

## Chemical Cross-Linking, Surface Compressional Modulus, and Viscosity of *n*-Octadecyltrimethoxy Silane Monolayers

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Monomolecular-thin films prepared at an aqueous interface continue to provide an attractive means to form well-defined molecular assemblies for surface modification and ultrathin-film applications. For these purposes, high-molecular weight, polymeric Langmuir–Blodgett films<sup>1</sup> have the potential of being more robust materials compared to their low-molecular weight analogues. Of course, the same entanglement of polymer backbones which gives rise to the transient network formation and attractive mechanical properties in bulk polymeric materials is less effective in a quasi-two-dimensional LB layer. Several groups have considered cross-linking monolayers as a means of enhancing properties of these materials.<sup>2a–f</sup> We recently demonstrated that an extended network formed from polymerization of bolaform alkyylaniline monolayers results in a sufficiently stable and flexible material in which individual self-supporting monolayers could be drawn from the water surface as thin films and fibers of macroscopic size.<sup>3</sup> Can the chemical transformations in these types of reactions be more quantitatively correlated to the resulting physical properties?

In this work, we present some insight on the network formation of amphiphilic *n*-octadecyltrimethoxysilane (OTMS, CH<sub>3</sub>(CH<sub>2</sub>)<sub>17</sub>-Si(OCH<sub>3</sub>)<sub>3</sub>) at air/water interfaces by measuring changes in compressive mechanical properties and surface rheology of the reacting system in real time. Such measurements should be broadly applicable to reactive amphiphiles.

In bulk solutions, alkoxy silanes are well-known to undergo acid- or base-catalyzed hydrolysis and to form siliceous materials.<sup>4</sup> Polysilsesquioxanes, RSiO<sub>3/2</sub>, offer intriguing models to examine this; as in this work, the R group can be strongly hydrophobic. Such materials form oligomeric cage, polymeric ladder, and three-dimensional network structures depending upon reaction conditions and the nature of the R group.<sup>5</sup>

Langmuir monolayers of OTMS at the air/water interface have been reported<sup>6a,b</sup> to form a condensation product. While the molecular weight and architecture of the product have not been reported, some have suggested that OTMS and similar materials should form linear<sup>6a,7</sup> rather than network polymers due to the 2D restrictions in the environment around the silane headgroup.

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(1) Miyashita, T. *Prog. Polym. Sci.* **1993**, *18*(2), 263.

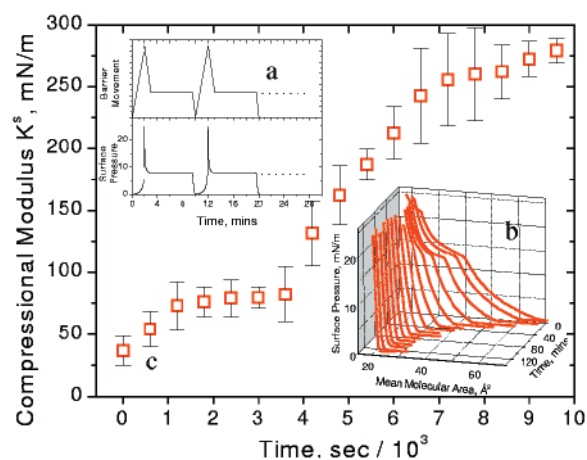
(2) (a) Miyano, K.; Veyssié, M. *Phys. Rev. Lett.* **1984**, *52*(15), 1318. (b) Heger, R.; Goedel, W. A. *Supramol. Sci.* **1997**, *4*, 301. (c) Kölchens, S.; Lamparski, H.; O'Brien, D. F. *Macromolecules* **1993**, *26*, 398. (d) Sisson, T. M.; Lamparski, H. G.; Kölchens, S.; Elayadi, A.; O'Brien, D. F. *Macromolecules* **1996**, *29*, 8321. (e) Zhang, L.; Hendl, R. A.; Cozzi, P. G.; Regen, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 1(7), 1621. (f) Schoberl, U.; Magnera, T. F.; Harrison, R. M.; Fleischer, F.; Pflug, J. L.; Schwab, P. F. H.; Meng, X. S.; Lipiak, D.; Noll, B. C.; Allured, V. S.; Rudalevige, T.; Lee, S.; Michl, J. *J. Am. Chem. Soc.* **1997**, *119*, 9(17), 3907.

(3) Kloppner, L. J.; Duran, R. S. *J. Am. Chem. Soc.* **1999**, *121*, 1(35), 8108.

(4) Parikh, A. N.; Schivley, M. A.; Koo, E.; Seshadri, K.; Aurentz, D.; Mueller, K.; Allara, D. L. *J. Am. Chem. Soc.* **1997**, *119*, 9(13), 3135.

(5) Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T. *Chem. Rev.* **1995**, *95*, 1409.

(6) (a) Vidon, S.; Leblanc, R. M. *J. Phys. Chem. B* **1998**, *102*, 1279. (b) Brittt, D. W.; Hlady, V. *J. Phys. Chem. B* **1999**, *103*, 2749.



**Figure 1.** (a) Example of two cycles of the oscillatory compressive stimuli applied to the reacting monolayer; the bottom curve represents the measured surface pressure response. (b) Pressure–area isotherms from which the plot in (c) was calculated. Obtained between 0 and 25 mN/m at 25 °C. (c) Surface compressional modulus of OTMS during reaction on a pH 3.5 subphase and at  $\Pi = 8$  mN/m.

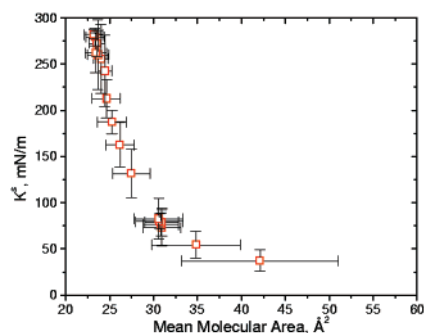
**Experimental.** All monolayer and polymerization studies were conducted on KSV LB5000 equipment at 25 °C using trough and barriers made of PTFE. The surface pressure ( $\Pi$ ) measurements were obtained using the Wilhelmy plate technique. High-purity water (resistivity  $\geq 18$  M $\Omega$ -cm) from a Milli-Q (Millipore) filter system was used, and the pH was adjusted with HCl. *n*-Octadecyltrimethoxy silane (>95%) obtained from Gelest Inc. was used as received. Isotherm studies (not shown) reproduced previously published work.<sup>6</sup>

**Surface Compressional Modulus and Reaction.** The surface compressional modulus of an insoluble monolayer is a measure of the film stiffness and generally should increase as molecular weight increases. The modulus was obtained by applying brief mechanical stimuli in situ during the course of the hydrolysis and condensation reactions. This was accomplished by introducing periodic compression–expansion cycles as shown schematically in Figure 1a. Each compression–expansion cycle gave rise to two isotherm curves; Figure 1b is a plot of the resulting surface pressure/area/reaction time curves describing the compression cycles. Each curve is an instantaneous record of mechanical properties at a defined point in the chemical reaction. The surface compressional modulus is defined as  $K^s \equiv -d\Pi/d \ln A$  where  $\Pi$  is the surface pressure and  $A$  is the molecular area in the film.<sup>8</sup> In the work,  $K^s$  was calculated directly from the slope of the condensed region of the corresponding isotherm, at  $\Pi \approx 20$  mN/m. Between compression–expansion cycles (~80% of total reaction time) the monolayer was maintained at isobaric conditions of  $\Pi = 8$  mN/m. Control experiments at isobaric conditions determined that the mechanical stimulus did not measurably change the reaction kinetics.

As shown in Figure 1c,  $K^s$  for the reacting monolayer increases about 10-fold with polymerization time in a nonlinear manner. At the start of the reaction,  $K^s$  has a value of 30 mN/m, increasing to plateau at about 70 mN/m from 20 to 60 min. The modulus then increases sharply and eventually becomes more constant at a value of about 280 mN/m. The sharp jump in the modulus near the end of the reaction suggests that a threshold degree of reaction is required to attain a critical concentration where entanglements

(7) Sjöblom, J.; Stakkestad, G.; Ebeltoft, H.; Friberg, S. E.; Claesson, P.; *Langmuir* **1995**, *11*, 2652.

(8) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid-Gas Interfaces*; Interscience Publishers: New York, 1966; pp 24–25.



**Figure 2.**  $K^s$ , the surface compressional modulus vs mean molecular area of the reacting system calculated from data in Figure 1. Surface area is expressed as area per Si atom in the monolayer.

or network links appear. This is in agreement with the percolation nature of network formation and the scaling argument proposed by de Gennes<sup>9</sup> and Stauffer.<sup>10</sup> Surface rheology results of other 2D network materials by Veyssié and co-workers,<sup>2a,11</sup> and more recently by Rehage<sup>12a,b</sup> support these findings.

Additional molecular insight is obtained by plotting  $K^s$  versus the mean molecular area as shown in Figure 2. The initial modulus increase observed in Figure 1c can now be attributed to an approximately 50% decrease in surface area, consistent with the methoxy-alcohol transformation expected from the hydrolysis reaction. The magnitude of the modulus may also be meaningful; for example, compressed monomolecular films of other common simple surfactants such as stearic acid<sup>13</sup> ( $C_{17}H_{35}COOH$ ) and 1-decanol<sup>14</sup> ( $C_{10}H_{21}OH$ ) have surface compressional moduli of  $1000 \pm 200$  and  $2500 \pm 500$  mN/m, respectively. Several explanations are possible for the low magnitude of the modulus of the current system. The modulus value is consistent with a soft, flexible monolayer material<sup>15</sup> which may arise because cross-links between  $sp^3$  Si atoms are restricted to the interfacial plane compared to a more rigid architecture in 3D cross-linked silica materials. Alternatively, during the time frame of the experiment, the system may still be in an inhomogeneous state and domains of close-packed and polymerized areas coexist with a liquid expanded (LE) phase. The overall compressional modulus measured, may be limited by the compressibility of LE phase at domain boundaries rather than that within individual close-packed domains. As the reaction progresses, the LE phase continuously transforms into close-packed domains, and these domains may coagulate, hence, the increase in modulus. The ultimate magnitude of the modulus may reflect how defect-free the resulting film is and may thus be kinetics-dependent.

**Surface Viscosity and Reaction.** Real-time surface viscometry was performed using a flow-trough canal.<sup>16a,b</sup> For a monolayer with significant surface viscosity such as the cross-linking system being studied, the surface viscosity  $\eta_s$  can be calculated from  $\eta_s(t) = \Delta \Pi w^3 / 12LQ(t)$  where  $w$  and  $L$  are the width and length of the canal,<sup>17</sup> respectively. The area flow rate  $Q(t)$  is calculated from  $Q(t) = \Delta A_f / \Delta t$  where  $\Delta t$  is the time interval of measurement

(9) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: New York, 1979.

(10) Stauffer, D. *Phys. Rep.* **1979**, *54*, 2.

(11) Rehage, H.; Schnabel, E.; Veyssié, M. *Makromol. Chem.* **1988**, *189*, 2395.

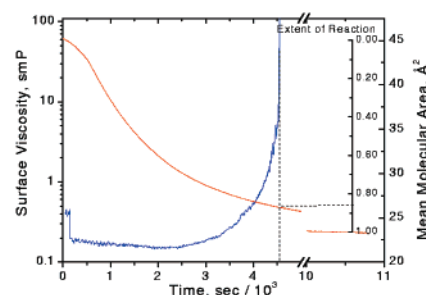
(12) (a) Burger, A.; Leonhard, H.; Rehage, H.; Wagner, R.; Schwoerer, M.; *Macromol. Chem. Phys.* **1995**, *196*, 1. (b) Rehage, H. Veyssié, M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 439.

(13) This work. Data obtained over a water subphase with pH  $\approx$  5.8.

(14) Zakri, C.; Renault, A.; Rieu, J.-P.; Vallade, M.; Berge, B.; Legrand, J.-F.; Vignault, G.; Grübel, G. *Phys. Rev. B* **1997**, *55*(21), 14163.

(15) Crisp, D. J. *J. Colloid Sci.* **1946**, *1*, 161.

(16) (a) Harkins, W. D.; Kirkwood, J. G.; *J. Chem. Phys.* **1938**, *6*, 53. (b) Sacchetti, M.; Yu, H.; Zografis, G. *Rev. Sci. Instrum.* **1993**, *64*, 1941.



**Figure 3.** Surface viscosity and area relaxation of OTMS in a pH 3.5 subphase during reaction (units of surface viscosity are milliPoise, smP =  $g\ s^{-1}$ ). The ordinate scales at the right side correspond to the isobaric area relaxation curve.

and  $\Delta A_f$  is the change in area, measured by barrier displacement, in the high-pressure side of the canal. Since the measurement is on a reacting system, the area change due to the reaction should be deconvoluted from the area change due to the actual flow of material across the canal, that is,  $A_f = (MMA)_t[A_o/(MMA)_o - A_t/(MMA)_t]$  where  $A_o/(MMA)_o$  is the original number of molecules and  $A_t/(MMA)_t$  is the remaining number of molecules at time  $t$  in the high-pressure side.<sup>18</sup> The difference is then multiplied by the mean molecular area at that point of the reaction.

The surface viscosity profile of the reacting system is shown above in Figure 3, overlaid against an isobaric area relaxation curve to show the progress of the reaction as it relates to the viscosity profile.

The initial surface viscosity is consistent with that of small amphiphilic molecules such as stearic acid which was measured at 0.34 smP. After the initial compression, a slight initial viscosity drop was reproducibly noted starting at  $t \approx 200$  s and may be evidence of the hydrolysis that occurs resulting in replacing methoxy with hydroxy groups.

As the reaction proceeds, viscosity slowly increases and then rapidly diverges. Extrapolation of this vertical segment to the horizontal time axis yields the gelation point, approximately 75 min after the reaction was started. This point corresponds to the same time at which the compressional modulus is increasing. The divergence of the surface viscosity is a manifestation of a cross-linking reaction and not just the formation of a linear polymer.<sup>19</sup>

Additional chemical insight is provided assuming that the area change per chemical reaction is constant; the resulting inset scale then gives an approximation of the extent of reaction as monomer converts to product, even though the exact chemical nature of the product is not completely known. The extrapolation of the gel point line corresponds to about 85% of the extent of reaction. The fact that this is significantly above a random 2D percolation threshold and that an initial slow increase precedes the gelation point may indicate that a substantial fraction of the network is made of linear, ladder-like segments with occasional cross-linking; nonetheless its monomolecular thickness and flexible nature add to possible architectures of polysilsesquioxanes.

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(17) Canal edges were angled at  $72^\circ$  to compensate for PTFE/water contact angle. Width and length were 1.35 and 93.78 mm, respectively.

(18) Mean molecular area at time  $t$ ,  $(MMA)_t$ , was obtained independently by isobaric relaxation of OTMS at identical conditions and no flow.

(19) Rolandi, R.; Dante, S.; Gussoni, A.; Leporatti, S.; Maga, L.; Tundo, P. *Langmuir* **1995**, *11*, 3119.