

Self-Assembled Polymer Films for Controlled Agent-Driven Motion

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ABSTRACT

Reliable stimuli-responsive materials make up a vital part of molecular medicine and on-chip diagnostics. Here, we describe such a material which exhibits rapid, large-amplitude, reversible deformations and which is formed in a simple, one-material, one-step, self-assembly process. The material is a polymer network comprised of discrete molecular actuators which anisotropically expand in response to their driving stimuli. Tuning the relative orientation of the actuators with respect to one another creates expansion variations throughout a sample, and this is exploited to induce macroscopic motion. The deformation directions are pre-engineered by the molecular positioning, and extremely fast response times and high sensitivity are observed. We describe water- and pH-controlled motion, and we anticipate that the techniques are extendable to other biologically or industrially relevant agents.

Molecular medicine and lab-on-a-chip components require stimuli-responsive materials and actuators. The targeted drug delivery concept, for example, could be achieved by the controlled, in vivo opening of micro drug reservoirs in the vicinity of disease-specific molecules or conditions. In addition, mixing and flow control have been recurring issues for on-chip diagnosis, and improved schemes for molecular detection and response are considered beneficial. In these fields, polymeric materials have many advantages over the traditional microelectromechanical system (MEMS) technologies;^{1–4} larger responses to weak stimuli are generally possible, designs are easy to implement, inexpensive, and consistent with scaling to production, and an enormous range of material properties (including suitability to aqueous operation and biological inertness) are available. In our case, liquid crystalline polymers are utilized in order to achieve orientational control over the components of a monolithic network.

Polymeric actuators based on liquid crystal (LC) networks generally respond to external stimuli by contracting along the director, and most commonly, this stimulus is ferroelectric,^{5,6} piezoelectric,⁶ thermal,^{7,8} or photonic^{9–11} in nature. In the case of thermal actuation, uniaxial contractions greater than a factor of 3 have been observed.⁷ In this case, increasing molecular disorder with temperature, especially at the nematic-to-isotropic transition, creates distortion of the polymer chains and, consequentially, macroscopic con-

traction along the director. Photonic actuation is based on a similar principle, but in this case, order variations are the result of photoisomerization of light-sensitive molecules embedded in the liquid crystal matrix. Aligned liquid crystal networks, however, have never previously been adapted to actuation based on a chemical stimulus, and it is this effect which is targeted in this paper.

The formation of pH- or water-controlled actuators is based on two simple concepts: an aligned liquid crystal network consisting of both covalent and secondary bonds, and stimulus-controlled molecular switching between acidic and neutral states. Chemical bonds are required that can be reversibly broken under the action of an agent, and therefore units such as hydrogen bonds are incorporated into the chemical structure of the monomers. These individual molecules do not have the rodlike conformation that is necessary to induce liquid crystalline behavior; however their ability to pair under the formation of hydrogen bridges stabilizes the necessary LC phases.^{12–14} This is conceptually shown in Figure 1a. The network order can be permanently fixed by attaching reactive groups to the ends of the mesogens and photopolymerizing the monomers while they are in the nematic phase.^{15,16} After a sufficiently rapid photopolymerization (Figure 1b), the polymer network retains the order of the monomers, effectively freezing in the liquid crystalline alignment of the system. In our case, the breakable chemical bonds are pairs of hydrogen bonds formed between carboxylic acid units, and the bond strength is sufficient to withstand immersion in water without significant deformation. Breaking the hydrogen bonds requires a reaction with

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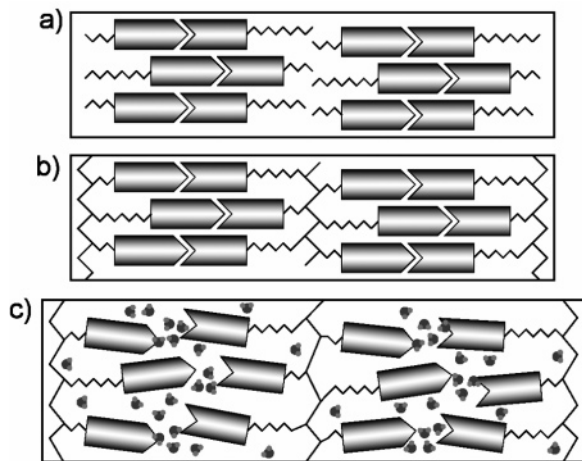


Figure 1. Formation of an aligned hygroscopic layer. In fabricating a water-sensitive actuator, linear benzoic acids (a) are aligned in the nematic state and polymerized into an organized network (b). Treating the network with a strong base converts the system into an aligned hygroscopic film (c).

a base, and thus under sufficiently alkaline conditions, the network is converted into a polymer salt and the hydrogen bonding is eliminated (Figure 1c). The salt retains less of the nematic order, and this causes a macroscopic, pH-induced deformation. Exposure to acids restores the hydrogen-bonded diacid and the original film dimensions.¹⁷

Humidity-controlled motion is expected after the network has been converted into a salt. The salt network is much more hygroscopic than the original hydrogen bonded network and begins swelling under humid conditions. The individual salt units act as molecular actuators, expanding preferentially perpendicular to the local director, and since the molecules are prealigned in the LC phase, the primary swelling directions are controllably established during polymerization. When many molecular actuators are combined in parallel, a large macroscopic expansion is expected perpendicular to the director in combination with a smaller expansion parallel to it. As above, the system may be deactivated by a short acid treatment, restoring the hydrophobic state and making the system relatively insensitive to water uptake.

Most commonly, liquid crystal actuators produce uniaxial deformation, whereas notable applications such as drug delivery and lab-on-a-chip components would actually benefit from a bending deformation. This deformation mode was recently demonstrated in response to a thermal stimulus using heavily cross-linked, monolithic polymer networks having gradients in the local director orientation.¹⁸ It is this principle that is employed here to induce large-scale deformations controlled by a chemical rather than physical stimulus. Overall, the water- or pH-induced expansion remains small, but macroscopic bending motion may be easily engineered into the system by prealigning the LC units. Three configurations for controlled bending are depicted in Figure 2. The uniaxially aligned film of Figure 2a responds equally to water or pH in all regions of the film and will only elongate by a small amount when presented with a uniform stimulus. Differences in the pH or humidity of the upper and lower surfaces, however, are sufficient to induce a large bending

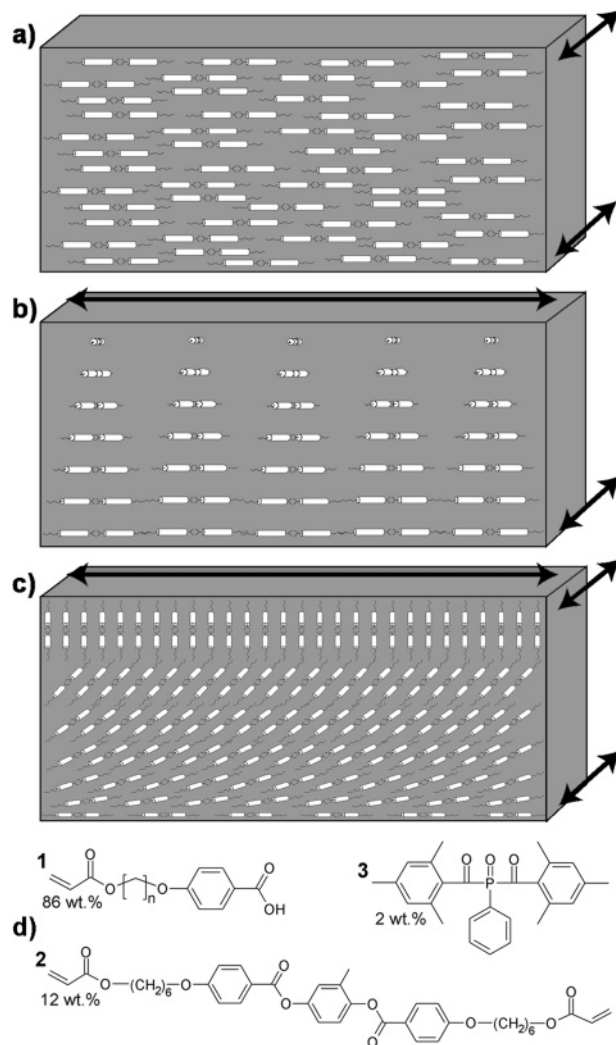


Figure 2. Director orientation configurations for bending motion. In the presence of water, a uniaxially aligned network (a) will preferentially elongate perpendicular to the local LC director. In the twisted (b) and splayed (c) configurations the 90° director rotation between the film boundaries leads to expansion mismatches on the upper and lower surfaces and, consequently, an overall bending behavior. Arrows indicate the preferred expansion directions. The composition of our specific photopolymerizable mixture is shown in part d. **1** is generally a 1:1:1 (by weight) mixture of acids with $n = 3, 5,$ and 6 . The mixture has a nematic phase between 15 and 96 °C. It is isotropic above 96 °C and crystallizes at 15 °C.

behavior. The twisted (Figure 2b) and splayed (Figure 2c) configurations do not require environmental gradients to produce macroscopic motion. In both cases, the preferred expansion directions on the opposite surfaces of a film are offset by 90°, and in the presence of a uniform stimulus, this results in expansion gradients over the thickness of the film and an overall bending behavior analogous to that of thermal deformation in a metallic bilayer. In all cases, permanent liquid crystalline cross-linkers without breakable secondary bonds may be incorporated into the network to increase the mechanical coherence of the actuator and to promote shape reversibility upon removal of the water analyte.

To implement the principle, the mixture shown in Figure 1d was photopolymerized with UV radiation. Molecule **1**

containing the humidity-sensitive group is in fact a mixture of three homologues in a 1:1:1 ratio (aliphatic lengths of $n = 3, 5,$ and 6) to decrease the crystallization temperature and widen the liquid crystalline temperature range in the monomeric state. Molecule **2** acts as a permanent cross-linker, providing chemical resistance, promoting mechanical stability, and also suppressing the formation of smectic phases, which interfere during polymerization. Polymerization was UV initiated at a temperature ($60\text{ }^{\circ}\text{C}$) within the nematic phase of the mixture while the molecules were ordered in the uniaxial or twisted configurations. An FTIR analysis of infrared absorption peaks at $809, 965,$ and 985 cm^{-1} (which are characteristic of excitations of the $\text{C}=\text{C}$ double bond in the acrylate group)¹⁹ shows that absorption at these wavenumbers is strongly reduced following UV irradiation. This indicates that the concentration of $\text{C}=\text{C}$ double bonds is much lower and strongly implies the formation of a polymer network. During polymerization, the birefringence of the uniaxially oriented samples was not observed to drop appreciably, indicating that the order in the monomeric state is preserved in the polymer network. In one typical measurement, the birefringence dropped from 0.167 as a mixture of monomers to 0.163 as a polymer network, and the visual appearance of the films between polarizers did not change noticeably. Additional information regarding film construction, polymerization conditions, FTIR measurements, and an analysis of the network order is available in the Supporting Information.

As a polymer, the network is aligned, hydrogen bonded, and rigid, but it is also hydrophobic and resists swelling in most solvents. Following polymerization, the films were treated with 0.1 M KOH for 20 s to convert a fraction of the carboxylic acid groups into potassium carboxylate groups, forming a hygroscopic network. The KOH treatment reduces the order of the network but does not eliminate it. Typical birefringence values drop from 0.16 to 0.085 , while the optical signature of uniaxial or twisted samples between crossed polarizers is preserved. Comparing FTIR spectra in the region from 1800 to 1300 cm^{-1} before and after treatment in KOH shows the conversion of a hydrogen-bonded diacid into a potassium salt. Absorption peaks of interest are located at 1733 cm^{-1} (associated with $\text{C}=\text{O}$ stretching of the free non-hydrogen-bonded esters),^{20,21} 1682 cm^{-1} ($\text{C}=\text{O}$ stretching in cyclic carboxylic acid dimers),²¹ 1547 cm^{-1} (anti-symmetric COO^- stretching),²² and 1395 cm^{-1} (symmetric COO^- stretching).²² Peaks at 1682 cm^{-1} , which are indicative of hydrogen bonding, are slowly eliminated during KOH treatment, while the carboxylate ion peaks at 1547 and 1395 cm^{-1} grow strongly. This is direct evidence that KOH penetrates the network, deprotonating the acid groups and breaking up the reversible hydrogen bonds. Sample FTIR spectra may be found in Figure 3.

After activation, the films exhibit a strongly anisotropic response to water. In Figure 4, the expansion of a uniaxially aligned film after full immersion in water is shown parallel and perpendicular to the nematic director, and it can be seen that the perpendicular expansion is significantly greater than expansion in the parallel direction. The observed actuation

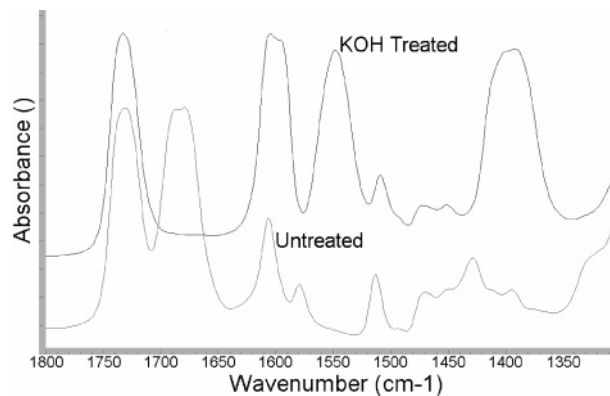


Figure 3. FTIR spectra of poly(**1**) in the region of 1800 to 1300 cm^{-1} before and after treatment in KOH solution.

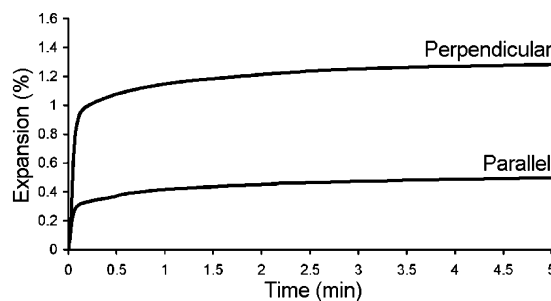


Figure 4. Preferential expansion of the photopolymer mixture. After photopolymerization, samples treated with KOH preferentially expand in water perpendicular to the director. The expansion curves were generated by immersing clamped KOH-treated films in water at time $t = 0$ and subsequently measuring the length of the sample.

behavior is consistent with this. After activation, uniaxially aligned films rapidly bend away from sources of water vapor about an axis oriented parallel to the liquid crystalline director and in the plane of the film. When exposed to water vapor on the opposite surface, the films also bend away from the vapor source, as is consistent with an anisotropic swelling mechanism. This is shown as a video in the Supporting Information. When fully immersed in water, uniaxial films do not show evidence of strong curling. Twisted films exhibit strong biaxial curling when exposed to a directional vapor source, curling about one in-plane axis when exposed from one side and the perpendicular in-plane axis when exposed from the other. This is also shown as a video in the Supporting Information. After full immersion in water, twisted films typically show strong curling about one of the two axes (most often the shorter one). In all cases, the bending is extremely rapid, having time constants on the order of seconds. The response of twisted films to relative humidity variations in a homogeneously humid air environment is shown in Figure 5. Uniaxially aligned films remain relatively unaffected by the variations, while twisted films show a strong, reversible response over the full range of humidity.

These systems consist of a monolithic network, and they are sensitive to both pH and humidity. The deformation axes may be accurately controlled by preinducing alignment in the nematic phase (i.e., twisted configurations), and the

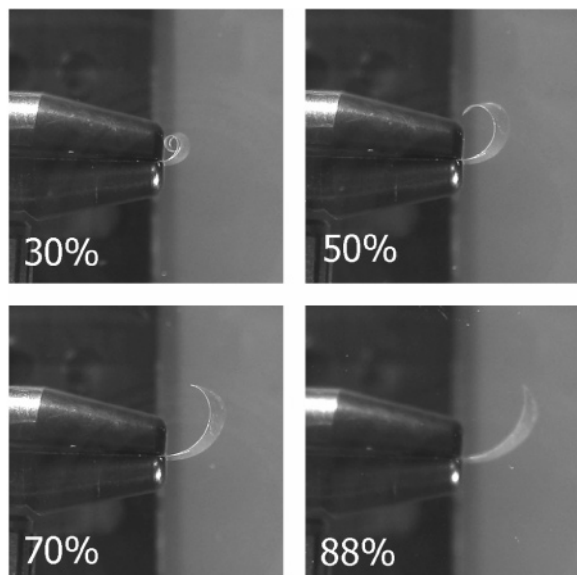


Figure 5. Images of a twisted film under the relative humidity conditions shown.

mechanical integrity and stimuli sensitivity may be tuned by varying the ratio of permanent to reversible chemical bonds in the network. As an added advantage, the actuators are composed of densely cross-linked polymers, which makes them better suited than typical elastomeric actuators to performing useful work as a part of, for example, a microfluidics system. The fact that the networks are formed by photopolymerization enables easy structuring and integration of the active elements into devices by lithographic means. The fast and large scale deformation which is observed in these systems also provides new opportunities to design for additional molecular stimuli. Secondary bonds other than the dicarboxylic acids can be included, and these will respond to pH stimulation differently than the particular molecules described here. The simple acid-to-salt reaction could also be replaced with a reaction that sensitizes the network to various biomolecules, laboratory reagents, or environmental gases. Chemical receptors specific to a target molecule would be implanted into the anisotropic LC network, and with this effect, one can envision large-scale polymer actuation directly stimulated by various molecular targets.

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Supporting Information Available: Two real-time videos of the motion generated in twisted and uniaxial polymer films, detailed fabrication and experimental information, and FTIR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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