

Experimental

The monomers **IIa** and **IIb**, and the precursor polymers **Ia** and **Ib**, were prepared according to literature procedures [5,6a]. For example, 1,4-phenylene dimethylene-bis-(tetramethylene sulfonium chloride) **IIa** was synthesized by adding 15 ml tetrahydrothiophene to 10 g α,α' -dichloro-*p*-xylene in 150 ml methanol. The reaction mixture was kept at 50 °C for 4 days and then concentrated to gelation. The bis-sulfonium salt was precipitated by addition of 250 ml of ice-cold acetone and isolated by filtration. The precursor polymers were synthesized by dissolving the 0.02 mol of bis-sulfonium salts in 200 ml of water. The solution was stirred for 0.5 h under nitrogen at 0–2 °C and a stoichiometric amount of 1 N NaOH solution was added and vigorously stirred for 0.5 h. The reaction mixture was neutralized with 1 N HCl. The solution was homogenized and dialyzed (MW cutoff 12,000) at 4 °C for 10 days.

Sol-gel-PPV glass composites were prepared as follows:

Method 1. Titania sols containing the precursor polymers **Ia** and **Ib** were prepared by dissolving 5 ml of titanium tetraethoxide in 20 ml ethanol and 5 ml glacial acetic acid and refluxing for 3 h [15]. After cooling a solution of 0.7 dry wt.-% **I** was added. Films were then deposited on glass substrates by dip-coating using a withdrawal speed of 20 cm/min. After drying of the film for 24 h, the elimination reaction was carried out by heating at 250 °C at 10^{-6} torr.

Method 2. Titania sols were prepared as above and 2.9 g of monomer **IIa** was added. The zirconia sol was prepared by dissolving 5 ml of zirconium tetrapropoxide in a 4 ml acetic acid/10 ml 1-propanol solution. Hydrolysis took place by slowly adding 6 ml of a 1:2 by volume water/acetic acid solution. 2.5 g of **IIa** was then added, along with further addition of the water/acetic acid solution as required, to retain a clear solution. After film deposition by dip coating as described above, polymerization was carried out by dipping the film in base (5 N NaOH or Triton B). Residues of the base were removed by washing the film in ethanol. Immediately after dipping the film in ethanol, the typical yellow color was generated.

Waveguide films were prepared by method 2. The refractive index was measured using a He-Ne laser in the so-called Kretschmann geometry [17]. In this method the film is coated onto a 45 nm silver layer, and the laser light coupled through the silver to the guided modes. The angular positions of these modes allow the determination of the thickness and the index of refraction of the film.

The fluorescence from the guided modes was measured using planar leaky light-guides [17], and recorded using a Zeiss MMS1 spectrometer. The exciting laser was an Omnichrome 543-150BS 100 mW Ar ion laser operating at 488 nm. PL spectra were recorded on a Perkin Elmer luminescence spectrometer LS 50. Analysis for sulfur in the composite films was carried out by using a Link 10000 EDS connected to a JEOL 840 SEM.

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Fabrication of Three-Dimensional Micro-Structures: Microtransfer Molding**

By Xiao-Mei Zhao, Younan Xia, and George M. Whitesides*

This paper describes a new technique—microtransfer molding (μ TM)—for forming complex, three-dimensional microstructures of organic polymers and ceramics. In this technique, microstructures are formed by filling microchannels on the surface of an elastomeric mold with a liquid precursor, and then bringing the mold into contact with a planar or contoured substrate. The liquid precursor is caused to solidify in situ either thermally or photochemically. The elastomeric mold is then peeled away, leaving the resulting microstructures on the surface of the substrate. Figure 1 outlines a representative process.

Photolithography,^[1] molding,^[2–4] embossing,^[5–7] and related techniques^[8–10] are commonly used in fabrication of microstructures of polymeric materials. Photolithography is an extremely useful technique that can routinely generate micrometer- to submicrometer-sized structures. It is, however, restricted to planar substrates, small areas (per exposure), and specialized polymers. Molding and embossing have been used primarily in forming patterns in polymeric materials with feature sizes in the region of 1–50 μ m; these techniques are now being reexamined for their utility in forming sub-micrometer and nanometer-scale features with very promising initial results.^[6,7]

We have recently described a technique for forming microstructures in polymers and sol-gel systems: micro-molding in capillaries (MIMIC).^[11] MIMIC fabricates microstructures by generating a network of capillaries by contact of an elastomeric master with a surface embossed with an appropriate relief structure, and allowing liquid precur-

*] Prof. G. M. Whitesides, X.-M. Zhao, Y. Xia
Department of Chemistry
Harvard University
12 Oxford Street, Cambridge, MA 02138 (USA)

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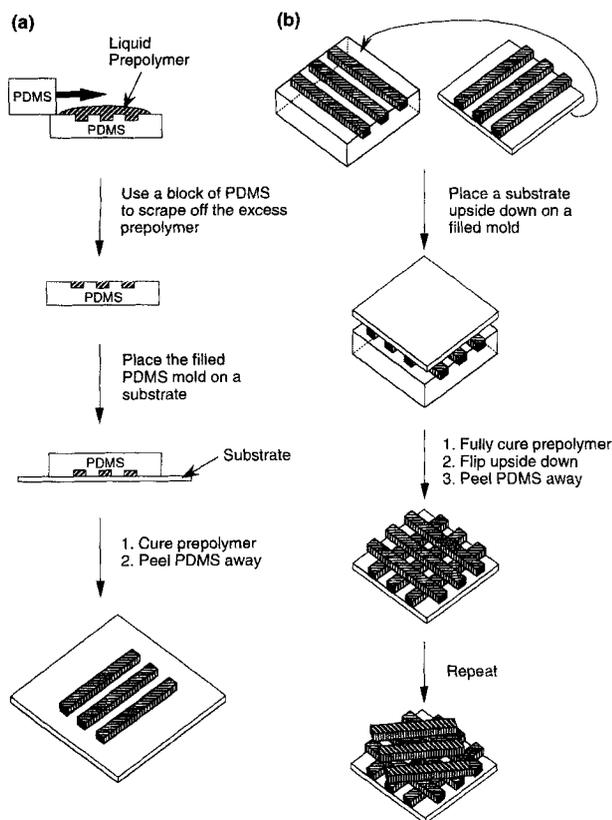


Fig. 1. A schematic diagram of microtransfer molding (μ TM) for fabrication of a) one-layer microstructures, and b) three-layer polymeric microstructures.

sor to fill the channels by capillary action. It is experimentally simple, and capable of forming structures down to approximately $2\ \mu\text{m}$ in size. It has the disadvantage that it is relatively slow. The rate of filling of the capillaries by the liquid prepolymer is inversely proportional to the distance over which the liquid has traveled. It normally takes hours for a prepolymer with viscosity = $300\ \text{cP}$ to fill in a $1\ \text{cm}$ -long capillary. In our experience, the maximum length of a channel that can be filled is $\sim 1.5\ \text{cm}$. Moreover, it relies on capillary filling and requires a continuous network of capillaries; it cannot, therefore, make isolated patterns or patterns on contoured surfaces.

μ TM has many useful characteristics. First, it is rapid: it can replicate microstructures from an elastomeric mold within five minutes. Second, μ TM can generate both isolated and interconnected structures. Third, μ TM can make microstructures on contoured surfaces—a characteristic that is essential for fabricating 3-D structures layer by layer. Fourth, μ TM can make functional microstructures over a large area: as an example, we have filled $3.5\ \text{cm}$ -long channels. Fifth, structures made of two-component materials (i.e., a polymer doped with a dye) using μ TM have a uniform concentration of the dopant over the whole pattern; similar structures fabricated using MIMIC may have a gradient of concentration in the components along the direction of filling, due to the adsorption of one component by

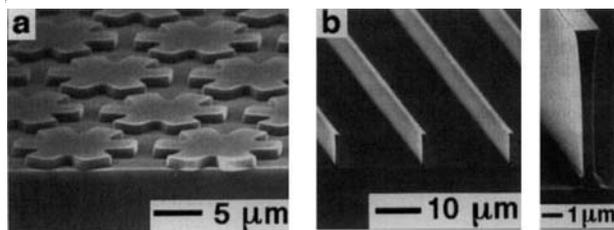
the PDMS master as the prepolymer fills the channels. Sixth, μ TM is applicable to a wide range of materials. We have successfully made microstructures of both polymers and ceramic precursors (spin-on glass, ZrO_2) on a range of substrates (glass, Ag, Au, Si, Si/SiO₂). Because μ TM is a fast process, it is much less sensitive than MIMIC to a change in viscosity of the prepolymer over the time the process is being carried out. For example, it can fabricate $3\ \text{cm}$ -long polymeric waveguides using a heat-curable polymer whose viscosity increases rapidly after the prepolymer is mixed with its initiator.

Figure 1a shows a schematic procedure used for μ TM. We fabricated an elastomeric mold (usually from poly(dimethylsiloxane), PDMS) with a relief structure on its surface using the procedures developed for use in microcontact printing (μ CP).^[12,13] The thickness of the PDMS mold used here was controlled to be $< 2\ \text{mm}$ to ensure the flexibility of the mold. A drop of liquid prepolymer was placed on the patterned surface of the mold and the excess prepolymer was removed. The most general procedure for removing excess polymer was to scrape it away using a piece of flat PDMS; alternatively, with appropriate structures, the excess polymer could be removed by blowing it off the surface of the mold with a brisk stream of nitrogen. When necessary, after using a flat piece of PDMS to remove excess polymer, a stream of nitrogen could be used to blow away a few visible drops of prepolymer left on the raised areas of the mold. The filled mold was placed in contact with a substrate. The prepolymer was then fully cured thermally or photochemically and the mold was peeled away. The whole process, except for the cure of the prepolymer, took less than 5 min.

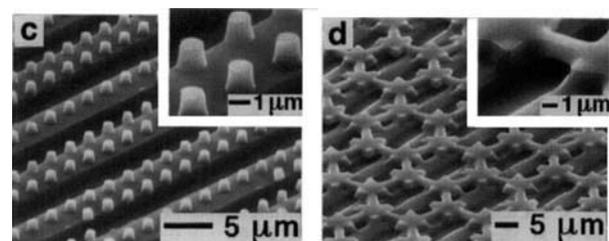
Figure 1b outlines the process used to fabricate multi-layer structures using μ TM. A heat-curable liquid epoxy (F109CLR) in the surface relief structure of a PDMS mold was partially cured at $65\ ^\circ\text{C}$ for 25 min. The pre-cure of the prepolymer increased its viscosity, and thus greatly reduced the possibility that the prepolymer in the grooves of the mold would be drawn into gaps in the microstructure of the first layer by capillarity. A substrate, the surface of which had already been patterned with one layer of a microstructure, was placed upside down onto the mold with a pre-cured, filled relief structure. The whole system was then fully cured at $25\ ^\circ\text{C}$ for 24 h. The PDMS mold was peeled away and a two-layer microstructure was obtained. The process was repeated to make the third layer.

μ TM is able to generate both isolated and interconnected microstructures using a broad range of materials. Figure 2a shows an SEM image of a pattern of isolated stars of UV-curable polyurethane on Ag. The features had flat edges and acute angles. μ TM can also make interconnected structures. The lines shown in Figure 2b were made of spin-on glass^[14] on a Si wafer. The cross-section of the SiO₂ lines was inverse trapezoidal because the lines of polymer on the photoresist master that we used to make the PDMS molds also had the same shape. Polymers are generally not suitable

1-layer microstructures



2-layer microstructures



3-layer microstructures

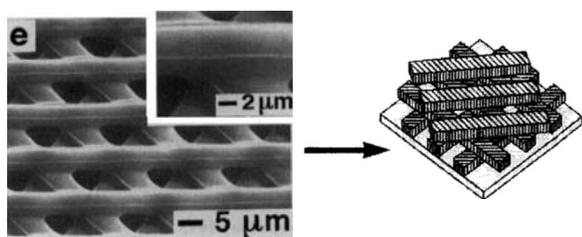


Fig. 2. Microstructures fabricated using μ TM. a) An SEM image of a fractured sample showing a pattern of isolated stars of UV-cured polyurethane (NOA 73) on Ag. b) An array of parallel lines of spin-on glass on Si with an aspect ratio (height/width) of ~ 8 . c) A two-layer structure: isolated microcylinders ($1.5 \mu\text{m}$ in diameter) on $5 \mu\text{m}$ -wide lines, supported on a glass cover slide. d) A two-layer structure: a continuous web over a layer of $5 \mu\text{m}$ -wide lines, supported on a glass cover slide. e) A three-layer structure on a glass cover slide. The layers of $4 \mu\text{m}$ -wide lines are oriented at $\sim 60^\circ$ from each other. Structures in c–e were made of heat-cured epoxy (F109CLR). All the samples were coated with $\sim 20 \text{ nm}$ of Au before the SEM images were taken.

ble materials with which to make structures with high (e.g. ~ 8) aspect ratios due to their fragility. The maximum height of the structures we have made is $\sim 9 \mu\text{m}$, and highest aspect ratio for these structures is ~ 8 .

The most significant advantage of μ TM over other techniques of microfabrication is the ease with which it can fabricate microstructures on non-planar surfaces. Figure 2c shows microcylinders ($\sim 1.5 \mu\text{m}$ in diameter) of thermally cured epoxy fabricated on an array of $5 \mu\text{m}$ -wide lines. It was also possible to make a continuous polymeric web over separated polymeric lines (e.g., Fig. 2d). The mechanical strength of the epoxy limited the type of structures that we were able to make: continuous polymeric webs could only be fabricated over polymeric lines that were separated by a distance that was less than 2.5 times the smallest dimension of the microstructures in the web. Otherwise, the free-standing parts of the web were torn off during the step in which the PDMS mold was peeled away from the cured polymer.

We used μ TM to fabricate 3-layer structures (Fig. 1b). A typical example is shown in Figure 2e. As explained previously, pre-cure in fabrication of the 2nd and 3rd layers (Fig. 1b) increased the viscosity of the prepolymer in the grooves of the PDMS mold and thus helped to prevent the liquid precursor from being pulled by capillarity into the empty spaces in the structures of previous layer(s). Even when fabricated with care, the edges of lines shown in Figure 2e were still a little softened and blurred. Three-dimensional microstructures are interesting for possible use in areas such as optics (for example, photonic band gap structures),^[15,16] and tissue engineering.^[17]

μ TM is able to make microstructures with much larger linear dimensions than MIMIC. Figure 3 shows the top (a)

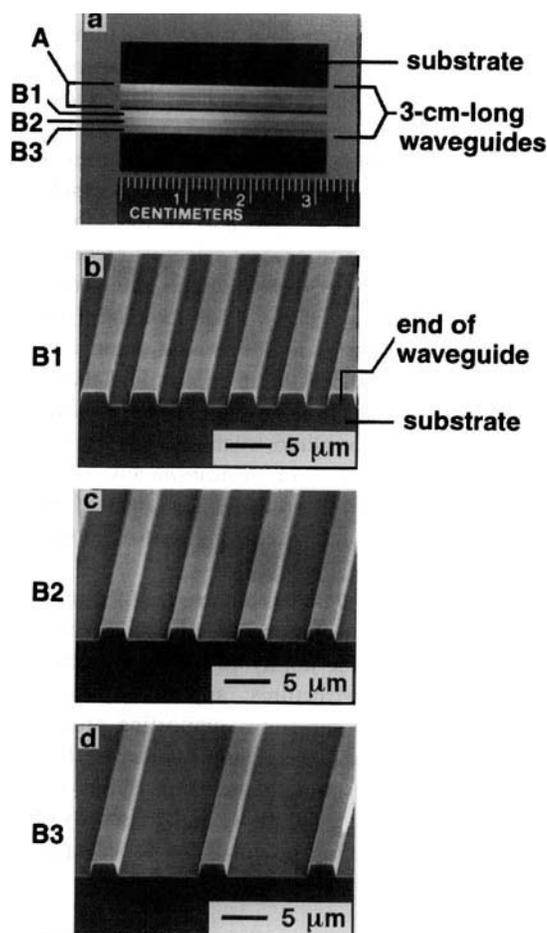


Fig. 3. a) A photograph of an array of 3 cm-long waveguides fabricated on Si/SiO₂. The waveguides were made of UV-curable polyurethane (NOA 73). b–d) SEM images of ends of the waveguides. The photograph (a) was taken when the sample was illuminated with a table lamp. The pattern used had an array of different sized channels and spacings: these structures give rise to different patterns of refracted light in this photograph. As shown in (a), there are two $0.4 \text{ cm} \times 3 \text{ cm}$ areas (area A and area B) of waveguides, and three parallel subsections (subsection 1, 2, and 3) in each area. The size of the waveguides in area A was $2.6 \mu\text{m} \times 1 \mu\text{m} \times 3 \text{ cm}$ (width \times height \times length), and in area B was $3 \mu\text{m} \times 1 \mu\text{m} \times 3 \text{ cm}$. The ends of the waveguides in section B1, B2, and B3 are shown in SEM images (b), (c), and (d), respectively. The arrangement of waveguides in area A is the same as that in area B except that the widths of the waveguides are different ($2.6 \mu\text{m}$ in area A and $3 \mu\text{m}$ in area B, respectively).

and side (b–d) views of 3 cm-long waveguides of polyurethane (NOA 73) fabricated on a silicon wafer covered with a 2 μm -thick layer of thermal silicon dioxide (Si/SiO_2). Light from a laser was coupled into a waveguide by butting the end of the optical fiber against the end of the waveguide.^[18] These waveguides ($n = 1.545$) with cross-sections of $\sim 3 \mu\text{m}^2$ supported multi-mode transmission of light with $\lambda = 633 \text{ nm}$ or 488 nm . We have made 3 cm-long waveguides using polyurethanes, epoxies, and rhodamine-doped polyurethanes and epoxies. A dye-doped waveguide emitted green light from fluorescence when light ($\lambda = 0.488 \mu\text{m}$, blue) propagating in a waveguide excited the dopant.

μTM has limitations. Microstructures fabricated on a flat surface using μTM may have a thin ($< 0.1 \mu\text{m}$) film between polymeric features; we assume this film is formed by some combination of transfer of prepolymer from the raised surfaces of the mold, and capillary wicking of prepolymer from the relief structures. The film is sometimes too thin to be visible under a SEM, but it prevents the underlying substrate, such as Si, from being attacked by chemical etchant. When we wished to use the polymeric microstructures as resists to control selective etching of the underlying substrate, we removed this interfering film successfully using O_2 reactive ion etching (RIE) (44 W, 13 sccm, 180 mTorr). Even without removing this film, however, μTM is successful in applications that are insensitive to its existence. One example is the fabrication of multilayer structures or microstructures on contoured surfaces (Fig. 2c–e). In this type of fabrication, any small amount of liquid prepolymer left on the raised areas of the mold appears to retract to the preexisting contoured surface by capillarity.

We believe that μTM has a number of features that make it attractive as a technique in fabrication of microstructures: simplicity; the ability to fabricate both single- and multi-layer microstructures; applicability to non-planar substrates, and to substrates supporting preexisting complex microstructures; speed; applicability to the fabrication of structures over large areas; compatibility with a broad range of materials; insensitivity to the viscosity of these materials—all suggest the potential for broad applications in microfabrication.

Experimental

The elastomeric mold was made from poly(dimethylsiloxane), (PDMS, Sylgard 184, Dow Corning, Silicone Elastomer) as described previously [12,13]. The filled thin ($< 2 \text{ mm}$ thick) PDMS mold was brought carefully into contact with the substrate to prevent air bubbles from being trapped between the mold and the substrate. We have used UV-curable polyurethanes (NOA 73, Norland Products; J-91, Sumner Optics), heat-curable epoxies (F109CLR, F109, F114, Tra-Con), rhodamine-doped polymers (NOA 73, J-91, or F109CLR, saturated with rhodamine 590 chloride, Exciton), and precursors for SiO_2 , and ZrO_2 to make microstructures on various substrates, such as Ag, Au, glass, Si, and Si/SiO_2 . Photo-curable polymers were irradiated with a UV light (Type 7825-34, Canrad-Hanovia 450 W medium-pressure, Hg vapor lamp) for 25 min, with samples placed at the distance of ~ 1 –

2 cm from the lamp. Heat-curable polymers were cross-linked at 65°C for 4 h or at 25°C for 24 h. The composition of the spin-on glass was 25 % of the mixture of tetraethylorthosilicate (TEOS)/water (pH 1, using HCl as catalyst) = 1/2, and 75 % of ethanol. The precursor of ZrO_2 was a suspension of the precursor polymer for ZrO_2 (Chemat Technology) in ethanol (10 % w/w). After the filled mold and the wafer were brought into contact, the solvent in the precursor of SiO_2 or ZrO_2 was evaporated by heating on a hot plate at 100°C for 20 min.

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Microemulsion Polymerization: New Surfactant Systems by Counterion Variation**

By Markus Antonietti,* and Hans-Peter Hentze

Polymerization in microemulsions allows the synthesis of ultrafine polymer latices in a size range $5 \text{ nm} < R < 50 \text{ nm}$ with a narrow particle size distribution.^[1,2] The chemical nature of the very large surface area of such latices, of up to $300 \text{ m}^2/\text{g}$, is easily controlled by simple copolymerization with functional co-monomers, resulting in surfaces with high densities of functional groups.^[3,4]

One big disadvantage of this polymerization technique which prohibits larger scale technical application is that large amounts of surfactant are usually required, typically 1 to 3 g surfactant per gram of polymer. In addition, microemulsions are formed only by a few surfactants.^[2] The great

[*] Prof. M. Antonietti, H.-P. Hentze
Max-Planck-Institut für Kolloid- und Grenzflächenforschung
Kantstrasse 55, D-14513 Teltow-Seehof (Germany)

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