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Segregation of Block Copolymer Micelles to Surfaces and Interfaces

Kenneth R. Shull*

*Almaden Research Center, IBM Research Division, 650 Harry Road,
San Jose, California 95120-6099*

Karen I. Winey

*Department of Polymer Science and Engineering, University of Massachusetts,
Amherst, Massachusetts 01003*

Edwin L. Thomas

*Department of Materials Science and Engineering, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139*

Edward J. Kramer

*Department of Materials Science and Engineering, Cornell University,
Ithaca, New York 14853*

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ABSTRACT: Surface and interface segregation of block copolymer micelles in a model system has been observed. The distribution of a diblock copolymer within a high molecular weight homopolymer matrix phase was determined quantitatively by forward recoil spectrometry. Cross-sectional transmission electron microscopy showed that excess copolymer segregation to the homopolymer/homopolymer and homopolymer/vacuum interfaces was due to the preferential segregation of block copolymer micelles to these interfaces. We argue that the segregation of block copolymer micelles is a manifestation of attractive interactions between polymer brushes, and between polymer brushes and a free surface, which are important in high molecular weight homopolymer matrices.

Introduction

The practical application of block copolymers is often hindered by the formation of block copolymer micelles in a homopolymer matrix phase. Consider, for example, the emulsification of immiscible polymer blends by the addition of block copolymer. Typically, copolymer is added to a blend of immiscible homopolymers that have affinities for separate blocks of the copolymer. Copolymer chains segregate to the interface between phases,¹ thereby reducing the interfacial tension^{2,3} and enhancing the mechanical strength of the interface.⁴⁻⁶ The interfacial properties are determined by μ_c , the copolymer chemical potential, which is generally limited by the formation of block copolymer micelles in one or both of the homopolymer phases. Micellization therefore places a fundamental limitation on the utility of block copolymers as interfacial agents. A microemulsion characterized by a vanishing interfacial tension between opposing phases can, for example, only be obtained when μ_c is greater than some critical value.

Block copolymer micelles are also important in that they are the basic structural units of the ordered morphologies observed in pure copolymer melts. Spherical, cylindrical, or lamellar microdomain morphologies can be viewed as spherical, cylindrical, or lamellar micelles that have condensed to form the appropriate ordered phase. A detailed understanding of the behavior of block copolymer micelles may therefore yield important insights into the nature of block copolymer melts in general.

In a recent publication,¹ it was argued that block copolymer micelles have a tendency to segregate to preexisting interfaces, provided that the matrix homopolymer molecular weight is sufficiently high. This conclusion was based on measurements of the depth distribution of

copolymer chains in thin film samples. Observation of excess copolymer at homopolymer/vacuum and homopolymer/homopolymer interfaces was attributed to the segregation of micelles to these interfaces. In the present paper we describe an electron microscopy study that directly confirms this interpretation.

Experimental Section

The block copolymer used was a diblock copolymer of deuterated polystyrene (dPS) and poly(2-vinylpyridine) (PVP), with degrees of polymerization of 391 for the dPS block and 68 for the PVP block and an overall polydispersity index of 1.03. The homopolymer matrix with which the copolymer was blended was polystyrene with a degree of polymerization of 6000. Thin-film bilayer samples were prepared by first spin casting 1000-Å PVP homopolymer layers (degree of polymerization \approx 6000) from acetic acid solution onto sodium chloride crystals. Blends of PS homopolymer and dPS/PVP copolymer were spun directly onto these PVP layers from toluene solutions, and these bilayer samples were annealed under vacuum at 178 °C for 24 h to allow the copolymer distribution to equilibrate. Forward recoil spectrometry (FRES)^{7,8} was used to determine the total integrated excess of the diblock copolymer at the free PS surface and at the PS/PVP interface. Details of this aspect of the experiment are described in ref 1.

The structures of the surface and interface regions were observed by cross-sectional transmission electron microscopy. The bilayer samples were floated off the sodium chloride crystals onto a water bath, where they were subsequently picked up on partially cured epoxy substrates. Water swelled the PVP layers, and the resulting stresses caused much of the PVP homopolymer layer to be lost in the water bath before the samples were picked up on the epoxy substrates. The substrates were then fully cured at 60 °C. The epoxy tended to mix with any remaining PVP, but the PS overlayer was not disturbed. The samples were sliced normal to the film surfaces to thicknesses of \sim 500 Å. These cross sections were then placed on copper grids, stained by

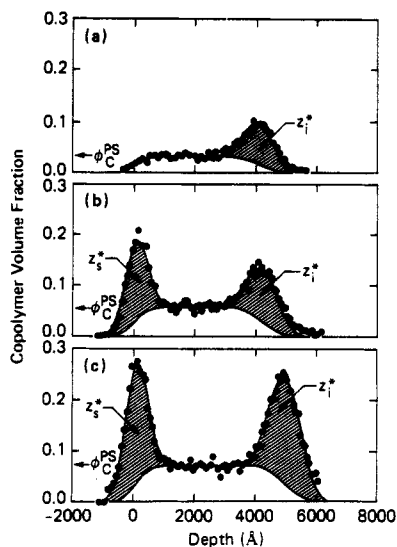


Figure 1. Depth distribution of the PS/PVP block copolymer in three different bilayer samples, as measured by forward recoil spectrometry: (a) $\phi_c^{ps} = 3.2\%$, $z_i^* = 100$ Å, $z_s^* = 0$. (b) $\phi_c^{ps} = 5.7\%$, $z_i^* = 134$ Å, $z_s^* = 150$ Å. (c) $\phi_c^{ps} = 7.0\%$, $z_i^* = 270$ Å, $z_s^* = 240$ Å.

exposure to methyl iodide vapor, and observed with a JEOL 100 CX microscope operated at 100 kV.

Results and Discussion

Copolymer chains segregate to the PS/PVP homopolymer interface, and in general there is an integrated interfacial copolymer excess, z_i^* . This segregated copolymer layer is in equilibrium with the copolymer in the bulk PS matrix phase, such that each value of ϕ_c^{ps} , the equilibrium copolymer volume fraction in this bulk PS phase, is associated with a unique value of z_i^* . When ϕ_c^{ps} is less than a critical volume fraction, equal to approximately 4.5% for this system, measured values of z_i^* are in excellent agreement with predictions from a detailed self-consistent mean-field theory of polymer interfaces in the presence of block copolymer.^{1,9} Copolymer segregation in this regime is driven by the tendency for each block of the copolymer to exist in the phase with which it is compatible. Figure 1a shows the measured depth distribution of the dPS/PVP copolymer in a bilayer sample which has $\phi_c^{ps} = 3.2\%$. The hatched area represents z_i^* , which is equal to 100 Å for this sample. The width of the peak designated by the hatched area is determined by the FRES depth resolution (800 Å) and not by the actual thickness of the segregated layer, which is of the same order as z_i^* .

When ϕ_c^{ps} exceeds 4.5%, copolymer segregates to the free PS surface in addition to the PS/PVP interface. Figure 1b shows the copolymer distribution for a sample for which $\phi_c^{ps} = 5.7\%$. Here $z_i^* = 134$ Å, and there is also a surface copolymer excess, z_s^* , which is equal to 150 Å. At higher values of ϕ_c^{ps} , z_i^* and z_s^* increase dramatically. Figure 1c shows the copolymer distribution for a sample with $\phi_c^{ps} = 7\%$. Here z_i^* has increased to 270 Å and z_s^* has increased to 240 Å.

It was argued previously that the excess interface and surface copolymer segregation is due to the preferential segregation of micelles to the surface and interfacial regions,¹ so that the critical value of 4.5% for ϕ_c^{ps} is closely related to ϕ_{cmc}^{ps} , the critical micelle concentration in the PS phase. Methyl iodide stains the PVP units of the block copolymer preferentially, such that the micelle cores

appear as dark spots in the TEM micrographs. None of these dark spots were seen for the sample with $\phi_c^{ps} = 3.2\%$, a result that is consistent with our interpretation that this concentration is lower than ϕ_{cmc}^{ps} . Figure 2 shows a cross section of the sample with $\phi_c^{ps} = 7.0\%$. The micellar cores are clearly visible in rows at the free PS surface and at the PS/epoxy interface. (The PS/epoxy interface corresponds to the PS/PVP interface in the original bilayer samples.) The intermicellar spacing is very uniform, which suggests that the micelles pack on an ordered lattice. Micrographs taken from different tilt angles confirm that the micelles are indeed spherical, as one would infer from the circular projections shown in Figure 2. The larger dark spots near the PS/epoxy interface are domains of residual PVP homopolymer, whereas the white spots are most likely voids resulting from air being trapped at the PS/epoxy interface during sample preparation. Figure 3 is a schematic representation of the sample shown in Figure 2 as it existed immediately following the annealing treatment, when the PVP layer was still intact. The epoxy interacts with PVP but not with PS (or dPS). The micelles at the PS/PVP interface are shielded by a layer of dPS and are therefore not affected by the epoxy.

Careful analysis of Figure 2 indicates that the micelle core radius, R_{core} , is approximately equal to 60 Å. Determination of the intermicellar spacing is complicated by the fact that different slices through an ordered packing arrangement will give different values for this quantity. An estimate of 300 Å for the intermicellar spacing is obtained from Figure 2, and we expect this figure to be accurate to within 30%. The predicted micelle size for the dPS-PVP diblock copolymer can be obtained from the equation for Q , the number of copolymer chains per micelle¹⁰

$$Q = \frac{\sqrt{\chi} N_c g a^3 \rho_0}{0.337 - 0.194 g^{1/3}} \quad (1)$$

where N_c is the overall copolymer degree of polymerization, g is the ratio of the core block degree of polymerization to N_c , a is the statistical segment length, ρ_0 is the segment concentration given by the reciprocal of the segmental volume, and χ is the Flory parameter describing the thermodynamic interaction between the core and corona segments. The following equations relate Q to R_{core} and $R_{micelle}$, where $R_{micelle}$ is the overall radius of the spherical micelle:

$$\frac{4\pi R_{core}^3}{3} = \frac{Q g N_c}{\rho_0} \quad (2)$$

$$\frac{4\pi R_{micelle}^3}{3} = \frac{Q N_c}{\rho_0} \quad (3)$$

Equations 1–3 are valid when N_h , the homopolymer molecular weight, is much greater than the corona block molecular weight, i.e., $N_h/(1-g)N_c \gg 1$, such that the micelle corona contains very little homopolymer. The appropriate values of the parameters for the system studied here are $N_h = 6000$, $N_c = 459$, $g = 0.148$, $\chi = 0.11$,¹ $a = 6.7$ Å,¹¹ and $\rho_0 = 9.4 \times 10^{-3}$ mol/cm³.¹² The condition $N_h/(1-g)N_c \gg 1$ is satisfied, and combination of eqs 1, 2, and 3 gives $R_{core} = 78$ Å and $R_{micelle} = 147$ Å. The micellar spacing and micellar core radius obtained from Figure 2 are in excellent agreement with these predictions if the micelles are in contact with one another such that the micelle diameter is given by the measured intermicellar spacing.

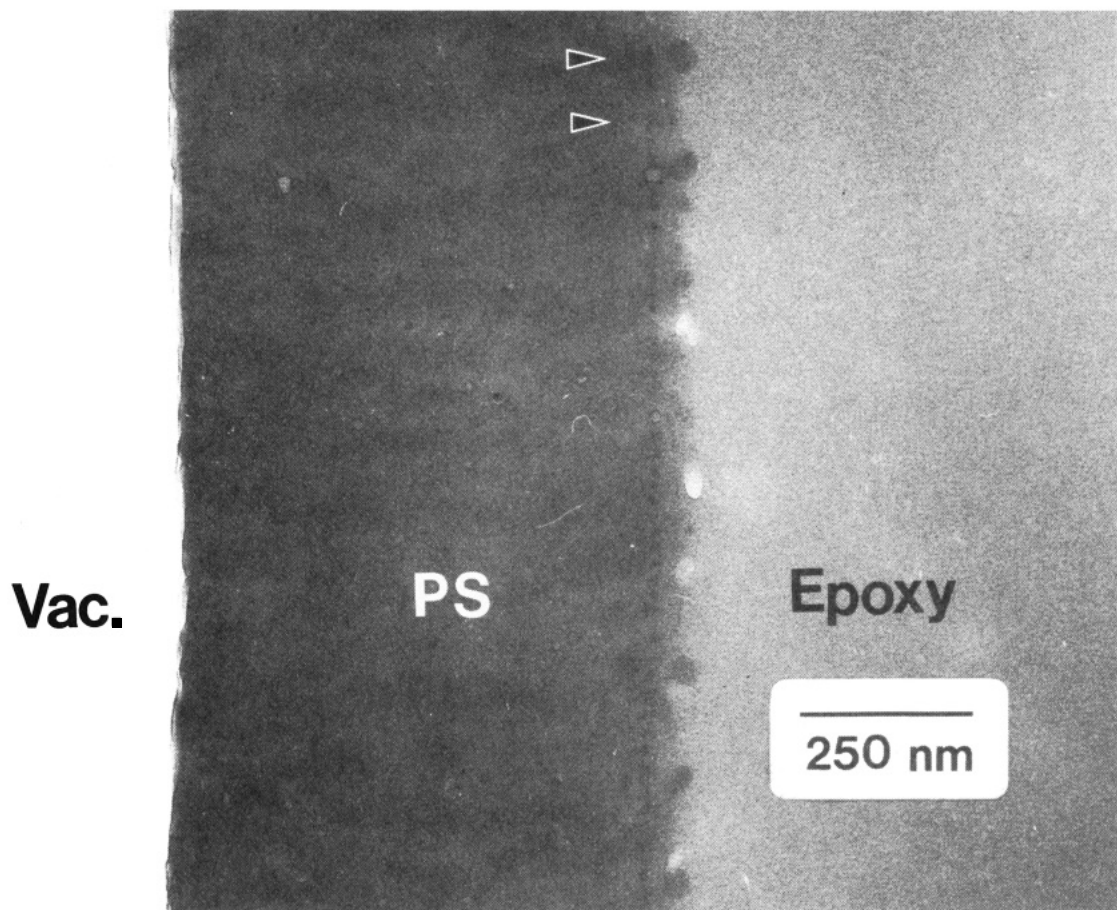


Figure 2. Micrograph showing a cross section through a sample with $\phi_c^{ps} = 7.0\%$. Micelle cores are visible as the small dark spots at the PS/epoxy interface (corresponding to the original PS/PVP interface) and at the PS/vacuum interface. A second layer of micelles has formed in the region between the two arrowheads.

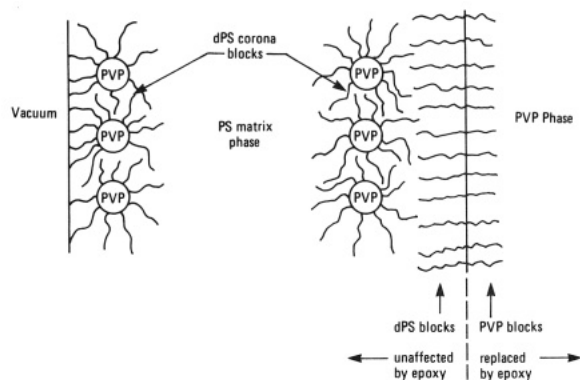


Figure 3. Schematic representation of the sample shown in Figure 2 as it existed immediately following the annealing treatment. The region not affected by the subsequent sample preparation is indicated.

As described in ref 1, the surface segregation of the block copolymer micelles is not driven by an interaction between the PVP segments and the free surface. In fact, the PVP cores are offset from the free surface by the dPS from the micelle coronas. This aspect of our interpretation was experimentally verified by X-ray photoelectron spectroscopy (XPS), which is only sensitive to the composition of the sample within 50 Å of the free PS surface. No nitrogen was detected for a sample with $z_s^* = 240$ Å, indicating that the volume fraction of PVP segments in this surface region is no greater than 5%, where this limit is imposed by the sensitivity of the XPS measurement. If the micelle cores were directly adjacent to the free PS surface, one would

expect that the surface PVP volume fraction would be at least 15%, which is the volume fraction of PVP in the neat copolymer.

The micellar coronas consist of dPS "brushes", or end adsorbed polymer layers, which extend into the high molecular weight PS phase from a narrow interfacial region. A similar dPS brush extends into the PS phase from the PS/PVP interface. The interfacial segregation of the micelles is a manifestation of an attractive interaction between polymer brushes, and the surface segregation of the micelles is due to an attractive interaction between polymer brushes and the free surface. As discussed in detail in refs 1 and 7, there are two origins of the attractive interaction between these polymer brushes. The first stems from the small but unfavorable enthalpic interaction between the dPS segments in the brushes and the normal (nondeuterated) PS segments in the surrounding homopolymer. The second stems from the entropy loss of the homopolymer matrix chains in the vicinity of interfaces and can be associated with gradient terms in the expression for the free energy. Segregation of micelles to the free surface is driven by these entropic contributions, by the lower surface free energy for dPS as opposed to PS, and perhaps by a tendency for chain ends, present in relatively high concentrations in the outer portion of a micelle, to segregate to the free surface. In low molecular weight matrices the interactions between the micelles and the surface or interface are dominated by the matrix osmotic pressure and are strictly repulsive.

Interactions between micelles in high molecular weight matrices are also attractive, and the aggregation of mi-

celles at a surface or interface is similar to the deposition of atoms on a smooth surface. Micelles form preferentially at steps, favoring the formation of a nearly complete layer of micelles before the next layer begins to form. The arrowheads in Figure 2 point to a region at the PS/PVP interface where a second layer of micelles is beginning to form. The appearance of several layers at the interface corresponds to the development of a bulk, three-dimensional microdomain morphology at this interface. The homopolymer is not soluble in all proportions in these bulk morphologies, and the appearance of an attractive interaction between micelles is accompanied by the onset of macrophase separation of micelle/homopolymer mixtures as $N_h/(1 - g)N_c$ increases.

The microdomain packing in a two-dimensional structure consisting of a single layer of segregated micelles may be quite different from the microdomain packing in a three-dimensional structure. For example, spherical domains of neat block copolymers in very thin films order in a hexagonal array, whereas the bulk microdomain morphology is a body-centered cubic array of spheres.¹³ The packing arrangement is determined by the loss of configurational entropy associated with the requirement that the bulk density remain constant. The optimum packing arrangement for satisfying this requirement is different for two- and three-dimensional arrays and is also affected by the inclusion of homopolymer. Kinning and co-workers have, for example, found that spherical micelles at relatively high concentrations in low molecular weight matrices order on a simple cubic lattice.¹⁴ As mentioned above, interactions between micelles in these low molecular weight matrices are dominated by the matrix osmotic pressure and are purely repulsive. The ordering behavior of micelles in two and three dimensions when the interactions are attractive and homopolymer is present is not well understood, since most studies of micelle formation have been carried out in low molecular weight homopolymer matrices.¹⁴⁻¹⁶

Finally, we point out that micellar systems are ideally suited for studying the interactions between polymer brushes. This is because the micelles are not rigid objects but are made up of many individual block copolymer chains. Equilibration in micellar solutions is accomplished through the motions of these individual chains, which exist at a concentration approximately equal to the critical micelle concentration. Thus, the rate at which two micelles attain their equilibrium separation with respect to one another can be much greater than it is for the equivalent solid particles with chains grafted to the particle surfaces. Equilibrium thermodynamic measurements of micellar distributions can then be used to determine whether or not the forces between polymer brushes are attractive or

repulsive, even when these forces are much too small to be measured directly.

Conclusions

Surface and interface segregation of block copolymer micelles has been clearly demonstrated. The segregation is a manifestation of an attractive interaction between polymer brushes, and between a polymer brush and a free surface, in high molecular weight homopolymer matrices. These interactions can be used to grow block copolymer microdomain structures at interfaces that have two- or three-dimensional character and suggest ways in which the interactions between polymer brushes in high molecular weight matrices can be studied.

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