Photoactuators based on liquid crystal elastomers or networks are smart materials that show photoinduced motions. However, their crosslinked networks make their repair or reprocessing difficult. Here, a healable and reprocessable photoactuator is fabricated using entangled high-molecular-weight azobenzene-containing polymers (azopolymers) that are non-crosslinked. A series of linear liquid crystal azopolymers with different molecular weights are synthesized. The low-molecular-weight azopolymers (5–53 kg mol$^{-1}$) cannot form freestanding photoactuators because their polymer chains lack entanglements, which makes them hard and brittle. In contrast, flexible and stretchable actuators are fabricated using high-molecular-weight azopolymers (80–100 kg mol$^{-1}$) that exhibit good processability because of the polymer chain entanglements. The azopolymer photoactuators show photoinduced bending based on photoinduced trans–cis isomerization of the azopolymers on the irradiated side. The experiments show not only photoinduced phase transitions or changes in the order parameters but also photoinduced solid-to-liquid transition of the azopolymers resulting in shape changes and mechanical responses. Thus, photoinduced solid-to-liquid transition is a new mechanism for the design of photoactuators. Moreover, the azopolymer photoactuators are healable and reprocessable via solution processing or light irradiation. Healability and reprocessability prolong lifetimes of photoactuators are important for materials reuse and recycling, and represent a new strategy for the preparation of smart materials.

1. Introduction

Actuators based on liquid crystal elastomers (LCEs) or liquid crystal networks (LCNs) show mechanical responses and shape changes under the stimulation of external stimuli, such as heat and light.[1] They are promising materials for artificial muscles,[1a,2] microrobots,[3] microfluidics,[4] oscillators,[5] and sensors.[6] The advantages of controlling actuators with light are that light has a high spatiotemporal resolution and that the photomechanical response represents a novel way for solar energy conversion.[1a,4,7] Photoactuators are usually prepared by introducing photoswitchable chromophores, such as azobenzene, into networks of LC polymers.[1e,2a,4a,8] The photoisomerization of azobenzene groups in a network can induce phase transitions or changes in the order parameter or changes in glass transition temperature ($T_g$), resulting in a mechanical response.[1a,4,7] Photoactuators need to be fabricated into different shapes, sizes, and architectures for different applications. However, the crosslinked networks of photoactuators make them insoluble and unmeltable.
Thus, it is difficult to reshape, reprocess, or reuse crosslinked photoactuators. Additionally, photoactuators are susceptible to mechanical damage, while repairing damaged photoactuators can prolong their lifetimes. The development of reprocessable and healable photoactuators can address the abovementioned problems. With the development of dynamic/reversible bonds,[9] reconfigurable LCEs and LCNs have been prepared.[2b,10] For example, Zhao and coworkers developed a rearrangeable azobenzene-containing LCN using exchangeable ester bonds,[10c] which is reprocessable at high temperatures in the presence of a catalyst. Photoactuators based on dynamic/reversible bonds showed that healability and reprocessability are important for materials design and can make photoactuators have new applications. However, healing and reprocessing via heating lack spatial resolution and are inconvenient in many cases. The development of photoactuators that can be precisely reprocessed and healed at ambient temperature is desirable but poses a challenge.

Here, we demonstrate the preparation of healable and reprocessable photoactuators using entangled linear azopolymers (Figure 1a). Our azopolymer actuators can be healed and reprocessed using solution processing or light irradiation at ambient temperature. The entangled linear azopolymers are soluble so that healing and reprocessing are achieved via solution processing. In addition, we demonstrated photoinduced healing and reprocessing of azopolymer actuators based on photoinduced reversible solid-to-liquid transitions. Several groups[11] and our group[12] reported that some azobenzene-containing small molecules or low-molecular-weight azopolymers can be switched between solids and liquids by light. For fabricating actuators, entangled high-molecular-weight azopolymers are better suited than small molecules or low-molecular-weight azopolymers because of their better processability and improved mechanical properties (Figure 1b,c). However, photoinduced reversible solid-to-liquid transitions for entangled high-molecular-weight azopolymers were not investigated before.[13] Driven actuators via photoinduced reversible solid-to-liquid transitions have not been demonstrated. In this work, we demonstrate entangled azopolymers with a molecular weight of 100 kg mol⁻¹ that show photoinduced reversible solid-to-liquid transitions. The polymer chain entanglement enables fabricating processable, robust, stretchable, and flexible actuators that are healable and reprocessable under light irradiation. Moreover, the well-accepted mechanism for photoactuation of photoresponsive liquid crystal polymers is that photoisomerization induces phase transitions or changes in the order parameter. Here, we demonstrate that photoinduced solid-to-liquid transition in our azopolymer contributes to light-induced mechanical responses and shape changes. This mechanism provides a new strategy for the design of advanced photoactuators.

2. Results and Discussion

We prepared azopolymers with different molecular weights—whose abbreviations are listed in Table 1—using atom transfer radical polymerization (ATRP) and recycling gel permeation chromatography (GPC) (Figure S1, Supporting Information). These azopolymers are polyacrylates with a flexible spacer and an azobenzene group on the polymer side chain (chemical structure in Figure 1a). We measured their molecular weights and polydispersity indices using GPC, determined their glass transition temperature (Tg) values and phase transition temperatures using differential scanning calorimetry (DSC), and observed their mesophases using polarized optical microscopy (POM) (Figures S2–S5, Supporting Information). Pertinent properties of the azopolymers are summarized in Table 1. The number-average molecular weights (Mn) of the azopolymers range from 5 to 100 kg mol⁻¹. The Tg values of the trans azopolymers increase from 48 to 80 °C with molecular weight. Additionally, all azopolymers exhibit liquid crystal phases above their Tg values.

To fabricate photoactuators, we prepared freestanding films by drop-casting azopolymer solutions on Teflon substrates and peeling the dried films off using a sharp knife (Figure 1c; Figure S6, Supporting Information). The azopolymers with molecular weights from 10 to 53 kg mol⁻¹ broke during the peeling process; therefore, freestanding films could not be obtained. In contrast, azopolymers with high molecular weights (80 and 100 kg mol⁻¹) could be peeled off, and freestanding films were obtained using the same procedure. We attribute their different processabilities to polymer chain entanglements. The critical entanglement molecular weight of the azopolymer calculated using Wool’s model[14] was 68 kg mol⁻¹ (Supporting Information). Low-molecular-weight azopolymers, which lacked entanglement, were hard and brittle; entangled high-molecular-weight azopolymers were tough and possessed good processability (Figure 1b,c). The freestanding film of P1-100k was highly transparent and flexible (Figure 1d,e). The stretch force to break a P1-100k film (5 mm × 1.5 mm × 130 µm) was ≈5 N (Figure S7, Supporting Information). Moreover, P1-100k was reprocessable at elevated temperatures. A freestanding film of P1-100k was elongated by 19 ± 3% at 90 °C via stretching (Figure 1f). POM images showed that the alignment of azobenzene mesogens was achieved via stretching (Figure S8, Supporting Information). All these properties enabled fabricating processable, robust, stretchable, and flexible actuators using P1-100k.

The photoresponsiveness of azopolymer films was studied using UV-vis absorption spectroscopy (Figure 2; Figure S9, Supporting Information). Upon UV irradiation, the π−π* absorption band of trans azobenzene groups at ≈332 nm decreased. Correspondingly, the n−π* absorption band of the cis isomer at ≈446 nm increased with the irradiation time. These changes showed that UV irradiation induced a trans→cis isomerization. Subsequent visible-light irradiation reverted the spectral changes back, which indicated that the cis azobenzene groups were switched back to the trans ones. Therefore, the photoisomerization of the azopolymer film was reversible.

Furthermore, we investigated the photomechanical response of P1-100k films (Figure 3). First, we studied a stretched P1-100k film (7 mm × 2 mm × 10 µm, Figure 3a), in which the azobenzene mesogens were aligned along the stretching direction (Figure S8, Supporting Information). UV irradiation of the stretched film induced bending toward the UV light source. The bending angle was 62° after irradiation for 10 min. Subsequent blue-light irradiation induced bending away from the blue-light source, and the film changed back to the upright position after blue-light irradiation for 50 s. Next, we studied an unstretched polydomain film (7 mm × 2 mm × 10 µm, Figure 3b), in which
the azobenzene mesogens in each tiny domain may have different orientations (Figure S8, Supporting Information). UV irradiation of the unstretched film also induced bending toward the UV light source. The bending angle was 26° after irradiation for 10 min. The film returned to its original position with subsequent blue-light irradiation for 10 min. Compared with the stretched P1-100k film, the unstretched one presented a slow bending rate and a small bending angle. The rate was slower than the reported azobenzene-containing actuators that were aligned.\textsuperscript{[1e,2b,4a,8a]} The results suggested that the alignment of azobenzene mesogens enhanced the photomechanical response. This result is coincident with the fact that liquid crystal mesogens in LCEs and LCNs are usually aligned when preparing actuators.

Different from conventional LCEs or LCNs that are crosslinked, our entangled azopolymer P1-100k was not...
crosslinked via covalent bonds. Thus, P1-100k can be reprocessed at elevated temperatures (Figure 1f) or using solution processes (Figure 4). As a proof of concept, we fabricated a rectangular film of P1-100k by drop-casting the azopolymer solution on a Teflon substrate, drying, and peeling the film from the substrate (Figure 4a). To reshape the object, we dissolved the rectangular film by the solution process and prepared a triangular film. Using the solution process, we again

Table 1. Certain properties of azopolymers with different molecular weights.

| Azopolymer | $M_n$ [kg mol$^{-1}$] | PDI | $T_g$ [°C] | Phase transitions [°C] |
|------------|----------------------|-----|-----------|------------------------|
| P1-5k      | 5                    | 1.41| 48        | G 48 LC 1, 88 I        |
| P1-10k     | 10                   | 1.41| 60        | G 60 LC 1, 98 LC 1, 110 I |
| P1-15k     | 15                   | 1.39| 65        | G 65 LC 1, 102 LC 2, 108 I |
| P1-25k     | 25                   | 1.35| 70        | G 70 LC 1, 105 I       |
| P1-35k     | 35                   | 1.29| 77        | G 77 LC 1, 109 LC 2, 117 I |
| P1-53k     | 53                   | 1.11| 80        | G 80 LC 1, 111 LC 2, 118 I |
| P1-80k     | 80                   | 1.11| 80        | G 80 LC 1, 108 LC 2, 113 I |
| P1-100k    | 100                  | 1.15| 80        | G 80 LC 1, 111 LC 2, 118 I |

$M_n$, number-average molecular weight; PDI, polydispersity index; $T_g$, glass transition temperature; GPC, gel permeation chromatography; DSC, differential scanning calorimetry; G, glass; LC 1, liquid crystal phase 1; LC 2, liquid crystal phase 2; and I, isotropic phase. $M_n$ and PDI were measured using GPC. $T_g$ values and phase transition temperatures were determined using the DSC second heating curves.

Figure 2. UV–vis absorption spectra of a spin-cast P1-100k film before irradiation, after UV irradiation (365 nm, 3.4 mW cm$^{-2}$, 1 min) and after subsequent visible light irradiation (470 nm, 0.7 mW cm$^{-2}$, 1 min).

Figure 3. Photoinduced reversible bending of P1-100k films. Photomechanical responses of a) stretched (with 2 N) and b) unstretched P1-100k films under UV (365 nm, 51 mW cm$^{-2}$) and subsequent blue-light (470 nm, 9 mW cm$^{-2}$) irradiation.
of unstretched films, we further studied the photomechanical responses (see below).

When a P1-100k film with a thickness of 10 µm is irradiated with UV light, only the azobenzene groups on the irradiated side isomerize. This action is because the absorption coefficient of the trans azopolymer at 365 nm is as large as \(2 \times 10^4 \text{ cm}^{-1}\), and the top layer with a thickness of 1 µm absorbs 99% of the incident UV light. As photoisomerization takes place, the absorption coefficient at 365 nm decreases by \(\approx 60\%\) in the cis-rich state. While the incident light may penetrate deeper, the top 3 µm thick layer of a cis-rich film absorbs more than 99% of the incident UV light; the azopolymer layer at the bottom of the film could not be excited with UV irradiation. The film forms a bilayer structure under UV irradiation: the bottom layer of the film does not change, but the top layer changes into a cis-rich state. Thus, we analyzed the mechanical properties of the top layer to elucidate the bending mechanism.

We performed nanoindentation measurements on a P1-100k film (thickness: 10 µm) to study how light irradiation influences the mechanical properties of the top layer (Figure 5a). The loading-pause–unloading displacement curves of the trans P1-100k film showed that the film possessed a hard surface (Figure 5b). After contact with the tip, the loading force increased with the displacement while the adhesion force was negligible. The elastic modulus and hardness were 1150 \(\pm\) 120 and 68 \(\pm\) 30 MPa, respectively (Table S1, Supporting Information). Subsequently, the film was illuminated with UV light, and the top layer was converted into a cis-rich state. The loading-pause–unloading displacement curves of the cis-rich P1-100k film were measured (Figure 5c). The adhesion force increased to \(\approx 2.27\) mN, indicating that cis-rich P1-100k was more adhesive than trans P1-100k. The elastic modulus and hardness were 212 \(\pm\) 40 and 3 \(\pm\) 1 MPa, respectively (Table S1, Supporting Information), which showed that cis-rich P1-100k was considerably softer than trans P1-100k. Additionally, the loading-pause–unloading displacement curves of cis-rich P1-100k were different from those of trans P1-100k. After the tip contacted the sample during the approach process, the slope of the curve gradually increased with the displacement. In the unloading process, the adhesion force exhibited a maximum at \(\approx 1950\) nm. Further withdrawal of the tip gradually decreased the force to 0. These results revealed that cis-rich P1-100k was a viscous material that formed a meniscus with the tip. Afterward, cis-rich P1-100k was converted back to trans-rich P1-100k via blue-light irradiation. The loading-pause–unloading displacement curves of the regenerated trans-rich P1-100k film (Figure 5d) were similar to those of the as-prepared trans P1-100k film (Figure 5b). The elastic modulus and hardness were 737 \(\pm\) 153 and 48 \(\pm\) 18 MPa, respectively (Table S1, Supporting Information). This experiment showed that the mechanical properties of P1-100k were photoswitchable.

The large change in mechanical properties of P1-100k under light irradiation is because P1-100k exhibited a photoinduced solid-to-liquid transition (Figure 5e). We have demonstrated that low-molecular-weight azopolymers (\(M = 9.9\) and 27 kg mol\(^{-1}\)) exhibit photoinduced reversible solid-to-liquid transitions.\(^{12,13}\) The liquid cis azopolymers are viscoelastic polymer melts.\(^{12,13}\) Here, we found that the high-molecular-weight azopolymer P1-100k also exhibited this property. Trans

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(relevant figures and text)
P1-100k had a $T_g$ (≈80 °C) higher than room temperature and was thus a solid; while cis-rich P1-100k had a $T_g$ (≈7 °C) lower than room temperature and was thus a liquid (Figure 5f; Figures S13–S15, Supporting Information). In addition, we observed the powders of isotropic P1-100k changed from isotropic solid to isotropic liquid under UV irradiation (Figures S16 and S17, Supporting Information). No liquid crystal to isotropic transition was involved in the photoinduced solid-to-liquid transition of P1-100k powders under UV irradiation (365 nm, 51 mW cm$^{-2}$, 20 min). Scale bar: 10 µm. f) DSC first heating curves of trans P1-100k and cis-rich P1-100k. The $T_g$ value of cis-rich P1-100k was substantially lower than that of the trans version. The cis content determined by $^1$H NMR was ≈87%.

Figure 5. Photoinduced solid-to-liquid transition demonstrated by nanoindentation, optical microscopy, and DSC. a) Schematic illustration: studying a P1-100k film before irradiation, after UV irradiation and after subsequent blue-light irradiation using nanoindentation (see Supporting Information for the experimental details for nanoindentation). Loading-pause–unloading displacement curves of the P1-100k film before irradiation b), after UV irradiation (365 nm, 51 mW cm$^{-2}$, 15 min) c), and after subsequent blue-light irradiation (470 nm, 9 mW cm$^{-2}$, 15 min) d). e) The photoinduced solid-to-liquid transition of P1-100k powders under UV irradiation (365 nm, 51 mW cm$^{-2}$, 20 min). Scale bar: 10 µm. f) DSC first heating curves of trans P1-100k and cis-rich P1-100k. The $T_g$ value of cis-rich P1-100k was substantially lower than that of the trans version. The cis content determined by $^1$H NMR was ≈87%.

Thin films or coatings prepared using P1-100k are healable based on photoinduced reversible solid-to-liquid transitions (Figure 6a). To demonstrate healing, a scratch on a P1-100k actuator was locally irradiated with UV light (365 nm, 51 mW cm$^{-2}$, 20 min) (Figure 6b–iii). Because UV irradiation induced flow in the azopolymer, the scratch disappeared (Figure 6biii). Then, visible light (470 nm, 9 mW cm$^{-2}$, 20 min) switched the healed P1 back to the solid state, completing the healing process (Figure 6biv). When a new scratch appeared in the same area of the film (Figure 6bv), it was healed again with light (Figure 6bvi). Atomic force microscopy (AFM) images also showed that light irradiation can heal scratches on a P1-100k film (Figure S19, Supporting Information). P1-100k films could be repeatedly healed with light. Thus, the photoinduced reversible solid-to-liquid transitions facilitate repairing damaged actuators.
Furthermore, we cut azopolymer actuators and healed the actuators in two ways. First, we demonstrated photowelding of an actuator that was cut into two pieces (Figure 6c). Both pieces of the actuator were illuminated with UV light (20 min, 365 nm, 51 mW cm$^{-2}$). The UV illuminated sides were pressed together and the joint was irradiated using blue light (20 min, 470 nm, 9 mW cm$^{-2}$). The welded actuator showed photoinduced bending (Figure 6d). Second, we demonstrated heat-induced healing of a cut actuator (Figure S20a, Supporting Information). The repaired actuator showed photoinduced bending (Figure S20b, Supporting Information).

Photoinduced solid-to-liquid transitions also enable the reprocessing of azopolymer actuators with high spatial resolution. Microstructured actuators show potential for applications such as transport devices, microactuators, and coatings with switchable adhesion and friction.$^{1g,16}$ P1-100k is a promising material for microstructured photoactuators because it has good reprocessability and it does not need alignment for photoactuation. We fabricated microstructured photoactuators via photopatterning (Figure 7a). First, a P1-100k film was prepared by drop-casting an azopolymer solution onto a Teflon substrate. Then, a mask was placed on top of the film. The film was illuminated with UV (365 nm, 51 mW cm$^{-2}$, 20 min) and blue light (470 nm, 9 mW cm$^{-2}$, 20 min) through the mask. After the removal of the mask, well-defined microstructures were created (Figure 7b). The microstructured photoactuator was obtained by peeling the film from the Teflon substrate. Light irradiation of the side without any microstructures induced bending of the microstructured photoactuator (Figure 7c). The photoactuation led to the bending of the microstructures. Before irradiation, a flat array of the microstructures was observed (Figure 7d), and after UV irradiation (365 nm, 51 mW cm$^{-2}$, 20 min), the actuator was bent toward the light source. Part of the microstructures were out of the focal plane of the optical microscope; therefore, a curved array of microstructures was obtained (Figure 7e). After blue-light irradiation (470 nm, 9 mW cm$^{-2}$, 20 min), the microstructured photoactuator returned to the initial state (Figure 7f). This experiment demonstrates a facile way to fabricate microstructured photoactuators.

3. Conclusion
In conclusion, we prepared healable and reprocessable photoactuators using entangled linear azopolymers that show photoinduced reversible solid-to-liquid transitions. Compared with nonentangled azopolymers, the entangled azopolymers exhibited improved mechanical properties and (re)processability. Freestanding azopolymer films were fabricated as photoactuators. The alignment of azobenzene mesogens in the photoactuators was achieved by stretching at 90 °C. Both aligned and nonaligned azopolymer films revealed photoinduced
reversible bending. The photoinduced reversible solid-to-liquid transitions contributed to the photoinduced bending of the nonaligned azopolymer films. The azopolymer actuators can be reprocessed and reshaped via conventional methods, such as heating or solution processes. Different from conventional methods, photoinduced reversible solid-to-liquid transitions enable the healing and reprocessing of azopolymer photoactuators with light at ambient temperature and in the absence of any solvent. Scratches on the azopolymer actuators were healed with light, and microstructures on the actuators were fabricated via photopatterning. The microstructured azopolymer actuator showed photoinduced bending, which induced a reversible distortion of the microstructures. The combination of polymer chain entanglements and photoinduced reversible solid-to-liquid transitions provide a new strategy for designing actuators with good reprocessability and healability.

4. Experimental Section

Synthesis and Characterization: The synthesis and characterization of the azopolymers are described in the Supporting Information.

Preparation of Photoactuators and Photoactuation: The azopolymer P1-100k was dissolved in cyclopentanone, and the polymer solution was drop-casted on a Teflon substrate. Then, the film was dried under vacuum at 40 °C overnight. A freestanding film was obtained by peeling it off using a sharp knife. The freestanding film was cut into an appropriate size for photoactuation experiments. To study the photomechanical response, the bottom of the freestanding film was fixed, and the film was irradiated using UV (365 nm, 51 mW cm\(^{-2}\)) and blue light (470 nm, 9 mW cm\(^{-2}\)). The bending processes were recorded using a camera.

Photoinduced Healing: A scratch on P1-100k films was made using an AFM tip controlled by a micromanipulator. The scratch was locally irradiated with UV light (365 nm, 51 mW cm\(^{-2}\), 20 min), which induced a solid-to-liquid transition. Then, blue-light irradiation (470 nm, 9 mW cm\(^{-2}\), 20 min) solidified the sample. The healing processes were recorded using optical microscopy and AFM.

Photopatterning: P1-100k was dissolved in cyclopentanone, and the solution was drop-casted on a Teflon substrate. After the film was dried, a mask was placed on top of the film. The film was irradiated with UV (365 nm, 51 mW cm\(^{-2}\), 20 min) and blue light (470 nm, 9 mW cm\(^{-2}\), 20 min). The microstructures were formed after the light irradiation and removal of the mask from the sample surface.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

actuators, azobenzene, photoswitches, polymers, self-healing

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