Synchrotron Studies of Oligomer and Polymer Assemblies on Elastomeric Substrates

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Tuning the surface characteristics of materials, including lubrication or wetting, has become of paramount interest in many everyday applications. For example, in some situations surfaces are required to be completely wettable, such as the surfaces of metals before paint deposition, in other applications one needs to prevent the surfaces from being wettable. Examples of the latter include non-stick layers, marine antifouling coatings, surfaces of car windshields or frying pans, etc.

Deposition of self-assembled monolayers (SAMs) composed of end-functionalized alkanes is a widely used method of tuning the surface wettability. For example, the surface of silica or gold can be decorated with SAMs made of silane-based or thiol-based molecules, respectively. While simple to perform, this methodology usually produces surfaces, which contain numerous structural defects. When exposed to polar liquids, such as water, these defect-containing SAMs usually surface reconstruct as the water molecules penetrate through the imperfections in the SAMs. These non-desirable surface reconstruction effects can likely be minimized (or even completely prevented from occurring) by increasing the packing density of the SAMs through increasing the density of the grafting points at the surface. However, tailoring the grafting density of the SAM chains is not an easy task because as mentioned earlier, SAMs are formed through self-assembly processes that are governed by the chemical and structural nature of the SAM molecules the means of their attachment to the substrate.

We have recently developed a method for controlling the grafting densities of molecules on surfaces. Specifically, we demonstrated that the combination of the self-assembly with mechanical manipulation of the grafted molecules on surfaces provides means of fabricating MAMs (”mechanically assembled monolayers”). In order to provide a proof of concept, we have created MAMs by assembling semifluorinated (SF) alkanes and showed that these produce superhydrophobic surfaces with superior long-lasting barrier properties. The method for fabricating superhydrophobic MAMs is schematically shown in the upper portion of Figure 1. First, a pristine poly(dimethyl siloxane) (PDMS) network film was prepared. After chemically removing any non-cross-linked oligomers, the film was cut into small strips (≈ 1 x 5 cm²) and mechanically uniaxially stretched by a certain length, Δx. Subsequent exposure to ultraviolet/ozone (UVO) treatment produced hydrophilic PDMS surfaces (PDMS-UVO) composed mainly of hydroxyl groups. The SF chlorosilane molecules, F(CF2)n(CH2)xSiCl3 (F8H2), were deposited from vapor onto this stretched substrate to form an organized SAM. Finally, the strain was released from the PDMS-UVO film, which returned to its original size, causing the grafted F8H2 molecules to form a densely packed MAM. To remove weakly physisorbed F8H2 molecules the samples were thoroughly washed in warm (≈ 60°C) deionized (DI) water for 1 minute and dried with nitrogen.

Figure 1: The upper panel show schematic illustrating the technological steps leading to the production of MAMs (“mechanically assembled monolayers”). The lower part denotes the dependence of DI water contact angle, θ, on F8H2-MAM samples on the degree of stretching of the PDMS substrate before the UVO treatment, Δx. The inset shows the corresponding contact angle hysteresis (defined as the difference between the advancing and receding DI water contact angles). The lines are meant to guide the eye. Also shown are photographs of a DI water droplet spreading on the F8H2-SAM and F8H2-MAM (Δx=70%) surfaces.
The bottom part of Figure 1 shows the dependence of the advancing contact angle of DI water, \( \theta_a \), of F8H2-MAM on the PDMS substrate extension, \( \Delta x \). The results in Figure 1 show that as \( \Delta x \) increases, \( \theta_a \) increases (hydrophobicity of the surfaces increases) and reaches a maximum at \( \Delta x \approx 70\% \) and then decreases slightly for \( \Delta x > 70\% \). The inset to Figure 1 shows the corresponding DI water contact hysteresis values (the difference between the advancing and receding DI water contact angles). The hysteresis decreases with increasing \( \Delta x \), reaches a minimum at around \( \Delta x \approx 60\% \), and then increases for \( \Delta x > 70\% \). The results in Figure 1 provide first round information about the packing of F8H2 in the F8H2-MAMs. As \( \Delta x \) increases from 0%, the number of the F8H2 groups per unit area increases, which in turn results in closer chain packing within the MAM. At \( \Delta x \approx 60 - 70\% \), the molecules are already densely packed. With \( \Delta x > 70\% \), the molecules in the MAM must begin to corrugate as a layer. The latter behavior gives rise to an enhanced molecular roughness and causes the contact angle hysteresis to increase.

Experiments aiming at investigating the stability of the MAMs – in particular the resistance of the F8H2-MAMs to surface reconstruction – revealed that these possess long-lasting superhydrophobic properties that do not deteriorate even after prolonged exposure to DI water. Specifically, while \( \theta_a \) on the F8H2-MAM fabricated on the unstretched substrate dropped almost immediately after a short DI water exposure (hours), indicating that the F8H2 chains surface reconstructed, the wettability of the F8H2-MAM samples immersed for 7 days in DI water and stored for 6 months in a Petri dish under ambient laboratory conditions decreased only by \( \approx 5\% \).

We used carbon K-edge near edge X-ray absorption fine structure (NEXAFS) spectroscopy to study the molecular orientation of the MAMs surfaces. NEXAFS involves the resonant X-ray excitation of a K or L shell electron to an unoccupied low-lying antibonding molecular orbital of \( \pi \) symmetry, \( \sigma^* \) (and \( \pi \) symmetry, \( \pi^* \)). The initial state K shell excitation gives element specificity, while the final-state unoccupied molecular orbitals provides bonding or chemical selectivity. Because of the fixed geometry and governing of the \( 1s \rightarrow \sigma^* \) (and \( 1s \rightarrow \pi^* \)) excitations by dipole selection rules, the resonance intensities vary as a function of the direction of the electric vector \( \mathbf{E} \) of the incident polarized X-ray relative to the symmetry of the molecule. The NEXAFS experiments were carried out on the U7A NIST/Dow Materials Soft X-ray Materials Characterization Facility at the National Synchrotron Light Source at Brookhaven National Laboratory (NSLS BNL). The set up at NSLS BNL is capable of measuring both the partial electron yield (PEY) NEXAFS and the fluorescence yield (FY) NEXAFS spectra. By simultaneously detecting both the PEY and FY NEXAFS signals, whose probing depths are \( \approx 2 \) and \( \approx 100 \) nm, respectively, the orientation of the molecules on the surface and in the interior of the sample can be resolved.

No measurable fluorine signal could be detected in the FY NEXAFS spectra of the SF-MAMs suggesting that the UVO treatment and subsequent MAM deposition did not modify the interior of the PDMS. On the other hand, the PEY NEXAFS data revealed a strong peak at 292.0 eV, corresponding to the \( 1s \rightarrow \sigma^* \) PEY NEXAFS spectra were taken in the direction parallel and perpendicular to the stretching direction; in all cases the PEY NEXAFS spectra were collected at the normal (\( \theta = 90^\circ \)) and grazing (\( \theta = 20^\circ \)) incidence geometries, where \( \theta \) is the angle between the sample normal and the polarization vector of the x-ray beam. A detailed analysis of the NEXAFS data performed using models presented elsewhere provided information about the average tilt angles of the fluorocarbon helix, \( \langle \phi_{\text{helix}} \rangle \). Figure 2 shows the values of the average tilt angles of the fluorocarbon helix, \( \langle \phi_{\text{helix}} \rangle \), that were determined from PEY NEXAFS spectra collected from F8H2-MAMs with \( \Delta x = 0\% \) (squares) and \( \Delta x = 70\% \).
(circles). The data shows that $<\tau_{F,\text{flex}}>$ measured along and perpendicular to the stretching direction on the F8H2-MAM sample prepared on unstretched PDMS-UVO substrate, was $\approx 5^\circ$ and $\approx 4^\circ$, respectively. Thus, the FyH2 molecules are oriented almost perpendicular to the PDMS-UVO substrate, which is in accord with the orientation of F8H2-SAM deposited on a SiO$_2$ substrate.\textsuperscript{5} The analysis of the PEY NEXAFS spectra from F8H2-MAM with $\Delta \chi = 70\%$ revealed that $<\tau_{F,\text{flex}}>$ measured along the stretching direction is $\approx 38^\circ$ and $<\tau_{F,\text{flex}}>$ collected perpendicular to the stretching direction was $\approx 21^\circ$. The NEXAFS experiments thus showed clearly that as $\Delta \chi$ increased, the F8H2 chains tilted away from the sample normal in the stretching direction. The fact that $<\tau_{F,\text{flex}}>$ increased from $\approx 4^\circ$ to $\approx 21^\circ$ as $\Delta \chi$ increased from 0% to 70% can be attributed to the slight compression of the sample perpendicular to the uniaxial stretch.

NEXAFS has proven invaluable for providing molecular-level information on chain mobility in the SF-MAMs exposed to DI water. As mentioned earlier, the F8H2-MAMs prepared on unstretched PDMS-UVO substrates ($\Delta \chi = 0\%$) stand almost perpendicular to the sample surface. However, the data in Figure 2 shows that when exposed to DI water, the chain orientation starts to disappear very rapidly and after about 1 day of DI water exposure, the F8H2-MAMs with $\Delta \chi = 0\%$ disorient completely. The behavior of the F8H2-MAMs prepared on PDMS-UVO substrates with $\Delta \chi = 70\%$ is very different. Specifically, the NEXAFS data reveal that $<\tau_{F,\text{flex}}>$ on samples exposed to DI water for up to 7 days is virtually indistinguishable from that measured on the same specimen before the DI water exposure. These results thus provide further evidence that the F8H2 molecules in MAMs with $\Delta \chi = 70\%$ are closely packed and mechanically interlocked; this interlocking hinders the chain’s tendency to move and reconstruct on the MAM surface. We attribute this unusual behavior to the extremely high packing densities of the MAMs – values that can only be achieved using this novel assembling method.

Very recently, we have extended the MAM technology to produce: i) polymer brushes with variable grafting densities using MAPA (=“mechanically assisted polymer assembly”) by performing the polymerization directly on the pre-stretched PDMS substrate, and ii) molecular gradients with tailorable surface properties. In both these projects, NEXAFS has proven invaluable in characterizing the chemistry and in the case of the molecular gradients also the molecular orientation of the anchored oligomers.

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References and notes

7. Due to the nature of the polarization dependencies of the NEXAFS signal intensities one cannot distinguish between a completely disoriented sample and a sample, whose chains are all tilted by $54.7^\circ$, the so called, “magic angle” [6].
9. We note that the tilt angle determined from NEXAFS represents an average value. There is no straightforward way to discriminate between the case of all chains homogeneously tilted by the same angle and the case of a disordered system with a broad distribution of tilt angles. Hence, we express our results on the orientation of the SF moieties in terms of the average tilt angle of the fluorocarbon part of the single SF groups, $<\tau_{F,\text{flex}}>$.

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