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The SNS Liquids Reflectometer

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The SNS Liquids Reflectometer [1], installed as one of the first instruments at the Spallation Neutron Source, has now been functional for more than a year. This instrument is designed to view liquid and solid surfaces in specular, off specular, and near-surface small angle scattering geometries. The guide system supplies 2 Å < λ < 16.5 Å neutrons at vertical incident angles ranging from $0° < \alpha_i < 5.5°$ for free liquid surfaces and up to 45° for solid surfaces. Three bandwidth choppers, synchronized with the spallation source and operating at 15–60 Hz, provide neutrons in bandwidths ranging from 3.5–14 Å at a fixed incident angle onto a sample. The sample stage enables all of the motions necessary for positioning liquid and solid surfaces, while the detector arm directs a position-sensitive detector to view the sample at specular or off specular angles up to 90° and can scan out of the specular plane by up to 30°.

We have been entertaining users since summer 2007, in advance of truly efficient instrument operation. We applaud our users for their patience and for their appetite for such amusements. With the help of the SNS instrument chopper, data acquisition, and data analysis support groups, we have developed procedures and software for aligning the instrument and collecting and reducing data. Recently, carrying out these tasks has advanced from being moderately painful to approaching tolerable, and we see "not terribly unpleasant" on the horizon. We have designed, fabricated, and continue to refine a growing suite of solid/air, solid/vapor, and solid/liquid sample holders (Figure 1). The small wet chemistry lab (Figure 2), located adjacent to the instrument control hutch, has proven useful, particularly the vacuum oven and Langmuir-Blodgett trough.

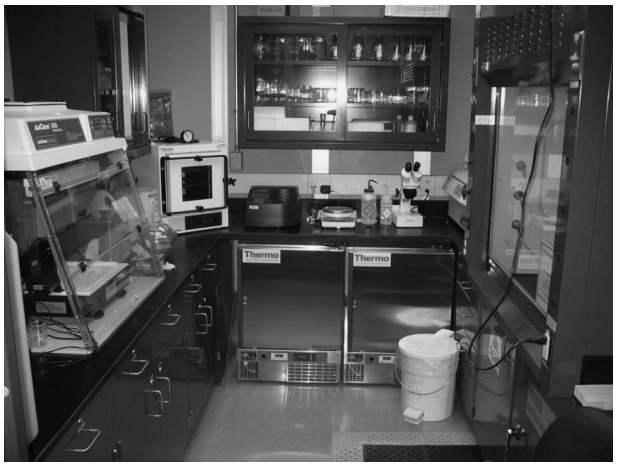

Figure 2. The SNS Liquids Reflectometer sample preparation laboratory. A fair bit of gear resides within our 10 m^2 (clockwise from left): Langmuir-Blodgett trough inside laminar flow hood, ultrasonic cleaner, spin coater, vacuum oven, freezer, refrigerator, UV-visible spectrometer, balance, microscope, glassware, centrifuge, fume hood, de-ionized water supply (off screen to right). (Photo courtesy of ORNL)

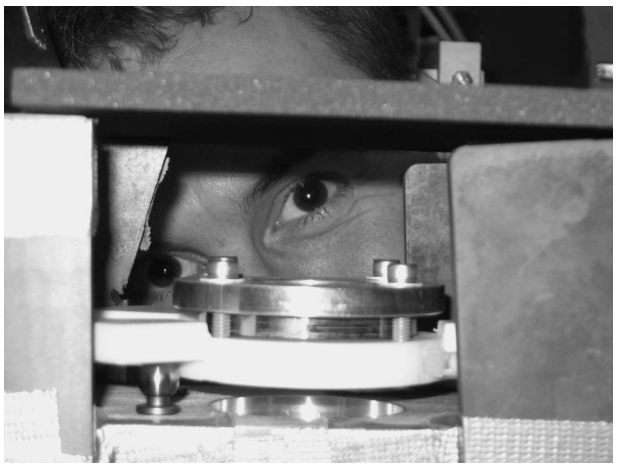

Figure 1. Mike Kilbey (Clemson U.) imitates a neutron detector and looks to a bright future beyond the solid/liquid sample cell mounted on the goniostat. (Photo courtesy of ORNL)

Progress in shielding and data reduction enabled us to reach specular reflectivities in the 10^{-7} range during the last run cycle. Figure 3 shows the specular reflectivity collected from a deuterated polymer film with the accelerator running

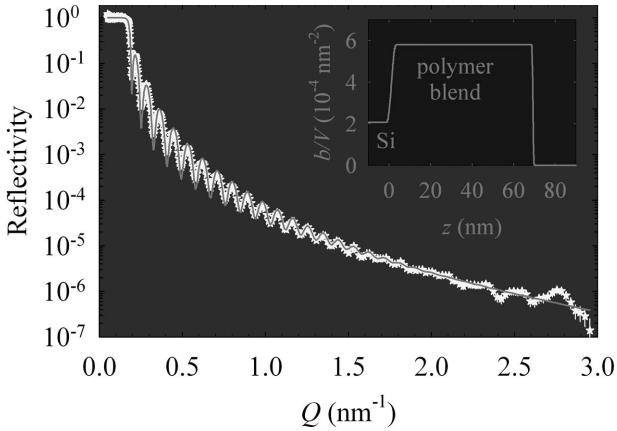

Figure 3. Specular reflectivity from a 67.5-nm-thick film consisting of a mixture of 80% deuterated polymethylmethacrylate (dPMMA) homopolymer and a polymer composed of polyethylene oxide (PEO) branches attached to a PMMA backbone (sample prepared by O. Swader and M. Dadmun at U. of Tennessee).

at 100 kW and 30 Hz, using a wavelength band 0.2 nm < λ < 0.9 nm and four incident angles (θ = 0.2°, 0.5°, 1.25°, and 3°) – recall that wavevector transfer $Q = 4\pi \sin\theta / \lambda$. The film, spin-coated onto a silicon substrate, contains a mixture of deuterated polymethylmethacrylate (dPMMA) homopolymer and a polymer composed of polyethylene oxide (PEO) branches attached to a PMMA backbone. The film, consisting of 80% dPMMA, is 67.5-nm thick and very smooth, featuring a Gaussian surface roughness of 0.6 nm. We collected the complete four-incident-angle data set in about 70 minutes.

Our first published experimental results [2] involve polyelectrolyte multilayers. Polyelectrolyte multilayers (PEMs) represent a new class of nanostructured materials obtained through alternating self-assembly of water-soluble polymers at solid-liquid interfaces. The use of weak polyelectrolytes as film constituents allows one to produce films that are responsive to variations of the external pH. The mechanism of response of weak polyelectrolyte multilayers

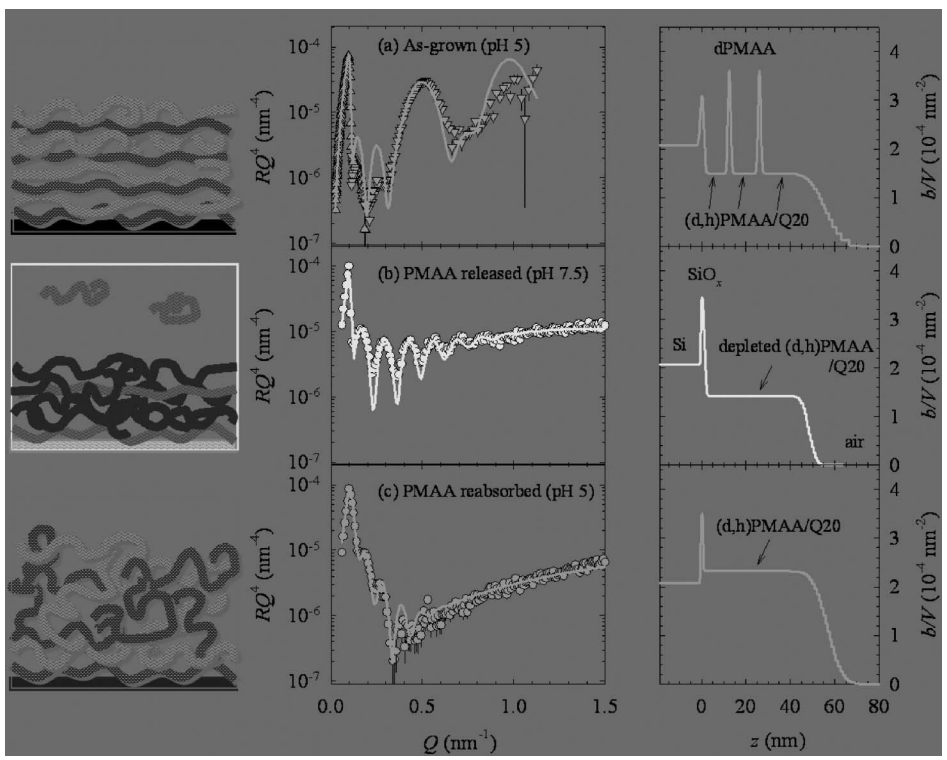

Figure 4. Neutron reflectivity data (left) and fitted scattering-length-density profiles (right) obtained experimentally for dry $[(Q20/PMAA)_4/(Q20/dPMAA)]_4$ films—every fifth PMAA layer is deuterated to enhance neutron contrast. (a) Deposited at pH 5, data collected using 0.2 nm < λ < 1.6 nm neutrons at two different incident angles (0.2° and 0.9°) using the Spallation Neutron Source Liquids Reflectometer. (b) After exposure to pH 7.5, collected at National Institute of Standards and Technology (NIST) NG-7 reflectometer at fixed wavelength λ = 0.475 nm. (c) After solution pH reduced back to that of deposition (pH 5), collected at NIST. All three samples were deposited on Si substrates with 1–2–nm-thick native oxide layers. The as-deposited film (a) exhibits intrinsic disorder, with only the first two of the four marker dPMAA layers forming discernable layers. Upon exposure to pH 7.5 (b), 38% of the PMAA dissolves into solution. The dissolved polymer is re-absorbed (c) after the solution pH is lowered back to 5.

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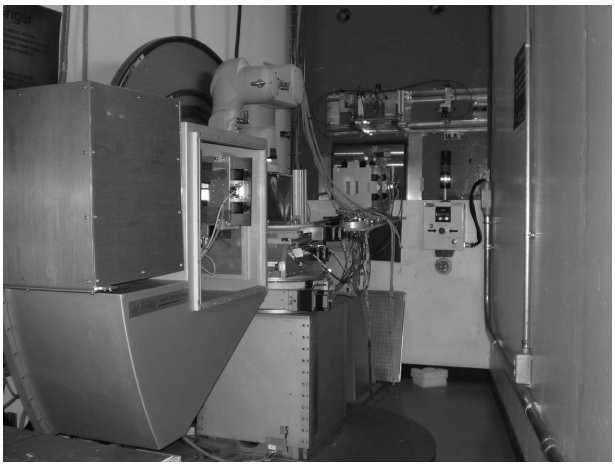

Figure 5. The SNS Liquids Reflectometer, mid-upgrade (from the left): the detector in its shielding box, background-reduction slits, sample goniostat on its elevator, the robotic sample changer, and the incident table and collimation (center right). The sample magazine will be mounted on the rail system above the guide exit on the wall on the upper right. (Photo courtesy of ORNL)

(wPEMs) to pH variation occurs via a pH-induced accumulation of excess charge within wPEMs. When the environmental pH changes in the region close to the apparent pKa of a weak polyacid or a polybase, a significant amount of charge of one sign is created within the wPEM. This charge can be then used, for example, to bind and release low molecular weight compounds such as dyes or drugs as well as to fabricate novel metal-containing inorganic nanocomposite materials. As a result of pH-induced electrostatic stress within the film, wPEMs swell and change their morphology. Rubner et al. [3] reported that weak polyelectrolyte multilayers exhibit interesting pH-switchable discontinuous swelling transitions. This pH-induced variation of charge within wPEM coatings also lies at the heart of the use of such coatings for control of electroosmotic flow in microchannels. Porous films have been produced from weak polyelectrolyte multilayers (wPEMs) as a result of ionic strength and pH variations and, more recently, environmentally-triggered morphological variation in wPEMs was used to produce films with controlled porosity for anti-reflection coatings. Figure 4 shows as-cast, released, and re-absorbed states of a PEM multilayer measured by neutron reflectivity at SNS and the National Institute of Standards and Technology.

We have a number of other interesting projects in the works, involving bio-inspired polymer films, surface segregation in branched polymer blends, and nanoscale structure of looped polymer brushes made from highly branched stars. In the next run cycle, which began in April 2008, we hosted our third round of users, who have proposed an exciting slate of experiments that will continue to challenge our capabilities.

We are commissioning the Langmuir trough, installing a robotic sample changer, and significantly upgrading the beamline shielding. The Langmuir trough is long overdue and will enable us to function truly as a liquids reflectometer. The robotic changer (Figure 5), when it becomes available in the summer of 2008, will run as many as 18 samples automatically and thus provide users with some badly needed sleep. With shielding improvements and our scheduled accelerator power ramp-up, we hope to add another decade of dynamic range in specular reflectivity. Future challenges include collecting, reducing, and modeling off specular and near-surface small angle scattering. The instrument is designed to access a vast parameter space; we are happy to report visiting the first smallish strip of it.

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