Interfacial Segregation in Disordered Block Copolymers: Effect of Tunable Surface Potentials

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The response of disordered P(*d*-S-*b*-MMA) diblock copolymers to variable strength surface fields has been studied by neutron reflectivity. Surface interactions were controlled by end grafting P(S-*r*-MMA) random copolymers with various styrene contents onto Si substrates. The degree interfacial segregation of the block copolymer was proportional to the surface potential. A first-order transition in the degree of segregation was observed as the brush composition was varied. Conditions were found which yielded neutral boundary conditions *simultaneously* at the vacuum and substrate interfaces. [S0031-9007(97)03464-9]

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The presence of a surface or interface can strongly influence the phase behavior, morphology, and kinetics of a multicomponent simple or complex fluid. One component typically has a lower interfacial energy than the others, leading to phenomena such as critical point wetting [1,2] and surface enrichment [3], surface directed spinodal decomposition [4–6], and surface-induced ordering and orientation [7–10]. Studies of these phenomena have typically focused on the behavior of two-component systems (denoted *A* and *B*) at interfaces where the interfacial energy difference $\Delta\gamma = \gamma_B - \gamma_A$ is large, such as the free surface or the interface with a solid phase. The interesting case of a neutral interface, where $\gamma_A = \gamma_B$, is normally inaccessible even near a critical point.

Surface segregation in disordered symmetric diblock copolymers has been studied theoretically [11,12]. The volume fraction $\Phi_A(r)$ of component *A* in the bulk is equal to the average value $\langle\Phi_A\rangle$. Adjacent to an interface, however, an excess of the lower interfacial energy block is predicted. The excess volume fraction of *A*, $c(z) = \Phi_A(z) - \langle\Phi_A\rangle$, has the form $c(z) = c(0)\cos(2\pi z/L)\exp(-z/\xi)$, where z is the distance from the interface and $c(0)$ is the excess of *A* at $z = 0$. In the linear response regime [small $\Delta\gamma$ and $c(0)$] [13],

$$c(0) = 2\xi l_p(\gamma_B - \gamma_A)/kT\,. \tag{1}$$

$c(0)$ can be positive or negative depending on the sign of $\gamma_B - \gamma_A$. The period L and decay length ξ are related to the degree of polymerization N and the Flory-Huggins segmental interaction parameter χ_{AB}. At the order-disorder transition ξ becomes infinite and L equals the lamellar period. The "packing length" l_p (typically several angstroms) is defined in terms of the monomer volume and statistical segment length [12].

Precise control of $\Delta\gamma$ can be achieved by end grafting a layer of an *A*-*B* random copolymer, denoted P(*A*-*r*-*B*), onto a surface, forming a random copolymer brush [14–16]. Each chain in the brush consists of a random sequence of *A* and *B* monomers where *f*, the *A* monomer fraction, can be specified in the synthesis ($0 < f < 1$). If the grafting density is sufficiently high, then a polymer placed in contact with the modified surface interacts only with the brush. The interfacial energy of homopolymer *A* with the brush, denoted γ_{Af}, decreases monotonically with increasing *f*. The opposite behavior occurs for homopolymer *B*. In the $N \rightarrow \infty$ limit, $\gamma_{Af} = (1 - f)\gamma_{AB}$ and $\gamma_{Bf} = f\gamma_{AB}$ [17]. Therefore,

$$\Delta\gamma = \gamma_{AB}(2f - 1) \tag{2}$$

can vary from γ_{AB} at $f = 1$ to $-\gamma_{AB}$ at $f = 0$. At an intermediate value of f, $\Delta\gamma = 0$. Thus by accurately controlling the composition of the random copolymer brush, a *neutral* surface can be realized.

Here this surface modification technique is applied to the study of interfacial segregation in disordered diblock copolymers. Random copolymers of styrene and methylmethacrylate, with $M_w \sim 10\,000$ Daltons and $M_w/M_n \sim 1.1$–1.8, were synthesized [18], and their characteristics are reported in Ref. [14]. The random copolymers were end grafted from the melt onto polished silicon substrates by reaction of the terminal OH group on the copolymer chain with the native surface oxide layer [14]. This yielded a dried film thickness of 4–5 nm, after repeated rinsing with toluene to remove unreacted chains, corresponding to a grafting density of $\sim$3 nm^2 per chain. A P(*d*-S-*b*-MMA) diblock copolymer ($M_w = 32\,000$ and $M_w/M_n = 1.04$) was prepared anionically, using perdeuterated styrene for neutron contrast. The volume fraction of styrene was 65%, as determined by C$_{13}$ NMR. Diblock copolymer films $\sim$170 nm thick were spin coated onto a series of substrates, each grafted with a random copolymer brush of different styrene content *f*. The samples were annealed at 150 °C for 24 hours and quenched to room temperature. Neutron reflectivity measurements were made on the NG7 reflectometer at the National Institute of Standards and Technology using a neutron wavelength λ of 4.75 Å. The instrumental resolution $\Delta Q_z/Q_z$ was ~5%, where $Q_z = (4\pi/\lambda)\sin\theta$ and θ is the grazing angle of incidence.

Neutron reflectivity profiles of P(*d*-S-*b*-MMA) films on polymethylmethacrylate (PMMA) ($f = 0$) and polystyrene (PS) ($f = 1$) brushes are shown in Fig. 1(a). Above a critical value of $Q_z = 0.014$ Å^{-1} the reflectivity decreases rapidly and oscillates with a period $\Delta Q_z = 2\pi/d$ where d is the thickness. The broad maximum in the reflectivity profile centered at $Q_z \sim 0.029$ Å^{-1} results from the periodic variation of $c(z)$ near the substrate and free surface.

The reflectivity data were fit using the Parrat formalism [19,20], assuming a model concentration profile of the form

$$c(z) = c(0)\cos(2\pi z/L)\exp(-z/\xi) + c(d)\cos[2\pi(d-z)/L]\exp[-(d-z)/\xi]. \quad (3)$$

The difference between the measured and calculated reflectivities was minimized by iteratively adjusting the model parameters. Equation (3) models $c(z)$ with independent composition oscillations at both the vacuum and substrate interfaces and is valid when $d \gg 2\xi$. For the P(*d*-S-*b*-MMA) films studied here $d \sim 1700$ Å, $\xi \sim 200$ Å, and $L \sim 270$ Å. With $\Phi_s(z) = \langle\Phi_s\rangle + c(z)$ and $\Phi_M(z) = 1 - \Phi_S(z)$, the total scattering length density $(b/V) = \Phi_S(b/V)_S + \Phi_M(b/V)_M$. The room temperature scattering length densities of *d*-PS and PMMA are 6.37×10^{-6} Å^{-2} and 1.03×10^{-6} Å^{-2}, respectively. The brush, native oxide, and silicon substrate were modeled by individual layers. All model parameters were allowed to vary. However, only $c(d)$, the styrene excess at the brush interface, varied in a systematic manner with the brush composition. All other parameters were constant.

The b/V profiles shown in Fig. 1(b) differ in that the oscillations at the substrate are 180° out of phase with each other. As expected, the *d*-PS block of the diblock copolymer segregates to a PS brush, and the PMMA block segregates to a PMMA brush. The lower surface tension component *d*-PS segregates to the vacuum interface in both cases. The best-fit values of $c(0)$ and $c(d)$ from all of the samples studied are shown in Fig. 2. $c(0)$ is independent of the brush composition, while $c(d)$ exhibits a more dramatic and interesting behavior. $c(d)$ increases linearly with *f* above an intercept of $f \sim 0.6$, and saturates to $c(d) \sim 0.3$ (near the maximum value of 0.35 for this block copolymer) as $f \rightarrow 1$. However, there is a sharp discontinuity in $c(d)$, for $0.63 \geq f \geq 0.58$ going from weak *d*-PS segregation $[c(d) = 0.05]$ to strong PMMA segregation $[c(d) = -0.30]$.

If $\Delta\gamma$ varies smoothly with *f*, then, from Eq. (1), $c(d)$ should pass smoothly through zero at the value of *f* corresponding to a neutral interface, where $\Delta\gamma = 0$. This assumes that the block copolymer interacts only with the random copolymer brush and does not sense the substrate. PMMA has a strong affinity for silicon oxide, while PS normally dewets from silica surfaces. Thus, a P(S-*r*-MMA) brush between an oxide substrate and a PMMA layer (either a PMMA homopolymer or the PMMA block of a copolymer) is potentially unstable against penetration by the PMMA through the brush to the substrate [21]. This is possible due to the relatively

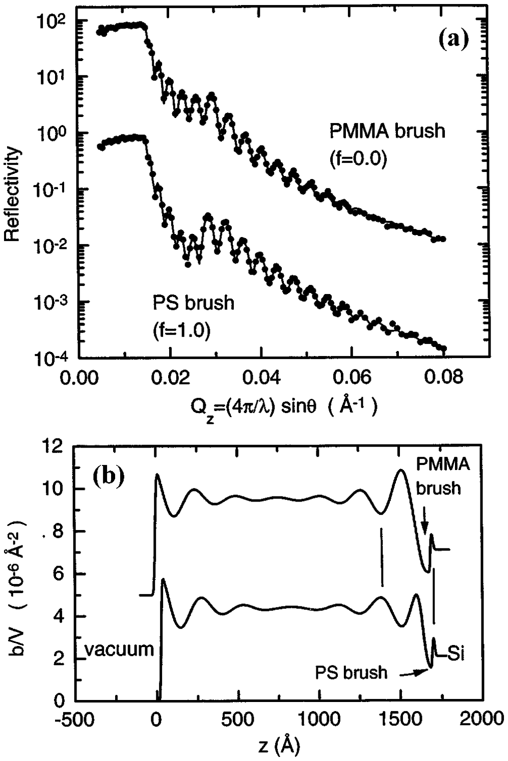

FIG. 1. (a) Reflectivity data from P(*d*-S-*b*-MMA) films on substrates coated with end-grafted PMMA ($f = 0$) and PS ($f = 1$) brushes. The points are the data, and the lines are calculated from the best-fit scattering length density profiles shown in (b). The model used to generate and fit the b/V profiles is discussed in the text.

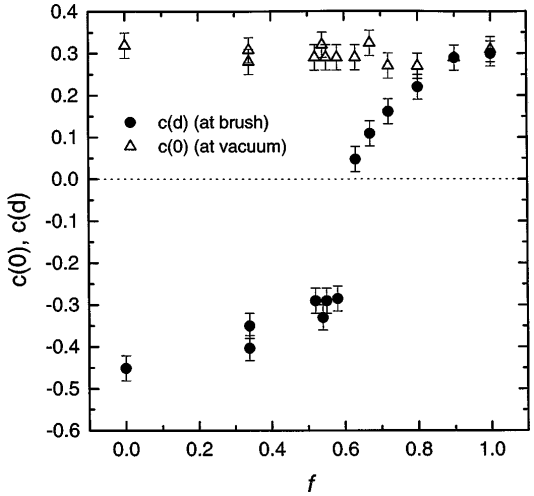

FIG. 2. The interfacial excess of *d*-PS at the vacuum interface [$c(0)$, triangles] and adjacent to the random copolymer brush [$c(d)$, circles]. There is an equal excess of *d*-PS at the vacuum interface for all of the samples, due to the lower surface tension of *d*-PS. The *d*-PS excess adjacent to the brush decreases with decreasing *f*, and undergoes a first-order transition at $f \sim 0.6$.

low grafting density of the amorphous brushes. The associated stretching of the brush and the increased number of S and MMA contacts represent entropic and enthalpic barriers, respectively, which oppose the penetration of PMMA into the brush.

The observed first-order wetting transition at $f \sim 0.6$ (Fig. 2), therefore, corresponds to the onset of penetration of the PMMA block through the brush to the substrate, as the enthalpic barrier to penetration is reduced. Experiments with *d*-MMA homopolymer films on P(S-*r*-MMA) brushes show a behavior similar to that of P(*d*-S-*b*-MMA), whereas PS homopolymer films on random brushes do not exhibit this behavior [22], in keeping with the above interpretation.

The interfacial energy difference $\Delta\gamma(f) = \gamma_{Mf} - \gamma_{Sf}$ was found to follow Eq. (1) [15] qualitatively, with $\gamma_{SM} = 0.8$ ergs/cm^2 and $d(\Delta\gamma)/df = 2\gamma_{SM} \sim 1.6$ ergs/cm^2. $\Delta\gamma$ was equal to zero at $f = 0.57 \pm 0.05$ rather than at $f = 0.5$ (indicating that χ_{AB} is concentration [23] and composition [24,25] dependent). The linear increase of $c(d)$ observed here, for $f > 0.6$ (Fig. 2), is thus qualitatively consistent with theory [13]. However, from Eq. (2) $dc(d)/df = (2\xi l_p/kT)d(\Delta\gamma)/df \sim 3.7$, using $d(\Delta\gamma)/df = 1.6$ ergs/cm^2, $l_p = 3.4$ Å, $\xi = 200$ Å, and $T = 425$ K, whereas experimentally $dc(d)/df \sim 1.5$ for $0.6 < f < 0.8$ (Fig. 2). Thus, the observed degree of segregation is approximately 2.5 times smaller than predicted. This may be due in part to the fact that the diblock copolymer used in this study is not symmetric—the S block is almost twice as long as the MMA block. Segregation of either block to a planar interface therefore necessitates some stretching and compression of the longer and shorter blocks, respectively, in the direction normal to the interface, which will tend to suppress segregation relative to the case of a symmetric diblock copolymer.

Segregation at the vacuum interface is driven by the difference in the surface tensions of PS and PMMA, γ_S and γ_M, respectively. Though differing by at most a few percent [26], $\gamma_S < \gamma_M$ over most of the temperature range between 100 and 200 °C [9,10]. However, γ_M decreases more rapidly with temperature than γ_S [26]. Therefore, $\Delta\gamma = \gamma_M - \gamma_S$ decreases with increasing temperature. Consequently, studies of segregation at the free surface of the same diblock copolymer were performed as a function of temperature from 125 to 250 °C, in an evacuated heated cell. Samples were coated onto both a bare substrate and a substrate with an $f = 0.65$ brush, providing strongly interacting and nearly neutral substrate surfaces, respectively. The scattering length densities were corrected for thermal expansion in analyzing the data.

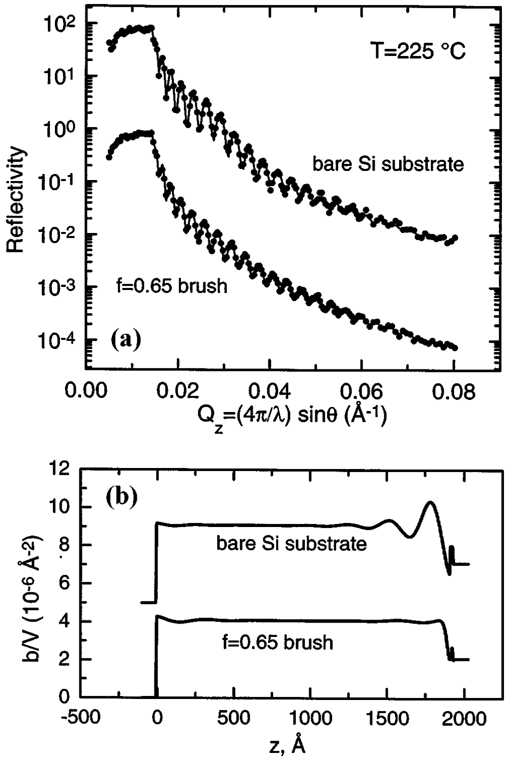

FIG. 3. (a) Reflectivity data from P(*d*-S-*b*-MMA) films on a bare substrate, and on a substrate with an $f = 0.65$ brush, taken at $T = 225$ °C. Note the almost total absence of the broad peak at $Q_z = 0.029$ Å^{-1}, which arises from interfacial segregation, in the $f = 0.65$ brush sample. Points are data; lines are calculated from the scattering length density profiles shown in (b).

Figure 3 shows reflectively data for both samples at 225 °C. While the reflectivity of the sample on the bare substrate clearly shows a broad peak associated with interfacial segregation and the resulting periodic variation of $c(z)$, this peak is almost completely absent in the data from the $f = 0.65$ brush sample. The best-fit scattering length density profiles [Fig. 3(b)] indicate no segregation at the vacuum interface in either sample at this temperature, and the same is true at the $f = 0.65$ brush interface [to within the uncertainty in determining $c(0)$]. The absence of segregation at the free surface at this temperature is due to the disappearance of $\Delta\gamma = \gamma_M - \gamma_S$, and is not due to a reduction of χ_{SM}. This is demonstrated by the presence of strong PMMA segregation adjacent to the bare substrate at 225 °C, with L and ξ values similar to those observed at 150 °C (consistent with the extremely weak measured temperature dependence of χ_{SM} [27]). Segregation at the free surface was fully restored when the temperature was lowered (see Fig. 4), ruling out sample degradation.

The degree of segregation at both film surfaces is plotted as a function of temperature in Fig. 4, for the sample on the $f = 0.65$ brush. The degree of segregation at the brush $[c(d)]$ has almost no temperature dependence, while $c(0)$ decreases with temperature and goes to zero above 225 °C. Consequently, neutral boundary conditions can be obtained *simultaneously* at both the vacuum and substrate interfaces by choosing an appropriate brush composition and temperature. It should be noted that isotopic labeling causes small changes in the surface tensions [3], and the temperature at which $\Delta\gamma = 0$ may therefore depend upon the isotopic labeling of the components.

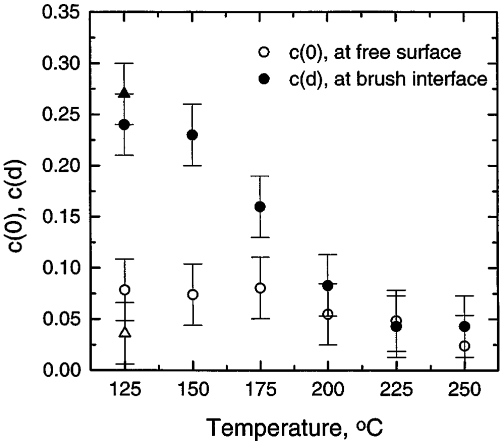

FIG. 4. Best-fit *d*-PS interfacial excess versus temperature for the film on an $f = 0.65$ brush, at the vacuum and brush interfaces. Strong *d*-PS segregation to the free surface was restored when the temperature was lowered to 125 °C (triangles), ruling out sample degradation as the cause for reduced segregation at high temperatures.

In conclusion, these studies have shown that surface interactions of P(S-*b*-MMA) block copolymers at the vacuum and substrate interfaces can be precisely tuned and, in fact, completely neutralized. Using end-grafted P(S-*r*-MMA) random copolymers, quantitative control over the interfacial interactions at the substrate can be achieved. The data presented support a linear variation of surface segregation with the strength of the surface potential $\Delta\gamma$. Evidence for a first-order transition in the degree of segregation was observed, which results from the attraction of the PMMA block to the substrate and the *f*-dependent free energy barrier presented by the brush. While we have demonstrated these effects using block and random copolymers of PS and PMMA, related studies should be possible with many other systems. The surface tension difference of PS and PMMA at the vacuum interface can be tuned and neutralized by varying the temperature. While this behavior is fortuitous, it allows independent control of the interface potential at both film surfaces, making the system studied here particularly useful for studies of interfacial effects in thin films of block copolymers and blends.

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