

Supramolecular Photoresponsive Polyurethane with Movable Crosslinks Based on Photoisomerization of Azobenzene

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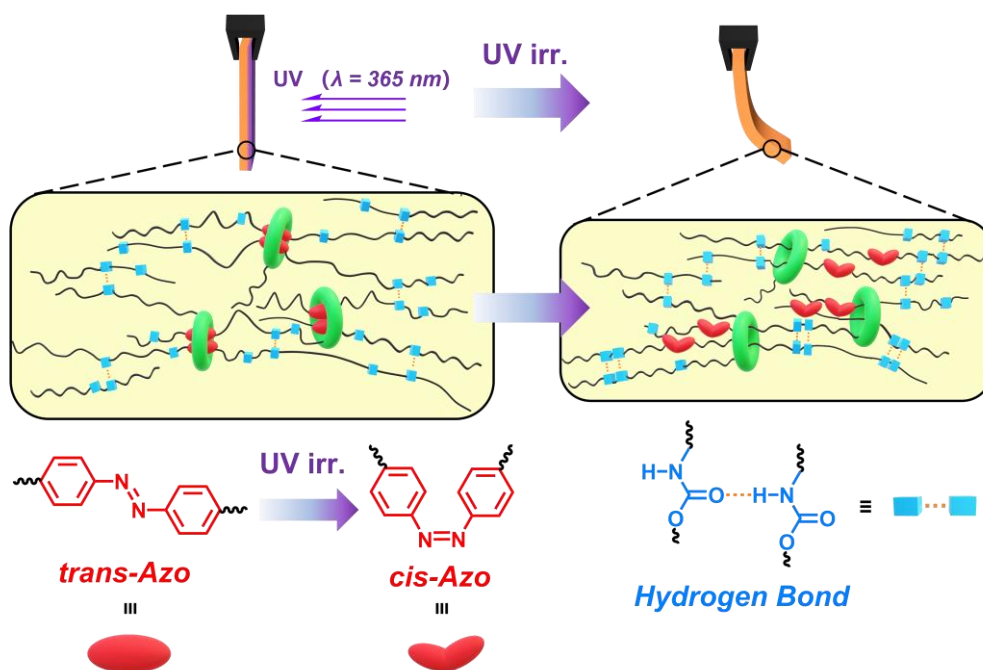
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Abstract

Light-driven actuators are widely used for smart devices such as soft robots. One of the main challenges for actuators is achieving rapid responsiveness, in addition to ensuring favorable mechanical properties. Herein, we focused on photoresponsive polyurethane (CD-Azo-PU) based on controlling the crystallization of the hard segments in polyurethane (PU) by complexation between azobenzene (Azo) and cyclodextrins (CDs). CD-Azo-PU incorporated polyurethane as the main chain and a 1:2 inclusion complex between Azo and γ CD as a movable crosslink point. Upon ultraviolet light (UV, $\lambda = 365$ nm) irradiation, the photoresponsiveness of CD-Azo-PU bent toward the light source (defined as positive), while that of the linear Azo polyurethane (Azo-LPU) without TAc γ CD-diOH as a movable crosslinker bent in the direction opposite the light source. The bending rates were determined to be 0.058°/s for CD-Azo-PU and 0.027°/s for Azo-LPU, indicating that the bending rate for CD-Azo-PU was faster than that for Azo-LPU. By incorporating movable crosslinks into CD-Azo-PU, we successfully achieved specific photoresponsive actuation with an enhanced rate.



TOC. Concept figure for the photoresponsive CD-Azo-PU.

Keywords: Polyurethane, Hydrogen bonding, UV irradiation, Photoresponsive, Movable crosslink, Supramolecular materials.

1. Introduction

Soft robots, capable of working in extreme and hazardous environments such as the deep sea¹, mining¹, and disaster scenarios², have gained significant scientific attention as a safer substitute for human intervention. One approach to developing soft robots is the utilization of stimuli-responsive materials³, which can change their shape, stiffness and other properties through internal structural changes in response to stimuli, such as moisture⁴⁻⁵, temperature⁶, electricity⁷⁻⁹, and light¹⁰⁻¹¹. Photostimuli are particularly intriguing due to the salient features of light: remote and contactless triggering with ease of spatial, temporal, directional, and intensity control¹². Photoinduced deformation at macroscopic scales has been observed for various polymer systems containing photochromic moieties, such as azobenzene (Azo) derivatives¹³⁻¹⁸. Azo-containing polymers are capable of deforming shapes due to changes in the conformation of polymeric chains based on photoinduced regulation of the orientational order¹⁹, free volume (physical aging)²⁰, crystallinity²¹⁻²³, and crosslinking points²³. Among these, the regulation of the crosslinking points particularly based on supramolecular chemistry could be a feasible way to control the bending behavior of photoresponsive materials because crosslinking points formed by noncovalent interactions, such as hydrogen bonding²⁵⁻³⁰, coordination bonding³¹, hydrophobic forces³²⁻³³, π - π interactions³⁴⁻³⁶ electrostatic effects³⁷, and host-guest interactions³⁹⁻⁴⁵, easily respond to stimuli due to their weak binding energies⁴⁶.

Cyclodextrin (CD) is a representative molecule used in host-guest chemistry. CD has a cavity to accommodate guest molecules, enabling the formation of reversible inclusion complexes with appropriate guest molecules. Our prior work has primarily focused on utilizing host-guest complexes, specifically CD and photoresponsive guest molecules (Azo or stilbene), to produce novel photoresponsive materials. This approach enables the creation of reversible and movable

crosslinks which regulates the responsiveness through control of the density and locations of crosslinking points, respectively. The expansion–contraction and selective assembly of hydrogels⁴⁷, sol–gel transitions⁴⁸ and photoresponsive actuation of xerogels⁴⁹⁻⁵¹ have been achieved. In a similar manner, actuation in nylon (polyamide) has also been achieved by incorporating a complex of γ CD and Azo as a movable crosslinker⁵². However, actuation in crystalline polymers exhibit low responsive deformation due to their high crystallinity⁵³. Here, we focused on polyurethane (PU) because the crystallinity or physical crosslinking density in PU can be readily modulated by controlling the composition of soft and hard segments. The versatile design of photoresponsive PU based on host-guest chemistry is used to enhance the photomechanical properties, thereby strengthening its utility in robust soft robotics applications.

Herein, we successfully prepared photoresponsive polymeric materials (CD-Azo-PU) with a 1:2 complex composed of γ -cyclodextrin (γ CD) and Azo as movable crosslinks in the PU backbone based on supramolecular chemistry. Introducing a small amount of γ CD as a movable crosslinker enabled an adjustable bending direction and increased bending rate by regulating the Azo distribution within the hard segment domains in the CD-Azo-PU material with enhanced flexibility. This method provided a highly tunable approach to design photoresponsive materials for soft robotics, which could facilitate the development of multifunctional photoresponsive materials.

2. Results and discussion

2.1 Preparation of photoresponsive PUs

Fig. 1a shows the chemical structures of photoresponsive PU materials with movable crosslinks; these were prepared by a two-step polymerization method (**Scheme S1-2**). We selected γ -cyclodextrin (γ CD) as a movable crosslinker because γ CD formed a 1:2 inclusion complex with *trans*-Azo⁵³⁻⁵⁵. Photoisomerization to *cis*-Azo causes the dissociation of the 1:2 complex between γ CD and *trans*-Azo; therefore, we controlled the complexation of γ CD and Azo by photostimuli. The PU materials were prepared by two steps method. Firstly, the excess hexamethylene diisocyanate (HDI) and dibutyltin-diacetate (DBTDA) were added to a dichloromethane (DCM) solution of TAc γ CD diol monomer (TAc γ CD-diOH)⁵⁵, Azo diamine (Azo-diAm)⁴⁹, and poly(tetrahydrofuran) (PTHF: $M_n = 1,000$). The mixing and polyaddition reaction produced isocyanate-terminated chains. Secondly, the isocyanate-terminated chains were elongated after the addition of propane-1,3-diol (PDO) as a diol chain extender; PDO was added at 25 °C and the solution was allowed to stand for 24 hours. The DCM polymer solution was poured into a mold and dried at room temperature overnight to obtain the photoresponsive PU films (CD-Azo-PU). Linear Azo PU (Azo-LPU; **Fig. 1b**) was also prepared by a similar two-step polymerization method (**Scheme S1-2**). The ¹H nuclear magnetic resonance (NMR) measurements of CD-Azo-PU and Azo-LPU showed that the mol% values of γ CD and Azo among all repeating units were approximately 2 and 4, respectively. (**Fig. S1-S2**)

In the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra, the isocyanate absorption peak at 2270 cm⁻¹ disappeared, and the absorption peaks at approximately 1683 cm⁻¹ and 1722 cm⁻¹, attributed to the carbonyl (C=O) groups, appeared after polymerization for all PU

materials. (**Fig. S3**). Comparable molecular weights of CD-Azo-PU ($M_n = 49,000$) and Azo-LPU ($M_n = 72,000$) were confirmed by gel permeation chromatography (GPC) (**Fig. S4 and Table S1**).

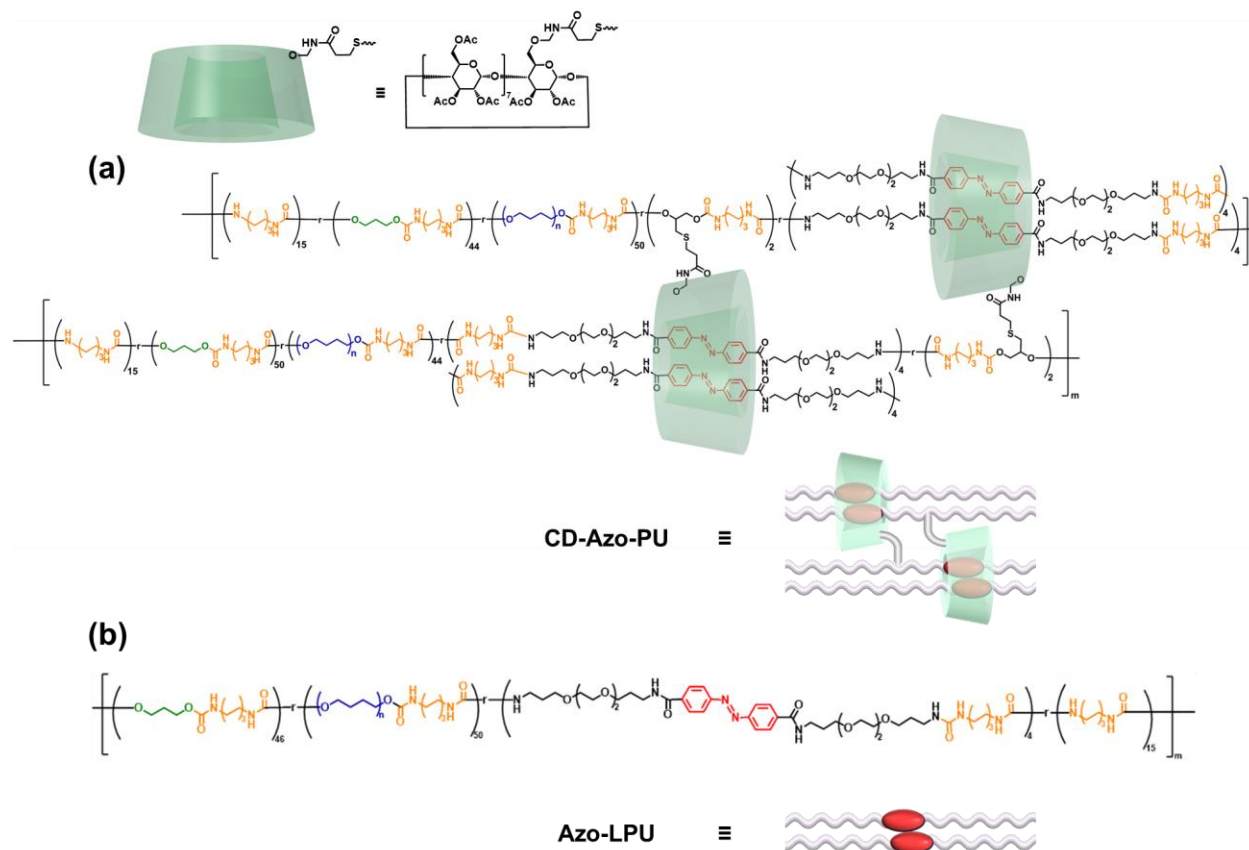


Figure 1. Chemical structures of the PU materials. (a) CD-Azo-PU and (b) Azo-LPU.

2.2 Photoresponsive properties of CD-Azo-PU and Azo-LPU

Fig. 2 demonstrates the photoresponsiveness of the CD-Azo-PU and Azo-LPU films ($20 \times 5 \times 0.7 \text{ mm}^3$) in relation to actuation upon ultraviolet (UV) light irradiation; the UV light was delivered by a Xenon lamp with a bandpass filter, λ of 365 nm, and radiation intensity of 0.26 mW/cm^2 at a distance of 10 cm. **Fig. 2a** depicts the actuation of CD-Azo-PU and Azo-LPU in response to photostimuli. Photoresponsive actuation of CD-Azo-PU and Azo-LPU was evaluated in terms of the flexion angle (θ). The positive direction of θ was designated as bending toward the light source. Upon UV light irradiation, CD-Azo-PU bent toward the light source within 5 min (**Fig. 2b**). Conversely, Azo-LPU bent away from the light source. **Fig. 2c** displays the flexion angles of CD-Azo-PU and Azo-LPU during a 5-minute period under UV irradiation, followed by a 5-minute period in the dark. CD-Azo-PU has a maximum flexion angle of 5.0° , whereas Azo-LPU has a maximum flexion angle of -2.3° . The initial bending rate (R_0) was calculated from the slope of the flexion degree versus irradiation time within the first 50 s (**Fig. 2d**). CD-Azo-PU displayed a higher initial bending rate R_0 of $0.058^\circ/\text{s}$ compared to the R_0 value of $0.027^\circ/\text{s}$ displayed by Azo-LPU. Moreover, CD-Azo-PU exhibited a larger maximum θ of 5.0° compared to that of 2.0° for our previous work⁵², the photoresponsive nylon with a 1:2 complex composed of γCD and Azo as movable crosslinks (Nylon- γCD -Azo) (**Fig. 2e**).

To investigate the relationship between the isomerization rate and bending rate, we used UV-visible (Vis) spectroscopy to monitor the photoisomerization of the Azo group in both CD-Azo-PU and Azo-LPU (**Fig. S5~S6**). Irradiation with UV light ($\lambda = 365 \text{ nm}$) decreased the intensity of the $\pi-\pi^*$ transition band of the Azo group within 80 min, and the $n-\pi^*$ transition band appeared, indicating that the Azo unit exhibited photoisomerization and photoinduced deformation. Interestingly, the pseudo-first-order plots of the photoisomerization of the Azo units indicated

comparable *trans*-to-*cis* isomerization rates of $k_1 = 9.0 \times 10^{-4} \text{ s}^{-1}$ (CD-Azo-PU) and $k_2 = 7.0 \times 10^{-4} \text{ s}^{-1}$ (Azo-LPU) (**Fig. S5~S6 and Table S2**). These findings indicated that CD-Azo-PU exhibited a faster bending response despite having a comparable isomerization rate compared to Azo-LPU. Accordingly, the fast-bending rate exhibited by CD-Azo-PU could be attributed to the structural properties of polymeric chains with γ CD as a movable crosslinker.

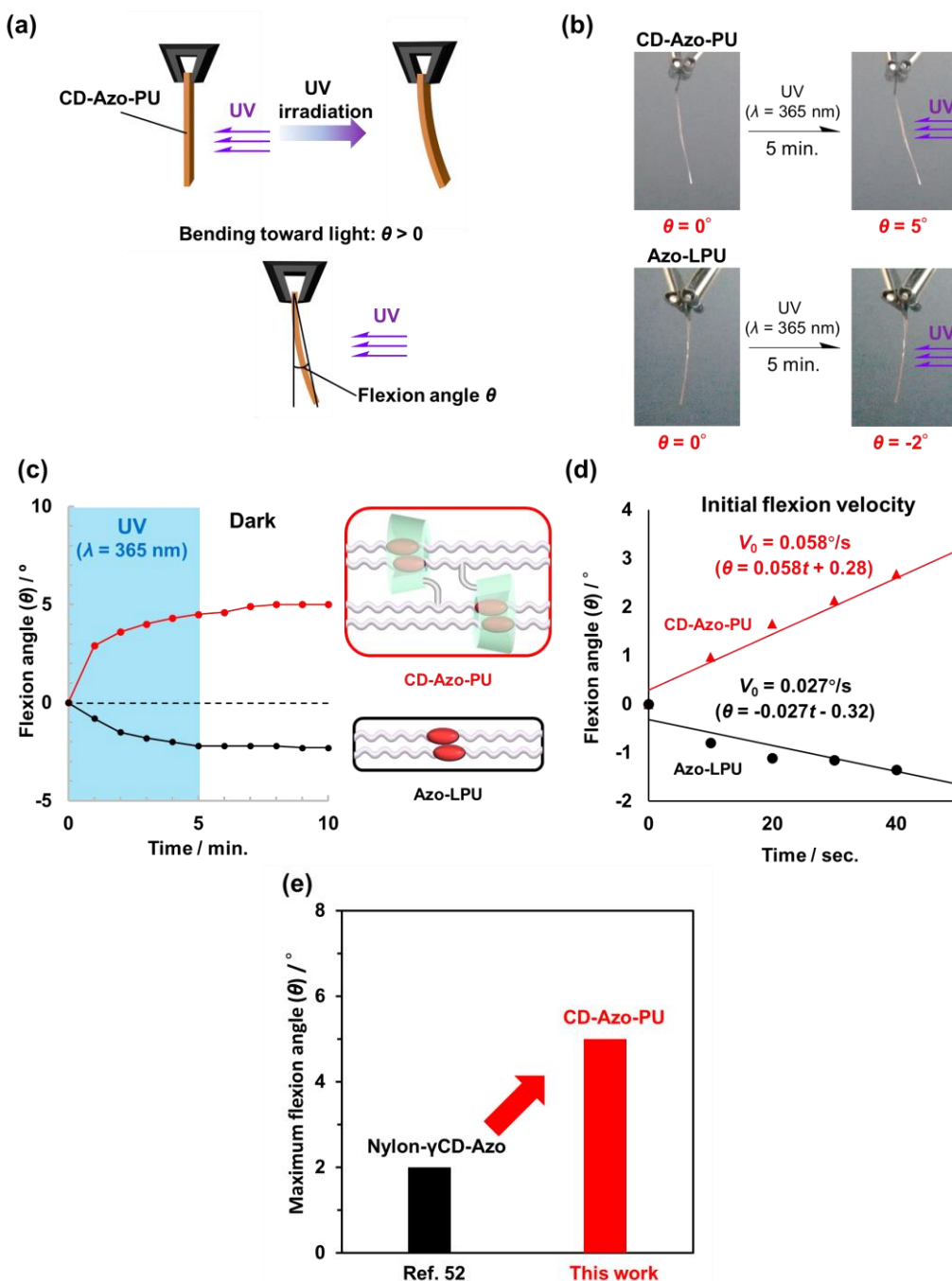


Figure 2. Photoresponsive properties of polyurethane materials containing Azo. **(a)** Schematic illustrations for evaluating the photoresponsiveness of the polyurethane materials. The photoresponsiveness was evaluated in terms of the flexion angle (θ). **(b)** Snapshots of the light irradiation tests of CD-Azo-PU ($20 \times 5 \times 0.7$ mm³) and Azo-LPU ($20 \times 5 \times 0.7$ mm³). **(c)** Flexion angles of CD-Azo-PU and Azo-LPU during UV light irradiation for 5 min. and subsequently placed in the dark for 10 min. **(d)** Bending rate of CD-Azo-PU and Azo-LPU during UV irradiation calculated based on their initial 50 s of bending behavior. **(e)** Maximum flexion angle of CD-Azo-PU compared to our previous work, Nylon- γ CD-Azo⁵².

2.3 Photoresponsive hydrogen bonding change in CD-Azo-PU and Azo-LPU observed by in situ ATR-FTIR testing

Hydrogen bonding in CD-Azo-PU and Azo-LPU was expected to change in response to photoisomerization of the Azo moiety. To further investigate the underlying mechanism responsible for the enhanced photoresponsiveness and the opposite bending behavior of CD-Azo-PU, ATR-FTIR spectroscopy was conducted to probe hydrogen bonds of the C=O groups in both CD-Azo-PU and Azo-LPU.

When C=O groups in PUs form hydrogen bonds, a potential shift in their infrared absorption peak could occur. This C=O stretching region contained three distinct contributions: free C=O groups at 1719 cm^{-1} , disordered hydrogen-bonded C=O groups at 1698 cm^{-1} , and ordered hydrogen-bonded C=O groups at 1682 cm^{-1} (**Fig. 3 (a, b, and c)**). The latter two groups would indicate the formation of hydrogen bonding within PUs in disordered or ordered hard segments⁵⁵⁻⁵⁸.

In PU, the shorter diol and Azo diamine chains combined with the isocyanate; in this case, PDO, HDI, Azo are considered the “hard segment,” which could contribute to the formation of the hydrogen bonds in PUs. The long diol chain segment, exemplified here by PTHF, is often referred to as the “soft segment”⁵⁸. Photoisomerization of the Azo moiety localized within hard segments could influence the photoresponsiveness of CD-Azo-PU and Azo-LPU.

Fig. 3d and 3e show the ATR-FTIR spectra of CD-Azo-PU and Azo-LPU in the 1600 to 1800 cm^{-1} range before and after a 5-minute UV light irradiation; the spectra were normalized to the C-H stretching bond peak near 2850 cm^{-1} . **Fig. 3f and 3g** display changes in peak intensities of free, disordered, and ordered hydrogen-bonded C=O groups before and after UV irradiation at room temperature for 5 min., where red and green bars signify increases and decreases in absorbance, respectively. In CD-Azo-PU, the peak intensities of the ordered hydrogen-bonded C=O groups

decreased by approximately 20%, while those of the disordered hydrogen-bonded and free C=O groups increased by approximately 10% after 5 min of UV irradiation. A similar but more notable trend was observed in Azo-LPU; the peak intensities of ordered hydrogen-bonded C=O groups decreased by nearly 40%, and the peak intensities of disordered hydrogen-bonded and free C=O groups increased by 30% after 5 min of UV exposure.

These results indicated that the Azo moiety existing within ordered hydrogen bonds in CD-Azo-PU and Azo-LPU could trigger dissociation of hydrogen bonding through photoisomerization from *trans*-Azo to *cis*-Azo due to alterations in the polarity and molecular symmetry of Azo molecules¹³⁻¹⁴. The change in the photoresponsive hydrogen bonding in CD-Azo-PU was less significant after a 5-min exposure to UV light irradiation compared to Azo-LPU. The observed outcome can be attributed to the *trans*-Azo moiety complexed with γ CD⁵⁵ in CD-Azo-PU. As our previous studies have shown that the PU with γ CD as a movable crosslinker tend to dissociate due to the bulky size of γ CD⁵⁵. Similarly, the *trans*-Azo moiety complexed with γ CD in CD-Azo-PU have a bulky size and thereby disturb the formation of hydrogen bonds involving the *trans*-Azo moiety. Upon exposure to UV light irradiation, *cis*-Azo in CD-Azo-PU was released from γ CD cavity, which enabled the formation of hydrogen bonding involving the *cis*-Azo moiety. Consequently, the extent of the photoinduced changes in hydrogen bonding in CD-Azo-PU was smaller than that observed in Azo-LPU.

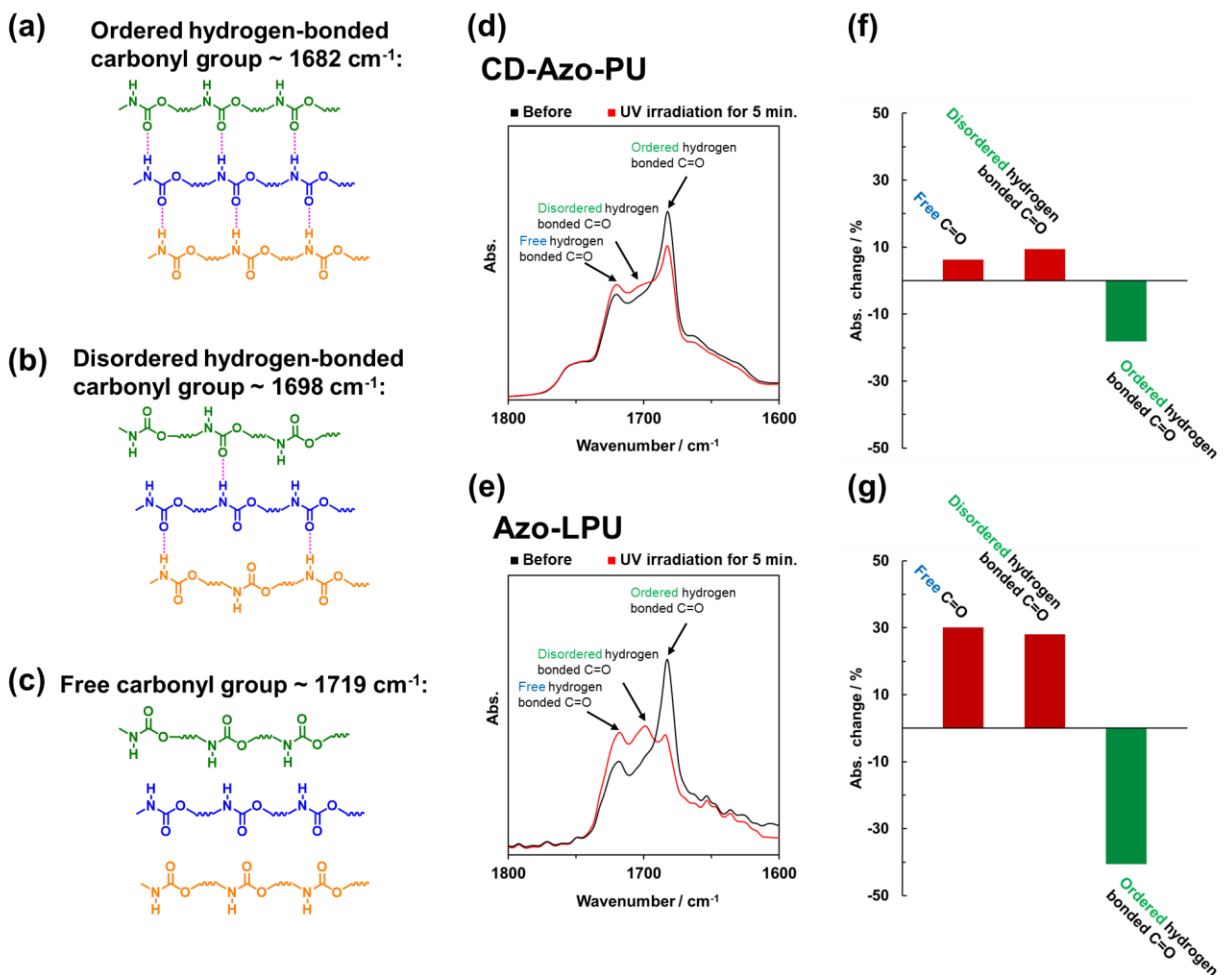


Figure 3. Proposed structure of the (a) ordered hydrogen-bonded region, (b) disordered hydrogen-bonded region and (c) free C=O region. Partial ATR-FTIR spectra of (d) CD-Azo-PU and (e) Azo-LPU showing hydrogen bonding behaviors before and after UV irradiation for 5 min. The absorbance change of the ordered hydrogen-bonded C=O, disordered hydrogen-bonded C=O and free C=O of (f) CD-Azo-PU and (g) Azo-LPU before and after UV irradiation for 5 min.

2.4 Photoresponsive crystallinity change in CD-Azo-PU and Azo-LPU observed by DSC measurements

Differential scanning calorimetry (DSC) was conducted to investigate changes in the crystallinity of CD-Azo-PU and Azo-LPU upon exposure to UV irradiation. Crystallization in PUs may occur when the hard segment possesses suitable symmetry and arranges itself into the crystalline domains⁵⁸. The enthalpy of melting (ΔH_m) was directly measured by DSC through the integration of the area under the endothermic peak in the thermogram. ΔH_m demonstrated distinct melting peaks of partially crystallized hard segments for the PU materials. This structural arrangement potentially regulates both the rate and direction of bending in CD-Azo-PU and Azo-LPU.

Fig. 4a shows the DSC thermogram from the first scan for CD-Azo-PU and Azo-LPU before and after 5 min of UV light irradiation. The glass transition temperature (T_g), melting temperature (T_m) and ΔH_m derived from the DSC thermograms are summarized in **Table 1**. After exposure to UV light irradiation for 5 min, the ΔH_m value for CD-Azo-LPU showed a substantial increase of 42.9%, rising from 9.8 J g⁻¹ to 14.0 J g⁻¹. In contrast, the ΔH_m for Azo-LPU experienced a decrease of 15.3%, dropping from 17.7 J g⁻¹ to 15.0 J g⁻¹ (**Fig. 4b**). The photoisomerization of Azo aggregated in hard segments in Azo-LPU from the *trans* to *cis* state promoted the dissociation of hydrogen bonding, further disturbing the formation of crystalline domains in Azo-LPU. This result was in good agreement with the ATR-FTIR results discussed above, which indicated that Azo-LPU bent away from the light source due to a decrease in crystallinity upon exposure to UV light irradiation, leading to an expansion of its exposed surface.

However, the crystallinity of CD-Azo-PU increased, and dissociation of hydrogen bond was inhibited upon UV irradiation (**Fig. 3d, 4a**). This result was attributed to the part of the *trans*-Azo

moiety complexed with γ CD in CD-Azo-PU that exited from the γ CD cavity through photoisomerization from *trans*-Azo to *cis*-Azo induced the increased crystallinity and minor hydrogen bond dissociation. Subsequently the *cis*-Azo rearranged within the well-organized hard segment in the crystalline domains in CD-Azo-PU, ultimately increasing the crystallinity. Additionally, the observed increase in the T_m in CD-Azo-PU, from 63.3 °C to 67.4 °C, supported the enhanced crystallinity following UV light irradiation. These results demonstrated that CD-Azo-PU bent toward the light source because of increased crystallinity following UV irradiation, resulting in a contraction of its exposed surface.

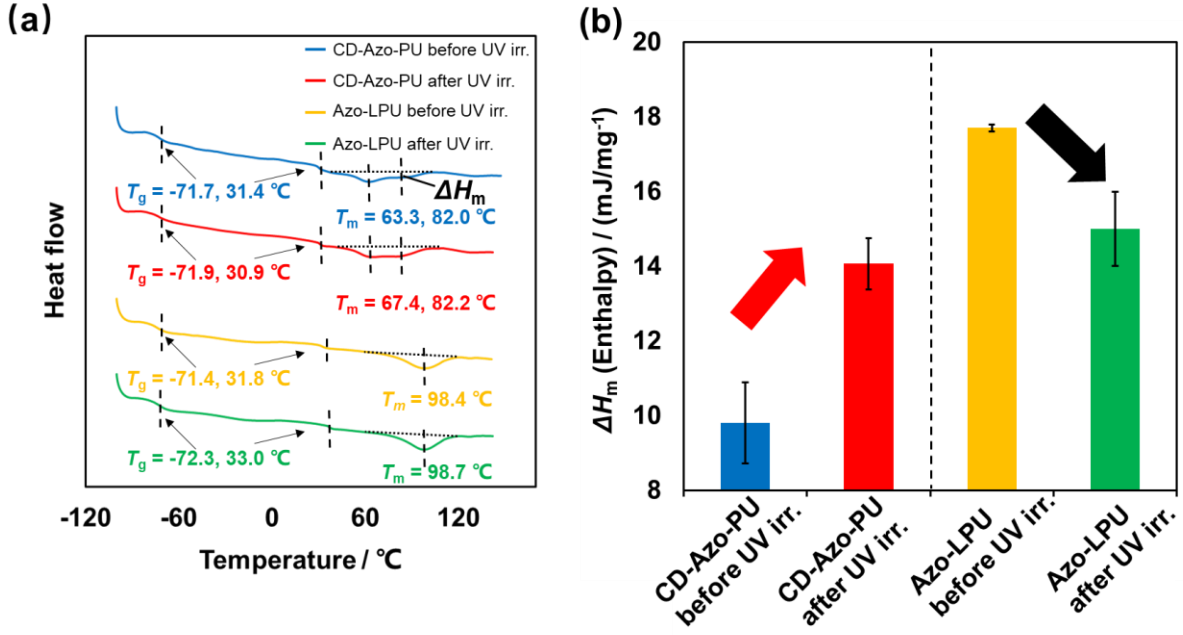


Figure 4. (a) DSC curves of the 1st scan for CD-Azo-PU and CD-Azo-PU before and after UV light irradiation for 5 min. The temperature range was from -100 °C to 150 °C, and the heating rate was 10 °C/min. (b) Change in the enthalpy of melting (ΔH_m) of CD-Azo-PU and Azo-LPU before and after UV light irradiation.

Table 1. T_g , T_m and ΔH_m of the 1st scan for the photoresponsive PU materials before and after UV light irradiation.

Sample	T_{g1}	T_{g2}	T_{m1}	T_{m2}	ΔH_m (Enthalpy)
	°C	°C	°C	°C	mJ mg ⁻¹
CD-Azo-PU	-71.7 ± 0.1	31.4 ± 1.5	63.3 ± 0.5	82.0 ± 1.1	9.8 ± 1.0
CD-Azo-PU-UV	-71.9 ± 0.5	30.9 ± 1.5	67.4 ± 2.2	82.2 ± 1.8	14.0 ± 0.7
Azo-LPU	-71.4 ± 0.3	31.8 ± 0.7	98.4 ± 0.2	-	17.7 ± 0.1
Azo-LPU-UV	-72.3 ± 0.3	33.0 ± 3.7	98.7 ± 0.7	-	15.0 ± 1.0

2.5 Correlation between the crystallinity and bending rate

We have discussed the bending direction. Herein, we compared the crystallinity of CD-Azo-PU and Azo-LPU before UV irradiation to investigate the correlation between crystallinity and bending rate.

Before UV irradiation, CD-Azo-PU had two T_m values at 63.3 °C and 82.0 °C, with a ΔH_m of 9.8 J g⁻¹, while Azo-LPU had a higher T_m at 98.4 °C and a higher ΔH_m of 17.7 J g⁻¹ (**Fig. 4a**). The lower T_m and ΔH_m of CD-Azo-PU could be attributed to the reduced degree of hard segments organized in the crystalline domains due to the inclusion of γ CD with Azo and the large size of TAc γ CD itself, which inhibited the formation of hydrogen bonds⁵⁵. These results indicated that the polymeric chains in CD-Azo-PU were able to move more freely than those in Azo-LPU. Consequently, CD-Azo-PU with low crystallinity showed faster bending kinetics than Azo-LPU with high crystallinity, even with comparable isomerization rates (**Fig. S5~S6**).

2.6 Proposed mechanism of photoresponsive behavior

The different bending behaviors of CD-Azo-PU and Azo-LPU after UV light irradiation can be clarified by the proposed internal structural changes, as shown in **Fig. 5**. The UV light, being unable to permeate the opposite side, is absorbed solely on the surface of the photoresponsive PUs⁴⁷. Consequently, CD-Azo-PU and Azo-LPU bend in response to UV light due to either the expansion or contraction of the irradiated surface, while the volume of the nonexposed areas remains constant. The resultant strain between the exposed and unexposed areas induces the bending behavior of CD-Azo-PU and Azo-LPU. Bending toward the incident light indicates surface contraction, while bending away indicates surface expansion.

Specifically, in CD-Azo-PU, UV light irradiation causes the Azo units to rearrange within well-packed hard segments in the crystalline domain in CD-Azo-PU after exiting from γ CD complexes, thereby enhancing the crystallinity of CD-Azo-PU (**Fig. 5a**). The crystallinity detected by DSC appears as the melting of the well-organized hard segment of PU. An increase in the well-organized hard segments causes denser physical crosslinks and contraction of irradiated surfaces. Furthermore, the end-to-end distance of the Azo molecules decreases following isomerization from *trans*- to *cis*-form, resulting in the surface contraction of CD-Azo-PU and subsequent bending toward the incident light.

In contrast, for Azo-LPU, after UV irradiation, the aggregation of the Azo units dissociates, leading to considerable dissociation of the ordered hydrogen-bonded C=O groups and a reduction in the crystallinity of Azo-LPU (**Fig. 5b**). Similarly, a decrease in the well-organized hard segments causes looser physical crosslinks and expansion of the irradiated surfaces. Thus, the irradiated surface of Azo-LPU expands and bends away from the incident light.

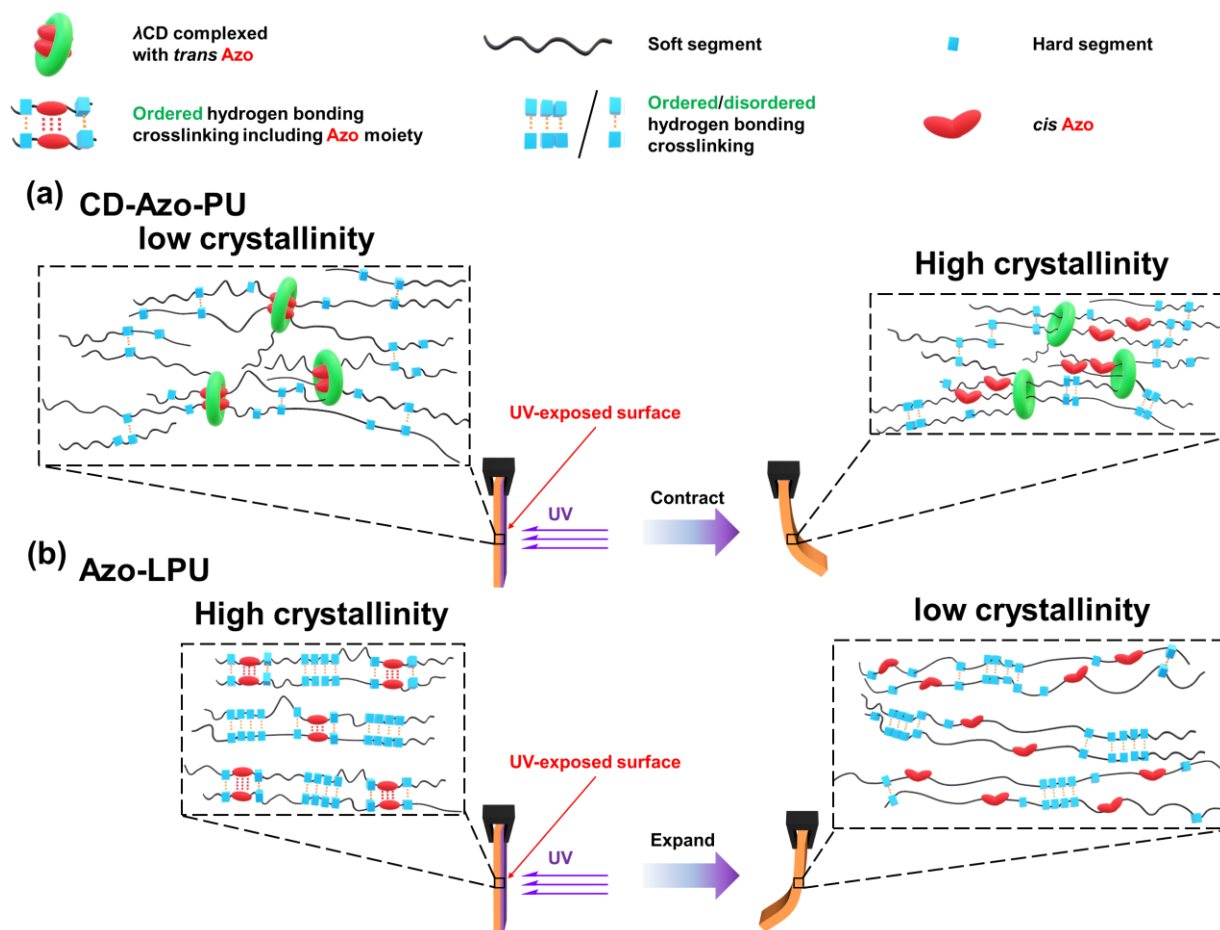


Figure 5. Proposed mechanism of the photoresponsive behavior of (a) CD-Azo-PU and (b) Azo-LPU. Upon UV irradiation, *trans*-Azo isomerized to *cis*-Azo, and the Azo moiety existing in the hard segment dissociated, leading to expansion of the film in the case of Azo-LPU. In contrast, γ CD formed a complex with the *trans*-Azo and slides along the polymeric chains, leading to contraction of the film in the case of CD-Azo-PU.

3. Conclusion

We investigated the photoinduced deformation of two Azo-containing PU materials, namely, CD-Azo-PU with Azo and γ CD serving as movable crosslinking points and the linear Azo-LPU. We demonstrated that introducing γ CD as a movable crosslink in CD-Azo-PU changed the bending direction and caused an increased bending rate in response to UV irradiation.

Upon exposure to UV light, the photoisomerization of Azo from the *trans* to *cis* state in Azo-LPU could trigger the dissociation of hydrogen bonding and disturb the formation of the crystalline domains, leading to a decrease in crystallinity. In contrast, in CD-Azo-PU, the dissociation of hydrogen bonds was less pronounced due to the complexation of the Azo moieties with γ CD. Instead, the part of Azo that was initially complexed with γ CD exited from the γ CD cavity upon UV irradiation, rearranged within the well-organized hard segments, and contributed to an increased crystallinity. The differential responses in the crystalline domains of CD-Azo-PU and Azo-LPU upon UV irradiation led to contrasting bending behavior. For CD-Azo-PU, the increased crystallinity caused the UV-exposed surface to contract, resulting in film bending toward the light source. Conversely, the decrease in crystallinity in Azo-LPU expanded the exposed surface, causing the film to bend away from light.

Our study provided insights into the different bending mechanisms of photoresponsive PU materials. The findings indicated that the bending direction and rate in response to UV irradiation could be controlled by manipulating the crystallinity of the PU materials through photoisomerization of the Azo moieties and their supramolecular interactions with γ CD in the system. This knowledge could be used to design and develop new photoresponsive materials with tailored photoresponsive properties for various applications, including light-driven actuators and soft robotics.

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Conflict of Interests

The authors declare no conflicts of interest.

Supporting Information

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

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