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Real-Time Grazing Incidence X-ray Diffraction Studies of Polymerizing *n*-Octadecyltrimethoxysilane Langmuir Monolayers at the Air/Water Interface

Stephen R. Carino, Holger Tostmann, Royale S. Underhill,
Jennifer Logan, Gayanga Weerasekera,[†] Jeffrey Culp,
Mark Davidson,[‡] and Randolph S. Duran*

Butler Polymer Laboratory, Department of Chemistry and
Department of Materials Science and Engineering
University of Florida, Gainesville, Florida 32611

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Introduction. Alkylsilanes are widely used as components in hybrid materials[1] and to modify surface properties. For example, Finnie et al.[2] imprinted hydrophobic alkylsilane patterns on silicon oxide surfaces. Similarly, Zheng et al.[3] have utilized alkoxysilanes as a passivating layer for subsequent patterned assembling of gold nanoparticles. Numerous other groups[4] have studied the formation of alkylsilane thin films on silicon and metal oxide surfaces. Fundamental questions regarding the growth mechanism of these materials persist, in particular, the effect of the cross-linking reaction between individual silane molecules on the quality and molecular architecture of the resulting film. Dutta[5] and several others[6] have observed that silane on SiO_2 undergoes island growth as manifested by the invariant film thickness over the duration of deposition. However, several other spectroscopic studies[7] indicated homogeneous growth modes, where the film thickness was observed to increase with deposition time. Carraro et al.[8] have shown that these two conflicting mechanisms are actually temperature dependent and may be a consequence of a phase transition taking place in the transient Langmuir monolayer film at the substrate−solution interface. Another possibility, as originally proposed by Sagiv[9] and corroborated by Silberzan,[10] is the hydrolysis and possible cross-linking of the silane while still physisorbed as a Langmuir monolayer onto the hydration layer of the oxide surface. This process is assumed to precede the actual chemical anchoring of the silane functional group to the substrate.[11] Here, we examine the dynamics of formation of polyalkylsiloxane from *n*-octadecyltrimethoxysilane [OTMS, $CH_3(CH_2)_{17}Si(OCH_3)_3$] monolayers at the air/water interface. Primarily, we intend to show the feasibility of real-time grazing incidence X-ray diffraction (GIXD) studies with sufficient time-resolution to follow structural changes induced by a moderately fast polymerization reaction. Such investigations should be of relevance to understanding the underlying chemical changes involved. To our knowledge this is the first time structural evolution and polymerization of a self-assembled monolayer at the air/water interface have been investigated in situ. Advances in synchrotron science and beamline instrumentation at third generation synchrotron sources should make this kind of investigation feasible on a wide variety of surface reactions.

Due to the formation of siloxane bonds from the reactive methoxy substituents, adsorbed OTMS molecules can be laterally constrained from moving at the surface. This assertion was supported by atomic force microscopy studies of self-assembled monolayers which showed a larger degree of disorder at higher temperatures, where the chemical reactivity is enhanced.[12] In such cases, the resulting molecular ordering is more glasslike than crystalline as cross-linking interferes with the in-plane reorganization of the monolayer following deposition.

As a Langmuir monolayer, polymerization of the OTMS monolayer can be readily controlled by pH and surface concentration.[13] Since the water interface is amorphous and lacks surface groups capable of forming directional chemical bonds, no substrate-induced in-plane positional ordering should occur. In this case, positional order is totally dependent on the intrinsic molecular packing induced by noncovalent interaction between the aliphatic chains and the polymerization of the headgroups of OTMS.

Experimental Section. Grazing incidence X-ray diffraction experiments were performed at the surface of a Langmuir trough aligned to a high-brilliance X-ray beam of the MRCAT undulator at the Advanced Photon Source (APS) synchrotron at Argonne National Laboratories (Argonne, IL). The incident X-ray beam was tuned to 11.0 keV ($\lambda = 0.113$ nm). To achieve surface sensitivity, the angle of incidence was kept below the critical angle of total external reflection (2.3 mrad for the air/water interface; see the Supporting Information for more details).

Results and Discussion. Previous work has shown that the reaction of the silane groups of the OTMS to form a 2D-polysiloxane network is essentially complete in 1 h at pH 1.5.[14] As the pH increases toward neutrality, the time for the OTMS to react and form a polysiloxane monolayer increases. At pH 4, the time it takes for the mean molecular area to relax to its final value of 21 ± 2 Å^2 is approximately 6 h, as can be seen in the area relaxation curve in Figure 1. This is within experimental error to the value of 20 Å^2 reported by Fontaine et al.[14] and may be representative of the ultimate packing of the alkyl chains, and/or the reacted siloxyl headgroups.

Initially, an in-plane diffraction scan of the reacted OTMS monolayer was recorded over a wide range of K_{xy} to identify all in-plane peaks. A first-order diffraction peak centered at around $K_{xy} = 15.2$ nm^{-1} was found, corresponding to an in-plane spacing of 4.76 Å in real space and an area per alkyl chain of 19.6 Å^2. These values are characteristic for hexagonal packing of alkyl chains[15] and consistent with previous experiments as discussed in the Supporting Information.

Having established the position of the in-plane diffraction peak, the range of the diffraction scan was limited to ±2° of the first-order diffraction peak. Together with the short counting time due to the high brilliance of the incident beam, a time resolution of

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* To whom correspondence should be addressed at the Department of Chemistry.

[†] Current Address: Center for Disease Control & Prevention, 4770 Buford Highway, NE, Building 17, Mailstop F-17, Atlanta, GA 30341-3724.

[‡] Department of Materials Science and Engineering.

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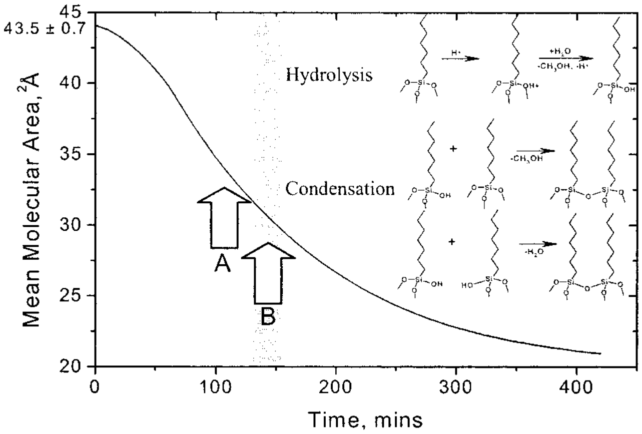

Figure 1. Area relaxation of OTMS at pH 4.0 and $\pi = 8$ mN m^{-1} and $T = 25$ °C. Arrow A points to the onset of the diffraction peak; arrow B indicates the window of gelation time from 2D viscometry. The inset shows the hydrolysis and condensation reactions for OTMS.

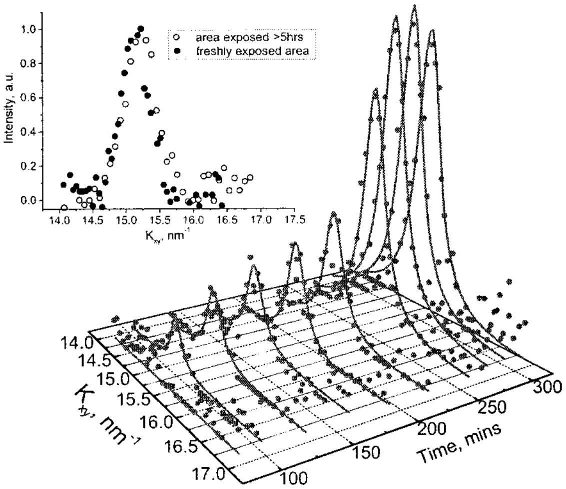

Figure 2. Real-time X-ray diffraction peaks of the reacting OTMS system. Signals obtained prior to $t = 88$ min are not shown; for clarity, only approximately every other scan is shown. Inset: Diffraction peaks of the same film area after cross-linking and 5 h of X-ray irradiation compared to an unirradiated surface ~15 min later, revealed by lateral displacement of the trough surface.

approximately 17 min was obtained between consecutive diffraction scans. This allowed the evolution of the hydrolysis/condensation reaction to be followed in situ in a kinetics experiment. The change in surface structure with time after spreading a monolayer onto a clean water subphase is shown in Figure 2.

Initially, there is no evidence of order, as represented by the absence of X-ray scattering peaks in the first 100 mins. The onset of ordering is manifested by the appearance of a fairly symmetrical peak observed at $K_{xy} = 15.24$ nm^{-1}, becoming resolvable at a MMA of 32.6 ± 2.3 Å^2 as shown in the isobaric area relaxation curve in Figure 1. This peak grows in intensity, leveling off at reaction times consistent with the end of the reaction as measured by isobaric area change. To our knowledge, this is the first time a direct link between macroscopic surface pressure data and microscopic diffraction surface structure data has been established as a function of time for a floating Langmuir monolayer.

The chemically interesting feature of the data is that the position of the peak does not change substantially with time, indicating that the spacing between the alkyl chains in the crystalline regions is constant. It is reasonable to assume that in the beginning of the reaction small domains of ordered alkyl chains form, giving rise to a weak scattering peak. Interestingly, the onset of a detectable diffraction peak occurs at surface areas significantly larger than the MMA attributed to the alkyl chain as reported by Fontaine et al.[14] In fact, at such surface areas (corresponding to about 50% conversion), one would anticipate that the alkyl chains would be liquidlike and not ordered. Arrow A in Figure 1 also illustrates that diffraction also occurs prior to the gel point, whose measurement is described in the Supporting Information. The appearance of the single peak so early in the reaction, corresponding to such a large MMA, supports the notion of a formation of ordered domains. Such results clearly demonstrate the value of obtaining direct structural data by GIXD to elucidate the mechanism of film formation on a molecular level. These ordered domains most probably consist of fully hydrolyzed and partially condensed silane molecules dispersed in primarily disordered and partially reacted OTMS, consistent with the results obtained by Rondelez et al.[11b] The ordering clearly occurs while the monolayer is macroscopically fluid. Finally, upon conclusion of the reaction, the domains coalesce producing a strong coherent surface scattering signal.

Another remarkable feature of this measurement is the exceptional chemical stability of the OTMS system to X-ray irradiation. As an illustration, the inset in Figure 2 shows a diffraction scan recorded at pH 4 and $\Pi = 8$ mN/m after more than 5 h of reaction and irradiation; the second curve was obtained 15 min later from the same monolayer, but with the beam laterally displaced by about 1.5 cm, exposing a "fresh" area that had not previously been irradiated. These results indicate that the immense (~10^{13} photons/s incident to the hutch) flux of 11 keV photons on the film did not break significant numbers of Si−O or Si−C bonds, or that any cleaved bonds reform almost quantitatively.

Summary. We have shown that high-brilliance synchrotron radiation can be used to take comparatively fast in-plane diffraction scans to follow a surface reaction in situ. The alkyl chains in OTMS spread on a clean water subphase self-assemble in small domains showing a characteristic in-plane spacing. Such a mechanism appears possible at fluid interfaces and thus in the absence of any anchoring to a solid substrate. The short-range positional order between the alkyl chains does not significantly change during the course of the reaction. The increase in intensity of the diffraction peaks with time can be interpreted either as an increase in the number of such ordered domains or the transformation of the smaller domains into larger organized assemblies as the polymerization progresses.

Overall, these kinetics experiments have shown the potential of fast GIXD scans to study the surface dynamics of a variety of reactive amphiphile systems. It should be noted that the experimental setup described for these initial measurements is not yet optimized for highest brilliance and overall experimental speed. Further optical and detection enhancements such as the use of an area detector being currently planned should easily allow the scan time required for similar quality diffraction data to be reduced significantly.

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Supporting Information Available: Extended description of the experimental setup (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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