

## Micro-Actuators: When Artificial Muscles Made of Nematic Liquid Crystal Elastomers Meet Soft Lithography

Axel Buguin,<sup>†</sup> Min-Hui Li,<sup>†</sup> Pascal Silberzan,<sup>†</sup> Benoit Ladoux,<sup>‡</sup> and Patrick Keller<sup>\*,†</sup>

*Institut Curie, CNRS UMR 168, 26 rue d'Ulm 75248 Paris Cedex 05, France, and Matière et Systèmes Complexes, Université Paris 7, CNRS UMR 7057, 2 Place Jussieu 75005 Paris, France*

Received November 3, 2005; E-mail: patrick.keller@curie.fr

The search for “smart materials” that respond to external stimuli (pH variations, ion concentration, temperature, electric field, etc.) by changes in shape or size has recently attracted considerable attention from the material research community.<sup>1–3</sup>

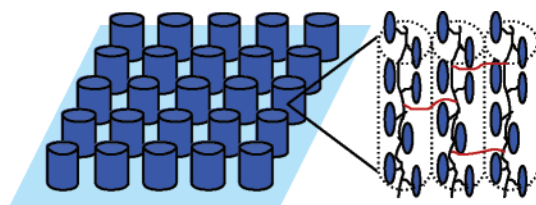
In addition to the obvious attractiveness of such studies in basic science, smart materials have many potential applications of great interest, including serving as the key building block for fabrication of sensors, micro-robots, micro-pumps, and actuators.

Some years ago, de Gennes<sup>4,5</sup> first proposed using nematic liquid crystal elastomers as “artificial muscles”. The idea was to make use of a conformational change of the polymer backbone at the nematic to isotropic phase transition<sup>6</sup> as the motor for a macroscopic contraction. On the basis of de Gennes’s idea, several thermo- and photoresponsive nematic liquid crystal elastomers have been produced.<sup>7,8</sup> For our part, we have developed actuators using side-on nematic liquid crystal elastomers.<sup>9–11</sup>

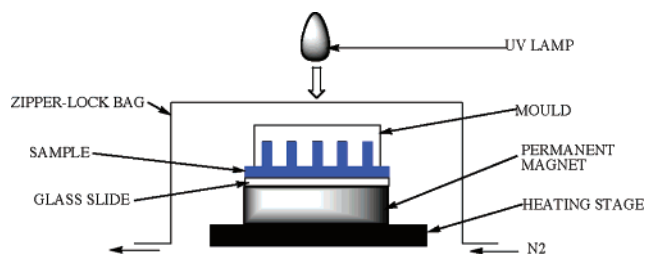
However, all the systems described so far are “macroscopic”, that is, their size is in the millimeter/centimeter range. For numerous applications involving surface-responsive materials, such as microfluidics, micro- or nanometer-sized actuators are desirable and present an alternative to more classical responsive materials, such as piezoceramics, that have their own limitations (small displacements, need of high voltages, and incompatibility with solvent). Making use of a soft lithography technique called replica molding,<sup>12</sup> we have succeeded in creating micron-sized responsive pillars made of nematic liquid crystal elastomers.

The required soft poly(dimethylsiloxane) (PDMS)-made molds were prepared by standard photolithography techniques. Briefly, a layer of a negative photoresist (SU08) deposited on a silicon wafer was exposed to UV light through a photomask (under a mask aligner) and developed to obtain, in relief, the desired pattern: an array of pillars 20  $\mu\text{m}$  in diameter and 100  $\mu\text{m}$  in height. The liquid polymer (PDMS-Sylgard 184; Dow Corning) was then poured into this mold. After cross-linking and peeling, the elastomeric replica (consisting now of an array of holes) was used itself as a “soft mold”. It exhibits two main properties, essential for what follows: its transparency to UV light and its softness which facilitates mold removal.

The main difficulty in producing responsive pillars made of nematic liquid crystal elastomer was the creation of the nematic liquid single crystal elastomer.<sup>7</sup> If we wanted pillars to contract when the nematic elastomer underwent the nematic to isotropic phase transition, we must be able to align the nematic director, and thus the polymer backbone, parallel to the long axis of the pillars (Figure 1). Such an organized structure can be performed by the application, before polymerization/cross-linking, of a suitably oriented magnetic field<sup>13</sup> on the nematic mesophase via a small permanent magnet.



**Figure 1.** Schematic representation of an array of nematic elastomer-made pillars, showing the macromolecular organization in each pillar.



**Figure 2.** Experimental setup used to prepare the responsive pillars.

A small amount of a mixture comprised of the nematic side-on acrylate monomer, (4'-acryloyloxybutyl)-2,5-di-(4'-butyloxybenzoyloxy)benzoate<sup>9</sup> (89.5 mol %), a cross-linking agent, 1,6-hexanediol diacrylate (10 mol %), and a photoinitiator, 2-benzyl-2-(dimethylamino)-4'-morpholinobutyrophenone (0.5 mol %) was heated to the isotropic phase (100 °C) on a microscope slide positioned atop a rare earth permanent magnet ( $\approx 1$  T NdFeB rare earth magnet) (Figure 2).

The soft mold was then gently pressed down on the melted sample, which filled the inner structure of the mold. To keep an inert atmosphere above the sample, the whole set up was then sealed in a zip-lock bag under a nitrogen flow. The temperature was then slowly decreased ( $-0.5$  °C/min) down to 60 °C, the temperature at which the sample is in its nematic phase.<sup>9</sup> During the cooling process, the applied magnetic field ensured the alignment of the nematic director parallel to the long axis of the pillars.

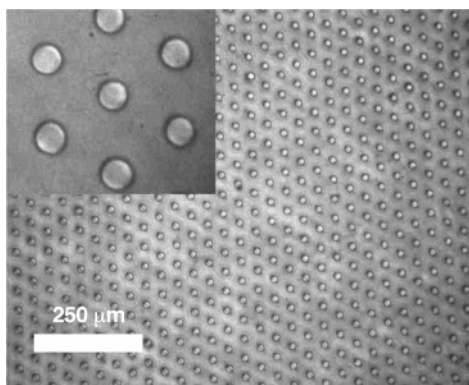
Keeping the temperature constant at 60 °C, the sample was then irradiated through the mold using a UV lamp (30  $\text{mW}\cdot\text{cm}^{-2}$ ,  $\lambda = 365$  nm; ELC-4001 light curing unit; Electro-Lite Corporation) for 30 min to promote the photopolymerization—photo-cross-linking of the monomer mixture. After cooling to room temperature, the PDMS mold was peeled off, leaving a thin glassy polymer film covered by a regular array of pillars, as seen by optical microscopy (Figure 3).

The soft mold was used several times without visible degradation in the quality of the obtained arrays.

When heated under the microscope, the focused picture of the top surfaces of the pillars became out of focus when the nematic to isotropic transition temperature of the elastomer was reached (around 120 °C). Cooling down to the nematic phase restored a

<sup>†</sup> Institut Curie.

<sup>‡</sup> Université Paris 7.



**Figure 3.** Top view (under an optical microscope) of the pillar pattern obtained by the imprint in the nematic liquid crystal elastomer. (Inset) Zoom on the structure (pillar diameter = 20  $\mu\text{m}$ ).



**Figure 4.** An isolated pillar heated (from left to right, the temperatures are 100, 120, and 130  $^{\circ}\text{C}$ ) exhibits a contraction along its major axis of the order of 35%. Ten heating cycles (at least) do not affect this behavior.

clear picture of the pillar tops. Each pillar seemed to behave as a small actuator.

However, at this stage, we could not exclude that the contraction was due (in full or in part) to a thin responsive elastomer layer located under the pillars.

To better characterize the contraction of the posts, on a small area of the array, the pillars were cut off with a razor blade. When heated above the nematic to isotropic transition temperature, the monodisperse cylinders, suspended in silicon oil to prevent them from sticking on the glass surface, underwent a contraction that was in the order of 30–40% (Figure 4). The cylinders went back to their original size after cooling below the isotropic to nematic transition temperature (see movie S.1 in Supporting Information).

These experiments clearly demonstrate that we have successfully prepared an array of micron-sized nematic liquid crystal elastomeric pillars that are able to contract and expand in response to small temperature changes around a well-defined transition temperature. Moreover, the size reduction improves thermal exchanges with the external medium and the time response of the contractile polymer; placed slightly above the nematic to isotropic transition temperature, a sudden cooling (by blowing air on the sample) shows qualitatively that this response is far faster than 1 s.



**Figure 5.** Contraction of isolated pillars cut from an array made with a mold with holes 2  $\mu\text{m}$  in diameter and 7  $\mu\text{m}$  in depth (from left to right, temperatures are 110, 115, and 130  $^{\circ}\text{C}$ ).

By reducing the characteristic size of the patterns (involving more sophisticated microfabrication methods developed for biophysics applications<sup>14</sup>), we have obtained similar results with pillars of 2  $\mu\text{m}$  in diameter and 7  $\mu\text{m}$  in height (Figure 5). However, those very small objects are much more difficult to manipulate individually than the previous ones.

These micron-sized actuators have many potential applications including the following: (1) the fabrication of active surfaces where small geometric variations often result in drastic changes of the surface properties (roughness, wettability, adhesion, etc.); (2) the achievement of small elementary “muscles” that can be manipulated individually and be used in micro-pumps or micro-robots.

Work is in progress to further explore the possible applications of these new thermally stimulated micro-actuators and to apply this new procedure to the preparation of light, magnetic field, or electric field stimulated micro-actuators.

**Acknowledgment.** This research was supported in part by CNRS (PIR “Microfluidique et Microsystèmes fluidiques”) (ACI “Nanosciences”) and by Institut Curie (PIC “Physique du Vivant”). We thank Dr. J. Plastino for her critical reading of the manuscript.

**Supporting Information Available:** A movie S1 (corresponding to Figure 4) showing the contraction and extension of a thermostimulable micro-actuator. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) *Electroactive Polymer (EAP) Actuators as Artificial Muscles-Reality, Potential and Challenges*, 2nd ed.; Bar-Cohen, Y., Ed.; SPIE-The International Society for Optical Engineering: Bellington, WA, 2004.
- (2) Yerushalmi, R.; Scherz, A.; van der Boom, M. E.; Kraatz, H. B. *J. Mater. Chem.* **2005**, *15*, 4480–4487.
- (3) Madden, J. D. W.; Vandesteeg, N. A.; Anquetil, P. A.; Madden, P. G. A.; Takshi, A.; Pytel, R. Z.; Lafontaine, S. R.; Wieringa, P. A.; Hunter, I. W. *IEEE J. Oceanic Eng.* **2004**, *29*, 706–728.
- (4) de Gennes, P. G. *C. R. Acad. Sci. Paris* **1975**, *281b*, 101.
- (5) de Gennes, P. G. *C. R. Acad. Sci. Paris IIB* **1997**, *324*, 343.
- (6) Cotton, J. P.; Hardouin, F. *Prog. Polym. Sci.* **1997**, *22*, 795–828.
- (7) Warner, M.; Terentjev, E. M. *Liquid Crystal Elastomers*; Oxford University Press: New York, 2003.
- (8) Xie, P.; Zhang, R. *J. Mater. Chem.* **2005**, *15*, 2529–2550.
- (9) Thomsen, D. L.; Keller, P.; Naciri, J.; Pink, R.; Jeon, H.; Shenoy, D.; Ratna, B. R. *Macromolecules* **2001**, *34*, 5868–5875.
- (10) Li, M. H.; Keller, P.; Li, B.; Wang, X.; Brunet, M. *Adv. Mater.* **2003**, *15*, 569–572.
- (11) Li, M. H.; Keller, P.; Yang, J.; Albouy, P. A. *Adv. Mater.* **2004**, *16*, 1922–1925.
- (12) Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550–575.
- (13) de Gennes, P. G.; Prost, J. *The Physics of Liquid Crystals*, 2nd ed.; Oxford University Press: New York, 1995; p 117.
- (14) du Roure, O.; Saez, A.; Austin, R. H.; Buguin, A.; Chavrier, P.; Silberzan, P.; Ladoux, B. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 2390–2395.

JA0575070