

Self-Assembly of Octadecyltrichlorosilane Films on Mica

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Synopsis

Self-assembled films of octadecyltrichlorosilane (OTS) have been deposited on freshly cleaved mica. A combination of argon plasma pretreatment, long adsorption times in solution, and a posttreatment at a moderate temperature (60°C) were required to form homogeneous OTS layers exhibiting good adherence to the mica. This process is more complex than the procedure required to form similar layers on glass. Advancing contact angles of water droplets ranged from 113 to 116°, with receding angles of 107 to 110°.

INTRODUCTION

A large and growing interest has been shown recently in the formation and properties of self-assembled monolayers—films only one molecule thick that form spontaneously on a solid substrate from a low-concentration (about 1 mM) liquid solution.^{1,2} Much recent work has been carried out by Sagiv,³⁻⁵ Allara,⁶⁻⁸ and Nuzzo.^{6,8} The properties of these films, which are made up of tightly packed, oriented molecules,^{3,4,7} compare well with those of Langmuir-Blodgett films.⁴ They are also, in general, easier to make; the latter requires a careful dipping procedure, while self-assembled monolayers only require that the substrate be dipped in a surfactant-containing solution for a certain amount of time. In addition, there exists the possibility of manipulating certain film properties, such as surface energy and density, by varying the solution concentration, substrate properties, and so on.

The types of materials exhibiting self-assembly vary, but all include a chemical group on one end of the molecule that interacts with the substrate, making substrate properties very important.³ These interactions may involve physisorption, as in the case of a fatty acid end group, or chemisorption, in which specific chemical bonds are formed between the substrate and the adsorbed molecule. Molecules that form covalent bonds with the substrate have received special attention due to their expected physical and chemical resilience.

A covalently bonding film of special interest recently is made from octadecyltrichlorosilane [$\text{CH}_3-(\text{CH}_2)_{17}-\text{SiCl}_3$], or OTS. Ideally, in an organic solution the chlorine groups are lost due to hydrolysis with small amounts of water that are present. A monolayer forms very quickly and is held in place by surface pressure at the solution-solid interface until covalent stabilization has taken place¹ (presumably there is an activation energy involved). On contacting the substrate, one hydroxyl group on the OTS-derivative molecule

reacts with a hydroxyl group on the surface, yielding water, and bonding the molecule to the substrate. The remaining hydroxyl groups on the molecule react with those on adjacent molecules of the monolayer, thus producing a continuous, crosslinked film. Another model of film formation holds that crosslinking takes place before adsorption onto the surface.⁹ This scheme could help to explain any film roughness that may be observed.

Sagiv³ has successfully formed films of OTS on Ge, Si, ZnSe, and glass, with the external character of the completed films being more or less identical. This is to be expected, since their surfaces are all composed solely of tightly packed hydrocarbon chains.

The object of this research is to develop a process for the consistent formation of tightly packed OTS monolayers on atomically smooth mica, which has not been done before. The motivation behind this work is the formation of very smooth, inert films of low surface energy, both for use in ensuing tribological studies and as a prelude to the study of other self-assembled films.

EXPERIMENTAL

Materials

A solution of 80% by volume bicyclohexyl, 12% CCl₄, and 8% CHCl₃ was used to dissolve OTS at a concentration of 2.0 mM. The bicyclohexyl (purchased from Aldrich Chemical Co. under the name dicyclohexyl) was filtered through an alumina column before use. All other solvents were distilled. The OTS (purchased from Petrarch Systems) was used as received.

Attempts were made to keep excess water out of the OTS solution, lest it cause excess hydrolysis of the OTS. Addition of OTS to the solution and the handling of solutions were performed in a nitrogen-filled glove box.

Muscovite mica (purchased from Ashville-Schoomaker) was used as the substrate. Cleaving of mica samples was performed by hand in air inside a laminar flow hood. Only mica that showed no imperfections or steps was used. Samples having areas of several square centimeters could be cleaved with little difficulty. Thickness of samples had no bearing on these experiments.

Film Formation

Films of OTS on mica were made using many different sequences of surface treatment, with varying success. The most successful of these involved exposing freshly cleaved mica to a 100-W Ar plasma for 10 min using a Harrick model PDC-23G plasma cleaner. The mica was then put in the OTS solution as quickly as possible. Adsorption was allowed to proceed for from 15 to 24 h.

The films were then removed from the OTS solution and rinsed in distilled cyclohexane, in order to remove retained solvent and traces of unreacted OTS. The samples were next put in a vacuum oven at 60°C and about 13 torr for 1–3 h to further remove any retained solvent and to encourage reaction of the OTS.

Characterization of a finished film was mainly carried out by visual observation and by measurement of the advancing and receding contact angle of a

water droplet on the film. The latter was carried out using a protractor eyepiece mounted on a microscope having a magnification of 10. Some films were also analyzed using Fourier-transform infrared spectroscopy (FTIR) in the transmission mode.

RESULTS AND DISCUSSION

The first concrete conclusion reached in this investigation was that it is much more difficult to form a film on mica than it is to form a film on glass. If an ordinary glass slide is cleaned of organic contaminants on its surface and is dipped in the aforementioned OTS solution for 5–15 min, a film is formed that sheds the solvent fairly well when it is pulled from the solution. The shedding of the solvent is a desirable film trait. The contact angle of a water droplet advancing across the surface, the advancing contact angle, is greater than 90° , and the water droplet is round and smooth at the film–droplet–air interface.

Mica under this same treatment shows contact angles of less than 90° that decay very rapidly (in minutes) to much lower values ($30\text{--}50^\circ$). The water droplets are not round and often have rough edges, suggesting incomplete film formation. Longer adsorption times raise the value of the initial contact angle, but do not halt the decay and do cause the retention of solvent by the film. Obviously, there is something about mica that impedes good film formation. It is hypothesized that the decay of an initially high contact angle is due to a lack of bonding between the OTS and the mica, so that the hydrophobic film is pushed out of the way or penetrated by water.

The lack of adherence to mica when compared to the good results seen with glass is puzzling; mica and glass contain many of the same chemical constituents. The difference in behavior may be rooted in structural differences. Glass has an open, amorphous structure and is rough on the microscopic level whereas mica has a dense, crystalline structure along its cleavage planes and is atomically smooth.

Another possible cause for the difference in behavior may be the relative number of hydroxyl groups available for bonding on the surface. These do not occur naturally in glass since ordinary glass is formed at temperatures where all water is driven off. However, hydroxyl groups may adsorb onto the surface due to the large number of metallic ions normally present in a glass. Mica has fewer metallic ions, and, although it has some naturally occurring hydroxyl groups in its structure, they are not present on its cleavage plane. However, mica does have a polar surface, which should lead to some adsorption of hydroxyl groups.

Heating of a coated substrate at moderate temperatures, and later under vacuum, was found to provide two beneficial effects. It (1) encouraged the removal of solvent retained on or in the film and (2) assisted in the covalent bonding within the film and between the film and substrate. The latter was perceived as occurring since films coming straight from the OTS solution were easily damaged by abrasion.

Exposure of mica to an argon plasma before adsorption of OTS dramatically increased both the advancing and receding contact angles and the

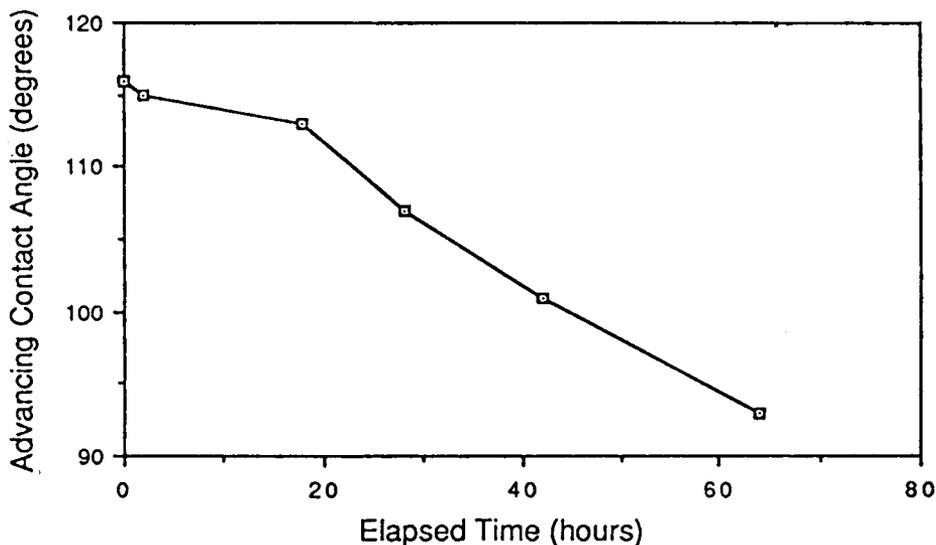


Fig. 1. Advancing contact angle of a water droplet on an OTS film, plotted against elapsed time of measurement.

resiliency of the films. It is not understood exactly why, though it may be due to a certain degree of surface roughening or disordering (which would make mica appear more like glass on the atomic level), ionization of the surface, or simple sputter cleaning.

Also required to form good films were adsorption times on the order of 20 h, though this tended to cause more solvent retention. Contact angles started out much higher and decayed over many hours or days with these long adsorption times.

With the experimental procedure outlined previously, OTS films having advancing contact angles of 113–116° and very long decay times could be made, as seen in Figure 1. The film and droplet were kept in an air environment at a relative humidity approximating 100%. Much of the decay observed was attributed to organic contamination of the water droplet. The receding contact angles ranged from 107 to 110°. The hysteresis between the advancing and receding angles was attributed to either (1) an acquired surface roughness due the argon plasma treatment or gelled OTS attached to the surface or (2) incomplete reaction of the OTS in the dry environment, leading to “sticking” between the water droplet and the film. The expulsion of HCl from OTS films for an extended period of time (days) has been deduced by the corrosion of aluminum foil covering a beaker containing OTS-coated material.

Despite this, water droplets showed excellent mobility on the surfaces; they moved freely across the film when the film was tilted or when led around by a needle. They were also nicely shaped, with no rough edges.

Some of the films were characterized using FTIR in the transmission mode. A typical absorbance spectrum is shown in Figure 2. The results have been ratioed to those of bare mica. This particular sample was soaked in an aqueous NaOH solution (pH 12) for 24 h prior to the OTS adsorption step in an attempt to introduce more hydroxyl groups onto the mica. The major

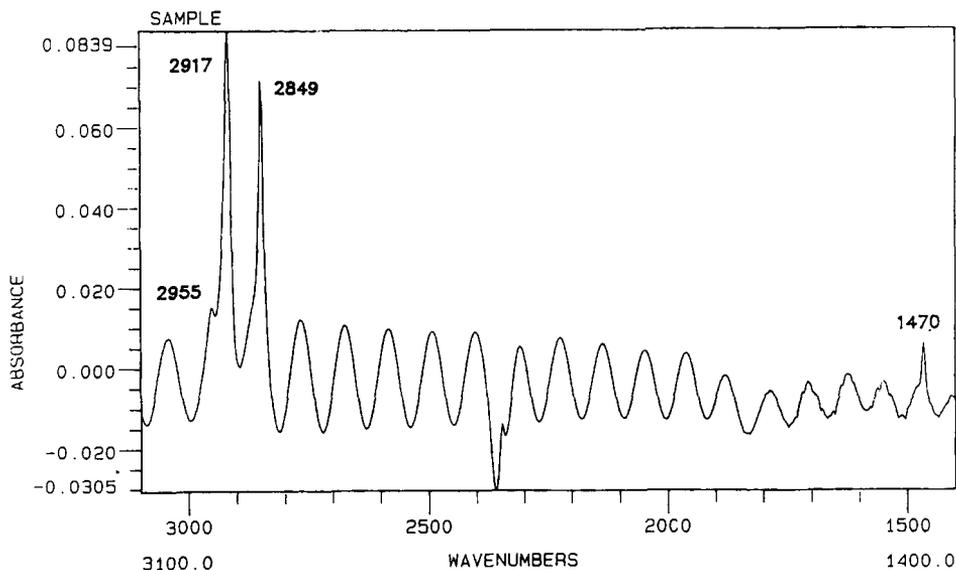


Fig. 2. FTIR absorbance spectrum of an OTS film. The important peaks are labeled. The oscillations are due to interference across the mica.

peaks are at 2917 and 2849 cm^{-1} , with smaller peaks occurring at 1470 and 2955 cm^{-1} . These are characteristic of OTS and have been noted before,³⁻⁵ but also correspond to peaks for bicyclohexyl, the main solvent. The oscillatory phenomenon in Figure 2 is due to reflection within the mica specimen.

CONCLUSIONS

Films of octadecyltrichlorosilane may be formed on mica substrates by self-assembly, resulting in an advancing contact angle of 113–116° and a hysteresis of about 6°. This was done using a combination of argon plasma pretreatment, long adsorption times, and a posttreatment at a moderate temperature (60°C) under vacuum.

These films are, as yet, rather crude. Research is presently underway to deposit OTS films on mica without the argon plasma treatment, by the deliberate introduction of more hydroxyl groups on the surface.

It is also hoped to find other systems exhibiting self-assembly without the harmful HCl byproduct and prolonged reaction of the chlorosilane group present on OTS. These films will find use as low-energy, inert surfaces as well as in tribological studies of very smooth surfaces.

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