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

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Introduction

Fundamental questions regarding the growth mechanism in alkylalkoxysilanes persist, in particular, the effect of the cross-linking reaction between individual silane molecules on the quality and molecular architecture of the resulting film. Here, we examine the dynamics of formation of polyalkylsiloxane from n-octa-decyl-tri-methoxy-silane [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 and structural 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 by in situ GIXD.

Methods and Materials

Grazing-incidence x-ray diffraction experiments were performed on OTMS spread at the surface of a Langmuir trough. 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). It had been shown previously that the reaction of the silane groups of the OTMS forming a 2D-polysiloxane network is essentially complete in 1 h at pH 1.5.[1] At pH 4, the time needed 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 Fig. 1.

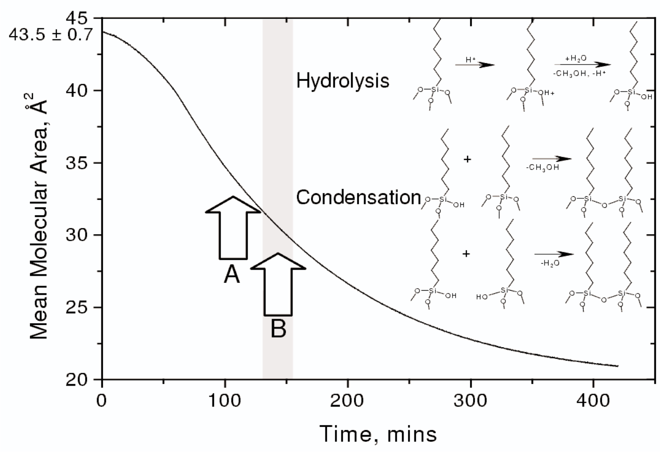

FIG. 1. Area relaxation curve of OTMS on water at pH 4. Arrow A points to the onset of ordering as detected by GIXS; arrow B indicates the gel point as determined by 2D canal viscometry. The inset shows the hydrolysis and condensation reaction for OTMS.

Results

Initially, in-plane diffraction scans of the reacted OTMS monolayer were recorded over a wide range of K_{xy} in order 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 a mean molecular area (MMA) per alkyl chain of 19.6 $Å^2$. These values are characteristic for hexagonal packing of alkyl chains[2] and consistent with previous experiments.

During the first 100 min, there is no evidence of order, as represented by the absence of x-ray scattering peaks. The onset of diffraction became resolvable at an MMA of 32.6 ± 2.3 $Å^2$ as shown in the isobaric area relaxation curve in Fig. 1. As shown in Fig. 2, the 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.

Discussion

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 from the isobaric area measurement, i.e., ordering is observed with

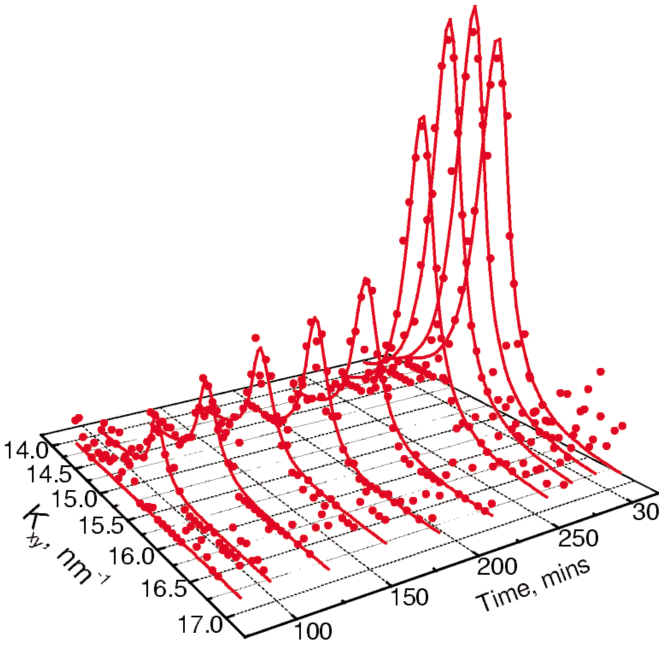

FIG. 2. Real-time GIXS of reacting OTMS on water.

GIXS before it is discernible in macroscopic experiments. Arrow A in Fig. 1 also illustrates that diffraction also occurs prior to the gel point, determined from canal viscometry. 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.[1] 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. A detailed discussion of this experiment is given elsewhere.[3]

Acknowledgment

We acknowledge support from the Petroleum Research Fund, KSV Inc., the NSF ERC on Particle Science and Technology, and the Advanced Photon Source. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

[1] P. Fontaine, M. Goldmann, and F. Rondelez, Langmuir **15**(4), 1348-1352 (1999).

[2] P. Tippmann-Krayer, R. M. Kenn, and H. Mohwald, Thin Solid Films **210**(1-2), 577-582 (1992).

[3] S.R. Carino et al., JACS **123**, 767-769 (2001).