

No Intrinsic Depletion Layer on a Polystyrene Thin Film at a Water Interface

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Using neutron reflectivity, we found that there is no intrinsic depletion layer at a deuterated polystyrene (dPS) film and deuterium oxide (D₂O) interface. A spun-cast film is susceptible to contamination on its surface from its surroundings during sample preparation. A contamination layer of hydrogenated organic material will be detected as a reduced scattering length density layer at the interface. We demonstrate that, by careful treatment of the film, contamination would be the primary cause of the reduced scattering length density layer at the interface.

Introduction

The interfacial structure of hydrophobic surfaces in contact with water has attracted a lot of interest in the past few years. The origin of hydrophobic forces has implications in many fields, including protein folding and colloidal systems. Theoretically, it has been proven that the hydrophobic force arises from a reduced density layer of water near large enough hydrophobic substrates.¹ The thickness of the layer has been calculated to a few angstroms using molecular dynamic simulation.² This layer could be considered to be a precursor of air nanobubbles. Air nanobubble formation on hydrophobic surfaces in aqueous media has become widely explored as a general phenomena. Nanobubble formation has been recognized by observing strong and stepwise long-range attractive interactions between macroscopic hydrophobic surfaces in aqueous media.³ Direct images of nanobubbles of 20–30 nm height have been obtained using tapping mode AFM at the silane-modified glass–water interface.⁴ Nanobubbles were found on various surfaces such as hydrophobic silane-modified surfaces and also inorganic surfaces including gold,⁵ graphite,⁶ and mica.⁷

Recently, hydrophobic polymer surfaces were used to study interfacial structures at the water interface.^{8,9} Using neutron reflectivity, they found a few-nanometers-thick layer with reduced scattering length density (SLD) between a deuterated polystyrene (dPS) film on Si and the D₂O interface. From the point of view of neutron reflectivity experiments, a reduced SLD layer at a dPS/D₂O interface can be interpreted as either a lower water density layer (i.e., depletion layer) or a hydrogenated contamination layer adsorbed on the dPS film. Polymer films are susceptible to contamination on their surfaces from the open air environment

during sample preparation. Therefore, careful treatment in preparing the film would be necessary to find the origin of the reduced SLD layer at a dPS/D₂O interface.

In this letter, we show that for carefully prepared dPS films there is no evidence of a reduced SLD layer in neutron reflectivity experiments at the dPS/D₂O interface. The adsorption of hydrogenated contaminants and/or oxidation on the dPS film during sample preparation might be responsible for the reduced SLD layer.

Experimental Section

Deuterated polystyrene (dPS) films were prepared by spin coating either from toluene or deuterated toluene (*d*-toluene) solution on freshly cleaned Si blocks (105 mm diameter and 13 mm thickness). Si blocks were thoroughly cleaned in piranha solution. Coated film thicknesses were about 500 Å. All of the films were carefully dried in a dish for an hour right after spin casting. To investigate the annealing effect, the dried films were annealed at 70 °C for 2 h or 160 °C for 24 h in an oil-free vacuum ($\sim 10^{-3}$ Torr) oven. The samples were then placed in a homemade liquid cell filled with D₂O. The cell was cleaned with deionized water and dried with nitrogen gas before use. Visible air bubbles trapped inside the liquid cell were carefully removed before neutron reflectivity measurements. The liquid cell temperature was controlled to ± 0.5 °C in the temperature range of 20–50 °C by a thermostat circulator during the measurement.

Neutron reflectivity measurements were performed on the NG7 horizontal reflectometer at the NIST (National Institute of Standards and Technology) Center for Neutron Research (NCNR). The sample and scattering geometry are schematically drawn in Figure 1a (lower inset). The neutron scattering intensity was collected along the specular reflection direction and plotted as a function of the *z*-directional scattering wave vector, $Q_z = (4\pi/\lambda)\sin\theta$ where the neutron wavelength is $\lambda = 4.75$ Å and θ is the incident angle to the substrate.

Results and Discussions

Neutron reflectivity is a very sensitive technique for detecting a low SLD layer at a dPS/D₂O interface where the SLD of dPS (6.42×10^{-6} Å⁻²) is well matched to that of the bulk liquid (SLD of D₂O = 6.36×10^{-6} Å⁻²). The calculated reflectivity shows only very weak Kiessig oscillations that result from the small difference between the SLDs of dPS and D₂O as shown in Figure 1a. However, even a 2-Å-thick low SLD layer at the interface gives rise to apparent Kiessig oscillation in the reflectivity profile where the corresponding layer SLD profile is depicted in Figure 1a (upper inset).

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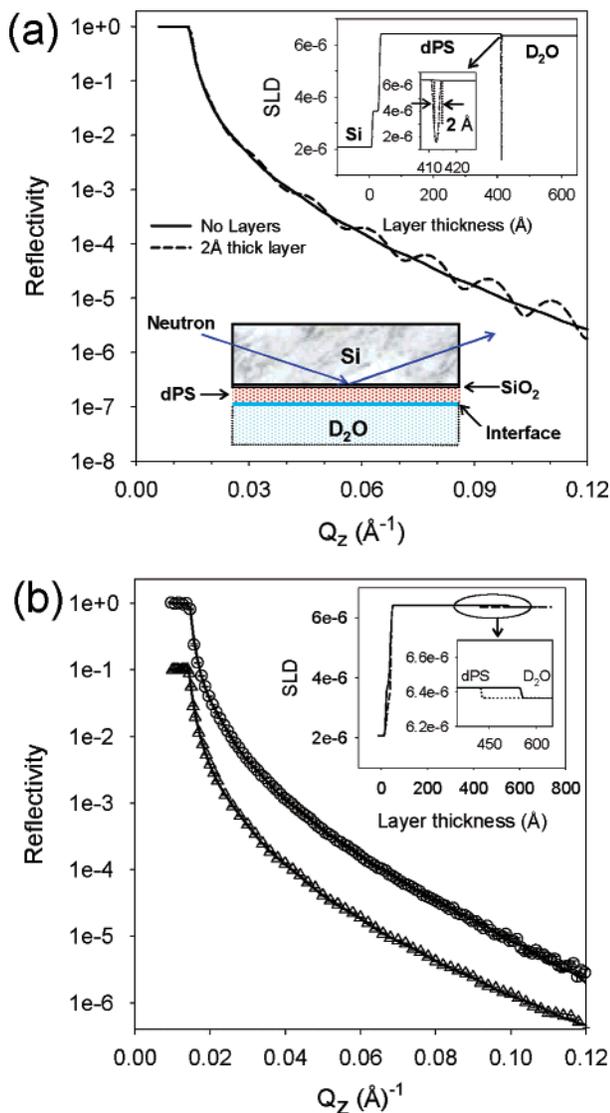


Figure 1. (a) Calculated reflectivity profiles when there is no low SLD layer (solid line) and a 2-Å-thick layer with an SLD of 1.68×10^{-6} (dashed line) at a dPS/D₂O interface. The corresponding SLD profiles are in the upper inset. Schematic sample geometry is shown in the lower inset. (b) Neutron reflectivity profiles are plotted as a function of Q_z for two dPS films that have been prepared from deuterated toluene (circle) and toluene solutions (triangle). Solid lines are the fit where the corresponding SLD profiles are in the inset.

We test the existence of a low SLD layer at a dPS/D₂O interface using neutron reflectivity. To minimize any residual solvent, the spun-cast dPS films were kept for a few hours in a clean dish, and then the film was assembled in the liquid cell filled with D₂O. In Figure 1b, neutron reflectivity profiles measured at 20 °C are plotted as a function of Q_z for two dPS films that were prepared from deuterated toluene (circle) and toluene (triangle) solutions. Solid lines are fits where the corresponding SLD profiles are shown in the inset with solid and dotted lines for the films prepared from *d*-toluene and toluene solutions, respectively. The exact thickness of the dPS films has been determined using neutron reflectivity at the dPS/H₂O interface by exchanging the bulk liquid from D₂O to H₂O in the same liquid cell after we measured the film at the dPS/D₂O interface. Apparently, no distinct oscillations were detected in the reflectivity profile, indicating that there is no low SLD layer (i.e., depletion layer) formed at the interface as described in Figure 1a. Additionally, there is no difference in reflectivity on the dPS films prepared from

d-toluene and toluene solution, implying that there is no residual solvent effect at the interface. Therefore, we conclude that low SLD material has been neither adsorbed nor created at the dPS/D₂O interface. This result is inconsistent with the previous reports^{8,9} where a low SLD layer at a dPS/D₂O interface was found using neutron reflectivity.

Contamination from Sampling Environments. In the previous section, before the reflectivity measurement, we kept the spun-cast dPS film in a clean dish, which also minimized dPS films' contact with the open air environment and therefore the adsorption of hydrogenated organic contaminants from the air was minimized. In this section, we purposely exposed the dPS films to an open air environment while we measured the film thickness using neutron reflectivity at an air interface for approximately 4 h, and then the film was assembled into the liquid cell. In Figure 2a, we plot the reflectivity profile of the dPS film/air interface; its thickness is obtained as 430 Å from the fit (solid line), and its corresponding SLD profile is shown in the inset. In Figure 2b, we plot the reflectivity at the D₂O interface for the dPS film that has been exposed to open air. The film was kept in the liquid cell for a day at room temperature and then measured once again in order to confirm the stability of the low SLD layer in water. The reflectivity profiles show distinct Kiessig oscillations and are apparently unchanged for a day. From the fit, the SLD profile shown in the inset is obtained. We found that a 2-Å-thick low SLD layer with an SLD of $(1.55 \pm 0.1) \times 10^{-6} \text{ Å}^{-2}$ exists at the dPS/D₂O interface, and there is neither accumulation nor destruction (i.e., dissolution in water) of the low SLD layer at least for 1 day in D₂O, implying that the low SLD layer has not originated from contamination of the liquid cell. From Figures 1 and Figure 2, therefore, it is concluded that the low SLD layer originates from hydrogenated contaminants adsorbed on the dPS film from an air open environment and not from a depletion layer.

The fit with the lowest statistical chi-square (χ^2) value could also be obtained from a thicker layer with higher SLD combinations because of the accuracy of the data, as shown in Figure 2c. The corresponding SLD profiles at the interface are plotted in Figure 2d. The lowest χ^2 value of 11.1 was calculated for the combination of (2 to 5)-Å-thick layers with corresponding SLD values of $(1.55\text{--}4.46) \times 10^{-6}$ at the interface. The χ^2 value increased for layers more than 6 Å thick. We expect that the hydrogenated contamination layer at the interface exists in the form of a continuous film of at least 2 Å thickness, or the contamination layer could be swollen by D₂O and could form a thicker layer with higher SLD.

Annealing Effects. Newly spun-cast dPS films were treated at high temperature in order to evaporate residual solvent completely or to relax the residual stress originating from the spin-casting process. During the heat treatment, the film starts to experience adsorption of hydrogenated organic materials and/or oxidation on the surface. The oxidation becomes especially severe when the films are annealed at higher temperature. To investigate these effects, the spun-cast film was annealed under two different conditions instead of keeping it in a dish. In the first method, the film was annealed at 70 °C for 2 h, which removed any residual toluene. In the second, the film was annealed at 160 °C for 24 h, where the annealing temperature is higher than the glass-transition temperature (T_g) of PS ($T_g \approx 100 \text{ °C}$). It is noted that all annealing was performed under a vacuum of 10^{-3} Torr using an oil-free pump. In Figure 3a and b, we plot the reflectivity of the annealed dPS films under these two conditions. There is no Kiessig oscillation in Figure 3a. Apparently, annealing at 70 °C for 2 h did not induce a detectable

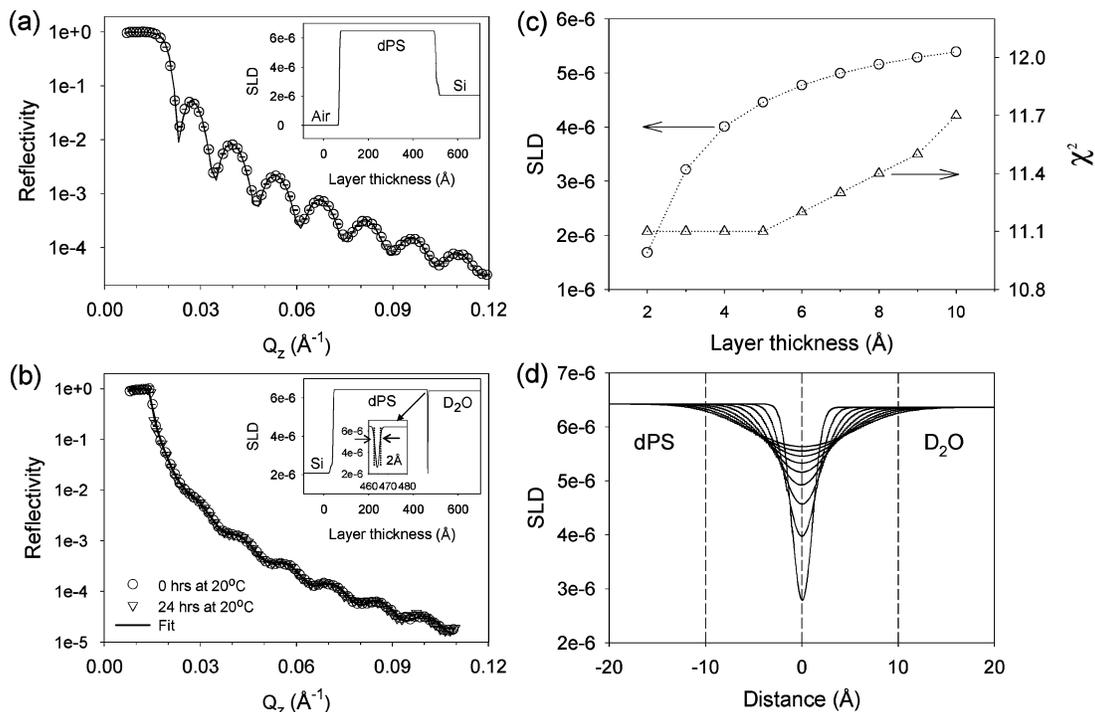


Figure 2. Neutron reflectivity profile of a dPS film exposed to air for 4 h measured (a) at the air interface and (b) at the D_2O interface. Solid lines are the fit, and their corresponding SLD profiles are in the insets. (c) Alternative fit to the reflectivity in b are shown where SLD and statistical chi-square (χ^2) values for each fit are plotted vs the interfacial layer thickness, and (d) their corresponding SLD profiles at the interface are plotted.

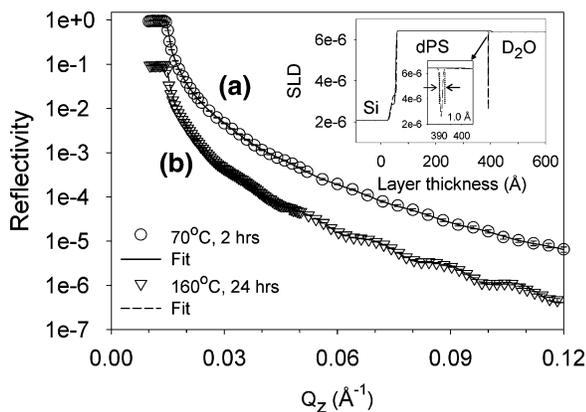


Figure 3. Neutron reflectivity profiles for dPS films at the D_2O interface after annealing (a) at 70 °C for 2 h and (b) at 160 °C for 24 h in an oil-free vacuum at 10^{-3} Torr.

amount of hydrogenated organic materials adsorbed or oxidized at the surface. In Figure 3b, however, we observed distinct Kiessig oscillations. Its corresponding SLD profile is shown in the inset. A 1- \AA -thick low SLD layer exists at the interface from annealing at 160 °C for 24 h.

Effects of Measuring Temperature. We further confirmed the stability of the interface as a function of temperature and time in the liquid cell. The dPS film used was prepared from *d*-toluene solution and annealed at 70 °C for 2 h under vacuum. In Figure 4a and b, the reflectivity profiles are unchanged without any evidence of oscillations even after prolonged exposure up to 2.5 days to D_2O at 20 °C in the liquid cell, where the temperature was elevated from 20 to 50 °C and returned to 20 °C over a period of 2 days.

Conclusions

Using neutron reflectivity, we found that no low SLD layer (i.e., depletion layer) exists at a dPS/ D_2O interface even for films

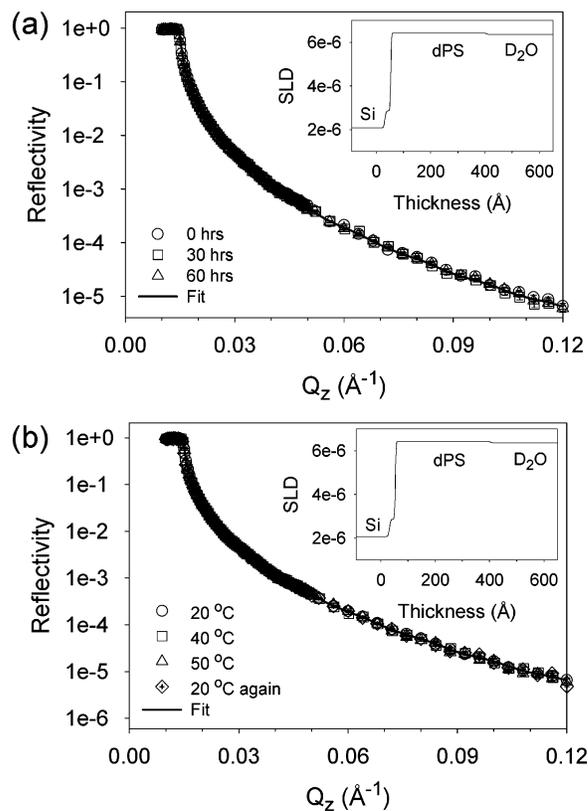


Figure 4. Neutron reflectivity profiles for dPS films at the D_2O interface measured (a) for prolonged exposure to D_2O for up to 60 h at 20 °C and (b) at temperatures of 20–50 °C.

exposed to D_2O for up to 2.5 days at temperatures of 20–50 °C. For dPS films that have been exposed to an open air environment for a few hours or annealed at high temperature in vacuum, distinct oscillations appear in the reflectivity profiles as a result

of a low SLD layer at the D₂O interface, indicating that a low SLD layer originates from hydrogenated contamination and/or oxidation of the DPS surface during sample treatment. It is noted

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that chemical analysis such as X-ray photoelectron spectroscopy (XPS) would be necessary when scrutinizing airborne contamination and annealing-induced oxidation. This nonobservation of an air layer at a water–hydrophobic solid interface agrees with the ellipsometric results of Mao et al.¹⁰ and Takata et al.¹¹

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