Use of Minimal Free Energy and Self-Assembly To Form Shapes

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Patterned self-assembled monolayers (SAMs) of alkanethiolates on gold films were used as constraining elements in forming shapes, in a strategy based on minimizing interfacial free energy. Circular right cylinders, catenoids, and other related shapes having centimeter dimensions were formed from poly(dimethylsiloxane) (PDMS) in a system comprising patterned SAMs and an aqueous solution of sodium chloride whose density equaled that of the polymer. These shapes were fabricated without using complementary, three-dimensional molds: the final form adopted by the PDMS was a minimum free energy shape with certain features of the shape set by the wetting of the pattern in the SAM by the PDMS. Using previously formed polymeric shapes and patterned SAMs as constraining elements, a cylinder fused with a catenoid, a cylinder fused with a truncated cone, two truncated cones fused together, and a truncated cone fused with a hemisphere were fabricated. Applying a magnetic field gradient influenced the final shape of the polymer by generating an effective spatial gradient in the density of the solution. Without using SAMs as constraining elements, convex-concave and double convex lenses were formed at interfaces of two immiscible liquids. Shapes with micrometer dimensions were fabricated by microcontact printing of patterned SAMs and self-assembly of a polymer on these patterns. These procedures produced shapes such as arrays of channel waveguides (with width of a few micrometers) and microlenses (with diameter of 1–2 μm).

Introduction

The formation of shapes is one of the most fundamental operations in materials science.[1–4] A wide variety of operations—casting, molding, machining, welding, and joining—have as their purpose the formation of shapes. These operations have been developed to an extraordinary degree of sophistication and are ubiquitous throughout materials and manufacturing processes. This degree of development not withstanding, there are excellent reasons to consider new methods for forming shapes. Among the methods that would be most useful are those that produced complex shapes without the requirement for first forming complementary molds or dies, that avoided significant surface finishing steps, that were applicable to forming shaped objects over a wide range of sizes (especially—in specific applications in fabrication of microstructures—sizes having dimensions of micrometers), and that could be used with materials having difficult mechanical properties (for example, soft gels and elastomers).

The objective of the work described in this paper is the exploration of one alternative strategy for the formation of shapes: that is, self-assembly. In this type of procedure, the shape adopted by the material is a consequence of the minimization of its free energy, typically as a result of minimization of interfacial free energy under the influence of surface tension, just as soap bubbles adopt shapes to minimize the surface energy for a given volume and boundary conditions.[5] In a process based on self-assembly, the shape forms spontaneously and represents a thermodynamic minimum (or an approach to thermodynamic minimum), rather than an arbitrary nonthermodynamic minimum. The adoption of regular, surface-minimizing shapes in liquids under the influence of surface tension can be found in inorganic and organic crystals, cell membranes, and biopolymers.[6–8] A number of manufacturing processes have also used this strategy of minimizing surface areas explicitly or implicitly: examples are forming metal spheres in microgravity,[9,10] casting or forming large mirrors,[11] pulling optical fibers from molten glass,[12,13] forming smooth glass surfaces by floating liquid glass on the surface of liquid metal,[14] and forming microlens arrays.[15] We wished to explore the range of shapes that could be produced by imposing more complex constraints on the system than those represented

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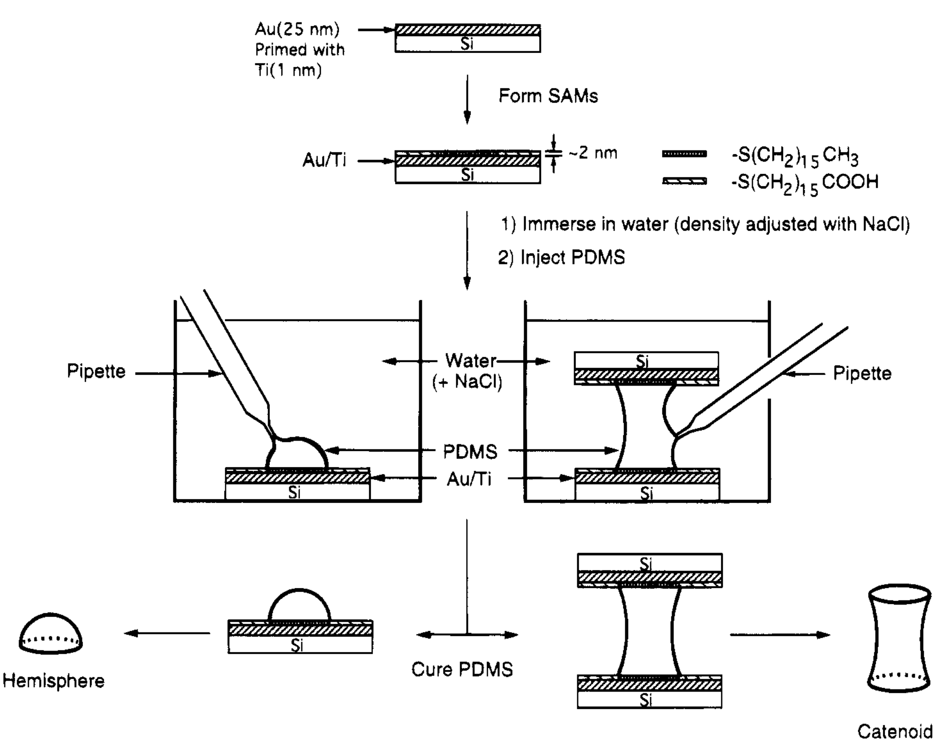

Figure 1. Schematic representation of the process used to fabricate minimum free-energy surfaces.

by these examples, and then the potential of these strategies for forming shapes with micrometer dimensions, and for application to organic materials. Our immediate objective is to develop a practical method of forming transparent objects, having dimensions from centimeters to micrometers, with optical surfaces, for use in photonic systems.

As a step toward this objective, we began our explorations by focusing on shapes that can be produced at the larger and more easily examined end of this range (dimensions of ~1 cm). As a model material, we have used poly(dimethylsiloxane) (PDMS), since it has a number of useful properties: it has good transparency.[16] It is noncrystalline and thus shows no tendency to phase separate into optically heterogeneous regions and scatter light. It is elastomeric. On cross-linking, it retains its dimensions and does not undergo a large change in density. The strategy in this work is based on the use of interfacial free energies to determine shapes. Our intent was to increase the degree of control over shape that could be achieved at thermodynamic equilibrium by building a number of controllable constraints into the system. First, we used the tendency of interfaces to minimize their area to determine shapes. Second, we typically carried out the cross-linking (or the shape-determining) step while the polymer was supported by a nonreactive, immiscible fluid medium whose density relative to that of the polymer could be controlled (for PDMS, we used water containing inorganic salts to adjust the density). In this circumstance, the effects of gravity could be minimized, and if desired, nongravitational forces could be introduced using magnetic or electric fields and components having different magnetic or electric susceptibilities. Third, through the choice of the polymer, we minimized the production of heat and accompanying changes in density and distortions in shape that would accompany an exothermic cross-linking step. Fourth, by using a water–PDMS interface as one important component of the system, we maximized the magnitude of the interfacial free energy available to be used in the determination of shape (the relevant interfacial free energies are water/air = 72.8 dyn/cm,[17] PDMS/air = 21.6 dyn/cm,[18] and PDMS/water = 40.4 dyn/cm).[19]

Results and Discussion

Cylinders, Catenoids, and Related Shapes. A schematic representation of the basic procedure we have used is sketched in Figure 1. Several types of constraints were used to determine the shapes: the area and shapes of the surfaces wet by the PDMS, the density of the supporting aqueous solution, and the magnitude of superimposed magnetic field (and apparent density) gradients. The wettable area of the constraining solid surfaces was provided by self-assembled monolayers (SAMs) on gold. Using an alkanethiolate SAM prepared from $HS(CH_2)_{15}CH_3$, hydrophobic regions were patterned on a thin gold film by contact printing;[20,21] a second, hydrophilic monolayer was formed around these hydrophobic regions using $HS(CH_2)_{15}COOH$. These surfaces were placed in an aqueous medium with density appropriately adjusted through addition of inorganic salts; if the density of the medium was matched to that of PDMS, the influence of gravity on the shape of the polymer disappeared, and the shape

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(16) The transmission efficiency is greater than 80% for $\lambda > 400$ nm for a 2.54 mm film (Publication No. 10-177-87, Dow Corning, Midland, MI, 1987).

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(19) This interfacial free energy was calculated from the contact angle, θ, of PDMS (104°) and the Young's equation, $\gamma_{SV} = \gamma_{SL} - \gamma_{LV} \cos \theta$.

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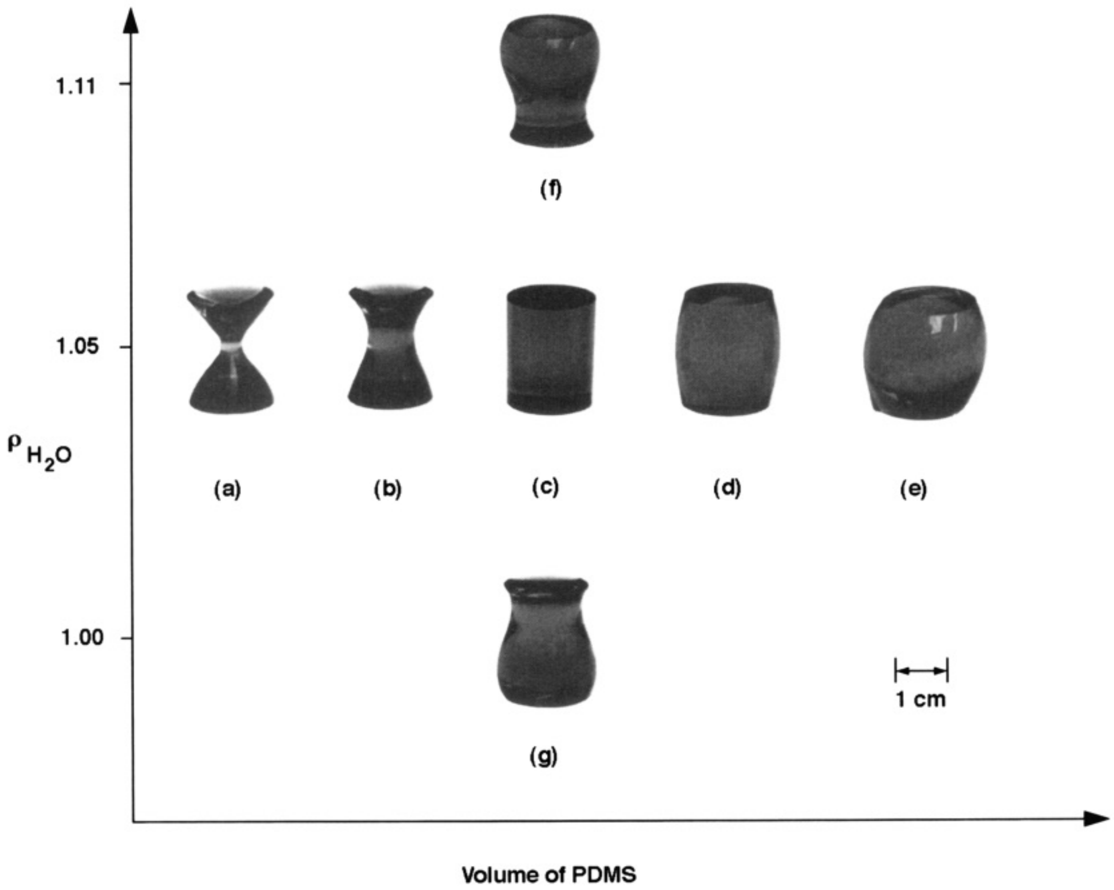

Figure 2. Shapes generated using two parallel, circular constraints wetted by PDMS. The volume of PDMS is normalized. Shapes *a*–*e* are generated in a medium of constant density, with $\varrho_{\mathrm{water}} = \varrho_{\mathrm{PDMS}}$, by varying the volume of PDMS. Shapes *f*, *c*, and *g* are generated by changing the density of the medium at constant volume of PDMS.

was determined only by the volume, the shape of the constraint, and the minimization of liquid–liquid interfacial free energies. A known volume of the liquid precursor (a commercially available prepolymer of PDMS, Sylgard 182) used to produce cross-linked PDMS was brought into contact with the hydrophobic regions of the surface(s) while the system was immersed in the aqueous medium; the hydrophobic polymer preferentially wet the hydrophobic regions of the surface but did not spread over the hydrophilic regions. The position of the objects that supported the patterned SAMs was fixed relative to one another, and the liquid polymer was allowed to cross-link to form an elastomeric solid. After cross-linking had proceeded sufficiently to fix the shape of the object in the aqueous medium, it was removed from the medium, separated from the constraining surfaces, and allowed to cure completely at room temperature for 24 h (or at 65 °C for 2 h). During cross-linking, PDMS undergoes a small change (~1–2%) in volume, and the overall shape of the polymer is maintained. The shape that was produced by this process was, thus, determined by fixing shapes of the contacts between the liquid and surfaces through patterning and preferential wetting and by allowing minimization of the interfacial free energy (that is, minimization of the surface area) of the system to determine the remaining surfaces. Since these are minimum free-energy surfaces, they are optically smooth.[22]

Figure 2 shows representative shapes formed by these processes. The shapes were formed in two planar, parallel surfaces having coaxial, circular hydrophobic patterns. In this system, the polymer minimized the surface area by adopting a catenoidal shape or a hyperboloid of one sheet. As the volume of polymer was increased for a fixed separation between the plates and area of the hydrophobic constraints, the surfaces of the PDMS pieces passed through a family of catenoids, *a*–*e*. A special case *c* exhibited a 90° contact angle of the PDMS with the surface: the resulting shape is a right circular cylinder. By varying the density of the aqueous media used to surround the PDMS, asymmetrical curvatures were obtained: *f* and *g*.

Non-right-circular cylinders were made by displacing one constraint (that is, one PDMS-wettable area) relative to the other in the plane of the parallel surfaces (Figure 3). Horizontal cross sections of *a*–*c* are isometric: that is, they have the same shape and size. When one surface was used instead of two, hemispheric shapes were formed. Figure 4 shows these shapes made using only one constraining surface: (a) a hemisphere, (b) a hemisphere fused with a square bottom, and (c) a hemisphere fused with a hexagonal bottom. The elastomeric character of PDMS allows these shapes to act as deformable lenses, where the focal length can be changed by compressing or stretching the lens.

Once these shapes are fabricated, they can themselves act as constraining surfaces for the formation of more complex structures. Figure 5 shows representative shapes, made in a multistage fabrication. First, elementary shapes such as cylinders, truncated cones, and catenoids were prepared in the procedure described

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(22) An analysis of these shapes by atomic force microscopy revealed that the outer surfaces are "smooth": no edges, folds, or defects of the dimension >0.1 μm were observed; Kim, E.; Whitesides, G. M.; Lee, L.; Smith, S.; Prentiss, M., submitted for publication in *Adv. Materials*.

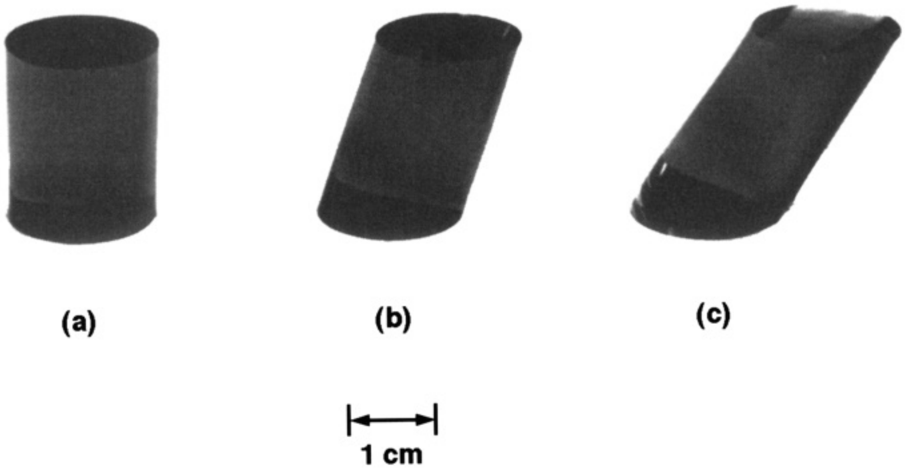

Figure 3. Various cylindrical shapes.

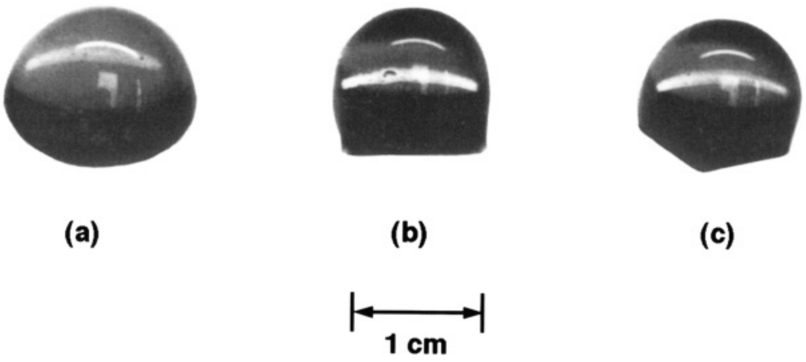

Figure 4. Various shapes from one constraint.

earlier. Using the flat, circular, hydrophobic surfaces of these structures and SAMs with circular hydrophobic patterns as constraining elements, the same procedure was used to fabricate more complex shapes: Figure 5a–c shows such structures. Figure 5a was fabricated using a polymeric cylinder and a SAM; 5b was prepared using one flat surface of a PDMS truncated cone and a SAM having a circular pattern; and 5c was prepared using one flat surface of a cylinder and a SAM having the circular pattern that was the same dimension as the end of the initially formed shape but placed at 45° relative to the top surface of the polymer. Figure 5d was prepared by only one constraining element, a PDMS shape that was a truncated cone. These shapes are only representatives of the many possible combinations of cylinders, catenoids, hemispheres, and other shapes that might be assembled using this type of procedure. Individual components of these "grafted" structures form chemical bonds (siloxanes) at the point of connection and maintain strong adhesion.

Other Forces. In addition to the forces of interfacial free energy, surface tension, and gravity, other types of forces can also be used to determine shapes in this type of procedure. One such force is that experienced by a diamagnetic object suspended in a paramagnetic medium and subjected to a magnetic field gradient.[23,24] In this situation, the apparent density of paramagnetic solution in the region of a magnetic field gradient is higher in the high-field region than in the low-field region (that is, its ability to support an object by buoyant forces is greatest when the magnetic field is highest). Figure 6 shows the effect of an applied, inhomogeneous magnetic field on the shape of the polymer. In the system we have used here—where the magnitude of the magnetic field is approximately constant over the volume of the PDMS (that is, the field gradient is low)—the shape adopted by the PDMS is similar to that formed in a more dense diamagnetic solution in the absence of a magnetic field. More complex shapes can be formed by using tailored magnetic fields and field gradients in the region of the shape being formed.

In a related procedure, one can add magnetic particles (such as magnetite) to the polymer and apply the magnetic field to influence the shape. We have carried out this type of procedure only with a magnetic field, but suspending particles with high dielectric constants in a polymer of low dielectric constant and superimposing an electric field gradient during curing should also influence shapes.

Lenses. Another type of shapes that can be fabricated by minimizing interfacial free energy is a lens.[14,25] In Figure 4, hemispherical planoconvex lenses were prepared by curing drops of polymer on the surface patterned with circular templates of SAMs. Here we injected a liquid prepolymer into the interface between two liquids that are immiscible with one another and with the liquid prepolymer; the shape of the PDMS lens was determined by a combination of interfacial and gravitational energies.

A series of convex–concave (or meniscus) lenses[26,27] were prepared with this procedure. Two liquid media

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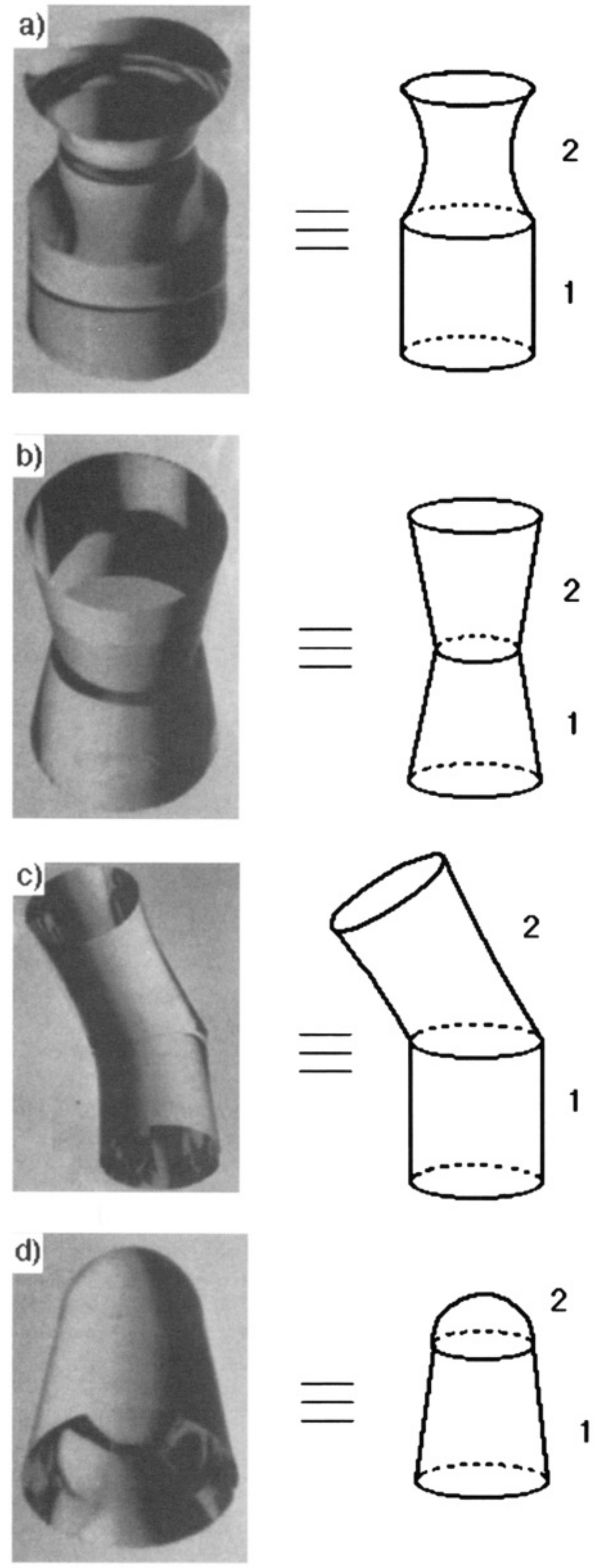

Figure 5. Secondary shapes generated using preformed shapes as constraints. (a) Shape formed by joining a catenoid and a cylinder. It was made using one end of a right cylinder and a circular element of a SAM as the constraints. (b) Shape formed by joining two truncated conical shapes. (c) Shape formed by joining a cylinder and a catenoid at 45° relative to one another. (d) Shape formed from a truncated cone. The diameter of the circular end section of these shapes is approximately 1 cm. In each shape, the number "1" indicates the pieces that was formed first, and "2" indicates the part that was added in the second step.

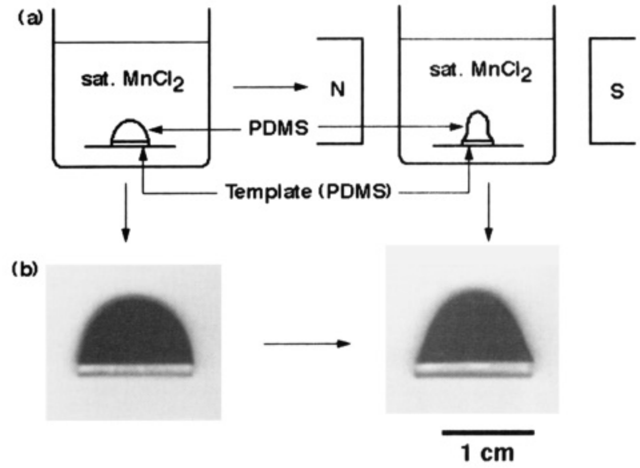

Figure 6. Using magnetic force to influence shape. (a) Schematic representation of the process. The constraint for this process was a PDMS film (Sylgard 182, Dow Corning) of a circular pattern. (b) The cross sections of the resulting shapes. The shapes are black due to a dark filling in the polymer (Sylgard 170, Dow Corning). The molarity of manganese(II) chloride in saturated aqueous solution is approximately 13 M. The magnetic field was applied using an iron horseshoe magnet; the maximum field strength (H) was approximately 4 kG, with magnetic field gradient $\mathrm{d}H/\mathrm{d}z \approx 2$ kG/cm.

that were immiscible with one another and with the liquid prepolymer of PDMS were selected: water and mercury. The density of water was adjusted with sodium chloride. The prepolymer of PDMS wets mercury completely, and the meniscus of mercury provided a template for the concave part of a lens. Under water, PDMS assumes a shape that minimizes the total free energy of the system. This system is a complex one, since five interfaces—mercury/glass, polymer/glass, water/glass, mercury/polymer, and polymer/water—and three gravitational terms—mercury, polymer, and water—are involved. The end result is that the interface between PDMS and mercury is concave, and that between PDMS and water is convex.

The overall size of the lenses were determined by the diameter of the test tube. A one-component, UV-cured PDMS (Optigard Q3-6662 or Q3-6696, Dow Corning) proved to be the most useful prepolymer to use in this type of fabrication (they are designed to be used in optical systems and contain little or no fillers). Figure 7A illustrates this process; the cross sections of representative lenses are also shown, together with the approximate focal length of each lens.

Double convex lenses could, in principle, also be prepared using two different immiscible polar solvents. Brine and different alcohols—methanol, 2-propanol, 1-butanol, and cyclohexanol—were used to illustrate the principle. Figure 7B shows the shape of lenses formed in different solvent systems. The quality of lenses prepared in this manner was not as good as the lenses shown in Figure 4, and the surfaces of these lenses had irregularities in shape and cloudy regions. Further development of this system would be required before it becomes useful in practice.

Microfabrication. The idea of determining shapes by minimizing surface free energy can be extended to fabricate small structures (micrometer scale). Because

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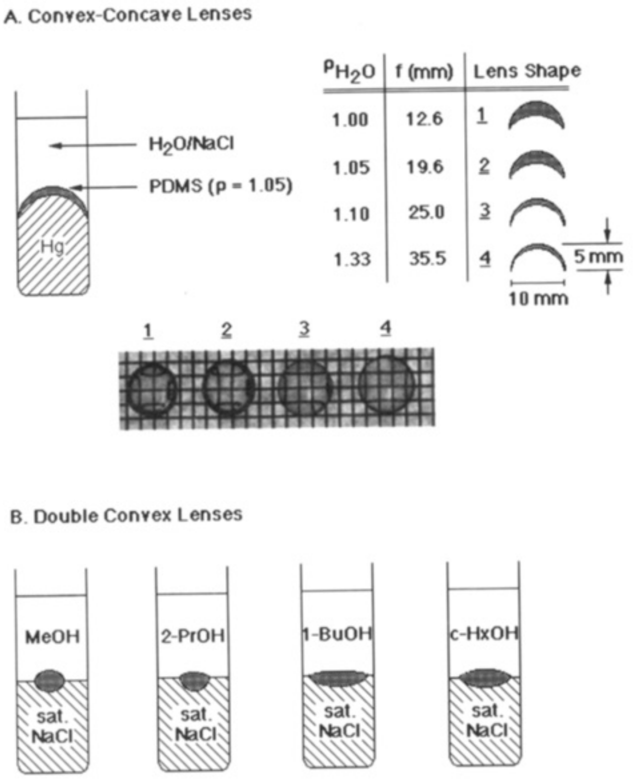

Figure 7. Fabrication of lenses. The shapes of lenses are approximated. (A) Schematic representation and photographs of convex–concave lenses. Photographs show the lensing properties of the lenses that are placed with their convex surfaces down, on a surface with perpendicular lines. Densities of aqueous solutions were adjusted by adding NaCl. The focal length of each lens was determined by shining a parallel beam through the lens from the concave side and finding the distance at which the beam was focused. The numbers (**1**, **2**, **3**, and **4**) in the table correspond to the same number in the photographs of the lenses. (B) Double convex lenses. MeOH, methanol; 2-PrOH, 2-propanol; 1-BuOH, 1-butanol; c-HxOH, cyclohexanol; sat. NaCl, saturated aqueous NaCl solution.

the forces that determine shapes remain constant to very small dimensions (certainly <100 nm), this type of procedure should be particularly useful in fabricating small objects with curved surfaces. Minimization of interfacial free energies has been used previously to fabricate arrays of microlenses by melting patterned polymer resists,[28] photocuring small drops of a polymer on a hydrophobic surface,[29] and thermally curing small drops of PDMS on a fluorinated surface.[30] The procedure we have explored for making small shapes involves the use of patterned SAMs having regions of different interfacial free energy to constrain the shape of the drops of prepolymer.

Microcontact printing (μCP) provides a convenient, efficient way of patterning SAMs.[20,21,31] Once a pattern consisting of hydrophobic and hydrophilic SAMs has been printed on gold, one can deposit an organic polymer selectively on the desired region of the surface. Organization of polymer on the patterned, *hydrophobic* surface has been described previously;[32] here, we describe a system in which the polymer is organized by wetting *hydrophilic* regions of the surface. Self-organized polymeric structures were formed as the result of minimizing interfacial free energy. Several polymers have been successfully used in this process: UV cured polyurethane (NOA 60 or 61, Norland) and PMMA (J-91, Summer), thermally cured PMMA (Norvlac resin), and thermally cured epoxy resin (Devcon). The best results were obtained with the UV-cured polymers because minimal shrinkage was observed with them.

Structures fabricated in this process may be useful in other applications. Polymeric, linear structures such as those shown in Figure 8a,b act as optical wave guides and have been used as masks in etching.[33] Microlens arrays (Figure 8c,d) focus light.[32] The lens array in Figure 8c was fabricated by μCP: a square pattern was generated by making two imprints of patterns of parallel lines at 90° relative to each other. Figure 8d shows another lens array made with a different surface pattern[34] (shown on the right top corner); even at this scale, all structures have smooth surfaces. We believe that it will be possible to fabricate a broad range of microstructures using this versatile process.

Conclusion

Self-assembly provides a method of making certain types of complex shapes without complementary molds or dies. There are many advantages to this procedure. It is possible to determine the shape of structures with a high degree of control using a combination of simple geometrical constraints, interfacial free energies, gravitational force, and magnetic or electric field gradients, in combination with differences in magnetic and dielectric properties of the materials in the system. A complex shapes can be generated in multistage processes, using preformed polymeric shapes. In principle, these procedures are scaleable to small dimensions (100 nm or less). The structures fabricated by this process have optically smooth surfaces that may be particularly useful to optical systems, and the flexibility in selecting different organic polymer provides an ability to optimize the utility for a specific optical system. The most important limitation of this process is that it has only limited ability to make flat surfaces without using solid constraining surfaces; the ability to form shapes with sharp angles is also limited. Making a hemisphere is straightforward; making a cube would be very difficult; making a spiral screw seems virtually impossible at present. It is, therefore, a technique that is applicable to only certain classes of shapes.

SAMs of thiolates on gold offer one method of generating constraints for three-dimensional shapes, but monolayers on other surfaces may prove useful. Siloxane on glass, silane on PDMS, and others may extend this procedure to other systems. We have shown that μCP is the most convenient way of patterning SAMs;

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(34) An interesting characteristic of these lens arrays is that small drops of polymer remained next to each microlens, on the hydrophobic region of the surface. This pattern reflect the dynamic breaking of a thin film of liquid polymer during the assembly of the polymer on the surface. It suggests another potential new avenue to microfabrication: that is, combining thermodynamic systems with dynamic ones.

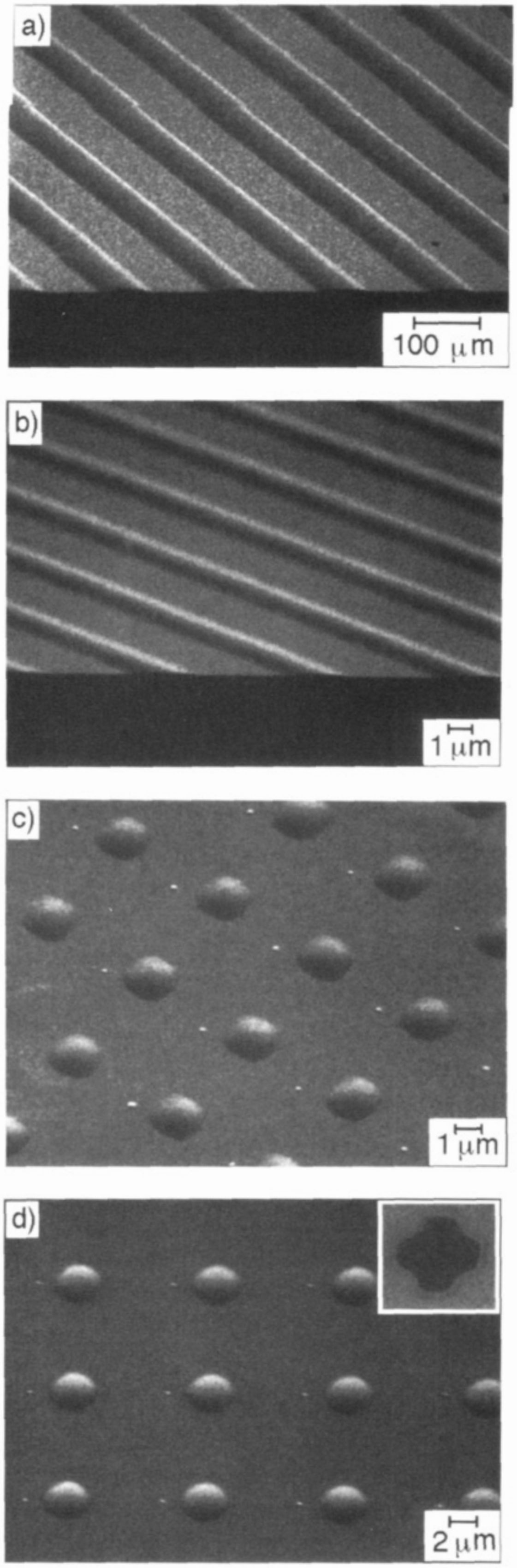

Figure 8. Microstructures fabricated using μCP and self-assembly of a polymer precursor. (a) Fracture view of polymeric lines (PMMA) ca. 45 μm wide and 3 μm high. (b) Fracture view of polymeric lines (PMMA) ca. 1.5 μm wide and ~0.3 μm high. (c) Microlens array made by μCP two line gratings at 90° relative to each other: the distance between lines was approximately 2 μm. (d) Microlens array made from μCP the pattern displayed at the right top corner. Note that some detail of the pattern is lost during the directed assembly of the polymer on the regions it wets.

however, other techniques such as microwriting,[35,36] electron-beam and UV lithography,[37,38] and micromachining[39] can offer other ways of generating constraints on gold and other surfaces. We have qualitatively demonstrated characteristics of shapes fabricated by various procedures, and finite element analysis[40] may provide a quantitative approach to relating the shape of the final structure to the various constraints defining the system.

Experimental Section

Materials. Thiols were available from previous studies or prepared by the procedure reported elsewhere.[41] Gold substrates were prepared by e-beam evaporation (rate: 1 Å/s, 250 or 500 Å) at a pressure of 1×10^{-7} Torr, using titanium as an adhesion promoter (rate 0.5 Å/s, 10 Å). The support for the metal layers was a polished single-crystal silicon wafer (Silicon Sense, Test grade). Macroscopic structures of PDMS were made with Sylgard 182 (Dow Corning), and macroscopic lenses were prepared with UV-curable PDMS (Optigard Q3-6662 or Q3-6669, Dow Corning). Before using PDMS and water, they were degassed separately under reduced pressure (20 mTorr) for 20 min. A prepolymer of polyurethane (NOA 60 or 61, Norland) and PMMA (J-91, Summer) were used as received.

Methods. Large features (~cm) of patterns were printed on gold using contact printing.[20,21] Stamps were made by standard lithographic fabrication procedures available as commercial services (Logan Stamp Works, Boston, MA). Ink pads for stamping were prepared by moistening a piece of lint-free cloth with a 1 mM solution of hexadecanethiol in ethanol.[20] Stamps used in μCP were made of PDMS (Sylgard, 184, Dow Corning).[20,21,31] They were "inked"[20] with an ethanolic solution of hexadecanethiol (2 mM) and placed in contact with the surface of the gold substrate for 5–10 s. The sample was rinsed with ethanol (~10 mL) and dried under a stream of N_2.

Photocurable polymers were irradiated with a UV light: Canrad-Hanovia 450 W medium-pressure, Hg vapor lamp (Type 7825-34, ACE Glass) with a water-cooled, quartz housing. Scanning electron microscopy was carried out with a JEOL JSM-6400. Polymeric structures were covered with gold by sputtering (Hummer II, Technics) before analyses by SEM.

Formation of Macroscopic Shapes of PDMS. A hydrophobic constraint on a gold film was patterned by contact printing.[20] A commercially fabricated stamp, which contained a circular pattern (1.3 cm diameter), was inked with hexadecanethiol in ethanol (1 mM). By contacting the stamp and gold (pressure ~30 g/cm^2; light finger pressure) for 5 sec at rt, the thiol was transferred to the gold substrate (250 Å, 10 Å Ti on silicon). The rest of the gold surface was rinsed with HS-$(CH_2)_{15}COOH$ in ethanol (~5 mL, 1 mM) to render it hydrophilic. After washing the derivatized surface with EtOH and water, it was placed under water whose density had been adjusted (to $\varrho \sim 1.05$ g/cm^3) by adding a saturated solution of NaCl. If more than one constraining surface was used, the relative location of the surfaces was adjusted. When a drop of prepolymer of PDMS (10:1 mixture of Sylgard 182 and Sylgard Curing Agent 182) was placed on the surface using a pipet, it preferentially wet the hydrophobic region ($-CH_3$ terminated SAM). After an appropriate volume of the polymer

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had been added, the density of water was fine tuned to match the density of PDMS by adding aqueous solution of saturated NaCl. The polymer was cured thermally. After the shape of the polymer was fixed (~12 h), it was removed from the aqueous medium, separated from the gold surface, and allowed to cure completely at 65 °C. This procedure was also carried out using UV-curable PDMS (Optigard Q3-6669) and curing photochemically.

Influencing Shapes Using Magnetic Forces. In a degassed solution of saturated aqueous $MnCl_2$ (from $MnCl_2 \cdot 4H_2O$, $M \approx 13$), a circular template (diameter = 1 cm) made of PDMS was placed (a patterned SAM on gold can also be used as a template). A degassed mixture of 1:1 Sylgard 170 A and Sylgard 170 B (Dow Corning) was transferred onto the PDMS template using a pipet and the polymer allowed to organize itself on the template. The system was then placed in a magnetic field ($H \approx 4$ kG) generated by a "horseshoe"-shaped permanent magnet. The entire volume of polymer was placed in between the two poles of the magnet ($dH/dz \approx 2$ kG/cm). The polymer was cured at room temperature for 2 h under the influence of the magnetic field, and the polymeric shape was removed from the aqueous medium and cured for additional 2 h at 60 °C.

Formation of Macroscopic Lenses. *Convex–Concave Lenses.* Mercury (3 mL) and aqueous NaCl solution (5 mL) were added to a test tube (diameter = 1.0 cm). The density of the water was adjusted by varying the concentration of the NaCl solution. A known volume of polymer (1 mL, Optigard Q3-6662 or Q3-6669) was added to the interface between the mercury and aqueous layers. After the polymer had organized itself at the interface, it was cured by placing the test tubes containing the polymer under a UV light (30 min at 15 cm away from the source). *Double-Convex Lenses.* The same procedure was used to make these lenses, except aqueous, saturated solution of NaCl and organic solvents (methanol, 2-propanol, *n*-butanol, and cyclohexanol) were used.

Patterning SAMs by μCP and Fabrication of Shapes Having Micrometer Dimensions by Self-Assembly. Elastomeric stamps were fabricated according to a published procedure.[20,21] This procedure was carried out *in air*, and a similar procedure was used to assemble organic materials, *under water*, on the patterned SAMs.[32] The stamp made of PDMS was "inked" with an ethanolic solution of $HS(CH_2)_{15}CH_3$ (1 mM) using a cotton swab, and the excess solvent was evaporated. Then the stamp was placed in contact with the gold surface for a few seconds. After removing the stamp, the gold surface was washed (~2 mL) with an ethanolic solution containing $HS(CH_2)_{15}COOH$ (1 mM). The patterned gold substrate was washed with ethanol and water and dried in a stream of N_2. A drop of a polyurethane prepolymer (NOA 60 or 61, Norland Optical) or a PMMA prepolymer (J-91, Summers Optical) was placed on the patterned gold surface using a pipet, and the excess polymer was removed either by tilting the surface at an angle to drain off the excess, or with a gentle stream of N_2. The prepolymer assembled selectively onto the hydrophilic region (−COOH) of the surface. The polymer was cured by exposing to the UV light for 30 min at 5 cm away from the source.

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