Photo-Induced Bending Behavior of Post-Crosslinked Liquid Crystalline Polymer/Polyurethane Blend Films

Xinlei Pang, Bo Xu, Xin Qing, Jia Wei,* and Yanlei Yu*

Photoresponsive blend films with post-crosslinked liquid crystalline polymer (CLCP) as a photosensitive component and flexible polyurethane (PU) as the matrix are successfully fabricated. After being uniaxially stretched, even at low concentration, the azobenzene-containing CLCP effectively transfers its photoresponsiveness to the photoinert PU matrix, resulting in the fast photo-induced bending behavior of whole blend film thanks to the effective dispersion of CLCP. Specifically, the blend film shows photo-induced deformations upon exposure to unpolarized UV light at ambient temperature. The film unbends after thermal treatment, and the randomly orientated mesogens in the film can be realigned by the mechanical stretching, which endows the film with a reversible deformation behavior. The photosensitive blend film possesses favorable mechanical property and good processability at low cost, and it is a promising candidate for a new generation of actuators.

1. Introduction

Smart materials have drawn wide attention from scientists and engineers in recent years due to their fascinating properties. Compared with ceramics and shape-memory alloys, it is known that polymers are one of the most promising materials in view of their intriguing characteristics such as good processability, moderate mechanical strength, and potential to form free-standing films with thickness from nanometers to centimeters.[1,2] Of them, as a combination of both the mesogen order of liquid crystals (LCs) and the elasticity of polymer networks, crosslinked liquid crystalline polymers (CLCPs) distinguish themselves from other polymers in possessing superior properties such as anisotropy, self-assembly, stimuli-responsiveness, and molecular cooperation effect.[1,3–12] CLCPs that can undergo controllable and reversible shape change in response to external stimuli are desirable for

a variety of practical applications and definitely merit further investigations. The incorporation of azobenzene chromophore into CLCPs gives rise to photo-induced deformations such as uniaxial contraction/expansion and high-speed bending.[13–22] The photomechanical effect resulting from photoresponsive CLCP is useful in the development of actuators.

There has been growing interest in designing and studying photoresponsive composite films by combining CLCPs with commercial polymers, which will reduce cost and enlarge the scopes of the applications of CLCPs.[23,24] Ikeda and co-workers reported various double-layer films through the lamination of azobenzene-containing CLCP layers on the flexible polyethylene (PE) plastic sheets. As a result, the rotation of a light-driven plastic motor as well as 3D movements such as an inchworm walk and a flexible robotic arm motion was successfully achieved.[25,26] Additionally, a visible-light-driven plastic microrobot composed of CLCP/PE bilayer films could manipulate the object that is about ten times heavier than its own weight effectively.[27] However, these photoresponsive double-layer actuators with an adhesive layer generally suffer from delamination of the two layers after long-term exposure to light source, which results in a decreased lifetime.

In fact, another useful method has also been proposed to prepare the photoresponsive composite films by dispersing liquid crystalline polymers (LCPs), LC molecules, or azo compounds in the amorphous polymers. Yu and co-workers achieved the photomechanical conversion in polymer-dispersed LCs (PDLCs) like hybrid films with LCP particles dispersed in polyvinyl alcohol (PVA), yet the responsive rate was very low because of the high glass transition temperature of LCP.[28,29] They prepared various photomobile composite films via doping LC molecules or azo compounds to the polymer. Owing to the immiscibility between the small molecule and the polymer, the poor dispersion inevitably occurred in the hybrid film, which further dramatically decreased the mechanical properties of the composite films and impeded their applications to some degree.[29–31]

Undoubtedly, the improvement of the miscibility between a photoabsorbent and the polymer matrix will bring the promotion of mechanical properties and bending behaviors of the resulted blend films. Involvement of photoresponsive CLCP to polymer substrate by the dispersion method will provide

X. L. Pang, B. Xu, X. Qing, J. Wei
Department of Materials Science
Fudan University
220 Handan Road, Shanghai 200433, China
E-mail: weijia@fudan.edu.cn

Prof. Y. L. Yu
Department of Materials Science and State Key Laboratory of Molecular Engineering of Polymers
Fudan University
220 Handan Road, Shanghai 200433, China
E-mail: ylyu@fudan.edu.cn

ADVANCED
SCIENCE NEWS
www.advancedsciencenews.com

Macromolecular
Rapid Communications
www.mrc-journal.de

an effective way to endow the polymer matrix with excellent photoresponsiveness. However, one-step crosslinking of CLCP films in the glass cell constrains the fabrication of composite films. Remarkably, the post-crosslinking method provides an opportunity to give a feasible and ingenious way to prepare CLCP/polymer blend films. Zhang and co-workers reported a series of CLCPs and homopolymers with N-hydroxysuccinimide carboxylate-substituted azobenzene groups, which enables the post-crosslinking of polymer chains with 1,6-hexanediamine under mild conditions after a film-formation process.[32–34] Our group synthesized a block copolymer PEO-b-PAZO bearing an easily crosslinkable azobenzene mesogen. The obtained CLCP fibers and films showed reversible photodeformations upon alternating irradiation with UV and visible light, which was the first report on the photo-induced deformations of CLCP films by the post-crosslinking process.[3] Furthermore, our group prepared two types of CLCPs with different azotolene concentrations, and the post-crosslinking process enabled the fabrication of the CLCP films and fibers with different shapes and dimensions.[23]

In this work, we fabricated a series of low-cost and fast responsive blend films by incorporating crosslinkable PAZO bearing N-hydroxysuccinimide carboxylate substituted azobenzene moieties to flexible polyurethane (PU). Upon 365 nm UV light irradiation, the stretched crosslinked blend films showed fast bending behaviors toward the actinic light along the stretching direction even at room temperature due to the effective dispersion of CLCP in the PU matrix. It is

expected that many other general polymer materials can also be used for fabricating blend films with photoresponsive PAZO.

2. Experimental Section

2.1. Synthesis of Crosslinkable Side-Chain Liquid Crystalline Homopolymer PAZO

The CLCP with N-hydroxysuccinimide carboxylate-substituted azobenzene moieties as side chains is named as PAZO for convenience (**Figure 1**a).[33,34] It is worth noting that a long spacer containing 11 methylene groups results in a higher monomer reactivity and a faster response to light sources.[18,23,33] The PAZO was synthesized via the conventional free radical polymerization of LC monomers on the basis of the similar procedures reported previously.[3,33]

2.2. Preparation of the Crosslinked PAZO/PU Blend Films

As shown in Figure 1b, the un-crosslinked PAZO/PU blend films were prepared as follows: a certain amount of PAZO was added to the N,N-dimethylformamide (DMF) solution of PU (100 mg mL^{-1}). PU was purchased from Sigma-Aldrich (No 81367, Selectophore), and its structure is shown in Figure S1 (Supporting Information). Then, the homogeneous mixture was directly cast onto the dry and clean glass substrates. After the solvent being completely evaporated, the free-standing films were obtained by peeling them off the glass substrates. Various weight ratios of PAZO/PU of the blend films are studied at 1.5/98.5, 1.7/98.3, and 9/91, respectively. The presence of the reactive
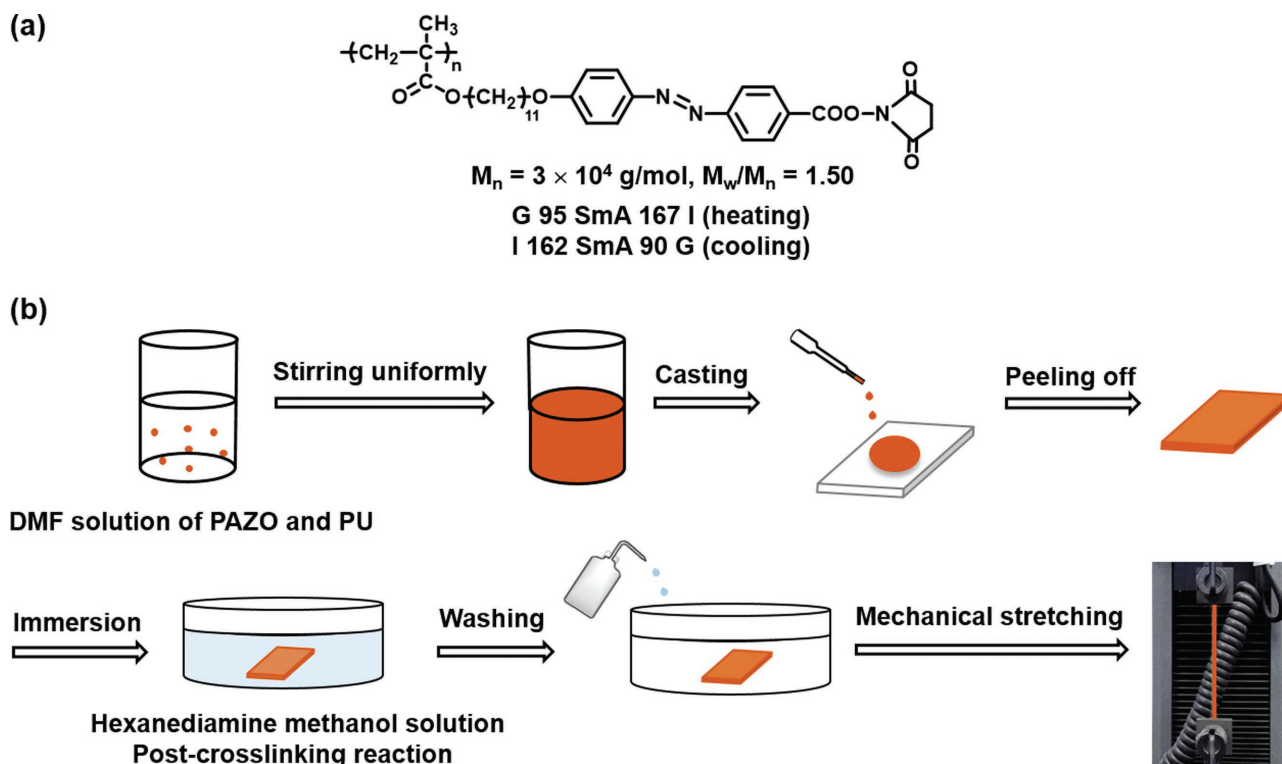

Figure 1. a) Chemical structure of the crosslinkable side-chain liquid crystalline homopolymer PAZO. M_n: number-average molecular weight; M_w: weight-average molecular weight; G: glassy phase; SmA: smectic A phase; I: isotropic phase. b) Preparation process of PAZO/PU blend films.

N-hydroxysuccinimide carboxylate groups makes the blend films' further post-crosslinking possible.

A typical post-crosslinking procedure is given as follows: the above-obtained un-crosslinked blend film was immersed into the 1,6-hexaniamine solution in methanol with a fixed concentration of 0.5 mg mL^{-1}, and this chemical crosslinking reaction was allowed to take place at ambient temperature for 4 h. After being washed with methanol and distilled water several times and then dried at room temperature for 12 h, the crosslinked blend films with smooth surfaces were successfully obtained.[33] The occurrence of the crosslinking in the blend films was confirmed by the difference of solubility between the crosslinked film and the uncrosslinked one (Figure S2, Supporting Information).[33] In addition, it has been demonstrated that the optical transparency of most of the azobenzene polymer films is hardly affected by the post-crosslinking process, which is highly important for their practical applications.[34] The PAZO/PU blend films mentioned below are crosslinked unless otherwise specified.
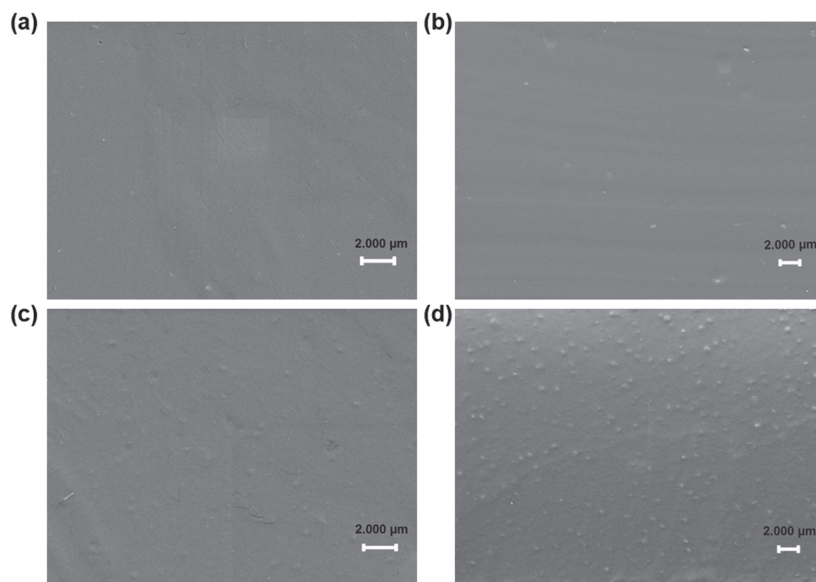
2.3. Characterization

The molecular length for the fully extended side-chain liquid crystalline unit of PAZO was evaluated by ChemBio 3D Ultra software. The mesomorphic property of PAZO was characterized with a polarizing optical microscope (POM, Leika, DM2500p) equipped with a Mettler hot stage (Model FP-90 and FP-82). The stretching process was performed with a tensile machine (Instron, Series 5943) under ambient temperature condition. The *trans–cis* photoisomerizations of azobenzenes in the tetrahydrofuran (THF) solution of PAZO and blend film (PAZO/PU = 1.5/98.5) were investigated by a UV–vis scanning spectrophotometer (Perkin Elmer, Lambda 650). In this process, a 365 nm UV lamp (OmRon, ZUV-C30H) and a 470 nm visible light lamp (CCS, PJ-1505-2CA, HLV-24GR-3W) were used. The orientation of azobenzene groups was evaluated by polarized UV spectroscopy. In addition, the thicknesses and the pictures of bending behaviors of the blend films were determined by an ultradepth 3D microscope (Keyence, VHX-1000C).

3. Results and Discussion

3.1. Mesomorphic Properties of PAZO

The mesomorphic properties of PAZO were first studied by using both differential scanning calorimetry (DSC) and POM. As shown in Figure S3a,b (Supporting Information), the isotropization occurred at 167 °C upon heating. When cooled from the isotropic phase, a clear LC texture was observed at 140 °C. In addition, the glass transitions at 95 and 90 °C were observed in the third heating scan and the third cooling scan, respectively.

The liquid crystalline mesophase of PAZO was further investigated with 1D wide angle X-ray diffraction (WAXD) (Figure S3c, Supporting Information). The first and second scattering peaks at $2\theta = 2.84°$ and $2\theta = 5.90°$ were observed at ambient temperature, with the radio of $1/d_1$ to $1/d_2$ being 1/2, revealing the presence of a long-range ordered lamellar structure with a layer spacing $d = 3.11$ nm ($d = \lambda/(2 \sin \theta_1)$). This d value is in agreement with the calculated molecular length for the fully extended side-chain liquid crystalline unit of PAZO

Figure 2. FESEM micrographs of a) the surface and b) the cross-sectional morphologies of the pure PU film; c) the surface and d) the cross-sectional morphologies of the blend film (PAZO/PU = 9/91).

(3.07 nm), which suggests that PAZO features a smectic A structure (Figure S3d, Supporting Information).

3.2. Surface and Cross-Sectional Morphologies of Pure PU Film and Crosslinked PAZO/PU Blend Films

The miscibility between the blending components is of vital importance in influencing the morphologies and performances of blend films. As shown in **Figure 2**a,b, the pure PU film exhibits the uniform surface and cross-section morphology, which were evidenced by the field emission scanning electron microscope (FESEM). Notably, when PAZO was added to the PU matrix, the surface morphology of the blend film (PAZO/PU = 9/91) is relatively smooth, suggesting a good dispersion of PAZO in the PU matrix (Figure 2c). In addition, as presented in Figure 2d, the cross-sectional morphology of blend film shows homogeneously dispersed aggregations, which is mainly originated from the PAZO. Therefore, in the obtained blend film, PAZO is presented in the form of LCP domains in the PU matrix. For comparison, the monomer of PAZO was also used to fabricate blend films. As shown in Figure S4 (Supporting Information), the small molecules only congregate on the surface of the blend film (AZO monomer/PU = 9/91) and fail to disperse uniformly within the polymer matrix. The inevitably immiscibility between the small molecules and the polymer matrix was also mentioned in previous report.[31] Furthermore, the dispersion of PAZO in the PU matrix was investigated with transmission electron microscope (TEM) by using an ultrathin section technique. The TEM micrographs of the pure PU film (Figure S5a,b, Supporting Information) and the blend film (PAZO/PU = 9/91; Figure S5c,d, Supporting Information) indicate the good dispersion of PAZO in the PU matrix, which is consistent with the FESEM result in Figure 2.

Table 1. Mechanical properties of pure PU films and PAZO/PU blend films.

	Young's modulus [MPa]	Maximum tensile strength [MPa]	Elongation at break [%]	Fracture energy [MJ m^{-2}]
PU	6.20 ± 0.79	49.87 ± 6.46	1346 ± 96	279 ± 45
PAZO/PU = 9/91 un-crosslinked	6.93 ± 2.08	26.11 ± 3.29	1029 ± 95	148 ± 20
PAZO/PU = 9/91 crosslinked	6.58 ± 2.25	24.66 ± 3.55	1624 ± 179	240 ± 29

3.3. Mechanical Properties of Pure PU Film and PAZO/PU Blend Films

Photoresponsive CLCPs have extensive application prospects in the field of microfluidics and artificial muscles.[26,27,35] Therefore, the favorable mechanical properties of CLCP materials are necessary. **Table 1** summarizes the data acquired from the mechanical tests. The uniform film samples with similar dimensions of 3 mm × 1 mm × 30 µm have been used unless explicitly mentioned.

As presented in Table 1, the pure PU film shows good mechanical properties with the maximum tensile strength of 49.87 ± 6.46 MPa, and its elongations at break reached around 1346%. Thus in the PAZO/PU blend films, PU as the host material can provide favorable mechanical properties for the whole blend system. It should be mentioned that poly(methacrylate)-type azobenzene polymers have rigid characteristics because of their backbones.[34] Compared with the pure PU film, blend films (PAZO/PU = 9/91) show higher Young's modulus but smaller tensile strength. The PAZO domains shown in FESEM images act as defects in the PU matrix under uniaxial tensile loading, causing the reduction in strengths of the blend films. Furthermore, particular attention is paid on the obvious effect of the post-crosslinking reaction on the mechanical properties of blend films. Compared to the un-crosslinked blend films, the average of the elongations at break and fracture energies of the crosslinked ones increase 57.8% and 62.2%, respectively.

3.4. Stretching-Induced Orientation of Crosslinked PAZO/PU Blend Films

The mesogens in PAZO are randomly orientated since no LC alignment was induced during the film-forming process. No photo-induced bending behavior of the blend film was observed upon irradiation with UV light because of the small volume change induced by randomly distributed mesogens.[28–31] If the materials possess any anisotropy, their deformation in response to light source can be induced in an anisotropic way with preferential direction of the orientation. Consequently, in order to obtain a large photomechanical behavior, homogeneous orientation of azobenzene moieties in the PAZO/PU blend film is highly important.[31] Zhao et al. reported the mechanical-induced orientation of azobenzene side-chain LCPs with the aid of supporting film,[36,37] but it is not widely applied to azobenzene-containing LCP with poly(methacrylate) backbone because it is difficult to fabricate stretchable films. However, mechanical-induced orientation was suitable for the stretching of the PAZO/PU blend films at room temperature, which was benefited from flexible and stretchable PU as the host material. All the samples were stretched to 400% extension, i.e., a draw radio of 5 (the draw radio is defined as the length after stretching over that before stretching). The orientation of azobenzene groups in the PAZO domains was determined for a stretched blend film (PAZO/PU = 1.5/98.5) as a model by polarized UV–vis spectra. The $\pi \rightarrow \pi^*$ transition of azobenzene moiety dominated the absorption peak centered around 338 nm of the stretched blend film, and the absorption of parallel ($A_{//}$) was larger than that of perpendicular polarization ($A_{\perp}$) (**Figure 3**a), while no obvious difference was observed in the pure stretched PU film (Figure S6, Supporting Information), illustrating that most of the azobenzenes in the blend film were preferentially oriented along the stretching direction. In addition, the soft segments of PU oriented preferably parallel to the stretching direction according to the reported work.[38]

3.5. Photochemical Isomerization of PAZO/PU Blend Film

The photoisomerization of azobenzene chromophore is at the origin of the attractive properties of polymers containing
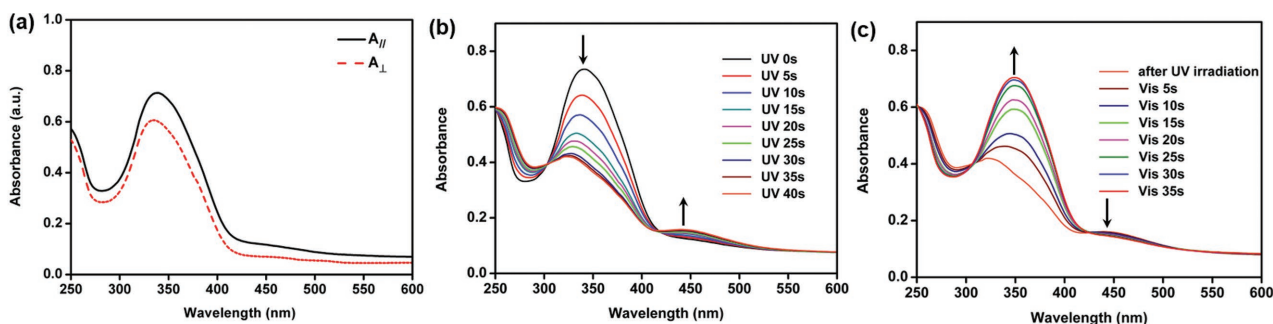

Figure 3. a) Polarized UV–vis absorption spectra of the stretched blend film (PAZO/PU = 1.5/98.5; thickness = 24 µm; elongation rate = 400%). b) UV–vis absorption spectral changes in dependence of time for the crosslinked blend film (PAZO/PU = 1.5/98.5) at 25 °C with irradiation of 365 nm UV light (power density = 8 mW cm^{-2}) and c) with irradiation of 470 nm visible light (power density = 10 mW cm^{-2}).

**ADVANCED
SCIENCE NEWS**
www.advancedsciencenews.com

**Macromolecular
Rapid Communications**
www.mrc-journal.de

azobenzene mesogens. As Figure 3b shows, upon firstly irradiating with 365 nm UV light, the blend film (PAZO/PU = 1.5/98.5) underwent *trans–cis* isomerization. With the passage of irradiation time, the intensity of the $\pi \rightarrow \pi^*$ transition band around 342 nm decreased, while the intensity of the $n \rightarrow \pi^*$ transition around 442 nm increased slightly until a photostationary state was eventually reached. The existence of isobestic points is typical for the presence of two distinct absorbing species in equilibrium with each other and meanwhile demonstrates that no side reaction took place during the photoisomerization process.[32,33,39] As shown in Figure 3c, irradiating the thermodynamically less stable *cis*-isomer with visible light at 470 nm brought about the *cis* to *trans* back isomerization. In addition, the photoisomerization of azobenzene moieties of the PAZO in the blend film was in consistent with that in the THF solution ($c = 4 \times 10^{-5}$ mol L^{-1}) (Figure S7, Supporting Information). These results suggest that PAZO exist in the blends is able to generate the photoisomerization in response to UV and visible light.

3.6. Photo-Induced Bending Behaviors of PAZO/PU Blend Films

The mechanism of the photo-induced bending behavior of the stretched crosslinked blend film is similar to that of the pure LCP films.[40] Upon irradiation with unpolarized 365 nm UV light (about 27 mW cm^{-2}), the *trans–cis* isomerization and alignment change of the azobenzene moieties occur in the blend film. Because of the high extinction coefficient of the azobenzene moieties at the irradiation wavelength, the actinic UV light hardly permeates through the film. As a result, the contraction of the PAZO domains is generated only in the surface layer, causing the fast bending behavior of the whole blend film (PAZO/PU = 9/91) toward the actinic light as a result of the driving effect of the dispersed PAZO domains to the PU

matrix (**Figure 4**a; Video S1, Supporting Information).[1,5,13] A bending angle (the bending angle is used to determine the tip displacement angle between the starting position and the tip end position of the film) of about 144° was obtained after being irradiated for 6 s. This result shows that the response rate of the blend film is comparable to that of the pure LCP film, while the content of the LCP used in the blend film is much smaller than that of the pure LCP film, which greatly decreases the preparation cost of the photoresponsive materials. Furthermore, irradiating the bent film from the opposite side with UV light at the same intensity also allowed bending behaviors toward the light source. After several cycles, longer irradiation did not induce obvious deformations of the blend film anymore because of the *trans–cis* photoisomerization of azobenzene moieties in the PAZO. In addition, blend film (PAZO/PU = 1.7/98.3) with a lower content of photoabsorbent also showed a fast photo-induced bending behavior. As shown in Video S2 (Supporting Information), upon exposure to UV light (about 8 mW cm^{-2}) for 40 s, a bending angle of about 160° was obtained. This result suggests that upon irradiation with UV light at extremely low intensity, the blend film shows even much faster responsive rate than the previously reported PVA-based films containing 4.5 wt% of the LCP and the photothermally responsive PU-based composite film.[28,31] This is one of the most prominent advantages of the present blend system. As comparison, the photodeformation behavior of the stretched blend film made of PU and un-crosslinked PAZO was also investigated. As shown in Video S3 (Supporting Information), upon exposure to 365 nm UV light (35 mW cm^{-2}), the stretched un-crosslinked blend film (PAZO/PU = 1.7/98.3) bent toward the light source, but the bending angle was very small with a fast degradation. This phenomenon suggests that the absence of crosslinking networks results in the lack of the cooperative motion of molecular chains in the PAZO domains.
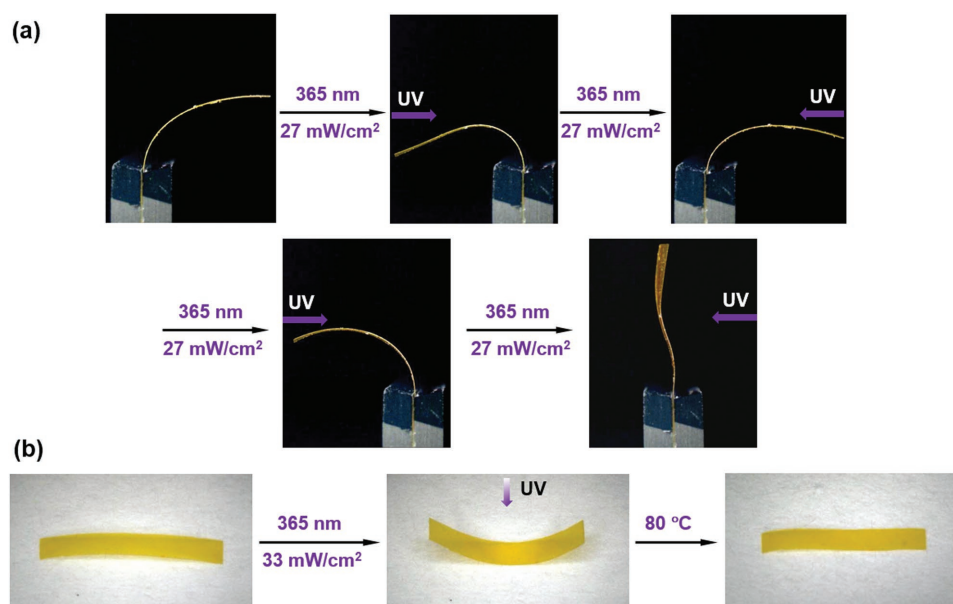

Figure 4. a) Photo-induced bending behaviors of blend film (PAZO/PU = 9/91, 6 mm × 1 mm × 35 µm) upon irradiation with 365 nm UV light. Irradiating the bent film from the opposite side also allows bending behavior toward the light source, with the arrow indicating the direction of irradiation, and this process can be repeated. b) Thermal recovery of the bent film occurred at 80 °C.

When the UV light was switched off, thermal treatment induced the bent film back to its original state (Figure 4b) due to the destroying of the hydrogen bonds between the hard segments and the soft segments in PU. Meanwhile, the back-isomerization of azobenzene moieties occurred with heat, but the ordered state initially induced by the stretching could not be achieved again directly. Since the un-crosslinked PAZO is brittle and easily damaged by the mechanical stretching, the PAZO domains are crosslinked before the mechanical stretching. Thus, the alignment formed is not fixed by chemical crosslinking networks. Once the alignment in the PAZO domains is destroyed in deformation process, the order is not able to recover even though the *cis–trans* isomerization happened. The alignment of azobenzene moieties could be achieved again by mechanical stretching at room temperature. The restretched blend film showed a photoresponsive behavior similar to that of the former. Therefore, the photoresponsive performances of the blend films reported in this paper are completed in a reversible way.

4. Conclusions

In summary, a series of UV-light responsive blend films with the crosslinkable PAZO as a photoactive component and a flexible PU as the polymer matrix were successfully fabricated by simple solution casting. The existence of reactive *N*-hydroxysuccinimide carboxylate-substituted azobenzene mesogens in the PAZO provides a good way to crosslink polymer chains in films under mild conditions. After mechanical induced orientation, the small volume change induced by the aligned azobenzene moieties upon UV irradiation at low intensity could be amplified to the whole blend system due to the good dispersion of photoactive CLCP, thus efficiently achieving the fast photo-induced deformations in a few seconds or tens of seconds. Commercially available PU with excellent flexibility as the host material provides good film formation and mechanical properties for the present system. In particular, the blend film (PAZO/PU = 1.7/98.3) with a lower content of PAZO was also able to undergo fast photo-induced bending behaviors upon exposure to UV light at ambient temperature, which was significantly faster than the previously reported composite films. Since the obtained PAZO/PU blend films possess many intriguing merits such as easy fabrication process, low cost, and well-controllable dimensions, numerous applications of the light-driven soft actuators on a large scale are possible. Furthermore, this method reported here also sets up a good example for the further combination of functional CLCP with other commercial polymers, which will greatly reduce the cost of photoresponsive actuators.

Supporting Information

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

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Keywords

[1] T. Ikeda, J. Mamiya, Y. Yu, *Angew. Chem., Int. Ed.* **2007**, *46*, 506.
[2] F. Cheng, Y. Zhang, R. Yin, Y. Yu, *J. Mater. Chem.* **2010**, *20*, 4888.
[3] J. A. Lv, W. Wang, W. Wu, Y. Yu, *J. Mater. Chem. C* **2015**, *3*, 6621.
[4] J. I. Mamiya, A. Yoshitake, M. Kondo, Y. Yu, T. Ikeda, *J. Mater. Chem.* **2008**, *18*, 63.
[5] Y. Yu, T. Ikeda, *Angew. Chem., Int. Ed.* **2006**, *45*, 5416.
[6] D. Q. Liu, C. W. M. Bastiaansen, J. M. J. Den Toonder, D. J. Broer, *Angew. Chem., Int. Ed.* **2012**, *51*, 892.
[7] H. Zeng, D. Martella, P. Wasylczyk, G. Cerretti, J. C. Lavocat, C. H. Ho, C. Parmeggiani, D. S. Wiersma, *Adv. Mater.* **2014**, *26*, 2319.
[8] J. Wei, Y. L. Yu, *Soft Matter* **2012**, *8*, 8050.
[9] X. Qing, L. Qin, W. Gu, Y. Yu, *Liq. Cryst.* **2016**, *43*, 2114.
[10] T. J. White, D. J. Broer, *Nat. Mater.* **2015**, *14*, 1087.
[11] E. K. Fleischmann, R. Zentel, *Angew. Chem., Int. Ed.* **2013**, *52*, 8810.
[12] H. Finkelmann, *Angew. Chem., Int. Ed.* **1987**, *26*, 816.
[13] Y. L. Yu, M. Nakano, T. Ikeda, *Nature* **2003**, *425*, 145.
[14] H. Finkelmann, E. Nishikawa, G. G. Pereira, M. Warner, *Phys. Rev. Lett.* **2001**, *87*, 015501.
[15] M. H. Li, P. Keller, B. Li, X. G. Wang, M. Brunet, *Adv. Mater.* **2003**, *15*, 569.
[16] Y. Yu, M. Taketo, M. Jun-ichi, I. Tomiki, *Angew. Chem., Int. Ed.* **2007**, *46*, 881.
[17] R. Y. Yin, W. X. Xu, M. Kondo, C. C. Yen, J. Mamiya, T. Ikeda, Y. L. Yu, *J. Mater. Chem.* **2009**, *19*, 3141.
[18] Y. Y. Zhang, J. X. Xu, F. T. Cheng, R. Y. Yin, C. C. Yen, Y. L. Yu, *J. Mater. Chem.* **2010**, *20*, 7123.
[19] W. Wu, L. Yao, T. Yang, R. Yin, F. Li, Y. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 15810.
[20] Z. Jiang, M. Xu, F. Li, Y. Yu, *J. Am. Chem. Soc.* **2013**, *135*, 16446.
[21] J. A. Lv, W. Wang, J. Xu, T. Ikeda, Y. Yu, *Macromol. Rapid Commun.* **2014**, *35*, 1266.
[22] Z. Yan, X. M. Ji, W. Wu, J. Wei, Y. L. Yu, *Macromol. Rapid Commun.* **2012**, *33*, 1362.
[23] Y. Liu, W. Wu, J. Wei, Y. Yu, *ACS Appl. Mater. Interfaces* **2017**, *9*, 782.
[24] T. Ube, T. Ikeda, *Angew. Chem., Int. Ed.* **2014**, *53*, 10290.
[25] M. Yamada, M. Kondo, J. Mamiya, Y. Yu, M. Kinoshita, C. J. Barrett, T. Ikeda, *Angew. Chem., Int. Ed.* **2008**, *47*, 4986.
[26] M. Yamada, M. Kondo, R. Miyasato, Y. Naka, J. Mamiya, M. Kinoshita, A. Shishido, Y. L. Yu, C. J. Barrett, T. Ikeda, *J. Mater. Chem.* **2009**, *19*, 60.

[27] F. Cheng, R. Yin, Y. Zhang, C.-C. Yen, Y. Yu, *Soft Matter* **2010**, *6*, 3447.

[28] H. Yu, C. Dong, W. Zhou, T. Kobayashi, H. Yang, *Small* **2011**, *7*, 3039.

[29] L. Yu, Z. Cheng, Z. Dong, Y. Zhang, H. Yu, *J. Mater. Chem. C* **2014**, *2*, 8501.

[30] Z. Cheng, T. Wang, X. Li, Y. Zhang, H. Yu, *ACS Appl. Mater. Interfaces* **2015**, *7*, 27494.

[31] L. Zhou, Q. Liu, X. Lv, L. J. Gao, S. Fang, H. Yu, *J. Mater. Chem. C* **2016**, *4*, 9993.

[32] L. Fang, G. Han, J. Zhang, H. Zhang, H. Zhang, *Eur. Polym. J.* **2015**, *69*, 592.

[33] X. Li, R. Wen, Y. Zhang, L. Zhu, B. Zhang, H. Zhang, *J. Mater. Chem.* **2009**, *19*, 236.

[34] G. Han, H. Zhang, J. Chen, Q. Sun, Y. Zhang, H. Zhang, *New J. Chem.* **2015**, *39*, 1410.

[35] J. A. Lv, Y. Liu, J. Wei, E. Chen, L. Qin, Y. Yu, *Nature* **2016**, *537*, 179.

[36] S. F. Rubin, R. M. Kannan, J. A. Kornfield, C. Boeffel, *Macromolecules* **1995**, *28*, 3521.

[37] S. Fu, Y. Zhao, *Macromolecules* **2015**, *48*, 5088.

[38] H. Ishihara, I. Kimura, K. Saito, H. Ono, J. Macromol, *Sci. Phys.* **1974**, *B10*, 591.

[39] M. Niemann, H. Ritter, *Makromol. Chem.* **1993**, *194*, 1169.

[40] C. J. Barrett, J.-I. Mamiya, K. G. Yager, T. Ikeda, *Soft Matter* **2007**, *3*, 1249.