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Adsorption of Copolymer Chains from a Melt onto a Flat Surface

Peter F. Green*

Sandia National Laboratories, Albuquerque, New Mexico 87185

Thomas P. Russell

IBM Almaden Research Center, San Jose, California 95120

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ABSTRACT: We have investigated the segregation of symmetric polystyrene–poly(methyl methacrylate) (PS–PMMA) diblock copolymers at interfaces formed between different polymer melts and flat, impenetrable surfaces using elastic recoil detection (ERD). Situations in which the copolymers were allowed to adsorb onto silicon (Si) from PS melts of varying degrees of polymerization, P, were examined. Over the range of concentrations studied, the excess copolymer chains per unit area at the interface, $\varphi^*(0)$, was found to be independent of P, for $P > N_c$, where N_c is the degree of polymerization of the copolymer chains. At very low concentrations, $\varphi^*(0)$ exhibited a strong linear dependence on φ_c, the equilibrium volume fraction of chains in the bulk of the homopolymer. For $\varphi_c \geq 0.012$ ($\varphi^*(0) \approx 42$ Å), $\varphi^*(0)$ became virtually independent of φ_c. This value of $\varphi^*(0)$ corresponded to the interface excess at which the Si surface became saturated with PMMA segments. The energy of interaction between a copolymer chain and the surface was determined to be of order k_BT. Interfacial segregation of the copolymers was not observed when the homopolymer host was PMMA, poly(vinyl chloride), or a blend of PS and poly(phenylene oxide). No segregation of the copolymers was observed at PS/gold interfaces. On the other hand, segregation of the PS–PMMA copolymers at PS/Al interfaces was very strong.

Introduction

Diblock copolymers exhibit interesting physical properties which are exploited for a variety of technological applications. They behave like surfactants and as a result are utilized for the steric stabilization of colloidal particles in coatings, for example.[1] In a typical scheme employed for colloidal particle stabilization, a segment of a diblock copolymer that exhibits a chemical affinity for the particle surface is allowed to adsorb on the surface of the particle while the other block extends into solution. The adsorption of copolymer chains on the surface of the particles imparts steric stabilization. The surfactant-like behavior of block copolymers has been exploited in other ways. Copolymers have been used to improve the fracture toughness of the interface between immiscible polymers.[2–4] The interface is strengthened when each block extends into the phase in which the interactions are most favorable. The degree of strengthening depends on the density of chains at the interface, the number of entanglements per block length, and the strength of the interactions between the blocks and the appropriate phase of the mixture. The addition of small quantities of the appropriate diblock copolymer to incompatible polymer mixtures also reduces the interfacial tension of the system.[5,6] This further improves the mechanical properties of the system. Block copolymers may also be used for selective membrane applications[7–9] because they exhibit varying bulk morphologies.[10]

Earlier we investigated the segregation of polystyrene (PS)–poly(methyl methacrylate) (PMMA) diblock copolymers to the interface of high molecular weight PS and PMMA homopolymers.[11] At low concentrations, the number of copolymer chains per unit area at the interface between the homopolymers depended linearly on the volume fraction of chains in the bulk. The driving force for the interfacial segregation is a lowering of the total free energy of the system. When the copolymers segregate to the interface, the number of unfavorable contacts between the homopolymer phases is reduced. This reduction in free energy is typically larger than the increase in free energy that results from the accompanying reduction in combinatorial and conformational entropy.[12] Leibler accounted for this behavior using a scaling approach.[13] He viewed the free energy of the chains at the interface as having three main contributions: (1) the translational entropy that accounts for the confinement of the chains in two dimensions; (2) the entropy of mixing between the copolymers at the interface and the homopolymer phases; and (3) the fact that the concentration of copolymer chains is sufficiently high that they overlap and interact with each other; they may stretch in order to reduce the number of unfavorable interactions. Of course, the structure of the interface is determined by the minimization of the free energy with the chemical potential of the chains at the interface equated to that of the chains in the bulk.

Others have investigated the segregation of copolymer chains near interfaces in melts. The segregation of copolymer chains near the interface of immiscible homopolymer layers has been investigated experimentally by Shull et al.[14] and by Dai et al.[15] Here they studied the polystyrene–poly(vinylpyridine) (PVP) system. In addition, Russell et al. have investigated the segment density distributions of diblock copolymers at homopolymer interfaces.[16,17] Theoretical investigations of this problem have also been done by Shull and Kramer[18] and by Noolandi and Hong.[12]

The phenomenon of the adsorption of copolymers from solution onto a surface has received considerable attention both experimentally and theoretically.[19–29] While there has been work on the adsorption of end-functionalized polymers from a melt onto a solid surface,[30,31] virtually no studies have addressed the adsorption of nonfunctionalized chains. In this paper, we address the adsorption of symmetric PS–PMMA diblock copolymer chains from polymer melts onto different impenetrable surfaces.

Experimental Section

The materials used in this study are as follows. The copolymers were fully deuterated, symmetric, PS–PMMA diblocks comprised of 262 segments. The fraction of PS segments on the copolymer

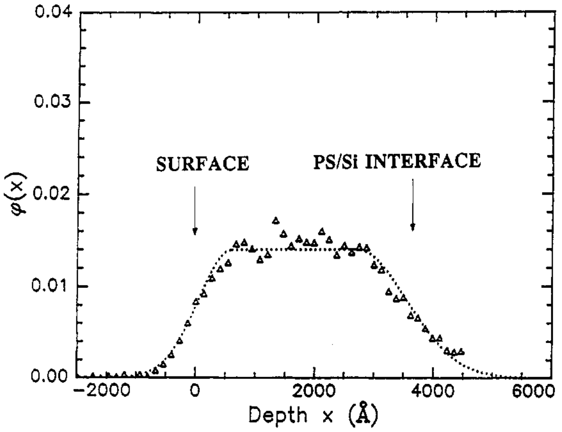

Figure 1. Volume fraction versus depth profile of the deuterated copolymer chains in an as-cast PS film.

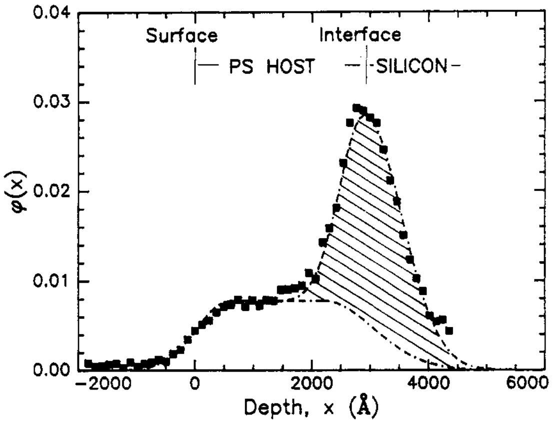

Figure 2. Segregation of the copolymer chains at the PS/Si interface after annealing at 165 °C for 65 h. The hatched region is the surface excess, $\varphi^*(0)$.

was 0.51. The homopolymers were poly(vinyl chloride) (PVC), poly(methyl methacrylate), polystyrene, and a blend of PS and poly(phenylene oxide) (PPO). The molecular weights of the polystyrenes, of narrow molecular weight distributions, were 5.0×10^4, 1×10^5, 2.3×10^5, and 1.8×10^6. The molecular weight of PPO was 5×10^4, and its polydispersity was less than 2. The molecular weights of PVC and PMMA were 1×10^5 and 5.0×10^5, respectively. Their polydispersities were less than 1.05. Polymer/nonpolymer interfaces were formed between the homopolymers mentioned above and silicon. Interfaces were also formed with Si surfaces on which gold and aluminum layers were evaporated.

In these experiments, very small quantities of the copolymer, a few weight percent or lower, were blended with a homopolymer. Using a photoresist spinner, a solution of the polymer was spun onto a wafer. The resulting films that were produced, after the solvent evaporated, were approximately 4000 Å. Note that the Si surfaces were not pretreated to remove the native oxide layer before the polymer was solution cast on them. Elastic recoil detection (ERD)[32-34] was then used to determine the volume fraction versus depth profile of the copolymer chains in the homopolymer host before and after the samples were annealed at temperatures above the glass transition temperatures of the homopolymer hosts.

Results and Discussion

The triangles in Figure 1 represent the volume fraction versus depth profile of the deuterated copolymer chains in the PS host of the as-cast film. The average volume fraction was 0.014. After annealing at 165 °C for 65 h, the copolymers segregated to the PS/silicon interface of the sample. This is depicted in Figure 2 by the filled squares. The excess of copolymer chains at the interface, $\varphi^*(0)$, is given by

$$\varphi^*(0) = \int_{\text{interface}} [\varphi(x) - \varphi_c]\, dx \tag{1}$$

where $\varphi(x)$ is the volume fraction of copolymer chains as a function of depth, x, within the sample and φ_c is that of the copolymer chains in the bulk. The hatched region represents $\varphi^*(0)$. The number of copolymer chains per unit area at the interface, Σ^{-1}, was obtained from eq 1 using

$$\frac{1}{\Sigma} = \frac{\varphi^*(0)\,\rho}{N_c} \tag{2}$$

N_c is the number of monomer segments per copolymer chain, and ρ is the number of segments per unit volume of a copolymer chain.

An expression relating $1/\Sigma$ to φ_c may be obtained by following the approach used by Leibler, mentioned in the Introduction.[13] In general, the density of copolymer chains at an interface is determined by equating the chemical potential of the chains at the interface to their chemical potential in the bulk. However, the equilibrium thermodynamics is affected by the kinetics of the adsorption of the copolymer chains at the interface when the chains are able to aggregate to form micelles in the bulk at concentrations above the critical micelle concentration (cmc). An expression for the free energy of the copolymer chains at the interface may be obtained by considering the situation in which one block (PMMA) is adsorbed on the Si surface and the other (PS) extends into the homopolymer (PS) phase. The thickness of the adsorbed layer is assumed to be much smaller than the radius of gyration of the copolymer chain. This is not an unreasonable assumption since this has been shown to be the case for the adsorption of these chains onto a quartz substrate from solution.[19] The free energy of the copolymer chains at the interface may be approximated by

$$\frac{F}{k_B T} = \frac{\delta}{\rho a \Sigma} + \frac{1}{\rho a \Sigma}\left[f_{el}(L) + \ln\left(\frac{N}{\rho a \Sigma}\right) + \frac{L\Sigma\rho}{P}\left(1 - \frac{N}{L\Sigma\rho}\right)\ln\left(1 - \frac{N}{L\Sigma\rho}\right)\right] \tag{3}$$

where N is the number of PS segments per copolymer chain and P is the number of segments per homopolymer chain. The first term on the right-hand side of this equation represents the interaction of the copolymer chains with the interface; $\delta k_B T$ is the interaction energy per PMMA block in contact with the Si surface. If the density of copolymer chains at the interface is sufficiently large so the chains can overlap and interact, then they may stretch, as discussed earlier. This is represented by an elastic energy contribution $f_{el}(L) = (3/2)L^2/Na$, where L is the distance that the nonadsorbing segment, PS, extends into the homopolymer phase. The entropy of mixing between the copolymer chains at the interface and the PS homopolymer chains in that region is represented by the fourth term on the right-hand side of eq 3. The third term in this equation is also entropic, and it reflects the fact that the copolymers are restricted to two dimensions.

We can calculate the chemical potential of chains at the interface for the situation in which the density of chains at the interface is sufficiently low that the segments (PS) that extend from the interface are unable to overlap and interact. The free energy for this situation is obtained by neglecting the elastic energy contributions in eq 3. It also follows that $L^2 = Na^2$ (unperturbed PS blocks). The chemical potential of the chains in the interfacial region is obtained using $\partial F/\partial Q$ (at constant area), where Q =

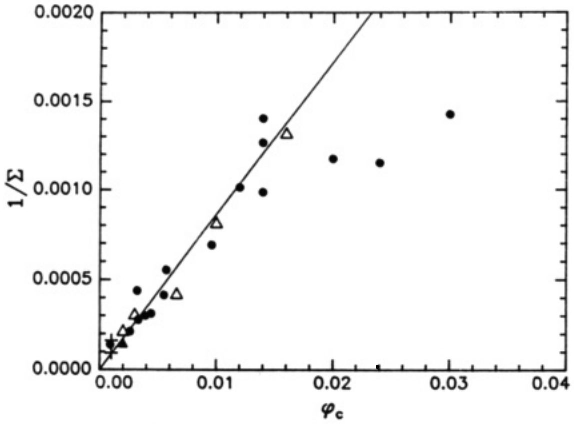

Figure 3. Dependence of the number of chains per unit area at the interface, $1/\Sigma$, as a function of φ_c. The different hosts represent the PS host degrees of polymerization: $P = 1000$ (triangles), $P = 6000$ (+), and $P = 17\,300$ (filled circles).

$1/a\rho\Sigma$ is the number of copolymer chains at the interface

$$\frac{\mu_{\rm inf}}{k_{\rm B}T} = \left(\delta + 1 - \frac{N}{P}\right) + \ln\left(\frac{N}{\rho a\Sigma}\right) - \frac{N}{P}\ln\left(1 - \frac{N^{1/2}}{\rho a\Sigma}\right) \tag{4}$$

Since the volume fraction of chains in the bulk is very small, the chemical potential of copolymers in that region may be approximated by[18]

$$\frac{\mu_{\rm c}}{k_{\rm B}T} = \left(\varphi_{\rm c} + 1 - \frac{N}{P}\right) + \chi N + \ln\varphi_{\rm c} \tag{5}$$

The relation between φ_c and $1/\Sigma$ is obtained by equating the two chemical potentials

$$\ln\varphi_{\rm c} + \chi N = \ln\frac{N}{\rho a\Sigma} - \frac{N}{P}\ln\left(1 - \frac{N^{1/2}}{\rho a\Sigma}\right) + \delta \tag{6}$$

Figure 3 shows a plot of $1/\Sigma$ as a function of φ_c for the copolymers adsorbing from PS hosts of differing molecular weights. Three cases are repesented in this figure. The circles and triangles represent the situations in which the copolymer chains were in a host of PS of $P = 17\,300$ and of $P = 1000$, respectively. The plus symbols represent the case where the PS host was composed of chains of $P = 6000$. At very low concentrations, $1/\Sigma$ exhibits a linear dependence on φ_c, while it becomes virtually independent of φ_c for $\varphi_c \geq 0.012$ ($\varphi^*(0) = 42$ Å or equivalently $1/\Sigma = 0.001$ Å^{-2}). This transition could result from a saturation of the Si surface by PMMA segments. On the other hand, it could result from the formation of micelles which would affect the kinetics of the segregation process appreciably. Hence, this volume fraction ($\varphi_c = 0.012$) might appear to be the critical micelle concentration (cmc).

To gain some insight into the abrupt change in the dependence of $1/\Sigma$ on φ_c at $\varphi_c = 0.012$, the behavior of the chains at the PS/Si interface could be contrasted with that at the interface between PS and PMMA homopolymers. This comparison is shown in Figure 4. The open circles represent the situation at the PS/PMMA homopolymer interface. This data was taken from ref 11. It is clear that the regime over which $1/\Sigma$ varies linearly with φ_c is much larger in the PS/PMMA case. This follows from the fact that the conformation of the copolymers at both interfaces should be very different, as shown in Figure 5. In the homopolymer/homopolymer (PS/PMMA) case, each copolymer block extends into the appropriate homopolymer phase with which its interactions are most favorable. At the PS/Si interface, the PMMA segments lay relatively flat on the Si surface while the PS segment extends into the PS phase. In this latter situation, the chains occupy a larger surface area of the interface. It is therefore possible that the saturation of the surface could be responsible for the abrupt change in the dependence of $1/\Sigma$ on φ_c at $\varphi_c \approx 0.012$. To be certain, however, we should explore the possibility that φ_c could be the critical micelle concentration.

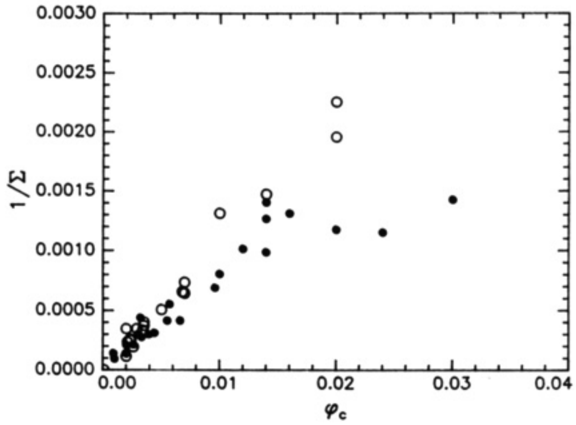

Figure 4. Comparison of the $1/\Sigma$ vs φ_c for the segregation of the copolymer chains at PS/Si interfaces (●) with that at PS/PMMA interfaces (○). The data for the segregation at the PS/PMMA interfaces were taken from ref 11.

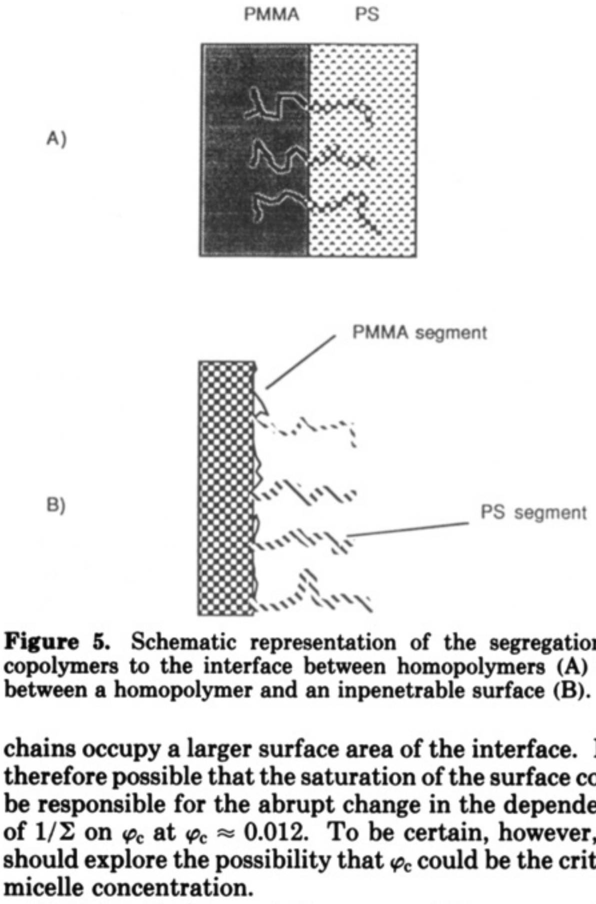

Figure 5. Schematic representation of the segregation of copolymers to the interface between homopolymers (A) and between a homopolymer and an inpenetrable surface (B).

If micelles had formed, the core would be composed of PMMA segments and the corona would be composed of deuterated PS segments. As discussed in ref 14, there is a strong driving force for the segregation of such micelles to segregate to the free surface. This driving force arises in part from the fact that d-PS has a slightly lower surface energy than the PS matrix chains. It is also well documented that there is a slight incompatibility between d-PS and PS segments. The samples in our study were annealed for a sufficiently long period of time for micelles to migrate to the free surface. There is no evidence of d-PS chains at the free surface, hence the absence of micelles. However, in studies where higher molecular weight PS–PMMA ($N_c = 1200$) copolymers were used, we have observed d-PS segments at the free surface of the sample which suggests that micelles had formed. Longer chain copolymers show a stronger tendency to aggregate to form micelles than do the short-chain copolymers. We can calculate a critical micelle concentration for the two symmetric copolymers of $N_c = 1200$ and $N_c = 262$. Since these chains are symmetrical, one expects that the resulting micelles should exhibit a lamellar morphology. Following Shull et al., we can write down the chemical potential of such micelles

$$\frac{\mu_{\mathrm{cmc}}}{k_{\mathrm{B}}T} = 0.67(\chi N_c)^{1/3}(5.64 - g)^{1/3} \qquad (7)$$

where $g = N_{\mathrm{PS}}/N_c$. Using eqs 4 and 7, together with the fact that $g = {}^1/_2$, we determined that $\varphi_{\mathrm{cmc}} \approx 0.03$ for the copolymer chains of $N_c = 262$. The average concentration of chains in the bulk is smaller than this value. On the other hand, $\varphi_{\mathrm{cmc}} \approx 1.7 \times 10^{-12}$ for the copolymer of $N_c = 1200$. Based on the results of these simple estimates, it is indeed reasonable to conclude that the point at which $1/\Sigma$ becomes virtually independent of φ_c is not due to the formation of micelles. It is reasonable to suggest that it resulted from a saturation of the PS/Si interface by the PMMA segments.

Equation 6 was used to compute the line drawn through the data in Figure 3. The segmental density, ρ, was taken to be the same for PS and PMMA. The parameters used to compute the line were $\rho = 0.042/\text{Å}^3$, $N = 262$, $P = 17\,300$, and $\chi = 0.038$. This value of χ was taken from our earlier paper.[11] In essence, the only adjustable parameter was δ, and we determined that it had a value of 0.6. This value is not unreasonable for the energy of interaction between a polymer chain and a Si surface. This interaction energy should be of order $k_{\mathrm{B}}T$ or less. Note that eq 6 is valid only for very low concentrations. If the density of copolymer segments at the interface was very high, then the chains may interact and stretch. If that were the case, then the full expression for the free energy, which incorporates the elastic energy contribution, would have to be used. In this situation the saturation that one observes is fundamentally different from what is addressed in this paper.

We may now address the effect of molecular weight. Based on the data in Figure 3, it is clear that the molecular weight of the host has a minor effect on the interface excess of copolymer chains. Given the values of P used in these experiments, the theoretical prediction, eq 6, is consistent with this observation. It should be emphasized, however, that despite the fact that the equilibrium excess of chains at the interface is not affected appreciably by the length of the host chains ($P > N$), the kinetics of the processes is. The "tube" renewal effects, which alter the diffusivity of the probe chains, are considerably more important for the shorter chain PS hosts.[34]

In order to study the effects of the chemical interactions in the system on the ability of the chains to segregate to an interface, we examined a number of other systems. We investigated the behavior of these copolymer chains near PMMA/Si, PVC/Si, and PS/PPO blend/Si interfaces. The copolymers were not observed to segregate at any of these interfaces. We also examined the behavior of the copolymers near a PS/Au interface and determined that there was no segregation of the copolymer chains to this interface. On the other hand, the attraction of the PS–PMMA copolymers toward PS/Al interfaces was very strong. We found this attraction to be much stronger than the PMMA/Si interaction, which is not surprising. These observations demonstrate that whether interfacial segregation occurs depends not only on the interactions between the copolymer segments and the substrate but also on those interactions between the homopolymer and copolymer segments and between the homopolymer segments and the substrate.

Conclusion

We have demonstrated that the PMMA blocks of PS–PMMA copolymers exhibit an affinity for the PS/Si interface. $1/\Sigma$ exhibited a linear dependence on φ_c. At a bulk concentration of $\varphi_c \approx 0.012$ ($\varphi^*(0) = 43$ Å, $1/\Sigma = 0.001$ Å^{-2}), $1/\Sigma$ became independent of φ_c. This is the concentration at which the Si surface became saturated with PMMA segments.

The adsorption of these copolymers to the PS/Si interfaces was compared with that at PS/PMMA homopolymer interfaces. As expected, considerably more chains segregated to the PS/PMMA interface than at the PS/Si interface. This follows from the fact that the equilibrium conformation that the copolymers adopt at these interfaces is necessarily different. The effective cross-sectional area occupied by the copolymers at the PS/Si interface is much larger than that at the PS/PMMA interface. While the molecular weight of the PS host had very little effect on the equilibrium excess of chains at the interface, it had considerable influence on the kinetics of the segregation process.

Based on the results of this study, it is clear that an affinity for one block of a copolymer, or an end group of an end-functionalized polymer, is not a sufficient condition for segregation of a chain to a surface. The nature of the interactions between the copolymer (or end-functionalized polymer) and the homopolymer as well as those between the homopolymer and the surface is also very important.

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Registry No. PS–PMMA (block copolymer), 106911-77-7; PMMA (homopolymer), 9011-14-7; PVC (homopolymer), 9002-86-2; PS (homopolymer), 9003-53-6; PPO (SRU), 9041-80-9; Si, 7440-21-3; Au, 7440-57-5; Al, 7429-90-5.