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Self-assembled monolayers for liquid crystal alignment: simple preparation on glass using alkyltrialkoxysilanes

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A simple procedure for the preparation of octadecylsiloxane self-assembled monolayers (SAMs) on float glass substrates is described. The method utilizes commercial octadecyltriethoxysilane, OTE: n-$C_{18}H_{37}Si(OCH_2CH_3)_3$, as the SAM precursor, with deposition accomplished in toluene solution using *n*-butylamine as catalyst. This synthetic approach obviates the use of the problematic trichlorosilanes typically required for the preparation of high quality SAMs, and is characterized by a wide 'process window,' utilizing off-the-shelf reagents without special handling.

1. Introduction

In the initial phase of a project exploring self-assembled monolayers (SAMs) for liquid crystal (LC) alignment [1], a method for the preparation of high quality alkane SAMs on float glass microscope slides was sought. Requirements for these monolayers included high thermal and mechanical stability, ease of preparation, and a simple approach for spatial patterning of the SAMs on a hydrophilic surface. In addition, it was desirable that the basic method for monolayer formation be extendable to the synthesis of functionalized surfaces where the SAM precursors would require purification and could be expensive.

'Silanization' with trialkoxysilanes has been used as a process for modification of glass surfaces for many years [2]. In the context of nematic and smectic LC alignment, such silanization of indium tin oxide (ITO) coated glass substrates is a classic method for creating homeotropic LC cells [3]. Unfortunately, it is not possible to infer the structure (topography, monolayer vs. multilayer, uniformity) of these surfaces since typically no surface characterization aside from the LC alignment itself is reported in the early papers. It is clear that high quality surfaces are not required for the achievement of homeotropic alignment, since relatively thick layers of lecithin spun onto ITO/glass substrates from ethanol solution are also often used to obtain homeotropic LC cells [3].

More recently, true self-assembled monolayers have been shown to provide an excellent, very flexible approach for the control of surface structure and properties [4–8]. The most well studied SAMs are heteroepitaxial thiolates on crystalline gold or other metal films [6, 7, 9]. These monolayers have very homogeneous and well understood structures, and since the metal layers are typically very thin, this system can

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provide transparent substrates with well controlled surface properties. Indeed, thiolate SAMs on gold are proving very useful in novel applications of LCs specifically involving unique LC alignment properties achievable on the SAMs [10, 11]. For our purposes, however, this class of monolayers is simply too fragile, both thermally and mechanically [6*b*, 12, 13].

The Sagiv-type siloxane SAMs [4], which can be prepared on glass substrates, seem to provide an excellent compromise between structural uniformity and thermal and mechanical stability. While their structures are less homogeneous than those of the heteroepitaxial thiolates on gold, being formed on amorphous hydroxylated substrates, siloxane SAMs are of remarkably high quality. This is due in part to the apparently facile formation of layered organic/siloxane two-dimensional sheets. For example, it has been shown that such sheets form in solution, eventually giving three-dimensional layered crystalline polymeric solids [14].

The most well studied synthesis of alkylsiloxane SAMs employs a solution of alkyltrichlorosilane in a hydrocarbon solvent. The chain length of the alkyl group is important, with 10–20 carbons being optimum. Hydroxylated substrates such as silicon with a layer of native oxide on the surface, or glass, are then coated by simple immersion in this 'dipping solution' for a specified period of time and at a specified temperature. The coated substrates are then typically rinsed to remove weakly bound polymer (often mechanical cleaning is also applied) and allowed to 'cure' at room temperature for 24–48 hours.

The mechanism of SAM formation is thought to involve self-assembly of monomer or small oligomer units on the surface in a non-covalent manner to give well ordered monolayer domains or islands on the surface surrounded by bare substrate or disordered precursor films on the surface [15–17]. This mechanism is similar to that involved in the formation of Langmuir–Blodget films of long chain amphiphiles at the air–water interface [18]. Chemical reactions then result in covalent attachment and crosslinking of the alkylsiloxane molecules. Eventually the regions between domains fill with ordered monomers, which become incorporated into the polymer sheet. The curing process after deposition is thought to allow completion of the final stages of the polymerization process.

Completed SAMs prepared from trichlorosilanes contain no chlorine [19] and probably few SiOH units. The signatures of a 'high quality alkyl SAM' include a film thickness of close to the fully extended length of the monomer units, a low concentration of *gauche* bends in the tails, and a small average tilt of the tails from the surface normal. Lack of pinholes is cited as an important feature of the highest quality SAMs, though from the point of view of LC alignment this is probably not critical. The best SAMs are prepared under class 100 clean room conditions, but for our purposes, simple laboratory ambient conditions must be adequate.

The method for SAM synthesis involving alkyltrichlorosilanes as the key starting materials suffers from several drawbacks. Specifically, the quality of the target monolayers is highly dependent upon subtle, hard to control variables, most importantly the purity of the starting trichlorosilanes and the water content of the dipping solution. The latter is especially problematical, since it is critical that the water content be above a certain value, but still kept very small (a water concentration in the dipping solution of $0.15\,\mathrm{mg\,ml^{-1}}$ has been suggested as optimum) [6*b*, 17, 20–22]. Avoidance of these problems represents one of the reasons the thiolate/gold system has found such broad acceptance.

Also, the trichlorosilane SAM precursors are very unstable with respect to reaction with nucleophiles such as water, making them difficult to store, and requiring their purification by distillation; silica gel chromatography cannot be applied to the purification of trichlorosilanes. For alkylsiloxane SAMs such as octadecylsiloxane on various substrates, the prototype and most well studied example, the required octadecyltrichlorosilane (OTS) starting material is inexpensive and relatively easy to purify by distillation. But, if more complex monolayers are desired, this method for SAM synthesis can become very expensive and wasteful, since only a tiny fraction of the organic starting material actually ends up in the 'product' monolayers.

These problems were recently addressed by Sukenik *et al.* [23], who described an approach to functionalized SAM formation whereby functionalized trimethoxysilane SAM precursors are converted in a high yield penultimate step into trichlorosilanes using trichloroacetyl chloride. This is advantageous since the trimethoxysilanes are much more stable than trichlorosilanes towards hydrolysis and also towards an interesting variety of organic transformations involving nucleophiles, including for example an Arbuzov reaction converting the primary alkyl bromide moiety of $\mathrm{Br(CH_2)_{15}Si(OCH_3)_3}$ to a dimethylphosphonate grouping by heating with trimethylphosphite, $\mathrm{P(OCH_3)_3}$.

In general, the trimethoxysilanes could be purified by chromatography on silica gel with good recovery if $\mathrm{Si(OCH_3)_4}$ was added to the chromatography solvent system. Finally, after SAM deposition, unreacted trichlorosilane could be recovered by re-conversion to the trimethoxysilane with methanol, followed by chromatographic purification as described above.

An alternative approach for avoiding the problems associated with trichlorosilane precursors would be to utilize a trialkoxysilane directly as the SAM precursor. Wöll *et al.* have reported details of a direct comparison between the structure of SAMs obtained from OTS and SAMs obtained directly from *n*-octadecyltrimethoxysilane (OTMS) on oxidized Si(1 0 0) surfaces using near edge X-ray absorption fine structure and X-ray photoelectron spectroscopies [24]. Their synthesis, which utilized ethanol as the solvent for the dipping solution with no other additives, was similar for both the trichloro- and the trimethoxy-silane derivatives. In both cases they state that these substrates 'tend to form self-assembled monolayers which are oriented almost perpendicular to the surface.' The OTS-derived SAMs are reported to have an average tail tilt of $0^\circ \pm 5^\circ$ from the surface normal, while the OTMS-derived SAMs have an average tail tilt of $20^\circ \pm 5^\circ$. While these results are extremely interesting, the fact that the trichlorosilane should react with ethanol to produce mixed chloroethoxysilanes with concomitant formation of HCl *in situ* complicates interpretation of the results. Our own experiments with trialkoxysilanes-derived SAMs deposited from alcohol solvents were unsuccessful, as described below.

Herein we present an effective and very simple method for the formation of SAMs directly from trialkoxysilanes utilizing octadecyltriethoxysilane as exemplar. The deposition of high quality layers on hydroxylated silica surfaces is achieved in toluene by catalysis of the SAM formation with *n*-butylamine. This procedure has the significant advantage that all the necessary reagents can be used as obtained commercially, and the depositions are accomplished under ambient conditions. In this way it is possible for groups without specialized organic synthesis experience or equipment to obtain octadecylsiloxane SAMs on convenient substrates in a very simple, inexpensive manner.

2. Experimental

2.1. *General and Characterization*

OTE was purchased from Aldrich, Hül America or United Chemical Technologies, Inc. Toluene and *n*-butylamine were reagent grade from Aldrich Chemical Co. All starting materials and reagents were used without further purification. AFM images were taken on a Nanoscope II (figures 1 and 2) or Nanoscope III (figure 3). Transmission FTIR spectra were obtained on a Thermo-Nicolet Nexus 670 spectrometer. The sum-frequency spectra were recorded with equipment based on a design that was originally demonstrated at Exxon [25]. The source is a 6 ns, 10 Hz pulsed YAG, frequency doubled and pumping a tunable dye laser that is converted to the infrared by stimulated Raman scattering in molecular hydrogen. The visible beam comes from a small fraction of the frequency-doubled YAG at 532 nm. The sum-frequency radiation is collected through a spatial and spectral filter, detected with a photomultiplier, and signal averaged. Data are recorded at each IR wavelength by tuning the dye laser [26].

Water contact angles on the SAMs were measured by two methods. Method one involved advancing a water droplet from a micropipet on a horizontal substrate at the focal plane of a film strip projector. The projected image was photographed and the contact angles were measured by a best-fit curve analysis. Method two involved using a syringe to advance a small water droplet on a horizontal SAM-coated surface, and taking a series of about 100 digital photomicrographs of the advancing droplet using a video camera positioned such that the images were taken parallel to the surface. An image analysis program was then used to measure the contact angles from these images. Contact angles were measured on several samples and at several locations on each slide.

Float glass microscope slides manufactured by Erie Scientific Corp. were purchased by special order from Fischer Scientific. If the order does not specify float glass (which has a green tint when viewed from the side), then 'white' glass slides may be shipped. In our hands, monolayers made on white glass slides were typically less solvophobic. Dipping of the slides was accomplished using an uncovered Coplin Staining Jar (specified as 60 ml, Wheaton Science Products). Slides were typically cleaned with a fresh piranha solution composed of 30% aqueous H_2O_2 and concentrated H_2SO_4 (1:1 v/v). The sulphuric acid was added to the hydrogen peroxide solution, and the slides were then immediately immersed into the warmed cleaning solution. No external heating of the solution was used. After 15–20 min, the slides were removed from the cleaning solution, rinsed with distilled water and dried in a stream of nitrogen until they appeared dry (60 s) just prior to the SAM deposition. Silicon(1 0 0) wafers were cut into strips and cleaned as above just prior SAM deposition.

2.2. *SAM deposition procedure*

To a '60' ml Coplin staining jar containing 35 ml of toluene were added 1.5 g of OTE and 0.5 ml of *n*-$BuNH_2$, both via syringe. The jar was then nearly filled with toluene for a total volume of ~70 ml. The total capacity of the jars is about 75 ml. Between one and five freshly cleaned float glass slides were then immersed in the dipping solution. The jars are made such that the slides do not touch each other or the walls of the jar (except at their edges) during deposition. After 90 min, the substrates were removed from the dipping solution with forceps, and rinsed with clean toluene. The samples were then wiped with a Kim Wipe wet with toluene, rinsed again with fresh toluene, and dried with a nitrogen stream. The slides were then allowed to cure for 24 h at 100°C in a vacuum oven ($\sim$25 in. Hg) before use. An oil-free vacuum pump was used with the oven, and care was taken not to contaminate the surface of the slides during the cure.

As mentioned above, the process window for this procedure seems quite wide. Good surfaces, by the transmission FTIR (on silicon substrates) and contact angle criteria, were also obtained without physical rubbing of the slides after deposition, and without high temperature curing. Qualitatively, based upon hundreds of preparations, we feel that the physical rubbing and cure procedures produce slightly better surfaces by our criteria. Many experiments involving optimization of the temperature of the dipping solution during deposition showed that good SAMs could also be obtained if the solution was held at 40–45°C. However, monolayers prepared from heated dipping solutions were not found to be consistently better than those obtained by dipping at room temperature. In our hands, the best monolayers were obtained when the dipping solutions were 'fresh' (less than several hours old). SAMs prepared by subsequent depositions from a batch of used dipping solution were inferior to those produced in the first deposition, as evidenced by contact angle measurements.

3. Results and Discussion

Initial experiments aimed at producing SAMs on float glass microscope slides from trialkoxysilanes involved simple substitution of *n*-octadecyltriethoxysilane (OTE) for OTS used in reported literature procedures [3, 27]. Dipping slides into alcohol or hydrocarbon solvents containing 0.5–2%. OTE with or without acetic acid catalyst gave 'monolayers' of very poor quality as evidenced by their lack of solvophobicity, and water contact angles of less than 90°. Further characterization of these surfaces by atomic force microscopy (AFM) shows them to be quite rough in the z direction (normal to the surface) when a $1 \times 1\ \mu m^2$ area was imaged, as shown in figure 1A. The size of the structures on the surface appear consistent with the 'multilayers' often reported in failed monolayer preparations. When the smoothest part of the substrate imaged in figure 1A (close to the right corner of the image) was scanned at higher resolution ($0.1 \times 0.1\ \mu m^2$ area), roughness was still clearly evident, as shown in figure 1B, consistent with the undesired polymerization away from the surface in the third dimension.

While the details of all the kinetic and thermodynamic factors contributing to the formation of SAMs are not fully understood, it seemed reasonable to consider (i) the stability of the Si–O bonds in OTE relative to Si–Cl bonds in trichlorosilane precursors, and (ii) the resulting slowness of the alkoxysilanes to react at the glass surface to form covalent links to the glass and crosslinks in the octadecylsiloxane polymer, to be key issues. A simple solution to this problem was suggested by the fact, well known in the 'functionalized silica gel' chromatography community, that the presence of amine or other bases catalyses the reaction of alkyltrialkoxysilanes with hydroxylated silica surfaces. For example, while amines were shown not to react with trimethoxymethylsilane (TMMS) in solution, added catalytic amounts of primary and secondary amines were shown to most effectively catalyse the reaction of the TMMS with the silica gel Cab-O-Sil MS75 (fully hydrated) in toluene, affording maximum loading of the TMMS on the silica surface [28].

This approach to enhancing the reactivity of surface silanol groupings towards alkyltrialkoxysilanes also seemed attractive for the promotion of SAM formation. Indeed, when a small amount of *n*-butylamine was included in a toluene/OTE dipping solution, the quality of the resulting monolayers improved dramatically. Several variations on this basic procedure for synthesis of SAMs on float glass have been explored, affording the following key generalizations.

First, if care is taken to dry the solvent and reagents, and the reaction is run under 'dry conditions,' with flame-dried glassware and under an inert atmosphere, low quality surfaces result. This is quite consistent with the many reports of the requirement for small amounts of water in the SAM dipping solutions, as mentioned above. It did not prove productive, in our hands, to start with dried solvents then add water to the system to optimize SAM formation. Instead, the best results were obtained by simply utilizing reagent grade materials as received from the suppliers.

Second, over a period of time (several weeks), the quality of monolayers obtained from freshly prepared dipping solutions degraded appreciably as evidenced by water contact angle measurements. This was found to be due to changes occurring in the siloxane starting material, which was typically stored in a desiccator, but was manipulated without taking special precautions against atmospheric moisture. Careful distillation of the OTE was effective at re-enabling the synthesis of high quality SAMs; this distillation, however, proved quite inconvenient. In our hands, when the quality of SAMs prepared from a stock sample of OTE begins to

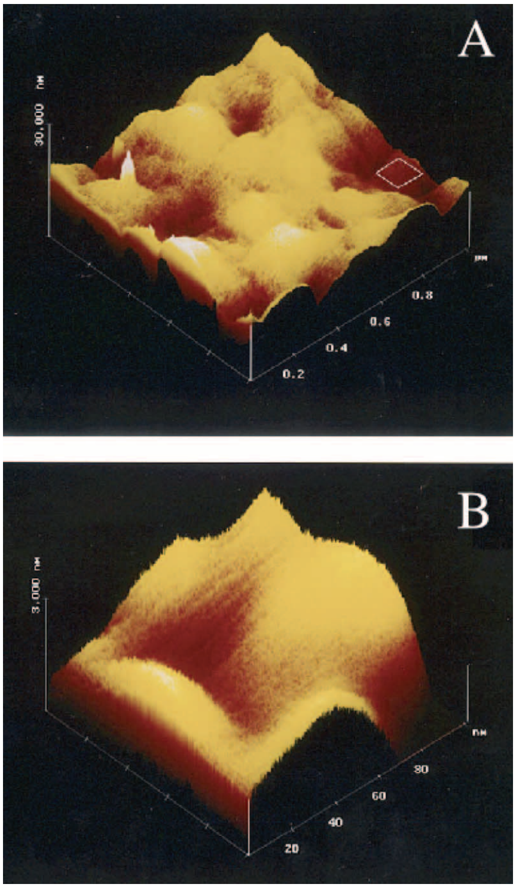

Figure 1. Typical AFM images of 'multilayer' surfaces prepared using OTE as the SAM precursor without amine catalysis. A: image of a 1 × 1 µm^2 area showing features in the z direction on the order of 300 Å in size; B: image of the 'smoothest' part of the surface shown in figure 1A (0.1 × 0.1 µm^2 area indicated by the white border) showing features in the z direction on the order of 30 Å in size.

degrade, we simply switch to a new batch of OTE starting material.

Characterization of the SAMs on float glass produced by this class of procedures has been accomplished by AFM, water contact angle measurements, and sum-frequency generation studies. In addition, SAMs grown on Si(1 0 0) substrates by the same procedural type were characterized by transmission Fourier transform infrared (FTIR) spectroscopy. The latter technique is a standard method allowing direct comparison of the SAMs created using the present approach with those prepared using OTS-based procedures.

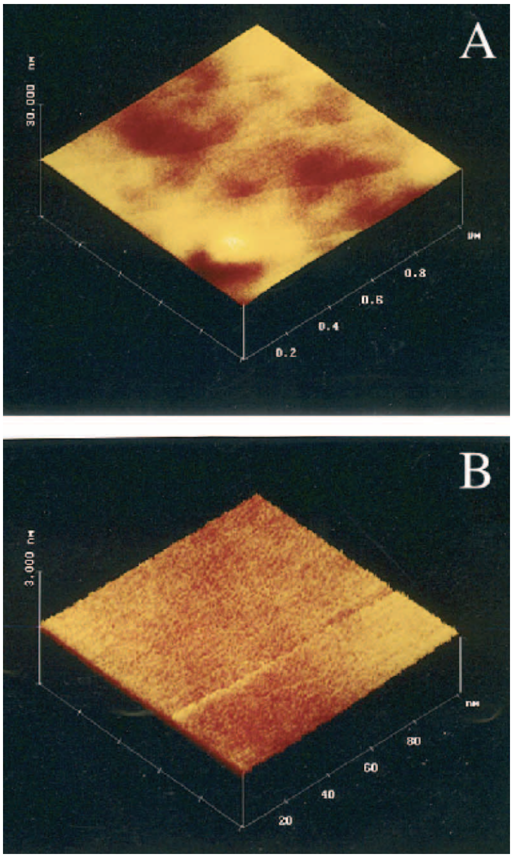

Figure 2. Typical AFM scans of a good SAM. A: image of a 1 × 1 µm^2 area showing no discernible topography of the monolayer in the z direction; B: image of a 0.1 × 0.1 µm^2 area showing roughness on the order of 2 Å in the z direction. The linear features, or grooves, apparent in both images were also observed on clean regions of untreated float glass under identical imaging conditions, suggesting that these grooves did not originate in the SAM synthesis, but were present on the surface of the glass prior to SAM formation. The groove in figure 2B appears to be about 4 Å deep and about 35 Å wide.

AFM scans of SAM surfaces prepared by the present process (simple contact mode) were of the same smoothness as the float glass substrates (conformal), as expected for a true monolayer (figure 2). These data show that the formation of multilayers does not occur due to the presence of the *n*-butylamine. However, the AFM images do not indicate the packing density of the octadecyl groups in the monolayers, since low packing densities with large tail tilts would also be conformal to the substrate surface.

Not surprisingly, the tin and non-tin sides of the float glass (coated or uncoated) are easily distinguished by AFM. The tin side of float glass can be determined by irradiation of a slide using a UV lamp such as those used for visualization of spots on TLC plates. In a darkened room, a distinct green fluorescence can be seen only from the tin side of the slide. In the experiments reported herein, the tin side of each slide was identified using this technique and distinguished

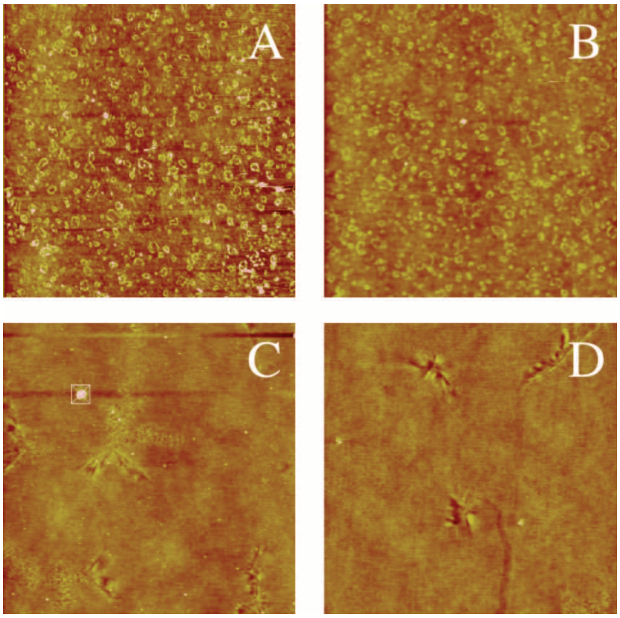

Figure 3. $10 \times 10\,\mu m^2$ AFM images of the tin and non-tin sides of float glass slides. A: bare non-tin; B: SAM-coated non-tin glass surfaces. The RMS (*Rq*) roughness computed from these images were 0.62 and 0.28 nm, respectively. C: bare tin, and D: SAM-coated tin side glass surfaces. The RMS roughness computed from these images were 0.32 and 0.18 nm, respectively. It is believed that the RMS roughness in these images is dominated by defects, and the differences observed in images A–D are not considered significant.

using a diamond scribe. As can be seen in the 'wide angle' AFM images in figure 3 ($10 \times 10\,\mu m^2$ image area), the tin side of bare float glass has fewer topographical features per unit area than the non-tin side. As expected for SAM-coated glass, the AFM images of the coated surfaces are essentially identical to those of the bare glass. It has been reported that the hydroxyl group density on the tin side of float glass is higher than that on the non-tin side. If this fact has an influence on monolayer formation, it could not, however, be seen by AFM.

A previously reported AFM study of SAMs prepared using the present procedure [29], which had been patterned using UV photolithography [30], suggests a 'step height' between the SAM domains and the hydrophilic surface obtained by irradiation, of about 10 Å in tapping mode. The octadecyl tails are about 25 Å long in the all anti conformation, suggesting a substantial tail tilt in the SAMs. As discussed in detail in [29], however, it is likely that the apparent step height is an artifact of the AFM experiment. Further work exploring the dependence of apparent step size on loading force and scan rate in the AFM experiment are in progress in order to develop a better understanding of the observed friction-free step sizes in the UV photopatterned SAMs.

The wetting behaviour of SAM-coated surfaces is a simple yet sensitive probe of SAM quality. Indeed, a good indication of the quality of the monolayer is provided immediately upon removal of the substrate from the dipping solution due to the well-known 'solvophobic' nature of alkylsiloxane SAMs. In a successful preparation, when the slide is removed from the dipping solution, the toluene 'sheets off' the slide, which then immediately appears dry. Advancing water contact angles on fully cured SAMs were measured on several samples and at several locations on each slide. In all cases the tin side of the slides was characterized by wetting behaviour. Contact angles were measured in two ways, both involving homemade apparatus. One method involved projection of the shadow of the droplet onto a screen, and analysis of the resulting image. The second method involved analysis of a sequence of photomicrographs of a small advancing water droplet taken from the side. The first method consistently gave values ranging from 111° to 120° for successful preparations, while the second method gave values ranging from 105° to 110°. These values are in agreement with those reported in the literature for densely packed SAMs with small tail tilts [6]. For comparison, SAMs prepared with 'old' siloxane starting material, as mentioned above, typically showed water contact angles of less than 100°. Several dozen slides were characterized by wetting behaviour on both the tin and non-tin sides. In these comparisons, the tin side typically showed a slightly larger contact angle than the non-tin side (though not always). This is probably due to the smoother topography of the tin side relative to the non-tin side of the slides.

SAMs on float glass prepared by this procedure were also examined using sum-frequency generation (SFG) [31]. As shown in figure 4, the data indicate that the density of *gauche* defects in the monolayers is small. In addition, analysis of the terminal methyl group orientation in the SAM by SFG spectroscopy gives an indication of overall tail tilt. The intensity of the r- (antisymmetric) methyl stretch vibrations, whose local hyperpolarizability symmetry characteristics are well known, were analysed as a function of the polarization of the input light. Making reasonable assumptions about the nature of the statistical distribution of Euler angle rotations that represents the ensemble of methyl groups in the sample, the parameters of that distribution can be extracted from the SFG data. The SFG results indicate that the average tilt of the terminal methyl group from the surface normal in these SAMs is about 36°. This value is consistent with the axis of the

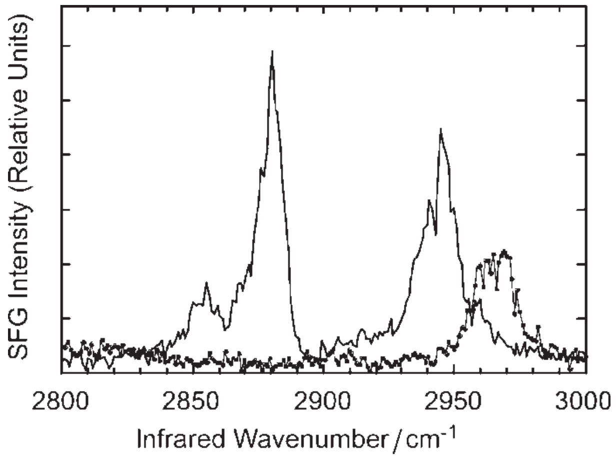

Figure 4. Vibrational spectrum, obtained through s-polarized sum-frequency generation, of an octadecylsiloxane monolayer assembled on float glass using the present procedure; s-polarized visible, p-polarized infrared incident beams (solid), p-polarized visible, s-polarized infrared incident beams (dotted). The feature at 2855 cm^{-1} is an indication of a very small concentration of *gauche* defects. Orientation of the chain end is determined from the polarization behaviour of the mode at 2960 cm^{-1}.

chains being very close to perpendicular to the sample surface.

In order to compare the SAMs produced by the present procedure more directly with those reported in the literature, SAMs were prepared on Si(1 0 0) substrates using the present method and analysed by transmission FTIR spectroscopy. As indicated in figure 5, the spectra are in good agreement with typical measurements on high quality OTS SAMs [32]. The frequencies obtained for the asymmetric and symmetric CH stretches provide a measure of the concentration of *gauche* bends in the chains. The peak frequencies for these modes are reported to be in the range 2915–2920 and 2846–2850 cm^{-1}, respectively, for highly ordered, all-*trans* extended alkyl chains and about 2924 and 2856 cm^{-1} for disordered chains. The measured peak positions, as shown in figure 5, are at the high end of the expected ranges for ordered chains, and in reasonable agreement with typical measurements on OTS SAMs prepared using the best procedures. Advancing contact angles of 105°–110° measured for these SAMs on Si(1 0 0) by method two were also in good agreement with those prepared in this laboratory using OTS, and those in the literature.

Finally, it should be noted that SAMs prepared by amine-catalysed deposition of trialkoxysilanes have proven useful in several interesting applications. Rogers *et al.* showed that photopatterned octadecylsiloxane SAMs, where the monolayers were prepared by an early variation of the present procedure, could be used to prepare surfaces patterned with a variety of proteins [33]. More recently, Clark and Lee have demonstrated a very elegant and novel approach to nematic LC alignment utilizing photopatterned octadecylsiloxane SAMs prepared by the present procedure, thereby proving the utility of these surfaces for LC alignment [34]. SAMs prepared by the present method have proven useful as solid substrates for the transfer of freely suspended smectic LC films, which were then studied by AFM [35]. Finally, we have reported novel smectic LC alignment modes using mechanically rubbed OTE SAMs prepared by the present procedure [36].

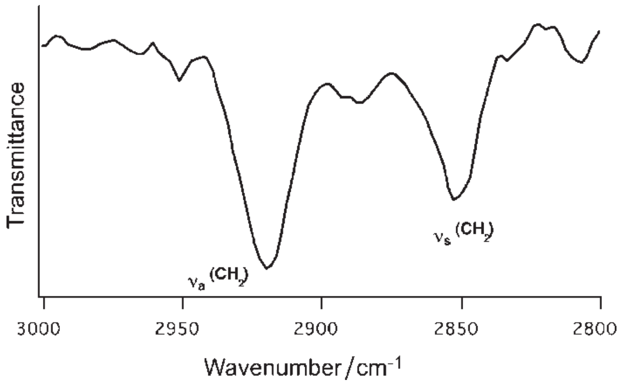

Figure 5. Typical transmission FTIR spectrum in the CH stretch region obtained from SAMs on Si(1 0 0) prepared by the present procedure. The peak centered at 2919 cm^{-1} was assigned to the asymmetric methylene C–H stretch, ν_a (CH$_2$), while the peak centered at 2850 cm^{-1} was assigned to the symmetric methylene C–H stretch, ν_s (CH$_2$).

4. Formation mechanism

Amine catalysis of the reaction of alkylalkoxysilanes with silicon oxide surfaces is a very well known process [28]. More recently, pyridine [37] and ammonia [38] have been shown to catalyse the chemical vapour deposition of conformal ultrathin silicon dioxide films on smooth substrates. For example, in a process involving successive gas phase additions of $SiCl_4$ and H_2O to a hydroxylated surface, the temperature necessary for the deposition was lowered from >900 to 330 K, and the required reactant fluxes were also lowered [38].

In the work of Blitz *et al.*, directed towards understanding the catalytic effect of ammonia and amines on the reactions of methyltrimethoxysilane with silica gel [28], it is reported that ammonia has no detectable interaction with the siloxanes in toluene. At the same time, it was shown that ammonia catalyses the direct condensation of unhydrolysed siloxanes on silica gel in the absence of adsorbed water. These results were taken to mean that the ammonia must influence the reaction of the siloxane–OCH_3 groups with the surface SiOH groups directly.

Possible mechanisms for the formation of SAMs from OTS include, on one extreme, the original proposal of Sagiv that the trichlorosiloxane is hydrolysed in solution to a trihydroxysilane [4]. This material then behaves as an amphiphile, forming the islands of SAM on the surface as imaged by *in situ* AFM. Covalent attachment to the Si–OH groups on the surface then occurs in a second, slower process. Alternatively, the trichlorosilane itself could form a Langmuir-like film on the surface. If this were the case, however, it is hard to see why there is such a strict need for water in the dipping solution. Between these extremes, it is possible that mono- or di-hydroxychlorosilanes form the monolayers.

It seems unlikely that the triethoxysilyl grouping of OTE itself would be polar enough to drive the formation of Langmuir-like monolayer islands. While the evidence is indirect, an attractive scenario for SAM formation by the method presented here involves, first, formation of a low concentration of octadecyldiethoxyhydroxysilane in solution. This material then forms non-covalent monolayer islands on the glass surface. The amine selectively catalyses the reaction of surface SiOH groups with $C_{18}SiOCH_2CH_3$ groups in the islands, providing covalent attachment. The amine may also catalyse the crosslinking of $C_{18}SiOH$ groups with $C_{18}SiOCH_2CH_3$ groups.

5. Conclusions

An especially simple procedure for the formation of octadecylsiloxane SAMs on float glass is presented. The synthesis exploits the relative stability of the triethoxysilane relative to the more commonly used trichlorosilanes, in combination with the catalytic effect of added *n*-butylamine. A mechanism involving monolayer formation mediated by formation and selective deposition of a monohydroxydiethoxysilane intermediate, followed by amine catalysed covalent attachment to the surface is proposed.

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