Hollow, nanoscale SiO$_2$ particles were recently prepared using similar procedures; see M. Gieng, T. Ung, L. M. Liz-Marzan, P. Mulvaney, Adv. Mater. 1997, 11, 84. A liquid core provides reconfigurability: the properties of a dye may depend on external factors such as solvent, temperature, or pH, and can be bleached optically or electrochemically. Liquid-core waveguides fabricated using solutions of dyes can therefore be made sensitive to small changes in the environment, and can be actively controlled. Solutions of laser dyes enable stimulated emission. The recent interest in micro-total analysis systems (μTAS) has stimulated research efforts in fabrication of chip-sized microfluidic devices for chemical and biological analyses. Microfluidic structures are microfabricated structures equipped to perform various transport and sensing operations on liquids. Chip-based liquid-core waveguides can be fabricated by the same microfabrication techniques that are used in the development of microfluidic devices for microanalytical applications. Spectrometric analytical devices based on liquid-core waveguides present a long optical path length and are therefore sensitive to small concentrations of analytes.

Soft lithographic techniques use elastomeric stamps and molds prepared by molding poly(dimethylosiloxane) (PDMS) on surface relief structures formed by photolithography. We have previously described the use of these PDMS molds for the preparation of supported and free-standing patterned polymeric structures. A recent application of these fabrication techniques has been the preparation of polymeric waveguides and optical elements such as waveguides couplers by molding procedures relying on PDMS molds.

In the work described here, the elastomeric PDMS is an integral part of the waveguide structure rather than a fabric-
cation tool used to assemble the waveguide. The conformal contact of an embossed PDMS structure with a substrate (glass, PDMS, silicon) generates arrays of micron-sized channels that can be filled with liquids. When the liquid in the channels has an index of refraction slightly higher than that of PDMS (~1.41),[13] light coupled into a channel is confined within that channel and guided through the liquid phase by internal reflection at the fluid/solid interface.[2]

Figure 1 illustrates the procedure followed for the fabrication of the PDMS structures used in the preparation of liquid-core waveguides in PDMS cladding. A thin film of photoresist (2–20 µm) was patterned by photolithography. Contact photomasks generated by rapid prototyping[14] were used for the preparation of structures with lateral features ≥20 µm, and commercial chrome masks were used for the preparation of structures with features <20 µm. The patterned photoresist film was passivated by gas-phase silanization, and used as a master for the molding of PDMS.[1] Glass slides (1 mm thick) were used to define reservoirs at each end of the array. The reservoirs facilitated the handling of liquids used as the core of the waveguides. The molding of PDMS against the glass slides generated optically flat PDMS surfaces, and minimized optical losses due to scattering of light by rough surfaces. After curing, the PDMS structure was removed from the photoresist master and the glass slides removed from the PDMS. The negative of the photoresist pattern was embossed on the surface of the PDMS structure. The embossed PDMS and a flat slab of PDMS were oxidized in a RF plasma cleaner (60–75 s) and brought into contact. Plasma oxidation of the embossed PDMS and the flat PDMS substrate enhanced adhesion and enabled irreversible sealing of the PDMS.[15,16] Plasma oxidation of PDMS generates a thin layer of silanol groups on its surface.[16] We believe that dehydration of silanol groups between opposing surfaces generates strong Si–O–Si bonds that are responsible for the irreversible sealing. The area of contact between the PDMS bas-relief structure and its substrate is maximized by the conformability of PDMS. Provided that the index of refraction of the substrate is lower than that of the liquid to be used as the core of the waveguide, other substrates can be used, including glass, Si/SiO2, or polymeric surfaces.

Figure 2a is a photograph of a PDMS structure prepared as described above. Figure 2b is a scanning electron micrograph of the cross-section of a PDMS structure prepared by sealing against a flat piece of PDMS a second piece of PDMS embossed with 8 µm ridges spaced by 2 µm. Sealing of the ridges against the flat substrate defined channels of microscopic dimensions (2 × 1 µm²). The interface between both pieces of PDMS is not distinguishable from bulk PDMS by scanning electron microscopy: the plasma oxidation procedure appears to modify the surface of PDMS without affecting its bulk properties. Figure 2c is an optical transmission micrograph of the cross-section of an array of channels filled with a mixture of glycerol and water of index of refraction (nD ~ 1.4175) higher than that of PDMS (nD ~ 1.41). The bright spots indicate that light is confined in the liquid phase and guided. High index fluids that were used include a commercial index-matching oil (nD ~ 1.515), a 60% solution of potassium thiocyanate in water (nD ~ 1.46), and mixtures of glycerol/water (nD ~ 1.333–1.474), 1,3-propanediol/water (nD ~ 1.333–1.440), and 1,3-propanediol/ethanol (nD ~ 1.360–1.440). The index of refraction of the mixtures are bracketed by the indices of the pure liquids and were measured prior to use.

The liquids spontaneously filled the channels by capillary action. Factors that affect the time required to fill the chan-
channels are the viscosity of the liquid, the surface energy of the PDMS, and the dimensions of the channels (cross-section and length). Oxidation of the PDMS by plasma treatment raised the surface energy of PDMS (the advancing contact angle of water on oxidized PDMS is ~0°) and facilitated spontaneous filling of the channels by capillary action. Whereas 25 mm long channels of large cross-section (20 &times; 50 &mu;m²) filled in less than 1 min, channels of smaller cross-section required more time for filling over shorter distance (~1 h for 15 mm). The high viscosity of glycerol/water mixtures also prevented the fluid from flowing out the channels, effectively trapping the fluid within the channels.

Figure 3 illustrates the procedure followed to characterize the output of the waveguides. Coupling of the light into the waveguides was achieved by focusing a He–Ne laser light on the end of the channels, or by bringing an optical fiber in close proximity to the end of the array. The latter procedure is illustrated in Figure 3.

Figure 4 shows photographs of the output of waveguides (20 &times; 50 &mu;m²) as a function of lateral positioning of an optical fiber used to couple light into the guides. Light was detected at the end of the channels only when the fiber was directly adjacent to the input of a guide. This observation establishes that light was guided through the fluid-filled channels. Selection of a particular waveguide within an array was accomplished by shifts in the lateral position of the fiber (Fig. 4a–c). Light was scattered by the PDMS cladding when the end of the fiber was not directly adjacent to the end of a fluid-filled channel (Fig. 4d).

The number of modes (optical paths through the waveguides) is determined by the dimensions of the guiding medium and the difference in index between the guiding medium (liquid) and the cladding (PDMS). The dimensions of the waveguides (20 &times; 50 &mu;m²) studied in Figure 4 are such that these guides are multimode (~10⁴ modes estimated).

We tried to prepare single-mode waveguides from channels of smaller cross-section (~1 &times; 3 &mu;m²). Figure 5 shows photographs of the output of such waveguides. Waveguides can be selected by shifting the position of the array with respect to the focused laser beam. If the light is focused on the PDMS wall separating two channels, no guiding takes place and no light is detected at the output (Fig. 5b). Figure 5d shows that the output of the waveguide is asymmetric. This result indicates that several optical paths exist that enable guiding of the light through the fluid-filled channel: this waveguide is still, therefore, multimode (~5 modes estimated). An accurate determination (at least three digits) of the index of refraction of the PDMS cladding would, however, enable the fabrication of liquid-core single-mode waveguides by preparing solutions of appropriate index of refraction.

The optical losses of the waveguides can be separated into transmission losses and coupling losses. The transmission losses of the waveguides are primarily due to three factors: the optical losses of the fluid, the surface roughness of the PDMS cladding, and the losses in the PDMS cladding. The coupling losses are due to scattering, reflections, mode mismatch, and misalignment. In our case, the observed losses were dominated by coupling losses.

In conclusion, we have demonstrated a convenient method of fabrication of liquid-core waveguides. Light is guided through a liquid phase of high index of refraction (~1.41–1.51) confined in channels of microscopic dimensions (~2–1000 &mu;m²) defined in PDMS of lower index (~1.41). A wide range of waveguide structures (interferometers, waveguide couplers, waveguide arrays, etc.) can be prepared by this approach.

Open channels are fabricated by sealing a piece of PDMS presenting a bas-relief structure against a flat piece of PDMS. The PDMS bas-relief structures are prepared by molding PDMS against photolithographically patterned masters. Irreversible sealing is achieved at room temperature. Sealing is promoted by plasma oxidation of PDMS.
Fig. 3. Schematic diagram of the optical coupling set-up using an optical fiber to couple light into liquid-core waveguides. High index fluid trapped in micron-sized channels by capillarity guide light by total internal reflection. The output of the channels is imaged with a CCD camera.

Fig. 4. a)–c) Photographs of the output of $20 \times 50 \mu m^2$ waveguides as a function of lateral position of the optical fiber used to couple light into the guide. Selection of the waveguide is accomplished by shifting the end of the fiber laterally. Light is coupled into and guided through the fluid-filled channels when the end of the optical fiber is directly facing the end of a channel. d) No output was observed when the end of the fiber was purposely misaligned with the fluid-filled channels. The light was focused on the PDMS cladding directly above the end of a channel.

Fig. 5. Photographs of the output of $1 \times 3 \mu m^2$ waveguides as a function of the lateral position of the input laser beam. a) Light was coupled into a waveguide by focusing the laser beam onto the end of a fluid filled channel. b) The laser beam was displaced laterally so that the beam was on the PDMS wall separating the two adjacent channels: no guiding is observed. c) Further translation of the laser beam onto the next fluid-filled channel results in guiding. d) A small displacement of the laser beam coupled into this guide results in an asymmetric output from the waveguide, indicating multimode behavior.
and is further enabled by conformal contact of PDMS with a substrate. Flexible structures can be prepared by sealing a piece of PDMS presenting a bas-relief structure against a PDMS substrate. Integration of these liquid-core waveguides on chip-based microfluidic devices is facilitated by the room-temperature sealing procedure.

The liquid-core waveguides described in this paper have a quasi-rectangular cross-section (2–1000 μm²) and an optically transparent cladding. The rectangular cross section of the waveguides combined with the transparent cladding allows undistorted imaging, through the cladding, of the fluid core of the waveguides, as opposed to cylindrical waveguides where distortions are introduced by lensing. Imaging capability provides added functionality in microanalytical systems.

Liquid-core waveguides offer a wide range of useful characteristics. The tailoring of the optical properties of the waveguide can be achieved by control of the optical properties of the fluid. Fluids with different index of refraction or absorption properties can be used to fill individually addressable channels. Various pumping techniques can be devised to fill the channels (capillary action, pressure or vacuum, electroosmotic flow, electrophoretic pumping, or mechanical deformation of the elastomeric PDMS).[17,20–23] Integration of a fluid-handling system to a liquid-core waveguide would allow rapid reconfiguration of the optical properties of the waveguides.

The ease of fabrication of these liquid-core waveguides, combined with previously developed soft lithographic techniques and rapid prototyping, open the way for the fabrication of various optical devices based on microfluidic systems.

**Experimental**

**Materials:** Poly(dimethylsiloxane) (Sylgard 184) was purchased from Dow Corning (Midtown, MD). Glyceol (nD 1 – 1.474) and 1,3-propanediol (nD 1 – 1.440) were purchased from Aldrich. Ethanol (nD 1 – 1.360) was purchased from Pharmco. Aqueous mixtures were prepared from deionized water (nD 1 – 1.335). Potassium thiocyanate was purchased from Mallinkrodt. A 60% KSCN aqueous solution has an index of refraction of ~1.46. Immersion oil (Type A, Code 1248, nD 1 = 1.515) was purchased from Cargille Laboratories. Microset 1110 photoresist was purchased from Shipley (Malborough, MA).

**Procedure:** The procedures used to generate PDMS stamps and molds have been reported previously [1]. Photoresist masters were prepared by photolithographic patterning of thick films (~20 μm) of photoresists generated by spin-coating at 1500 rpm. The masters were passivated by gas phase silanization. PDMS (10:1 PDMS:catalyst) was cast and cured (60 °C, 8–12 h) on the photoresist masters. Flat slabs of PDMS were prepared by curing PDMS against a silicon wafer. Before sealing, PDMS was oxidized by plasma treatment in a RF plasma cleaner for 60–75 s. Two freshly oxidized pieces of PDMS sealed spontaneously upon contact. The channels filled by capillary action. Mixtures of glycol/water, 1,3-propanediol/water, and 1,3-propanediol/ethanol were prepared at room temperature and thermally equilibrated prior determination of their index of refraction and use.

**Instrumentation:** Photolithography was performed with Karl Suss mask aligner. Plasma oxidation treatments were performed in a RF plasma cleaner (Harrick, PDC-23G). Scanning electron micrographs were taken on a JSM-6400 JEOL scanning electron microscope operated at 15 kV. The structures were sputtered with gold using an argon plasma sputter (Hummer II, Technics Inc.) for imaging purposes. Optical micrographs were taken using a Leica DMRX microscope equipped with a CCD camera and a frame grabber. Index of refraction of fluids were measured at room temperature using a Bausch & Lomb refractometer. Optical experiments were performed using a 15 mW He–Ne laser operating at 633 nm (Melles-Griot 05-LHP-925). Light from the laser was coupled into a single mode optical fiber. The output of the fiber was aligned with the end of the liquid core waveguide using a modified fiber coupling stage (Thor Labs model MDT611). A 20X microscope objective imaged the output of the waveguides onto a CCD camera (Sony, SSC-M374).

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[18] When the difference in index between the cladding and the guiding medium is high, the number of modes can be estimated from the cross-section of the waveguide. In the present case (20 × 50 μm² cross-section), the waveguide has ~20 (l/2) × 50 (l/2) modes, that is 10⁷ modes at 0.633 μm.
[19] The index of refraction of PDMS may present small variations as a function of the exact conditions of preparation (amount of catalyst, temperature and length of curing).