness of adding copolymers to polymer films to promote adhesion and wettability [13, 14].

Adsorption of copolymers and their conformation when confined to a substrate influence thin-film adhesion. At similar nonadsorbing block degree of polymerizations or N_B, triblock copolymers exhibit a lower grafting density than diblock copolymers because triblocks generally have more loops (*i.e.*, excluded volume), whereas diblocks can crowd more efficiently at the polymer/melt interface (*cf.* Figure 1) [15]. Moreover, Hamley *et al.* [8] showed that pure diblock copolymer films have slower hole-growth rates than pure triblock copolymer films because diblocks have a greater grafting density. However, for films consisting of a polymer matrix blended with either diblocks or triblocks, the copolymers can adsorb to the interface and form entanglements with the free matrix chains. The goal of this article is to determine whether the addition of ABA or BAB triblock copolymers to homopolymer films can enhance film stability relative to films containing diblock copolymer additives [14]. An underlying issue is whether triblocks can migrate to the substrate and participate in anchoring the coating to the substrate. Thus, the interfacial excess of triblock copolymer is a good indicator that the additive will stabilize the coating *via* entanglements with matrix chains [16].

The adsorption of triblocks at the solid/solution interface has been investigated. Kim and Jo [17] developed a grand canonical Monte Carlo model to simulate the thermodynamics and micellization of triblock copolymers at constant volume fraction of anchoring block, f_A and degree of polymerization, DOP. As expected, if the B block is nonadsorbing, ABA copolymers display B loops that bridge the anchored A blocks, whereas BAB copolymers exhibit dangling tails of B with an anchored central A block as represented in Figures 1a and 1b, respectively. Nomenclature was chosen to be consistent with the triblocks in this study, where multiples of M and N are used to denote the degree of polymerizations of A and B blocks, N_A and N_B, respectively. This

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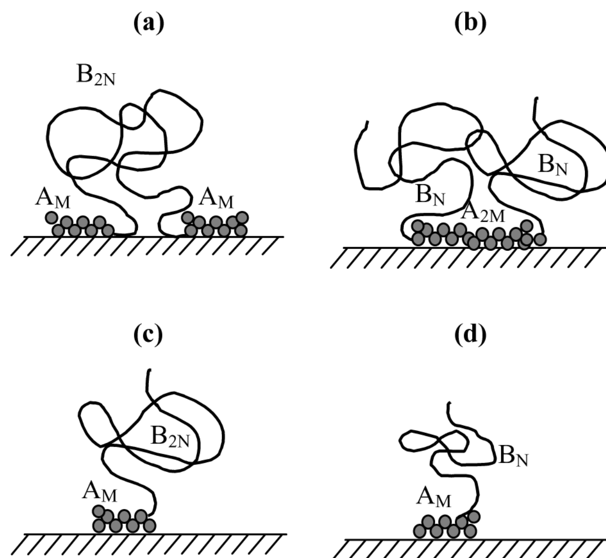

FIGURE 1 Schematic representation of chain conformation of ABA and BAB triblock copolymers and AB diblock copolymers at a substrate. For the ABA architecture, a bridge or looped conformation is expected, whereas for BAB and AB copolymers a tail conformation is expected. A and B represent anchoring and nonadsorbing blocks, whereas multiples of M and N represent the DOP of these blocks, respectively.

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model also predicts high critical micelle concentration for triblocks, relative to diblocks, suggesting that more triblock can be added to stabilize coatings.

For diblock copolymers in nonselective solvents, Marques *et al.* [18] and Guzonas *et al.* [19] found that the relative sizes of the A and B blocks determine the structure of the adsorbed layer. For $N_B >> N_A$, adsorption is dominated by the length of the dangling B block and, correspondingly, the grafting density of chains attached to the wall, σ, decreases with increasing N_B because of crowding. However, as the molar fraction of A blocks, $f_A = N_A/(N_A + N_B)$ increases, the structure of the adsorbed layer becomes dominated by N_A and σ begins to increase.

Griffiths *et al.* [20] investigated the adsorption of amphiphilic diblock and triblock copolymers onto polystyrene latex spheres from aqueous solution. They found that chain architecture was only a weak factor for BAB copolymers but important for ABA, where A is the hydrophobic (anchoring) block. In the latter case, the diblock $A_{2M}B_N$ (*cf.* Figure 1c) formed a thicker and denser layer than the triblock $A_MB_NA_M$. Moreover, ABA copolymers form a denser layer than BAB

copolymers. Based on maximizing coverage, these studies suggest that diblocks will perform better than triblocks and that the location of the anchoring block is an important consideration in chain architecture (*i.e.*, ABA is better than BAB).

Dorgan *et al.* [21] studied adsorption of end-attaching triblock and diblock copolymers to silicon oxide from toluene. In their studies, the adsorption behavior of triblocks with a bridge conformation was investigated and compared with diblocks (*cf.* Figures 1a, 1c, 1d). The triblock copolymers had short, anchoring poly(ethylene oxide) (PEO) end blocks and a long polystyrene (PS) middle block (ABA), whereas the diblock copolymers consist of a PEO block of fixed length and varying PS lengths. The diblock copolymers followed the expected scaling law, $\sigma \propto 1/N_A$. However, for ABA copolymers, σ scaled as $1/(R_{g_B}/R_{g_A})^2$, where R_{g_A} and R_{g_B} are the radii of gyration of A and B blocks, respectively. Thus, the adsorption behavior of ABA copolymers is dominated by the size of the nonadsorbing B block and σ decreases as N_B increases. An important finding from this study is that end-attaching triblock copolymers can form brush structures when adsorbing from a nonselective solvent onto a selective surface.

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Wetting and dewetting of thin liquid films have been topics of long-standing interest. A series of articles in *The European Physical Journal E* [22] reviews the current understanding about how and why thin films rupture. Interestingly enough, the mechanism responsible for film rupture is still open for debate. Most dewetting studies have focused on thin (~100 nm) polymer films deposited on either hard (*e.g.*, silicon) or soft (*e.g.*, another polymer) substrates. A few studies have attempted to improve film stability by adding end-grafted molecules or block copolymers to the homopolymer matrix. As noted in a previous study [13], diblock copolymers are effective stabilizing agents because they decrease the capillary driving force for dewetting and adopt brush conformations that enhance entanglements at the matrix/adsorbed diblock copolymer interface. Surprising, the thermodynamic work of adhesion is the same for self-adhesion of diblocks and triblocks at the same f_A [23], suggesting that dewetting should be similarly effected by the addition of diblocks or triblocks.

The goal of this article is to investigate whether triblock copolymers can stabilize films more effectively than diblock copolymers. Morover, two triblock architectures, ABA and BAB, are investigated to understand whether "loops" or "dangling ends" form more effective brushes. Finally, to be effective, the triblock copolymers must adsorb to the substrate at high enough coverage to prevent or retard dewetting. Thus, the failure of the some ABA copolymers to prevent dewetting may be attributed to insufficient anchoring block length.

TABLE 1 Molecular Characteristics of ABA and BAB Copolymers

Name	M_w (g/mol)	N_B	N_A	f_A (%)	PDI
$A_{M/3}B_{2N}A_{M/3}$	95,900	895	$2\times(14)$	3.0	1.09
$A_MB_{2N}A_M$	143,500	1285	$2\times(49)$	7.1	1.14
$A_{M/10}dB_{4N}A_{M/10}$[a]	226,500	2013	$2\times(5)$	0.4	1.22
$dB_NA_{2M}dB_N$[a]	141,500	$2\times(581)$	115	9.0	1.36

[a]"d" indicates that block is deuterated.

2. EXPERIMENTAL PROCEDURE

2.1. System

Triblock copolymers were prepared with an anchoring block molar fraction, f_A, and two different architectures, ABA and BAB (*cf*. Figures 1a and 1b). For all triblock and diblock copolymers, A represents poly (methyl methacrylate) (PMMA) blocks, which are attracted to the silicon oxide, SiO_x, substrate, whereas B represents the hydrophobic PS blocks, which do not interact strongly with SiO_x [16, 24–26]. Two triblock copolymers have similar A blocks, DOP, and f_A, but different chain architecture, namely, $A_MB_{2N}A_M$ and $B_NA_{2M}B_N$ (*cf*. Figures 1a and 1b). Table 1 contains the molecular characteristics of the triblock copolymers based on SEC and NMR. To simplify nomenclature, we set $M \sim 50$ and $N \sim 500$.

To investigate the effect of f_A on the dewetting kinetics, ABA triblocks were investigated with an A block that decreases from M to $M/10$ (*cf*. Table 1). The dewetting from blends containing triblocks was also compared with previous results for blends containing A_MB_N and A_MB_{2N} diblock copolymers [14]. Table 2 lists the diblock copolymer characteristics. The matrix is PS, a nearly neutral environment for the dPS blocks, with DOP, $P_1 = 306$, and the polydispersity index (PDI) ≤ 1.03 (Pressure Chemical, Pittsburgh, PA, USA). Note that all triblock copolymers in this article have $N_B > P_1$.

TABLE 2 Molecular Characteristics of AB Copolymers

Name	M_w (g/mol)	N_B	N_A	f_A (%)	PDI
A_MdB_N[a]	50,000	445	37	8.0	1.21
A_MdB_{2N}[a]	110,000	933	44	4.5	1.05

[a]"d" indicates that block is deuterated.

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As noted in Tables 1 and 2, two of the triblocks and both diblocks contain deuterated PS nonadsorbing blocks. This labeling provides contrast for depth-profiling studies. Note that these adsorption studies used a PS matrix with DOP, $P_2 = 1923$, and PDI ≤ 1.06 (Pressure Chemical) to prevent dewetting. To ensure that the interfacial characteristics were independent of matrix DOP, all blends followed $P_2 > 2N_B$ for $P_2 = 1923$ [16].

2.2. Sample Preparation

Dewetting and adsorption studies were performed on films containing a mixture of PS and triblock copolymer deposited on SiO_x surfaces. The SiO_x surfaces were prepared by first etching the as-received silicon wafers for 3 min in a hydrofluoric acid–water solution (1:7) to remove the native oxide. These wafers were placed in an ultraviolet ozone cleaner for 10 min to grow a clean SiO_x surface [14].

For dewetting experiments, polymer films were prepared by spin-casting a solution of 2.0 wt.% polymer in toluene at 2000 rpm for 60 s on SiO_x. Either 10 or 1 vol.% triblock was blended with the PS matrix, $P_1 = 306$. Films were dried in a vacuum oven at 110°C for 12 h to remove solvent. The ellipsometric thickness was ~83 nm for 10 vol.% and ~79 nm for 1 vol.% films. The PS–diblock blend films contained 1 vol.% copolymer.

Samples were annealed in a Mettler FP90 hot-stage (Mettler, Columbus, OH, USA) preheated to 175°C and examined by an optical microscope (OM) linked to a video camera and VCR. The hole diameter and density were measured as a function of annealing time. By plotting hole diameter, D, *versus* annealing time, t, the hole-growth rate, v, was determined. The growth rate was determined at early times during linear growth. The hole diameter was measured until holes touched. A Digital Instrument Dimension 3000 atomic force microscope (AFM) (Santa Barbara, CA, USA) was used to image the hole-floor morphology and roughness. The root-mean-square, RMS, roughness values were determined over a 5 μm × 5 μm area using Nanoscope V5.12 (Santa Barbara, CA, USA) software.

For the adsorption studies, the polymer films were prepared by spin-coating a solution of 3.0 wt.% polymer in toluene at 2000 rpm for 60 s on SiO_x. The solutions were filtered to remove dust particles. Blends contained 5 vol.% triblock copolymer with a PS (P_2 = 1923). Only blends with the deuterated triblocks $A_{M/10}dB_{4N}A_{M/10}$ and $dB_NA_{2M}dB_N$ (*cf.* Table 1) were studied. The ellipsometric thickness values were 162 nm and 176 nm, respectively. Samples were annealed in a vacuum oven at 175°C for 5 days to attain equilibrium [24, 25].

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LE-FRES experiments on films containing 5 vol.% diblock copolymer (*cf.* Table 2) were previously reported [16].

Low-energy forward-recoil spectrometry (LE-FRES) was used to determine the interfacial excess, z^*, of the copolymer. Details have been given elsewhere [27]. Using 2.0 MeV He^+ at 15° incident and exit angles with respect to the film and a 6-μm Mylar® stopper filter, the depth resolution was 55 nm at the surface and 63 nm at a depth of 180 nm beneath the surface. The minimum z^* value is ~0.5 nm.

3. RESULTS AND DISCUSSION

3.1. Dewetting

3.1.1. Addition of ABA Triblocks to Homopolymer Films

Three ABA triblock copolymers were prepared as described in Table 1. These triblock copolymers have a long nonadsorbing block relative to the matrix (*i.e.*, $N_B > P_1 = 306$). The anchoring block lengths are 5, 14, and 49, corresponding to f_A's = 0.4, 8.0, and 7.1. Two of these triblocks have similar N_B, $A_M B_{2N} A_M$, and $A_{M/3} B_{2N} A_{M/3}$.

Figure 2 shows D *versus* t for films containing 10 vol.% triblock copolymer, $A_{M/3} B_{2N} A_{M/3}$ (open circles) and $A_{M/10} B_{4N} A_{M/10}$ (solid squares), as well as pure PS (solid triangles). For all cases, D initially increases linearly [9, 11] with t, and after approximately 30 min slows down* to $D \sim t^{0.70}$, $D \sim t^{0.67}$, and $D \sim t^{0.70}$, respectively, in good agreement with the expected $D \sim t^{2/3}$ behavior [11, 28, 29]. Although the addition of the ABA copolymers does not prevent dewetting, the hole-growth rate is much slower than in the pure PS case where D becomes ~550 μm before impinging after 100 min. Hole impingement is delayed in the triblock case. However, because the nucleation density of holes is slightly larger in the triblock systems, holes reach diameters of ~320 μm and 310 μm, respectively, before impinging. The hole-growth rates, v, are ~3.3 μm/min, 3.1 μm/min, and 7.5 μm/min, respectively. No dewetting was observed for films containing 10 vol.% $A_M B_{2N} A_M$ for times up to 16 h. Figure 3 shows how v decreases as f_A increases. For blends containing 10 vol.% triblock, dewetting is observed for $0\% < f_A < 4\%$. However, for the triblock copolymer with $f_A = 7.1\%$, films are stable, demonstrating that the length of the anchoring end blocks relative to the nonadsorbing middle block is an important factor in adhesion promotion.

*For simplicity, Figure 2 shows D *vs.* t; however, plots of log D *versus* log t for $A_{M/3} B_{2N} A_{M/3}$, $A_{M/10} B_{4N} A_{M/10}$ and pure PS film show slopes of 0.7, 0.67, and 0.7, respectively.

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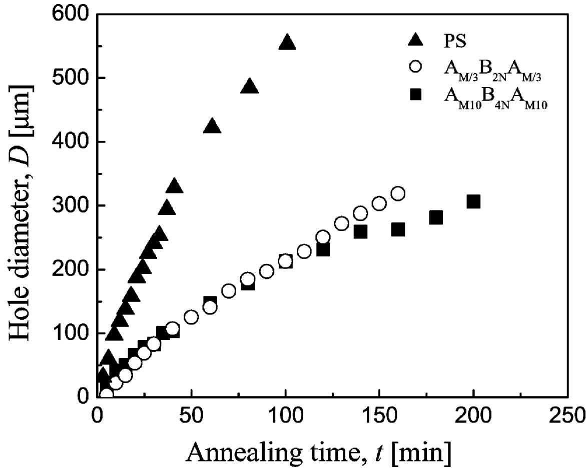

FIGURE 2 Hole diameter, D, as a function of annealing time, t, for pure PS film with $P_1 = 306$ (closed triangles) and PS–ABA blends containing 10 vol.% of $A_{M/3}B_{2N}A_{M/3}$ (open circles) and $A_{M/10}dB_{4N}A_{M/10}$ (solid squares). The film containing 10 vol.% of $A_{M/10}dB_{4N}A_{M/10}$ was stable against hole growth.

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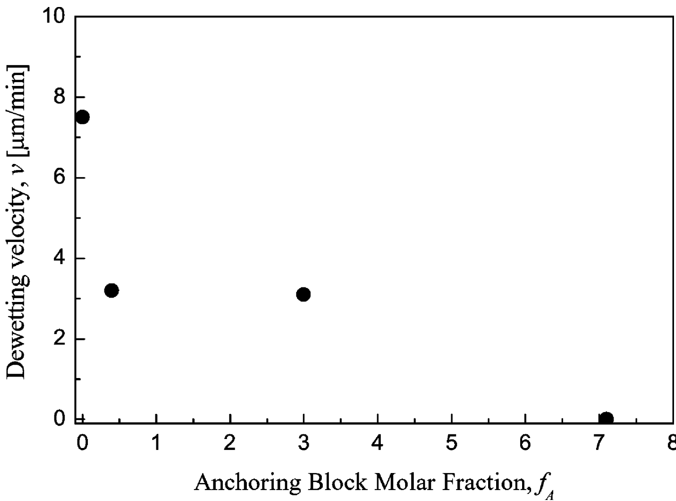

FIGURE 3 Hole growth rate, v, as a function of anchoring block molar fraction, f_A, for PS–ABA blend films containing 10 vol.% triblock copolymer and PS ($P_1 = 306$). In the plot $f_A = 0\%$ corresponds to the pure PS film and $v = 0$ corresponds to the stable PS–$A_M B_{2N} A_M$ film.

To complement hole-growth studies, AFM was used to investigate the morphology of the hole floor inside the rims. For films containing $A_{M/3}B_{2N}A_{M/3}$, $A_{M/10}B_{4N}A_{M/10}$, and pure PS, the RMS roughness values are 1.0 nm, 6.0 nm, and ~0.3 nm, respectively. Relative to the roughness of bare SiO_x (~0.2 nm) [14], these values for triblock films are supporting evidence that the hole floors are covered with residual polymer. This result is consistent with autophobic dewetting [8, 9] of PS from a surface with a high grafting density of adsorbed chains. The residual polymer can be explained by a model that describes dewetting of blend films containing diblock copolymer [14]. In this model, viscous dissipation during hole growth takes place at the interface between the bulk and adsorbed layers, instead of between the solid substrate and adsorbed layer. Thus, as the rim retracts to expose substrate, mounds of adsorbed chains are left behind.

Figures 4a and 4b show the cross-sectional analysis of the hole floor for the triblock copolymer systems $A_{M/3}B_{2N}A_{M/3}$ and $A_{M/10}B_{4N}A_{M/10}$, respectively. These cross-sectional images are characteristic of three or more holes for each system. Figures 4a and 4b show a rough surface with peaks corresponding to polymer mounds. For the $A_{M/3}B_{2N}A_{M/3}$ system (Figure 4a), the hole floor is covered with discrete patches about 4.0 nm high, whereas for $A_{M/10}B_{4N}A_{M/10}$ (Figure 4b), the features are much higher, about 10 nm. In a previous study [13], polymer patches were found to develop at the contact line between the receding rim wall and the hole floor. The larger patches suggest that disentanglement of the free PS matrix chains from the $A_{M/10}B_{4N}A_{M/10}$copolymer brush

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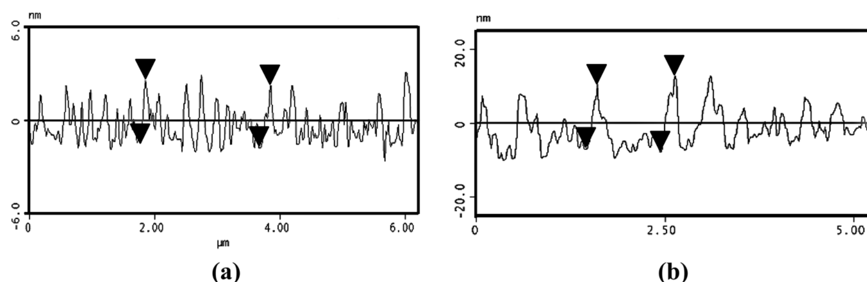

FIGURE 4 AFM cross-section images (a, b) of the hole floor of PS–ABA films containing 10 vol.% triblock where $f_A = 3.0$ (a) and $f_A = 0.4\%$ (b). The PS matrix has $P_1 = 306$ and the substrate is SiO_x. The cross-section images show patches of polymer across the hole floor for both systems. Triangles denote selected maxima or minima in film height.

is more strongly hindered than when the B mid-block is much shorter (*i.e.*, $2N$). This observation is consistent with the slightly slower hole growth for the $A_{M/10}B_{4N}A_{M/10}$ system.

3.1.2. ABA, BAB, and AB Chain Architecture

To understand the effect of chain architecture on dewetting, triblock copolymers of $A_MB_{2N}A_M$ and $dB_NA_{2M}dB_N$ were prepared with similar values of f_A, namely 7.1 and 9.0, respectively. The former architecture is expected to result in a brush with a bridge conformation (*cf.* Figure 1a), whereas a $dB_NA_{2M}dB_N$ brush would have two extended tails (*cf.* Figure 1b). The dewetting of these triblock systems is compared with diblock copolymers, A_MdB_N and A_MdB_{2N}. The A_MdB_N has an N_B approximately half of the B block length of both triblock copolymers, but a similar f_A, 8.0, whereas A_MdB_{2N} has a N_B similar to both triblock copolymers, but with about half the fraction of adsorbing units, $f_A = 4.5$. The triblock and diblock molecular characteristics are given in Tables 1 and 2, respectively. To be consistent with previous experiments with diblock copolymers, 1 vol.% triblock copolymer was added to a PS matrix with $P_1 \sim 306$. Thus, for all copolymers, $N_B > P_1$. Recall from the previous section that PS films with 10 vol.% of $A_MB_{2N}A_M$ are stable up to 16 h.

PS films containing any of the four additives are found to be stable. Namely, the addition of only 1 vol.% of either $A_MB_{2N}A_M$ or $dB_NA_{2M}dB_N$ prevents dewetting for times up to 16 h. Thus, architectures resulting in bridge or tail conformations at similar values of f_A are effective stabilizers. For films containing 1 vol.% A_MdB_N ($f_A \sim 8\%$) or A_MdB_{2N} ($f_A = 4.5\%$), dewetting is also arrested [14]. The diblocks have the tail conformations represented in Figures 1d and 1c, respectively. In summary, for these diblocks and triblocks, with $N_B > P_1$ and $f_A > 4\%$, dewetting is completely suppressed independent of copolymer architecture.

3.2. Adsorption of Triblock and Diblock Copolymers

The interfacial characteristics of a copolymer absorbed at the melt/substrate interface are governed by the molecular characteristics as well as monomer–monomer and monomer–substrate interactions. The parameters include the degrees of polymerization of the matrix P, the nonadsorbing block N_B, and the adsorbing block N_A. The interaction parameters are the Flory–Huggins segment–segment interaction parameter and the interaction energies between each segment type and the substrate. Interfacial excess, z^*, is defined as the area

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under the volume-fraction profile, $\phi(z)$, which is in excess relative to the bulk volume fraction of adsorbed polymer, ϕ_∞:

$$z^* = \int_0^\infty dz[\phi(z) - \phi_\infty]. \tag{1}$$

The grafting density of chains attached to the wall, σ, and the average distance between grafted chains, D, is determined from the experimentally measured z^*:

$$\sigma = z^* \rho N_{\mathrm{av}}/(N\mathrm{m}) \tag{2}$$

and

$$D = \sigma^{-1/2} \tag{3}$$

where N is the number of segments of adsorbed chains, ρ is the polymer density, m is the relative molecular mass, and N_{av} is Avogadro's number. The degree of chain stretching is reflected in D. For example, the adsorbed chains adopt a mushroom-like conformation if chains are far apart or $D >> R_{g_B}$, where R_{g_B} is the radius of gyration of the dPS block [30]. For $D \sim R_{g_B}$, adsorbed polymers can form "clusters," whereas, for $D < R_{g_B}$ chains must extend because of excluded volume.

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Figure 5 shows the dPS volume-fraction profile, $\phi_B(z)$, for a film containing 5 vol.% $dB_NA_{2M}dB_N$ in a PS matrix with $P_2 = 1923$. Within the resolution of LE-FRES, segregation of $dB_NA_{2M}dB_N$ to the film surface is not significant. However, $dB_NA_{2M}dB_N$ does segregate to SiO_x with a $z^* = 2.6$ nm. The solid line represents a uniform bulk concentration or ϕ_∞ in Equation (1). Figure 6 shows $\phi_B(z)$ for a film containing 5 vol.% $A_{M/10}dB_{4M}A_{M/10}$ in a PS matrix with $P_2 = 1923$. Segregation of $A_{M/10}dB_{4M}A_{M/10}$ to the film surface is not observed. Moreover, segregation to SiO_x is small and only slightly broadens the back edge to yield $z^* \sim 0.6$ nm, which is close to the sensitivity limit of LE-FRES. The solid line represents a uniform bulk concentration, $\phi_\infty = 0.05$. The yield beyond 210 nm is statistical noise. The z^* values for $dB_NA_{2M}dB_N$ and $A_{M/10}dB_{4M}A_{M/10}$ are consistent with the dewetting behavior for films containing these additives. Namely, in the former case, hole growth was completely suppressed, whereas, in the latter, holes grew until they touched.

The surface excess of A_MdB_N and A_MdB_{2N} copolymers from a PS melt were previously reported [14]. As in the triblock system, 5 vol.% copolymer and a PS matrix with $P_2 = 1923$ were used. The interfacial properties of the diblock and triblock copolymer systems

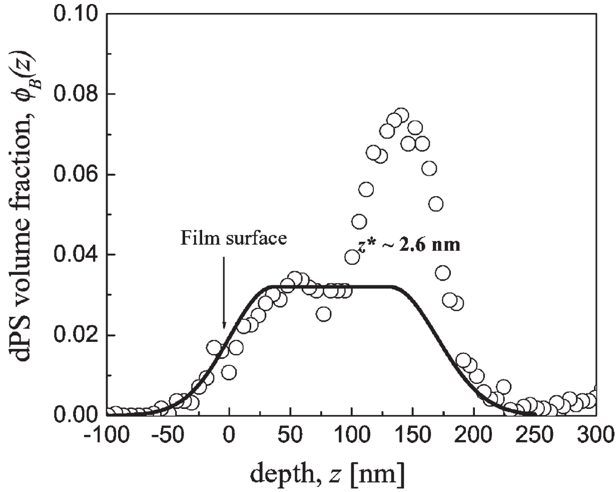

FIGURE 5 LE-FRES volume-fraction profile of the dPS block in a PS–$dB_N A_{2M} dB_N$ film annealed for 5 days at 175°C (open circles). The PS matrix has $P_2 = 1923$. The volume fraction of dPS in the as-cast sample is 0.05. The solid line represents a uniform concentration. The arrow indicates the position of the film surface and z^* is given by the area between the solid line and symbols.

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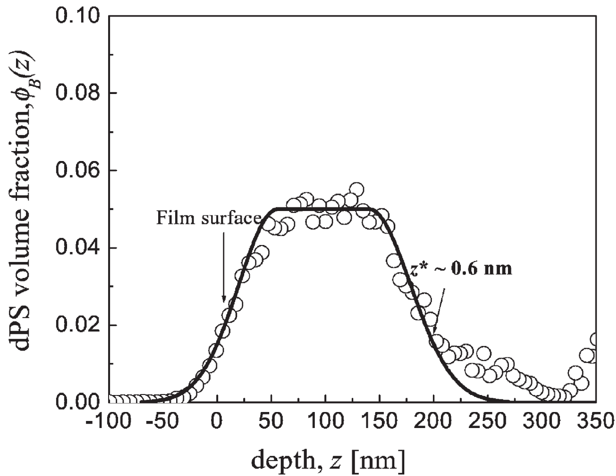

FIGURE 6 LE-FRES volume-fraction profile of the dPS block in PS–$A_{M/10} dB_{4N} A_{M/10}$ film annealed for 5 days at 175°C (open circles). The PS matrix has $P_2 = 1923$. The volume fraction of dPS in the as-cast sample is 0.05. The arrow indicates the position of the film surface. The z^* is not large enough to produce a peak but rather gives rise to a broadening of the back edge.

TABLE 3 Interfacial Properties of Films Containing AB, ABA, and BAB Copolymers

Name	M_w (g/mol)	f_A (%)	N_B	z^* [nm]	σ [chains/nm^2]	D/R_{g_B}
A_MdB_N	50,000	8.0	445	4.0	0.055	0.75
A_MdB_{2N}	110,000	4.5	933	6.0	0.040	0.60
$A_{M/10}dB_{4N}A_{M/10}$	226,500	0.4	2013	0.6	0.002	1.8
$dB_NA_{2M}dB_N$	141,500	9.0	$2 \times (581)$	2.6	0.015	0.87

are shown in Table 3. Of the four deuterated additives, only the $A_{M/10}dB_{4M}A_{M/10}$ copolymer was unable to prevent dewetting. Analysis of D/R_{g_B} suggests a potential explanation. For $A_{M/10}dB_{4M}A_{M/10}$, D is greater than R_{g_B} and the ABA chains are isolated from their neighbors and adopt a mushroom-like conformation. However, for $dB_NA_{2M}dB_N$ and both diblock additives, D is less than R_{g_B} and chains overlap with their neighbors, resulting in a stretched, brush-like conformation. Thus, these three additives may impart stability to coatings by decreasing the capillary driving force for dewetting (*i.e.*, lower interfacial tension) and adopt brush conformations that enhance entanglements with matrix chains. The former contribution has been nicely described for end-grafted chains added to a solvent system [31] and the effect of brush density, molecular weight, and free chains [32]. One aim of the present study is to understand how entanglements between matrix chains and either tails or loops from the tethered block copolymer hinders or prevents film dewetting.

A comparison of interfacial properties in Table 3 shows that diblocks adsorb more strongly than triblocks (*i.e.*, more chains per unit area), in good agreement with adsorption behavior in solutions [20, 21]. Although the number of different copolymers is limited, some trends can be established. Diblocks show higher values of z^*, suggesting that they can be more easily accommodated at the melt/SiO_x interface than triblocks (*i.e.*, less excluded volume). Comparing the A_MdB_N and $dB_NA_{2M}dB_N$ copolymers with similar values of f_A, the diblock has almost four times the number of chains per unit area. This sparse grafting of the triblock results from the longer anchoring and nonadsorbing blocks (*i.e.*, N_A and N_B are twice as large for the triblock). Comparing the A_MdB_{2N} and $dB_NA_{2M}dB_N$ copolymers with similar total nonadsorbing block lengths, the diblock has almost three times the grafting density and 30% closer spacing between chains. This result shows that the tail of the diblock is more strongly stretched than either tail of the triblock, even though the former is twice as long as the latter [20, 21].

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Thus, based on adsorption studies, diblock copolymers are expected to be more effective thin-film stabilizing agents than triblock copolymers with similar block lengths. For the diblocks, in particular $A_M dB_N$ and $A_M dB_{2N}$, the coverage increases by 50% as N_B doubles, as shown in Table 3. These results suggest that the addition of diblocks that have a relatively large N_B should be more effective in improving thin-film stabilization. For copolymers with $N_B >> N_A$, Marques *et al.* [18] and Guzonas *et al.* [19] have shown that adsorption is dominated by the nonadsorbing block length and increases as N_B increases. As a final note, the complementary triblocks $A_M B_{2N} A_M$ and $dB_N A_{2M} dB_N$ prevented dewetting. Although the interfacial properties of $A_M B_{2N} A_M$ cannot be measured, solution studies [20] show that ABA copolymers form a denser adsorbed layer than BAB copolymers of similar size. If true in the melt, higher z^* values are expected for $A_M B_{2N} A_M$ copolymers, suggesting that this copolymer is more effective in stabilizing thin films than $dB_N A_{2M} dB_N$. Further studies are needed to support this hypothesis.

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4. CONCLUSIONS

The effect of triblock chain architecture and anchoring block molar fraction on dewetting and adsorption was investigated. Adding ABA triblocks (bridge), BAB triblocks (tail), and AB diblocks with $f_A > 4\%$ stabilize films for annealing times up to 16 h regardless of architecture. However, for $f_A < 4\%$, dewetting is observed for thin-blend films containing ABA triblocks. Thus, f_A is an important parameter in selecting copolymer additives for thin-film stabilization and should have a value greater than 4% for copolymers with $N_B > P$. The length of the nonadsorbing block, N_B, strongly influences the interfacial properties of AB and BAB copolymers adsorbed to the melt/substrate strate interface. Although films containing 1 vol.% $dB_N A_{2M} dB_N$, $A_M dB_N$, or $A_M dB_{2N}$ are stable, the z^* values increase from 2.6 to 4.0 to 6.0, respectively. In the melt, stronger adsorption of diblock copolymers in comparison with triblock copolymers is consistent with adsorption from solution [20, 21] and suggests that diblocks are more effective than triblocks in improving thin-film stability.

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