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Observation of chain stretching in Langmuir diblock copolymer monolayers

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We report observations of chain stretching in diblock copolymer monolayers on the surface of a selective solvent. Using neutron reflectivity, we have studied the concentration profile of the submerged block over a large range of surface density σ (chains per area) for two different molecular weights. The observed increase in the layer thickness is weaker than the $\sigma^{1/3}$ prediction of mean-field and scaling theories for the limiting behavior, but is in agreement with recent numerical self-consistent-field calculations by Whitmore and Noolandi [Macromolecules **23**, 3321 (1990)].

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For many years, the behavior of polymers near surfaces and interfaces has been an area of active study. Layers of polymers attached at one end to a surface, a case important for industrial applications, are of particular recent interest [1]. Such *tethered* layers are commonly formed by two different methods: polymer end-grafting [2–5] and selective adsorption of one block of a diblock copolymer [6–10]. The resulting structures vary as a function of the surface density σ (chains per area). For small σ, the so-called *mushroom* regime, the average distance between the polymers is large. Neighboring polymers do not interact and the average dimension of the tethered polymer perpendicular to the surface is approximately the free polymer radius of gyration R_g. As σ increases, the neighboring chains begin to interact and the polymers stretch perpendicular to the surface to reduce excluded-volume interactions. In the limit of strong stretching, the so-called *brush* regime, both scaling and mean-field theories predict that the layer height h^* in a good solvent is proportional to $M\sigma^{1/3}$, where M is the molecular weight of the tethered chain [11,12]. This scaling has been supported by molecular-dynamics simulations for sufficiently high σ [13]. However, the values of σ in the simulation are difficult to compare to real systems due to important simplifications. On the other hand, sufficient quantitative modeling has been incorporated into recent numerical self-consistent-field (SCF) calculations to allow quantitative comparison with real systems [14]. Over a somewhat smaller range of σ, yet still covering well into the interacting regime, the limiting behavior was not observed. Rather, the dependence of h^* on σ was weaker than $\sigma^{1/3}$ and did not follow a power law.

A number of experiments have been performed to examine the dependence of the layer height on M_w and σ for tethered chain systems. However, it is our view that there has yet to be a clear determination of the individual dependencies. In order to discuss previous work, we represent the surface density in reduced units of $\sigma^* = \sigma/\sigma_0$, where $\sigma_0 = 1/\pi R_g^2$ is the surface density at which neighboring tethered polymers should begin to overlap [1]. Using small-angle neutron scattering, Auroy *et al.* have examined polydimethylsiloxane (PDMS) chains end-grafted onto the surface of porous silica. In an initial report [3], they found good agreement with the limiting scaling relation in the form of a plot of $h^*/\sigma^{1/3}$ vs M_w for $12 < \sigma^* < 70$. However, this plot is very insensitive to the σ dependence and thus is mainly a test of the M_w dependence. In addition, both M_w and σ were varied simultaneously, so it was not possible to determine the individual dependencies. In a subsequent report focusing on the σ dependence, Auroy *et al.* [5] prepared a series of grafted layers covering a large range of surface densities ($2 < \sigma^* < 50$) for a single molecular weight. Their data showed the onset of stretching to occur in the range $12 < \sigma^* < 30$. Since the data in the stretched regime are limited to two points, the σ dependence cannot be determined.

Field *et al.*, studying diblock copolymers selectively adsorbed onto a solid surface by neutron reflectivity, also reported a nearly linear dependence of $h^*/\sigma^{1/3}$ on M_w for data in which M_w and σ were varied simultaneously [9]. We note, however, that the range of $4 < \sigma^* < 7$ in their study was much lower than that for Auroy *et al.* [3]. More recently, Field *et al.* examined four selectively adsorbed diblock copolymers in which the length of the adsorbed block was varied while the length of the tethered block was held constant [10]. In this way, they were able to vary σ while keeping M_w constant. They observed a small increase in the layer thickness over the examined range ($1.3 < \sigma^* < 5$), but reported a qualitative change in the shape of the profile between samples corresponding to $\sigma^* \approx 3.7$ and $\sigma^* \approx 4.8$. This was interpreted as the transition between the mushroom and brush regimes. These results are in apparent disagreement with the SCF calculation of Whitmore and Noolandi ($0.6 < \sigma^* < 6$) [14], who did not see a qualitative change in the profile.

Finally, Kent *et al.*, studying Langmuir diblock copolymer monolayers at the liquid-air interface by neutron reflectivity, varied the surface density of a tethered chain system for a single molecular weight over the range $1.3 < \sigma^* < 4.2$ [15]. In this range, the dependence of h^* on σ was found to be weaker than the predicted limiting scaling behavior.

In view of the disparity of behavior that has been reported with respect to the variation in the tethered layer as a function of σ, we report the dependence of h^* on σ for two tethered chain molecular weights where the surface density is varied over a wide range ($1 < \sigma^* < 10$) for each sample. To do this, we have employed Langmuir diblock copolymer monolayers at the liquid surface where σ can be varied continuously. The copolymers are highly asymmetric in order to access a large range in σ. We observe that the form of the profile is qualitatively the same over the entire range of σ. In addition, the data do not conform to the limiting scaling behavior over this range. However, both the form of the profile and the dependence of the layer thickness on σ and M_w are well described by the numerical SCF calculation of Whitmore and Noolandi [14].

In our study, we have used polydimethylsiloxane-polystyrene (PDMS-PS), which forms a monolayer at the air surface of ethyl benzoate (EB), a selective, good solvent for PS. The surface tension (γ) of EB lies in between that of PS and PDMS ($\gamma_{\rm EB} = 34$ dyn/cm, $\gamma_{\rm PDMS} = 20$ dyn/cm, $\gamma_{\rm PS} = 40$ dyn/cm) [15]. Since $\gamma_{\rm EB} > \gamma_{\rm PDMS}$, there is a strong driving force for the PDMS block to remain at the surface while the fact that $\gamma_{\rm PS} > \gamma_{\rm EB}$ ensures that the PS block does not adsorb at the surface, a problem frequently encountered in end-grafted polymer systems. Two PDMS-PS diblock copolymers with a perdeuterated PS block were studied: 4.5-60 (Polymer Labs, England) and 15-175 (Polymer Standard Service, Germany), where the numbers denote the molecular weights (in kg/mol) of the PDMS and PS blocks, respectively. The polydispersity of each specimen was 1.1 and both samples were used as received. Ethyl benzoate was purchased from Aldrich and vacuum distilled before use.

Monolayers of PDMS-PS were formed at the air surface by depositing a small dry grain of the copolymer onto the surface of the solvent. This avoided the use of an organic spreading solvent and the possibility of its partial retention in the monolayer. The surface density σ was either increased by adding grains of polymer or decreased by aspirating the surface. The reflectivity data were collected for 4–6 h periods for a total time of up to 16 h. The stability of the layer was monitored by measuring the surface tension before and after each reflectivity measurement. Usually, the surface tension remained constant within 0.2 dyn/cm during any given scan and, in this case, the data sets were checked for reproducibility and then combined to obtain better statistics. The surface pressure ($\gamma_{\rm EB} - \gamma$) varied between zero and 8 dyn/cm for the smallest and largest σ values, respectively.

The neutron reflectivity was performed on the time-of-flight reflectometer DESIR at the ORPHEE reactor (Laboratoire Léon Brillouin, Saclay, France). The sample was contained in a Teflon trough ($14 \times 4 \times 0.4$ cm^3), which was completely enclosed to minimize loss of organic subphase by evaporation. The neutron beam passed through 1-mm quartz windows to enter and exit the chamber containing the trough. Data were collected at a fixed angle of incidence θ and a variable neutron wavelength λ. The corresponding scattering vector is given by $q = 4\pi \sin\theta/\lambda$. For the 4.5-60 specimen, θ was 8.7 mrad, while for 15-175, two different angles of 10.5 and 21 mrad were used to obtain a larger range of reflectivity. The neutron wavelengths ranged from 3 to 18 Å, and the resolution (full width at half maximum) was given approximately by $\Delta q/q = 0.06$. The largest q values were 0.025 Å^{-1} for 4.5-60, and 0.045 Å^{-1} for 15-175, which correspond to a range of reflectivity of three and four orders of magnitude, respectively. Since the scattering length density of PDMS is closely matched to that of air, only the deuterated PS block submerged in the solvent is detected.

The reflectivity for two widely different surface densities of the 15-175 sample are shown in Fig. 1. In order to emphasize the major features in the data, we have plotted the ratio of the reflectivity from the monolayer covered surface to the model Fresnel reflectivity for the solvent, the latter being in agreement with the pure solvent data. Since the PS block is deuterated and the solvent is hydrogenated, the reflectivity increases from the solvent value with increasing surface density, thus leading to values of the reflectivity ratio greater than unity. The solid lines correspond to the reflectivity calculated for a parabolic concentration profile according to Ref. [12] as follows:

$$\phi(z) = \phi_s[1 - (z/h^*)^2] , \qquad (1)$$

where ϕ_s is the surface concentration, z is the distance from the surface, and h^* is the layer height. The

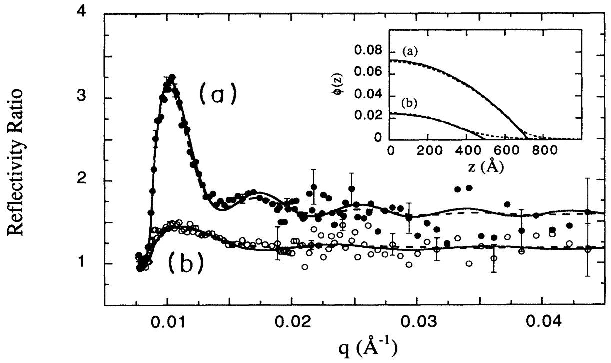

FIG. 1. Ratio of the reflectivity from the 15-175 PDMS-PS specimen to the Fresnel curve for the EB solvent as a function of q for two widely different surface densities. The error bars represent the statistical error of selected points. The two data sets, (a) and (b), were fitted with a parabolic profile (solid lines) and a parabolic profile with a weak exponential tail (dotted lines). The corresponding concentration profiles are shown in the inset.

reflectivity was computed by dividing the profile into 2-Å slabs and calculating the reflected waves at each interface using the Fresnel equations [16]. The best-fit parameters were determined by minimization of χ^2 using the Marquardt algorithm. Typical values of χ^2 were in the range 1–2. In addition to the profile of Eq. (1), we have fit a number of other profiles to the data, including a parabolic profile with an exponential tail, an error function, and a profile similar to that in Eq. (3) but with a variable exponent [9]. While there were slight improvements in the fits over the pure parabola in some cases, as shown in Fig. 1, our conclusions are not dependent on which of these profiles is selected. Therefore, in the following, we will discuss results from fitting to Eq. (1). A further note is that the fits for the 15-175 series are virtually the same when only the reflectivity up to $q=0.025$ Å^{-1} (i.e., the q range for the 4.5-60 series) is used for the fitting. In addition, we are not able to detect a roughness typical of an organic liquid surface (5 Å) or a small depletion layer in our q range. A detailed discussion of the fitting procedure will be given elsewhere.

In contrast to the results of Field *et al.* [10], we observe no qualitative change in the shape of the profile over the range of σ. For example, there were no trends toward increasing χ^2 values or systematic deviations in the residuals with decreasing σ for fits involving any of the profiles mentioned above. On the other hand, fits to our data using the *mushroom* profiles of Field *et al.* led to much larger χ^2 values and systematic deviations in the residuals, even at the lowest σ values. We note that this is in qualitative agreement with numerical SCF calculations [14,17], molecular dynamics [13], and Monte Carlo [18] simulations, in which the profiles closely resemble a parabolic function with a smooth tail and a small depletion layer close to the surface over a range of σ covering weakly to strongly interacting chains.

The surface density was determined from the integral of the reflectivity profiles as

$$\sigma=(\rho N_A/M_w)\int_0^\infty \phi(z)dz \ , \tag{2}$$

where ρ is the melt density of the PS block and N_A is Avogadro's number. The highest attainable σ values are limited by the stability of the monolayer, while the smallest σ values are limited by the experimentally detectable difference between the observed reflectivity and that of the pure solvent. A minimum 10–20% deviation from the pure solvent curve was found to be necessary to obtain parameters without excessively large error bars.

In Fig. 2(a), we have plotted h^* as a function of reduced surface density σ^* $(=\sigma\pi R_g^2)$ for the 4.5-60 and 15-175 specimens [19]. For 4.5-60, h^* is nearly constant for $\sigma^*<2$ and then increases by about 30% over the range $2<\sigma^*<9$. The value of the reduced surface density where the increase appears to begin, $\sigma^*\sim 2$, corresponds to an average radius per chain of $0.7R_g$. For 15-175, h^* increases by 50% over the range $2<\sigma^*<11$. Due to the weaker signal for this specimen at low σ^*, there is a larger error in h^* and the onset of stretching cannot be precisely determined. We remark that our values for h^* are entirely consistent with previously reported results for tethered PS chains in good solvents [6–10,15] at similar values of σ^*. On the other hand, the gradual increase in h^* over this range is in contrast to the results of Auroy *et al.* [5], who observed no change in h^* over this range in σ^* for tethered PDMS chains in a good solvent.

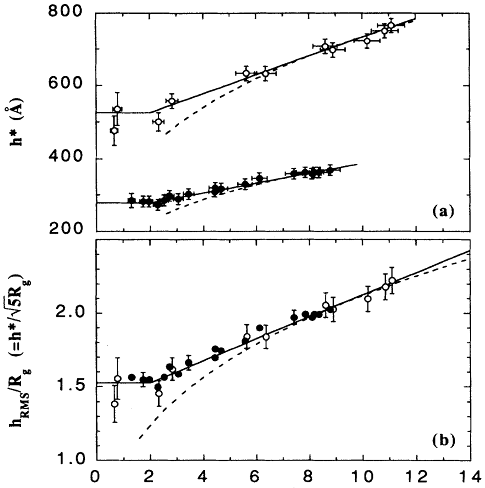

FIG. 2. (a) Plot of layer thickness h^* vs reduced surface density σ^* for the 15-175 (open circles) and 4.5-60 (filled circles) PDMS-PS diblock copolymers. For $\sigma^*>2$, the solid line represents Eq. (3). The dashed curves represent the limiting scaling behavior of $h^*\sim M_w\sigma^{1/3}$. (b) Reduced layer thickness $h_{\rm rms}/R_g(=h^*/\sqrt{5}R_g)$ vs σ^*, with the same data and fits as in (a). The error bars include an uncertainty of ±5% in M_w.

For both samples, the data for $\sigma^*>2$ appear to increase linearly with σ^* according to the following empirical expression:

$$h^*/R_g=A(1+B\sigma^*) \ . \tag{3}$$

The fitted values of the coefficients are $A=3.1\pm0.1$ and $B=0.055\pm0.002$, where the uncertainty is the difference between fitted values for the two polymers. Thus, over the present range of σ^*, the amount of stretching varies roughly linearly with the crowding among the tethered PS blocks. This point is further illustrated in Fig. 2(b), where $h_{\rm rms}=h^*/\sqrt{5}$ is the root-mean-square dimension of the PS blocks perpendicular to the surface, calculated for the parabolic profile.

The dashed lines in Fig. 2 represent calculated curves which follow $h^*\propto M_w\sigma^{1/3}$, the scaling prediction for highly stretched chains. We have arbitrarily adjusted the constant of proportionality in this relation to match the data for the highest σ^* values. From this comparison, we conclude that the data do not follow the limiting behavior over the majority of the present range of σ^*. In particular, the data have a dependence on σ which is weaker than $\sigma^{1/3}$. Comparison to the $\frac{1}{3}$ power law is most appropriate for the highest σ^* values where the PS blocks are more strongly stretched. However, to determine whether the data are deviating from Eq. (3) and tending toward $\sigma^{1/3}$ behavior (dashed lines in Fig. 2), a range extending to even higher σ^* is required.

Since the present data do not follow the limiting scaling prediction, we have fit the data with the following relations in which the power-law exponents were allowed to vary:

$$h^* = CM_w^{\beta}\sigma^{\alpha} , \quad (4)$$

$$\phi_s = DM_w^{\tau}\sigma^{\delta} . \quad (5)$$

The two pairs of exponents (β,α and τ,δ) are not independent, however, as $\alpha+\delta=1$ and $\beta+\tau=1$ from Eqs. (1) and (2). Using the data for $\sigma^*>2$, α was determined to be 0.21 ± 0.01 and 0.24 ± 0.02 for the 4.5-60 and 15-175 samples, respectively, while δ was fitted to 0.79 ± 0.01 and 0.76 ± 0.02. Furthermore, by fixing $\alpha=0.22$ and $\delta=0.78$ for both polymers, we calculated $\beta=0.86$ and $\tau=0.14$. As shown in Fig. 3, these power laws for h^* and ϕ_s adequately describe the data for both polymers for $\sigma^*>2$. Thus, over the present range of σ^*, our results for h^* can be adequately represented by either the linear relation of h^*/R_g with σ^* in Eq. (3) or the power-law relation of h^* with M and σ in Eq. (4).

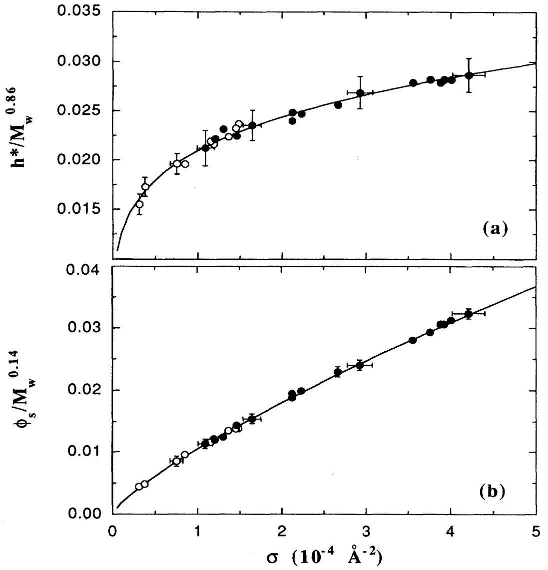

FIG. 3. (a) Plot of $h^*/M_w^{0.86}$ vs σ for the 15-175 (open circles) and 4.5-60 (filled circles) PDMS-PS diblock copolymers. The solid curve represents $h^*/M_w^{0.86}=0.16\sigma^{0.22}$. (b) Plot of $\phi_s/M_w^{0.14}$ vs σ. The solid curve represents $\phi_s/M_w^{0.14}=14\sigma^{0.78}$. The error bars include an uncertainty of ±5% in M_w.

We have compared the above results to recent SCF calculations by Whitmore and Noolandi [14]. These authors used a SCF scheme similar to earlier work by Muthukumar and Ho [17], but included a more detailed description of the self-consistent potential as well as specific material parameters which allow a quantitative comparison with experimental data for PS in a good solvent. They calculated concentration profiles for a tethered chain length corresponding to 60 kg/mol PS for a range of σ from 0.025 nm^{-2} to 0.0025 nm^{-2} ($0.5<\sigma^*<5$), and for a range of molecular weight from 21 to 73 kg/mol PS for $\sigma=0.023$ nm^{-2} ($1.4<\sigma^*<6$). While their data do not follow strict power laws, they give values for the scaling exponents in Eqs. (4) and (5) evaluated at various points over the range of surface density. Over the range $0.5<\sigma^*<5$ for the chain length corresponding to 60 kg/mol PS, α increases from 0 to 0.30, and δ decreases from 0.85 to 0.67. Over their range of molecular weight, β increases from 0.67 to just over 0.8 and τ decreases from about 0.2 to under 0.07. Our values ($\alpha=0.21-0.24$, $\delta=0.76-0.79$, $\beta=0.86$, $\tau=0.14$), which were fit over the entire range of σ and M, are in good agreement with these limits. Furthermore, they find only a moderate increase of the layer height (< 100%) and no abrupt transition between mushroom and brush states. This is entirely consistent with our observations.

In conclusion, we have investigated the stretching of tethered polymer layers over a large range in surface density. This is the first investigation where both the surface density and molecular weight have been varied independently. Over the range of σ examined, the data are well described by a linear relation $h^*=3.1R_g(1+0.055\sigma^*)$, or a power law of the form $h^*=0.16M_w^{0.86}\sigma^{0.22}$. Our data are not consistent with the limiting scaling behavior over the majority of the σ range, but the observed behavior is qualitatively described by recent numerical SCF calculations by Whitmore and Noolandi.

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