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Segregation of Chain Ends to Polymer Melt Surfaces and Interfaces

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The conformation of polymer chains in the melt near an impenetrable boundary has recently been studied by molecular dynamics[1] and off-lattice Monte Carlo simulations.[2-4] Both types of calculations show an enhancement of the chain end density within a distance of approximately two polymer segment lengths of the interface relative to the bulk. In the absence of preferential interactions between monomers and the interface, the segregation arises from minimizing the loss of conformational entropy near an impenetrable boundary; i.e., by positioning an end near the surface, only one unit rather than two is reflected.

In order to obtain an experimental measure of this effect, monodisperse ($M_w/M_n < 1.1$) polystyrene (PS) chains of molecular weight 63 000 with short blocks of deuterated polystyrene (dPS) ($M_w = 1300$) at each end were prepared. The block length was kept as short as possible, while yet producing sufficient neutron scattering contrast in order to minimize any preferential surface segregation due to isotopic effects.[5] The synthesis was carried out via living anionic polymerization of a purified styrene monomer in cyclohexane at 60 °C, utilizing *sec*-butyllithium as the initiator. The process was terminated using degassed methanol.

Samples were prepared by spin casting a layer of the triblock copolymer from toluene, approximately 2460 Å thick, onto a 6.4-mm-in.-thick by 50-mm-diameter Si wafer. The Si wafer was etched with HF acid to remove the native oxide. The resulting H passivated surface has been shown in separate segregation experiments on PS/dPS homopolymer blends to have no preferential interactions with either dPS or PS.[6] This is in contrast to the native oxide covered surface to which segregation of the dPS segment in symmetric triblocks of $M_w = 670\,000$ has been observed.[6,7] The sample was then annealed in the liquid state at 160 °C for 24 h in order to allow the chains to reach their equilibrium configurations in the melt.

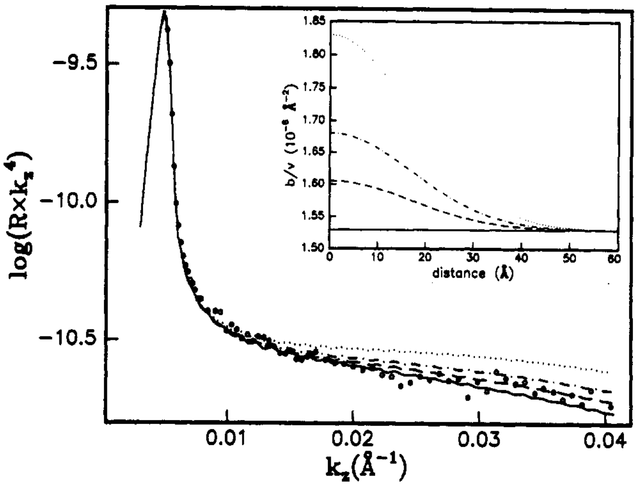

Figure 1. Neutron reflection profile for an annealed layer of dPS/PS/dPS (M_w = 1.3K/63K/1.3K) triblock. The line fits correspond to simulation assuming the deuterium distribution profiles shown in the inset. Inset: Scattering length density as a function of distance from the vacuum surface assuming no end segregation (—) and an enhancement factor of 1 (– –), 2 (– · · –), and 4 (· · ·) over the bulk concentration.

The segregation of chain ends at either the Si or vacuum interface, which would be manifested by an increase in the dPS concentration, was probed by neutron reflection on the POSY II reflectometer at Argonne National Laboratory. The neutron reflection technique is discussed in detail in ref 8. The distribution of ends at the interfaces was modeled in the following way: in the bulk, all segments of the chains are uniformly distributed and the volume fraction of deuterium is given by

$$\phi = 2N_D/N \qquad (1)$$

where N_D and N are the polymerization indices of the deuterated end segment and the polymer chain, respectively. If segregation of chain ends occurs at either the vacuum or Si interfaces, the excess deuterium in the near surface region, Z^*, is given by

$$Z^* = \alpha\left[\frac{2N_D}{N} - \left(\frac{2N_D}{N}\right)^2\right]a \qquad (2)$$

where $a = 6.7$ Å is the statistical segment length of PS and $\alpha + 1$ is the ratio of chain ends at the surface to that in the bulk. The first term in eq 2 accounts for the excess deuterated segments brought into the near surface region by the extra ends present at the surface. The second term accounts for the deuterated segments initially present in the uniform film but displaced in order to accommodate the extra segregated ends. It should be noted that eq 2 produces a maximum in Z^* when $N_D = N/4$ or when $^1/_4$ of each chain is deuterated at the ends. This type of triblock, for total $N = 2450$, was studied as well, with identical results.

Figure 1 shows the reflectivity data for the $M_w = 65\,600$ triblocks plotted as $\log(Rk_z^4)$ vs k_z, where k_z is the component of the incident neutron wave vector perpendicular to the sample surface and R is the reflectivity. Three different functional forms for the distribution of excess deuterium near the surface were studied, namely, an exponential decay, a square layer with an interfacial roughness of 10 Å, and a Gaussian distribution of variance $R_g/4$ and $2R_g$, where $R_g = a\,(N_d/6)^{1/2}$ is the radius of gyration of the deuterated end segment. In the case of the M_w = 65 600 triblock, the length of the deuterated segment was short enough that the χ^2 fit was not sensitive to the details of the functional forms and only varied with the total integrated excess, Z^*. The inset of Figure 1 shows the neutron scattering length per unit volume b/v, which is proportional to the volume fraction of deuterium as a function of distance from the vacuum interface for various

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Table I

amount of enrichment	Z^* (Å)	χ^2 (surface)	χ^2 (interface)
none ($\alpha = 0$)	0	1.98	3.60
twice ($\alpha = 1$)	0.2556	1.95	3.58
three times ($\alpha = 2$)	0.5112	2.35	3.84
four times ($\alpha = 3$)	0.7668	3.61	5.26

Gaussian profiles corresponding to Z^* with $\alpha = 0, 1, 2,$ and 3. The lines in Figure 1 are the reflectivity profiles derived from these functions, superimposed upon the experimental data (○). The roughness of the sample was determined independently from X-ray measurements as 6 and 8 Å at the Si and vacuum surfaces, respectively. The χ^2 values then calculated for various values of Z^* are listed in Table I. From Table I and Figure 1 we can see that the degree of end segregation is no larger than a factor of 2, corresponding to $\alpha = 1$.

In order to probe the degree of chain end segregation to an immiscible polymer interface, a bilayer sample was produced by floating a film approximately 935 Å thick of poly(bromostyrene) (PBrS) of $M_w = 96\,000$ on top of a 1590-Å-thick triblock layer of composition similar to the one discussed above. The bilayer was then annealed for 24 h at 160 °C. The interfacial width between immisicible bilayers[9] of PS and PBrS, both of molecular weight 96 000, was previously measured using X-ray reflection and found to be approximately 45 Å. Consequently, if chain end segregation were to occur, it would be concentrated in this layer. Calculated profiles (again in terms of the neutron scattering length) for this distribution for the case of no segregation and for $\alpha = 0$ and 2.5 are shown in the inset of Figure 2. It should be noted that PBrS and the triblock we are using are contrast matched in the bulk with respect to the neutron scattering length density, and hence no scattering will occur from the triblock/PBrS interface unless there is an excess of deuterium at the interface due to chain end segregation. The reflectivity data plotted as $\log(Rk_z^4)$ vs k_z, together with the calculations corresponding to the profiles in the inset, are shown in Figure 2. The χ^2 values for different values of α are tabulated in Table I. The results are similar to the ones discussed before for the single layer; namely, that the degree of segregation is no larger than a factor of 2. The measured experimental limits on the degree of segregation for both the vacuum and immiscible polymer interface are in good agreement with the predictions of both the molecular dynamics[1] and Monte Carlo simulations.[2-4]

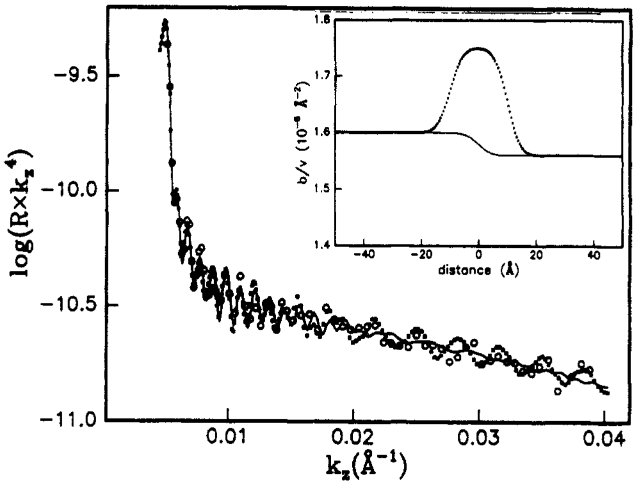

Figure 2. Neutron reflection profile for an annealed PBrS (M_w = 96K)/DPS/PS/DPS (M_w = 1.3K/63K/1.3K) bilayer sample. The line fits correspond to simulations assuming the deuterium distribution profiles shown in the inset. Inset: Scattering length density as a function of distance from the vacuum surface assuming no end segregation (—) and an enhancement factor of 2.5 (···) over the bulk concentration.

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