Highlights

Soft Actuators Based on Liquid-Crystalline Elastomers

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There is a growing interest in the development of artificial muscle-like actuators, which are ideal for the realization of biomimetic movements as they change their shapes and dimensions when a potential is applied. Polymer actuators play a leading role in this field because they provide such advantages as flexibility, light weight, low costs, and quiet operation compliance.[1] Various materials are under current investigation in this field, such as polymer gels,[1] conjugated polymers,[2] carbon nanotubes,[3] and dielectric elastomers,[4] and various chemical and physical stimuli have been applied to induce the responses of these materials, including pH, solvent composition, temperature, electric field, magnetic field, and light. Among these polymer soft actuation materials, gels and conducting polymers are most promising for applications in the field of biomimetic actuation. However, the low elastic modulus and low yield strength of gels provide important limitations for actuator performance, whereas for battery-like conducting polymers faradaic processes involving solid-state dopant diffusion and structural changes limit the rate, cycle life, and energy conversion efficiencies.

Recently, there has been a growing focus on the study of soft actuation materials based on liquid-crystalline elastomers (LCEs) as a result of their unique combination of the anisotropic features of liquid crystal (LC) phases and the rubber elasticity of polymer networks. In 1997, de Gennes et al. reported theoretical studies on the possibility of using LCEs as artificial muscles.[5] They proposed that a slight drop in the temperature across the isotropic (I)-to-LC transition is able to cause a strong uniaxial deformation of LCEs at nearly constant volume owing to a change in the LC order. Finkelmann and Kundler later reported that nematic LCE (NLCE) films containing polysiloxanes exhibited a spontaneous contraction along the director axis when heated toward the N-to-I phase-transition temperature (Figure 1).[6a] By synthesizing NLCE films through a hydrosilylation reaction of a monofunctional LC compound and a bifunctional LC polyether with poly(methylhydrogensiloxane), a shape change over 300% was obtained.[6b,c] This thermomechanical effect was also observed in side-on NLCE films and fibers that contained polyacrylate.[7a,b]

de Gennes also proposed the possibility of realizing an artificial muscle or actuator from an I–LC–I triblock copolymer.[5b] Accordingly, Li et al. chose side-on LC polymers to construct an LC domain aligned homogeneously throughout the whole sample and synthesized a side-on triblock elastomer by atom-transfer radical polymerization (ATRP). A thermally induced contraction of the elastomer was observed when the LC block underwent the N-to-I phase transition.[7c] In addition, Yusuf et al. investigated the thermomechanical properties of the LCEs swollen in an anisotropic solvent such as low-molecular-weight liquid crystals (LMWLCs).[8]

Recently, photoinduced contractions of LCEs incorporating azobenzene derivatives was achieved upon their irradiation with UV light.[9] This photomechanical effect was ascribed to the decrease in the order parameter caused by a photochemical reaction (*trans–cis* isomerization): the rodlike *trans*-azobenzene moieties stabilize the LC alignment, whereas the bent *cis* forms lower the LC order parameter (Figure 2a). Shortly afterwards, we succeeded in achieving a three-dimensional deformation (photoinduced bending) by using azobenzene-containing NLCE films swollen in suitable solvents or heated above their glass-transition temperatures (T_g) in air.[10] In this case, a contraction in the surface region only caused by the limitation of the absorption of photons contributes to the bending (Figure 2b). Other reports on photoinduced bending of LCEs followed subsequently.[11] These photoresponsive LCE materials are promising for applications as high-speed actuators, as the photochemical phase transition of azobenzene-containing LC polymers can be evoked on a timescale of nanoseconds under optimized conditions.[12] By using their deformations, one can convert light

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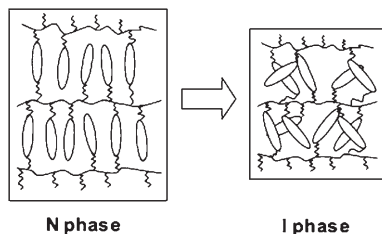E-mail: ylyu@fudan.edu.cn

Figure 1. Schematic illustration of the thermally induced contraction in LCEs. N = nematic; I = isotropic.
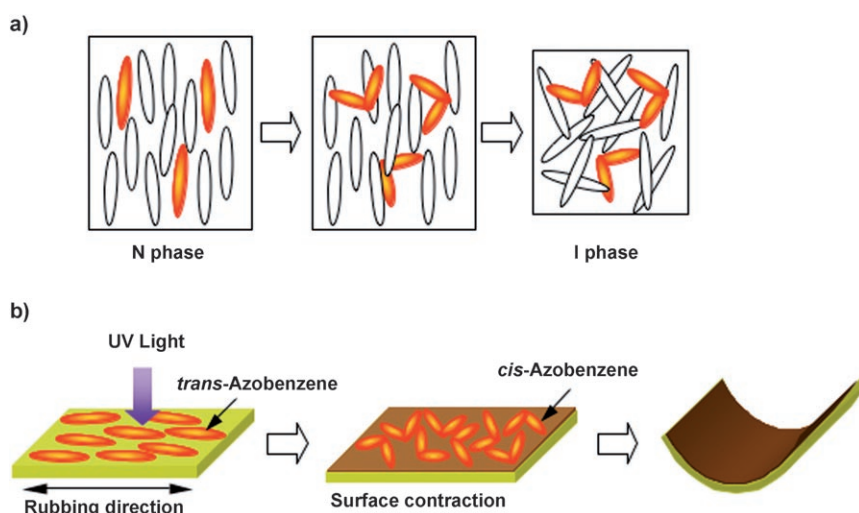
Figure 2. Photomechanical effects of the azobenzene-containing LCEs: a) the photoinduced contraction caused by a photochemical phase transition; b) plausible mechanism of the photoinduced bending behavior.

energy into mechanical power directly. Moreover, as their deformations are driven by light and thus require neither batteries nor controlling devices on the materials themselves, it should be simple to miniaturize the photochemical systems for potential application in driving micromachines and nanomachines.

Another useful property of LCEs is their shape change upon applying electric fields (electromechanical responses) owing to reorientation effects induced by an electric field. Zentel first reported tiny changes of LCEs swollen in LMWLCs under large fields in 1986.[13] Subsequently, Barnes et al. reported a 20% contraction of polydomain elastomers swollen in an isotropic LMWLC.[14] Kishi et al. reported quantitative results on shape changes of swollen polydomain LCEs under a dc electric field (0.3 V μm^{-1}).[15] Recently, Courty et al. demonstrated a fairly large electromechanical effect in an LCE embedded with carbon nanotubes upon using, however, a large applied field (1 V μm^{-1}).[16] Yusuf et al. reported measurable shape changes (maximum 13% contraction) in LCEs swollen with an LMWLC under small fields (0.01–1 V μm^{-1}).[17] Moreover, Zentel et al also investigated electromechanical responses in dry freestanding ferroelectric LCEs[18] and obtained 4% strain in ultrathin films (less than 100-nm thick) at only 1.5 V μm^{-1}.

The studies summarized above fully indicate that LCEs have a high potential to be applied as soft actuators, with such advantages as large deformations and high-speed, two- (contraction) or even three-dimensional (bending) actions. However, all the systems described so far have been macroscopic ones, with sizes in the millimeter/centimeter range. For many applications of stimuli-responsive materials involving LCEs, micro- or nanometer-sized actuators are desirable.

Keller and co-workers recently made an important contribution on creating microsized responsive pillars based on LCE materials by making use of a soft lithography technique called replica molding.[19] Figure 3a illustrates the experimental setup used to prepare the LCE pillars. The soft mold of poly(dimethylsiloxane) with an array of holes 20 μm in diameter and 100 μm in height was first prepared by standard photolithography techniques by using a negative photoresist. Then, the mold was pressed onto the melted monomer mixture, which consisted of a nematic side-on acrylate monomer and a crosslinker. The monomer mixture was slowly cooled to its N phase, and UV-light-induced polymerization was performed under a magnetic field to align the N director parallel to the long axis of
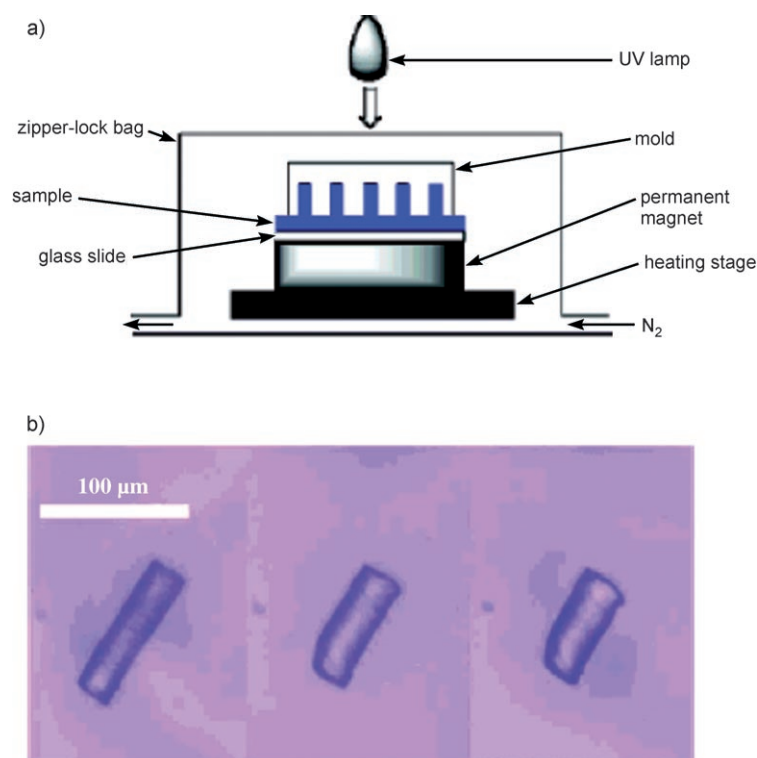

Figure 3. Thermomechanical effects of microsized LCE pillars prepared by a soft lithography technique. a) Experimental setup used to prepare the responsive pillars. b) An isolated pillar (20-μm diameter) heated at various temperatures exhibits 35% contraction along its major axis (from left to right, T = 100, 120, and 130°C).

the pillars. After photopolymerization, the soft mold was peeled off and the side-on LCE pillars were cut off. When heated from an N phase to an I phase, the pillars suspended in silicone oil underwent a contraction on the order of 30–40% (Figure 3 b). The contracted pillars could revert to their original size after cooling from the I phase to the N phase. With a decrease in the size of the pillars, this thermal deformation became faster (much less than 1 s) as a result of better thermal exchange with the external medium.

The work described herein summarizes the trend of using LCE materials as muscle-like actuators in response to temperature, light, and electric fields. Particularly, the work by Keller and co-workers constitutes a very important milestone in the field, as they put forward a new concept using a soft lithography technique to prepare micro-sized LCEs. Significant improvements have recently been reported in extreme-UV (EUV) resists.[20] Nested and isolated line resolutions approaching 30 nm and 25 nm, respectively, have been demonstrated. Therefore, we should be able to obtain nanosized LCE actuators with a further endeavor to apply the EUV lithography technique. However, it should be borne in mind that photochemically induced changes in LC orders by incorporating chromophores such as azobenzene into micro- and nanosized LCEs can lead to a faster deformation of the LCEs as compared to thermal deformation.

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