

Self-Organization of Organic Liquids on Patterned Self-Assembled Monolayers of Alkanethiolates on Gold¹

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Patterned, self-assembled, monolayers (SAMs) of alkanethiolates on gold organized two immiscible liquids—water and a hydrocarbon—in contact with the SAM into simple three-dimensional structures at its surface: the pattern in the wettability of the surface was thus reflected in the self-organized pattern of spatially-segregated liquids. The dimensions of the patterned structure (~2 nm perpendicular to the plane of the SAM) were amplified in the dimensions of the drops (2 μm) in the same direction. This strategy for the assembly of liquid features will be useful in building and controlling three-dimensional structure near the surface of self-assembled monolayer films. Microlense arrays illustrate this utility.

Introduction

This paper describes a procedure that uses patterned, self-assembled, monolayers (SAMs) of alkanethiolates on gold to organize two immiscible liquids—water and hydrocarbon—in contact with the SAM into simple three-dimensional structures at its surface. This demonstration is one step in extending the principle of molecular self-assembly to larger, mesoscopic, structures having micrometer-scale features in the direction perpendicular to the plane of the SAM.

Noncovalent interactions—hydrophobic, hydrogen bonding, ionic and van der Waals—provide an important organizing principal in nature at scales of length from the molecular (proteins, DNA)² to the macroscopic (wettability of feathers).³ Nonbiological uses of these interactions in the *design* of materials for specific functions is just beginning: examples include the transfer of Langmuir–Blodgett films to solid substrates for optical systems,^{4,5} the formation of nanocrystals of cadmium selenide as models for quantum boxes,^{6,7} and the use of polymer microspheres for controlled release of drugs.⁸

We have generated SAMs patterned into hydrophobic and hydrophilic regions with dimensions of 1–50 μm.⁹ Exposure of these patterned SAMs to two-phase systems comprising water and an immiscible hydrocarbon fluid resulted in the organization of each liquid around regions of different wettability. The pattern in the wettability of the surface was thus reflected in the self-organizing pattern of segregated liquids at the surface of the SAM. The dimensions of the patterned structure (~2 nm in the plane of the SAM) were amplified in the dimensions of the

drops (2 μm) perpendicular to the plane. We believe that this strategy for the assembly of liquid features will be useful in building and controlling three-dimensional structures near the surface of self-assembled monolayer films.

Experimental Section

Materials. Thiols and disulfides were available from previous studies.¹⁰ Transparent gold substrates were prepared by evaporation at (1 Å/s), using an electron beam, of 100 Å of gold (99.999%) onto titanium-primed (5 Å) silicon wafers (Silicon Sense) at a pressure of 1×10^{-7} Torr.¹⁰ Stamps were made of poly-(dimethylsiloxane) (Dow-Corning, SYLGARD Silicone Elastomer-184).^{11,12} A prepolymer of polyurethane, NOA 60 (1.56 refractive index; 300 cP viscosity at 25 °C), was used as received from Norland Products, Inc. (New Brunswick, NJ).

Patterned SAMs by Microcontact Printing. Elastomeric stamps were fabricated according to a published procedure.^{11,12} The stamps were inked with neat hexadecanethiol and placed in contact with the surface of the gold substrate for 5 s (Figure 1A). The derivatized sample was immersed in a solution of 50 mM bis(16-carboxyhexadecyl) disulfide for 10 s to cover the surface of the gold completely with SAMs (Figure 1B). The sample was rinsed with ethanol (~20 mL), and dried under a stream of nitrogen. The advancing contact angle of water (pH 5) in the hydrophilic areas was 10°; this angle was 112° in the hydrophobic areas.

Assembly of Organic Structures. A polystyrene Petri dish (100 × 15 mm, Fisher Scientific) was submerged in a 1-L beaker containing doubly distilled, deionized water. A glass tube with a diameter of 2 cm was suspended to half its length in the beaker and centered over the Petri dish: this glass tube contained the hydrocarbon and permitted the Petri dish to be transferred into or removed from the beaker without contamination from the organic liquid. A hydrocarbon liquid (~30 μL, hexadecane, NOA 60, heptane or styrene) immiscible with water was added to the glass tube (Figure 1C). The thickness of the hydrocarbon layer was ~100 μm.

The patterned SAM was lowered by hand through the organic phase (~3 s; ~1 cm/s) before coming to rest under water in the polystyrene dish; we did not investigate the sensitivity of this procedure to the speed of movement of the sample through the hydrocarbon–water interface. This dish was removed from the beaker while the sample remained submerged in the water it contained; this procedure allowed convenient manipulation of the sample and protected it from the air and from contamination by undesired contact with the hydrocarbon liquid.

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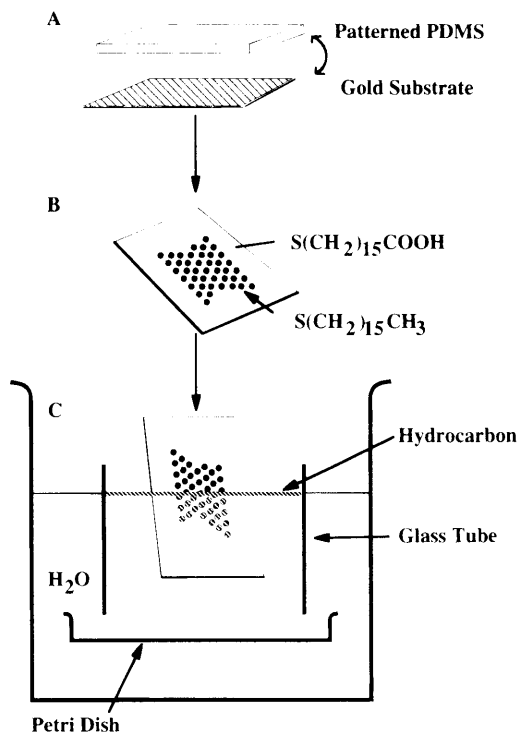


Figure 1. Procedure for the assembly of organic liquids on the surface of patterned SAMs. (A) An elastomeric stamp formed from poly(dimethylsiloxane) (PDMS) was inked by exposure to neat $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ and brought into contact with the gold substrate (100 Å thick) and removed. (B) The substrate was immersed in an ethanolic solution of $(\text{HOOC}(\text{CH}_2)_{15}\text{S})_2$ (50 mM) for 10 s, washed with 20 mL of ethanol, and dried under a stream of nitrogen. (C) Drops of hydrocarbon assemble on hydrophobic regions of the monolayer as it passes through an hydrocarbon-water interface.

Preparation of a Permanent Microlens Array: Polymerization of NOA 60. NOA 60 was assembled as liquid drops on the patterned surface of the SAM. It was cured with UV light from a Conrad-Hanovia 450-W medium pressure, mercury vapor lamp (type 7825-34 from ACE Glass) that had a water-cooled, quartz housing (type 7854B from ACE Glass). The sample, immersed under 5 mm of water, was ~3 cm from the immersion well of the UV lamp; the time of exposure of the sample to the lamp was 20 s.

Instrumentation. Scanning electron microscopy was done on a JEOL JSM-6400 scanning electron microscope. Images were acquired in the secondary electron imaging mode with an electron beam current of 2 nA.^{13,14}

Optical micrographs were obtained on an Olympus BH-2 microscope. Light was transmitted through the thin gold substrate. The objective lens (20×; ~0.22 numerical aperture) of the microscope was immersed in water; the image was captured with a charged-coupled camera (Sony) through a 15× relay lens and digitized with a frame grabber (RasterOps, Santa Clara, CA).

Atomic force microscopy (AFM) used a Topometrix TMX 2010 scanning probe microscope. The images were obtained using a cantilever made from silicon nitride in constant contact with the surface. The cantilever was scanned across the substrate at a rate of 100 $\mu\text{m}/\text{s}$ and with a constant force of 0.1 nN; data were collected in the forward part of the scan.

Contact angles of water and hexadecane were measured on a Ramé-Hart Model 100 goniometer at room temperature and ambient humidity. Advancing and receding contact angles were measured on at least 3 drops of each liquid per slide; contact angle data in the text represent the average of these measurements. A Micro-Electropipette syringe (Matrix Technologies) was used for dispensing and removing the liquids onto the SAMs (~1 $\mu\text{L}/\text{s}$).

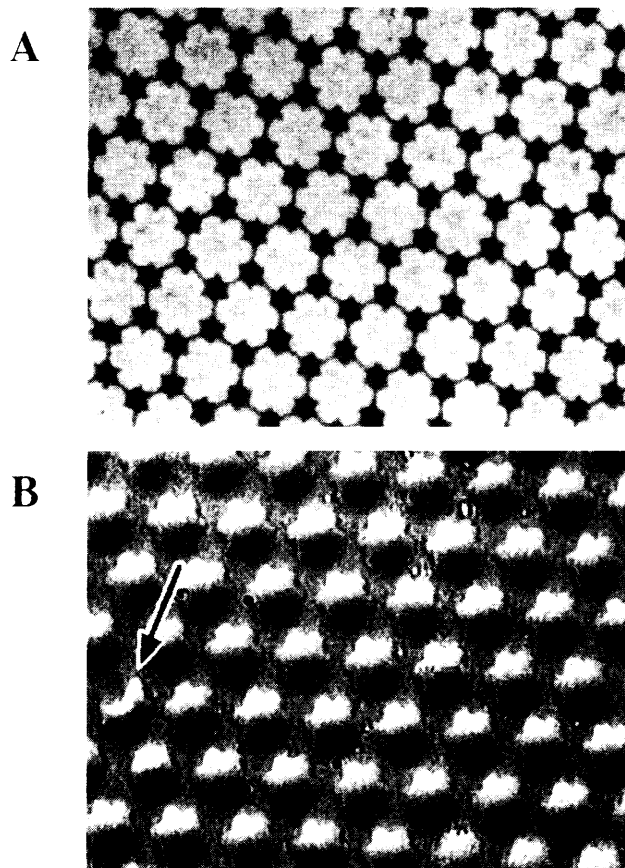


Figure 2. Results of patterning SAMs on gold and assembly of organic liquids on its surface. (A) Scanning electron microscopy (SEM) shows representative light (SAM of $\text{S}(\text{CH}_2)_{15}\text{CH}_3$) and dark (SAM of $\text{S}(\text{CH}_2)_{15}\text{COOH}$) regions patterned on the gold; lateral force microscopy showed that the border between these regions was sharp (width <200 nm). The intensity of oxygen on this patterned substrate, average over a 2.5 cm^2 region measured by X-ray photoelectron spectroscopy (XPS), was $30 \pm 3\%$ of the intensity for a monolayer of $\text{S}(\text{CH}_2)_{15}\text{COOH}$ on gold; this value is consistent with the area fraction of dark regions, 27%, in the SEM image. (B) Drops of $\text{CH}_3(\text{CH}_2)_{14}\text{CH}_3$, imaged by optical microscopy, conform under water to hydrophobic patches (light regions in Figure 1C) of the monolayer. The defect (arrow) on the left side of the image is probably due to an imperfection in the PDMS stamp used to pattern the surface.

X-ray photoelectron spectra were obtained on an SSX-100 spectrometer (Surface Science Instruments) using monochromatic Al K_{α} X-rays. The spot size was 3 mm^2 with an analyzer pass energy of 100 eV for measurements of O(1s); spectra were accumulated for 30 min. A 1 mm^2 spot and an analyzer pass energy of 50 eV were used for measurements of C(1s) and Au(4f); these spectra were acquired for 20 and 3 min, respectively.

Results

Parts A and B of Figure 1 show the scheme used to form patterned SAMs using an elastomeric stamp;^{11,12} a representative example of the resulting patterned substrate had well-delineated hydrophobic (light areas) and hydrophilic (dark areas) regions with spatially sharp (<1 μm) transitions in the functionality on the surface (Figure 2A). Exposure of these patterned SAMs to a two-phase liquid of hexadecane and water (Figure 1C) resulted in the organization of each liquid around regions differing in their wettability. Figure 2B shows that pattern in the SAM was mirrored and extended by the self-organizing pattern of segregated liquids at the surface of the SAM: the hydrocarbon wet hydrophobic regions, and water wet hydrophilic regions, preferentially.

The liquid structures were easily removed by lifting the sample from the aqueous phase and rinsing it with

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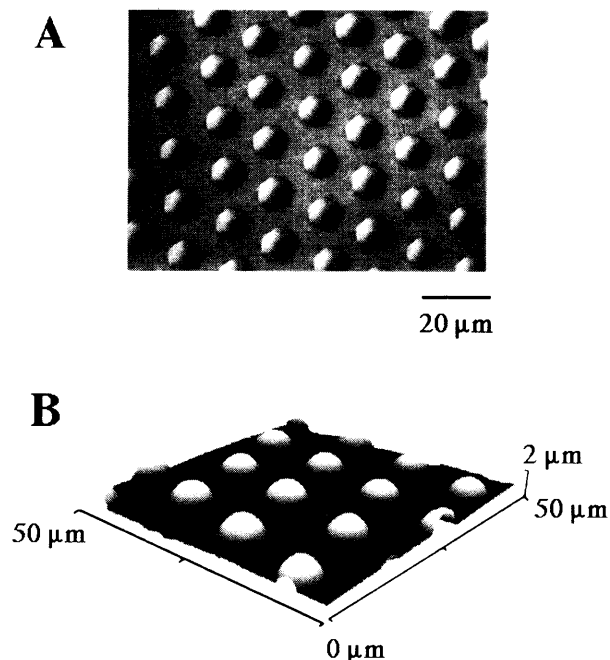


Figure 3. Permanent structures resulting from the assembly of an organic liquid on a patterned SAM. (A) SEM image of polyurethane structures made by assembly of a liquid prepolymer (NOA 60) on a patterned SAM (as in Figure 2A); the prepolymer was converted to a solid under water by exposure to UV light. (B) AFM image (constant force mode) of the cured polyurethane structures. The angle between the cured polyurethane and the surface, measured from this image, was $30 \pm 2^\circ$; the height of the polymerized drop was $1.5 \pm 0.1 \mu\text{m}$; the volume of these structures was $\sim 5 \times 10^{-14} \text{ L}$.

ethanol. Samples could be cycled dozens of times between air and the two-phase liquid, with rinsing between cycles, without a noticeable decrease in the resolution of the pattern. Patterns of organic liquids prepared by this technique were stable for weeks under water without detectable degradation in the pattern. Other organic liquids—styrene, heptane, and a prepolymer of polyurethane (NOA 60)—produced similar liquid structures on patterned SAMs. These liquid structures assembled onto SAMs remained stable even when the water phase was heated to 75°C . UV curing of patterns of NOA 60 gave permanent structures (Figure 3) although some of the structural features present before curing were lost on polymerization (probably due to shrinkage). These polymer structures allowed transmission and focusing of light transmitted through the substrate and were thus microlens arrays (Figure 4).¹⁵

Discussion

Organization of liquid structures and their detailed shapes on patterned SAMs was the consequence of minimization of interfacial free energy: hydrophobic regions preferred energetically to be wet by hydrocarbon or organic liquids; hydrophilic regions preferred to be wet by water. We have formed self-organized liquid structures on patterned SAMs with features down to $10 \mu\text{m}^2$ in size, although the technique can generate even smaller structures.

Fabrication of microlenses to focus, and to correct aberrations in the intensity of light from, diode lasers or optical fibers will provide a useful application of the concepts presented in this paper. Surface tension has already been exploited usefully in the fabrication of arrays

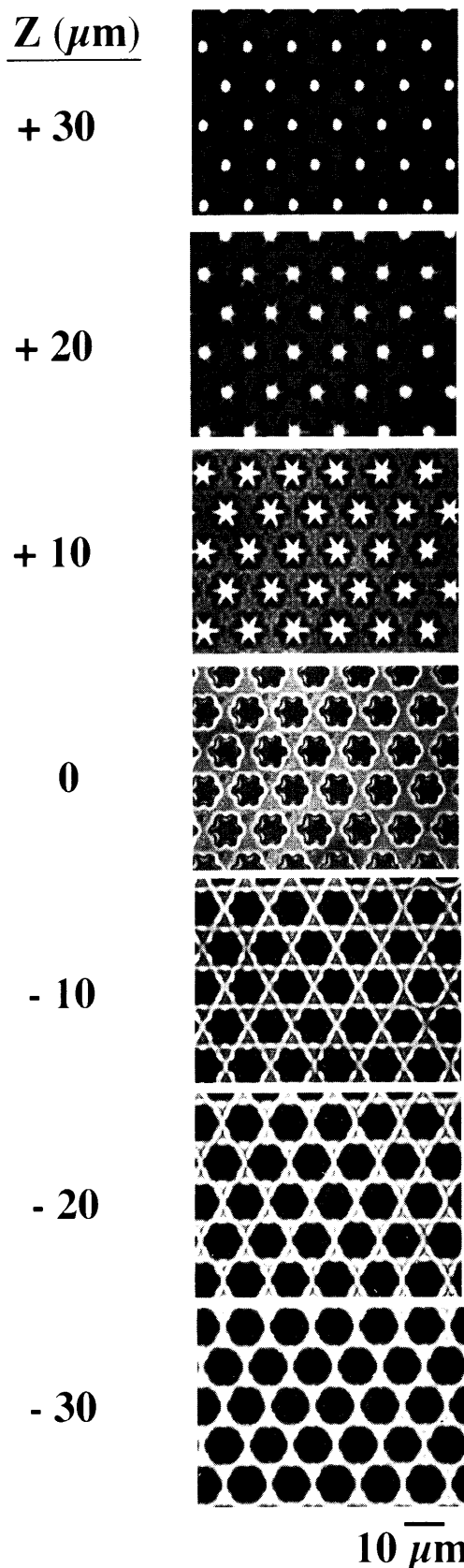


Figure 4. Polyurethane structures assembled on a patterned SAM on transparent gold are microlenses. The array of microlenses was illuminated from a point source of white light ($\sim 50 \text{ mm}$ from the gold surface; the black body temperature of the light was $\sim 4800 \text{ K}$) and observed from heights below (bottom three frames), at (middle frame), or above (top three frames) the gold surface using an optical microscope ($\sim 1200\times$). The lens in this array focused the source at $\sim 30 \mu\text{m}$ (top frame) from the plane of the sample; the f number of these lenses was thus $f/3$.

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of microlenses: polymer resists, patterned by exposure to light, form lenses on melting.¹⁶ Drops of a photocurable polymer placed on a hydrophobic surface do not spread and therefore form microlenses when a small volume ($< 1 \mu\text{L}$) of polymer is used.¹⁷ Laser ablation of polymers¹⁸ and ablation of polymers by high-energy beams of protons¹⁹ or other ions²⁰ have also been used to fabricate microlenses from organic materials, in addition to methods utilizing replication by molding or ruling a polymer.¹⁵ The strengths of the technique demonstrated in this work are its ease of use and the small scale, and parallel, formation of simple structures that reflect and amplify the pattern

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in wettability of the underlying substrate. Because of the high surface tension of water, structures with small radii of curvature are possible. Although we used patterned SAMs on gold as a model system, polymer substrates with areas of different wettabilities should, in principle, work well.

This technique of assembly also offers the possibility of delivering chemical reactants to specific, micrometer-scale regions on a surface without requiring precise manipulation to position the liquid. Complicated three-dimensional structures, or structures with sharp angles, probably will not be made by the our procedure. Application of finite element analysis to the calculation of shape of geometrically confined drops²¹ will be helpful for the design of mesoscale optical structures based on the combination of wettability and immiscible liquids.

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