Regulating the Photodeformation Behavior of Azobenzene-**Containing Polyimide via Thermal Treatment**

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light source) in side-chain azobenzene polyimides by adjusting the thermal treatment conditions. Different thermal treatments introduced variations in the internal free volume of the material, leading to two distinct deformation mechanisms under blue light exposure and resulting in opposite macroscopic deformation behaviors. By choosing appropriate thermal treatment methods, we fabricated actuators with specific functionalities and utilized the



correlation between deformation behavior and thermal treatment to demonstrate a detector for thermal history. This postsynthesis regulation of the photodeformation behavior offers a convenient and repeatable manner to engineer actuation on demand. KEYWORDS: photodeformation, azobenzene, thermal treatment, free volume, polyimide, actuator

1. INTRODUCTION

In nature, animals and plants produce complex and precise responses to environmental changes to better adapt to their ecological environments and survive. For instance, plants optimize their use of light resources through phototropic or negative phototropic growth mechanisms: phototropic growth in stems maximizes photosynthesis, while negative phototropism in roots anchors the plant and enhances water and nutrient absorption.¹ Inspired by these natural phenomena, researchers have been exploring ways to mimic such adaptive deformation behaviors in materials. Among these, azobenzenecontaining polymers are commonly used as photodeformable materials. The isomerization of azobenzene moieties under ultraviolet/visible light induces an asymmetric contraction or expansion in the materials, bringing different deformation behaviors such as bending away from or toward the light source.²⁻⁷ These materials hold significant potential applications in smart systems that require autonomous environmental responsiveness, offering innovative solutions that mirror the adaptive strategies found in nature.^{8–11}

To better imitate the complexity of biological morphogenesis, researchers have struggled with regulating photodeformation behaviors in azobenzene-containing polymers. When azobenzene chromophores are incorporated into liquid crystal polymers (azo-LCPs), the deformation behavior of the material can be altered by tuning the alignment of azobenzene.^{12,13} For instance, Ikeda et al.¹² discovered that the initial alignment of azobenzene significantly affects the bending direction of the azo-LCP films. When the azobenzene moieties are aligned parallel to the surface, the film exhibits an asymmetric contraction under UV light, resulting in bending toward the light source. Conversely, when the azobenzene moieties are oriented normal to the surface, the film undergoes an asymmetric expansion, leading to bending away from the light source. Additionally, Yu et al. revealed that the location of photoresponsive azobenzene in a side chain or cross-linker also played an important role in deciding their photoinduced bending direction.¹⁴ However, the limitation of these approaches is that the bending direction is typically unchangeable under the same stimulus once the azobenzene polymers are synthesized. That is, adjusting the bending direction using the above approaches requires a repreparation of material with different alignment or chemical compositions.

In contrast, utilizing postsynthesis treatment methods to adjust the bending direction will eliminate the need for synthesis of a distinct material. This allows the bending direction of materials to be switchable and makes the material more aligned

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Figure 1. (a) Chemical structure of s-DAC11AB-PI. (b) Under blue light irradiation (470 nm, 80 mW/cm²), SC-PI bent away the light source, while RC-PI bent toward the light source. The film size is 10 mm \times 2 mm \times 20 μ m.

with the definition of environmental adaptability. Thermal treatment is an effective postsynthesis treatment method, which has been extensively utilized on engineering properties of polymers, such as mechanical properties, ^{15–17} dielectric properties, ^{18,19} and other characteristics.^{20–22} Moreover, White et al.²³ discovered that thermal treatment conditions alter the molecular chain interactions and free volume of azobenzene-containing polyimide (azoPI), thereby affecting the photomechanical deformation angle of the films under polarized blue light irradiation.

Herein, we found that heat treatment not only changes the degree of deformation in azobenzene polymers but also enables controllable reversal of the deformation direction. We observed that side-chain azobenzene polyimide s-DAC11AB-PI (Figure 1a) films subjected to a slow cooling process after heating (designated as SC-PI) bend away from the light source under unpolarized blue light irradiation, whereas films that were rapidly cooled (designated as RC-PI) demonstrated bending toward the light source. Besides, the density experiments, along with positron annihilation lifetime spectroscopy (PALS), were applied to gain insights into the mechanism behind the different deformation modes. The deformation discrepancy arises from changes in the free volume within the polymer before and after light exposure, which is dependent on the thermal treatment conditions. Eventually, blue-light-responsive actuators referred to as "walker" and "cooling system detector" were constructed, thereby expanding the application scope of intelligent deformable materials.

2. MATERIALS AND METHODS

2.1. Materials. s-DAC11AB-PI, whose chemical structure is shown in Figure 1(a), was synthesized according to our previous work,²⁴ and the synthetic procedures are presented in the Supporting Information. Subsequently, the s-DAC11AB-PI films were heated above the glass transition temperature ($T_g = 147 \text{ °C}$) for 5 min and cooled at controlled rates. The films subjected to relatively slow cooling were designated as

SC-PI, while those subjected to relatively rapid cooling were designated as RC-PI.

2.2. Characterization of Photoresponsiveness. Before testing the photoinduced deformation ability of the material, s-DAC11AB-PI films underwent thermal treatment using a high-temperature micro heating stage (Mettler Toledo, HS82, CHE). The equipment's temperature range is from room temperature to 300 °C, with a heating rate of 0.1 to 20 °C/min. Subsequently, the film's response to blue light was tested using the HLV-24BL-3W blue light source produced by CCS Inc. This device is equipped with a PJ-1505-2CA controller and emits 470 nm visible light through an LED lamp head with a maximum light intensity of 120 mW/cm². During irradiation, the distance between the light source and the material was maintained at 5 cm. The deformation process of films under blue light, along with the changes in surface morphology and height, was recorded using a Canon EOS 70D DSLR camera and a super depth microscope (Keyence, VHX-1000C).

Additionally, the photoisomerization behaviors of the azobenzene groups in s-DAC11AB-PI were characterized by using a Lambda 650 UV/vis spectrophotometer manufactured by PerkinElmer. A polyamic acid (PAA) solution was spin-coated onto glass slides, followed by thermal imidization to prepare azoPI films (with the film thickness controlled to approximately 3 μ m, as shown in Figure S1). The films were then vertically positioned in the equipment for photoisomerization characterization. Finally, s-DAC11AB-PI films were cut into 10 × 5 mm pieces and vertically mounted between the clamps of a universal testing machine to measure their photoinduced stress. A prestress of 0.05 N was applied to the films before illumination, ensuring they remained vertical but unstressed. The films were then irradiated with blue light, fully covering the film surface with a light spot. The illuminated side of the film tended to bend, generating a tensile force on the clamps, which was measured as the photoinduced stress.

2.3. Characterization of Free Volume Using Positron Annihilation Lifetime Spectroscopy Measurements. The positron annihilation lifetime spectrum (DPLS3000) was utilized to measure the free volume of the materials. It employs a ²²Na positron radiation source with an activity of approximately 2×10^6 Bq. Upon β^+ decay, the source generated positrons with kinetic energy ranging from 0 to 540 keV, nearly simultaneously emitting a 1.28 MeV γ photon. The appearance of this γ photon served as the starting point for positron generation, while the occurrence of the 0.511 MeV annihilation γ photon marks the end point of positron annihilation. This time interval



Figure 2. Experiment images and schematic illustration of density changes of (a) SC-PI and (b) RC-PI under blue light irradiation for 60 s. The film size is $2 \times 2 \times 20 \ \mu$ m.

was considered as the positron lifetime. The sandwich structure was formed by placing the radiation source between samples, and measurements were conducted under ambient conditions at room temperature and pressure. The dimensions of the samples are $12 \text{ mm} \times 12 \text{ mm} \times 12 \text{ mm} \times 11 \text{ mm}$. After that, a total of one and a half million counts were recorded to obtain the positron annihilation lifetime spectrum for the samples. The system has a time resolution of 200 ps, and the acquired positron annihilation lifetime spectrum was analyzed by using the MELT-4 program.

The lifetime (τ_3) of *ortho*-positronium (*o*-Ps) was employed to calculate the nanohole radius of the free volume utilizing the established semiempirical relationship, given as

$$\frac{1}{\tau_3} = 2 \times \left(1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right) \right) \tag{1}$$

where τ_3 and *R* (nanohole radius) are expressed in ns and Å. ΔR is the empirical electron layer thickness (0.166 nm). The fractional free volume (f_v) is calculated using the following relationship:

$$f_{\nu} = CV_{f}I_{3} \tag{2}$$

where V_f represents the nanohole volume corresponding to the radius *R* calculated using eq 1. I_3 denotes the intensity (%) of the *o*-Ps pick-off lifetime component in the spectrum, and *C* is an empirical constant (0.018).^{25–27}

3. RESULTS AND DISCUSSION

3.1. Photodeformation Behavior of s-DAC11AB-PI with Slow Cooling or Rapid Cooling. To detect a possible influence of thermal treatment on the photodeformation behavior, we initially employed slow cooling (SC) to the heated s-DAC11AB-PI film (thickness: 20 μ m), with a heating temperature of about 200 °C and a cooling rate of 5 °C/min to room temperature. As shown in Figure 1b and Movie S1, the obtained SC-PI film exhibited a behavior of bending away from the light source upon exposure to nonpolarized blue light (470 nm, 80 mW/cm²), which means the expansion takes place on the irradiated surface of the film. Besides, the bending angle increased with increasing irradiation time (Figure S2a) and reached 69° after 25 s with no further changes. Additionally, the film exhibited an increased deformation angle with increasing light intensity (Figure S2b). This bending behavior was rapidly recovered by heating to above T_{g} . That is because raising the

temperature activates the molecular chains, causing them to move and return to their initial state.

We then employed rapid cooling (RC) to the heated s-DAC11AB-PI film with a cooling rate of 300 °C/min. As shown in Figure 1b and Movie S2, RC-PI exhibited bending toward the light source when irradiated with blue light (470 nm, 80 mW/ cm^2), which is opposite to the bending direction of SC-PI. This means contraction takes place on the irradiated surface of the film. Figure S3 illustrates the relationship between the bending angle of RC-PI and the light exposure time. The film exhibited a faster deformation rate and a larger bending angle than that of SC-PI. Upon light exposure, the bending angle of the film rapidly increased, reaching a maximum bending angle of 102° within 15 s. Eventually, this deformation can also be recovered by reheating the material followed by a desired cooling process (SC or RC) to customize the photodeformation direction again. This fulfills the concept that a single material can meet different demands and applications, which is ideal for reutilization and environmental protection.

3.2. The Mechanism behind the Deformation Discrepancy Induced by SC and RC. White et al. studied the deformation behavior of azoPI under polarized blue light after different thermal treatment conditions. They found that the cooling rate strongly affects the azobenzene photochemistry (*trans-cis-trans* isomerization) of azobenzene under polarized blue light. Rapid quenching introduces additional free volume, enhancing the deformation capability in the same direction.²³ In this work, we have discovered that when azoPI is exposed to unpolarized blue light, different cooling processes lead to opposite deformation behaviors by following different deformation mechanisms.

Critical to reversing the photodeformation direction is the reversal of volume change at the surface of the film under blue light irradiation. To clarify this, we characterized the density change of the SC-PI and RC-PI before and after irradiation through density experiments.²⁸ As shown in Figure 2a, the SC-PI film was placed in a saturated sodium chloride solution and sank to the bottom due to its higher density before being exposed to light. After irradiation with blue light (470 nm, 80 mW/cm²) for 60 s, the floating film indicates a decrease of film density induced by blue light exposure. In addition, to further validate the conclusion, topological deformations on the surface of SC-PI

films were recorded by capturing the deformations on a PDMS surface. The SC-PI films were placed on a glass substrate, and a precursor solution of PDMS was uniformly cast over their surface. As the PDMS cured, the deformations of the SC-PI under illumination were recorded.²⁹ Figure S4 displays the surface morphology of PDMS, showing uniform undulations corresponding to the structure of the mask template, thus proving that SC-PI film undergoes expansion. On the other hand, Figure 2b shows that the RC-PI is suspended in a solution of sodium chloride, which clearly demonstrates that the RC-PI possess a lower density than that of SC-PI. Subsequently, the film sank to the bottom after irradiation with blue light for 60 s (470 nm, 80 mW/cm²), indicating that blue light exposure increases the density of the film.

The opposite changes in density imply that distinct mechanisms underlie the photoinduced deformation behavior of the films subjected to different cooling processes. When the films were heated to a high temperature, the movement of molecular chains was promoted and the distance between the chains increased. For SC-PI, the slow cooling process allows for gradual relaxation of the polymer chains, leading to a densely packed arrangement of molecular chains. However, under blue light irradiation, the trans-cis-trans isomerization of azobenzene molecules forces the local polymer network to expand in order to accommodate the free volume requirements of azobenzene isomerization. As a result, the film bends away from the light source. This is similar to the reported free volume expansion mechanism of azobenzene materials.^{30–34} In contrast, the rapid cooling process freezes the molecular chain arrangement at a high temperature, maintaining the expanded state at room temperature. This restricts the free volume increase of RC-PI under blue light, forcing the film to adopt a free volume contraction mechanism. That is, the blue light irradiation promotes the isomerization of azobenzene, which gives polymer chains opportunity to move and pack densely. As a result, the reduced free volume causes contraction on the light-irradiated side, resulting in the film bending toward the light source. This free volume contraction mechanism under blue light has not been reported in room-temperature deformation to date. However, Barrett et al. found that azo-dipole pairing and aromatic stacking occur under blue light irradiation when azobenzene polymers are at high temperatures, which lead to film contraction. We hypothesize that the molecular arrangement of the film after the RC process is similar to that in the high-temperature state. As expected, RC-PI exhibits a similar change to azo-dipole pairing and aromatic stacking under blue light irradiation.³

To further validate the aforementioned statement, the free volume of polymer films was measured using PALS measurements. From PALS measurements, the radius of the free volume nanoholes can be calculated from eq 1, thus offering a precise method for the analysis of changes in the free volume from polymer systems. Table 1 provides the *o*-Ps lifetime (τ_3), free volume nanohole size, and fractional free volume of SC-PI and

Table 1. Free	Volume Parameters	Calculated b	y PALS
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Sample	τ_3 (ns)	R (Å)	$V_{f}(\text{\AA}^{3})$	f_v (%)
SC-PI before blue light irradiation	4.0	4.2	320.9	1.2
SC-PI after blue light irradiation	6.0	5.2	578.6	2.2
RC-PI before blue light irradiation	5.4	4.9	500.4	1.9
RC-PI after blue light irradiation	3.6	4.0	269.9	1.0

RC-PI before and after blue light exposure. The nanohole size distribution and free volume distribution of the films in different states are shown in Figure S5 and Figure 3. After blue light



Figure 3. Free volume nanohole size distribution for SC-PI and RC -PI films before and after blue light irradiation.

exposure (3 min, 80 mW/cm²), the fractional free volume of SC-PI increases, and the distribution widens, confirming the proposed mechanism of free volume expansion. Subsequently, the free volume of the film after the RC process is much larger than that after the SC process, demonstrating the influence of the different thermal treatment on the aggregated state of the material. And the fractional free volume of the film after RC treatment sharply decreases after blue light exposure, consistent with the proposed mechanism of free volume contraction under blue light.

Subsequently, taking advantage of thermal treatment not requiring material resynthesis, we can achieve reversible switching of photodeformation behavior by adjusting thermal treatment conditions. To further elucidate the role of thermal history relative to the photodeformation behavior, we also investigate the influence of heating temperature on the reversal behavior of the photodeformation direction. Starting at room temperature, the SC-PI film was heated to different temperatures and subjected to rapid cooling. The obtained films were irradiated with blue light (470 nm, 80 mW/cm²), and the deformation was recorded in Table 2, in which the irradiation of

 Table 2. Influence of Heating Temperature on Bending Direction

Heating temperature (°C)	RT	50	100	150	160	170	180
Bending direction	•		Bending away			Bending away/toward	Bending toward
					2		

the blue light is consistently from the right direction. We found the film remains bent away from the light source when the heating temperature is near the film's T_g ($< T_g + 20$ °C). When the temperature increases to above T_g ($> T_g + 20$ °C), the film exhibits swing between bending away and bending toward the light source, ultimately resulting in the film remaining in an intermediate state and staying stationary. Further increasing the temperature ($\geq T_g + 30$ °C) causes the film to undergo a directional change, bending toward the light source. These results prove that only when the heating temperature rises above T_g can the free volume of the film increase to a critical value, allowing for reversal of the deformation direction. Simultaneously, we also examined the influence of different cooling rates on the film's deformation behaviors (Table 3). It was found that

Table 3. Influence of Cooling Rates on Bending Direction



the film exhibited slight bending away behavior after it underwent a cooling rate of 10 $^{\circ}$ C/min. However, when the cooling rate was above 20 $^{\circ}$ C/min, the film bent toward the light source and exhibited a larger bending angle with the cooling rate increasing.

Overall, the photodeformation of s-DAC11AB-PI film under blue light is influenced by two mechanisms simultaneously, with the choice of mechanism depending on the initial free volume of the material. The deformation of SC-PI, with its inherently smaller free volume, is dominated by the mechanism of free volume expansion, while that of RC-PI, with a free volume exceeding the critical value, relies on the mechanism of free volume contraction. Determining the critical conditions for bending direction reversal lays the foundation for utilizing this phenomenon to achieve diverse functionalities in the future. The free volume within the material plays a critical role in deformation reversal. The side-chain azobenzene polyimide material reported in this study inherently possesses a relatively large free volume, allowing for its adjustment under thermal treatment conditions. Therefore, we inferred that such properties could be achieved as long as the free volume of the polymer is sufficiently large. However, main-chain azobenzene polyimides generally lack sufficient free volume and should not exhibit this characteristic. As far as we know, this deformation reversal phenomenon has not been reported in the polyimide with azobenzene in the main chain.

3.3. Actuators Based on Photodeformation of s-DAC11AB-PI Film under Blue Light. The essential requirement for preparing the actuator is a strong deformability. We found that a rapid cooling process not only offers the opportunities to reverse the deformation direction of a film but also enhances its deformability. To evaluate the photoresponsive ability of SC-PI and RC-PI, their ultraviolet-visible absorption spectra were recorded after 60 s of blue light exposure. As shown in Figure 4a and 4b, the RC-PI exhibits a more pronounced reduction in absorbance of the material at 365 nm compared to SC-PI after 60 s of blue light exposure (470 nm, 80 mW/cm^2). This is attributed to the larger free volume within RC-PI, which facilitates the isomerization reaction of azobenzene. As a result, under irradiation, the isomerization in RC-PI occurs more readily, enhancing both the speed and the magnitude of the photoinduced deformation of the film. Furthermore, we tested the photoinduced stress of SC-PI and RC-PI under blue light. At the moment of blue light exposure, the stress curve exhibited a sudden change with stress rapidly increasing. As the light exposure continued, the mechanical force of the film began to slowly increase, resulting in a photoinduced stress of approximately 1.3 MPa for SC-PI and 2.7 MPa for RC-



Figure 4. UV-vis absorption spectra of (a) SC-PI and (b) RC-PI before and after blue light irradiation for 60 s. (c) Photoinduced stress of two materials under blue light irradiation.



Figure 5. (a) The fabrication of an arch-shaped bilayer actuator. (b) Photographs of the "walker" moving and (c) schematic of the photoresponsive walking robot under blue light irradiation.



Figure 6. (a) Experimental setup and (b) schematic presentation of the cooling process detector fabricated from the s-DAC11AB-PI film.

PI. The large photoinduced stress of RC-PI enables the film to fabricate excellent light-driven actuators (Figure 4c).

Utilizing the strong deformability of RC-PI, we constructed a photoresponsive "walker" using a bilayer structure, which crawled forward on rough paper, as shown in Figure 5 and Movie S3. The bilayer structure can provide more adjustable motion behaviors for photodriven devices, such as rapid shape recovery rates, controllable motion directions, and self-propelled motion modes.^{36,37} Here, we endowed the RC-PI film with a "photoelastic" characteristic by bonding it with polyethylene (PE) through electrostatic interaction.²⁴ The film bent quickly toward light upon irradiation and then automatically returned to its initial state when the light was turned off.

The PE/RC-PI film was shaped to an arched structure through thermal shaping (Figure 5a). The front end of the actuator experiences greater friction than the rear end by controlling the contact area between the actuator and the rough paper. As depicted in Figure 5b and 5c, under blue light irradiation, the arched actuator stretches at both ends due to the photoinduced stress exceeding the friction at the ends. Upon removal of the blue light, the elastic recovery of the PE layer causes the lessfrictional rear end to retract, while the higher-friction front end remains stationary. This enables the actuator to crawl forward on the rough surface of the paper as a "walker" at approximately 0.2 mm/s. Based on the capability of the s-DAC11AB-PI film to exhibit opposite photodeformation direction according to different cooling rates, the potential application as a cooling process detector is illustrated in Figure 6 and Movie S4. The s-DAC11AB-PI film with a low-resistance conductive silver coating on both sides was used as a switch in the circuit system. When the film underwent a SC (<10 °C/min) process, the film with the conductive layer bent away from light as exposed to blue light, and it comes into contact with the left electrode, completing the circuit and causing the green light to illuminate. On the other hand, when the film underwent a RC (>20 °C/min) process, it bent toward the light source under blue light exposure, causing the red light to illuminate.

4. CONCLUSION

In summary, we present a method to easily enable the side-chain azobenzene polyimide to exhibit opposite photodeformation directions through thermal treatment. By applying rapid or slow cooling processes to the polyimide, different free volumes were introduced within the resulting polymer films. Under blue light irradiation, these differentiated free volumes led to distinct photodeformation mechanisms: for SC-PI, free volume expansion and for RC-PI, free volume contraction, resulting in opposite deformation behaviors. This variation in the free volume provides the polyimide with unique deformation characteristics, enabling a reversible switch in the bending direction. The principles elucidated here have the potential to advance the development of adaptive materials capable of complex, programmable responses to environmental stimuli and transform the design of smart devices and sensors that require precise bidirectional control.

ASSOCIATED CONTENT

Data Availability Statement

Data will be made available on request.

3 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.4c02399.

Experimental procedures, characterization, additional results (Figures S1–S5) PDF)

Movie S1: The deformation behavior of the s-DAC11AB-PI film; the film treated with SC exhibits bending away from the light source under blue light irradiation (MP4) Movie S2: The deformation behavior of the s-DAC11AB-PI film; the film treated with RC exhibits bending toward the light source under blue light irradiation (MP4)

Movie S3: The walker prepared from RC-PI crawls under blue light irradiation (MP4)

Movie S4: Utilizing the characteristic that films exhibit opposite deformation behaviors under different cooling rates, a circuit device was prepared to detect thermal treatment environments; after undergoing slow cooling environment, the green light turns on; after rapid cooling, the red light turns on (MP4)

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Author Contributions

Menghan Zhang: investigation, writing—original draft, formal analysis. Xuejie Sun: investigation, editing. Jia Wei: supervision, project administration, review and editing. Yanlei Yu: review and supervision.

Notes

The authors declare no competing financial interest.

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