

Direct Measurements of Polymer Depletion Layers by Neutron Reflectivity

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(Received 17 December 1990)

We present results of direct measurements of polymer depletion layers at the liquid/air interface using neutron reflectivity. The systems studied are semidilute solutions of polystyrene in toluene using polymers of different molecular weights. The thickness of the depletion layer d is found to be of the order of the correlation length ξ of the polymer in the bulk solution. We show, for the first time, the existence of a depletion layer at the free surface of a polymer solution when $\gamma_p > \gamma_s$, where γ_p and γ_s are surface tensions of pure polymer and pure solvent, respectively. We show also that the thickness of the depletion layer scales with the bulk concentration ϕ_b as $d \sim \phi_b^{-0.75}$.

PACS numbers: 78.65.Hc, 61.12.-q, 68.10.Jy, 78.20.Ci

The behaviors of flexible polymer chains in the vicinity of a wall have received much interest in both theoretical and applied aspects of interfacial science. The wall, which can be a solid, liquid, or gaseous interface, can be characterized under “adsorbing” ($\chi_s > 0$) or “nonadsorbing” ($\chi_s \leq 0$) depending upon the energies of the polymer-solvent, polymer-polymer, and polymer-wall interactions. χ_s is the differential-adsorption energy parameter which corresponds to the difference in free-energy transfer, to the surface, of a polymer segment and a solvent molecule from pure bulk polymer and pure solvent, respectively. [1] At the free surface of a solution (liquid/gas interface), polymer adsorption is governed by the surface tension of the pure polymer (γ_p) and that of pure solvent (γ_s). If $\gamma_p < \gamma_s$, polymer adsorption takes place. This is true for the case of poly(dimethylsiloxane) in toluene as demonstrated by surface-tension measurements [2] and by direct measurements of the adsorbed layer by neutron reflectivity [3]. If $\gamma_p > \gamma_s$ as in the case of polystyrene in toluene [2], or if $\gamma_p = \gamma_s$ ($\chi_s = 0$), the polymer is repelled from the surface. Under these conditions, due to the fact that the decrease in conformation entropy of the macromolecule in the vicinity of the wall is not compensated by an adsorption energy, steric repulsion between the molecule and the wall results in a depletion layer [4]. In the field of colloidal stability, it was shown for the case of both dilute [4] and semidilute [5] solutions that an overlap of two depletion layers can cause a net attraction between the two walls as a result of osmotic pressure. This area of colloidal stability control by nonadsorbing polymers as opposed to adsorbing polymers has received much attention in the recent past [6]. The study of interfacial depletion layers therefore encompasses both theoretical as well as practical interests.

Theoretical predictions of the concentration profile in the depletion layer by mean-field [7] and by scaling [8] approaches give the same qualitative results. In the dilute regime, the thickness of the depletion layer is of the

order of the radius of gyration of the free polymer coil. As the concentration increases and approaches coil overlap in the semidilute regime, the depletion layer decreases significantly to the order of the bulk polymer correlation length, ξ . This decrease in thickness is due to the increasing amount of work required to move a solute molecule from the depletion layer into the bulk solution against the increasing osmotic pressure. Experimentally, however, direct measurement of a polymer depletion layer, as expected, is considerably more difficult than that of an adsorbed layer. This arises from the fact that the concentration difference between the depletion layer and the bulk solution is often much smaller than that between adsorbed layer and bulk solution. Literature reports on the experimental determination of depletion layers are scarce [9]. To our knowledge, there has been no report of *direct* measurements of the depletion layer.

In this paper, we present for the first time results of *direct* measurements, using neutron reflectivity, of the average thicknesses of polymer depletion layers at the liquid/air interface (case of $\gamma_p > \gamma_s$). The technique of neutron reflectivity allows us to study nondestructively interfacial phenomena at molecular length scales. In addition, unlike fluorescent techniques, no foreign molecule is incorporated in the system, thus there is no possible chemical alteration of the samples.

The systems we have studied consist of semidilute solutions of protonated polystyrene in deuterated toluene. The molecular weights of the polymer samples are 47000, 133000, and 230000, with radii of gyration of 81, 145, and 195 Å, respectively. The concentrations of the polymer solutions range from $1.5\phi^*$ to $7.20\phi^*$ where ϕ^* , expressed in volume fraction of monomer, is the overlap concentration defined as $\phi^* = 3M_w/4\pi N_A (R_g^2)^{3/2}$. M_w is the molecular weight and R_g the radius of gyration at infinite dilution determined by low-angle light scattering.

Neutron reflectivity is governed by the same principles as those underlying any electromagnetic radiation in the

“s” polarization state. A vast amount of detailed description of neutron optics can be found in the literature [10]. When a beam of neutrons reaches an interface with a grazing angle of incidence θ_0 , it is reflected and refracted according to the laws of Descartes. The reflectivity, which is defined as the ratio of the intensity of the specularly reflected beam to the intensity of incident beam, is thus a function of the normal component $k_z = (2\pi/\lambda)\sin\theta_0$ of the incident wave vector (λ is the neutron wavelength). The normal component q of the refracted wave vector is related to k_z by

$$q^2 = k_z^2 - 4\pi(Nb)(z = \infty). \quad (1)$$

N is the number density and b the average coherent scattering length. For nonabsorptive materials, Nb is related to the refractive index n by [10] $n = 1 - (Nb/2\pi)\lambda^2$. $(Nb)(z)$ then, is the average coherent scattering length density at a distance z from the interface and $(Nb)(\infty)$ is that for the bulk solution.

The reflectivity $R(k_z)$ can be calculated from $\psi_q(0)$ and $\psi'_q(0)$, where $\psi_q(z)$ is the solution of the Schrödinger equation [10]:

$$\psi''_q(z) + q^2\psi_q(z) = V(z)\psi_q(z) \quad (2)$$

and which behaves as $\exp(iqz)$ for $z \rightarrow \infty$. $V(z)$ is the neutron interaction potential which is defined as $V(z) = 4\pi\{(Nb)(z) - (Nb)(\infty)\}$. For a two-component system of polymer P in solvent S , $V(z)$ can be rewritten in terms of the monomer concentration such that $V(z) = 4\pi\{\phi(z) - \phi(\infty)\}\{(Nb)_p - (Nb)_s\}$, where ϕ is the local monomer volume fraction. When $q^2 < 0 \leftrightarrow k_z < (k_z)_c = \sqrt{4\pi(Nb)(\infty)}$, total reflection occurs. When $k_z > (k_z)_c$, the reflectivity is calculated from [11]

$$R(k_z) = \left| \frac{ik_z\psi_q(0) - \psi'_q(0)}{ik_z\psi_q(0) + \psi'_q(0)} \right|^2. \quad (3)$$

For a homogeneous interface where the refractive index varies sharply as a step function from one medium to another, Eq. (3) is reduced to the Fresnel reflectivity [11]:

$$R_F(k_z) = \left| \frac{k_z - q}{k_z + q} \right|^2. \quad (4)$$

In the presence of surface roughness $\langle\sigma^2\rangle^{1/2}$, the Fresnel reflectivity is modified by a Debye-Waller factor giving [12]

$$R_F^i(k_z) = R_F(k_z)\exp(-4q^2\langle\sigma^2\rangle). \quad (5)$$

For liquid surfaces, roughness arises from capillary wave fluctuations, the degree of which depends upon the surface tension of the liquid. For the solutions used in this study, $\langle\sigma^2\rangle^{1/2}$ is measured to be about 5 Å; this value is included in the calculations of the reflectivity functions.

The experiments were conducted on the neutron reflectometer, CRISP, at the pulsed neutron source at the

Rutherford Appleton Laboratory, United Kingdom. The neutron wavelengths range from 0.5 to 6.5 Å. Two incident angles, $\sim 0.45^\circ$ and $\sim 0.90^\circ$, were used in order to increase the range of k_z . In this study, the experimental error $\delta k_z/k_z$ is about 6%.

Figure 1 shows reflectivity data [$\log R(k_z)$ vs k_z] for pure deuterated toluene (curve *a*) and for deuterated toluene containing protonated polystyrene [$M_w = 47000$, $\phi_b = 4\phi^*$ (curve *b*), $M_w = 230000$, $\phi_b = 3\phi^*$ (curve *c*)]. The dotted lines are the corresponding calculated Fresnel curves taking into account effects of surface roughness and instrumental resolution [$R_F^i(k_z)$]. Curve *a* shows that the reflectivity of pure solvent can be fitted to a Fresnel curve. Curves *b* and *c*, however, deviate from the Fresnel curves, showing clearly that the surfaces of the polymer solutions are not homogeneous. In order to fit the data of these polymer solutions, a depletion layer has to be incorporated into the calculation. The solid continuous lines are theoretical curves calculated with depletion layers with concentration profiles predicted by mean-field theory [7] where

$$\phi(z) = \phi_b \tanh^2(z/d). \quad (6)$$

ϕ_b is the monomer concentration in the bulk solution and

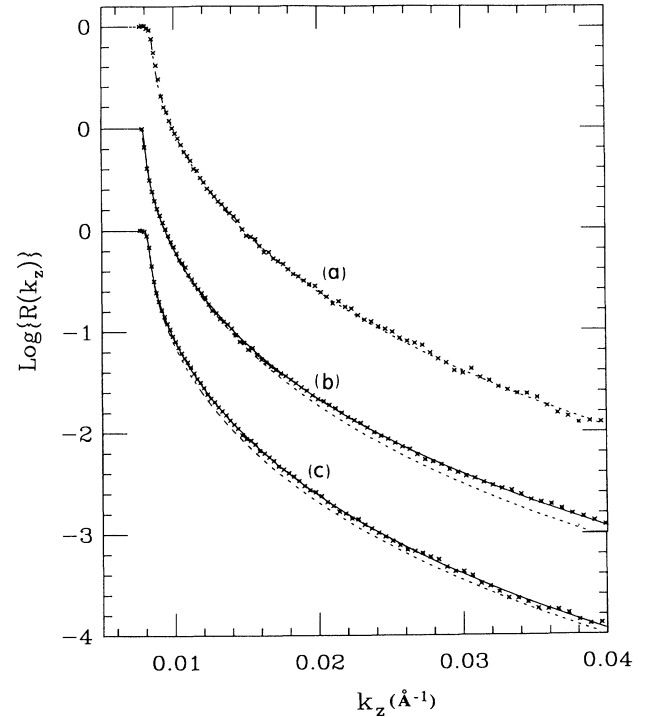


FIG. 1. Reflectivity data [$\log R(k_z)$ vs k_z] of pure deuterated toluene (curve *a*), protonated polystyrene in deuterated toluene ($M_w = 47000$, $4\phi^*$, $d = 28$ Å) (curve *b*), ($M_w = 230000$, $3\phi^*$, $d = 80$ Å) (curve *c*). The dotted lines are corresponding Fresnel curves; the solid lines are theoretical curves calculated with a depletion-layer profile predicted by mean-field theory [Eq. (6)].

d the extension of the depletion layer. The values of d are determined to be 28 and 80 Å for cases *b* and *c*, respectively.

In Fig. 2, the reflectivity data are represented as $\log\{R(k_z)/R_F(k_z)\}$. This representation of results shows more clearly the deviation of the experimental data from the Fresnel reflectivity (horizontal straight line at zero), and thus the effects of interfacial structure. The continuous lines through the data points [Figs. 2(a)–2(c)] are theoretical curves calculated with depletion layers using the concentration profile described by Eq. (6).

We have also used a simpler single-layer step profile to model the depletion layer. In this case, we find that the step profile appears to work when the thickness of the depletion layer is small, in the range of 25 to 30 Å. However, when the depletion layers are relatively large, in the range of 80 to 90 Å, the model breaks down, as shown in Fig. 2(d). This is because the cutoff for the extension of the depletion layer in the step profile is too abrupt, and for large layers produce oscillations within the range of k_z investigated. For smaller layers, the oscillations fall outside the range of k_z studied, giving an impression that the model gives a satisfactory fit. Notice that the oscilla-

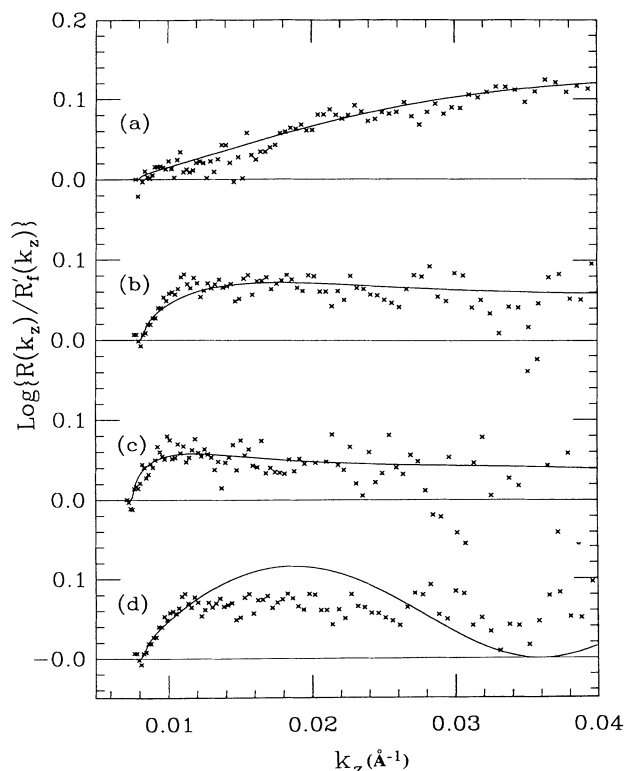


FIG. 2. Reflectivity data ($\log[R(k_z)/R_F(k_z)]$) vs k_z for polymer solutions (a) ($M_w=47000$, $4\phi^*$, $d=28$ Å); (b) ($M_w=230000$, $3\phi^*$, $d=80$ Å); (c) ($M_w=133000$, $1.5\phi^*$, $d=105$ Å). (a)–(c) are fitted with the mean-field profile; (d) is data of (b) fitted with a single-layer step profile.

tions are smoothed out when a continuous profile is used [Figs. 2(b) and 2(c)]. We point out that mean-field profile fits our data, but other models (such as scaling) may work just as well. Our data are sensitive to the difference between an abrupt step profile and a smooth continuous profile; however, they do not allow us to distinguish between different smooth profiles. This does not affect our present study since both mean-field and scaling theories predict d to be proportional to ξ . Our interest is to determine the average thickness of the depletion layer and its concentration dependence, the latter of which does not depend on the type of profile used.

Figure 3 (see inset) shows the variation of d with ξ evaluated from the relationship [13] $\xi/R_g=0.43(\phi_b/\phi^*)^{-0.75}$. The normalized thickness of the depletion layer d/R_g , plotted as a function of the normalized concentration ϕ_b/ϕ^* , is given in the same figure. The continuous straight line yields a slope of -0.75 . Thus we show, for the first time, that the thickness of the depletion layer at the free surface of a semidilute polymer solution follows the relationship

$$\frac{d}{R_g} \sim \left(\frac{\phi_b}{\phi^*} \right)^{-0.75} \quad (7)$$

as predicted by scaling considerations [8]. For dilute solutions where $\phi_b < \phi^*$, the depletion layer is predicted to be of the order of the radius of gyration and we expect

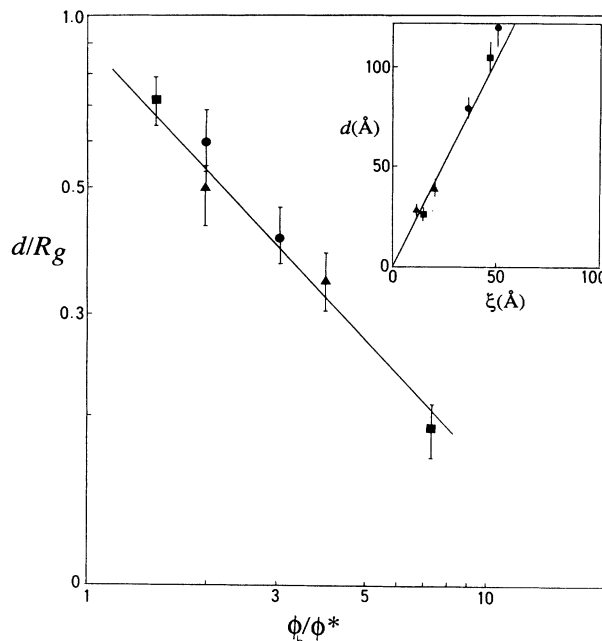


FIG. 3. Normalized depletion layer thickness d/R_g plotted as a function of normalized polymer concentration ϕ_b/ϕ^* [(\blacktriangle), $M_w=47000$; (\blacksquare), $M_w=133000$; (\bullet), $M_w=230000$]. The slope of the straight line is -0.75 . Inset: The relationship between d and ξ .

a significant dependence of d on the polymer molecular weight. However, in dilute solutions, the contrast between the depletion layer and the bulk solution becomes so small that it is not possible to deduce irrevocably the existence of a depletion layer from the reflectivity data.

In summary, neutron reflectivity has been used to measure *directly*, for the first time, polymer depletion layers at the liquid/air interface. These results show the existence of a depletion layer at the free surface when $\gamma_p > \gamma_s$. The overall thickness of the depletion layer is measured to be proportional to the correlation length of the polymer, ξ . We have also shown that the depletion layer at the free surface of a semidilute polymer solution follows the relationship $d/R_g \sim (\phi_b/\phi^*)^{-0.75}$ as predicted by scaling laws.

We are appreciative of the invaluable comments and suggestions that M. Daoud has given us in this study. We also acknowledge G. Jannink for his helpful remarks and interest in this work.

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