

Polymer microstructures formed by moulding in capillaries

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THE formation of patterned structures on micrometre-length scales is essential for the fabrication of many electronic, optical and mechanical devices¹. Patterning technologies are well established for semiconductors and metals, but are relatively undeveloped for organic polymers (with the notable exception of the specialized polymers used in photolithography¹). Polymeric replicas of some structures have been formed by filling them with monomers which are subsequently polymerized^{2,5}. But these procedures have important limitations, in that they usually involve the destruction of the template structure, or the resulting structures are not sufficiently regular for most applications. Here we describe a general moulding procedure which does not suffer from these limitations. For the mould we use the continuous network of channels formed when a substrate and a patterned elastomeric master are placed in intimate contact. A low-viscosity polymer precursor is placed in contact with the network, which then fills spontaneously by capillary action. After cross-linking the precursor, the master is removed (and can be reused), leaving a patterned polymer layer; depending on the choice of substrate, patterned free-standing films can be similarly produced.

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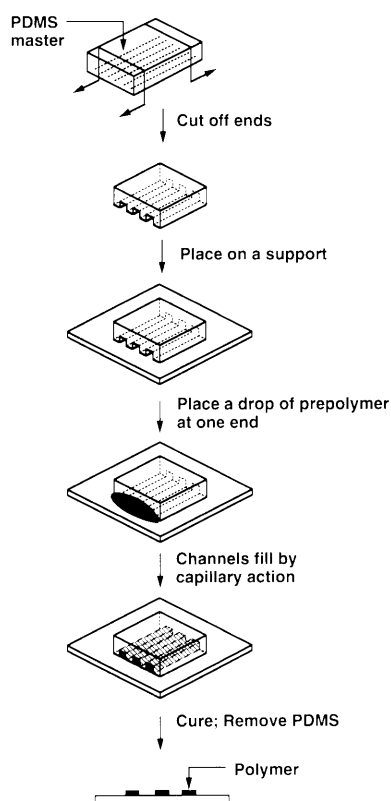


FIG. 1 Schematic diagram of capillary micromoulding of a pattern of parallel, rectangular channels. It is not necessary for both ends of the channels to be open: even if one end is closed, the channels fill with the prepolymer. The trapped air seems to escape by diffusing through the PDMS master.

Photolithography has successfully provided routes to planar and quasi-planar supported structures in the specialized polymers used as photoresists¹. Techniques for forming microstructures in structural and functional polymers would allow microfabrication of a broader range of organic materials. Here we describe a new procedure—micromoulding in capillaries (MIMIC)—for fabricating microstructures of polymeric materials (Fig. 1). We fabricate an elastomeric master that has a planar surface with a network of recessed channels by casting poly(dimethylsiloxane) (PDMS, Sylgard 184, Dow Corning) against a complementary relief structure (in turn prepared by photolithographic or non-photolithographic procedures)^{5, 8}. We cut the ends of this master so that the network of channels is open and allows the liquid prepolymer to enter. The master is placed on a support; the patterns in the surface of the master form a network of channels. When a drop of a liquid prepolymer is placed at one open end of this network, the liquid spontaneously fills the channels by capillary action. The initial rate at which a prepolymer of polyurethane (J-91, Summers) moved along a channel with approximate cross-sectional dimensions $3.0 \times 1.5 \mu\text{m}$ over a solid support of Si/SiO₂ was $\sim 0.5 \text{ mm min}^{-1}$. The prepolymers were cross-linked thermally (at 65 °C for 1–2 h, for thermally cured epoxies) or photochemically (thin PDMS films are optically transparent)⁹. Once the polymer had cross-linked sufficiently, the PDMS stamp could be removed from the support. These cross-linked polymers did not adhere to PDMS, and the patterned polymeric layer remained on the support.

This process generates negative replicas of the patterns on the surface of the master. Features having flat edges and acute angles can be prepared (Fig. 2*a, b*); the edge resolution obtained in the polymeric structure is determined by the PDMS stamp. We have

prepared samples with the complexity of those in Fig. 2 with macroscopic dimensions of several square centimetres.

MIMIC can also be used to fabricate free-standing films, using two procedures. In the first, the polymer structure is formed on a solid support and then freed by dissolving, melting or vaporizing that support. For example, Fig. 2*c* shows a complex patterned structure that has been removed from a Si/SiO₂ surface by dissolving the oxide layer in an aqueous solution of NH₄F/HF; the folding in the sample demonstrates its structural integrity. We have prepared other free-standing films by removing the support using appropriate conditions, such as dissolving

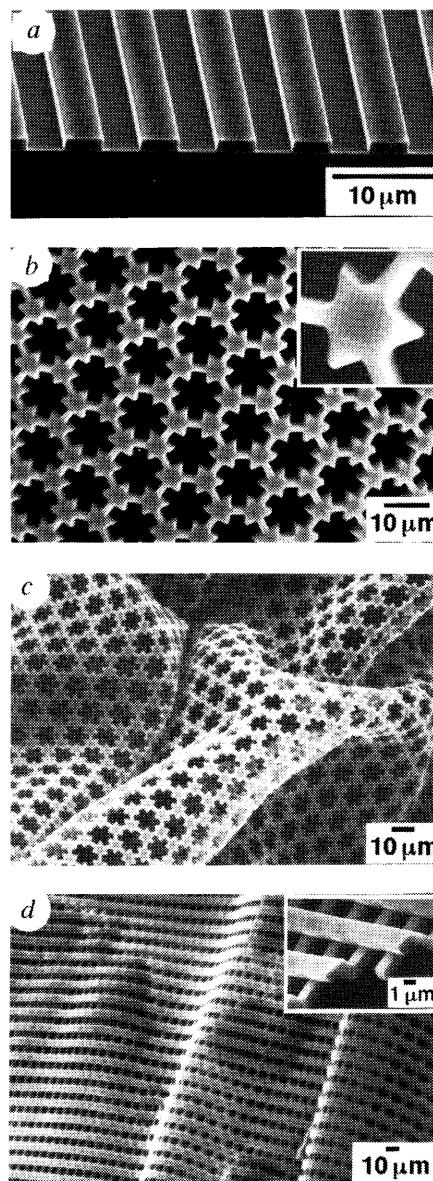


FIG. 2 Patterns fabricated by MIMIC. Patterns were sputtered with gold before imaging by scanning electron microscopy. The polymer used was photocured poly(methylmethacrylate). *a*, An oblique image of a fractured sample showing rectangular slabs of polymer on a gold film supported on Si/SiO₂. *b*, Image (captured at 30°) of more complex patterns on a silicon wafer. *c*, A free-standing film: the same film as in *b* was released from the surface by dissolving the SiO₂ layer in NH₄F/HF. The folding in this region of the sample was accidental, but illustrates the flexibility of the film. *d*, A free-standing polymeric structure fabricated in channels formed by conformal contact of two PDMS masters like those in *a*, using an orientation in which the grooves of the two masters were perpendicular. The two layers of the channels formed one interconnected polymeric structure (inset).

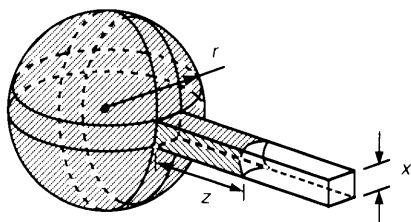


FIG. 3 A model for capillary micromoulding.

glass in HF, single-crystal NaCl and KCl in water, polymer films in solvents (for example, acetone for a film of a photoresist), or melting (paraffin film). In the second, the polymeric structure is formed between two PDMS masters. After filling with and cross-linking the precursor, the polymeric structure was removed from the master using Scotch tape or tweezers (Fig. 2*d*). This type of structure—two layers with independent structure in each—cannot be fabricated by photolithography in a single step.

The three components of the system used for MIMIC—the elastomeric master, the support, and the liquid prepolymer—must have certain characteristics. The master must be elastomeric, have a low surface free energy, and be unreactive towards the prepolymer. PDMS is sufficiently elastomeric that it makes conformal contact with supports that are rough on the 100-nm scale⁷; this contact limits the lateral spreading of the prepolymer by capillarity into the regions in contact with the stamp. Because the PDMS master and the support adhere without applying external force, the process reproduces features in the surface of the master accurately. Even the low interfacial free energy of the surface of the PDMS master ($\gamma_{\text{PDMS-air}} = 21.6 \text{ dyn cm}^{-1}$; ref. 10) is sufficient to maintain adhesion between the master and the support. The PDMS component has very low reactivity towards the prepolymers under the curing conditions used here. Its elasticity is sufficient to allow its separation from the polymeric microstructures; if it was not an elastomer, this separation could be difficult or impossible.

We have used many different supports in MIMIC, including Si, SiO₂ (both native and thermally grown), Ni, NiO, Ti, TiO₂, platinum, glass, gold, NaCl, and SiO₂ covered by self-assembled monolayers (SAMs), and films of organic polymers. It is often helpful that the surface energy of the support is higher than that of PDMS as this ensures selective adhesion of the polymer being moulded to the support (rather than to the master), but it may not be necessary. The ability to tune precisely the surface properties of SAMs on gold and SiO₂ (refs 11, 12) makes these supports particularly useful. The support need not be flat; we have successfully used curved surfaces (glass) with radii of curvature from 0.25 to 1.0 cm. A PDMS master formed as a thin ($\sim 100 \mu\text{m}$) film can adhere to a curved surface without losing the fidelity of the stamp. The support can also be a polymeric surface (with or without recessed patterns) (Fig. 2*d*).

The liquid prepolymer should have low viscosity ($< 400 \text{ cP}$) to allow flow through the capillary; it should have small volume changes ($< 3\%$) on curing; and it should wet the support (or the master, or both) at least partially; complete wetting, however, is not necessary. We have used several prepolymers successfully, for example ultraviolet-curable poly(methylmethacrylate) (SK-9, Summers Optical), ultraviolet-curable epoxies (UV15, UV15-7, Master Bond), heat-curable epoxies (F113, F114, TRA-CON), ultraviolet-curable polyurethanes (J-91, Summers Optical; NOA 60, 71, 72, 73, 88, Norland), heat-curable polyurethane (NOA 133, Norland) and ultraviolet-curable poly(methylacrylate) (SJ-7, Summers Optical). Photocurable polymers were irradiated with an ultraviolet light (Canrad-Hanovia 450 W medium-pressure, mercury vapour lamp Type 7825-34) for 10–20 min at a distance of 1–2 cm from the sample. It is important that the prepolymer has low viscosity and that it cross-links under achievable conditions.

The most important concept of MIMIC is that the liquid organizes and forms patterns as a result of capillary forces. The changes in interfacial free energies for a liquid moving from a spherical drop (radius r) into a hollow tube with a square cross-section (width x) are given by equations (1) and (2) (Fig. 3)^{13–15}. Here three surfaces are assumed identical (the PDMS) and one different (the support). The terms γ_{SV} , γ_{SL} and γ_{LV} are solid vapour, solid liquid and liquid vapour interfacial free energies, respectively; θ and θ' are the contact angles of the liquid prepolymer on the surface of PDMS and the support.

$$\Delta G = \gamma_{\text{LV}} \Delta A^{\text{sphere}} - f(\gamma_{\text{SL}}, \gamma_{\text{SL}}) \Delta A^{\text{channel}} \quad (1)$$

$$= x^2 \Delta z \gamma_{\text{LV}} / r - [3x \Delta z (\gamma_{\text{SV}} - \gamma_{\text{SL}}) + x \Delta z (\gamma_{\text{SV}} - \gamma_{\text{SL}})] \quad (2)$$

$$\approx -[3x \Delta z (\gamma_{\text{SV}} - \gamma_{\text{SL}}) + x \Delta z (\gamma_{\text{SV}} - \gamma_{\text{SL}})] \quad (3)$$

$$\approx -x \Delta z \gamma_{\text{LV}} (3 \cos \theta + \cos \theta') \quad (4)$$

When $r \gg x$ and the term due to the drop of liquid prepolymer can be neglected, equation (2) becomes equation (3) (or the equivalent, equation (4)). These equations demonstrate that this process is dominated by the free energies of the solid vapour and solid liquid interfaces. Only when $\gamma_{\text{SV}} - \gamma_{\text{SL}}$ (and/or $\gamma_{\text{SV}} - \gamma_{\text{SL}}$) are negative (a situation that normally correlates with high γ_{LV}) will the capillary not fill. As an approximation, this capillary force is positive, that is, the liquid spontaneously fills the capillary, for any value of θ and θ' between 0 and 90°; the liquid wicks through the capillary when the liquid wets or partially wets the inside of the capillary¹⁶. The capillary force is negative for liquids with high values of γ_{SL} and γ_{SL} ($\theta > 90^\circ$ and $\theta' > 90^\circ$); these liquids do not fill the capillary. If $\theta > 90^\circ$ and $\theta' < 90^\circ$, the balance of forces becomes ambiguous. An example of this last case is water when the master is PDMS, and the support is a partially hydrophilic SAM ($-\text{COOCH}_3$ terminated) on gold ($\theta = 105^\circ$; $\theta' = 60^\circ$); we need to add surfactant or an organic solvent such as ethanol ($\sim 5\%$ is sufficient) to the water to achieve flow through the capillary. The surface of PDMS may also be modified to increase the interfacial free energy and to ensure wetting by a liquid¹⁷. We usually allow the capillarity to fill the channels while they are oriented perpendicular to the force of gravity. If the channels were filled against (or with) the force of gravity, the force acting to fill the capillary will be reduced (or augmented) by $F' = x^2 h \rho g$, where h is the height of the liquid in the capillary, ρ the density of the liquid, and g the gravitational constant.

The surface tension and viscosity of the liquid, the size of the capillary, and the length of the channel determine the rate of liquid flow in the capillary (equation (5))¹⁵:

$$\frac{dz}{dt} = \frac{R \gamma_{\text{LV}} \cos \theta}{4 \eta z} = \frac{R (\gamma_{\text{SV}} - \gamma_{\text{SL}})}{4 \eta z} \quad (5)$$

where R is the hydraulic radius (the ratio between the volume of the liquid in the capillary section and the area of the solid and liquid interface), η the viscosity of the liquid, and z the length of the column of liquid. Our experimental results are qualitatively consistent with this relationship. Equation (5) indicates that the filling of very small capillaries will be slow because R will decrease as the dimensions of the capillary decrease. We have observed the filling of sections of capillary that were approximately $1.0 \times 0.1 \mu\text{m}$ in cross-section, but for a short distance only.

Capillary micromoulding has several useful differences from conventional photolithography as a method of forming polymeric microstructures. Photolithography requires two steps: forming (usually by spin coating) and patterning photoresist films. MIMIC requires one: forming and patterning the polymeric films occur simultaneously. Photolithography requires one exposure per structure; the master in MIMIC can be used many times, and photolithography is used only once (if at all) to make the master. Photolithography is limited to special classes of polymers and photosensitizers; MIMIC is applicable to most polymers with low viscosity. Photolithography is a two-dimensional

process: patterning layers with different thicknesses is impossible in a single step.

Micromoulding driven by capillarity is remarkable for its simplicity, for the fidelity with which the patterns present in the mould are preserved in the polymer, and for the effectiveness with which capillarity fills the channels. □

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