# Shape Actuation via Internal Stress-Induced Crystallization of Dual-Cure Networks

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Ⓢ Supporting Information

ABSTRACT: We demonstrate a single-phase, two-way shape actuator that, in the absence of an external load, elongates upon cooling and reversibly contracts upon heating. In a simple and straightforward process, a partially cross-linked, semicrystalline poly(ε-caprolactone) (PCL) network is melted, stretched to several hundred percent strain, and further cross-linked. Upon removal of the applied load, the elastic double network adopts a "state-of-ease" that retains part of its former strain. When cooled, internal stress-induced crystallization causes further elongation of configurationally biased chains. When heated, crystallites melt, and the sample returns to its equilibrium state-of-ease. Under optimized conditions, reversible actuation >15% strain can be reproducibly achieved, and samples can be cycled multiple times with highly uniform actuation with no observable creep. The mechanism behind such actuation was further confirmed via calorimetry and X-ray scattering.
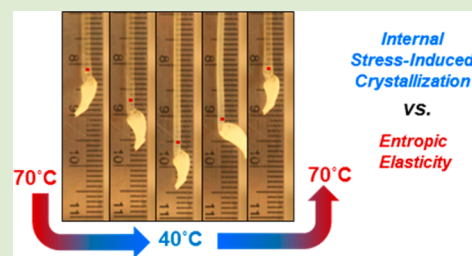
Shape-memory polymers (SMPs) form a class of actively moving polymers that can actively switch between two shapes upon the application of an external stimulus, typically heat.[1] A thermal-responsive shape-memory effect can be achieved by cooling an elastically deformed material through a thermo-reversible transition to bolster its internal cohesive energy density, thereby fixing the temporary shape. Upon heating, stored elastic energy is released, resulting in one-way shape recovery and the capacity to perform mechanical work.[2] In recent years, the engineering of SMPs has become incredibly sophisticated, and materials now can robustly memorize multiple temporary shapes[3−8] and can be triggered by various stimuli such as light, moisture, or applied magnetic fields.[9−11] However, many potential applications (e.g., artificial muscles and actuators) are constrained by the material's inherent one-way shape memory; in other words, conventional SMPs do not return to their temporary shape upon cooling, and they must be reprogrammed each cycle.

Strain-induced crystallization of semicrystalline polymers such as poly(ε-caprolactone) (PCL) can enable *two-way* shape memory: the ability to reversibly cycle between two shapes by varying temperature.[8,12,13] However, an external load must always be present to direct crystallization along a preferred direction. This concept can be extended to achieve stress-free, two-way shape actuators by joining a layer of pre-elongated shape memory polymer with a layer of unstretched elastomer.[14,15] The resulting composite has built-in stress to direct crystallization in the shape-memory layer, resulting in reversible bending upon thermal cycling. Recently, Behl et al. have demonstrated free-standing copolymer networks, with two-phase-separated crystallizable domains that are capable of reprogrammable and reversible bending.[16] In their approach, one set of crystallizable domains determines the shape-shifting geometry, while the other provides the thermally controlled

actuation capability. Liquid crystalline elastomers are also capable of reversible shape actuation by coupling mesogens to a lightly cross-linked network.[17,18] For example, stress-free shape actuation of drawn fibers to record strains of nearly 500% has been observed upon cycling through a mesophase transition.[19] However, since liquid crystal elastomers are inherently soft (typically $E' < 1$ MPa), they can experience irreversible creep. Moreover, liquid crystalline transitions usually involve small enthalpic changes (<5 J/g), and therefore, generating sufficient force for applications remains challenging.

Here, we demonstrate a single-phase, two-way shape actuator that, in the absence of an external load, elongates upon cooling and reversibly contracts upon heating. In a simple and straightforward process, a partially cross-linked, PCL network is melted, stretched to several hundred percent strain, and further cross-linked. Upon removal of the applied load, the elastomer adopts a "state-of-ease" that retains part of its former strain.[20] When cooled, internal stress-induced crystallization causes further elongation. When heated, crystallites melt, and the sample returns to its equilibrium state-of-ease. Under optimized conditions, reversible actuation of over 15% strain can be reproducibly achieved, and samples can be cycled multiple times with uniform actuation and no observable creep. The microscopic scenario giving rise to bidirectional shape switching was elucidated by X-ray scattering. We anticipate that these results, combined with further studies, will enable knowledge-based design of two-way shape actuators with even greater efficiency.

Our synthetic strategy relies on two orthogonal chemical reactions to achieve stagewise introduction of covalent cross-links at different strained states (see Figure 1 and Figure S1,
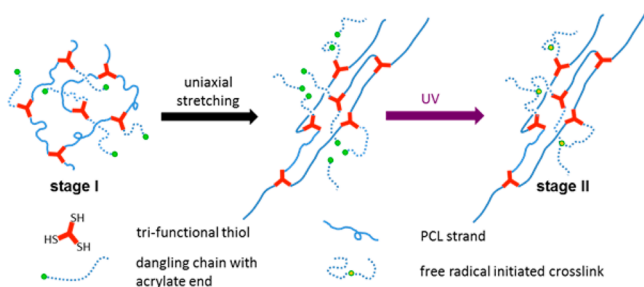

Figure 1. Cartoon showing preparation of dual-cure network stress-free actuators.

Figure 2. Actuation behavior of samples cured at an extension ratio of 650%. (a) A specimen with a gauge length of 8.3 cm (red dot), measured at 70 °C, under no external load, elongated to 9.7 cm, upon cooling to 40 °C, and reversibly returned to its initial length, upon heating to 70 °C. The white part on the bottom end of the sample is the grip used to hold the sample during MTS tests. The grip does not show actuation behavior. (b) Evolution of tensile extension over five cooling−heating cycles, showing 14% actuation.

Supporting Information, for synthesis details). The initial network was prepared using base-catalyzed and radical-free thiol−acrylate coupling of acrylate-functionalized prepolymers with multifunctional thiols (Stage I). The presence of prepolymer in stoichiometric excess leads to a known amount of unreacted and dangling acrylate end groups. A second population of cross-links was introduced by uniaxially stretching melted samples to prescribed extension ratios (λ = 2.0, 3.5, 5.5, 6.5, 7.5) and subsequently postcuring the stretched networks with UV irradiation (Stage II). Photogenerated free radicals initiate polymerization of the acrylate dangling ends to form new subchains that weave throughout the existing strained network. This stagewise establishment of the network was confirmed through observation of acrylate end-group consumption via Fourier transform infrared (FT-IR) spectroscopy (see Figure S2, Supporting Information).

The most intriguing aspect of our network design lies in its ability to configurationally bias chains for crystallization along a preferred direction. While there are many reports of architecturally similar "double networks" where additional cross-links are added in the deformed state,[21−25] the present study involves semicrystalline PCL chains that actively undergo stress-induced crystallization (elongation). During UV postcuring, dangling ends are relaxed and weave through the elastically deformed network before being reacted together to form permanent bonds and entanglements that stabilize strain within the network. Due to the newly introduced constraints, when the load is removed above the melting temperature, the network is unable to retract to its original, unstrained state. Instead, the network adopts an equilibrium "state-of-ease" that balances elastic stress from the original, load-bearing network strands with the entropic stress from newly formed subchains. Consequently, the original network strands are configurationally biased along the prestrain direction by internal stress arising from new entanglements and chemical bond constraints. When cooled, this internal stress facilitates crystallization of network chains along the biased direction, further elongating the material. This effect is fully reversible and is analogous to a two-way shape-memory polymer under a constant external load.

Shape actuation of dual-cured networks was evaluated using mechanical testing with temperature control, and an example is shown in Figure 2. Prior to thermal cycling, samples were deformed by a small amount (2−12%) and unloaded at 70 °C to remove any kinks that formed during film molding. After
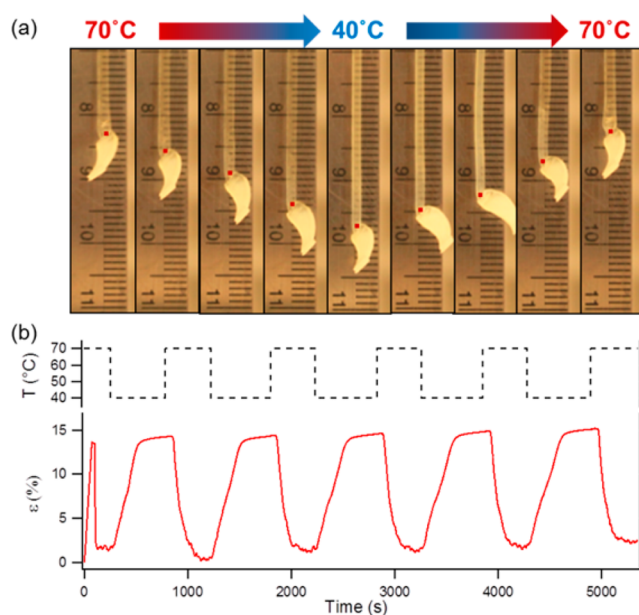
stress training, the original (zero-strain) shape was nearly recovered. The small residual strain should not be ascribed to plastic deformation because it is absent in subsequent cycles. Samples were then subject to five cooling−heating cycles between 40 and 70 °C under a negligible 0.01 N constant force (smallest load possible on the instrument). Upon cooling to 40 °C, the specimen self-elongates, caused by the crystallization of configurationally biased PCL chains. At the plateau of the cycle's elongation, the strain data are slightly sloped, indicating that the sample was not fully crystallized within the assigned cooling period. When heated to 70 °C, the sample contracted due to melting of shape-distorting crystalline domains. Shape actuation is fully reversible and is reproducible over several cycles. A significant dimensional change of 1.4 cm, corresponding to 17% strain, is apparent from the images in Figure 2(a) for a specimen photocured at 650% strain. This specimen reversibly actuated with one end fixed and the other unbounded. The actuation performance of specimens fabricated under different prescribed extension ratios is summarized in Table S1 (Supporting Information).

The semicrystalline, shape-actuating networks were interrogated by wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) (see Figure S3, Supporting Information) experiments. The former was conducted in transmission, to probe the degree of crystallinity and the degree of orientation. Scattered intensity was recorded as a function of the scattering angle 2θ and the azimuthal angle ϕ, defined as the angle between scattered radiation and the draw direction. PCL typically forms orthorhombic unit cells with polymer chains running along the crystallographic c-axis. When PCL is uniaxially stretched (cold-drawn) during crystallization, the c-axis of the unit cell aligns along the stretch direction. The (110) and (200) reflections are observed along the equator,
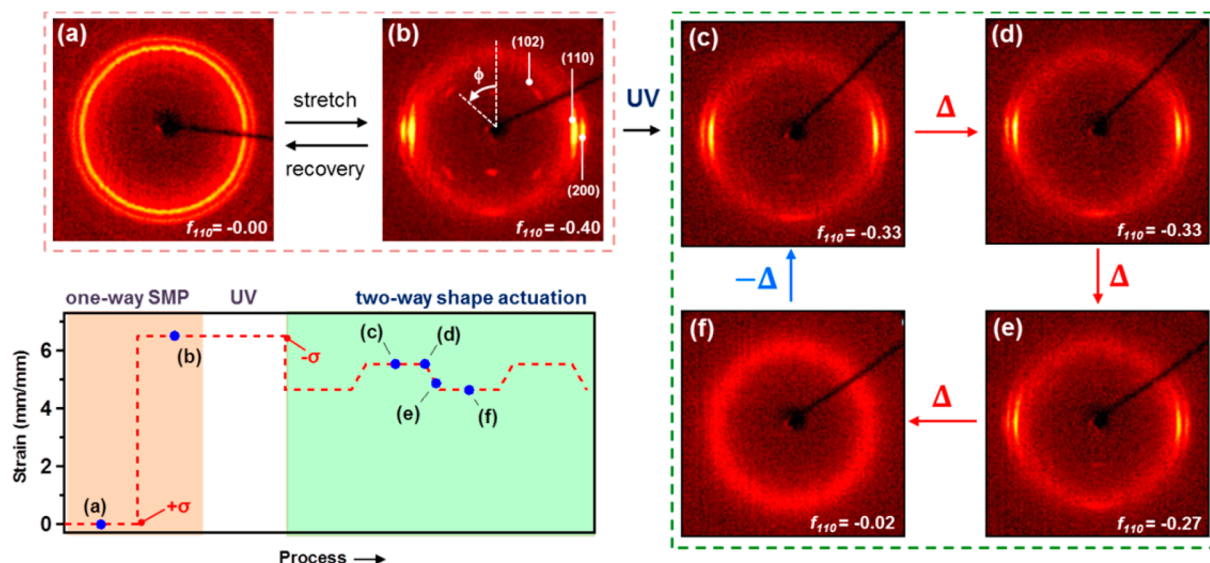
Figure 3. Measured sample dimensions and WAXS data illustrating how UV fixation transforms the specimen from a one-way shape-memory polymer to a two-way shape actuator. Bottom left: strain for a PCL Stage I network that is stretched to 650%, photocured, and thermally cycled without applied stress. The annotations $(+\sigma)$ and $(-\sigma)$ indicate when the load was applied and removed. The blue data points indicate measured strain values, and the dashed line is meant to guide the eye. The rest: evolution of WAXS patterns at different stages as the material is converted from one-way shape-memory polymer (red box) to a two-way shape actuator (green box): (a) Stage I network in the unstretched state. (b) Stage I network stretched to 650%. (c) The network after Stage II curing—UV irradiation at 650% strain—followed by unloading and cooling to room temperature. (d, e, and f) The same network after heating to 40 °C, 55 °C, and 70 °C, respectively. The Herman orientation factor of the (110) planes is included in each WAXS image.

and, for highly ordered samples, the (102) plane is observed as a weak four-point pattern.[26,27] The degree of orientation can be quantified by the azimuthal variation of diffracted X-rays from the (110) plane near $2\theta = 21.5°$ using Hermans' orientation factor[28]

$$f_{110} = \frac{(3\langle\cos\phi\rangle^2 - 1)}{2} \quad (1)$$

where

$$\langle\cos\phi\rangle = \frac{\int_0^\pi I_{110}(\phi)\cos^2\phi\,\sin\phi\,\mathrm{d}\phi}{\int_0^\pi I_{110}(\phi)\sin\phi\,\mathrm{d}\phi} \quad (2)$$

The factor f_{110} has limiting values of unity for perfect alignment, zero for random orientation, and $-1/2$ for alignment of (110) orientation vectors in the plane normal to the cold-draw direction but without a preferred direction within that plane.

Figure 3 shows a data-based illustration relating sample strain to PCL strand orientation at different stages of network preparation and subsequent shape actuation. Prior to UV irradiation, the partially cured PCL network behaves as a cold-drawable shape-memory polymer that can undergo stress-induced crystallization.[8,12] Mechanistically, stretching just beneath PCL's melting point reorients and disrupts crystallites and stretches network strands. Stretched network subchains have lower configurational entropy, and consequently, new crystals form that can fix the network's strain. If heated above the crystal's melting point, these crystals melt, and the material can elastically recover to its original shape. The WAXS pattern from the unstrained, lightly cross-linked network, containing unpolymerized dangling ends (Figure 3, state a), displays uniform orientation arcs for the two most prominent planes, the (110) (innermost) and (200) (outermost). The lack of

orientation in the unstretched sample ($f_{110} = -0.001$) originates from isotropic scattering from the stacks of randomly oriented chain-folded lamellae. When cold-drawn to 650% (Figure 3, state b), the scattered intensity concentrates at low angle along the meridian with $f_{110} \sim -0.40$, indicating a large amount of lamellae oriented along the stretch direction.

Samples can be transformed from a one-way shape-memory polymer to a two-way shape actuator by UV irradiation at fixed elongation above its melting point. Irradiation introduces new net points and converts dangling ends into elastically active subchains. The resultant specimen turned pale yellow in comparison to its previously milky white appearance due to the decomposition of loaded photoinitiator, DMPA. When unloaded, the sample's extension ratio decreased, and its WAXS pattern (Figure 3, state c) exhibited somewhat reduced orientation with $f_{110} \sim -0.33$. In this state, the new netpoints interfere with crystallization, and dangling ends are no longer available for undisrupted crystallization. Heating the specimen from 25 to 40 °C (Figure 3, state c to d) had barely any impact on the degree of orientation and elongation. However, by 55 °C, the scattering arcs from the oriented crystalline lamella blurred, and the sample dimension significantly shortened (Figure 3, state e). Further heating to 70 °C, well above its melting temperature, caused complete melting of PCL crystallites as indicated by the disappearance of the Bragg diffraction (Figure 3, state f). Furthermore, at 70 °C the sample further contracted to its equilibrium extension, which minimizes the total stretching free energy of all strands. Upon cooling, internal stress-induced crystallization of the dual cured network occurs, and the sample recovers its extended state (Figure 3, state c), completing its stress-free two-way shape actuation cycle.

In summary, we have disclosed a single-phase, poly(ε-caprolactone) shape actuator that reversibly shrinks and elongates along one dimension upon heating and cooling.

The actuator is simple and straightforward to prepare: cross-links between subchains are first introduced in the undeformed state (Stage I), and the resulting elastomer is further cross-linked, while stretched to several hundred percent, by polymerization of dangling ends containing acrylate functional groups (Stage II). The resulting network has built-in stress and anisotropy along the stretch direction, imparting a two-way shape memory effect in the absence of an external load. WAXS tests confirmed the ability of network subchains to transform between nearly isotropic coils and oriented crystals, upon thermal cycling. When cooled, the actuator elongates as crystallization further aligns PCL chains along the stretch direction, and when heated, the actuator contracts back to its state-of-ease. Thermal cycling is highly reproducible, and no evidence of mechanical creep was observed. The concept is versatile and can be applied to any polymer that exhibits strain-induced crystallization where cross-links are uniformly and controllably introduced in elongated states with built-in stress. The accomplishment of a thermally activated, one-dimensional stress-free actuation based on a single material (instead of a composite) will broadly benefit a range of technologies, especially biomedical devices, artificial muscles, and robotic system designs. Moreover, the obtained understanding of the stress-induced crystallization within an anisotropic network opens up new possibilities to engineering the long-existing "double networks" in creative ways.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials and characterization methods and supplemental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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