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Neutrality Conditions for Block Copolymer Systems on Random Copolymer Brush Surfaces

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ABSTRACT: The wetting behavior of P(S-*b*-I) and P(S-*b*-nBMA) thin films placed upon tunable P(S-*r*-MMA) brush surfaces is addressed. Homopolymer dewetting experiments show an increase in interfacial energy between PI and P(S-*r*-MMA) with increasing styrene fraction, while the interfacial energy dependence of PnBMA with brush composition was indeterminate. Reflection optical micrographs of block copolymer films cast on PS and PMMA brush surfaces show island/hole structures that are indicative of a parallel orientation of the block copolymer domains with respect to the film boundaries. The micrographs are identical in structure and are comprised of the same interference colors, indicating antisymmetric wetting conditions for films cast upon both PS and PMMA brush surfaces. Thus, for P(S-*b*-I) and P(S-*b*-nBMA) films cast upon PMMA brush surfaces, unfavorable wetting of the PS component occurs at the PMMA brush surface in order to avert PI/PMMA and PnBMA/PMMA interactions which are more unfavorable. Consequently, the dependence of the interfacial energy between PI or PnBMA with P(S-*r*-MMA) random copolymer brushes as a function of styrene content does not influence the behavior of these systems. The general wetting behavior of block copolymer films on random copolymer surfaces is discussed with specific attention being made to wetting condition inversions and neutral surfaces.

Introduction

It has been well established that the structure of diblock copolymer thin films is dictated by boundary conditions, in particular, commensurability and interfacial interactions.[1−6] Generally, preferential wetting of one block at an interface[1−4] occurs to minimize the free energy of the system, leading to a parallel orientation of the microdomains.[5,6] Symmetric wetting corresponds to the case where the same component wets both interfaces, whereas films having a different component wetting each of the interfaces corresponds to antisymmetric wetting. For unconfined films having a lamellar morphology, quantization of the film thickness to values of nL_0 and $(n + {}^1/_2)L_0$, for symmetric and antisymmetric wetting cases, respectively, where n is an integer and L_0 is the bulk lamellar period, occurs to alleviate frustration of the block copolymer domains induced by chain stretching or compression. This results in a terraced topography with surface features having heights of L_0.

Recently, Mansky et al.[7] showed that the surface characteristics of a substrate can be precisely controlled by anchoring P(S-*r*-MMA) random copolymers to silicon substrates, i.e., attaching random copolymer brushes. By varying the composition of the random copolymer, surfaces having characteristics ranging from PS to PMMA could be obtained. Tunability was demonstrated by dewetting studies of PS and PMMA homopolymer films placed upon the random copolymer brush surfaces. Dewetting occurred for samples having sufficient chemical mismatch between the homopolymer and random copolymer surface: PS homopolymer dewetted random copolymer surfaces having styrene fractions $f \leq 0.65$ and PMMA dewetted surfaces when $f \geq 0.50$. Contact angles between the homopolymer and random copolymer brush layer were measured for the dewetted structures, i.e., droplets, by AFM. Interfacial energies between PS and PMMA homopolymer with the random copolymer layer were extracted and found to decrease and increase, respectively, with increasing styrene fraction in the random copolymer brush. A condition of neutrality was obtained for random copolymer surfaces having a styrene fraction of 0.58 as these surfaces were found to be nonpreferential to PS and PMMA; i.e., the interfacial energies of PS and PMMA with the random copolymer layer were equal.

It was found that the orientation of the microphase-separated domains of a symmetric diblock copolymer of PS and PMMA, denoted P(S-*b*-MMA), on the random copolymer surfaces could be controlled by tuning the interfacial interactions.[8] For block copolymer films placed upon random copolymer brushes rich in PS, the PS block segregated to the random copolymer interface, leading to symmetric wetting. (The PS block segregates to the polymer/air interface due to its lower surface energy.) Conversely, P(S-*b*-MMA) films on PMMA-rich random copolymers showed antisymmetric wetting conditions due to the wetting of the random copolymer layer with the PMMA block. For block copolymer films cast on nonpreferential random copolymers, segregation of either PS or PMMA blocks to the random copolymer layer was arrested due to the balance of interfacial energies of the respective blocks with the random copolymer. This led to a perpendicular orientation of the

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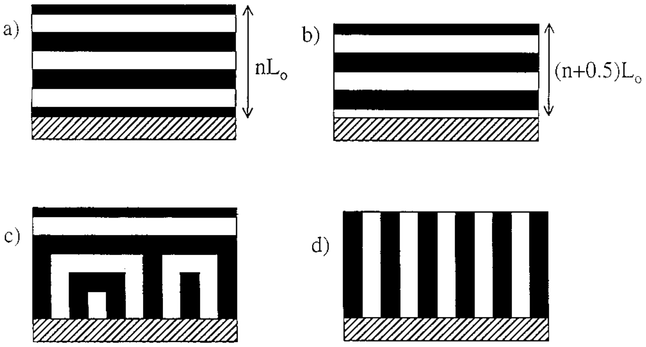

Figure 1. Block copolymer structures observed for films having (a) symmetric boundary conditions, (b) antisymmetric boundary conditions, (c) one nonpreferential and one preferential boundary surface, and (d) nonpreferential boundaries.

lamellar microdomains near the block copolymer/random copolymer interface. At the air surface, however, a parallel orientation is observed as the PS blocks segregate to the air surface, due to its lower surface energy as compared to that of PMMA, resulting in a mixed lamellar morphology. Thus, by varying the composition of the random copolymer brush surface, a conversion from symmetric to antisymmetric wetting occurs. The random copolymer composition at which this change occurs is synonymous with the nonpreferential random copolymer composition where the perpendicular orientation of the lamellae is induced. Finally, it has been shown that nonpreferential random copolymers localized to the air surface *eliminate* the preferential segregation of the PS block to the air surface. By utilizing this approach with the substrate grafted nonpreferential random copolymer, a block copolymer film can be confined between two nonpreferential interfaces, leading to a perpendicular orientation of the domains throughout the film thickness.[9,10] These four boundary conditions are shown schematically in Figure 1.

The strategy of localizing random copolymers to substrates, comprised of the same monomeric units, to control interfacial interactions is generic and can be applied to other polymer systems. By selecting random copolymers having the same chemical constitution as the block copolymer of interest, a nonpreferential interaction condition must exist at some random copolymer composition. Recent advances in “living” free radical polymerizations should provide pathways in synthesizing a variety of well-defined random copolymers.[11−16]

It may also be possible to use random copolymers brushes that are chemically distinct from the block copolymer of interest to control interfacial interactions; e.g., P(A-*r*-B) random copolymers may be utilized to control the orientation of microdomains consisting of P(B-*b*-C) or P(C-*b*-D) block copolymers. As discussed by Matsen,[17] a nonpreferential random copolymer should exist for systems where C and D have opposite affinities for A and B. This issue is addressed for two P(B-*b*-C) systems, poly(styrene-*block*-isoprene) and poly(styrene-*block*-*n*-butyl methacrylate), denoted P(S-*b*-I) and P(S-*b*-*n*BMA), respectively, with P(S-*r*-MMA) modified surfaces. The salient features observed in the P(B-*b*-C) systems can, of course, be directly related to the more general case of P(C-*b*-D) block copolymers.

Results

Prior to studying the behavior of P(S-*b*-I) and P(S-*b*-*nBMA*) block copolymer films on P(S-*r*-MMA) random copolymer surfaces, the interfacial interaction dependence of the PI and PnBMA homopolymer with the random copolymer surface was examined as a function of random copolymer brush composition. PI (M_w = 300 000, M_w/M_n = 1.05) and PnBMA (M_w = 28 000, M_w/M_n = 1.1) homopolymer films, having thicknesses of ~32 nm, were spin-coated onto random copolymer brush surfaces having thicknesses of ~5 nm with compositions ranging from pure PS to pure PMMA. The random copolymers are described in Table 1, and the preparation of the random copolymer brushes has been described elsewhere.[7] Films were annealed under vacuum at 80 °C for 3 days and then quenched to room temperature.

Table 1

f	M_w	M_w/M_n	f	M_w	M_w/M_n
1.00	9 800	1.11	0.58	9 600	1.80
0.90	11 000	1.39	0.52	10 700	1.79
0.80	10 600	1.30	0.34	8 900	1.57
0.72	10 350	1.50	0.00[a]	8 000	1.10
0.67	10 800	1.49			

[a] Synthesized via a group-transfer polymerization.

Optical microscopy of the films showed that the PI films dewetted the random copolymer brush surfaces when $f \geq 0.60$ but remained optically smooth otherwise. PnBMA films, on the other hand, remained optically smooth for all compositions of the random copolymer brush. The structures of the dewetted PI films were examined with a Digital Instruments atomic force microscope in the tapping mode. A typical dewetted PI film is shown in Figure 2 where $f = 0.8$. The heights and radii of the droplets were measured, and contact angles, θ, were obtained assuming a hemispherical shape.[18] The interfacial energy between the homopolymer and random copolymer brush can be related to the measured contact angle through Young’s equation,

$$\gamma_{If} = \gamma_f - \gamma_I \cos \theta_{If}$$

where γ_{If} is the interfacial energy between the PI homopolymer and the random copolymer, γ_I is the surface energy of PI, θ_{If} is the measured contact angle, and γ_f is the surface energy of the grafted copolymer which was approximated by the weighted average of the surface energy of PS and PMMA. It was observed that the PI contact angle increased with increasing f, as shown in Figure 3, indicating an increasing interfacial energy between the PI homopolymer and brush. The dependence of the interfacial energy of PnBMA on the brush composition could not be determined, since PnBMA wet the brush surface for all compositions.

With these results, the wetting behavior of diblock copolymer films was subsequently studied for symmetric P(S-*b*-I) and P(S-*b*-nBMA), having M_w = 18 000 and 85 000, respectively. For P(S-*b*-I), films having thicknesses of 88 nm were spin-coated onto PS and PMMA brush surfaces and annealed at 120 °C for 3 days. Upon annealing, the films ordered into lamellar sheets with a spacing corresponding to the bulk period, L_0, 17 nm. Due to the incommensurability of the original film thickness with L_0, islands or holes having heights of L_0 formed to alleviate frustration of the diblock copolymer domains upon both PS and PMMA brush surfaces. Comparison of the optical micrographs taken on P(S-*b*-I) films cast on PS and PMMA brush surfaces (Figure 4) shows that terraced structures of identical patterns and interference colors were observed, indicating that

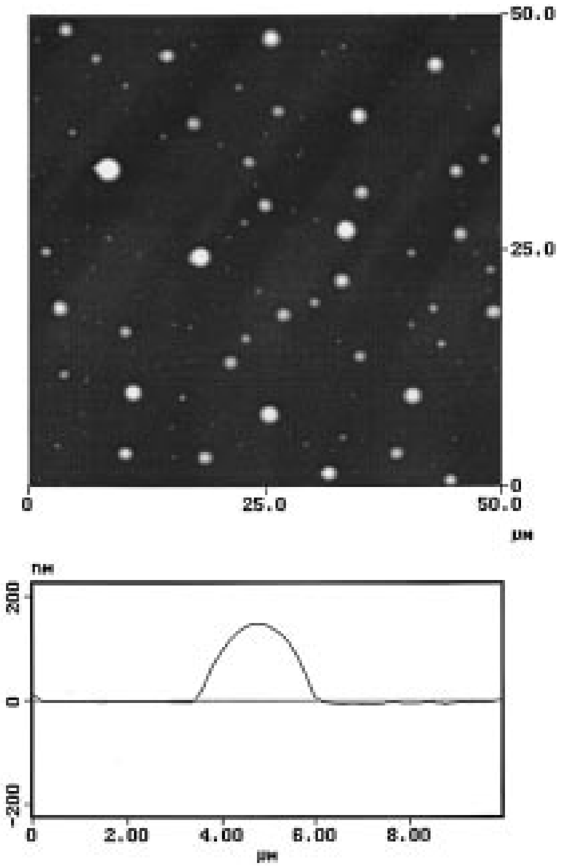

Figure 2. (a) Height contrast AFM image of dewetted PI droplets on PS brush surface. (b) Line scan measuring height and diameter of a PI droplet.

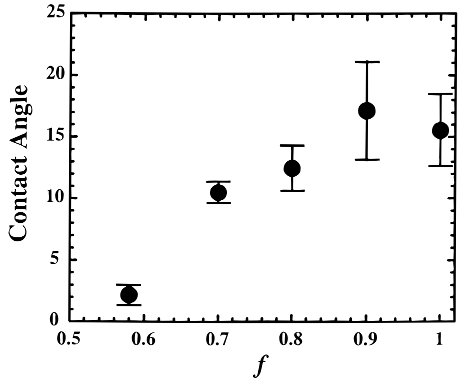

Figure 3. Contact angle dependence between PI droplets and P(S-*r*-MMA) random copolymer brush layer as a function of styrene fraction, *f*, in random copolymer.

the wetting conditions are the same. For films cast upon PS brush surfaces, the PS block segregates to the block copolymer/brush interface while the PI block segregates to the polymer/air interface (the surface energy of PI is less than that of PS), leading to antisymmetric wetting conditions. Since the optical micrograph for the film placed on the PMMA brush surface is identical to that obtained from the film placed upon the PS brush, antisymmetric boundary conditions must also be present for the film placed upon the PMMA brush surface. Thus, the PS block segregates to the brush interface regardless of the brush composition.

Similarly, P(S-*b*-nBMA) films, having thicknesses of 195 nm and a bulk lamellar period of 40 nm, were spin-coated onto PS and PMMA brush surfaces, annealed under vacuum at 185 °C for 3 days, and quenched to room temperature. Examination of the two films with optical microscopy (Figure 5) revealed matching surface patterns, indicating that these films also had identical boundary conditions. Since antisymmetric wetting can be inferred for the film cast upon the PS brush, i.e., PnBMA has a lower surface energy as compared to that of PS and segregation of the PS block to the PS brush layer is expected, the sample placed upon the PMMA brush surface must also have antisymmetric wetting conditions. Thus, the PS block segregates to the block copolymer/brush interface regardless of the brush composition. As a comparison, P(S-*b*-nBMA) films having film thicknesses of ~200 nm were cast onto a PS brush surface and an untreated silicon substrate and were annealed under identical conditions. The micrographs of these samples (Figure 6) clearly show contrasting surface patterns consisting of different interference colors due to the difference in wetting conditions. This is expected since the film placed upon the untreated silicon substrate has symmetric wetting boundary conditions due to the segregation of PnBMA to both film interfaces.[19,20]

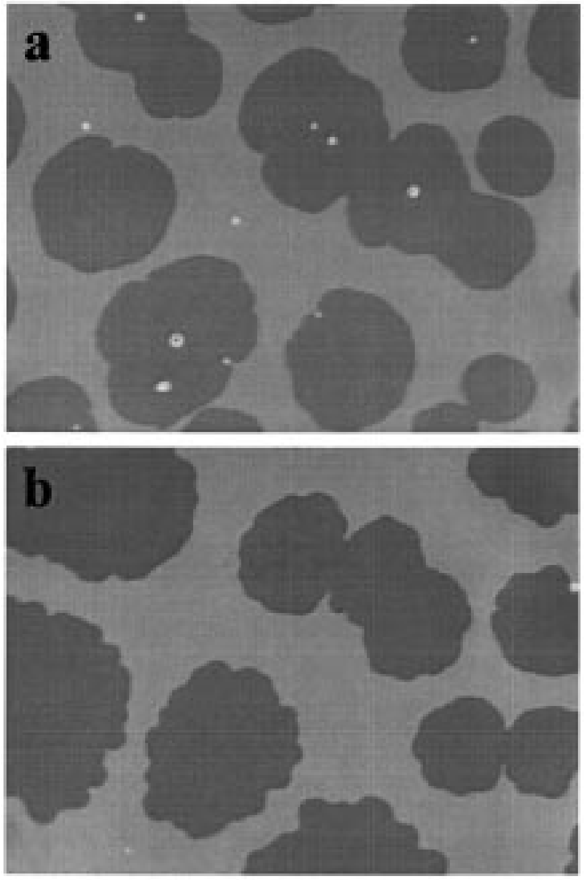

Figure 4. Optical micrographs of P(S-*b*-I) thin films on (a) PS and (b) PMMA brush surfaces. Image is 300 × 400 μm.

Discussion

The results can be summarized as follows. Antisymmetric wetting is observed for P(S-*b*-I) and P(S-*b*-nBMA) films cast upon PS and PMMA brush surfaces. For films placed upon PS brush surfaces, this is expected as the PS blocks segregate to the brush interface to minimize unfavorable PS/PI and PS/PnBMA interactions. However, for the films placed on PMMA brush surfaces, the

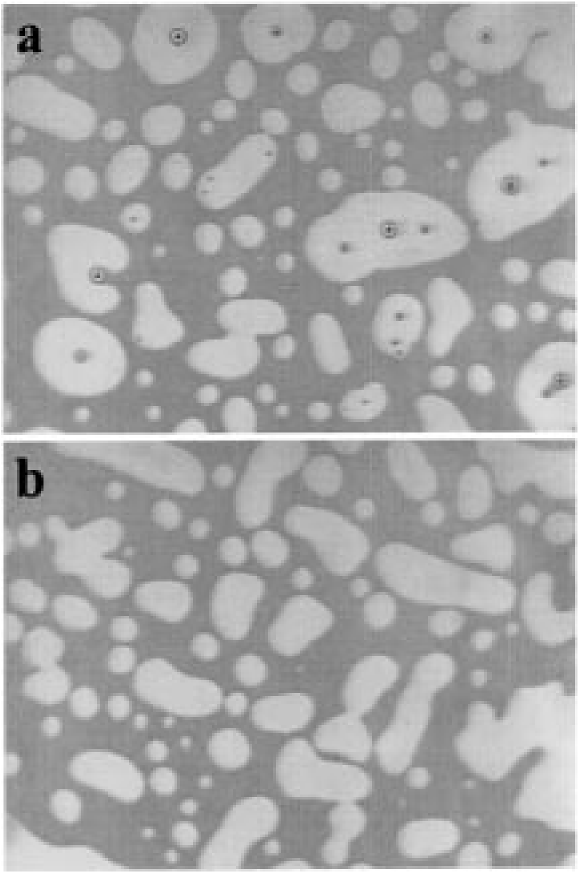

Figure 5. Optical micrographs of P(S-*b*-nBMA) thin films on (a) PS and (b) PMMA brush surfaces. Image is 300 × 400 μm.

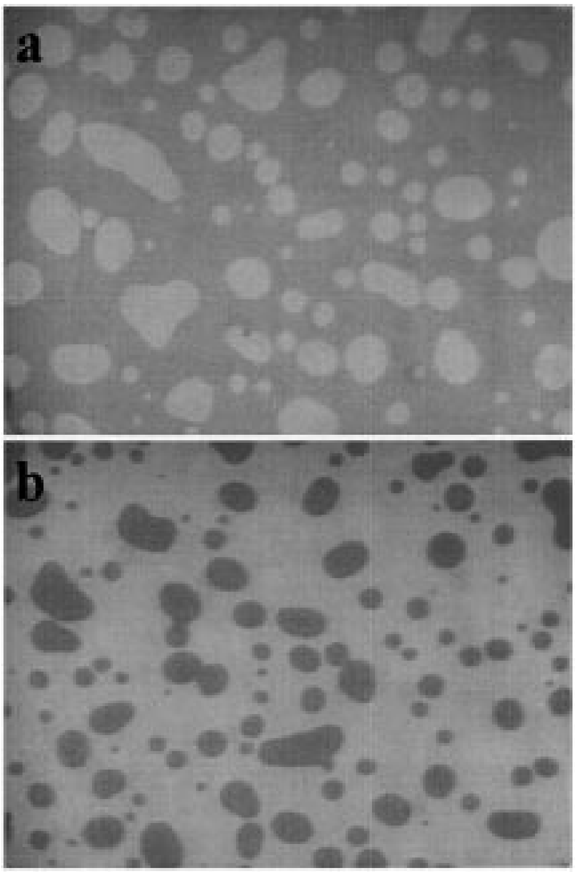

Figure 6. Optical micrographs of P(S-*b*-nBMA) thin films on (a) a PS brush surface and (b) a silicon substrate. Image is 150 × 200 μm.

PS blocks segregate to the PMMA brush layer to minimize unfavorable PMMA/PI and PMMA/PnBMA interactions which are *more* unfavorable than PS/PMMA interactions. Consequently, the systems adopt structures having a PS/PMMA interface which are normally unfavorable as PS typically dewets PMMA brush surfaces. Since a change from antisymmetric to symmetric wetting conditions does not occur as *f* decreases to zero, then for P(S-*b*-I) and P(S-*b*-nBMA), there is no composition of the brush that is nonpreferential.

The dependence of the interfacial energy of PI with the random copolymer is inconsequential for the P(S-*b*-I). From the contact angle experiments, the interfacial energy between PI and PS was found to be larger than the interfacial energy between PI and PMMA, i.e., $\gamma_{S,I} \geq \gamma_{MMA,I}$. Thus, the two block components have opposite affinities for the two random copolymer components. However, P(S-*b*-I) does not exhibit a conversion from symmetric to antisymmetric wetting, since the interfacial energy between PI and PMMA is still larger than that between PS and PMMA, i.e., $\gamma_{MMA,I} \geq \gamma_{S,MMA}$.

Random copolymer surfaces can be precisely tuned to control interfacial interactions. In some cases, a neutral or nonpreferential random copolymer composition may exist for a block copolymer, as shown previously for P(S-*b*-MMA) on P(S-*r*-MMA) surfaces. The neutral composition is the random copolymer composition where the interfacial energies between the respective blocks and the random copolymer are equal. This is shown schematically in Figure 7a for a P(A-*b*-B) on P(A-*r*-B) surfaces where the interfacial energies for the A and B blocks are plotted as a function of B fraction in the random copolymer, f_B. However, for a P(B-*b*-C) or P(C-*b*-D) placed on a P(A-*r*-B) surface, opposite affinities of the respective blocks for random copolymer components, A and B, do not guarantee a condition of neutrality at some value of f_B. This has been demonstrated for P(S-*b*-I) films on P(S-*r*-MMA) surfaces where the PI and PS blocks show opposite affinities for styrene and MMA units in the random copolymer, yet an inversion from symmetric to antisymmetric wetting is not found. This absence of a neutral composition is understood from the schematic diagrams shown in Figure 7b for the generalized case involving a P(C-*b*-D) system, where C prefers A, D prefers B, and yet $\gamma_{C,A} \geq \gamma_{D,A}$. Since there is no intersection between the interfacial energy curves at any f_B, the D block always segregates to the random copolymer surface, regardless of the copolymer composition. This figure can, of course, be applied to P(B-*b*-C) systems by simply substituting B for D and adjusting the *y*-axis such that the interfacial energy of B at $f_B = 1.0$ equals zero.

The existence of a P(A-*r*-B) nonpreferential surface for a P(C-*b*-D) block copolymer system does not necessitate that blocks C and D have opposite affinities for A and B. If both blocks interact preferentially with one of the random copolymer components, a nonpreferential surface may still exist if the interfacial energy dependence on random copolymer composition is significantly different for the two block components. This is depicted in Figure 7c where C and D both have preferential affinities for random copolymer component B and the interfacial energy of D with the random copolymer has a higher dependence on the random copolymer composi-

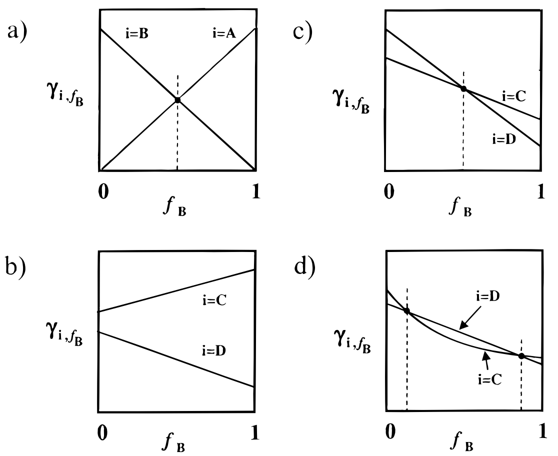

Figure 7. Schematics showing interfacial energy dependence of various block copolymer systems on P(A-*r*-B) random copolymer surfaces. The interfacial energy between each block and the random copolymer layer is plotted as a function of B fraction in the random copolymer brush layer for four cases. (a) Block copolymer, P(A-*b*-B), is composed of the same units as the random copolymer. A nonpreferential composition is guaranteed at some f_B and occurs at the intersection of the two curves (marked by the dotted line). (b) P(C-*b*-D) block copolymer system where C and D have opposite affinities for the random copolymer constituents and D has a lower interfacial energy with the random copolymer layer independent of brush composition. In this case, there is no intersection of the two curves, resulting in an absence of a nonpreferential composition. (c) P(C-*b*-D) block copolymer system where both C and D have more favorable interactions with B in the random copolymer and the interfacial energy dependence of D on f_B is larger than that of C. The intersection of the two curves represents the nonpreferential composition and is marked by the dotted line. (d) Example of a P(C-*b*-D) block copolymer system where the dependence of interfacial energy on composition for the C block is nonlinear and two neutral compositions are observed. It should be noted that these figures can be applied to P(B-*b*-C) systems by simply substituting B for D and adjusting the *y*-axis such that the interfacial energy of B at $f_B = 1.0$ equals zero.

tion, causing an intersection of the interfacial energy plots for C and D at some f_B.

The arguments presented above assume that the interfacial energy of a polymer with a random copolymer brush layer varies in a monotonic, linear manner with brush composition. For most systems, these assumptions are reasonable to determine whether there is a neutrality condition. However, for systems where the dependence of the segmental interaction parameter and, hence, the interfacial energy on composition is not monotonic, then a more complex behavior can be found. An example of this is shown in Figure 7d for a P(C-*b*-D) system, where the interfacial energy dependence of C with f_B is nonlinear and two intersections of the interfacial energy curves exist. For such a system, the D block segregates to the brush surface at high and low f_B while segregation of the C block occurs at intermediate compositions. Consequently, there are two brush compositions where neutrality is found. Since preferential wetting occurs by one block component at $f_B = 0$ and 1, the simple method of examining block copolymer wetting conditions at the two extreme compositions is insufficient in determining whether neutrality conditions exist. Nevertheless, it is expected that complex systems such as these are uncommon and that the assumption of linear, monotonic behavior is generally valid.

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