

Programming Shape-Morphing Behavior of Zwitterionic Polymer/Liquid Crystal Composite with Humidity-responsive Self-healing Performance

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Electronic Supplementary Information

Abstract In this study, a zwitterionic polymer/liquid crystals composite film with programming shape-morphing behavior and humidity-responsive self-healing performance was prepared by blending a zwitterionic polymer and liquid crystalline azobenzene compound in solution, followed by film-forming in a mold without tedious or multistep synthetic route. The as-obtained zwitterionic polymer/liquid crystal composite film exhibited programming shape-morphing behavior under different stimuli. In this process, the temporary shape of the composite film was memorized after the removal of the stimuli. Such characteristics would fit the requirements of intelligence and energy-saving for stimuli-responsive shape-changing materials. Moreover, the composite film showed humidity-responsive self-healing performances under wet conditions at room temperature. In summary, the simple design and preparation route of the zwitterionic polymer/liquid crystal composite film with programming shape-morphing behavior and mild condition-responsive self-healing performance look promising for the fabrication and practical application of novel photo-driven devices and soft robotics.

Keywords Zwitterionic polymer; Polymer/liquid crystals composite; Programming shape-morphing behavior; Humidity-responsive self-healing performance; Stimuli-responsive shape-changing

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INTRODUCTION

Mimicking the behaviors of some biological organisms who implement shape-morphing under variable conditions, such as fast snapping of Venus flytrap upon mechanical stimulation, blooming of water lily during day/night cycles, and change in skin wrinkles shape of caterpillars during movement, has become an important topic in academic circles.^[1–4] For instance, the development of stimuli-responsive shape-changing materials has recently attracted enormous interest because of their potential applications in artificial muscles, flexible microrobots, sensors or medical devices, etc. Over the years, various intelligent materials with such function have been explored and developed, including hydrogels,^[5,6] dielectric elastomer,^[7] shape-memory polymers (SMPs),^[8,9] and liquid crystalline polymers (LCPs).^[10–12] Among these stimuli-responsive shape-changing materials, LCPs have attracted increasing attention owing to their combined well-organized

liquid crystal structures with polymer properties and the distinctive characteristics under various stimuli, such as temperature, light, humidity, solvent, electric and so on.^[13–18]

Particularly, photo-responsive LCPs^[19] are attracting increased attentions of scientists. Various materials systems have been developed in past decades. Yu *et al.* proposed the strategy of fabrication photo-responsive polymer-dispersed liquid crystal (PDLC)-like hybrid films by efficient and simple blending of poly(vinyl alcohol) (PVA) and liquid crystals containing mesogenic azobenzene molecules.^[20–22] In this process, polymers used as the matrix endowed the material with good film-formation and mechanical properties, and liquid crystals as the dopants rendered the film with stimuli-responsive shape-morphing function. After mechanical stretching, the liquid crystals arranged homogeneously to yield a hybrid film with photo-induced shape-deformation similar to LCPs. However, although photo-driven PDLC-like hybrid films and most conventional cross-linked LCPs could hold temporary shapes under stimuli, the original state would be recovered in the short period after removal of the stimuli. The reason for this has to do with the recovery in the arrangement of liquid crystals or internal stress from the cross-linked

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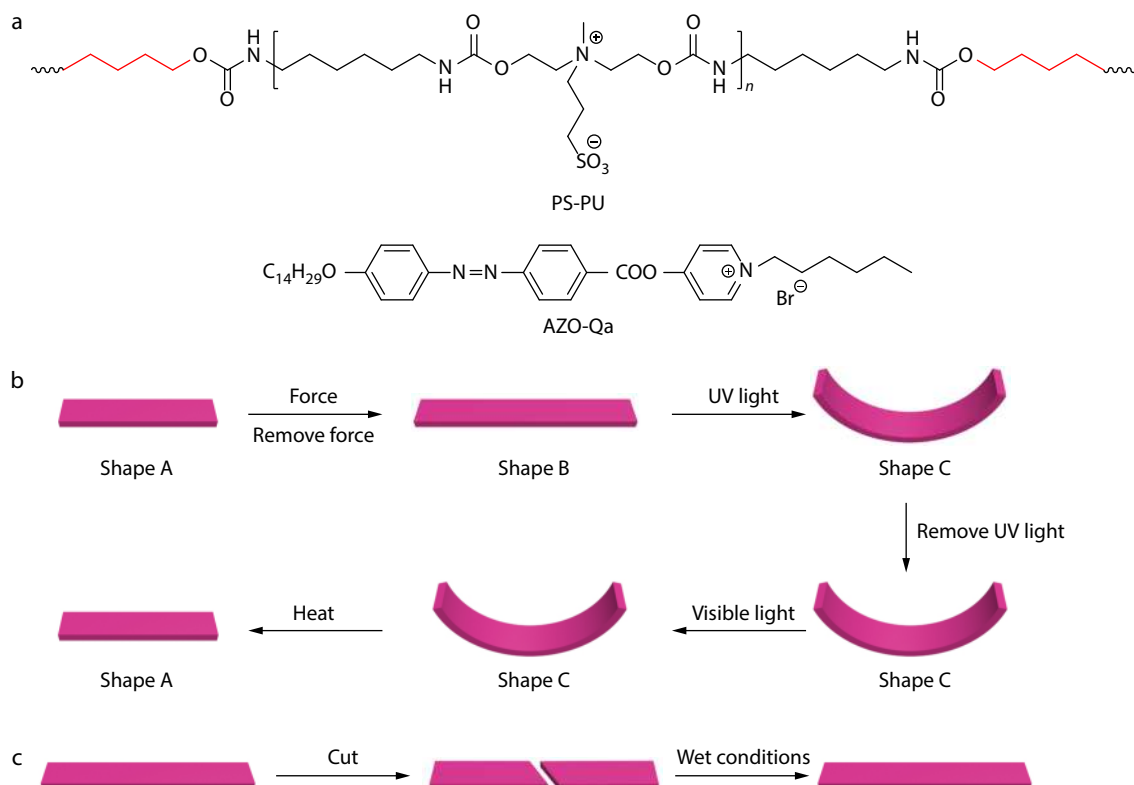
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polymer network.^[23] Such performances stating that temporary shapes cannot be held in the absence of stimuli have restricted the applications of such stimuli-responsive shape-changing materials. For example, soft mechanical porters fabricated by cross-linked LCPs may deform into yield bent shapes (like hooks) from flat shapes and could sling objects under UV light. To this end, the porters must constantly be irradiated with UV light during the work. If not, the porters would lose efficacy due to the recovery of flat porter shape in short time in the absence of UV light.^[24] Hence, successfully maintaining the bent shape of the porter combined with correct functioning after removal of UV light may be useful for intelligence and energy saving.

On the other hand, damages and defects, such as scratches, surface flaws, and cracks are inevitable in stimuli-responsive shape-changing materials during use.^[25] Therefore, self-healing or the capability of a material to recover from physical damage could prolong its service life in practical applications.^[26,27] Hence, the development of stimuli-responsive shape-changing materials with self-healing performances is of great practical and scientific significance. In this respect, some LCPs or polymer/liquid crystal composites with self-healing effects have been reported,^[28,29] such as hydrogen-bonded liquid crystal polymers,^[30,31] however, hydrogen-bonded liquid crystal polymers show self-healing and recyclable properties by breaking the hydrogen bonds only under specific conditions (higher temperatures).^[32] Overall, the self-repair property appeared in zwitterionic polymer/liquid crystal systems has not been investigated

comprehensively. The self-healing process and mechanism might be quite different from those under high temperature and high pressure.

Herein, a polymer/liquid crystals composite film with programming shape-morphing behavior and mild condition-responsive self-healing performance was developed. The composite film was fabricated by blending a zwitterionic polymer and liquid crystalline azobenzene in DMF solution, followed by film-forming in a mold without tedious and multistep synthetic routes. As shown in Scheme 1(a), the zwitterionic group sulfobetaine was grafted on the main chain of conventional polyurethane (PU) to form a zwitterionic polymer PS-PU. The low-mass mesogenic azobenzene compound Azo-Qa played the role of a photosensitive component, offering inner stress to endow the composite film with photo-responsive shape-morphing capability under UV light irradiation.^[33] Furthermore, the separation between the hard and soft segments in the zwitterionic polymer rendered the zwitterionic polymer/liquid crystal composite with a shape memory effect. This ensured memorization of the temporary shape of the composite films after the removal of the stimuli. The as-obtained zwitterionic polymer/liquid crystal composite film exhibited programming shape-morphing behavior under applied stimuli. Under mechanical stimulation (Scheme 1b), the composite film transformed into an elongated flat shape (shape B) from the original flat shape (shape A) and maintained the shape after removal of external force. Under UV light, the film deformed into a bent shape (shape C), which can be fixed after removal of the UV light or irradiation under



Scheme 1 (a) Chemical structures of PS-PU and Azo-Qa; (b) Schematic illustration of the programming shape-morphing behavior of PS-PU/Azo-Qa composite film under different stimuli; (c) Schematic diagrams of the humidity-responsive self-healing process of PS-PU/Azo-Qa composite film under wet conditions at room temperature.

visible light for some time. Under applied thermal stimulation, the composite film recovered its original flat shape (shape A). Also, the polymer matrix presented moisture-responsive properties due to the ultra-hydrophilicity of the zwitterionic moieties.^[34,35] The latter was contributed to the humidity-responsive self-healing performance of the zwitterionic polymer/liquid crystal composites (Scheme 1c). Overall, the design and preparation route of the zwitterionic polymer/liquid crystal composite film with programming shape-morphing behavior and mild condition-responsive self-healing performance in this work look promising for the fabrication and practical applications of novel photo-driven devices and soft robotics.

EXPERIMENTAL

Materials

Zwitterionic polyurethane (PS-PU) was prepared by the grafting reaction between conventional polyurethane and 1,3-propanesultone (PS) according to our previous report.^[33] The liquid crystalline azobenzene compound (Azo-Qa) was synthesized *via* quaternization between halogenated alkanes and tertiary amines. The detailed synthesis and characterization data are provided in the electronic supplementary information (ESI, Figs. S1–S6).

Fabrication of Zwitterionic Polymer/Liquid Crystal Composite Film

The PS-PU/Azo-Qa composite film was fabricated by first dissolving 2.0 g of PS-PU and 0.12 g of Azo-Qa in DMF (30 wt%). The obtained solution was then stirred for 4 h at 60 °C to ensure the homogeneous dispersion of the two components. Afterward, the as-prepared solution was poured into a Teflon mold and dried in a vacuum oven at 80 °C for two days to reduce the solvent. Finally, the composite film with a dimension of 60 mm × 25 mm × 0.7 mm was achieved by peeling off the mold.

Characterization and Measurements

Nuclear magnetic resonance spectroscopy (¹H-NMR, Bruker AV400, Switzerland) was used to confirm the molecular structures of the synthesized materials. To this end, deuterated dimethyl sulfoxide (d-DMSO) was employed as the solvent and tetramethylsilane as an internal reference at room temperature. The surface bondings were identified by X-ray photoelectron spectroscopy (XPS, VG multilab2000) analyses using X-ray source made of Al K α , X-ray gun with 15 kV voltage and 10 mA current, and photoelectron take-off angle of 90°. The phase structure of the liquid crystals was analyzed by X-ray diffractometer (XRD, D8 Advance, Germany) scanning in the range of 10° to 50° at a rate of 5 (°)/min. The thermal properties were evaluated by a differential scanning calorimetry (DSC-25, TA, USA) instrument under purged nitrogen gas over the temperature range of –40 °C to 200 °C and heating or cooling rate of 10 °C/min. The polarizing optical photomicrographs of the polymers were collected on a polarizing optical microscope (POM, Carl Zeiss, AxioVision SE64) equipped with a hot stage and accuracy of 0.1 °C (Linkam LTS420). The UV-visible (UV-Vis) spectra were obtained on a Lambda 950 (PerkinElmer, USA) spectrophotometer. Scanning electron microscopy (SEM) images were collected on a Thermo APREO S. Atomic force

microscopy (AFM) images were recorded on a Multimode 8 system (Bruker Dimension ICON, USA) under tapping mode and room temperature. The tensile tests were measured on a UT-2080 tensile machine (U-CAN UT-2080, Taiwan, China) at room temperature and tensile speed of 50 mm/min, and strain-stress curves were recorded for analysis. Dynamic mechanical analysis (DMA) data were used to quantitatively analyze the shape memory effect of the composite films. The samples were measured on a DMA Q800 (TA Instruments, USA) under controlled-force mode. The humidity-induced self-healing process was implemented in a constant temperature humidity chamber (HWS-150, Jinghong, China).

RESULTS AND DISCUSSION

Fabrication of PS-PU/Azo-Qa Composite Films

PS-PU/Azo-Qa composite films were prepared by direct film-forming from a solution containing certain amounts of homodispersed PS-PU and Azo-Qa in a mold. The chemical structures of PS-PU and Azo-Qa are presented in Scheme 1(a), and the schematic diagrams of the two components in the zwitterionic polymer/liquid crystal composite are illustrated in Fig. 1(a). Sulfobetaine (SB), as a common zwitterionic group, was incorporated into the backbone chain of conventional polyurethane through chemical bonding after the ring-opening reaction between alkyl sulfonic lactone and tertiary amine.^[36,37] NMR and XPS spectra show the formation of zwitterionic group in PS-PU and AZO-Qa (Fig. S4 in ESI). XRD spectra confirm the crystal structure of AZO-Qa at room temperature (Fig. S5 in ESI), and the H-NMR spectra clearly presents the molecular structure of Azo-Py and Azo-Qa (Fig. S6 in ESI). Accordingly, there should be strong electrostatic force between sulfobetaine and AZO-Qa. Azo-Qa exhibited a focal conic texture of the smectic phase under POM at 90 °C (Fig. S7 in ESI), with reversible *trans-cis* isomerization under the irradiation of UV and visible light (Fig. S8 in ESI). The DSC curves of PS-PU, Azo-Qa, and PS-PU/Azo-Qa composite are displayed in Fig. 1(b). The phase transition peaks of Azo-Qa and the glass transition peak of PS-PU were noticed in the DSC curve of PS-PU/Azo-Qa composite. Hence, the two components were in the state of microphase separation.^[38] The doping of Azo-Qa enhanced the tensile strength but slightly decreased the elongation at break (Fig. 1c). Compared to PS-PU, the phase separation rendered the polymer morphology of PS-PU/Azo-Qa composite rougher (Fig. 1d and Fig. S9 in ESI).^[39,40] Therefore, the variation in mechanical properties between PS-PU and PS-PU/Azo-Qa composite may be ascribed to the internal stress relief induced by the porous microstructure.^[41] Figs. 1(e) and 1(f) display the UV-Vis absorption spectra of PS-PU/Azo-Qa composite in DMF solution. Under UV light (λ =365 nm) irradiation, the liquid crystalline azobenzene molecules in the composite underwent *trans-to-cis* isomerization with a distinct decline in the characteristic absorption peak of the *trans* isomer. After irradiation with visible light (λ =450 nm), the UV-Vis absorption spectra returned to the initial state, demonstrating *cis-to-trans* isomerization. The reversible *trans-cis* isomerization of PS-PU/Azo-Qa composite under UV and visible light irradiation confirmed the photoresponsive properties of PS-PU/Azo-Qa composite in solution.

Programming Shape-morphing Behavior of PS-PU/Azo-Qa Composite Film

The homogeneous alignment of mesogenic moieties plays an

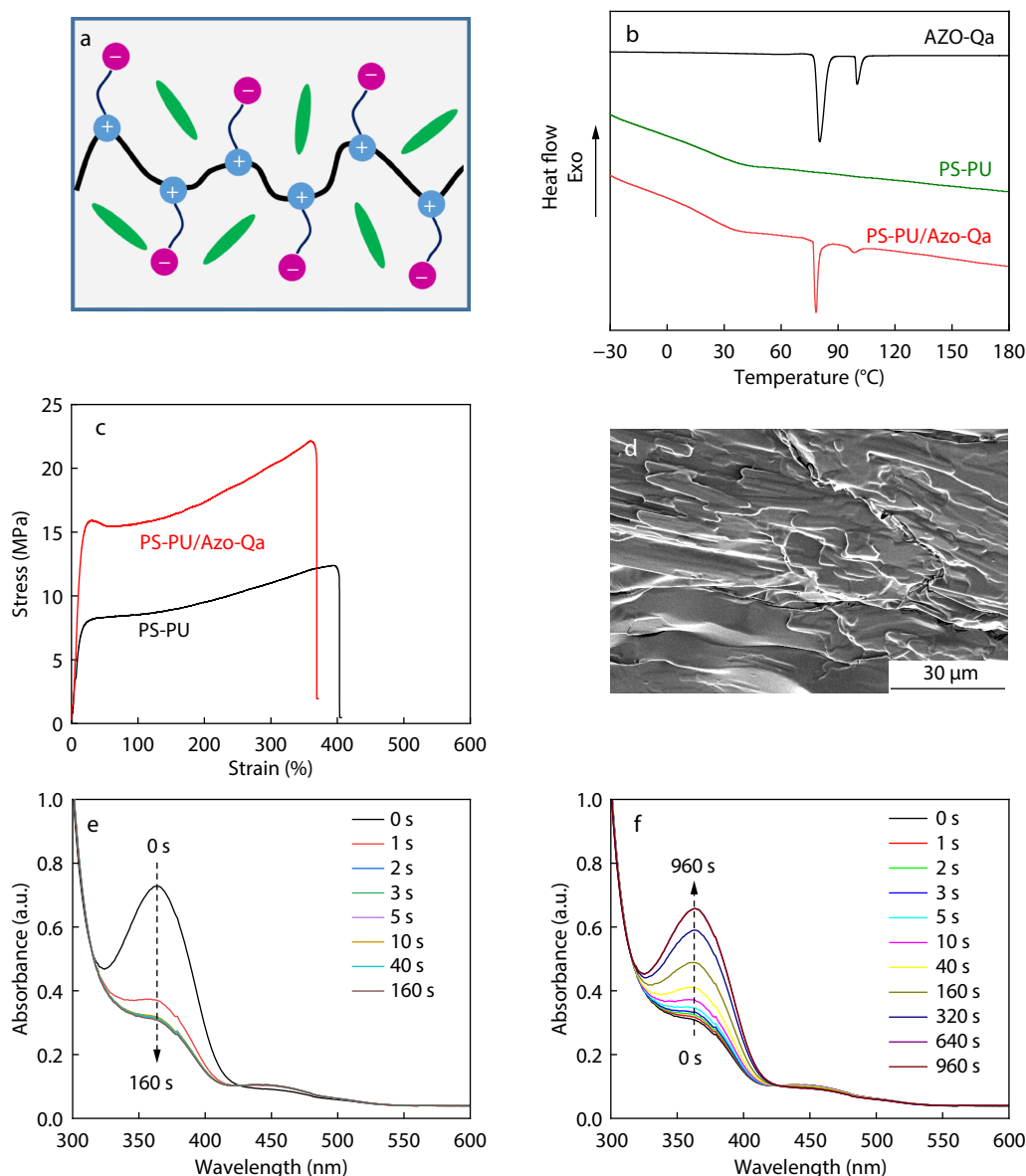


Fig. 1 (a) Schematic diagram of PS-PU and Azo-Qa in the zwitterionic polymer/liquid crystal composite; (b) DSC curves of Azo-Qa, PS-PU, and PS-PU/Azo-Qa composite; (c) The stress-strain curves of PS-PU film and PS-PU/Azo-Qa composite film measured at room temperature; (d) SEM image of the composite film. UV-Vis absorption spectra of PS-PU/Azo-Qa composite in DMF solution (2.0×10^{-6} mol/L) under irradiation with (e) UV light (365 nm) and (f) visible light (450 nm).

important role on LCP-based actuator films to achieve good light-induced shape deformation performance.^[10,23,42,43] In this experiment, mechanical stretching was employed to induce homogeneous alignment of Azo-Qa molecules in the composite film. According to the DSC curves in Fig. 1(b), the Azo-Qa kept its liquid crystalline phase between 80 and 100 °C, and the composite entered rubbery state above 35 °C. Therefore, the film was mechanically stretched at 80 °C as shown in Fig. 2(a). The liquid crystalline azobenzene molecules were driven to rearrange homogeneously along the direction of the external force. Next, the as-stretched films were held at the elongated status and slowly cooled to about 0 °C. As expected, the composite film presents a temperature-induced shape memory effect owing to the separation between the hard and soft

domains in the polymer matrix PS-PU.^[44,45] Fig. 1(b) shows that PS-PU has amorphous soft phase which might provide reversible phase to fix temporary strain. After grafting with AZO-Qa mesogens, the liquid crystalline phase can be kept because Azo-Qa mesogens would be separated into another aggregate phase. Whereas the netpoints of PS-PU formed by the strong electrostatic force or hydrogen bonding might be kept stable in the composite. As a result, the shape recovery ratio is only about 76.4% and the shape fixity ratio is around 95.5% in the composite film (Fig. 2b). Therefore, the elongated shape of the composite film can be memorized, and the alignment of Azo-Qa molecules can be maintained after the removal of the applied external force. Under POM, the composite film displayed randomly and uniformly distributed bright domains before and

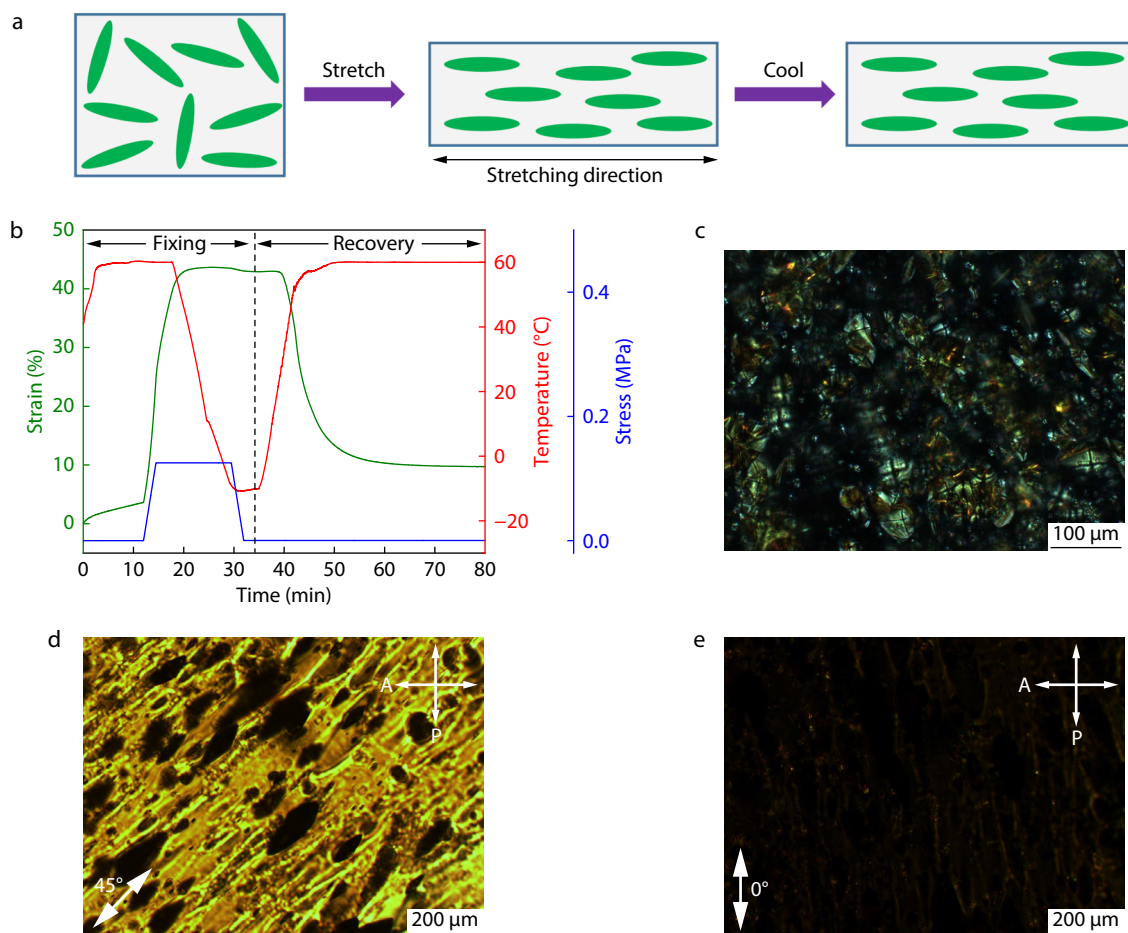


Fig. 2 (a) Schematic illustration of the mechanical stretching process and the evolution of the arrangement of Azo-Qa molecules in the composite film. The green ellipsoid represents the mesogenic azobenzene molecules. (b) Quantitative shape memory curve of PS-PU/Azo-Qa composite film obtained by DMA; (c) POM image of PS-PU/Azo-Qa composite film at 25 °C; (d, e) POM images of PS-PU/Azo-Qa composite film after mechanical stretching treatment with an elongation rate of 80%, the stretching direction of the sample parallel to one of the polarization direction and angle to the polarizer was 45°, respectively (A, analyzer; P, polarizer).

after stretching, respectively (Figs. 2c and 2d). In particular, the as-stretched composite film is bright for polarizers aligned at 45° to the stretching direction, while black for one polarizer aligned along the stretching direction (Figs. 2d and 2e). Hence, mesogenic azobenzene molecules in the as-stretched composite film were aligned homogeneously along the direction of the stretching force, as demonstrated by the periodic change in transmittance under POM.^[23,39,46] However, it should be pointed out that no obvious phase transition appears on POM at room temperature when UV irradiation was applied, since these homogeneous AZO-Qa molecules is in the state of crystalline phase. It also implied that the shape morphing of composite film does not ascribe to the liquid crystalline phase transition.^[47,48]

The programming shape-morphing behavior of PS-PU/Azo-Qa composite film is depicted in Fig. 3. The composite film transforms into shape B (elongated flat state) from shape A (flat state) after mechanical stretching (Figs. 3a and 3b), as well as deformed into shape C (bent state) upon UV light (365 nm, 50 mW/cm²) (Fig. 3c and Video S1 in ESI). Also, the composite film maintained shape C after removal of the UV light and even under irradiation with visible light for 10 min (Figs.

3d and 3e). Such performance is considerably different from the photo-induced shape-deformation of LCEs, where the bent shape recovered quickly to a flat shape upon visible light due to *cis-trans* isomerization of azobenzene moieties.^[23,24,49] The curved composite film morphs into a flat shape and almost recovers the original state of shape A after heating at 80 °C for a few minutes (Fig. 3f). Note that shape B and shape C could hold the state until the applications of another stimulus. Hence, the programming shape-morphing behavior of PS-PU/Azo-Qa composite film could be achieved by applying different stimuli, such as force, light and temperature.

The possible mechanism of the programming shape-morphing behavior of PS-PU/Azo-Qa composite film under different stimuli is presented in Fig. 4. The change in conformation of polymer chains dominated the shape-deformation of polymer materials.^[50] Therefore, the variation in the chain conformation of PS-PU/Azo-Qa composite film was employed to elucidate the mechanism related to the programming shape-morphing behavior for the composite film under different stimuli. Shape A (flat state) was obtained via the film-forming of PS-PU/Azo-Qa solution in a mold, leading to an entangled state of polymer chains and random arrange-

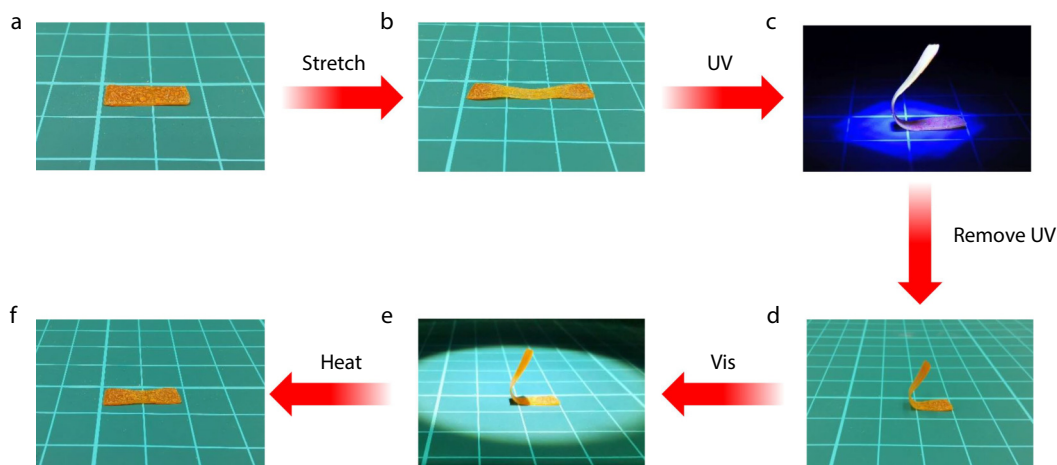


Fig. 3 Programming shape-morphing behavior of PS-PU/Azo-Qa composite film (the size of the grid on the background is 1.0 cm): (a) shape A, (b) shape B after stretching, (c) shape C under UV light, (d) shape C after removal of UV light, (e) shape C under visible light for 10 min, and (f) shape A after heating to 80 °C for a few minutes.

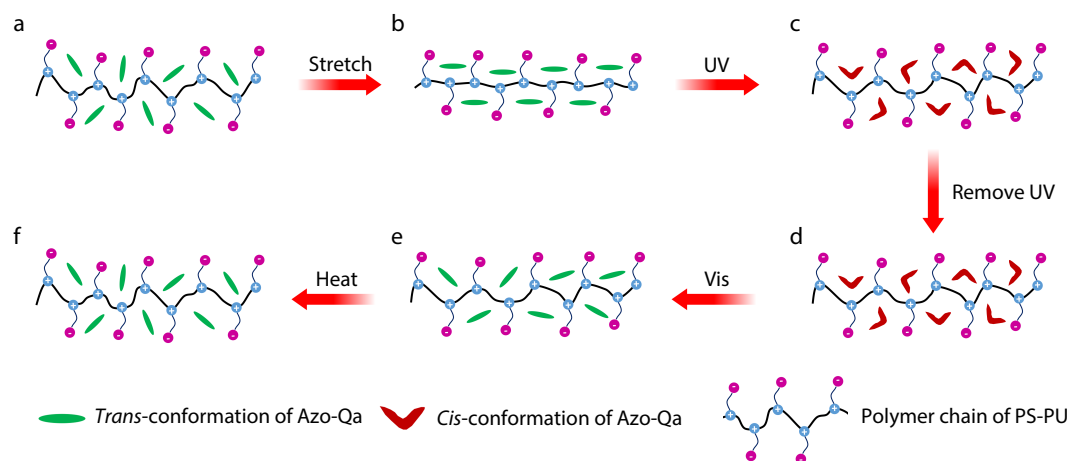


Fig. 4 Schematic illustration of the possible mechanism of the programming shape-morphing behavior of PS-PU/Azo-Qa composite film: (a) entangled polymer chain and random-arranged Azo-Qa molecules, (b) outstretched polymer chain and homogenous-arranged Azo-Qa molecules after stretching, (c) coiled polymer chain and random-arranged Azo-Qa (*cis* configuration) molecules under UV light, (d) coiled polymer chain and random-arranged Azo-Qa (*cis* configuration) molecules under UV light after removal of UV light, (e) coiled polymer chain and random-arranged Azo-Qa molecules after irradiation with visible light for 10 min, and (f) entangled polymer chain and random-arranged Azo-Qa molecules after heating to 80 °C for a few minutes.

ment of mesogenic azobenzene molecules in the original stage (Fig. 4a). After mechanical stretching at 80 °C and cooling to room temperature, the polymer chains are outstretched by external force and mesogenic azobenzene molecules are arranged homogeneously (Fig. 4b). Note that doping of Azo-Qa does not damage the separation between the soft and hard domains of PS-PU (Fig. S10 in ESI), conducive to the good temperature-induced shape memory effect of PS-PU/Azo-Qa composite film. Consequently, the outstretched polymer chains and homogenous-arranged Azo-Qa molecules can be maintained at room temperature after removal of the external force, and shape B (elongated flat state) can be memorized, since the soft domains provide a T_g of 35 °C as shown in DSC curves. Under UV light, Azo-Qa molecules in the composite underwent *trans*-to-*cis* isomerization, thereby disturbing the homogeneous arrangement of mesogenic moieties,^[17] as well as affording the internal stress to actuate

the motion of the polymer chains.^[33] The polymer chains started to coil, inducing local volume contraction of the film upon changes in the conformation of mesogenic azobenzene from *trans*-to-*cis* (Fig. 4c). Moreover, the large molar extinction coefficient of Azo-Qa led to penetration of the UV-light for only a few micrometers from the surface of the film. Hence, the side close to the UV light source was exposed to large amounts of UV-irradiation when compared to the backlight side, leading to greater volume contraction in that region. The variation in volume contraction rate in the composite film along the direction of UV light drove the film to bend toward the light source, similar to photo-driven mechanism of LCPs or PDLC films reported previously.^[12,21] Consequently, the composite film transformed into shape C (bent state) from shape B. After removal of the UV light, the coiled polymer chains were frozen due to suppression of the thermal motion of the polymer chain below T_g (Fig. 4d). Also, the bent state

shape C cannot be recovered to the flat state. On the other hand, the motion of the polymer chain was still restrained at room temperature even though the composite film was irradiated by visible light for 10 min and Azo-Qa molecules underwent *cis*-to-*trans* isomerization. Being different from the common azobenzene-containing LCPs, the inner force arising from the isomerization of Azo-Qa is too small to drive the motion of polymer chains of PS-PU in these composite films. As a result, the polymer chains were still maintained in the coiled state (Fig. 4e), while the bent state of shape C can be unchanged after irradiation with visible light for 10 min. Once heating to 80 °C for a few minutes, the thermal motion of the polymer chains was activated, and the coiled polymer chains started to recover their original states (Fig. 4f). As a result, the original flat state of the composite film was regained.

Humidity-responsive Self-healing Performance of PS-PU/Azo-Qa Composite Film

Self-healing is the capability of a material to recover from physical damage, such as abrasion, crack, fracture, and so on, which is contributed to prolonging the service life of smart materials in practical applications.^[25,51] Although many polymers exhibit self-healing behaviors under some conditions, the self-healing effect under mild conditions is still problematic for both academia and industry.^[52] More interestingly, PS-PU/Azo-Qa composite film in this work could repair cracks on its surface under wet conditions at room temperature without high-temperature environments, thereby different from most thermoplastic polymers.^[53] As shown in Figs. 5(a)–5(c), the crack made with a razor on the film surface starts to narrow after treatment under wet conditions at room temperature for 4 h.

The original crack almost vanished, leaving only a small scar after 12 h treatment. However, the crack in the composite film surface subjected to dry conditions at room temperature remained after treatment for 18 h (Fig. S11 in ESI). To further demonstrate the integral self-healing capability of PS-PU/Azo-Qa composite, the film was first cut into two pieces and then brought to contact at room temperature and 85% humidity controlled by a constant temperature humidity chamber. After 12 h treatment and drying in a low-temperature vacuum oven to remove moisture, the two pieces rebonded to form a refreshing film with the ability of manually stretching at a certain elongation (Figs. 5d and 5e). Encouragingly, the as-fresh integral composite film also exhibited a programming shape-morphing behavior under various applied stimuli. The as-healed composite film transformed into the elongate flat shape from the original flat shape after mechanical stretching, as well as deformed into a bent shape under UV light (365 nm, 50 mW/cm²) (Fig. 5f and Video S2 in ESI). These experimental results demonstrated that PS-PU/Azo-Qa composite film was featured humidity-responsive self-healing performance, providing a firm foundation for its practical applications.^[54]

A possible mechanism of humidity-responsive self-healing behavior was derived from the experimental data and is shown in Fig. 6. Since the zwitterionic polymers possess ultra-hydrophilicity due to the electrostatically induced hydration,^[34,35] the ultra-hydration capacity of sulfobetaine was identified as a critical factor in humidity-responsive self-healing performance of PS-PU/Azo-Qa composite film. Hence, after cutting the composite film into two pieces and then bringing them to contact at room temperature under wet

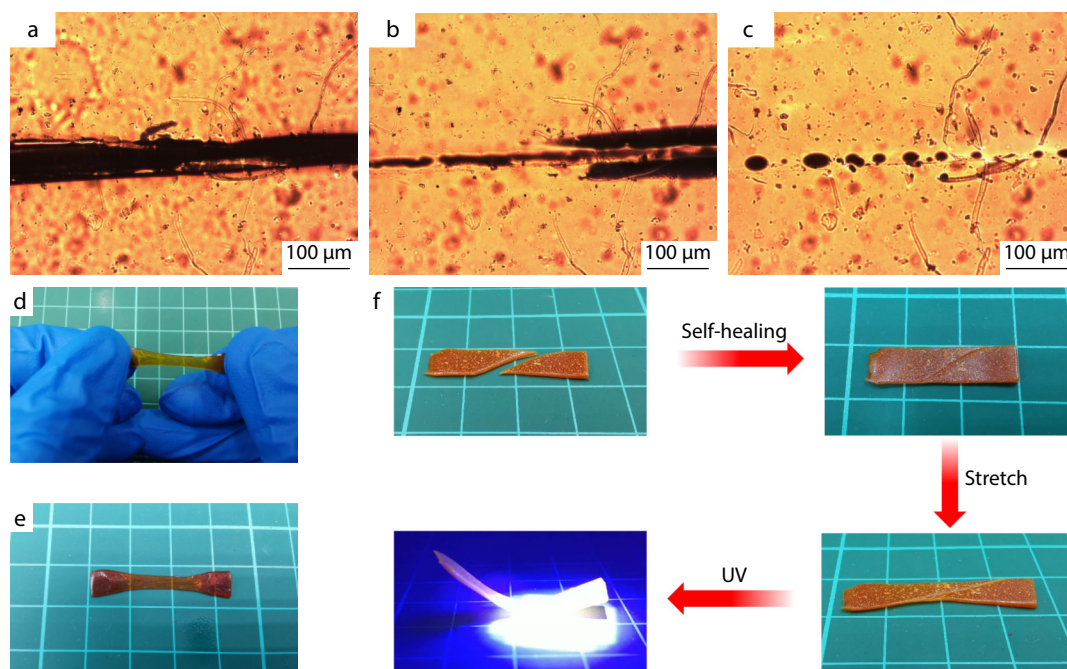


Fig. 5 Photomicrographs of PS-PU/Azo-Qa composite film under POM with plane-polarized light during the humidity-triggered self-healing process at different time intervals (the size of the grid on the background is 1.0 cm): (a) 0 min, (b) 4 h, and (c) 12 h; Photographs of the as-healed PS-PU/Azo-Qa composite film: (d) during and (e) after stretching process; (f) Photographs of the self-healing process of PS-PU/Azo-Qa composite film and programming shape-morphing behavior of a fresh film under force stimuli and UV light.

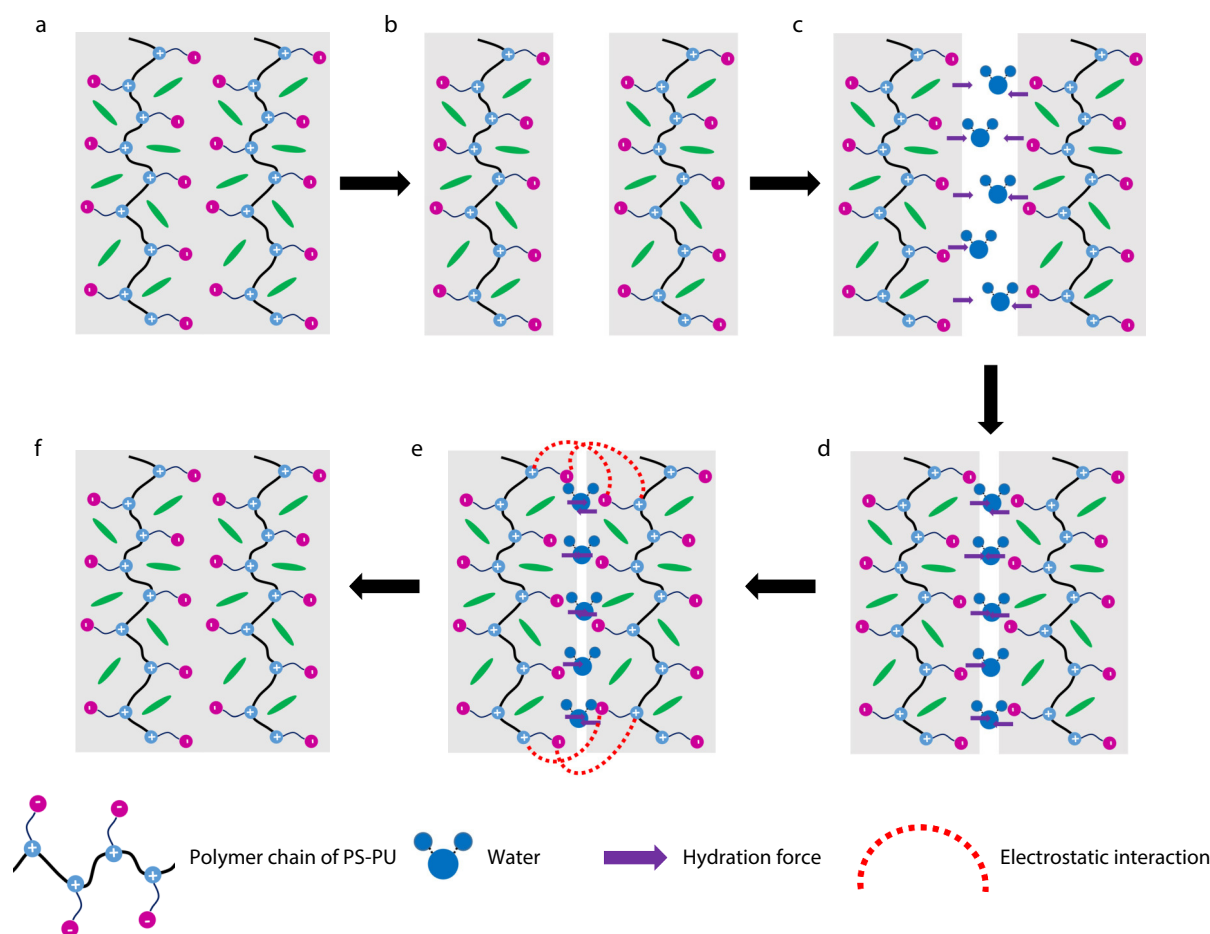


Fig. 6 Schematic illustration of the proposed humidity-responsive self-healing mechanism: (a) origin state, (b) two pieces obtained by cutting the film, (c) introduction of water under wet conditions, (d) narrowed gap between the two pieces under the moisture-induced plasticization effect and hydration force, (e) electrostatic interactions between positive and negative charges in zwitterionic moieties, and (f) afresh integral state after drying.

conditions, water was firstly adsorbed on the fracture surface due to the ultra-hydrophilicity of zwitterionic moieties.^[55] The introduction of water led to the drop of T_g and the polymer chains in the composite film achieved increased mobility under wet conditions due to the enhanced moisture-induced plasticization effect.^[56] Meanwhile, the hydration force between water and the zwitterionic moieties drags the polymer chains to motion toward the water-rich region (Fig. 6c). As a result, the gap between the two pieces gradually decreases under wet conditions (Fig. 6d). Once the gap was reduced to a certain extent, the electrostatic interactions between the positive and negative charges in zwitterionic moieties enhanced, thereby rebonding the two pieces (Fig. 6e).^[57] After drying, the afresh integral composite film can be obtained (Fig. 6f). Hence, the humidity-responsive self-healing performance of PS-PU/Azo-Qa composite film can be ascribed to the combined action of moisture-induced plasticization effect and electrostatic interactions between zwitterionic moieties.^[56,58,59]

CONCLUSIONS

In summary, a zwitterionic polymer/liquid crystals composite

film with programming shape-morphing behavior and humidity-responsive self-healing performance was successfully fabricated by blending a zwitterionic polymer and liquid crystalline azobenzene compound in solution, followed by film-forming in a mold without tedious and multistep synthetic routes. The low-mass mesogenic azobenzene as a photosensitive component afforded the inner stress to endow the composite film with photo-responsive shape-morphing capability under UV light. Also, the zwitterionic polymer as the matrix rendered the film with shape memory effect and moisture-responsive properties. The as-obtained zwitterionic polymer/liquid crystal composite film exhibited programming shape-morphing behavior under different stimuli, and the temporary shapes could be memorized after removal of the stimuli. The composites revealed also humidity-responsive self-healing performance under wet conditions at room temperature. Overall, the performances of zwitterionic polymer/liquid crystals composite film look promising for use as intelligence and energy-saving stimuli-responsive shape-changing materials in novel photo-driven devices and soft robotics.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2883-1>.

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