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In Situ Observation of Self-Assembled Monolayer Growth

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Introduction. Monolayers of amphiphilic organic molecules that form spontaneously on a solid substrate by adsorption from solution are known as self-assembled monolayers (SAMs) and have been intensely studied for the last decade as a powerful method of surface modification and functionalization. Although great progress has been made in the understanding of molecular arrangement[1−3] and even of phase transitions[4−6] in SAMs, very little is known about the initial growth process. Although early work on SAM formation supported a homogeneous growth mode,[7] recent *ex situ* infrared spectroscopy[6] and atomic force microscope (AFM)[8−10] studies on submonolayer SAMs indicate the presence of submonolayer islands on films removed from solution before completion. There has been understandable skepticism, however, about the connection between the structure of these "quenched" monolayers and that of the actual monolayer forming in solution, since the processes of removal, rinsing, and drying can dramatically affect the film morphology. We present the first *in situ* images of SAM growth (obtained by AFM) proving that the molecules aggregate into dense two-dimensional islands as the monolayer forms in solution. This discovery furthers the analogy between SAMs and films grown by molecular beam epitaxy and will eventually allow the application of well-developed theories of two-dimensional cluster growth to SAMs.[11,12] In addition, detailed studies of quenched films indicate that the surface coverage, for short times, is proportional to concentration $\times$ time$^{1/2}$.

In order to quantitatively separate features corresponding to a partial monolayer from those of the substrate, we have found it convenient to work with a featureless, atomically flat substrate—mica. SAMs of cross-linking alkylsilanes[8,13] as well as dialkyl ammonium salts[14] have previously been prepared on mica. We are using a single-chained, non-cross-linking alkyl phosphonic acid which is expected to bind strongly with the aluminum atoms in mica or alumina.

Experimental Details. We previously reported contact angle and AFM data demonstrating the formation of octadecylphosphonic acid (OPA) monolayers on mica substrates from tetrahydrofuran (THF) solution.[15] For *ex situ* observations, partial monolayers were removed from solution, rinsed for 30 s in THF, and blown dry with clean, dry nitrogen. Surface tension measurements were performed with a filter paper Wilhelmy plate and a NIMA (Coventry, England) surface tensiometer. AFM imaging of quenched films was performed under ambient conditions with a Nanoscope III AFM (Digital Instruments, Santa Barbara, CA) in contact or tapping mode. No damage due to imaging was observed with the low forces used (≤ 1 nN). In order to avoid surface contamination during *in situ* imaging, the deposition solution came into contact with only glass, PTFE Teflon, and a fluoropolymer Kalrez o-ring (Dupont). The details of image analysis have been previously reported.[15]

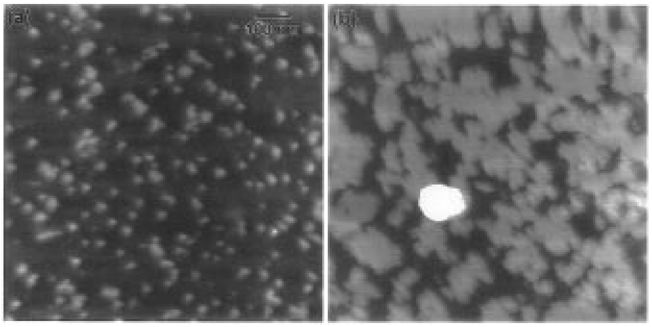

Figure 1. (a) AFM image obtained *in situ* during monolayer growth on mica in a 0.05 mM OPA solution after about 20 mins of exposure. The higher areas (lighter shades of gray) correspond to submonolayer islands of OPA whose tops are about 2 nm higher than the surrounding substrate. (b) AFM image of a different sample at a later stage of growth. The original islands have grown and coalesced. The large white particle near the center is typical of objects that were frequently seen in *in situ* images but were removed by rinsing since they were not observed on quenched films. They were often useful as location markers during growth.

Results. AFM images obtained of the SAM during actual growth conditions (Figures 1 and 2) prove that the monolayer forms by nucleation, growth, and coalescence of submonolayer islands. These are the first direct observations of SAM growth. Figure 1a shows a monolayer in contact with 0.05 mM OPA solution after about 20 min immersion. The islands of OPA are clearly visible indicating that the molecules aggregate into islands while they are still in solution, not as a consequence of rinsing or drying. Such islands do not form in control experiments in pure THF. The small (10−20 nm diameter) islands grow gradually while maintaining their general shape. The islands are not observed to move relative to each other. The growth is consistent with accretion at the island edges, implying the existence of unseen monomers (or other small species), on the "bare" parts of the substrate, which migrate to the islands and attach. Figure 1b shows an *in situ* image of a different sample that was captured at a later stage of growth. Many of the original islands have coalesced to form larger islands. The island size distribution of *in situ* images in their early stages (see supporting information) displays a well-defined peak at a length scale that evolves with time.

Occasionally, bubbles were observed to pass through the liquid cell during imaging, and the surface coverage increased discontinuously. Figure 2a shows a monolayer where a number of bubbles have passed through the liquid cell, and the coverage is, therefore, much greater than expected for simple nucleation and growth. This led us to suspect that monolayer material was deposited during the passage of the solution/air interface over the substrate. After the bubbles passed, growth in solution continued. Parts b and c of Figure 2 show the same area of the

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(1) Poirier, G. E.; Tarlov, M. J.; Rushmeier, H. E. *Langmuir* **1994**, *10*, 3383−3386.

(2) Camillone, N.; Eisenberger, P.; Leung, T. Y. B.; Schwartz, P.; et al. *J. Chem. Phys.* **1994**, *101*, 11031−11036.

(3) Poirier, G. E.; Tarlov, M. J. *J. Phys. Chem.* **1995**, *99*, 10966−10970.

(4) Fenter, P.; P. Eisenberger; K. S. Liang *Phys. Rev. Lett.* **1993**, *70*, 2447−2450.

(5) Allara, D. L.; Parikh, A. N.; Judge, E. *Chem. Phys.* **1994**, *100*, 1761−1764.

(6) Parikh, A. N.; Allara, D. L.; Azouz, I. B.; Rondelez, F. *J. Phys. Chem.* **1994**, *98*, 7577−7590.

(7) Wasserman, S. R.; Whitesides, G. M.; Tidswell, I. M.; Ocko, B. M.; et al. *J. Am. Chem. Soc.* **1989**, *111*, 5852−5861.

(8) Schwartz, D. K.; Steinberg, S.; Israelachvili, J.; Zasadzinski, J. A. N. *Phys. Rev. Lett.* **1992**, *69*, 3354−3357.

(9) Xiao, X.-D.; Liu, G.-Y.; Charych, D. H.; Salmeron, M. *Langmuir* **1995**, *11*, 1600−1604.

(10) Bierbaum, K.; Grunze, M.; Baski, A. A.; Chi, L. F.; et al. *Langmuir* **1995**, *11*, 2143.

(11) Amar, J. G.; Family, F.; Lam, P.-M. *Phys. Rev. B* **1994-II**, *50*, 8781−8797.

(12) Zinke-Allmang, M.; Feldman, L. C.; Grabow, M. H. *Surf. Sci. Rep.* **1992**, *16*, 377−463.

(13) Kessel, C. R.; Granick, S. *Langmuir* **1991**, *7*, 532.

(14) Liu, Y.; Wu, T.; Evans, D. F. *Langmuir* **1994**, *10*, 2241.

(15) Woodward, J. T.; Ulman, A.; Schwartz, D. K. *Langmuir* **1996**, *12*, 3626−3629.

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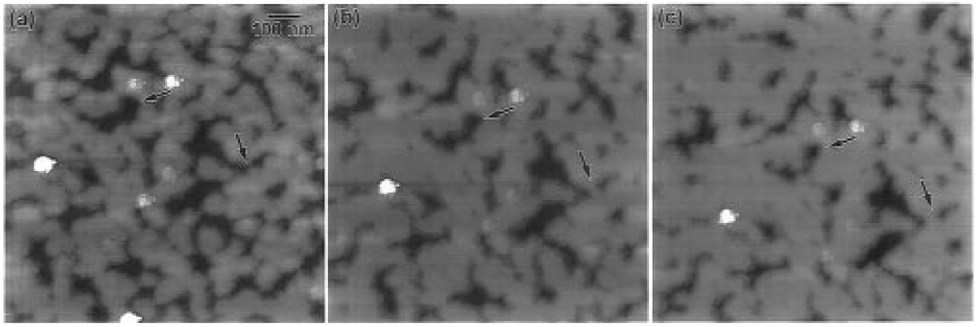

Figure 2. AFM images obtained *in situ* of a monolayer during growth in 0.10 mM OPA solution. (a) After only 5 min in solution, the coverage is much higher than expected due to material deposition from the solution/air interface. (b, c) The same area on the film (with some scanner drift) after an additional 3 and 7 min of exposure to solution, respectively. The holes that appeared in a are observed to fill-in gradually by film growth from the edges. The arrows guide the eye to the same positions on the film in each image. The darker borders surrounding the island edges may represent a real feature in the height profile—a sort of "ledge" at the island edge. However, as in any AFM image, the apparent profile of an edge is actually a convolution of the true profile and the (unknown) tip shape.

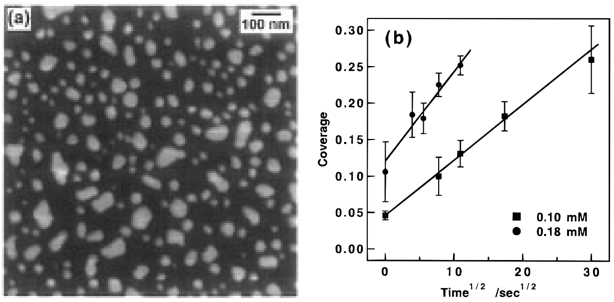

Figure 3. AFM image of a quenched monolayer that was exposed to 0.10 mM OPA in THF for 120 s. (b) The surface coverage of quenched films as a function of exposure time$^{1/2}$ for samples immersed in 0.18 mM solution (circles) and 0.10 mM solution (squares).

surface as in Figure 2a at subsequent times during which the growth was observed continuously. This sequence of time-resolved images directly demonstrates the growth process toward the end of monolayer growth.

The existence of an adsorbed (Gibbs) monolayer at the solution surface was confirmed by noting that the surface tension decreased approximately linearly (correct in the dilute limit)[16] with concentration by about 0.3 mN/m over the range 0−0.5 mM. To demonstrate that this Gibbs layer was transferred to the substrate (in a quasi-Langmuir−Blodgett process) during insertion and/or removal, we measured the monolayer coverage of substrates inserted into solution, removed immediately, and quenched. The observed coverage was much greater than expected for the total immersion time of less than 1 s. The surface coverage increased systematically with the number of dips, and the fraction of a monolayer deposited per dip was proportional to the solution concentration, about 0.05 per dip in 0.10 mM and 0.1 per dip in 0.18 mM solution.

The monolayer coverage as a function of immersion time and concentration was studied systematically on quenched films. Typical images (Figure 3a)[15] show that compact-shaped monolayer islands (1.8 ± 0.2 nm high) of OPA form on the surface. The compact island shape implies that the OPA molecules have sufficient mobility to rearrange in order to minimize the island perimeter, in contrast with octadecyltrichlorosilane monolayers which were observed to form fractal islands.[8] We attempted to determine the power of the first-order term in the kinetics of early growth by fitting the island coverage of quenched films with the phenomenological expression $\theta = \alpha t^{\nu} + \theta_0(1 - \alpha t^{\nu})$. The second term in the expression was added to account for the quasi-LB deposition. The exponent extracted from the fit was 0.47 ± 0.04 for 0.10 mM solution and 0.42 ± 0.10 for 0.18 mM solution. These exponents are consistent with $t^{1/2}$ behavior (see Figure 3b). The parameter θ_0 is related to the quasi-LB process and is approximately proportional to the concentration. The lines through the data in Figure 3b represent the best fits and have slopes $7.95(22) \times 10^{-3}$ s$^{-1/2}$ for 0.10 mM solution and $1.32(19) \times 10^{-2}$ s$^{-1/2}$ for 0.18 mM solution. The ratio of these coefficients is 1.7 ± 0.3, consistent with the concentration ratio of 1.8. The fitting function used was certainly not unique, and further detailed studies will be necessary to determine the growth kinetics.

Discussion. If every molecule that diffuses to the surface is adsorbed, the number of adsorbed molecules is given by $N \approx \rho_0(Dt/\pi)^{1/2}$,[17] where ρ_0 is the number density of the solute in bulk solution and D is the diffusion coefficient. Our data would be consistent with $D \approx 10^{-8}$ cm^2/s, significantly smaller than the expected $10^{-6}-10^{-5}$ cm^2/s for OPA in THF. We conclude that the coverage is not diffusion-limited.[18−20] In the weakly-adsorbing limit, on the other hand, the coverage is $\theta \approx kCt$, where k is an undetermined "sticking coefficient." This cannot explain the observed $t^{1/2}$ coverage kinetics. We suspect that the observed growth kinetics are due to the two-dimensional nucleation and growth process which generally follows a power law; however, the exponent depends on specific deposition conditions. We hope that future experiments over a wider range of solution concentration and temperature and with other solvents (changing viscosity) will shed light on this issue and allow us to determine the nature and rate of surface transport.

Conclusions. *In situ* AFM images of SAMs demonstrate that formation proceeds by nucleation, growth, and coalescence of submonolayer islands. The decrease in the surface tension of deposition solution with concentration in combination with observed coverage of substrates dipped quickly in solution indicates that monolayer material is transferred in a quasi-LB process during the removal of the substrate from solution. The time dependence of the coverage of quenched films show that the kinetics (for short times) of the monolayer island growth is proportional to concentration × time$^{1/2}$.

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Supporting Information Available: Island size distribution for the AFM image in Figure 1a (1 page). See any current masthead page for ordering and Internet access instructions.

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[16] Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; John Wiley & Sons: New York, 1990; p 88.

[17] Frisch, H. L.; Mysels, K. J. *J. Phys. Chem.* **1983**, *87*, 3988−3990.

[18] Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; et al. *J. Am. Chem. Soc.* **1989**, *111*, 321−335.

[19] Guyot-Sionnest, P.; Superfine, R.; Hunt, J. H.; Shen, Y. R. *Chem. Phys. Lett.* **1988**, *144*, 1−5.

[20] Cheng, S. S.; Scherson, D. A.; Sukenik, C. N. *J. Am. Chem. Soc.* **1992**, *114*, 5436−5437.