In Situ Observation of Monolayer Self-Assembly by FTIR/ATR

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The very uniform, robust, siloxane-anchored, ultra-thin films created by the spontaneous adsorption of long-chain alkyltrichlorosilanes provide well-defined systems for the study of monolayer structure[1] and present new possibilities for controlled surface modification.[2] Kinetic studies offer considerable insight into the growth mechanism of two-dimensional self-assembled molecular monolayers. We report herein the use of Fourier transform infrared spectroscopy (FTIR) in the attenuated total reflectance (ATR) mode for the in situ observation of the self-assembly of a monolayer of octadecyltrichlorosilane (OTS) on the surface of germanium.

The kinetics of alkyl thiol[3] and fatty acid[4] self-assembly has been examined by removing the deposition substrate from the medium containing the surfactant prior to optical characterization. While such ex situ strategies offer a measure of versatility, a nonperturbing, in situ observation allows for the direct, uninterrupted monitoring of the self-assembly process. Such an approach was used by Shen and co-workers,[5] who monitored OTS deposition on fused silica using sum frequency generation.

The deposition of OTS from bicyclohexane (BCH) solution onto a Ge surface is uncomplicated by any additional functionality in the hydrocarbon chain and is very well suited to in situ FTIR observation. The straight alkyl chains of the OTS and the rings of the BCH have nearly nonoverlapping CH_2 bending modes. The stability of OTS layers on Ge is comparable to that on Si, but Ge offers a wide optical window in the energy range of interest; the IR penetration depth in the ATR mode is sufficiently small to permit the detection of changes in the surface and near-surface concentrations of OTS and BCH in the presence of both compounds in the solution phase.

The in situ FTIR/ATR experiments were performed using a cell which provides for a closed volume of solution to be maintained over the ATR element. All spectra are displayed as the difference between the spectrum obtained at a given time and that of the dilute (8.4 mM) OTS/BCH solution acquired at the beginning of the experiment (which nearly corresponds to that of the neat solvent). Thus, spectral features associated with any species whose surface and near-surface concentrations increase or decrease with time will show growth in the positive or negative sense, respectively.

Figure 1 shows a series of sequential FTIR/ATR spectra in the region between 1480 and 1410 cm^{-1}, where the positive-pointing feature at 1467 cm^{-1} corresponds to the methylene bending mode of OTS and the negative-pointing counterpart at 1448 cm^{-1} is due to the cyclohexyl units of BCH. This series of spectra has two important features: (i) The monotonic increase in intensity of the OTS methylene bending mode as the deposition proceeds is paralleled by a monotonic decrease in the corresponding band of BCH. This is consistent with the replacement of BCH by OTS molecules at the interface. (ii) There is an isosbestic point at 1459 cm^{-1}, indicating that this replacement is quantitative. The minimal overlap of these two features makes it possible to obtain

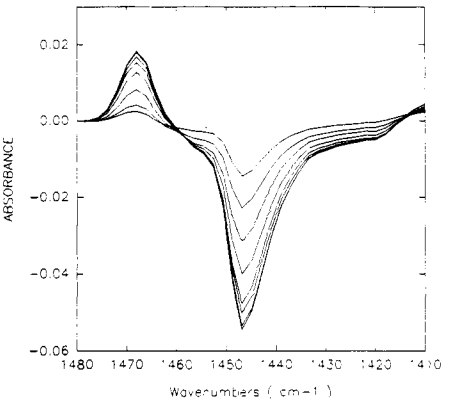

Figure 1. Time-difference FTIR/ATR spectra for the deposition of OTS from a BCH solution onto Ge for the following times (in minutes): 19, 43, 83, 163, 243, 323, 435, 495.

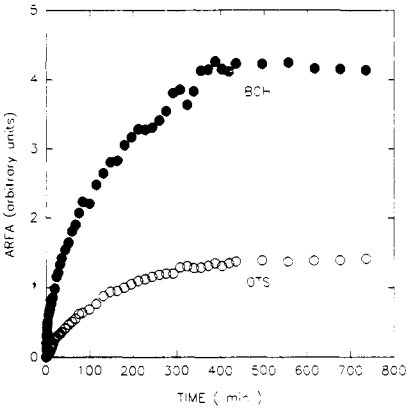

Figure 2. Plot of the area under the methylene bending bands of OTS and BCH as a function of time.

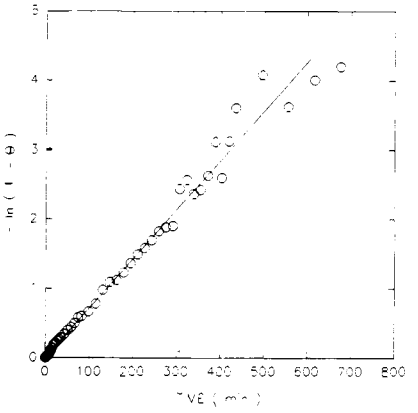

Figure 3. Plot of $-\ln(1-\theta)$ versus time (in minutes). The straight line represents the best fit to the experimental points (slope = 6.95×10^{-3}; correlation factor $r^2 = 0.99$).

reliable values of areas and/or peak heights for the majority of the deposition process.

A plot of the peak areas obtained from spectra recorded over more than 10 h is shown in Figure 2. Our analysis of this data relies on two assertions. The intrinsic rate of self-assembly is slow enough that the overall rate under our experimental conditions is not complicated by diffusion effects. Secondly, the number of molecules involved in the surface layer represents a small enough fraction of the total number of molecules in the reservoir that the change in the bulk concentration of the surfactant [S] is negligible even after monolayer formation is completed.

On the basis of the above assertions, these data are analyzed using a simple Langmuirian model, assuming that adsorption is irreversible (i.e., desorption is negligible), for which $d\theta/dt = k(1-\theta)$ where k is a first-order rate constant in s^{-1} and θ is the fraction

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of the surface covered by the adsorbate. Thus, plots of $-\ln(1-\theta)$ versus time should be linear, with a slope proportional to the intrinsic rate of self-assembly. Figure 3 shows such a plot, for which θ is calculated on the basis of data such as those depicted in Figure 2. As indicated, the data could be fit with a straight line (correlation factor $r^2 = 0.99$) with a near-zero intercept.[6] The value of the intrinsic rate constant for self-assembly ($k/[S]$) based on spectral areas for six independent runs at 296 K was $(1.15 \pm 0.26) \times 10^{-2}$ s^{-1} M^{-1}, which compared well with that calculated on the basis of the height of the peaks, $(0.95 \pm 0.18) \times 10^{-2}$ s^{-1} M^{-1}. That this value is smaller than the reported[5] for OTS deposition on fused silica presumably arises from reactivity differences between the oxide/hydroxide layers of silicon and germanium. However, in as much as OTS deposition provides a close-packed film with no pendant functionality influencing the deposition process, it constitutes a benchmark for understanding the self-assembly of other siloxane-anchored monolayer films.

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(6) During its initial stages, the rate of the deposition is the largest and the signals being observed are smallest. These factors introduce a large relative uncertainty in this part of the data compared to that obtained later in the deposition process. Despite the overall goodness of fit, close inspection of the early data reveals a possible deviation from linearity, a behavior that could be ascribed to the presence of a second class of surface sites displaying much faster kinetics. More detailed studies currently underway in this laboratory are expected to shed light on this phenomenon.

Solvent Effects on the Energetics of Prolyl Peptide Bond Isomerization

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The interconversion of cis (E) and trans (Z) isomers of peptide bonds that include the nitrogen of proline residues can give rise to a slow kinetic phase during protein folding.[1,2] This interconversion is catalyzed by the peptidyl-prolyl cis-trans isomerases (PPIases).[3,4] Two of these enzymes, cyclophilin and FK-506 binding protein (FKBP), have been studied extensively: (1) isotope effects[5] and analyses of mutant enzymes[6] suggest that the prolyl peptide bond does not suffer nucleophilic attack during catalysis, (2) calorimetry shows that binding to FKBP occurs with a large decrease in heat capacity,[7] and (3) structural studies of cyclophilin[8] and FKBP[9] reveal active sites composed of hydrophobic side chains.[10] Consequently, desolvation has been proposed as a significant contributor to catalysis by the PPIases.[11] This proposal is consistent with NMR line shape analyses of simple amides, which suggest that the rate of amide bond isomerization does indeed depend on solvent.[12] To assess the contribution of de-

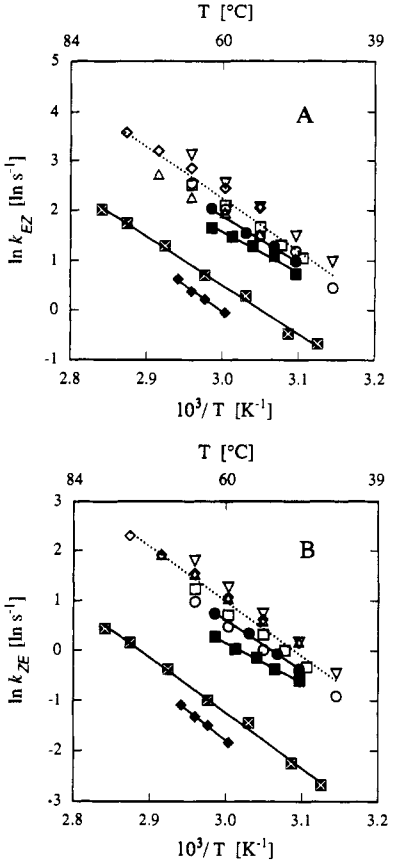

Figure 1. Arrhenius plots for the cis to trans (A) and trans to cis (B) isomerizations of **1** in different solvents. The solvents (dielectric constant at 25 °C) were as follows: ◇, dioxane (2.21); ○, benzene (2.27); ▽, toluene (2.38); ●, isopropyl alcohol (19.92); ■, ethanol (24.55); ◆, trifluoroethanol (26.14); □, acetonitrile (35.94); △, *N*,*N*-dimethylformamide (36.71); ⊠, water (78.30). Linear regression analysis is shown for each protic solvent (—) and all aprotic solvents (---).

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