X-ray Reflectivity Study of Polymer Confined by Two Hard Walls

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Introduction

It is of interest to measure directly the effects of confinement on the molecular ordering of polymers in thin films and near hard surfaces. The existence of "layering" in linear polymer melts under confinement has been surmised from both measurements with the surface forces apparatus (SFA)[1] and simulations.[2] Force measurements with linear polydimethylsiloxanes (PDMS)[1] show oscillations characteristic of layering, while those with melts of branched polybutadienes[3] show no oscillations. Experimental evidence for layering at a solid/liquid interface obtained using x-ray reflectivity (XR) has recently been published for the case of a liquid film of small molecules with a free surface[4] and an experimental report[5] records successful XR experiments to determine the layering of small molecules in a confined geometry where two solid/liquid interfaces are close together. In the work described below, the sample cell and approach developed by Sinha and coworkers for XR of the small molecule system are applied to first measurements on polymers, both PDMS and polybutadiene (PB).

Methods and Materials

Two polymer materials were considered. First, PDMS of weight average molecular weight 1675 g/mol and polydispersity 1.24 was studied. The PDMS chains are highly flexible, have no short chain branching, are chemically and oxidatively relatively inert, and have a viscosity comparable to that of water at this molecular weight. In order to consider the effect of branching, an anionically polymerized polybutadiene of molecular weight 8000 g/mol, polydispersity of M_w/M_n ~1.04 and ca. 94% 1,4 microstructure was studied as well. The PB was stabilized with a very small concentration of antioxidant according to standard protocols.

X-ray reflectivity is superbly sensitive to variations in electron density along the surface normal in a confined film, with the resolution of these variations limited by dynamic range, microroughness of the adjacent surfaces, and quality of the alignment of the confining plates. The key to making the measurements shown here was the use of a novel sample cell.[5] Dynamic range was maximized by using higher energy x-rays on an insertion device. Fine definition of the wall positions and minimization of wall scattering was accomplished by using highly polished silicon single crystals for both walls. The confining pressure was increased and the gap between the confining walls decreased by adjustment, with a torque wrench, of three micrometers controlling the position of the "upper" silicon crystal.

Results

The reflectivity experiments were performed at the Advanced Photon Source at Argonne National Laboratory on the 1-ID beamline using 30 keV photons. When the confining plates were sufficiently well aligned, a reflectivity curve could be measured. Curves were obtained for a range of pressures, and the first important result was that substantial changes in the gap thickness (as evidenced by the spacing of the Kiessig fringes in the reflectivity), occurred in a jump-wise fashion, consistent with Israelachvili's observation that the thickness of his PDMS confined layer was quantized. Between jumps the confining pressure was increased substantially with only subtle changes in the reflec-

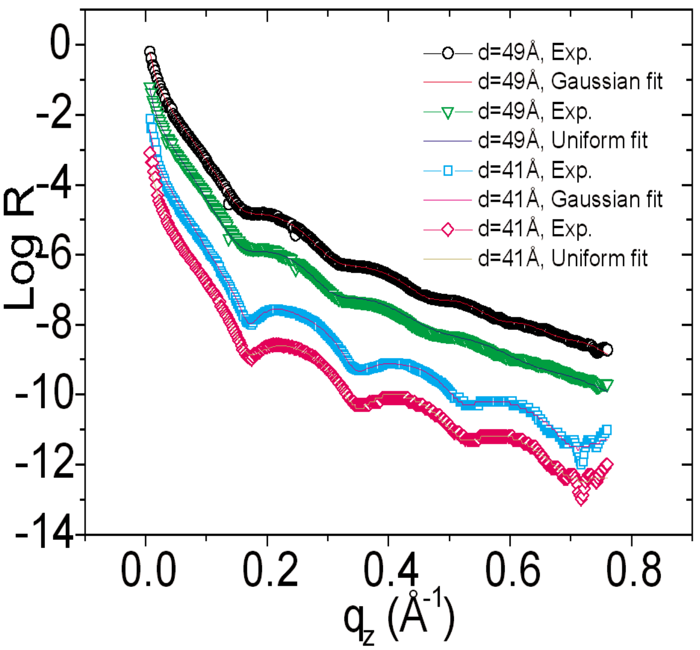

FIG. 1. Reflectivity curv from confined layers.

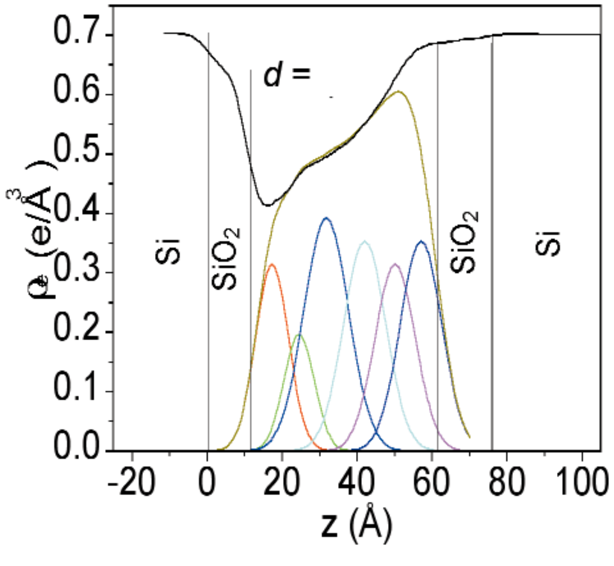

FIG. 2. Candidate electron density mode for polymer in a 49 Å gap.

tivity occurring. For the purposes of this report, we focus on the reflectivity curves obtained at gap spacings of 41 and 49 Å. These are shown in Fig. 1. No curves indicative of a well-defined spacing were obtained for the PB samples.

Discussion

Analysis of the reflectivity data is still in progress. However, some observations can already be made. First, none of the reflectivity curves is consistent with a uniform electron density profile in the film. Second, it is possible to model both data sets very well using model electron density profiles that are asymmetric and that envision electron densities of the PDMS layer that are substantially above the electron density known for bulk PDMS (0.31e/Å^3) for at least a portionof the layer. One electron density profile that fits the data for the 49 Å thick film very well is shown in Fig. 2. The shape of the electron density profile can be rationalized by assuming that it corresponds to six polymer layers, with a Gaussian distribution of electron density associated with each layer as suggested in Fig. 2. The breadths of the Gaussians next to the confining walls account not only for randomness in the position of the chains, but also for the very small roughness of the confining walls.

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