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A Convenient Route to Prepare Reactive Azobenzene-Containing Liquid Crystal Polymers and Photodeformable Fibers

Yan Chen, Quan Liu, Patrick Theato, Jia Wei, and Yanlei Yu**

Azobenzene-containing liquid crystal polymers (azo-LCPs) with reactive groups attract much attention due to the combined properties of liquid crystallinity, photoresponsivity and reactivity, which make them promising in designing intelligent photo-driven soft actuators. Herein, a post-polymerization modification strategy is used to prepare a series of reactive azo-LCPs using the trans-esterification reaction of poly(pentafluorophenyl acrylate) with functional alcohols. These reactive azo-LCPs show good capabilities in fabricating fibers via a simple thermal-drawing method and subsequent crosslinking reaction with diamine under mild conditions. Furthermore, the prepared fibers exhibit reversible deformation behaviors under the alternate irradiation of UV and visible light (365/530 nm). This facile synthetic strategy is expected to open up new possibilities for fabricating photo-driven actuators.

Azobenzene-containing liquid crystal polymers (azo-LCPs) as a kind of stimuli-responsive material have been widely used in fabricating intelligent actuators including artificial muscles,[1–3] soft robotics,[4–6] and microfluidics.[7–9] Recently, introducing reactive groups into azo-LCPs has aroused much interest because it allows a post-processing modification, which is hard to be realized in conventional crosslinked azo-LCPs.[10–16] For example, after the fabrication process, these reactive groups can be used in crosslinking reactions to improve the mechanical properties or functional modification to obtain more capabilities, providing a new possibility to construct intelligent soft actuators. As a consequence, various reactive groups such as hydroxyl,[11–13] *N*-hydroxysuccinimide esters,[14,15] and thiol groups[16] have been applied to azo-LCPs for different purposes. So far, most reactive azo-LCPs are synthesized by homopolymerization of azo monomers containing reactive substituents[14–16] or by copolymerization of azo monomers with reactive monomers.[17,18] However, these direct polymerization methods often suffer from limited group tolerance because many reactive groups may lead to side reactions or hinder the polymerization. Moreover, the synthesis of azo monomers exhibiting reactive substituents is usually complex and tedious, which dramatically limits the applicability of such reactive azo-LCPs. Therefore, an effective approach to generate reactive azo-LCPs is highly desirable.

Post-polymerization modification (PPM) of a precursor polymer bearing reactive groups provides a facile strategy to synthesize reactive azo-LCPs.[19,20] By partially modifying with azobenzene compounds, a polymer containing both azobenzene groups and reactive groups can be easily obtained. In addition, this approach enables the easy and highly efficient synthesis of a systematic library of LCPs from a single reactive precursor polymer. Recently, Zhao and co-workers designed a novel liquid crystal elastomer utilizing a styrene–butadiene–styrene (SBS) triblock copolymer as the reactive precursor polymer.[21] Through first modification by thiol groups and subsequent esterification reaction with azobenzene mesogens, the unresponsive SBS polymer was successfully converted into a photoresponsive LCP. However, this relatively cumbersome PPM route inevitably restricts their application. As demonstrated by Theato and co-workers, poly(pentafluorophenyl acrylate) (PPFPA) as a reactive precursor polymer can react with many functional groups including amines and alcohols under mild conditions, even near-quantitative conversion for most of the amines.[22,23] This high reactivity, companying with the excellent solubility and hydrolysis resistance, makes PPFPA an attractive platform for the preparation of libraries of functional polymers.[20] To date, various functional materials such as reactive surfaces,[24,25] amphiphilic nanogels,[26,27] and multi-responsive polymers[28,29] have been synthesized by PPM of PPFPA.

In this article, we provide an efficient method to synthesize reactive azo-LCPs, taking advantage of a trans-esterification

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PPM reaction of PPFPA with functional alcohols (**Figure 1**a). With all copolymers synthesized from a single reactive precursor polymer, they exhibited similar degree of polymerization and chain-length distributions, which is important for studying the relationship between composition and properties. The reactive pentafluorophenyl (PFP) ester in PPFPA fulfills a dual role: 1) it can be substituted by azobenzene group to endow the polymer with both liquid crystalline and photoresponsive properties, and 2) it can further react with diamines to result in a crosslinked polymer network. Now, utilizing a simple thermal-drawing of the reactive azo-LCP and a subsequent crosslinking process, photodeformable fibers with reversible bending behavior were fabricated (Figure 1b).

The design, synthesis, and chemical structure of the azo-modified PPFPA (PFAZO) are shown in Figure 1a, in which a hydroxyl-terminated azobenzene compound (AZO-OH) was chosen as functional alcohol. Through controlling the feed ratio of AZO-OH, three copolymers PFAZO-x ($x = 14\%$, 30%, 58%) with different azobenzene molar contents of 14%, 30%, and 58% were synthesized and their structural and component information was determined by ^{1}H NMR. As shown in **Figure 2**a, typical azobenzene proton signals (a, b) clearly emerged in all ^{1}H NMR spectra of the synthesized copolymers, demonstrating that the azobenzene moieties have been successfully attached to PPFPA. In addition, the absence of protons signal (c) of methylene attached to the hydroxyl group of AZO-OH at 3.6 ppm indicated that the residue AZO-OH had been removed from the products. The azobenzene contents (14%, 30%, and 58%, respectively) in three copolymers were calculated from the integration values of the resonance signals, and the details are shown in Figure S1–S3, Supporting Information. Furthermore, the existence of PFP esters in PFAZO, which is necessary for the post-functionalization of azo-LCPs, was verified by ^{19}F NMR spectra (Figure 2b) where all copolymers showed the typical PFP esters signals in the region of −150 to −165 ppm.

The successful PPM was also confirmed by Fourier transform infrared (FT-IR) spectroscopy (Figure 2c). The FT-IR spectra of the homopolymer PPFPA presented a characteristic C=O stretching absorption of PFP ester groups at 1780 cm^{-1}. Once partially modified with AZO-OH, a new C=O stretching absorption at 1735 cm^{-1} appeared. This particular signal proportionally increased as the mole equivalent of AZO-OH was increased, accompanied by the gradual decrease in absorption at 1780 cm^{-1}. Similar changes were also found in the aromatic C=C stretching absorption of PFP at 1518 cm^{-1} and the aromatic C=C stretching absorption of azobenzene at 1500 cm^{-1}.

The mesomorphic properties of PFAZO-x ($x = 14\%$, 30%, 58%) were analyzed with a combination of polarized optical microscope (POM), small-angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC). POM observation showed that all copolymers featured typical schlieren texture at room temperature, suggesting the formation of liquid crystal phase (**Figure 3**a). The SAXS spectra of PFAZO-14%, PFAZO-30%, and PFAZO-58% were obtained at room temperature (Figure 3b), in which all copolymers exhibited two scattering peaks (q_1 to q_2 being 1/2) and similar q_1 in the low-angle region, revealing the presence of a long-range ordered lamellar structure with layer spacing (d) around 4.10 nm ($d = 2\pi/q_1$). The DSC study revealed the thermodynamic properties of polymers (Figure 3c, Figure S4a, Supporting Information). Combining the observation of POM at varied temperatures (Figure S4b, Supporting Information), it can be concluded that the endothermic peak around 120 °C represents the transition between liquid crystal phase and isotropic phase. As the azobenzene contents were increased from 14% to 58%, the clearing temperatures of PFAZO increased from 116 to 130 °C, indicating the improved stability of the liquid crystal phase. In addition, all obtained copolymers exhibited elevated glass transition (T_g) compared with the precursor polymer PPFPA (Figure S4c, Supporting Information), which is due to the introduction of rigid azobenzene units.

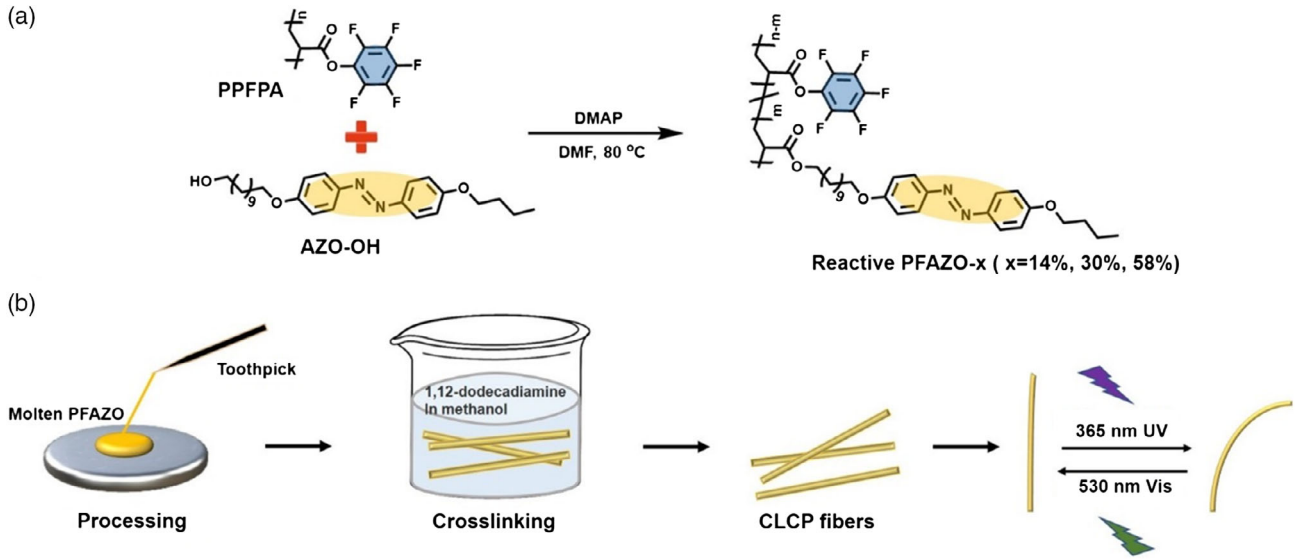

Figure 1. a) Trans-esterification reaction of PPFPA with varied equivalent of functional alcohol (AZO-OH) to produce three reactive copolymers PFAZO-x ($x = 14\%$, 30%, 58%) with different azobenzene contents. b) Experimental schematic to show the preparation procedures of the photoresponsive crosslinked liquid crystal polymer (CLCP) fibers.

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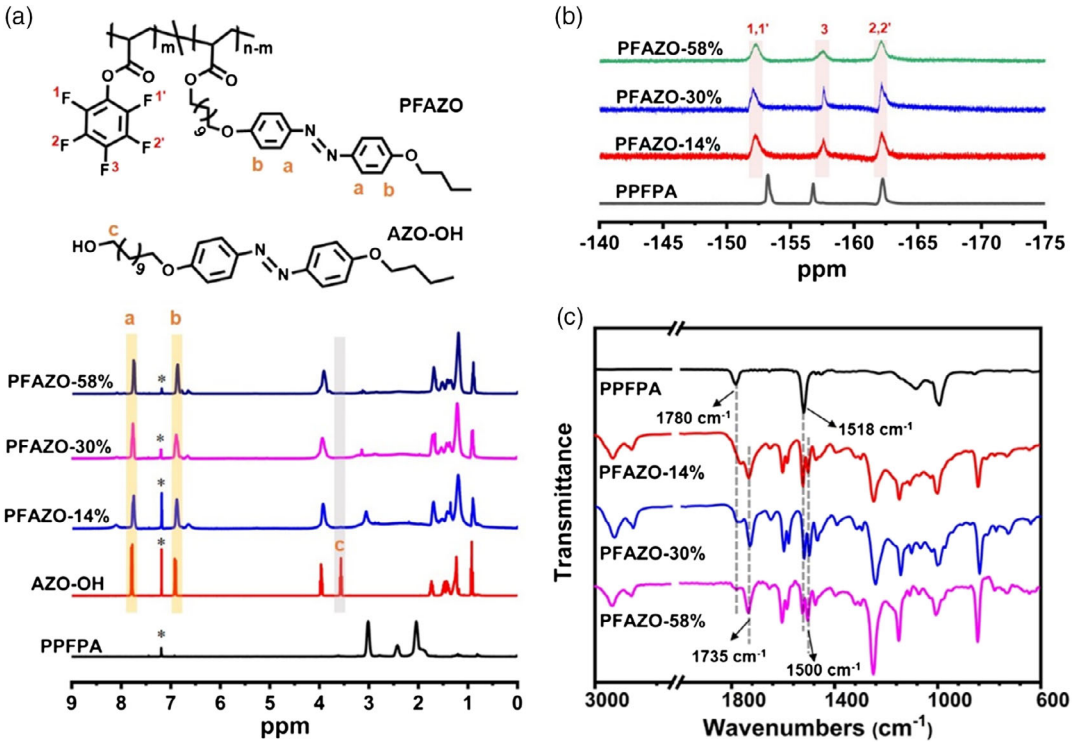

Figure 2. a) ^{1}H NMR spectra of PPFPA, AZO-OH, and PFAZO in $CDCl_3$. The peaks from the solvents are marked with the symbol *. b) ^{19}F NMR spectra of PPFPA and PFAZO in $CDCl_3$. c) FT-IR spectra of PPFPA and PFAZO.

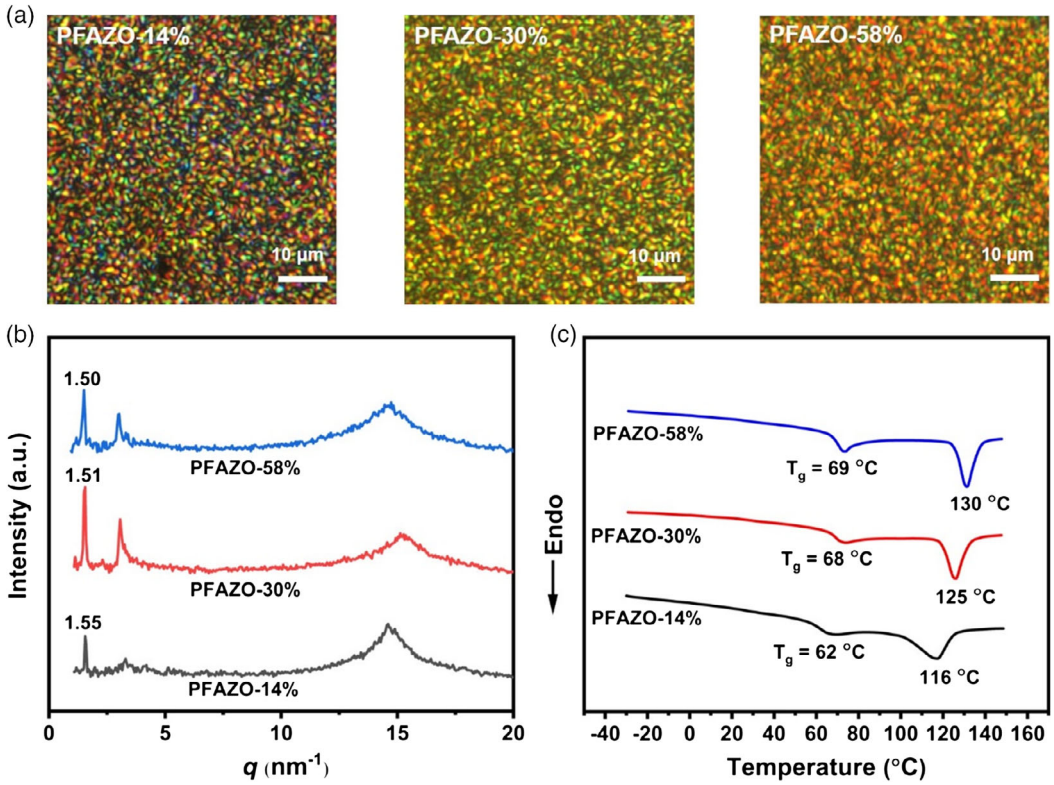

Figure 3. a) POM images of PFAZO at room temperature. b) SAXS spectra of the PFAZO powders at room temperature. c) DSC curves of the PFAZO from the second heating scan (10 °C min^{-1}).

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The photoisomerization of azobenzene is one of the attractive properties of azo-LCPs. As shown in **Figure 4**a, upon irradiation with 365 nm UV light, PFAZO-58% in CH_2Cl_2 solvent underwent a *trans–cis* isomerization. With the ongoing irradiation, the intensity of the $\pi \rightarrow \pi^*$ transition around 365 nm decreased, whereas the intensity of the $n \rightarrow \pi^*$ transition around 450 nm increased slightly until a photostationary state was eventually reached. The existence of isobestic points demonstrated the presence of two distinct absorbing species in equilibrium with each other and no side reaction took place during the photoisomerization process.[30] The *cis–trans* back isomerization was achieved through irradiating with visible light ($\lambda = 530$ nm) (Figure 4b). A similar photoisomerization process was observed for PFAZO-14% and PFAZO-30%, as shown in Figure S5, Supporting Information.

To build actuators with good photomechanical motion, the presence of crosslinking networks is essential for it helps to spread the forces produced by the photoisomerization of azo groups to the whole system.[31] Noteworthy, this crosslinking structure can be easily realized in PFAZO utilizing a secondary functionalization of the remaining PFP ester group. Here, three freestanding fibers (PFAZO-14%, PFAZO-30%, PFAZO-58%) with different azobenzene contents and crosslinking extent were fabricated by the first fabrication of the uncrosslinked azo polymer fibers through a simple thermal-drawing method and subsequent crosslinking reaction under mild conditions (Figure 1b). The detailed crosslinking reaction of PFP groups with diamine is presented in a schematic illustration shown in Figure 4c. According to previous studies, in the post-crosslinking system,

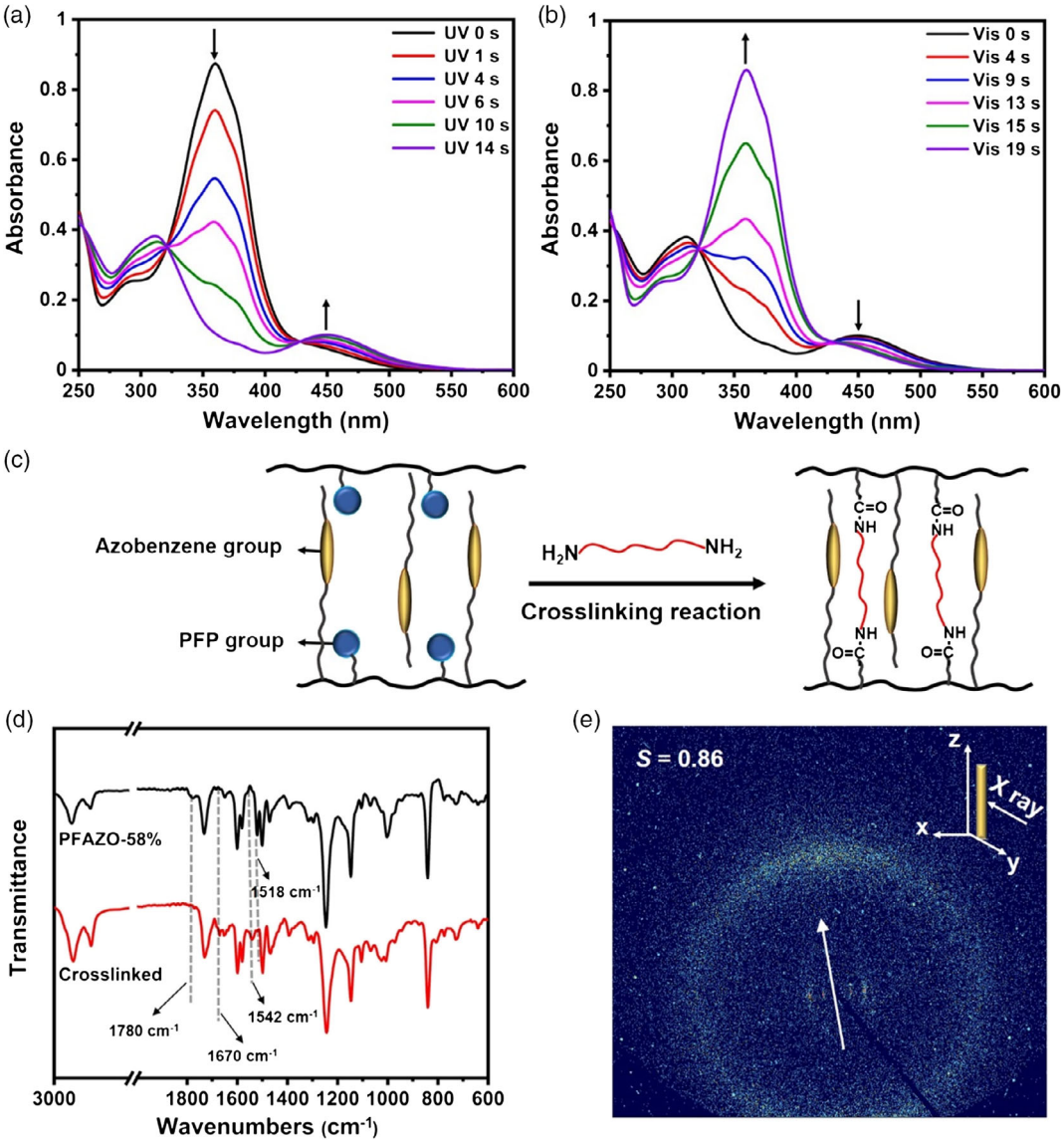

Figure 4. a,b) Changes in UV–Vis absorption spectra over time of PFAZO-58% in CH_2Cl_2 solution at 25 °C under irradiation with 365 nm light (10 mW cm^{-2}) or 530 nm light (20 mW cm^{-2}). c) Schematic illustration of the crosslinking reaction of PFP groups with diamine at room temperature. d) ATR FT-IR spectra of uncrosslinked PFAZO-58% and crosslinked PFAZO-58% fibers. e) 2D-XRD patterns and inserted orientation parameter values of the spontaneous orientation of the crosslinked PFAZO-58% fiber. The X-ray beam is perpendicular to the axial direction of the fiber.

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the extent of crosslinking in the fiber surfaces should be proportional to the contents of the crosslinkable group in the polymer.[15,31] Attenuated total reflection Fourier transform-infrared (ATR FT-IR) spectroscopy was performed to study the structural change on the PFAZO-58% fiber surface before and after its crosslinking with 1,12-dodecadiamine. As shown in Figure 4d, new absorptions around 1670 and 1542 cm^{-1} were observed after crosslinking, which corresponded to the C=O stretching and NH bending of the amide groups, respectively. This observation together with the disappearance of the absorption around 1780 and 1518 cm^{-1} (the PFP ester group from the uncrosslinked polymer) provides strong and direct evidence for the occurrence of the chemical crosslinking reaction of the PFP ester groups in the polymer via 1,12-dodecadiamine. The resistance of fibers against organic solvents also confirms the successful crosslinking (Figure S6, Supporting Information). The uncrosslinked fibers were dissolved in CH_2Cl_2 within 30 s, whereas the crosslinked fibers remained intact even after soaking in the same solvent for 30 min.

The preferential orientation of mesogens is of vital importance for LCPs to deform in the anisotropic manner under external stimuli.[32] Here, 2D X-ray diffraction (2D-XRD) was used to investigate the orientation of mesogens in the fibers (Figure 4e, Figure S7a,b, Supporting Information). In the low-angle region, all fibers showed similar diffraction arcs on the equator line, implying the formation of a smectic phase with normal directions of the smectic layer perpendicular to the fiber axial direction. In the high-angle region, two diffraction arcs on the meridian demonstrated the smectic A phase with mesogens orientation along the radial direction of the fiber. A schematic diagram of mesogen orientations (in a single layer) in the fiber is shown in Figure S7c, Supporting Information.

With the alignment of mesogens in a direction perpendicular to the fiber axis, these fibers are expected to bend away from the light source when exposed to UV light for the anisotropic expansion caused by the *trans–cis* isomerization of the azobenzene mesogens and the resulted disruption of alignment in the surface region (Figure S7d, Supporting Information).[33] The photoinduced bending behaviors of three crosslinked fibers (PFAZO-14%, PFAZO-30%, PFAZO-58%) are shown in **Figure 5** and Movie S1–S3, Supporting Information, in which all fibers showed reversible photoinduced bending behaviors upon irradiation with UV light and subsequent visible light. As reported, the photodeformation behaviors of the crosslinked fibers are related to the azobenzene contents and crosslinking degrees.[34–36] In this work, the PFAZO-14% fiber only presented a slight deformation (bending angle around 5°) because high crosslinking networks restrict the mobility of polymer chain and the low

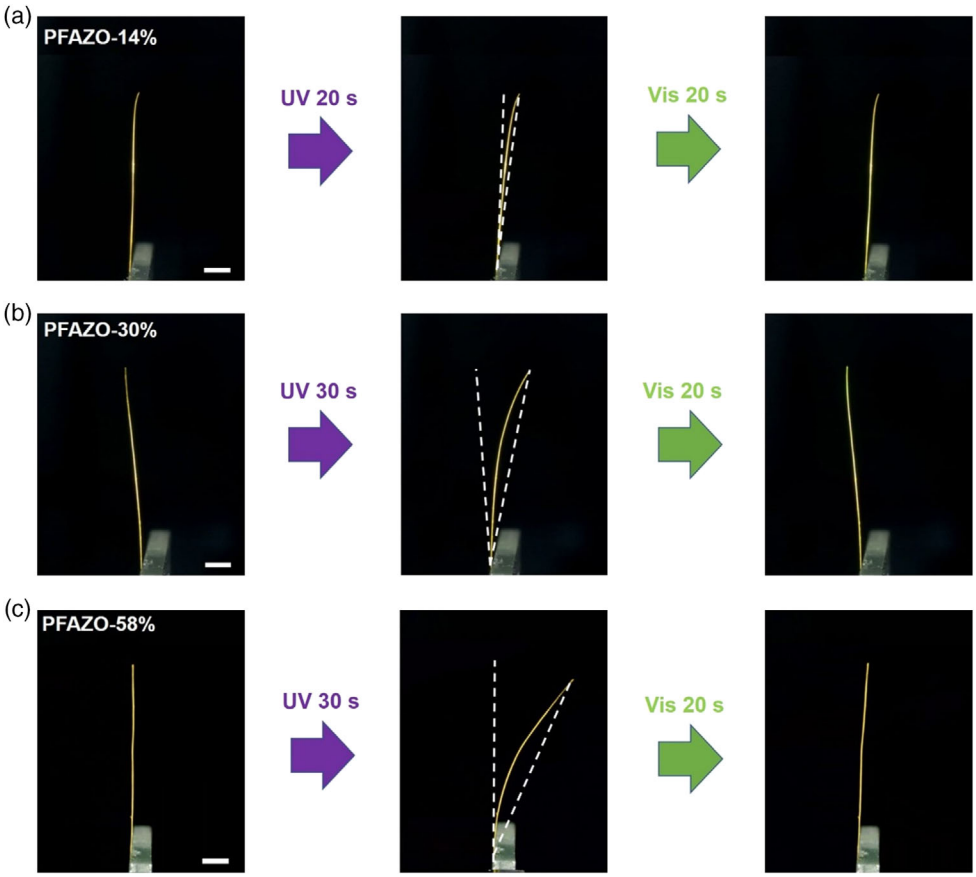

Figure 5. Photodeformation behaviors of a) PFAZO-14%, b) PFAZO-30%, and c) PFAZO-58% crosslinked fibers. The bending and recovery are induced by 365 nm UV light (10 mW cm^{-2}) and 530 nm green light (10 mW cm^{-2}). The maximum bending angles of PFAZO-14%, PFAZO-30%, and PFAZO-58% reach 5°, 20°, and 30°, respectively. The diameter of the fibers is about 20 μm, and the scale bar is 1 mm.

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azobenzene contents produce small photoinduced force.[34,35] Among all obtained fibers, PFAZO-58% fiber exhibited the largest bending angle, which is due to the synergistic effect between increased azobenzene contents and decreased crosslinking degree. When irradiated by UV light (365 nm, 10 mW cm^{-2}), it took 30 s for PFAZO-58% fiber to reach its maximum bending angle of 30°. The bent fiber could revert to its initial state upon irradiation with visible light (530 nm, 10 mW cm^{-2}) for 20 s. For comparison, the photodeformation behaviors of uncrosslinked fibers were also evaluated, which all showed negligible photomobility after irradiation with UV light. This phenomenon, along with other similar results in previously reported uncrosslinked fibers,[16,31] indicates the importance of crosslinking structure in the photo-driven actuating system.

In summary, we have provided a facile strategy to synthesize reactive LCPs with different azobenzene contents (14%, 30%, 58%) by PPM of the reactive precursor PPFPA. These copolymers exhibited stable liquid crystal phases and reversible photochemical behaviors. Moreover, they showed great capabilities in fabricating photodeformable fibers with high alignment order of azo mesogens through a simple thermal-drawing and subsequent crosslinking process with diamine. Among the obtained fibers, PFAZO-58% fiber with the highest azobenzene content and lowest crosslinking degree exhibited a maximum bending angle at room temperature. Collectively, this straightforward synthetic strategy, along with the remaining active PFP groups, renders PFAZO attractive candidates for introducing additional functionalities to design a wide range of flexible and multi-functional actuators.

Experimental Section

Synthesis of PPFPA: Precursor polymer PPFPA was synthesized according to a reported method.[37] PFPA (2.4 g, 10.1 mmol), 1,4-dioxane (3.8 mL), azobisisobutyronitrile (3.3 mg, 0.02 mmol) were added into a Schlenk flask. Afterward, the reaction was frozen and thawed three times, where liquid N_2 and N_2 gas were used for freezing and protection, respectively. The reactant was then stirred at 70 °C for 24 h. After cooling down with an ice bath, the crude product was added dropwise into methanol and then reprecipitated from tetrahydrofuran (THF) in methanol twice. The product was dried under vacuum to obtain a white powder product (Yield, 85%). The synthetic route is shown in Scheme S1, Supporting Information. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.10 (s, 1H, —CH—), 1.77–2.51 (br, 2H, —CH_2—); ^{19}F NMR (400 MHz, $CDCl_3$, δ): d/ppm: −162.28 (s, 2F), −156.78 (s, 1F), −153.25 (s, 2F). GPC (THF, 5 mL min^{-1}): $M_n = 1.82 \times 10^4$ g mol^{-1}, $Đ = 1.49$.

Synthesis of Compound 11-(4-((4-Butoxyphenyl) Diazenyl) Phenoxy) Undecan-1-ol (AZO-OH): Functional alcohol AZO-OH was synthesized according to the similar procedures reported previously,[38] with the synthetic routes as shown in Scheme S2, Supporting Information (Yield, 73%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.95−7.78 (m, 4H, aromatic), 7.05−6.87 (m, 4H, aromatic), 4.06−4.00 (dt, 4H, —CH_2O—), 3.60 (s, 2H, —CH_2—OH), 1.88−1.23 (m, 22H, —$(CH_2)_9$—, —$(CH_2)_2$—), 0.90 (s, 3H, —CH_3).

Synthesis of PFAZO: The PFAZO were synthesized by PPM of PPFPA with AZO-OH following a recently developed trans-esterification strategy.[39] First, the PPFPA (100.0 mg, 0.42 mmol, 1.0 eq. of PFP group) was dissolved in 1.0 mL of dry *N*,*N*-dimethylformamide. Then, AZO-OH of varied equivalents to PFP groups of PPFPA (0.25, 0.50, and 0.75 eq.) and 0.2 eq. of 4-dimethylaminopyridine were added under inert N_2 atmosphere. The mixture was stirred for 15 h at 80 ° and then precipitated in *n*-hexane. After redissolving the precipitate in THF and then reprecipitating in *n*-hexane twice, PFAZO with three different azobenzene contents were obtained. Furthermore, these copolymers were dried under a high vacuum at 45 ° overnight. The relevant characterization data are summarized in Table S1, Supporting Information.

Fabrication of Crosslinked Fibers: In a typical experiment, a small amount of the copolymer (20 mg) was heated to 150 ° 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 using a toothpick. The fibers were left at room temperature for about 1 h to be stabilized. The average diameter of the fibers was about 20 μm. Then the drawn fibers were immersed in a solution of 1,12-dodecadiamine in methanol (2×10^{-3} M) to undergo the chemical crosslinking reaction for about 1 h. After being washed with methanol several times and then dried at ambient temperature for 24 h, freestanding crosslinked fibers were finally obtained.

Characterization Methods: ^{1}H NMR and ^{19}F NMR spectra of the AZO-OH, PPFPA, and PFAZO were recorded on a Bruker DMX500 NMR spectrometer using tetramethylsilane as the internal standard and $CDCl_3$ as the solvent. FT-IR spectra and ATR FT-IR spectra were recorded on a Nicolet Nexus 470 spectrometer. The molecular weight as well as the polydispersity index were measured by gel permeation chromatography (GPC, Shimazu, LC-10ADvp) with THF as the eluent at a flow rate of 5 mL min^{-1}. The thermodynamic properties of PFAZO were determined by DSC (TA, Q2000) at a heating and cooling rate of 10 °C min^{-1}. The textures of PFAZO were evaluated with a POM (Leika, DM2500p) equipped with a hot stage (Linkam THMS600). SAXS measurements were carried out on a Bruker NanoSTAR SAXS system using Cu Kα ($\lambda = 1.542$ Å) as the radiation source. UV–Vis absorption spectra were measured with a UV–Vis absorption spectrophotometer (HITACHI, U-4100). 2D-XRD experiments of fibers were conducted on a small-angle/wide-angle diffractometer (Xeuss 2.0) with a 2D detector of Pilatus3R in transmission mode. Photographs and videos of the bending behaviors were taken by a super-resolution digital microscope (Keyence, VHX-1000C). 365 nm UV light was generated by an Omron ZUV-H30MC light source with a ZUV-C30H controller. Visible light (530 nm) was generated by a CCS HLV-24GR-3W.

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.

Data Availability Statement

Research data are not shared.

Keywords

photodeformations, poly(pentafluorophenyl acrylate), post-polymerization modifications, reactive liquid crystal polymers, soft actuators

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