

## Photodeformable Azobenzene-Containing Polyimide with Flexible Linkers and Molecular Alignment

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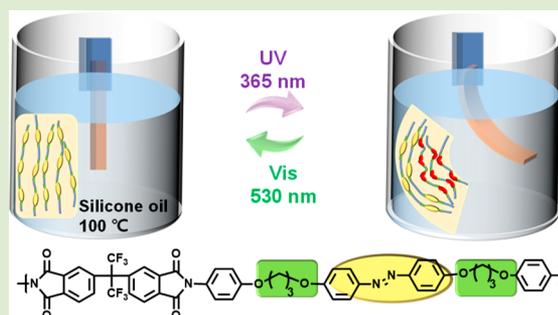
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**ABSTRACT:** Azobenzene-containing polyimides (azo-PIs) as photodeformable materials have attracted scientific attention in view of combining photoresponse and high performance (such as excellent mechanical and thermal properties). In the previously reported photodeformation of azo-PIs, polarized blue–green light was utilized to produce concerted motion of azobenzene moieties based on the mechanism of photoinduced reorientation. Herein, we explored a designed azo-PI undergoing photodeformation upon unpolarized light irradiation. The azo-PI film aligned by the hot-stretching process exhibited fast and reversible bending behavior under alternate ultraviolet (UV) and visible (vis) light irradiation, indicating the efficient nano-to-macroscopic propagation of molecular deformation of azobenzene. Besides, the aligned azo-PI film even bent in hot water (80 °C) and hot silicone oil (100 and 120 °C) with UV light irradiation.



Photodeformable polymers have drawn considerable attention due to the notable features of light stimulation for spatial, temporal, and directional control.<sup>1–3</sup> A prominent choice for fabricating photodeformable soft materials is incorporating photoswitchable chromophores into polymers, which is a well-established strategy for converting a molecular level motion into macroscopic changes. Azobenzene is a widely utilized chromophore that undergoes reversible *trans*–*cis* and *cis*–*trans* isomerization under UV/vis illumination. As the geometrical change of molecules ascribed to the isomerization of azobenzene can further be amplified to macroscopic deformation of polymers,<sup>4</sup> the azobenzene-containing polymers (azopolymers) with deformability have shown potential as artificial muscles,<sup>5,6</sup> sensors,<sup>7,8</sup> soft robots,<sup>9–15</sup> and micro-pumps.<sup>16,17</sup>

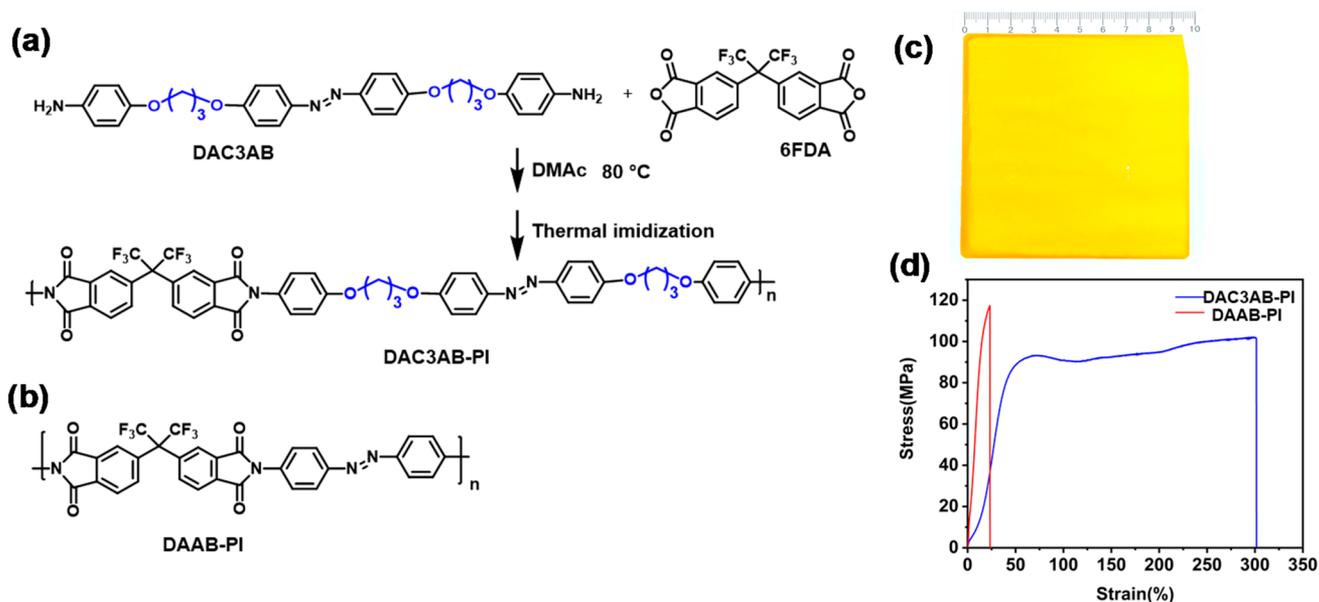
In the past few decades, azobenzene-containing liquid crystal polymers (azo-LCPs) have been extensively studied due to the fast response and large macroscopic deformation, which are facilitated by their features of the alignment and the cooperative effect of liquid crystals.<sup>18–26</sup> When irradiated with UV light, the *trans*–*cis* photoisomerization of azobenzene gives rise to the variation of the mesogens alignment, and the cooperative effect of aligned mesogens acts as amplifying nanoscopic molecular motions of azobenzene units into macroscopic deformations. The fascinating photodeformability of azo-LCPs attributed to their alignment has also inspired the exploration of a large deformation in nonliquid crystal polymers bearing azobenzene, which enriches diversity of azopolymers and provides benefits for adapting their utilization under different conditions.<sup>13–15,27–35</sup> Recent years have witnessed the interest in nonliquid crystal azopolymers like

azobenzene-containing polyimides (azo-PIs),<sup>13–15,27–35</sup> as polyimides (PIs) possess excellent mechanical and thermal properties.<sup>36</sup> In order to achieve the large deformation of amorphous and semicrystalline azo-PIs, polarized light was employed to align isotropic azobenzene moieties, that is, the *trans*-azobenzene is oriented orthogonally to the polarization direction after cycling *trans*–*cis*–*trans* isomerization upon polarized light irradiation (Weigert effect).<sup>28</sup> This photo-induced molecular alignment leads to the expansion or contraction of the network bearing azobenzene with respect to polarization and eventually results in the macroscopic deformation of the azo-PIs.

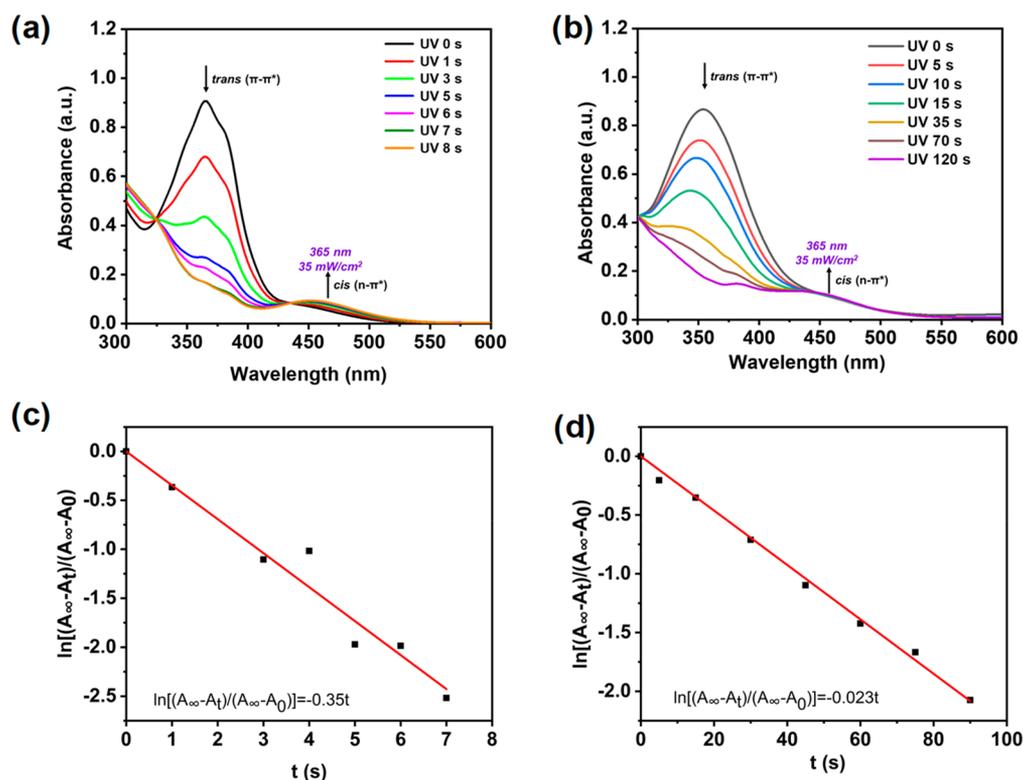
Utilizing unpolarized light to control deformation will make the manipulation more convenient, which has still not been implemented to azo-PIs. It is speculated that the random molecular chains in azo-PIs hinder the accumulation of the geometrical change of azobenzene under unpolarized light, for example, UV light. Therefore, the amplitude of macroscopic deformation is limited. As aforementioned, the concerted motion of azobenzene is advantageous to realize the anisotropic deformation in azopolymers. In order to realize large deformation under unpolarized light, alignment structures should be applied to the initial azo-PI before actinic

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**Figure 1.** (a) Synthesis of DAC3AB-PI via a two-step method. (b) Chemical structure of DAAB-PI. (c) The photograph of large-scale DAC3AB-PI film (thickness: 25  $\mu\text{m}$ ). (d) Stress–strain curves of the DAC3AB-PI (blue line) and the DAAB-PI films (red line).

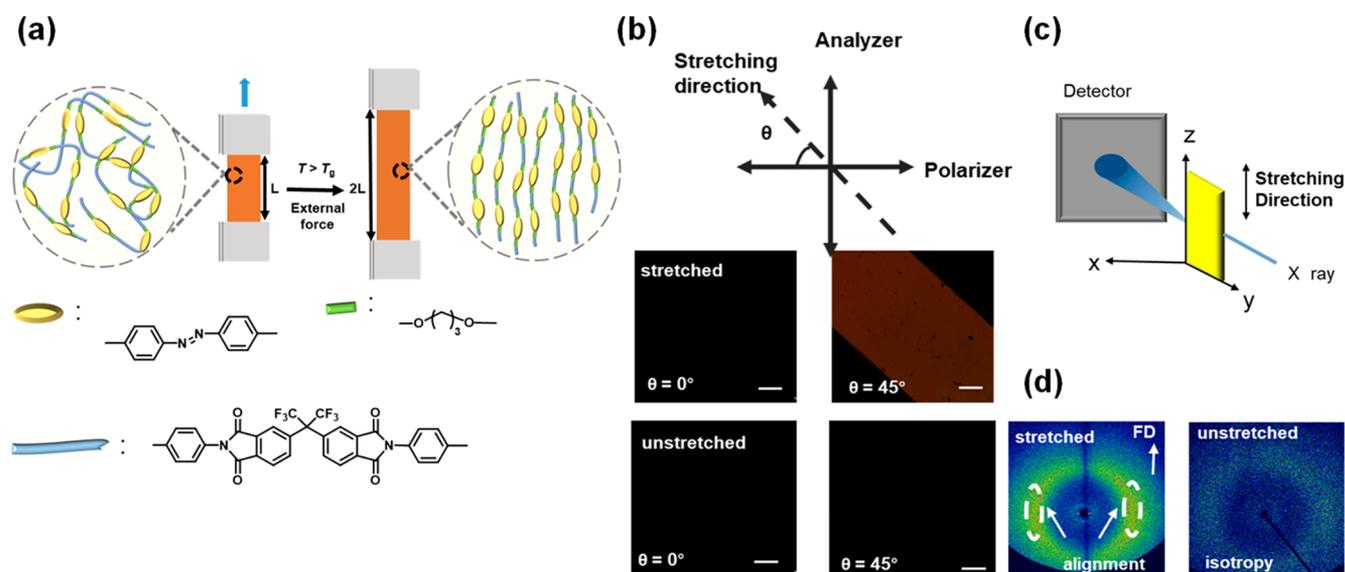


**Figure 2.** UV–vis absorption spectra of azo-PIs in NMP solution (ca.  $5.0 \times 10^{-5}$  mol L<sup>-1</sup>) upon exposure to UV light (365 nm, 35 mW cm<sup>-2</sup>): (a) DAC3AB-PI and (b) DAAB-PI. The intensity of the  $\pi \rightarrow \pi^*$  transition band around 360 nm decreases, while the  $n \rightarrow \pi^*$  transition band around 460 nm increases with the increment of irradiation time. Simulated lines (red) and measured points (black) for the *trans*–*cis* isomerization of (c) DAC3AB-PI and (d) DAAB-PI in NMP solution.

stimulus is employed. Stretching is proven to be a facile and efficient approach for the fabrication of aligned polymers, particularly for large-area treatments, which is capable of inducing the alignment of molecular chains along the stretching direction. White and Tan et al. previously reported a prestrained cross-linked azo-PI, which demonstrated a 2-fold

increase in photogenerated stress under irradiation of polarized 488 nm light.<sup>27</sup>

Wholly aromatic PIs are usually hard to be stretched near the glass transition temperature ( $T_g$ ) owing to their rigid structures and the strong interaction among polymer chains.<sup>37</sup> Herein, a semiaromatic azo-PI is constructed by introducing flexible linkers, facilitating the preparation of aligned film by



**Figure 3.** (a) Schematic illustration of hot-stretching process of DAC3AB-PI film above  $T_g$ . (b) Polarizing optical micrographs of the texture of the stretched DAC3AB-PI film (above) and unstretched (below) DAC3AB-PI film observed at ambient temperature. Scale bar: 200  $\mu\text{m}$ . (c) Schematic illustration of the films setup for 2D-WAXD testing. (d) 2D-WAXD patterns of the stretched DAC3AB-PI film (left) and unstretched DAC3AB-PI film (right); FD: film direction.

the hot-stretching process (Figure 1a). At the same time, the flexible linkers would accelerate *trans*–*cis* isomerization brought by the moderate reduction of molecular chain rigidity. The effects of hot-stretching on polymer chain alignment and the reversible bending behavior of the obtained film under alternate UV and green light irradiation are investigated. The azo-PI film even undergoes the photodeformation in hot water and silicone oil, which provides the potential for photocontrolled actuators in high-temperature environments.

Distinct from the previous work focusing on the photodeformation induced by *trans*–*cis*–*trans* reorientation with the polarized light excitation, we adopted unpolarized UV light to realize photodeformation enhanced by prestretching. First, the previously reported DAAB-PI was prepared with commercially available monomers 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) and 4,4'-diaminoazobenzene (DAAB; Figure 1b).<sup>31</sup> However, the rigid structures impede the stretchability of DAAB-PI with a low elongation ratio of 23% (Figure 1d), which is incapable of achieving the alignment by the hot stretching process. To address this issue, flexible linkers are introduced to the azo-PI to realize the facile fabrication of aligned film. As shown in Figure 1a,c, the azo-containing diamine monomer (DAC3AB) with flexible linkers was designed and copolymerized with 6FDA to prepare the large-scale DAC3AB-PI film. The obtained DAC3AB-PI exhibits an elongation ratio of  $\sim 300\%$  (Figure 1d), which is 10 $\times$  larger than that of DAAB-PI, offering an opportunity to obtain aligned azo-PI by stretching method.

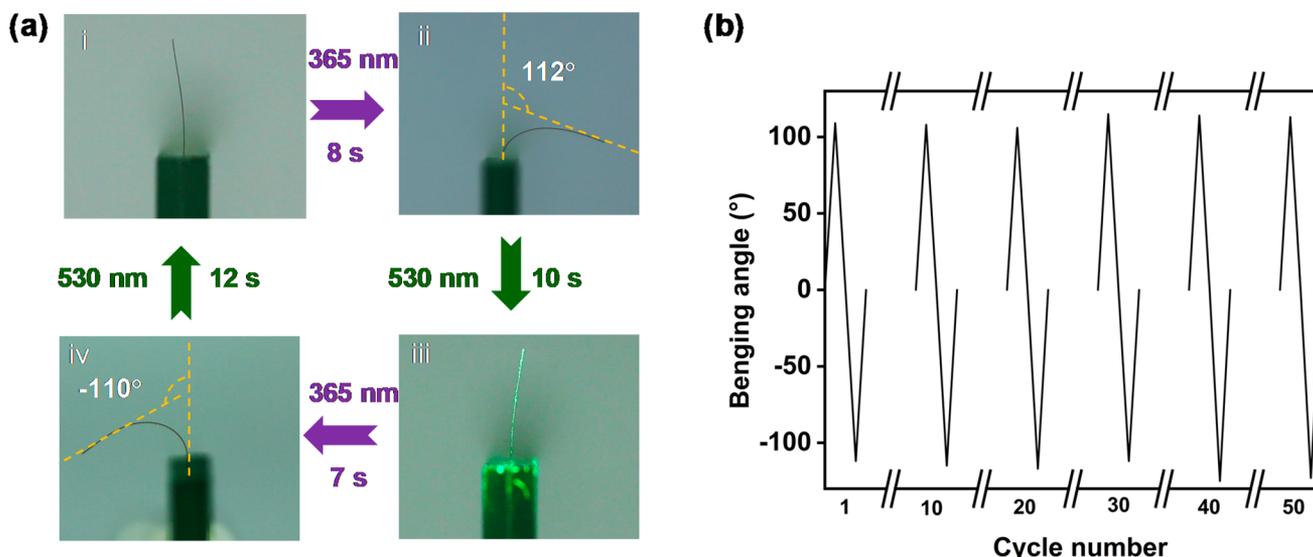
The flexible linkers are also anticipated to play an essential role in facilitating the *trans*–*cis* isomerization as the reduced rigidity of molecular chains. Figure 2a,b shows the photoisomerization of DAC3AB-PI and DAAB-PI in *N*-methyl pyrrolidone (NMP) solution under UV light irradiation (365 nm, 35 mW  $\text{cm}^{-2}$ ). Before the irradiation of UV light, a strong absorption band around 360 nm ascribed to the  $\pi \rightarrow \pi^*$  transition of *trans* form appears in both samples. After exposure to UV light, the intensity of the  $\pi \rightarrow \pi^*$  transition band decreases, while the intensity of the  $n \rightarrow \pi^*$  transition

band corresponding to the *cis* isomers around 460 nm increases with the irradiation time increasing. The intensity changes of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions suggest that both DAC3AB-PI and DAAB-PI undergo *trans*–*cis* isomerization under UV light irradiation. Remarkably, DAC3AB-PI undergoes faster isomerization, as the time required for reaching the photostationary state (PSS) of DAC3AB-PI and DAAB-PI was 8 and 120 s, respectively. To quantify the *trans*–*cis* isomerization rates of the azo-PIs, the first-order kinetic coefficient  $k_{tc}$  about the photochemical isomerization was introduced and calculated via time-resolved UV–vis absorption spectra as the following equation:<sup>38,39</sup>

$$\ln \frac{A_\infty - A_t}{A_\infty - A_0} = -k_{tc}t$$

where  $A_0$ ,  $A_t$ , and  $A_\infty$  are the absorbance values before irradiation, after irradiation for  $t$ , and at the photostationary state, respectively. According to the linear fitting (Figure 2c,d), the  $k_{tc}$  for DAC3AB-PI and DAAB-PI in NMP solution are calculated as 0.35 and 0.023  $\text{s}^{-1}$ , respectively. Compared to DAAB-PI, DAC3AB-PI exhibits a larger  $k_{tc}$  of photoisomerization under exposure to UV light with the same intensity, indicating a faster *trans*–*cis* isomerization in DAC3AB-PI solution. Because the azobenzene in DAC3AB-PI is adjacent to the flexible alkyl segments, the polymer chains are less constrained compared to that of DAAB-PI, which facilitates the configuration change of azobenzene under UV light irradiation. Another reason for the difference in isomerization rates is the difference in UV absorption caused by the introduction of ether groups between azobenzene and *N*-phenylphthalimide. As shown in Figure 2a,b, the  $\pi \rightarrow \pi^*$  absorption of the DAC3AB-PI is narrower than that of DAAB-PI and shows higher absorptivity at 365 nm, which is beneficial to the promotion of isomerization rates.

To further evaluate the *trans*–*cis* isomerization in the solid state, UV–vis spectra of azo-PI films were recorded under irradiation. The UV–vis spectra of the films (Figure S6) manifest the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  characteristic absorption at



**Figure 4.** (a) Reversible bending and unbending behavior of the stretched DAC3AB-PI film ( $5 \text{ mm} \times 1 \text{ mm} \times 20 \text{ }\mu\text{m}$ ) under alternate UV (365 nm,  $70 \text{ mW cm}^{-2}$ ) and visible light (530 nm,  $80 \text{ mW cm}^{-2}$ ) irradiation, respectively. The light was irradiated from the right side in the process i  $\rightarrow$  ii and ii  $\rightarrow$  iii, while the light was irradiated from left side in the process iii  $\rightarrow$  iv and iv  $\rightarrow$  i. Film position before (vertical yellow dash line) and after (sloping yellow dash line) UV light irradiation. The angle between the lines is the maximum bending angle of the film (positive value: bending toward right; negative value: bending toward left). (b) 50 photodeformation cycles of the stretched DAC3AB-PI film.

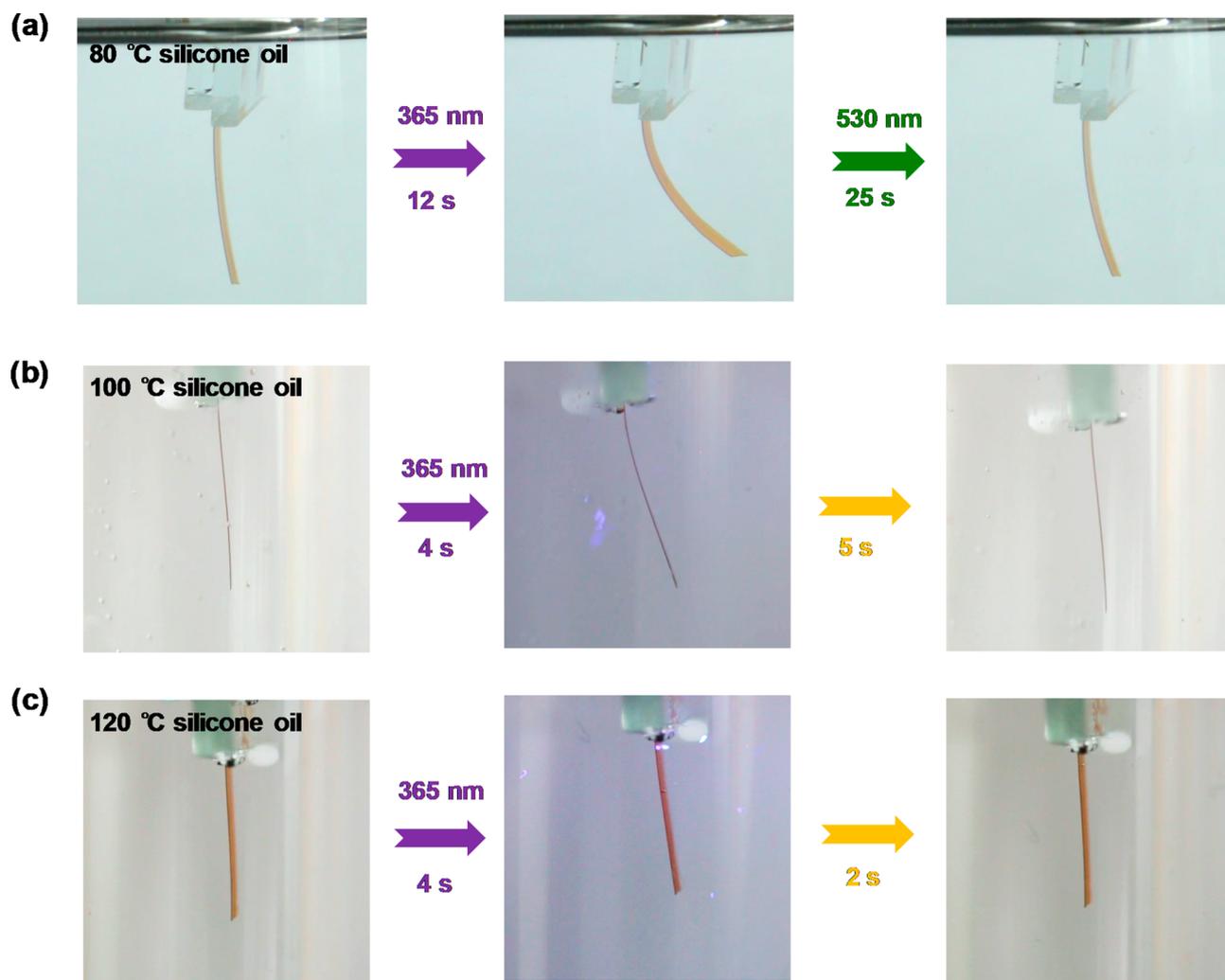
about 360 and 460 nm, respectively, which is similar to that of azo-PIs solution. Specifically, the irradiation time required to achieve PSS in the solid state of DAC3AB-PI (ca. 13 s) is significantly shorter than that of DAAB-PI film (ca. 120 s), which proves that the flexible linkers in DAC3AB-PI contribute to the faster isomerization rate either in solution or in the solid state.

Taking advantage of the stretchability of DAC3AB-PI endowed by the flexible chains, the obtained film was uniaxially aligned by hot-stretching. As illustrated in Figure 3a, the film was uniaxially stretched to a draw ratio of 2 (from L to 2L), followed by equilibrium for 3 h at  $250 \text{ }^\circ\text{C}$ , and was subsequently cooled slowly to ambient temperature. Polarizing optical microscopy (POM) and two-dimensional wide-angle X-ray diffraction (2D-WAXD) were used to evaluate the alignment of the film induced by the stretching process. As shown in Figure 3b, upon rotating the sample with respect to the analyzer, a periodic change from dark to bright field appears in the POM photographs of the stretched film. Instead, no periodic dark and bright change is shown in the case of unstretched film. The changes of the brightness indicate that an alignment emerges in the stretched film. 2D-WAXD was carried out by irradiating the film with the incident X-ray beam parallel to the  $y$  axis (Figure 3c). As revealed in Figure 3d, the obvious archlike diffractions located on the equator in the high angle region reveals that the film has a preferred alignment along the stretching direction. With respect to the unstretched DAC3AB-PI, the weak diffractions in the quadrants appear due to the random arrangement of polymer chains. According to the azimuthal integration in the high-angle region of 2D-WAXD patterns (Figure S7), the order parameter of the stretched film was calculated as about 0.9, while that of the unstretched film was nearly 0. It is clear from these results that stretching process induces the alignment and regularity of polymer chains parallel to the stretching direction.

To demonstrate the photodeformability of the aligned DAC3AB-PI film, a film with the size of  $5 \text{ mm} \times 1 \text{ mm} \times 20 \text{ }\mu\text{m}$  was exposed to unpolarized UV and visible light

irradiation. As shown in Figure 4a, when irradiated with UV light, the stretched DAC3AB-PI film bent toward the light source along the long axis, and the maximum bending angle reached  $112^\circ$  in 8 s (365 nm,  $70 \text{ mW cm}^{-2}$ ; Figure S8, Video S1). Due to the strong UV absorption of azobenzene moieties, the photoisomerization occurs only near the film surface at the irradiated side, which results in a contraction in the surface and leads to the bending behavior toward the light source. In contrast, the unstretched DAC3AB-PI film ( $5 \text{ mm} \times 1 \text{ mm} \times 23 \text{ }\mu\text{m}$ ) exhibited a small bending ( $4\text{--}5^\circ$ ) upon UV irradiation of 1 min (Figure S9). This clearly reveals that the alignment benefits the accumulation of the photomechanical effect that stems from the *trans*–*cis* isomerization in a specific direction and gives rise to a larger macroscopic deformation. Comparatively, the small photodeformation of the unstretched film is attributed to the absence of preferred alignment. The considerable difference of bending behaviors between the two films demonstrates the importance of alignment on the photodeformability of azo-PI. Meanwhile, it offers a strategy for realizing large photoinduced deformation in other non-liquid crystal azopolymers.

It has been proven that polymer chain entanglements in linear azopolymers play an important role in the reversible photodeformable behavior.<sup>40</sup> Besides, the alignment is expected to remain upon UV illumination as the *trans*–*cis* isomerization of azobenzene units is a localized motion. When irradiated with visible light, the entanglements in high-molecular DAC3AB-PI together with accumulated *cis*–*trans* photoisomerization in the alignment direction will give rise to the restoration of the initial shape. Accordingly, reversible bending behavior of the stretched DAC3AB-PI film was investigated. When exposed to visible light (530 nm,  $80 \text{ mW cm}^{-2}$ ), the bent film recovered to the initial state in 15 s, as the asymmetric contraction disappears owing to the reverse of azobenzene from bent *cis* isomers to the *trans* state (Figure 4a). Particularly, the maximum bending angle remained almost constant during the 50 deformation cycles of DAC3AB-PI (Figure 4b), revealing the excellent antifatigue properties. In



**Figure 5.** (a) Photographs of the stretched DAC3AB-PI film that exhibit bending and unbending behavior upon alternate irradiation with UV (365 nm,  $70 \text{ mW cm}^{-2}$ ) and green light ( $530 \text{ nm}$ ,  $80 \text{ mW cm}^{-2}$ ) in silicone oil at  $80 \text{ }^\circ\text{C}$ . (b, c) Photographs of the stretched DAC3AB-PI film that exhibit bending upon alternate irradiation with UV ( $365 \text{ nm}$ ,  $70 \text{ mW cm}^{-2}$ ) and subsequent unbending under heat stimuli at  $100$  and  $120 \text{ }^\circ\text{C}$ , respectively. The size of the film is  $8 \text{ mm} \times 3 \text{ mm} \times 20 \text{ }\mu\text{m}$ . The light was irradiated from the right side.

addition, the thermal relaxation behavior of bent film was illustrated in Figure S10. After removal of the UV light, the film reverts from  $112^\circ$  to  $70^\circ$  in 30 min and to  $10^\circ$  after 6 h in the darkness.

Introduction of flexible linkers into DAAB-PI inevitably brings a deterioration of thermal properties to some extent. However, the obtained azo-PI (DAC3AB-PI) still possesses relatively high  $T_g$  ( $\sim 195 \text{ }^\circ\text{C}$  by DSC,  $\sim 217 \text{ }^\circ\text{C}$  by DMA) and good heat resistance (5% decomposition temperature  $\sim 427 \text{ }^\circ\text{C}$ ; Figure S5). Besides the excellent photodeformability at ambient temperature, the azo-PI has the potential to allow for applications as actuators at elevated temperatures by virtue of its heat resistance. We evaluated the bending behavior of the stretched film in  $80 \text{ }^\circ\text{C}$  hot water, the film bent toward light resource and reached the maximum bending angle of  $45^\circ$  within 8 s (Figure S12a and Movie S3), then it reversibly recovered to its initial state within 15 s under subsequent green light irradiation ( $530 \text{ nm}$ ,  $80 \text{ mW cm}^{-2}$ ). Alternatively, because the *cis*-to-*trans* back isomerization also occurs under heat stimuli, the bent film reverted to its original state in 90 s after turning off the UV light (Figure S12b).

The photodeformation in more viscous liquid such as silicone oil under different temperatures was further investigated. As shown in Figure 5a and Movie S5, the film bent to  $45^\circ$  in approximately 12 s upon exposure to UV light. When the UV light was switched off, the film returned to the unbent state after 75 s without the visible light irradiation, whereas the subsequent green light illumination reduced the recovery time to 25 s (Figure S13, Figure 5a, Movies S5 and S6). In addition, the maximum bending angle decreased with the increase of the temperature. When the temperature of silicone was elevated to  $100 \text{ }^\circ\text{C}$ , the maximum bending angle decreased to  $22^\circ$  and reverted to initial state in 4 s after turning off the UV light (Figure 5b and Movie S7). As the rising temperature accelerates both *trans*-*cis* photoisomerization and *cis*-*trans* thermal isomerization, the deformation at high temperature is a dynamic equilibrium of both isomerizations.<sup>41</sup> The effects of temperature on the PSS and the *cis*-*trans* thermal relaxation were evaluated by UV-vis spectroscopy (Figure S14). When the temperature increases, there is a higher content of *trans* isomers at the photostationary state; thus, a smaller contraction is generated and a slight macroscopic deformation is induced. Despite the significant thermal back-isomerization,

a slight bending (around 5°) was still generated when the oil was heated to 120 °C, and an instant recovery was observed after removing the UV light (Figure S5c and Movie S8), which suggests the distinguished photodeformability of the azo-PI.

In conclusion, we have successfully obtained a stretched azo-PI with flexible linkers and demonstrated the large and reversible bending behavior under UV and visible light irradiation. It is worth noting that the alignment stemming from the hot-stretching strategy plays a critical role in amplifying the bending magnitude, which is contributed by the accumulation of the photomechanical effect generated from the azobenzene isomerization in a specific direction. The incorporation of flexible linkers facilitates the stretching process, as it serves a higher elongation ratio for rigid PI. Remarkably, thanks to the good thermal stability and mechanical properties of PI, the photodeformation of our azo-PI can also be realized in heated silicone oil. This work provides inspiration for designing promising actuators of azo-PIs for high-temperature applications.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.1c00040>.

Experimental procedures (Figures S1 and S2), polymer characterization (Figures S3–S5), additional results, and supporting movie captions (Figures S6–S14 and Movies S1–S8) (PDF)

Movie S1 (MP4)

Movie S2 (MP4)

Movie S3 (MP4)

Movie S4 (MP4)

Movie S5 (MP4)

Movie S6 (MP4)

Movie S7 (MP4)

Movie S8 (MP4)

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### Author Contributions

†These authors contributed equally to this work.

### Notes

The authors declare no competing financial interest.

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