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Thermal and UV Shape Shifting of Surface Topography

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Shape-memory materials are receiving much interest due to their mechanical response to external stimuli (e.g., stress, pH, temperature, electricity, and light).[1,2] Among these materials, liquid crystalline elastomers (LCEs) have a unique place, showing reversible shape-recovery effects with shape memory triggered by heat,[3]light,[4−6] or electricity.[7] This unique equilibrium feature originates from the combination of the rubber elasticity of the polymer network and the orientational ordering of liquid crystalline moieties.[8] LCEs show dramatic thermal strain up to 400%; however, the material needs to be aligned as a macroscopic monodomain, before shape-memory effects are observed.[8,9] LCEs containing azobenzene groups can be irradiated with polarized UV light, and domains with the same orientation will undergo trans−cis isomerization. The dependence of UV absorption on polarization relative to the director alignment can lead to a response in polydomain materials;[4] however, the issue of alignment of the nematic order on a macroscopic scale remains pivotal in the field of LCE actuators. One way around this problem of polydomain−monodomain alignment is to remain on lengthscales below the characteristic uniform domain size, $\square_D$. We recently reported that confinement of liquid crystalline polymers into nanoparticles is a powerful tool to make inherently shape-shifting structures.[10] Thus far, this confinement of LCEs in monodomains, which are typically of the order of a few micrometers or less,[11] has not been exploited.

Here, we demonstrate a facile method for trapping the LCEs in surface microstructures via molding. Each structure is automatically a monodomain because its size is below ξ_D, and thus its shape can be reversibly switched by temperature or UV irradiation.

Figure 1a illustrates the general experimental procedure to isolate LCEs into monodomain regions on a submicrometer structured surface. A silicon master containing 400-nm wide and 120-nm deep holes (700-nm wide at the top, see AFM cross section in Figure 1b) is used to mold the LCEs. We noted that all LCE replicas had lower aspect ratio features (60−90-nm high). This is due to the evaporation of solvent during the curing step. As a result (Figure 1c), the LCE material undergoes unidirectional drying inside the mold, which leads to an alignment of the mesogens in the plane of the film (see below). Importantly, due to the small diameter of the columns, the director is aligned uniformly in each of them. The molecular structures of the components used to prepare the photosensitive LCE used in this study are shown in Figure 2. Cross-linked networks are obtained by reacting the terminal vinyl groups of the DiUB cross-linker, the mesogenic moiety MBB as well as a BMAzo dye (for optical actuation), with the Si−H bond of the polysiloxane chain following a common route for making bulk nematic elastomers.[8] The details for replicating the silicon master are similar to those used for making composite h-PDMS stamps.[12] Briefly, 3.0 μL of LCE starting material is put on top of the silicon master, and cross-linked under saturated toluene vapor within the holes of the mold. PDMS (Sylgard 184) is then poured on top of the cured LCE to form a mechanically stable composite that can be peeled from the master. The clearing point of the LCE is around T_{NI} = 67 °C as measured by optical microscopy, almost the same as that of the bulk material.[5]

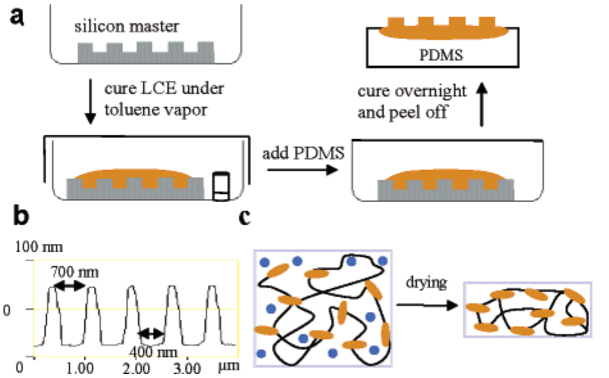

Figure 1. (a) Schematic illustration of LCE stamp preparation procedure. (b) AFM cross section of the master. (c) Illustration of the drying process of LCE posts inside the mold and concomitant alignment of mesogens.

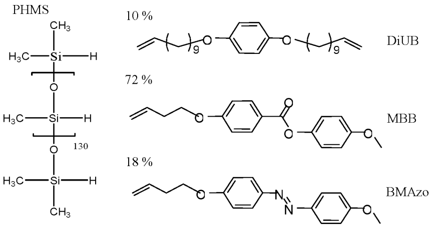

Figure 2. Chemical structures of compounds used in the preparation of the LCEs and their molar ratio.

Figure 3a shows the AFM image of an LCE surface patterned with approximately 700-nm wide and 40-nm high columns, or disks. The AFM image in Figure 3a is taken directly after release from the master. The replication is accurate and consistent over a large area of the surface. At this stage, the circular shape of the master has been imprinted into the elastomeric network, but the mesogens might not have formed the most favorable nematic state due to confinement of the master. Subsequently, the material is annealed at 55 °C (10 °C below its T_{NI}) for 10 min, to allow the elastomer film to adopt a nematic monodomain structure inside each column. This results in a significant distortion of the columns into “cigar-like” structures (Figure 3b). The AFM images show that long wavelength ripples form on the top surface of the stamps in the

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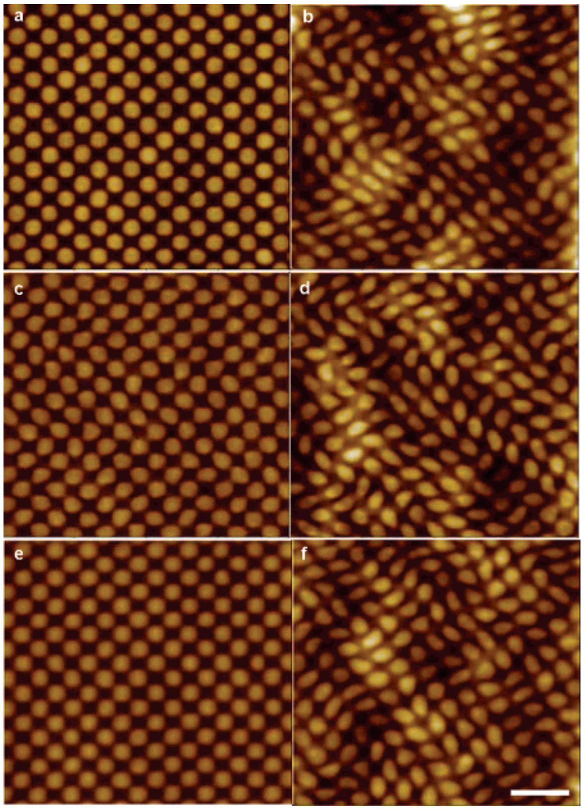

Figure 3. AFM images of (a) azo-LCE stamp after release from master; (b) annealing at 55 °C for 10 min; (c) annealing at 120 °C for 10 min, and quenched in liquid N_2; (d) annealing at 55 °C for 10 min; (e) 365-nm UV irradiation at 55 °C for 30 s; (f) annealing at 55 °C for 10 min in the dark; the white bar represents 2 μm; *z*-scale = 200 nm.

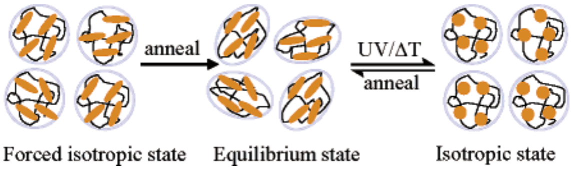

Figure 4. Thermal and UV shape shifting in azo-LCE disks.

nematic states; these are generated as a result of the development of stresses in the thin LCE films on top of the compliant PDMS substrate.

The shape of the surface features can be reversibly switched between cigar-like and circular column by cycling the material through a disordered-isotropic and ordered-nematic phase. This can be achieved using temperature as well as UV light.

When heated at 120 °C (well above the clearing temperature T_{NI}), the LCE loses its nematic order and forms circular columns to minimize the surface tension of the network, analogous to our earlier work on nanoparticles.[10] This morphology was fixed for imaging by rapidly quenching the sample in liquid nitrogen (Figure 3c). The general principle behind the molecular reorganization processes is illustrated in Figure 4.

This result indicates that the constraints of spontaneous elongation of small monodomain disks, randomly oriented in the plane and distorting the elastic substrate, thus leading to the loss of grid order, are removed above T_{NI}. After subsequent annealing at 55 °C for 10 min, the mesogenic components reorient and relax to the equilibrium cigar shape again (Figure 3d). This cycle can be repeated many times without obvious fatigue. This behavior is also observed on LCE stamps which did not contain azo moieties (see Supporting Information).

The introduction of the azobenzene group into the LCE network introduces the possibility of distorting the nematic phase by switching the N=N bonds from the trans to the cis conformation, thereby disrupting the alignment of the LC segments. A resulting photomechanical response has been well documented in bulk systems, with photoisomerizing groups chemically attached to the backbone,[5] or infused as a dye.[6] After distorted surface features were obtained via thermally annealing the stamps, the LCEs were exposed for 30 s to UV irradiation (365 nm). As a result of the conformational switching of the azobenzene moieties, the nematic order was disrupted and the original shape imposed by the master (circular features) was recovered (Figure 3e). The azobenzene isomerization is reversed via thermal treatment at 55 °C for 10 min in the dark, allowing the cigar-like structures to re-form (Figure 3f).

The reversible change in surface topography should enable the fabrication of configurable optical elements. Furthermore, since these transitions take place in elastomeric materials, they can be coupled to mechanical movements (i.e. it should be possible to move objects on these surfaces as well as change the shape of the pattern), which could find applications in a new generation of microfluidic devices.

Acknowledgment. We are grateful to Dr. D. Zhou for providing the silicon master. Z.Y. thanks the ORS and Gates Cambridge Trust for financial support.

Supporting Information Available: Details on experimental procedures, and AFM images of silicon master and PDMS stamp duplicated from the master. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA056866S