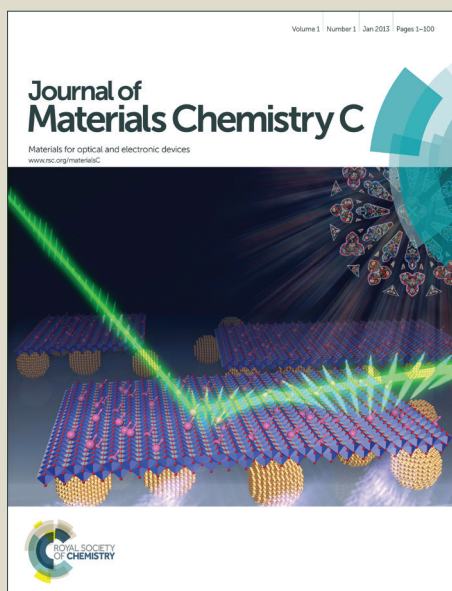


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COMMUNICATION

Reactive Azobenzene Liquid-Crystalline Block Copolymer as a Promising Material for Practical Application of Light-driven Soft Actuators

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Cross-linked liquid-crystalline polymers containing azobenzene have been drawing the great research interests of the scientists due to their significant values in design of light-driven soft actuators. However, poor processabilities due to the chemical cross-linking severely prevent their practical applications. Here, we designed and synthesized a novel reactive block copolymer PEO-*b*-PAZO bearing N-hydroxysuccinimide carboxylate substituted azobenzene groups. This copolymer is compatible with traditional polymer processing methodology including melt and solution processing methods, providing a facile way to prepare the photoresponsive films and fibers, and enabling post-crosslinking after processing through a mild reaction between N-hydroxysuccinimide carboxylate substituents and a difunctional amine. Most importantly, the prepared fibers and films showed reversible photodeformation regulated by alternating irradiation of UV and visible light (365 nm/470 nm). We envision that this novel liquid crystalline polymer will open up new possibilities for low-cost fabrication of high performance photo-driven actuators on a large scale.

Actuators that reversibly change their shape and/or size in response to external stimuli have been extensively studied for novel applications in wide-ranging industrial and medical fields.¹ Among them, the light-driven soft actuators are most attractive, because light as an external stimulus enables the remote control and gives rise to

rapid deformation of materials,^{1a,b} and polymers are one of the most promising materials for the fabrication and the engineering of the actuators due to their advantageous properties, such as their high processability, softness, easy fabrication characteristics, excellent corrosion resistance, and low manufacturing costs.² Several types of photosensitive polymers have been developed as soft actuator materials, including gels,³ shape-memory polymers,⁴ organic crystals,⁵ and cross-linked liquid-crystalline polymers (CLCPs).^{1a} In particular, the CLCPs are superior soft materials that possess both the order of liquid crystals (LCs) and the elasticity of polymer networks. With the aid of the CLCPs, it is possible to convert small amounts of external energy into macroscopic amounts of mechanical energy, which is essential for applications in actuators. By incorporating photochromic molecules such as azobenzene (azo) moieties into the CLCPs, deformations such as reversible contraction and expansion,⁶ and even bending^{7,8} have been induced by photochemical reactions of the azobenzene chromophores. Subsequently, numerous light-driven soft actuators such as swimmer,⁹ motor,¹⁰ oscillator,¹¹ microrobot,¹² artificial cilia,¹³ micropump,¹⁴ microvalve,¹⁵ inchworm and robotic arm¹⁶ have already been fabricated from the photoresponsive CLCPs.

Generally, there are two major methods to prepare the azo-CLCPs: the one step method and the two step method. In the former, the CLCPs are usually synthesized in conventional LC cells through common free radical copolymerization of acrylic monomers and crosslinkers; thus the size and the shape of the acquired CLCPs are limited and well-defined CLCPs are not easily obtained.¹⁷ In the latter, well-defined weak networks are synthesized in the first step, then these networks are stretched unidirectionally to align mesogens and establish order. In the second step, cross-linking reactions fix the network anisotropy.¹⁸ The advantage of the two step method is that the induced network anisotropy in the first step is reproducible; thus well aligned elastomers are achieved. However, the two step method is only suitable for producing the CLCPs with polysiloxane as the main chain. The both methods mentioned above are not

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applicable for widespread applications of the CLCPs as actuators due to their limitation of processability. A great challenge still remains about how to ameliorate the processability of the azo-CLCPs, which requires the precise coordination of rational molecular design strategy and processing methodology.

Lee et al. firstly reported an uncross-linked liquid-crystalline polymer (UCLCP) which exhibited reversible photoinduced bending behavior in various directions controlled by polarized UV light.¹⁹ Due to lack of chemical cross-linking, such properties of the UCLCP as strength, heat resistance, and reversibility are not good. Following, electron beam (EB) irradiation polymerization was employed to prepare the azo-CLCPs, which can be carried out without initiator at any temperature and any state of the monomers.²⁰ Although this approach shows excellent processing freedom compared with the previous methodology, it still remains some drawbacks for practical applications due to the requirement of unique and expensive processing equipment.

Herein, we designed a reactive block copolymer PEO-*b*-PAZO containing polymethacrylate, which bears N-hydroxysuccinimide carboxylate substituted azo groups, and poly(ethylene oxide) PEO (Fig. 1a). The molecular design strategy of the copolymer is based on two principal points: (1) N-hydroxysuccinimide substituents in the azo mesogens offer a superior approach after processing to post-crosslink polymer chains by using a difunctional primary amine under mild reaction conditions; (2) the introduction of a soft PEO block can supply enough free volume for the photoisomerization of the azo groups and the photochemical phase transition, enabling us to obtain more excellent photoresponsive CLCPs.²¹

Experimental

Synthesis and characterization of block copolymer PEO-*b*-PAZO: The block copolymer was synthesized by RAFT polymerization of a LC monomer, N-hydroxysuccinimide 4-[(ω-methacryloxyundecyloxy))phenylazo] benzoate, and a dithiobenzoyl-terminated PEO-based macro-chain transfer agent.

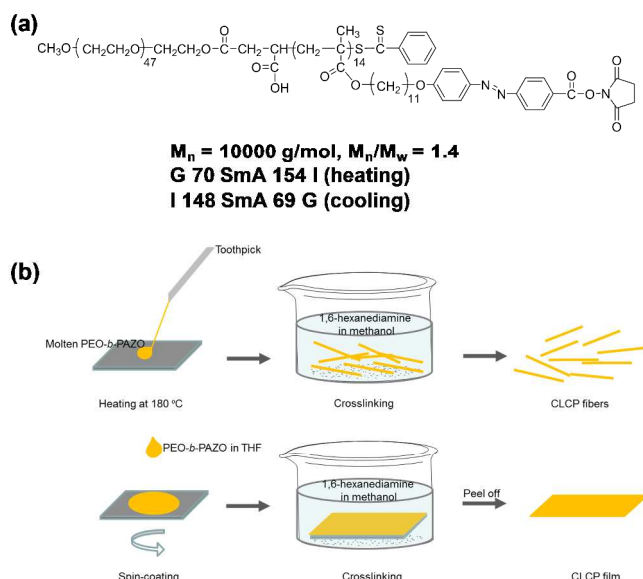


Fig. 1 (a) Chemical structure of the block copolymer PEO-*b*-PAZO used in this study. Mn: number-average molecular weight, Mw: weight-average molecular weight, G: glassy phase, SmA: smetic A phase, I: isotropic phase. (b) Experimental schematic to show the preparation procedures of the photoresponsive CLCP fibers and films.

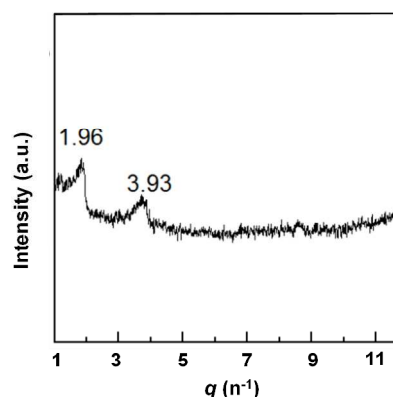


Fig. 2 SAXS spectrum of the block copolymer PEO-*b*-PAZO. The sample was cooled from 200 °C and then annealed at 140 °C for 1 h.

The LC monomer was synthesized according to the similar procedures reported previously (Scheme S1).^{22,23} Macro-chain transfer agent was synthesized according to the previously reported method (Scheme S2).²⁴ A glass tube was charged with macro-chain-transfer agent (102 mg, 0.05 mmol), 2,2'-azobisisobutyronitrile (1.5 mg, 0.01 mmol) and the LC monomer (500 mg, 0.61 mmol) in anhydrous tetrahydrofuran (THF, 2 mL); it was then degassed by three freeze-evacuate-thaw cycles and sealed in vacuo. The polymerization was carried out at 70 °C for 48 h. The block polymer was precipitated through the addition of the mixture into absolute diethyl ether, collected by filtration, and dried in a vacuum oven at 40 °C. Molecular weight as well as polydispersity index was measured by Gel Permeation Chromatography (GPC, Shimadzu, LC-10ADvp) with THF as the eluent at a flow rate of 0.8 mL/min. Thermodynamic properties of the LC monomer and the block polymer were determined by differential scanning calorimetry (DSC; TA, Q2000) at heating and cooling rates of 3 °C/min for the LC monomer and 10 °C/min for the block polymer, respectively. Three scans were applied to check the reproducibility. The optical anisotropy of the block polymer fiber was studied using a polarizing optical microscope (POM; Leica, DM2500p). 1D-SAXS experiments were performed with a small angle X-ray scattering (SAXS) instrument (Bruker NanoSTAR). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nexus 470 spectrometer.

Preparation of CLCP fibers: As shown in Fig 1b, the block copolymer fibers were drawn from a PEO-*b*-PAZO melt in its isotropic state. In a typical experiment, a small amount of the copolymer (20 mg) was heated to 180 °C on a glass substrate placed on a hot stage (Mettler, FP-90 and FP-82), then the fibers were prepared by quickly drawing out the melt with a toothpick. The fibers were left at room temperature for about 1 h to be stabilized. The average diameter of the fibers was about 100 μm. Then the drawn fibers were immersed into a solution of 1,6-hexanediamine in methanol (1×10^{-3} M) to undergo the chemical crosslinking reaction for about 2 h. After being washed with methanol several times and then dried at ambient temperature for 24 h, free-standing crosslinked fibers were finally obtained.

Preparation of CLCP films: A THF solution (8 mg/ml, 0.5 ml) of PEO-*b*-PAZO was cast onto a glass substrate using a spin coater at a low speed of 1200 r/min for 10 s. After the solvent was evaporated at ambient temperature for 1 h, a yellow polymer film was formed on the substrate. The obtained film was then immersed into a solution of 1,6-hexanediamine in methanol (1×10^{-3} M) and the chemical crosslinking reaction took place at room temperature for 4 h. After being washed with methanol several times and then dried at ambient temperature for 24 h, a free-standing CLCP film with the thickness

of about 20 μm was obtained by peeling off from the glass substrate (Fig. 1b).

Photoirradiation: For photoinduced bending experiments, a 365-nm UV LED (Omron, ZUV-C30H, 100 mW cm^{-2}) was used. Linearly polarized UV light (LPL) was obtained from the same instrument through a polarized UV filter. For unbending experiments, a 470-nm visible LED (CCS, PJ-1505-2CA, HLV-24GR-3W, 120 mW cm^{-2}) was used to irradiate the samples. Photographs of bending and unbending behavior were recorded with a digital camera (Olympus, VHX-500F).

Results and discussion

Mesomorphic property of PEO-*b*-PAZO

The copolymer PEO-*b*-PAZO showed a number-average molecular weight of $M_n = 1 \times 10^4$ g/mol with a molecular weight distribution of $M_w/M_n = 1.4$ (Figure S5). The mesomorphic property of PEO-*b*-PAZO was investigated by the combined techniques of DSC, POM, and SAXS. According to the DSC curves in Fig. S6, PEO-*b*-PAZO exhibits a phase transition at 154 $^{\circ}\text{C}$ (clearing point) in the heating process and at 148 $^{\circ}\text{C}$ in the cooling process. In addition, a glass transition at 70 $^{\circ}\text{C}$ and 69 $^{\circ}\text{C}$ was observed in the heating and cooling scan, respectively. The POM observation revealed the presence of a broken focal-conic fan-shaped texture when the melt of PEO-*b*-PAZO was heated to 140 $^{\circ}\text{C}$ and annealed for 60 min (Inset of Fig. S6), suggesting PEO-*b*-PAZO exhibits a smectic

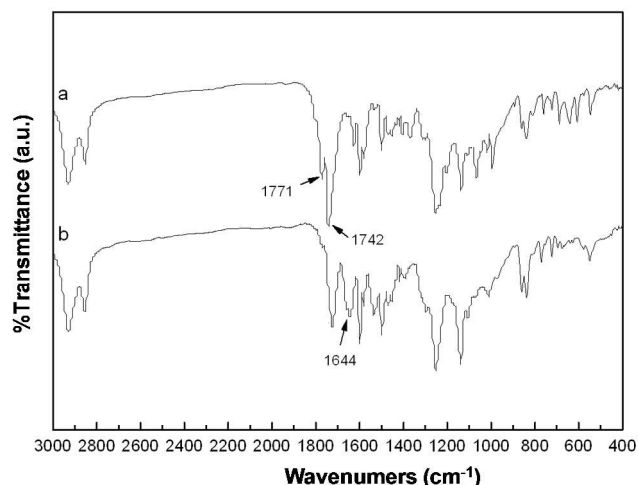


Fig. 4 IR spectra of the copolymer PEO-*b*-PAZO (a) and the crosslinked copolymer film (b).

phase.

Furthermore, the SAXS spectrum of PEO-*b*-PAZO was measured when the sample was cooled from 200 $^{\circ}\text{C}$ and annealed at 140 $^{\circ}\text{C}$ for 1 h (Fig. 2). The first and second scattering peak is $q_1 = 1.96 \text{ nm}^{-1}$ and $q_2 = 3.93 \text{ nm}^{-1}$, respectively, with the ratio of q_1 to q_2 being 1/2. This result demonstrates the presence of a long-range ordered lamellar structure with a layer spacing $d = 3.20 \text{ nm}$ calculated from the formula $d = 2\pi/q_1$. The d value agrees with the calculated side-chain length of PEO-*b*-PAZO (3.26 nm) perfectly, which implies that PEO-*b*-PAZO features a SmA structure.

Photochemical isomerization of PEO-*b*-PAZO

The photochemical isomerization of the crosslinked PEO-*b*-PAZO film prepared by the method demonstrated in the Fig. 1b was investigated. When irradiated with UV light at 365 nm, the PEO-*b*-PAZO film underwent trans-cis photoisomerization until a photostationary state was eventually reached (Fig. 3a). With the increase of irradiation time, the intensity of the $\pi \rightarrow \pi^*$ transition band around 350 nm decreased, whereas the intensity of the $n \rightarrow \pi^*$ transition band around 450 nm slightly increased. Fig. 3b shows the change on the UV-vis spectrum of the PEO-*b*-PAZO film under irradiation of visible light at 470 nm. It can be seen clearly that the PEO-*b*-PAZO film undergoes cis-trans back isomerization upon the visible light irradiation, but the finally recovered absorbance of trans-azobenzene is lower than that before the UV light irradiation, with the recovery of the trans-isomer being 98%. These results indicate that the CLCP film composed of PEO-*b*-PAZO is able to generate the photoisomerization in response to UV and visible light.

Photoinduced bending and unbending behavior

As shown in Fig. 1b, a freestanding CLCP fiber was prepared from the PEO-*b*-PAZO melt by dip-drawing method and then immersed into a solution of 1,6-hexanediamine in methanol to undergo the chemical-crosslinking reaction. Fig. 4 shows the IR spectra of PEO-*b*-PAZO and the crosslinked counterpart. The absorption band corresponding to the C=O stretch was observed 1644 cm^{-1} for the amide group, whereas the absorption band was observed at 1771 cm^{-1} and 1742 cm^{-1} for the N-hydroxysuccinimide ester in the uncrosslinked copolymer.

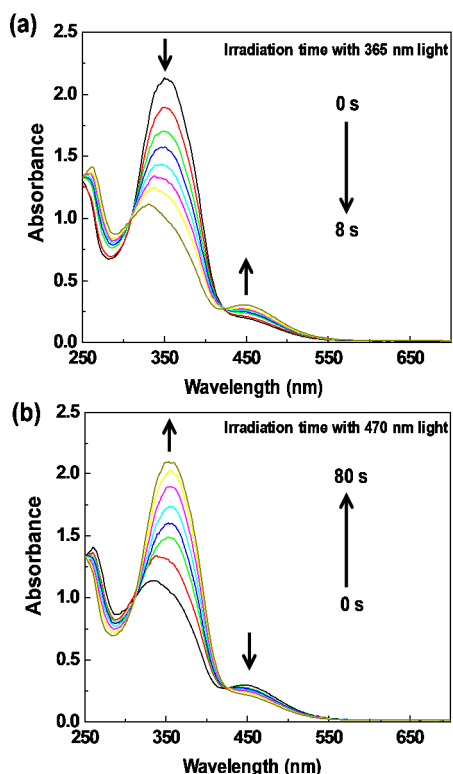


Fig. 3 Changes in UV-vis absorption spectra of the cross-linked PEO-*b*-PAZO film (the film thickness is 2 μm) at 25 $^{\circ}\text{C}$ in dependence of time: (a) upon irradiation with 365 nm light; (b) upon irradiation with 470 nm light at the photostationary state.

POM observation of the CLCP fiber was performed when the fiber was placed between crossed polarizers. Typical polarized optical micrographs are shown in Fig. 5a. The highest transmittance occurred at an angle of 45° between the polarization direction of either polarizer and the drawing direction, whereas the lowest transmittance appeared when the polarization direction was parallel to the drawing direction. Therefore, a periodic change of dark and bright images was observed by rotating the CLCP fiber with an interval of 45° . The results indicate that the mesogens are preferentially oriented to the drawing direction; therefore, the fiber can be called the monodomain CLCP fiber. The photoinduced bending and unbending behavior of the fiber was shown in Fig. 5b, when the fiber was heated to 80°C by a hot stage. As irradiated with 365 nm UV light, the fiber began to bend toward the light source along the fiber axis, and reached the maximum bending angle in 30 s. Then the bent fiber reverted to the initial flat state upon irradiation with 470 nm visible light in 3 min. Because of the alignment of the azobenzene mesogens along the fiber axis, irradiation with UV light leads to a reduction of the alignment order along the fiber axis in the surface of the CLCP fiber, which contributes to the bending deformation. In addition, the effect of heat on unbending behaviour was also studied, because the experiment was conducted at 80°C . Due to the thermal-induced disordered alignment, the CLCP fiber underwent back reaction indeed. However, the thermal-induced unbending behaviour was too slow and negligible compared with photo-induced recover process. This phenomenon testified that irradiation of visible light is necessary to trigger the back reaction within 3 minutes.

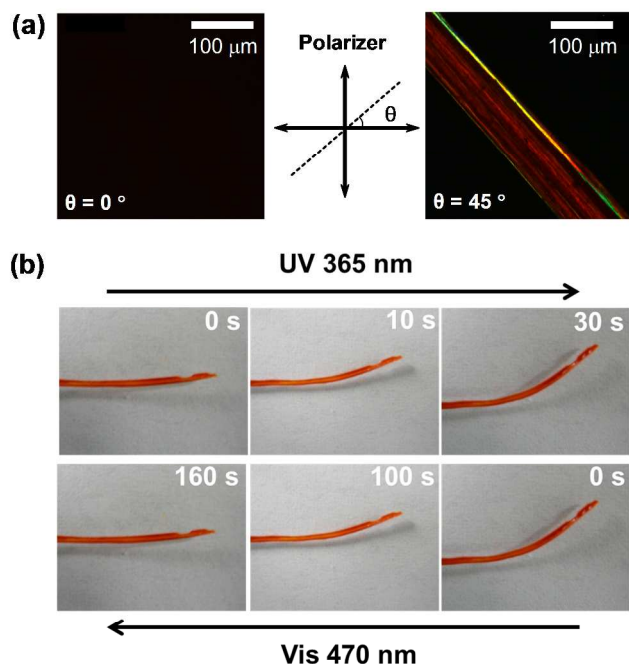


Fig. 5 (a) Polarizing optical micrographs of the texture of the CLCP fiber observed at room temperature. The black arrows indicate the directions of optical axes of the two polarizers, while the dashed line shows the drawing direction. (b) Images of photoinduced bending and unbending of the CLCP fiber upon irradiation with UV light at 365 nm (100 mW cm^{-2}) and visible light at 470 nm (120 mW cm^{-2}). The size of the fiber is $20\text{ mm} \times 100\text{ }\mu\text{m}$.

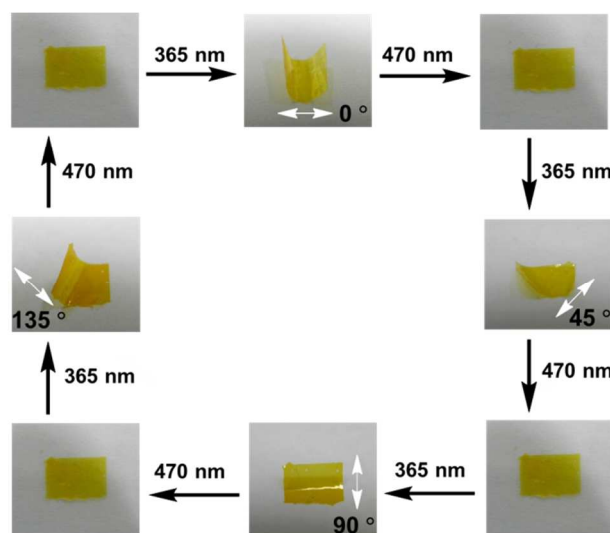


Fig. 6 Images of the precise control of bending direction of the CLCP film using linearly polarized UV light. White arrows in the images indicate the direction of polarized light. The size of the film is $4\text{ mm} \times 3\text{ mm} \times 20\text{ }\mu\text{m}$.

Furthermore, a freestanding CLCP film was fabricated by casting a THF solution of PEO-*b*-PAZO on a glass substrate, followed by the post-crosslinking reaction as well (Scheme S3). Since the obtained CLCP film was a polydomain film without pre-orientation, the CLCP film could undergo directional bending upon irradiation with linearly polarized light (LPL) by varying the polarization direction.^{3b} Fig. 6 shows a sequence of frames of bending behavior of the CLCP film heated to 80°C by a hot stage. The first frame in Fig. 6 shows the film before light irradiation. On irradiation with 365-nm LPL with a polarization direction at zero degree, the film bent towards the light source with the direction of bending parallel to the LPL direction, as shown in second frame in Fig. 6, counting clockwise. When the bent film exposed to visible light at 470 nm, it reverted completely to the initial flat state. Other bending behaviors of the film upon photo-irradiation with LPL directions at 45° , 90° and 135° are shown in the fourth, sixth and eighth frames of Fig. 6, respectively. Furthermore, the bent film could be restored from each bent state to its original flat state upon irradiation with 470-nm visible light. Moreover, the bending-unbending cycle was repeated without apparent fatigue. Similar to the case of the reported CLCP films,⁶ the bending of the film was ascribed to the contraction in the surface of film induced by the trans-cis isomerization of azobenzene and the alignment change of the mesogens with irradiation of UV light.

Conclusions

We successfully synthesized a novel reactive block copolymer PEO-*b*-PAZO, and prepared the monodomain CLCP fiber and the polydomain CLCP film through the mild chemical crosslinking reaction between PEO-*b*-PAZO and 1,6-hexanediamine at room temperature. Both of the CLCP fiber and film showed reversible photoinduced bending and unbending behaviors in response to UV and visible light, respectively. The monodomain CLCP fiber bent toward the light source along the fiber axis as well as the alignment direction of mesogens; therefore the fiber is able to bend toward

any direction when we change the irradiation direction of the incident UV light. On the other hand, the polydomain CLCP film underwent directional bending behaviors upon exposure to linearly polarized UV light. This reactive block copolymer with excellent processability allows fabrication of the freestanding CLCPs with good photomechanical properties and unlimited shape. Either melt or solution processing method also benefits the realization of widely practical applications of the CLCPs as light-driven actuators on a large scale.

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COMMUNICATION

Reactive Azobenzene Liquid-Crystalline Block Copolymer as a Promising Material for Practical Application of Light-driven Soft Actuators

An liquid-crystalline block copolymer composed of poly (ethylene oxide) methyl ester (PEO) and poly (methacrylate) bearing an N-hydroxysuccinimide carboxylate-substituted azobenzene mesogen was synthesized by RAFT polymerization. The freestanding fiber and film were prepared by facile techniques of dip-drawing or casting and thereafter immersing to undergo the post-crosslinking. Both of the CLCP fiber and film showed reversible bending and unbending behaviors in response to UV and visible light, respectively.

