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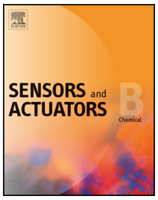

Shape changes in chemoresponsive liquid crystal elastomers

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ABSTRACT

Liquid crystal elastomers are ordered polymers that undergo reversible, anisotropic shape change in response to a number of stimuli, including heat, light, and solvent. In this study, we design liquid crystal elastomers that actuate both axially and torsionally in response to chemical stimuli. We characterize the response of uniaxially-aligned liquid crystal elastomer films exposed to a variety of chemical stimuli of varying quality. In each solvent, there is a contraction along the alignment direction paired with an expansion in the perpendicular directions. Torsional actuation is generated by patterning a twisted alignment through the thickness of the liquid crystal elastomer. These hierarchically-patterned materials reversibly transition from flat to helical with over 200°/mm of twist in chemical vapor. This response is stable for at least 100 cycles. Ultimately, this chemoresponse is combined with mechanical instability to make high-twist torsional actuators with peak velocities of almost 400 RPM.

1. Introduction

Shape-changing polymers enable complex mechanical motion where traditional machines are too large, dense, or expensive. These responsive polymers have been demonstrated as active elements in microfluidic valves [1–4], microactuators [5,6], and minimally invasive implants [7,8]. However, many polymeric actuators rely on large temperature changes in order to reach maximum potential. In natural materials, chemical energy gradients are widely used to drive shape change, such as osmotic pressure driving the closure of a Venus flytrap [9]. In synthetic materials, including a number of hydrogels [10–12] and polymer composites [13–15], chemoresponsive shape change is driven by anisotropic or spatially heterogeneous swelling. Liquid crystal elastomers (LCEs) are a class of responsive polymers in which molecular order can be programmed spatially and hierarchically to give rise to anisotropic shape change in response to stimuli, such as heat [16], organic solvents [17–19], or light [20–22]. By patterning the molecular orientation (director (n)), these actuators can morph from flat into a 3-dimensional shape [17,23,24]. LCEs are currently being explored for a variety of applications, including artificial muscles [25,26] and tactile displays [27,28].

The reversible shape change of LCEs has been characterized extensively for temperature changes, with strains of up to 400% and stresses of up to 300 kPa being observed [29,30]. However, these films often require temperatures near 75 °C, sometimes not reaching maximal shape change until 150 °C [17,31,32]. By comparison, chemoresponsive materials can be triggered isothermally. While the chemoresponse of densely crosslinked liquid crystal polymer networks in solvents has been studied, the stimulus response of these materials tends to be small in magnitude when compared to their elastomeric, lightly-crosslinked counterparts [33–35]. Fewer studies have leveraged the large swelling of LCEs, with many focusing on liquid crystalline solvents [17–19,36–40]. Here we investigate LCEs as chemoresponsive actuators by characterizing their intrinsic swelling properties in response to isotropic chemical stimuli, namely good solvents and good solvent vapors. Polarizing optical microscopy (POM) is used to characterize shape change as a function of the director orientation in response to solvents of different quality. We then leverage a recently described synthetic method [17] to program the director of LCE monoliths to generate torsional actuators based on these swelling properties. Ultimately, we demonstrate this torsional actuation is reversible and can reach high speeds.

2. Experimental

2.1. Reagents

The liquid crystal molecule 1,4-Bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (RM82) was purchased from Synthon Chemicals. The low molar mass liquid crystal, 4-(trans-4-pentylcyclohexyl) benzonitrile, acetone,

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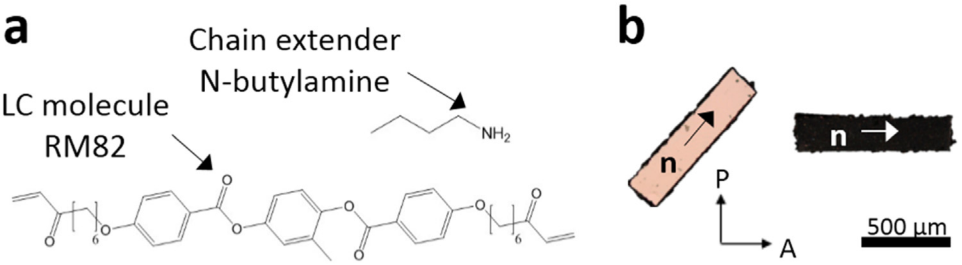

Fig. 1. (a) RM82 and *n*-butylamine used to synthesize LCEs. (b) POM of a LCE with planar alignment under crossed polarizers when the director (n) is both along the polarizer direction (dark) and at 45° to the polarizers (light).

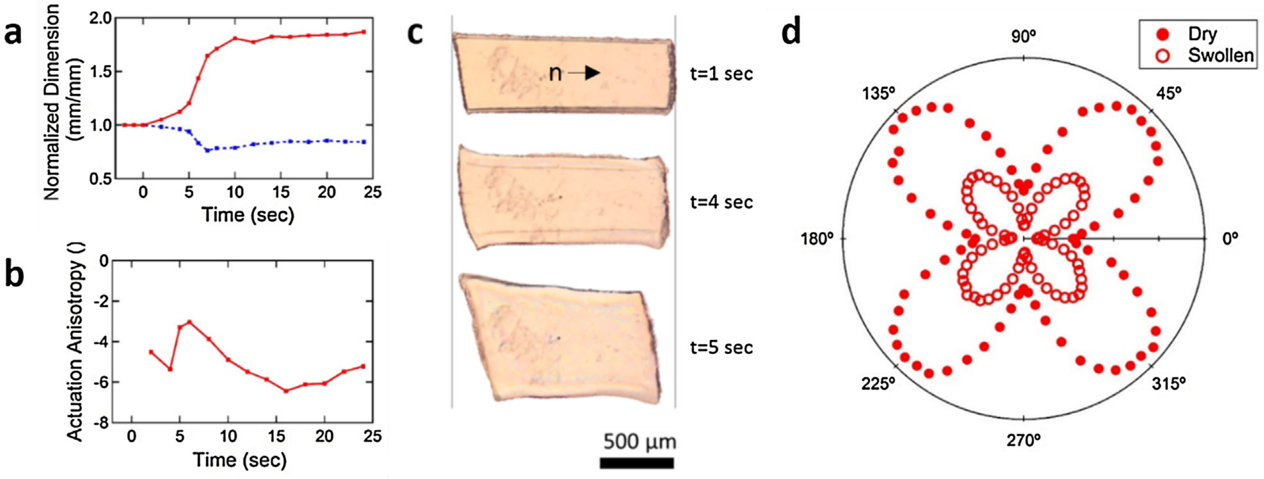

Fig. 2. (a) Representative curve of normalized dimension change of LCE in THF along (blue dashed line) and perpendicular (red line) to the director. (b) Representative curve of actuation anisotropy at each time point of swelling in THF as calculated in Section 2.4. Lines between points are added to guide the eye. (c) Images taken on an optical microscope show samples with planar alignment swollen in THF. Bounding lines are added to aid in capturing the shape change in relation to the original shape. (d) Relative transmittance of dry and swollen LCE samples in THF as a function of sample rotation when observed between crossed polarizers. Polarizers are along 0°/180° and 90°/270°. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

dimethylformamide (DMF), and *n*-butylamine were purchased from Sigma Aldrich. The photoinitiator Irgacure I-369 was donated by BASF Corporation. Elvamide for surface alignment was purchased from DuPont. Tetrahydrofuran (THF) was purchased from Fisher Chemical, and chloroform was purchased from Cambridge Isotope Laboratories, Inc. All reagents were of reagent grade and used without further purification.

2.2. Film synthesis & preparation

Cleaned microscope glass slides (50 mm × 25 mm × 1 mm) were coated with 0.15% Elvamide in methanol solution and rubbed by a microfiber cloth to generate a preferential direction for liquid crystal alignment. Cells were constructed by placing two glass slides separated by a 30 μm spacer to set polymer film thickness. An equimolar amount RM82 and *n*-butylamine were mixed with 1 wt% of photoinitiator I-369. For LCE gels, 10 wt% or 20 wt% of low molar mass liquid crystal was added to the described mixture. Aligned cells were filled by capillary action and kept for 12 h at 75 °C for neat films or 65 °C for LCE gel films. Then, oligomerized samples were crosslinked with 250 mW/cm^2 intensity of 365 nm UV light (OmniCure® LX400+, Lumen Dynamics) for 2 min.

2.3. Gel fraction

Gel fractions of the aligned LCE films (n = 3) were measured. LCE films were immersed in THF liquid for 24 h, then dried in the vacuum oven for 24 h at 60 °C. Masses were measured before immersion in THF and after removal from the vacuum oven. This procedure was repeated twice.

2.4. Polarizing optical microscopy

After synthesis, alignment of LCE films and gels was confirmed using POM. To determine the dimensional change of planar LCE samples in all solvents, samples were cut with an aspect ratio of 2, with the long axis along the director. Samples (n = 3) were placed in a glass channel to restrict sample movement, and solvent was added at the mouth of the channel. Swelling was directly observed in the microscope under crossed polarizers, and video (30 Hz) was taken to capture the shape change. Frames were analyzed from each video in ImageJ to measure dimensional change in each axis. Representative curves were chosen to illustrate transient shape change behavior. Total volume change at equilibrium (φ) was calculated as $\varphi = V/V_o$, where V is the swollen volume and V_o is the original film volume. This calculation assumes the dimensional change in the z-axis to be analogous to the axis perpendicular to the director. Actuation anisotropy (ξ) is calculated as $\xi = \frac{l_{f_\perp}}{l_{o_\perp}} / \frac{l_{f_\parallel}}{l_{o_\parallel}}$, where l_o is the original length and l_f is the length at each time point. The axis along the director is denoted by $\parallel$, and the axis perpendicular to the director is denoted by $\perp$.

Sample order parameter was qualitatively compared between samples using POM. Dry and swollen samples were imaged under crossed polarizers with images taken every 5° over a full rotation. Images were converted to greyscale in ImageJ, and the mean