


Soft Matter Hot Paper

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A Facile Strategy for the Development of Recyclable Multifunctional Liquid Crystal Polymers via Post-Polymerization Modification and Ring-Opening Metathesis Polymerization

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Abstract: Post-polymerization modification (PPM) offers a versatile approach for engineering multifunctional polymers, but this advantage has not been fully exploited to fabricate multifunctional liquid crystal polymers (LCPs). Here, we design a facile synthetic approach towards multifunctional LCP by combining the ring-opening metathesis polymerization (ROMP) with PPM, in which ROMP helps to prepare a reactive LCP precursor with high molecular weight, and PPM provides a facilitation to introduce functional groups into the precursor. Consequently, a photo- and humidity-responsive linear LCP (LLCP) is demonstrated to show the potential of this synthetic strategy to diversify functions of the LCPs. Under light irradiation and humidity changes, the deformation modes of the LLCP films are converted to complex shapes (bending, twisting, and curling). The obtained dual-responsive LLCP with high molecular weight possesses excellent processability and recyclability, making it possible to construct 3D shape actuators with programmable deformation behaviors under light/humidity.

Introduction

Liquid crystal polymers (LCPs) being able to adapt shapes in response to external stimuli (such as heat,^[1] light,^[2] moisture,^[3] and electric field^[4]) have emerged as one of the most competitive candidates in smart materials because of the combination of the programmable orientation of liquid crystals and the elasticity of polymer matrices.^[5] Advanced LCP materials with diversified functionalities have aroused many interests due to their ability to achieve multiple responses and complex shape changes.^[6] To date, the

commonly used method to synthesize a multifunctional LCP is by copolymerizing mesogens with demand functional monomers. However, this direct polymerization method suffers from limited group tolerance because many functional groups may lead to side reactions or hinder the polymerization, which inevitably limits the attained functional type of LCPs.

Comparatively, post-polymerization modification (PPM), in which chemical modification is conducted after the polymerization step, breaks the restriction of direct polymerization and provides an alternative route to introduce functional groups.^[7] This strategy is based on polymer precursors bearing reactive groups, which are transformed into other functional groups in subsequent steps, offering broader opportunities to diversify polymers. Up to date, many functional materials such as amphiphilic nanogels,^[8] smart surfaces,^[9] and multi-responsive nanofibers^[10] have been fabricated utilizing this strategy. However, the ascendancy of PPM in LCPs has not been fully exploited and most researches are focused on monofunctional LCPs. For example, Finkelmann et al. creatively utilized a commercial poly (methyl siloxane) as the precursor to have hydrosilylation reactions with mesogenic alkenes and crosslinkers, and obtained well-oriented liquid crystal elastomers with large stimuli-responsive deformation.^[11] Yang et al. attained side-chain LCPs by grafting mesogens onto poly-[3-mercaptopropylmethylsiloxane] through thiol-ene click chemistry, and investigated thermal-actuation effects of resulted films.^[12] Recently, Zhao and co-workers designed a liquid crystal elastomer exhibiting anomalous shape change through the “click” and esterification reactions of styrene-butadiene-styrene triblock copolymer.^[13] Unfortunately, these commercial reactive polymers usually have poor reaction efficiency or limited types of chemical reactions, which result in nonquantitative installation of functional groups or cumbersome synthetic routes.

Apart from using commercial reactive polymers as precursors, synthesizing highly reactive polymers and subsequently employing them to prepare advanced LCPs is more attractive due to the structural designability. Zhang et al. reported the synthesis of a series of reactive LCPs bearing azobenzene mesogens with N-hydroxysuccinimide esters and their applications in preparing crosslinked LCPs.^[14] Our group synthesized a liquid crystal block copolymer with N-hydroxysuccinimide esters as reactive groups, which was fabricated to fibers and films followed by the post-crosslinking reaction between N-hydroxysuccini-

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amide esters and difunctional amines.^[15] Compared to polymers grafting N-hydroxysuccinimide esters, pentafluorophenyl (PFP)-ester polymers are more reactive and exhibit excellent solubility in organic solvents.^[16] Therefore, we prepared photodeformable crosslinked LCPs by the sequential PPM of a PFP-containing homopolymer precursor.^[17] Above prior work was developed on (living) free radical polymerization and the obtained LCPs before post-crosslinking had low molecular weight (only about 10^4 g mol⁻¹), possessing unsatisfactory mechanical and stimuli-responsive properties due to the lack of sufficient chain entanglements as crosslinks. In this case, reactive groups in aforementioned LCPs were mostly utilized for post-crosslinking reactions to form chemically crosslinked networks, while the intrinsic advantages of PPM to multifunctionalize LCP precursors were not thoroughly exploited. To address this issue, a powerful polymerization technique is highly desirable to satisfy the requirement of high molecular weight reactive polymer, in which the reactive group is fully used to realize multifunctionalities.

Ring-opening metathesis polymerization (ROMP) is a powerful tool for designing well-defined linear polymers with high molecular weight.^[18] Recently, we synthesized a series of photodeformable linear LCPs (LLCPs) with excellent mechanical properties endowed by high molecular weight through ROMP.^[19] Herein, we propose to combine the respective advantages of ROMP and PPM to offer a new possibility for generating multifunctional LLCPs. Firstly, ROMP is used to synthesize a high molecular weight reactive LLCP, which renders the LLCP precursor with good mechanical properties even without chemical crosslinking. Furthermore, the existence of reactive groups makes the above LLCP to undergo efficient coupling reactions with functional groups via a PPM reaction. By integrating ROMP and PPM, we fabricated a photo- and humidity-responsive LLCP and explored its applications in recyclable multifunctional actuators.

Results and Discussion

A highly reactive LLCP precursor (PABPFP) with single-stimulus response was firstly synthesized via ROMP, followed by the further functionalized reaction between PFP ester and 4-aminobenzoic acid (Figure 1a). A monomer containing an azobenzene group and a long flexible chain was chosen to endow the polymer with photoresponse and liquid crystallinity (Scheme S1).^[20] We designed another monomer with PFP ester (Scheme S2) that has been extensively used in postpolymerization substitution due to the high reactivity and excellent hydrolysis resistance.^[21] PABPFP was prepared through copolymerizing the above two monomers via ROMP (Scheme S3), showing a controllable composition (the ratio of azobenzenes to PFP esters is 1:2, calculated by ¹H NMR in Figure S2). The molecular weight ($M_n = 2 \times 10^5$ g mol⁻¹, Figure 1b) of obtained PABPFP is an order of magnitude higher than that of LCPs^[14,15,17] synthesized by free radical polymerization. More importantly, PABPFP offers a platform for multifunctionalization

since PFP esters can be converted to various functional groups, while azobenzene-containing LCPs previously prepared by ROMP were designed as monofunctionalized photodeformable polymers.^[19]

Here, we demonstrated the multifunctionalization by preparing a dual-responsive LLCP (PABCOOH) through the aminolysis reaction of PFP esters and 4-aminobenzoic acids. The success of functionalization reaction to obtain PABCOOH was verified by NMR spectra, where the signals of PFP esters disappeared in ¹⁹F NMR spectra (Figure 1c) and new peaks related to acetamidobenzoic acids at 7.49 ppm and 8.91 ppm emerge in ¹H NMR spectra (Figure S2 and S4) after the aminolysis reaction. Mesomorphic properties of the PABPFP and PABCOOH samples were confirmed by both polarized optical microscopy (POM) with a hot stage and differential scanning calorimetry (DSC). POM photographs with corresponding phase transition temperatures exhibited obvious schlieren textures, revealing the presence of mesogenic phases (Figure S3). Compared with PABPFP precursor ($T_g \approx -4^\circ\text{C}$, $T_{iso} \approx 52^\circ\text{C}$), the obtained PABCOOH exhibited elevated glass transition temperature ($T_g \approx 29^\circ\text{C}$) and LC-to-isotropic phase transition temperature ($T_{iso} \approx 68^\circ\text{C}$), which are potentially due to the formation of hydrogen bonding interactions in the form of acidic dimers (Figure 1d). Furthermore, PABCOOH also possessed comparable molecular weight and degree of polymerization with the PABPFP precursor (Figure 1b), which ultimately led to robust mechanical property with 528 ± 25 MPa elastic modulus (Figure S5). We investigated the photoresponsivity of PABCOOH through UV-Vis absorption spectra under UV and visible light irradiation (Figure S6).

To construct multifunctional LLCP actuators with appreciable stimuli-response, the mesogens within the polymer must first be aligned with an applicable method. Compared with our previously studied LLCPs,^[19a-c] in which mesogens achieved alignment after thermal annealing, the PABCOOH here still exhibited a disordered state after the annealing process (Figure S7), presumably due to the existence of carboxyl groups. On the other hand, the linear structure and high molecular weight of PABCOOH bring about excellent processability and mechanical properties, making it possible to obtain oriented LCPs through hot-stretching (Figure 1e). A PABCOOH film was firstly fabricated by solution casting, which exhibited a polydomain state as shown in 2D X-ray diffraction (2D-XRD) (Figure S8). In order to achieve mesogen alignment, the film was stretched to 200% strain at 60°C (between T_g and T_{iso}) and kept for 10 min to totally release the stress generated in the stretching process. As investigated by 2D-XRD in Figure 1f, the split diffractions in both the low- and high-angle regions demonstrates the smectic A phase with the in-plane orientation of mesogens, and the order parameter S was calculated as around 0.83 from the azimuthal integration in the high-angle region of 2D-XRD patterns (Figure S9).

The highly-oriented azobenzene mesogens endow the monodomain LLCP film with excellent photodeformability. As shown in Figure 2a and Movie S1, upon UV irradiation (365 nm, 20 mW cm⁻²), the film (10 mm × 10 mm) bent

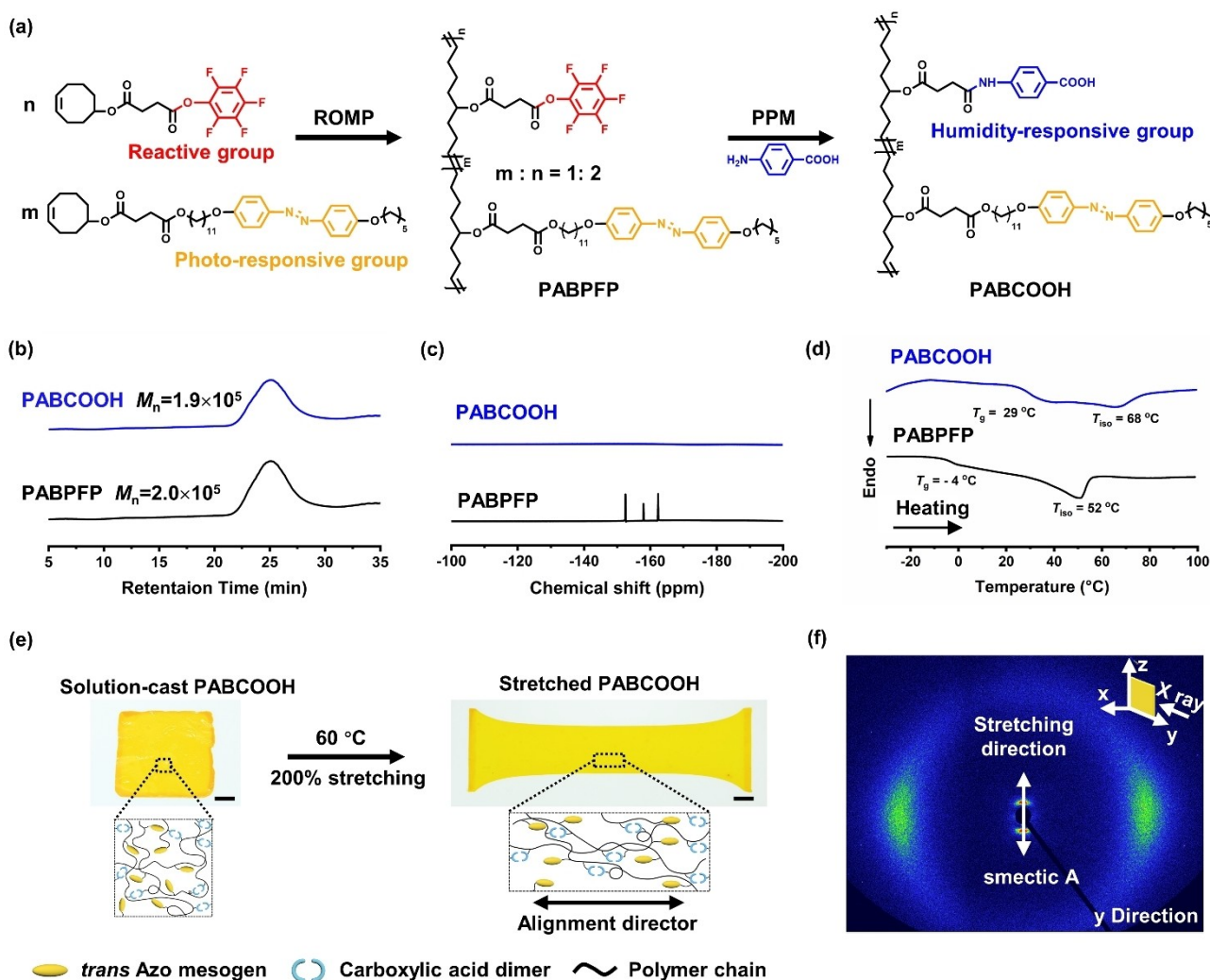


Figure 1. a) Synthetic route of the reactive LLCP precursor (PABPFP) and the dual-responsive LLCP (PABCOOH). b) Gel Permeation Chromatography (GPC) curves of PABPFP and PABCOOH, M_n number-average molecular weight. c) ^{19}F NMR spectra of PABPFP and PABCOOH. d) DSC curves of the polymers from the second heating scan. e) Schematic illustrations of the preparation of the stretched PABCOOH film (200% strain) via hot-stretching process. Scale bar = 10 mm. f) 2D-XRD patterns of the PABCOOH film with smectic A phase. Insertion: The incident X-ray beam is parallel to the y direction.

toward the light source along the mesogen alignment direction. This directional bending behavior stems from the fact that the *trans-cis* photoisomerization of azobenzene causes the film surface to contract along the mesogen alignment direction.^[22] Subsequent visible light irradiation made the bent film recover to the initial flat state as a consequence of *cis-trans* back isomerization, indicating that the photodeformation is reversible (Figure 2b-I).

The humidity-responsiveness of the LLCPS film was achieved by converting benzoic acid into corresponding hygroscopic carboxylic salt through base treatment.^[23] After selectively treating one side of the LLCPS film with 0.1 M KOH solution, the film bent toward the base-treated side along the perpendicular direction to the mesogen alignment director. This bending behavior is ascribed to the fact that the base treatment breaks the hydrogen bonds between the carboxylic dimers and converts them into carboxylic salt

(Figure 2b-II), resulting in the shrinking of the treated side,^[3] which is proved by Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy (Figure S10). The bent film was cut into strips (3 mm × 30 mm) to investigate the humidity-induced deformation behavior. When the relative humidity (RH) was increased from 20% to 80%, the bent strip gradually spread to a flat shape because of the swelling of the treated side with hygroscopic carboxylic salt (Figure 2c and Movie S2). The initial bending amplitude of the strip is influenced by the amount of destructed hydrogen bonds varied with treatment time in KOH solution.^[24] Figure 2d illustrates that the initial curvature ($1/r$) of strips becomes larger with the increase of treatment time, and all bent strips undergo stepwise unbending when the RH increases. The above investigation proceeded at uniform RH changes is deriving from one-side base treatment. In addition, base treatment on both sides of

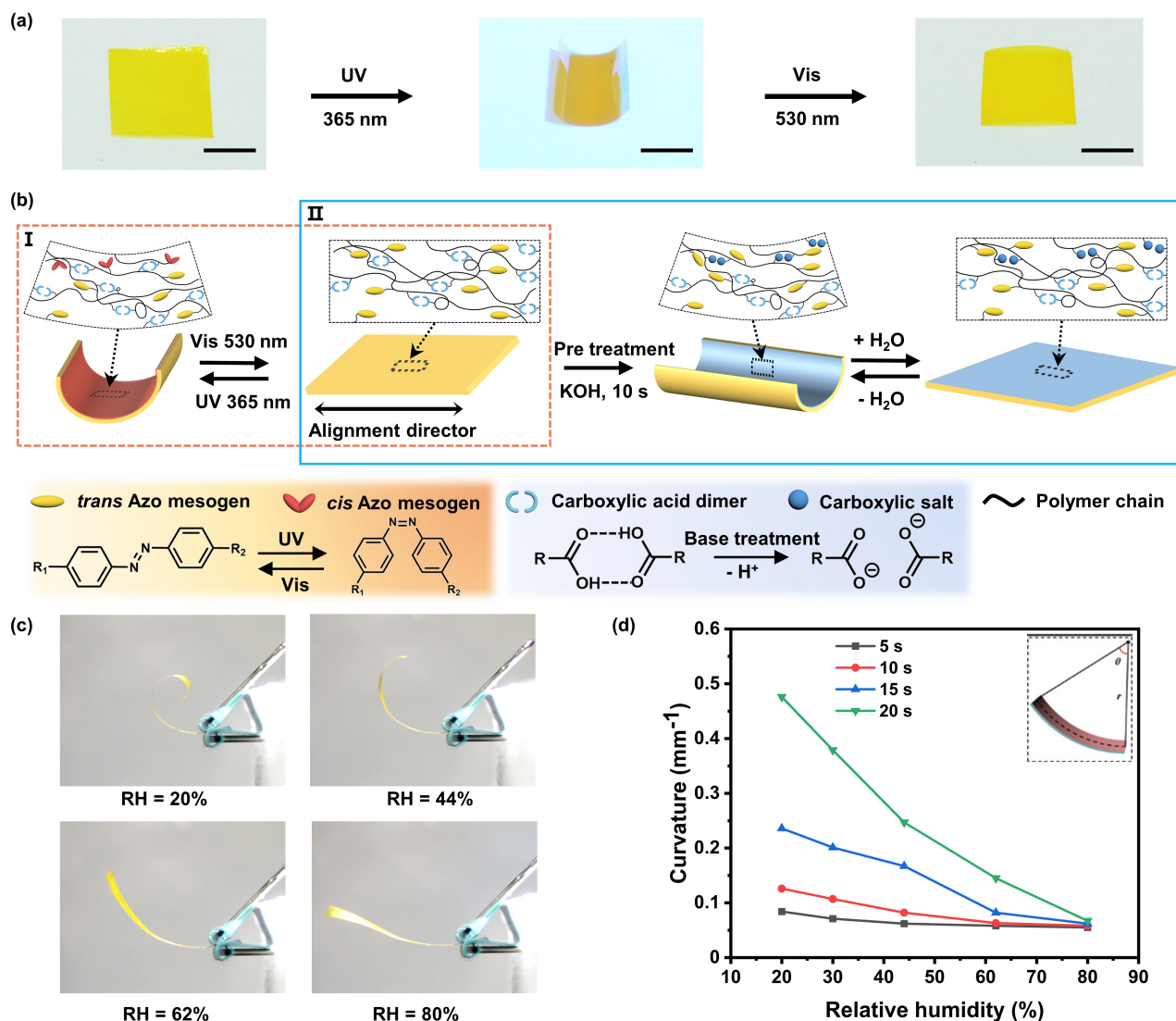


Figure 2. a) Photographs showing the bending and unbending behaviors of the monodomain PABCOOH film (10 mm × 10 mm) under irradiation with UV light (365 nm, 20 mW cm⁻²) and visible light (530 nm, 50 mW cm⁻²), respectively. Scale bar = 5 mm. b) Illustration showing (I) the photo-responsive and (II) the humidity-responsive deformation mechanisms of the PABCOOH film. c) Humidity-controlled unbending of the base-treated PABCOOH strip (3 mm × 30 mm). d) Curvatures (1/r) of the PABCOOH strips with different treatment time (5 s, 10 s, 15 s, and 20 s) of 0.1 M KOH solution as a function of RH.

the PABCOOH film endows these tailored strips with the deformation ability under a humidity gradient, specifically an approaching wet finger at arbitrary side drives the strip bending (Figure S11).

As shown in Figure 2b, the dual-responsive LLCPC film deformed along the mesogen alignment direction under UV light, while it bent vertically to that direction after KOH treatment at low RH and unbent at high RH. We speculate that the reason why the humidity-responsive deformation occurs vertically to the mesogen alignment is due to the anisotropic mechanical properties. That is, the PABCOOH film had a lower Young's modulus in the direction perpendicular to mesogen directors than in the parallel direction, leading to a facility for shrinkage/swelling along that direction. We further expanded the actuation modes of

stretched LLCPC strips by employing cutting angles at 0°, 45°, and 90° with the stretching direction (Figure 3a). The straightforward trimming led to variation of deformation behaviors, in which the tailored films with different offset angles displayed reversible bending, twisting, and curling with the light irradiation or RH changes from 44% to 80% (Figure 3b).

Furthermore, the linear structure without chemical cross-links of the dual-responsive LLCPC allows the preparation of arbitrary shapes through origami-like folds.^[25] Inspired by the activities of actinias (Figure 4a), we fabricated an artificial 3D actinian actuator to mimic anisotropic motions in response to stimuli. A flat monodomain PABCOOH film was folded and fixed at 60°C for 10 min to achieve a stable folding structure, which retained the uniaxial mesogen

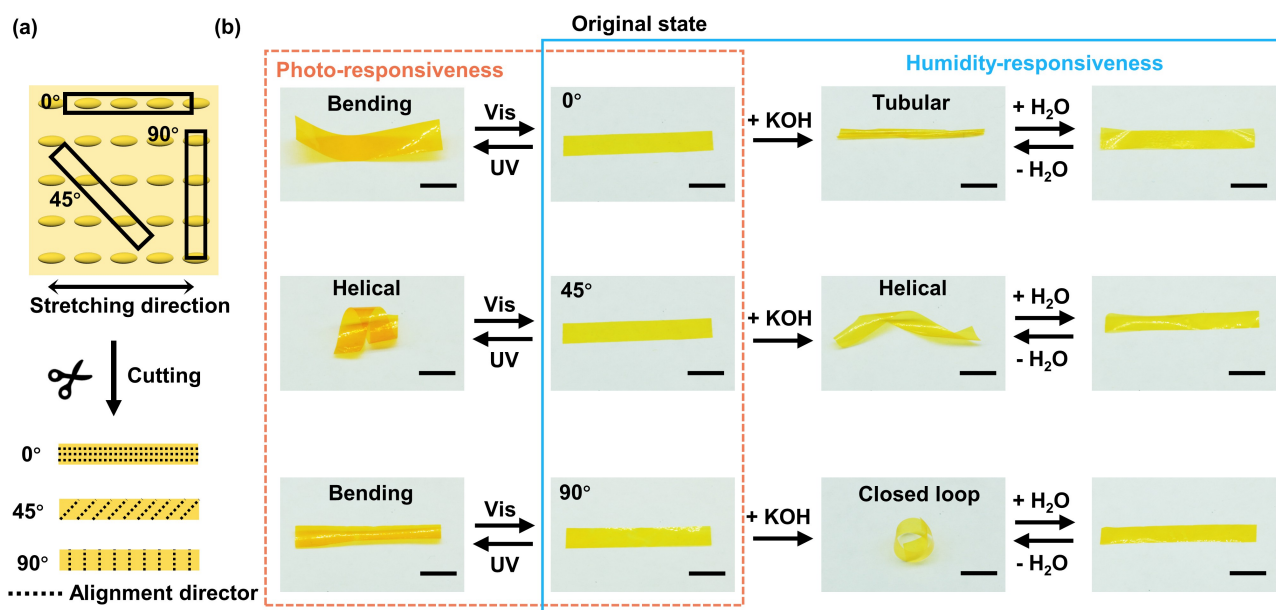


Figure 3. a) Schematic representation of cutting angles between the long axis of PABCOOH strip and the mesogenic director. b) Shape changes of PABCOOH strips (3 mm × 20 mm) by cutting a stretched film at different angles (0°, 45°, 90°) with respect to the mesogenic director under the photo-stimuli and humidity-stimuli with base pre-treatment independently. Scale bar = 5 mm.

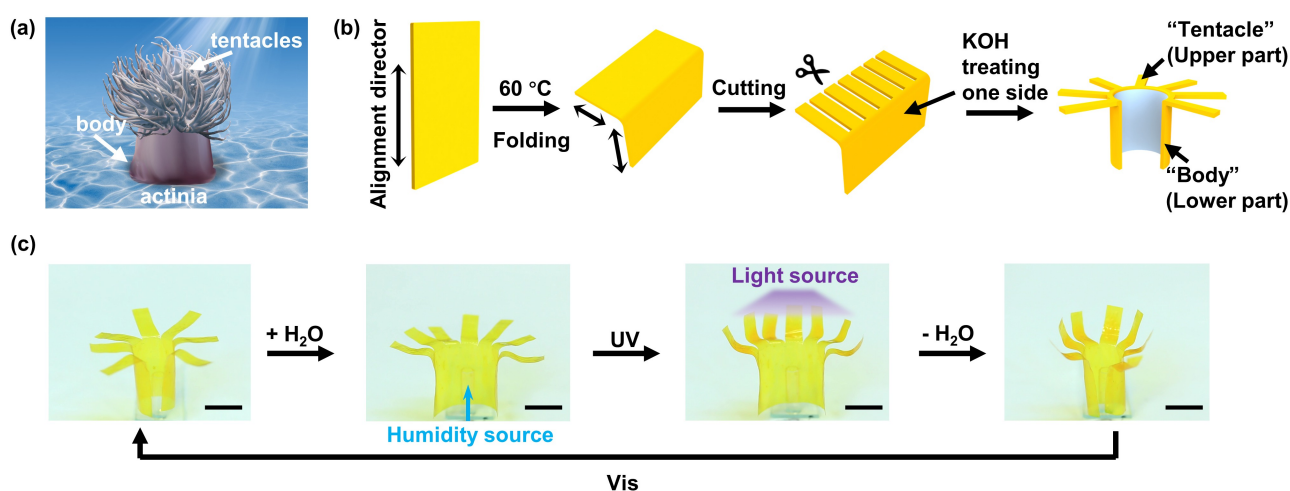


Figure 4. a) Scheme of an actinia with the body and tentacles indicated by white arrows. b) Schematic illustration of fabricating process of an artificial actinia. c) The programmable deformation of an artificial actinia under different stimuli. Scale bar = 10 mm.

alignment confirmed by 2D-XRD (Figure S12). The upper part of this structure was cut to mimic the “tentacles” of actinias (depicted by the dotted lines, parallel to the alignment director). One side of the lower part of the structure was treated by KOH solution for 10 s (marked with blue area) to form a tube shape, which represented the “body” part of actinias (Figure 4b). By taking advantage of the dual-responsiveness to light and humidity, programmable deformation modes in the artificial actinia were easily realized via controlling both stimuli simultaneously or separately (Figure 4c and Movie S3). When exposed to UV light, the “tentacles” bent toward the light source along the mesogen alignment direction, and recovered to the flat state using

visible light, realizing a “close” and “open” movement. The tube-shaped “body” tended to spread perpendicularly to the mesogen alignment direction after absorbing water and bend again when desorbing water, imitating the “swelling” and “shrinking” behaviors of the actual actinia body.

In addition, the LLC actuator also presents excellent recyclability, which is attributed to the absence of a chemical crosslinking (Figure 5a). The carboxylic salt in actinian actuator was reconverted into hydrogen-bonded diacid through HCl treatment. The success of acid treatment was proved by the FTIR spectra in Figure 5b, in which the absorbing peaks at 1582 cm⁻¹ and 1389 cm⁻¹ (related to the carboxylate ion) disappeared, while a new peak at 1701 cm⁻¹

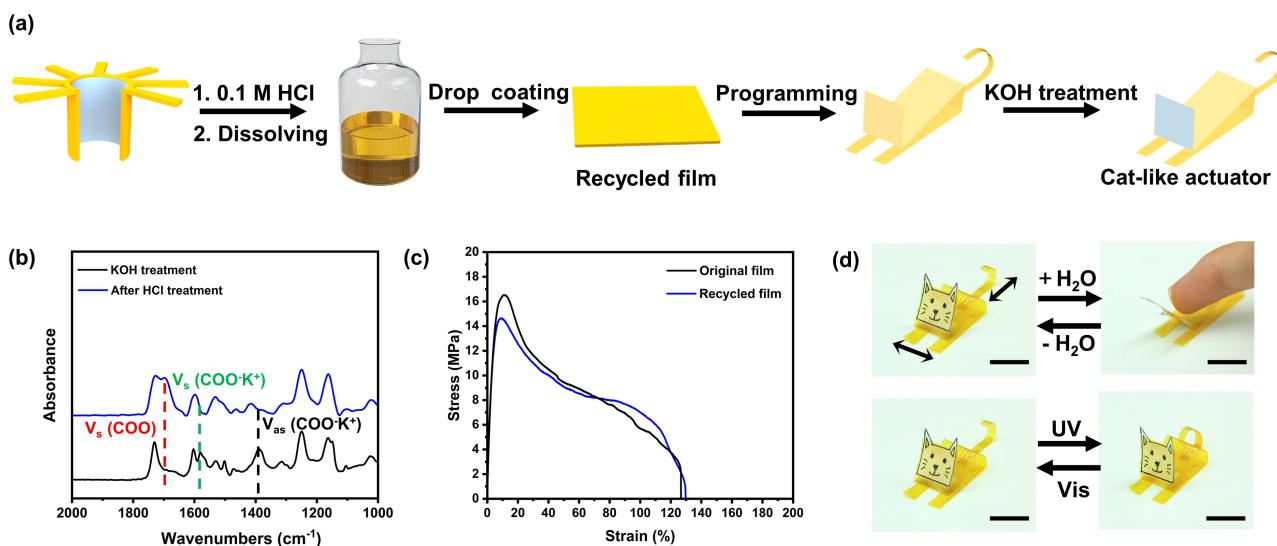


Figure 5. a) Schematic illustration of recycling the fabricated actuators through the HCl treatment, dissolving, and solution casting process. The recycled film was programmed to generate a cat-like 3D soft actuator. b) The FTIR spectra of the KOH-treated PABCOOH film (black), and the same film after HCl treatment (blue). c) Stress-strain curves of the original and recycled films of PABCOOH. d) Bionic deformation behaviors of “cat”, where double arrows indicate the mesogen alignment of “cat body” and “cat tail”. Scale bar = 10 mm.

appeared, elucidating that the salt was transferred to acid. After that, the acid-treated actuator was dissolved in organic solvent (e.g., tetrahydrofuran) and reprocessed to a new film through solution casting. The mechanical properties of the original and recycled films showed no significant difference, further demonstrating the recyclability of the films (Figure 5c). Utilizing the recycled LLCP, an artificial 3D cat was constructed through simple steps displayed in Figure S13. The “cat head” treated by KOH on both sides exhibited the humidity-responsive performance, where the bilateral KOH treatments allowed the film to remain flat shape rather than bending shape induced by selectively treating one side. Figure 5d shows the biomimic motion of “cat”: When a wet finger approached the “head”, it bent away from the finger due to the asymmetrical absorbance of moisture and recovered to the flat state after removing the finger. Additionally, the azobenzene groups endowed PABCOOH films with photo-responsive characteristic as verified via the “cat tail” motion, where the mesogen alignment was along the stretching direction. The photo-responsive “tail” presented reversible bending and unbending behaviors by alternating UV and visible light illumination.

Conclusion

In summary, we illustrated a facile synthetic route to construct multifunctional LCPs by combining ROMP and PPM. Copolymerization of azobenzene-containing monomer and the PFP ester-containing monomer by ROMP resulted in PABPFP copolymers with a combination of liquid crystallinity, photoresponsivity and reactivity. The versatile activated PFP ester is able to be quantitatively transformed into other functional groups, offering broader opportunities to structurally diversify LCPs. Based on these facts, a photo-

and humidity-responsive LLCP was synthesized through the aminolysis reaction between PFP ester and 4-aminobenzoic acid. Utilizing this LLCP with excellent processability and mechanical properties, recyclable 3D structure actuators with rational molecular alignment were fabricated, which showed sophisticated shape deformations under the stimulation of light and humidity. Apparently, the successful construction of the dual-responsive LLCP and actuators in this work is universal and can be extended to develop various multifunctional LCPs by simply tuning the type of modifiers, thereby accelerating the manufacture of intelligent actuators with multiple functionalities and complex deformations.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Humidity-Responsiveness · Linear Liquid Crystal Polymers · Photo-Responsiveness · Post-Polymerization Modification · Ring-Opening Metathesis Polymerization

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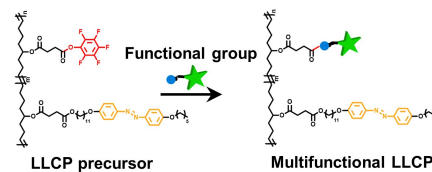
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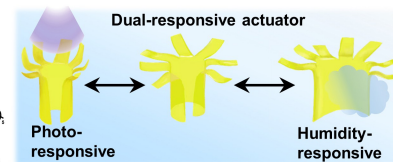
Soft Matter

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A Facile Strategy for the Development of Recyclable Multifunctional Liquid Crystal Polymers via Post-Polymerization Modification and Ring-Opening Metathesis Polymerization



We present a new synthetic strategy to combine the post-polymerization modification (PPM) and the ring-opening metathesis polymerization (ROMP) for designing multifunctional linear liquid



crystal polymers (LLCPs). A photo- and humidity-responsive LLCP is demonstrated to show the potential of this synthetic strategy to offer broader opportunities to structurally diversify LCPs.