

Crossover of a block copolymer brush in a polymer melt from a stretched to collapsed conformation

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The adsorption of block copolymers from a homopolymer melt is studied as a function of matrix molecular weight using neutron reflectivity and low energy forward recoil spectrometry. The block copolymer is poly(deuterated styrene-*block*-methylmethacrylate) (*dPS-b-PMMA*), which contains short MMA and long *dS* blocks. The MMA block adsorbs to the silicon oxide surface, whereas the *dPS* extends into the matrix chains. The *dPS-b-PMMA* is blended with a polystyrene matrix of molecular weight P . Volume fraction profiles and copolymer coverage (z^*) are investigated as a function of P . We find that z^* initially increases rapidly with P and remains almost constant for P larger than $2N_B$ (N_B is the number of *dS* segments). We also observe that the thickness of the adsorbed layer (L) as well as the interfacial width between the brush and the matrix (w) initially decrease rapidly with increasing P and become weakly dependent on P for $P > 2N_B$. By measuring z^* , L , and w as a function of P we observe a crossover from a stretched to collapsed brush at $P \sim 2N_B$. For $P > 2N_B$ the matrix chains are driven from the adsorbed layer by entropy. Self-consistent mean field predictions are in qualitative agreement with experimental results and provide an estimate for the MMA-wall interaction energy, $-8kT/\text{block}$. [S1063-651X(97)50609-X]

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Polymer adsorption onto a solid substrate plays a key role in determining the properties of adhesives, coatings, composites, and other engineered materials [1]. Adhesion of coatings to a variety of surfaces can be controlled using additives called adhesion promoters. These polymers adsorb preferentially to the polymer-solid interface and improve the interfacial properties. Strong attraction to the substrate on one hand and entanglement with the polymer matrix on the other make these polymers very attractive for tailoring the adhesion between polymer films and inorganic substrates [2]. Our goal is to control the conformation of adsorbed molecules at the melt-substrate interface so as to tailor the adhesive properties of coatings.

Polymer adsorption from a polymer melt has recently received theoretical [3,4] and experimental [5–13] attention. The effect of the adsorbing polymer concentration on the adsorbed amount (z^*) was investigated by Green and Russell [5] and Budkowski, Klein, and Fetters [6] for block copolymers, and by Zhao *et al.* [7] and Jones *et al.* [8] for end-functionalized homopolymers. From a practical and fundamental prospective, a key parameter governing polymer adsorption at a solid surface is the matrix degree of polymerization P . At the air-polymer interface, Budkowski *et al.* [9] found that the block copolymer thickness decreases as P increases. In their study, the stretched to collapsed transition was not investigated. For symmetric block copolymers, Green and Russell [5] reported that P had no significant effect on the z^* of poly deuterated(styrene-*block*-methylmethacrylate) over a limited range of P . Clarke *et al.* [10] used neutron reflectivity to determine the concentration profile of carboxyl end-functionalized deuterated polystyrene

(*dPS-COOH*) adsorbed onto silicon oxide. For a nearly constant graft density of *dPS-COOH*, the P of a polystyrene matrix was varied. Qualitatively, the brush thickness was found to be independent of P for $P > N$, the number of *dPS* segments. Because the brush thickness was not quantitatively evaluated, this study was only able to estimate the P corresponding to the crossover from the case where the matrix chains penetrate the brush to the case where the matrix chains are mainly expelled. Similarly, using neutron reflectivity, Nicolai *et al.* [11] measured z^* and the brush-matrix interfacial widths for *dPS-COOH* as a function of polystyrene matrix molecular weight; however, no clear transition was found in these studies. By measuring the brush thickness and width over a wide range of P 's we will show that this crossover occurs at $P \sim 2N_B$.

In this paper, we study poly(deuterated styrene-*block*-methylmethacrylate) (*dPS-b-PMMA*) adsorption at a PS-silicon oxide (SiO_2) interface using low-energy forward recoil spectrometry (LE-FRES) and neutron reflectivity (NR). The number of polystyrene (PS) segments, P , is varied systematically so a quantitative understanding of the interplay between P and *dPS-b-PMMA* adsorption can be gained. As P increases, the interfacial excess of *dPS-b-PMMA* (z_B^*), increases, and reaches a plateau near $P \sim 2N_B$, where N_B is the number of *dPS* segments. The adsorbed layer thickness (L) and the interfacial width (w) between the layer and matrix are both found to decrease with P , and become nearly independent of P for $P > 2N_B$. Quantitative analysis of z_B^* , L , and w reveals that the adsorbed chains go from a stretched conformation at low P to a collapsed one at $P > 2N_B$. A comparison of the *dPS-b-PMMA* volume frac-

TABLE I. Polymer characteristics.

Polymer	Number of segments	Polydispersity index	Source
<i>dPS-b-PMMA</i>	933 for <i>dS</i> ; 44 for MMA	1.05	Polymer Source, Inc.
PS	288–6246	1.03–1.06	Pressure Chemical

tion profiles with those from a numerical self-consistent mean field (SCMF) model shows that the interaction energy between the MMA block and SiO_x is $-8kT$.

The characteristics of the adsorbing and matrix polymers are given in Table I. The *dPS-b-PMMA* is a strongly asymmetric block copolymer having only 4.5 mole % of MMA. The short MMA block is known to adsorb to the SiO_x surface, whereas the long *dS* block adsorbs only weakly and is easily replaced by MMA segments [14]. To simplify the nomenclature in this paper, we will denote the adsorbing MMA block as *A* and the nonadsorbing *dS* block as *B*. To probe the various regimes, the values of *P* range from much shorter than N_B to much longer than N_B .

Substrates were prepared by etching a silicon wafer for 3 min in a 7% vol. hydrofluoric acid solution to remove the native oxide. The substrate was then placed in an ultraviolet ozone cleaner for 10 min, resulting in a clean 20 Å SiO_x film. Polymer films were prepared by spin coating a toluene solution of *dPS-b-PMMA* and PS on the substrate. As the matrix molecular weight increased, the solution concentration was decreased from 2.5% to 5% wt. in order to keep the film thickness constant. Samples were then dried in a vacuum oven for about 12 h at 80 °C. Film thicknesses as determined by ellipsometry were about 2000 Å. The volume fraction of *dPS-b-PMMA* in the as cast films was $\phi_\infty = 0.05$. All samples were annealed in a vacuum oven for 5 days at 174 °C.

The interfacial excess of the deuterated *B* block was determined by LE-FRES using a 2.0-MeV He^+ ion beam at 15° incident and exit angles with respect to the polymer film, and a 7.5 μm Mylar stopper foil. Under these conditions, the depth resolution ranged from about 450 Å at the surface to about 700 Å at 2000 Å beneath the surface. Conventional FRES [15] and LE-FRES [16] have been described elsewhere. For selected samples, the volume fraction profiles were measured by neutron reflectivity at the High Flux Isotope Reactor at Oak Ridge National Laboratory, and at the Intense Pulsed Neutron Source at Argonne National Laboratory on the MIRROR (HB3A) and POSYII reflectometers, respectively. The principles of NR have been described elsewhere [17]. For consistency, the LE-FRES and NR measurements were carried out on the same samples. The NR data sets were evaluated using the fitting procedure outlined in [18].

To complement the LE-FRES and NR measurements, a SCMF model was used to calculate the volume fraction profiles of the *B* block at the PS/ SiO_x interface. These calculations followed the procedure of Shull and Kramer [4] and were extended by us to study block copolymer adsorption at the polymer-solid interface. From the SCMF volume fraction profiles, the characteristics of the adsorbed layer can be determined, namely, z_B^* , *L*, and *w*. The SCMF input parameters are the segment numbers of the *A* and *B* blocks and the matrix polymer, the bulk volume fraction of the copolymer,

the interaction parameters χ_{AB} , χ_{AM} , and χ_{BM} , and the interaction energies between the substrate and polymer segments, namely, ε_A^s , ε_B^s , and ε_M^s . The index *M* denotes the matrix polymer. Since the *B* block and the matrix are *dPS* and PS, respectively, the interaction parameter χ_{BM} was set to 0. Similarly, the interaction of PS and *dPS* with SiO_x was neglected by setting $\varepsilon_B^s = \varepsilon_M^s = 0$. Using the known PS-PMMA interaction parameters [19], the values of χ_{AB} and χ_{AM} were taken as $\chi_{AB} = \chi_{AM} = 0.0367$ at 174 °C. Thus, the only unknown parameter is the interaction energy between the *A* block and the SiO_x . Therefore, by varying ε_A^s until the SCMF and experimental volume fraction profiles agree, the strength of the MMA interaction with the wall can be determined. A reliable method for measuring ε_A^s is of great importance because this parameter strongly influences adhesion.

Figure 1 shows z_B^* (solid circles) measured by LE-FRES as a function of *P*. As *P* increases, z_B^* increases rapidly, and then saturates at about 55 Å for *P* approximately equal $2N_B$. As *P* increases, the driving force for *dPS-b-PMMA* adsorption increases because the entropic penalty for matrix chains to reside near the substrate increases. For $P > 2N_B$, z_B^* stops increasing because the accessible sites for MMA adsorption are filled at $P \sim 2N_B$. Thus further increasing *P* does not increase the number of adsorbed *dPS-b-PMMA* chains. The inset in Fig. 1 shows z_B^* calculated from the SCMF model for $\varepsilon_A^s = -8kT/A$ block, where *k* and *T* are the Boltzmann constant and temperature, respectively. This value of ε_A^s originates from NR measurements discussed later. In qualitative agreement with experiments, the SCMF z_B^* increases rapidly

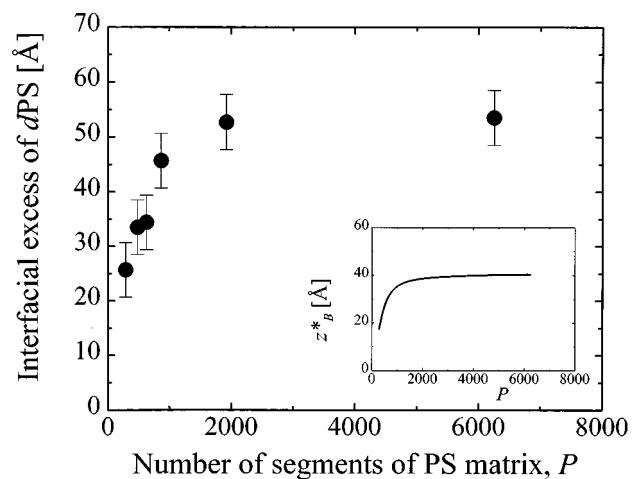


FIG. 1. Interfacial excess of *B* block (z_B^*) as determined from LE-FRES (solid circles). Inset: z_B^* calculated by SCMF model (solid line) for $\varepsilon_A^s = -8kT$. The segment-segment interaction parameters are given in the text. The error bars were obtained following [21].

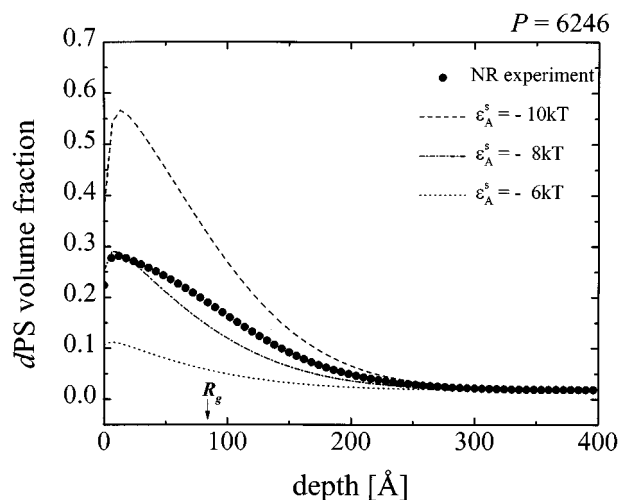


FIG. 2. Volume fraction profile of B block measured by NR (solid circles) for $P = 6246$. The PS/SiO_x interface is at depth 0. Lines represent the volume fraction profiles of B block calculated by SCMF for $\varepsilon_A^s = -6kT$ (dotted line), $-8kT$ (dash-dotted line), and $-10kT$ (dashed line). Segment-segment interaction parameters used in the SCMF are given in the text. The arrow indicates the radius of gyration of the B block (R_g).

at low P and saturates at $P \sim 2N_B$. Note that the SCMF model underestimates the magnitude of z_B^* by about 15 Å over the entire range of P . Recall that the slightly repulsive interaction between dPS and PS was neglected in the SCMF calculations. By including this interaction the dPS - b -PMMA chains would receive an additional driving force for leaving the bulk and consequently z_B^* would increase. In addition, the dS segments are preferentially attracted to silicon oxide over the PS segments [20] providing an additional increase in the calculated z_B^* . The incorporation of both contributions into the SCMF calculations is underway.

The B block volume fraction profile measured by NR (solid circles) is shown in Fig. 2 for a matrix with $P = 6246$ ($6.7N_B$). The PS-SiO_x interface is at depth 0. Figure 2 clearly shows that dPS - b -PMMA adsorbs strongly to the SiO_x surface, reaching a B volume fraction of 0.28 near the interface. Because of the finite sample thickness and appreciable z_B^* , the bulk volume fraction of the B block decreases from 0.05 before to 0.02 after annealing. The thin depletion layer at the interface is due to the presence of the adsorbed A chains (i.e., MMA). Because MMA contains only hydrogen, a depletion in the deuterium volume fraction profile is observed at the PS-SiO_x interface. For $P \gg N_B$, Fig. 2 shows that the adsorbed layer thickness is comparable to the B block radius of gyration ($R_g = 84$ Å), indicated by an arrow. Also shown in Fig. 2 are the SCMF volume fraction profiles of the B block for three different MMA-SiO_x interaction energies, namely $\varepsilon_A^s = -6kT$ (dotted line), $-8kT$ (dash-dotted line), and $-10kT$ (dashed line). Note that the profiles are extremely sensitive to the magnitude of ε_A^s . For $\varepsilon_A^s = -6kT$ the adsorption is very weak, whereas an increase in ε_A^s from $-6kT$ to $-10kT$ results in an almost fivefold increase in the B block concentration at the interface. For $\varepsilon_A^s = -8kT$ (dash-dotted line) the model profile is in best agreement with the NR profile (solid circles). This value of ε_A^s

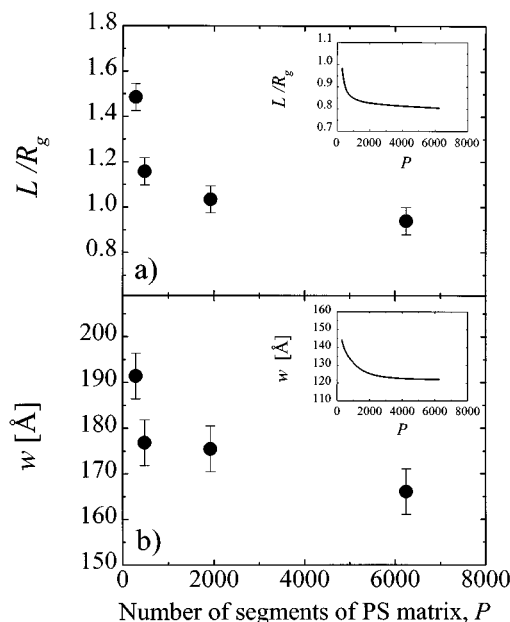


FIG. 3. (a) Normalized thickness of the adsorbed layer (L) determined from NR (solid circles). Inset: L calculated by SCMF for $\varepsilon_A^s = -8kT$. (b) Adsorbed layer-matrix interfacial width (w) determined from NR (solid circles). Inset: w calculated by SCMF for $\varepsilon_A^s = -8kT$. The error bars were obtained following [21].

($\pm 1kT$) was obtained consistently for all values of P . This result contrasts with the SCMF calculations of Clarke *et al.* [10], where ε_A^s held no physical significance. Note that in our calculations ε_A^s represents the interaction energy between the A block and the SiO_x substrate. Because all 44 MMA segments do not lie on the surface, the interaction energy per segment is unknown. For example, if every fourth MMA segment was attached to the surface, the strength of the MMA-SiO_x interaction would be about $-1kT$, a reasonable result.

Figure 3(a) shows the normalized adsorbed layer thickness (solid circles) as a function of P . The thickness is calculated from NR volume fraction profiles of the B block [$\phi(z)$] using

$$L = \frac{1}{z_B^*} \int_0^\infty [\phi(z) - \phi_\infty] dz,$$

where z is the distance from the PS-SiO_x interface. At low P , the adsorbed layer is about $1.5R_g$ thick, suggesting that the adsorbed chains extend from their unperturbed conformation and stretch into the matrix. As P increases, L/R_g quickly decreases and becomes nearly independent of P for $P > 2N_B$. Because the entropy of mixing decreases with increasing P , the matrix chains are progressively expelled from the layer. As a result, the adsorbed layer becomes thinner and compact. The inset of Fig. 3(a) shows L/R_g calculated by the SCMF model. Although the SCF model underestimates L by about 20% these results are in good qualitative agreement with experiments.

Figure 3(b) shows that the interfacial width between the adsorbed layer and the matrix (solid circles) behaves in a similar manner as L/R_g . The width is defined from the gra-

dient of the profile at the center of the interface. For low P , the interface is quite broad, $w = 190 \text{ \AA}$, suggesting that the nonadsorbing B block and matrix chains are highly entangled. As P increases, the matrix chains are expelled from the adsorbed layer. Thus, the interface becomes narrower and w decreases. For $P > 2N_B$, w becomes nearly constant. The inset to Fig. 3(b) shows how w from SCMF varies with P . Again, the SCMF prediction is in good qualitative agreement with experimental results, although the calculated values underestimate the experimental w by about 25%. A possible reason why both the SCMF L and w are less than their experimental values is our choice of ϵ_A^s . Figure 2 shows that the value of ϵ_A^s strongly influences the shape of the volume fraction profile. The interaction energy was chosen to provide the best agreement between SCMF and experimental profiles near the PS-SiO_x interface. Away from the interface, the agreement becomes worse and, in general, the SCMF profile is thinner and sharper than the experimental profile.

Figure 3 shows that for $P < 2N_B$ both L and w are very sensitive functions of P . In this regime the adsorbed chains are stretched and the matrix polymer penetrates deep into the adsorbed layer. As P becomes larger, the adsorbed layer collapses, and at $P \sim 2N_B$, we observe a transition into the regime where the adsorbed layer properties are almost independent on P . These results agree with the observation of Green and Russel [5] who found that the layer thickness was independent of P for $P \gg 2N_B$. Our results suggest that the adhesion of polymer coatings can be improved by adding block copolymer additives with sufficiently high molecular weights so that $2N_B > P$.

In summary, we have presented a systematic and quanti-

tative study of the stretched to nearly collapsed transition of d PS- b -PMMA chains adsorbed from a PS melt to a silicon oxide surface. The interfacial excess of d S block is found to increase with P , and to reach a plateau near $P \sim 2N_B$. The adsorbed layer thickness and the width of the layer/matrix interface are both found to decrease with P , and to become nearly independent of P for $P > 2N_B$. By rigorous comparison of the experimental volume fraction profiles with those from a SCMF model, the value of the MMA-SiO_x interaction energy is determined to be $\epsilon_A^s = -8kT$ per block. These results show that the effectiveness of PS- b -PMMA copolymers as adhesion promoters in PS coatings can be optimized by choosing PS block lengths which are greater than $\frac{1}{2}P$. Under these conditions the adsorbed chains are well entangled with the matrix chains and therefore the polymer coating is more securely anchored to the substrate.

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- [21] The results were obtained by minimizing the χ^2 between the experimental and simulated data. To estimate error bars, we varied the corresponding parameter (z^* , L , w) such that χ^2 increased by a factor of about 2.