Light-Fueled Climbing of Monolithic Torsional Soft Robots via Molecular Engineering

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Azobenzene-functionalized liquid crystalline polymer networks (azo-LCNs) are promising candidates for light-fueled contactless manipulation of miniaturized soft robots through embedding photoactive molecular switches into alignment-programmable LCNs. In particular, the 3D helical geometry of azo-LCNs is reported to achieve rapid photomotility by introducing rolling resistance. However, the maximum height of the obstacle that soft robot can overcome is limited by the helix diameter and the stress–strain responsivity. Herein, the helical diameter per unit length and photogenerated stress through molecular engineering of photoactive molecular switches are maximized. The carbon number of aliphatic spacers in the photoactive molecular switches is varied from two to eight to systematically investigate the structure–property–performance relations by studying the molecular geometry, physical properties of polymers, and photomotility of polymers. Furthermore, a finite-element analysis simulation is presented to understand the rolling locomotion of helical torsional soft robots. Through molecular engineering, the helix diameter per unit length of 0.2 mg soft robots is maximized, demonstrating high Young’s modulus ($\approx$2 GPa) and photogenerated stress ($\geq$1 MPa), as well as large velocity per body length, compared with the previously reported soft robots. Finally, the molecularly engineered soft robots successfully climb stairs, which is a key task in robotic systems.

1. Introduction

The photomechanical deformation of polymers has been demonstrated by embedding an azobenzene moiety into a light-responsive molecular switch that can perform both reversible trans (9 Å)–cis (5.5 Å) photoisomerization and cis–trans back-isomerization. In polymeric form, these molecular-level contractile and tensile stresses can be transferred into various macroscopic strain responses, such as bending,[2–7] twisting,[8–15] and three-dimensional (3D) shape-morphing,[16–18] according to their programmed molecular alignment. Current research literatures report azobenzene-functionalized liquid crystalline polymer networks (azo-LCNs) and elastomers (azo-LCEs) have mostly achieved passive-type photomotility through beam patterning or localized beam scanning.[19,20] In addition, unresponsive frames or polyurethane foam wheels have been used to prepare 3D structures and reduce contact areas with substrates for rapid photomotility.[21,22] Recently, Wie et al. demonstrated an
active-type photomotility of monolithic 3D helical soft robots\textsuperscript{[23]} and Jeon et al. proposed photomechanical jumping of azo-LCNs film\textsuperscript{[24]} upon irradiation with unpolarized and unpatterned light, a contrast to the programming external stimuli sources. As compared with cylindrical geometry, helical geometry is efficient in achieving rapid photomotility through the introduction of rolling resistance and an increase in rotational inertia per unit mass\textsuperscript{[23,25]} Rolling resistance can be reduced with a large helix diameter and a decrease in the area of contact between the helix and the substrate. In terms of helix turn numbers, a single-turn helix is desirable for maximizing the helical diameter per unit length. However, the helix loses its rolling capability once the number of turns dips below unity.\textsuperscript{[26]} In the case of a single-turn helix, torsional soft robot the contacts ground with number of contact points modulate between 1 and 2, minimizing the contact area. The helix diameter is closely related to the height of the obstacle that a soft robot can overcome; therefore, a single-turn helix is an effective design for minimizing rolling resistance while maximizing the limit of the soft robots’ z-directional reach.

In this study, we control the cross-link density of azo-LCNs by varying the spacer length of a photoactive molecular switch, ranging from two to eight, to regulate the number of turns as well as the helical diameter. Helical diameter can be increased using a higher cross-link density that restricts molecular deformation via chemical covalent bonding in the networks. However, a higher cross-link density can also compromise photomotility because of increased stiffness. Thus, a rational molecular design for optimization of cross-link density is essential. The manipulation of cross-link density has thus far been conducted mostly through an incomplete curing or via a formulation study with monofunctional monomers.\textsuperscript{[8,27–29]} These methodologies, however, intrinsically generate increased defects from dangling chain ends, resulting in an inefficient energy transfer. To counter these shortcomings, we tune the cross-link density by varying the spacer length of the photoactive molecular switch\textsuperscript{[16,28]} without using monofunctional groups or incompletely cured systems, a strategy that achieves high mechanical property and effective transfer of photogenerated stress. In addition, we optimize the geometric factors, including the twisted nematic (TN) offset angle between the nematic director and principle axis of films as well as the aspect ratio of soft robots. To better understand the mechanism of torsional motility in soft robots, we perform a macroscopic finite-element method (FEM) simulation. Finally, we demonstrate stair climbing of a 3D helical torsional soft robot that is able to overcome its own weight, perform an effective stress transfer along with modulation of contact points between 1 and 2.

2. Results and Discussion

The photomotility of helical soft robot consists of two type motions: 1) rolling motion when soft robot has more than 2 points which contact with ground and 2) torsional motion when number of contact points modulates between 1 and 2 (Figure 1a). As shown in Figure 1a, rolling soft robot is hard to locomote on discontinuous terrain in terms of overcome stair and huddle obstacles. Inertia driven rolling motion has photogenerated torque ($T_{ph}$) by reduction of rolling resistance from photostain. However, this force is not suitable for the helical soft robot to climb stairs when combine with small helical diameter ($D_h$) compared with height of step ($H$). In contrast, torsional soft robot continuously generates potential energy ($E_p$) to reach the next stair from the head of soft robot in the sequence of locomotion. Moreover, high photogenerated stress and high coil height enable soft robot to climb the stair obstacles. To explore effects of cross-linking density on the photomechanical responsivity of azo-LCNs, the number of carbon atoms ($n$) are tailored ranging from two to eight in the aliphatic spacer of the azobenzene-derived molecular switch (Azo-n; Figure 1b) which is then confirmed by an NMR analysis (Scheme S1, and Figure S1, Supporting Information). Then, the synthesis of Azo-n LCNs begins by copolymerizing the reactive liquid crystalline monomer, RM257, with the molecularly engineered photoactive azobenzene molecular switch which results in the molten mixtures entering nematic phase ($n = 5,6,7,8$; Figure 1c, further details about phase behavior described in Supporting Information and Figure S2, S3, Supporting Information). The azobenzene molecular switch is aligned along the reactive mesogen liquid crystalline molecular matrix. Upon exposure to UV light, the photoisomerization of azobenzene not only reduces the orientational order by changing the geometry of the excluded volume of molecules but also causes molecular contraction. The photomechanical stress propagates to the networked polymer matrix through the cross-linking points by collective molecular contraction whereby each chain becomes covalently connected. In the stress propagation step, highly cross-linked networks in the Azo-5 LCNs enables the azobenzene molecular switch to efficiently transmit photogenerated stress with minimal stress dissipation caused by the pull of the aliphatic carbon spacer (Figure 1d). Dynamic mechanical analysis (DMA) is utilized to elucidate the correlation between cross-linking density and photogenerated stress. To determine the cross-linking density ($\nu_c$) of the Azo-n LCNs, thermomechanical properties including storage modulus ($E'$) and glass transition temperature ($T_g$) are measured with the DMA (Figure S4, Supporting Information). The storage modulus in the rubbery plateau region is assigned as $E_{high}$ to calculate $\nu_c$, based on Flory’s rubber elasticity theory (Equation (1))\textsuperscript{[30]}

$$\nu_c = \frac{E_{high}}{3RT_{high}}$$

where $E_{high}$ is the storage modulus at temperature in the rubbery plateau regime ($T_{high}$) typically at glass transition temperature $T_g + 50 ^\circ C$ (where $T_g$ of each Azo-5,6,7,8 LCNs is 98, 102, 96, and 94 ^\circ C, respectively), and $R$ is the ideal gas constant. As expected, the cross-link density systematically decreased as the number of spacers in the molecular switch increased (Figure 1e and Table 1).\textsuperscript{[27,31]} In the case of Azo-8 LCNs, the longest azobenzene spacer results in the smallest cross-link density (8.47 mol m$^{-3}$) among the Azo-n LCNs. Conversely, for the Azo-5 LCNs, the shortest spacer results in the largest cross-link density (10.25 mol m$^{-3}$). The photogenerated stress response of unidirectionally aligned Azo-n LCNs is calculated and measured with irradiation of the broad-spectrum UV light (Figure 1f). The UV irradiation on azo-LCNs induces contractile stress that is parallel to the nematic director, detectable via a blocked force experiment conducted with the DMA.\textsuperscript{[32]} The highest photogenerated stress is measured from Azo-5 LCNs, along with the highest cross-link...
density and degree of trans–cis photoisomerization, as evident from the highest transition of absorbance at 365 nm over time (Figure S5, Supporting Information). Although Azo-n LCNs have relatively similar modulus at room temperature, photogenerated stress is highly dependent on effective stress transfer through cross-link points. The cross-link density affects photogenerated stress in how effectively contractile stress is transferred following the isomerization of azobenzene. Thus, photogenerated stress ($\sigma_p$) can be expressed as a function of cross-linking density ($\nu_e$) and fraction of cis azobenzene ($\rho_{cis}$) (Equation (2))

$$\sigma_p = B_n \cdot \nu_e \cdot \rho_{cis}$$

$B_n$ indicates the individual constant of each Azo-n LCN. The fraction of cis azobenzene is measured from normalized
UV–vis absorbance at 365 nm light (Figure S5 and S6, Supporting Information). The calculated photogenerated stress agrees with the measured photogenerated stress (Figure 1f).

The photoinduced motility of a liquid crystalline soft robot is shown in Figure 2. To induce this photomotility, broadband light (320–500 nm) is implemented for reversible trans–cis photoisomerization of an azobenzene moiety. The 365 nm wavelength light for π–π* absorption peak in trans–cis photoisomerization in conjunction with the light of 410 and 442 nm wavelengths is simultaneously irradiated for rapid regeneration of the trans isomer.[23] Owing to the absorbance difference between

| Sample | Azo conc. [wt%] | Azo conc. [mol%] | Tg [°C] | T_high [K] | E' high [MPa] | ν_e [mol m⁻³] |
|--------|----------------|-----------------|--------|-----------|--------------|-------------|
| Azo-5  | 10             | 11.5            | 98     | 421       | 107.6        | 10.3        |
| Azo-6  | 10             | 11.3            | 102    | 425       | 97.3         | 9.2         |
| Azo-7  | 10             | 11.0            | 96     | 419       | 92.4         | 8.9         |
| Azo-8  | 10             | 11.0            | 94     | 417       | 91.2         | 8.5         |

Figure 2. The mechanism of continuously rolling soft robot. a) The front and back alignment of azo-5 LCN utilized in simulation. b–d) Comparison of the (b) simulation models and experimental rolling motion of a soft robot on 2 mm × 2 mm grid. In tilted view (c) and top-down view (d) with 2 mm scale bar [+45° (F) to −45° (B)]. e) The displacement (top) of head (†), center of mass (‡), and tail (§) of azo-5 LCN and stress distribution (middle: head, bottom: tail, filled symbol: front surface, hollow symbol: back surface).

Table 1. Components and properties of Azo-n LCNs.

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trans-azobenzene (365 nm) and cis-azobenzene (n→π*, 410, 442 nm), photoisomerization behaviors can be estimated by measuring the UV–vis absorbance at specific wavelengths. As shown in Figure S5 and S6, Supporting Information, Azo-5 LCNs exhibit the highest isomerization ratio, followed by Azo-6, Azo-8, and Azo-7. The absorbance at 365 nm occurs in a photographically stationary state caused by the use of broad-spectrum UV light for perpetual photomotility rather than the monochromatic 365 nm light which results in complete trans–cis photoisomerization. In our experiments, the photomotility in torsional soft robots originates from the competition between photogenerated torque and rolling resistance in conjunction with the gravitational force under broadband wavelength light (Figure 2b in Figure S5 and S6, Supporting Information). Under exposure to actinic light (0.4 W cm⁻², 320–500 nm broad spectrum), the photoinduced torsional deformation of TN azo-LCNs with an offset angle of the nematic director is triggered by the photomechanical strain from trans–cis isomerization parallel to the nematic director. Moreover, the strain gradient is amplified through sample thickness. The flat Azo-5 LCN film [1 mm (W) × 15 mm (L) × 14 μm (T)] incidentally deforms into a helical coil as a result of the strain gradient. Then, the asymmetric helical coil experiences photogenerated torque (τₚ) and resultant gravitational force when the coil head exceeds the helical pitch. When net generated torque exceeds rolling resistance, the soft robot rapidly turns halfway as the coil head (red symbol in Figure 2e–i) drops to the ground along the torque axis by the conjunctive pulls of photogenerated torque and gravitational force (Figure 2b-i, c, d-i to ii, red region in Figure 2e). After a half turn of the soft robot, continuous light irradiation on the opposite side (white region in Figure 2d) regenerates the coil by photogeneration of the torque along the opposite side (Figure 2b-ii, c, d-ii to iv, orange region in Figure 2e). As shown in Figure 2e-ii, iii, the photogenerated stress at the front and back surfaces in both the head and tail inverses after a half turn of the soft robot. Then the coil is regenerated in line with the axis of molecular alignment along the reversed surface as photogenerated stress increases (orange region in Figure 2e). This dropping of the coil head and its regeneration occurs repetitively, resulting in a perpetual rolling locomotion. However, in the rolling experiments, a rapid and complicated nonlinear behavior hinders an intuitive understanding of the rolling mechanism. To elucidate this mechanism, we develop a simulation method using finite element analysis and compare its results with the experimental results of azo-LCNs (Figure 2b,e, S7 and Video S2, Supporting Information) that were derived following algorithm shown in Figure S7, Supporting Information. Previous attempts in the literature to implement the torsion through polarized light of LCNs with twisted nematic alignment as simulation had been limited due to the complexity of the shadowing effect from the transformed polymer at a large bending angle.¹⁹ In this study, there were many considerations taken for the shadowing and inertia effects, cis–trans back-isomerization, and damping by viscoelasticity. We demonstrate that the proposed finite element model would work for similar results without complicated multiscale simulation.

As rolling resistance is proportional to normal force, helical soft robotic systems have reduced weight and normal force at the identical helix diameter, different from cylinders and even hollow cylinders. Thus, the radius of curvature (or helix diameter) is the governing parameter for efficient photomotility, as rolling resistance is inversely proportional to the radius of curvature. Therefore, a large helix diameter from the 3D helical azo-LCNs is desirable to minimize rolling resistance. At an identical film length, the helical diameter can be maximized with reduced helical pitch and minimize contact points with the substrates. The number of contact points is also related to additional friction originating from helix imperfection (i.e., roughness of the substrate and soft robots). When contact points modulate between 0 and 1, the soft robot can be expected to demonstrate perpetual jumping motion, rather than rolling motion. Therefore, the soft robots require a helical pitch of at least 1, generating contact point modulation between 1 and 2 for successful rolling locomotion. A simple approach to decrease the helical pitch would be to reduce the length (or aspect ratio) of the coil. However, a film with a smaller aspect ratio is more difficult to deform into a helical coil. When photogenerated strain is insufficient and cannot exceed the helical pitch of 1, the Azo-n LCNs become twisted by light irradiation; however, the rolling phenomenon disappears below the critical aspect ratio. Aside from aspect ratio, the shear direction of photogenerated strain is also dependent on the offset angle in the TN Azo-n LCNs. Therefore, we consider both aspect ratio and molecular alignment of Azo-n LCNs. As shown in Figure S8, Supporting Information, we determine the threshold aspect ratio to roll with 1 mm (W) × 14 μm (T) Azo-n LCNs for different TN offset angles (from 0° to 90° at 15° intervals) and spacer lengths (from 5 to 8) in the molecular switches. The threshold aspect ratio tends to reduce at lower TN offset angles due to a larger helix diameter at an identical aspect ratio. As the spacer length increases, a reduced cross-link density results in a lower threshold aspect ratio at an identical offset angle. Importantly, TN offset angles also affect the uniformity of photomotility. Because TN geometry has a nematic director difference of 90° between the top and bottom surfaces of the film, an offset angle of 15° at the top indicates −75° offset angle at the bottom, denoted as 15°/−75°. Upon exposure to actinic light, the film experiences the largest helical diameter at an angle of 15° with the primary axis of the film. When photogenerated strain grows sufficiently large enough to overcome rolling resistance, the film coils and rolls. This rolling motion reverses the sign of the alignment angle, and the initial bottom part now becomes the top surface with +75° offset angle. The film has the largest light absorption at 75° along the alignment axis, which causes actuation into a different shape. This shape reconfiguration of the coil occurs continuously, resulting in the repetition of bimodal deformation for photomotility. In the case of 30°/−60° TN, rolling induces switching of the offset angle into 60°/−30°, where the contraction along 60° is dominant in the film. As the helix diameter is larger at 30° offset angle, the velocity of the 30°/−60° TN (or 60°/−30° TN) soft robot also becomes bimodal (Figure 3a and Video S3, Supporting Information). Unlike the asymmetric TN, the rolling locomotion of the symmetric 45°/−45° TN has no modulation of the offset angles and the contraction axes. Thus, the 45°/−45° TN demonstrates unimodal actuation and rolling velocity, as evident from Figure 3b. As clearly compared in Figure 3a,b, the different Δ displacement patterns over time between the front and back sides originate from the offset angles and resultant light absorption as well as actuation. The changes
in velocity of soft robots with various offset angles are shown in Figure 3c; a lower offset angle results in a higher rolling velocity. In comparison with the larger offset angle, the lower offset angle of azobenzene moieties forms the coil with larger diameters that induces the longer displacement of coil owing to a higher position of coil head. At 75°, a velocity of 0 mm s⁻¹ is recorded because it ceases the rolling after a single turn from the 15°/−75° TN. While the instantaneous velocities of 75°/−15° TN and 60°/−30° TN are faster than that of 45°/−45° TN, the average velocity of 45°/−45° TN (2.61 mm s⁻¹) is faster than that of the 30°/−60° and 60°/−30° TNs, which yields a value of 2.37 mm s⁻¹.

**Figure 3.** Continuously rolling soft robot. Photoinduced rolling motion of Azo-5 LCNs in TN geometry aligned with various offset angles with 2 mm × 2 mm grid and relative displacement of Azo-5 LCNs with a) +30°/−60° and b) +45°/−45° with 2 mm scale bar. c) Velocity of Azo-n LCN soft robots (aspect ratio 15) with different TN23 offset angles. d) Glass transition temperature-dependent photomotility of Azo-n LCNs. Azo-5 (●), Azo-6 (▲), Azo-7(▼), Azo-8 (+) LCNs. Velocity was calculated by measured displacement of the soft robot in the top-down recorded video via frame-to-frame measurement and overall time taken to roll once. The average and standard deviation of velocity was calculated from mean velocity of each rolling sequence. e) The normalized velocity for BL per second against body mass for various robotic systems. Rigid robots (●), pneumatic soft robots (▲), ionic polymer-metal composites (▼), hygromorphic polymers (●), shape memory alloy composites (▲), hydrogels (●), living snakes (+), and earthworms (*) compared with this the proposed model (★).
In addition to offset angles, temperature governs the photo-motility of viscoelastic soft robots regardless of spacer length in the molecular switches due to thermal back isomerization of azobenzene, as shown in Figure 3d. The photoinduced velocity of all Azo-n LCNs gradually increases until temperature falls slightly below \( T_g \) (\( T_g - 15 ^\circ C \)). Then, a significant reduction in velocity is observed for all Azo-n LCNs above the \( T_g \) due to a rapid segmental relaxation of rubbery polymers in conjunction with \( cis\)-\( trans \) back-isomerization, resulting in low photogenerated stress. \( cis\)-\( trans \) back-isomerization of azobenzene is known to be highly temperature dependent.[21] Here, impact of temperature is quite significant because a glassy viscoelastic liquid crystalline polymer network experiences a substantial modulus reduction from 2 GPa to 100 MPa throughout the polymer (Figure S4, Supporting Information). The effects of viscoelastic thermomechanical properties in polymers on photomotility are shown in Figure S9 and Video S4, Supporting Information. Well below the polymer \( T_g \) (\( T_g - 30 ^\circ C \)), glassy polymers hardly form a helical coil because of the high modulus (Figure S9a, Supporting Information), limiting strain responsivity. At elevated temperatures (\( T_g - 15 ^\circ C \)), a modest modulus drops of the polymeric soft robot results in maintenance of high coil height (Figure S9b, Supporting Information). At a glance, one may expect further enhancement of strain responsivity at elevated temperatures above \( T_g \) due to the drastically reduced modulus. However, at a high temperature (Figure S9c, Supporting Information), a low-height coil and oscillation of the soft robot are observed due to insufficient elastic modulus in conjunction with accelerated viscous relaxation and \( cis\)-\( trans \) back-isomerization. Furthermore, the aforementioned reduced coil height contributes to decreased velocity. The temperature of the heated azo-LCNs is measured at dynamic state under light irradiation (Figure S10, Supporting Information). Compared with nonirradiated soft robots, the temperature increases by \( 20 ^\circ C \) for the dynamic and by \( 40 ^\circ C \) for the stationary soft robots.

Light intensity also affects the velocity of photomotility (Figure S11, Supporting Information). As the light intensity increases, the helix regeneration of Azo-n LCN soft robot speeds up which, in turn, increases rolling velocity because intensity of UV light and visible light increases rates of \( trans\)-\( cis \) and \( cis\)-\( trans \) isomerization in azobenzene moieties. However, overly high light intensity of 0.5 W cm\(^{-2}\) results in helix regeneration before the drop of helix head that induces changes in the rolling direction toward the opposite direction (Figure S11b, Supporting Information). Under light irradiation, the azobenzene chromophore translates the absorbed photon energy into molecular contraction (isomerization) and temperature increases of LCNs under the photothermal effect. The

**Figure 4.** Overcoming obstacle motions of soft robot. a) Rolling motion of helical soft robot. b) Head-to-tail climbing motion of a torsional soft robot. c) Head-to-head climbing motion of a torsional soft robot when stuck in a gap. d) Continuous head-to-head step-climbing motion. Light intensity: 0.4 W cm\(^{-2}\), \( T_g - 15 ^\circ C \), 2 mm scale bar, (a,b,c) 2 mm step, (d) 1 mm step.
characteristics of temperature elevation in Azo-n LCNs during dynamic state are related to UV–vis absorbance behaviors at 365 nm, indicating that a smaller temperature rise in Azo-5 means more absorbance at 365 nm: energy demand in trans–cis isomerization. To avoid photothermal effects, the temperature of the Azo-n soft robot is fixed at Tg-15 °C (Figure S11a, Supporting Information).

For comparison with other rigid and soft robots,[34–64] we report the velocity of the optimized Azo-5 LCN soft robot (aspect ratio of 15, 45°/45°) operating at Tg-15 °C for body length (BL) per second against its body mass (Figure 3e). In general, the velocity of robotic systems tends to decrease proportionally with smaller body mass in a double-logarithmic plot. In particular, the molecularly engineered Azo-5 LCNs become outliers in comparison with other soft robotic systems with a velocity of 0.15 BL s-1 or 2.4 mm s-1 with only 0.2 mg of body mass.

Importantly, high photogenerated stress and low body weight mass enable the Azo-5 LCNs to climb large obstacles. As shown in Figure 4, rolling soft robot cannot incline 2 mm height step (Figure 4a). However, the 15 μm-thick torsional soft robot successfully climbs a 2 mm-height step in two different modes and multistep upon irradiation with a 0.4 W cm-2 broadband UV light. The first climbing mode occurs when the helix head penetrates below the step. The stuck head acts as a lever while the accumulated photogenerated stress at the surface of the helix head lifts up the entire Azo-5 LCN body with tail above the step. At the same time, Azo-6, 7, 8 LCNs cannot overcome their obstacles because the relatively low photogenerated torque does not allow enough force for the lift (Video S5, Supporting Information). The stuck head part then slips from the gap, and the Azo-5 LCN moves forward (Figure 4b and Video S5, Supporting Information). Another mode for step climbing is the act of the helix head going over the step while the tail remains below the step (Figure 4c and Video S6, Supporting Information). Although the soft robot has a single point of contact with the step at the middle point of its body, helical momentum of the head enables the helix head to move ahead of the step while the tightly coiled Azo-6 LCN with higher content of molecular switch cannot climb the step because its small helical diameter does not allow for the lifting up of head over the step height (Video S5, Supporting Information). It follows that the helix head lands upward of step by gravitational force. Then, the repetitive rolling of the Azo-5 LCN with the head placed on the step outweighs the weight of the soft robot below the step and lifts it up toward the step (Video S6, Supporting Information). Furthermore, the Azo-5 LCN successfully climbs the stairs, accomplishing a series of 1 mm-height steps. Again, the Azo-5 LCN soft robots clearly demonstrate modulation of contact points between 1 and 2. Although the narrow width of the steps provides very limited contact area for action-and-reaction, and a large difference between the contact points, the soft robot continuously climbs the stairs by overcoming its own weight (Figure 4d and Video S7, Supporting Information).

3. Conclusions

In summary, we demonstrate the effects of molecular engineering on the photomotility of soft robots comprising glassy Azo-LCNs. We systematically vary the number of spacer carbons in the azobenzene molecular switch and investigate their structure–property–performance relations. The parameters studied include both molecular and macroscopic properties: photoisomerization of the molecular switch, offset angle of the TN molecular geometry, cross-link density, thermomechanical properties, film aspect ratio, and glass transition temperature. Notably, the photomechanical active molecular switch with a shorter spacer length (Azo-5) provides effective stress transfer through denser cross-links, achieving larger photogenerated stress, higher coil height, and faster photomotility. Moreover, temperature is found to be a governing parameter for velocity of photomotility in all azo-LCNs soft robots due to the glass transition-dependent viscoelasticity of the LCNs in conjunction with back-isomerization of the molecular switch. Finally, we achieve agile and consistent photomotility with high coil height for effective step climbing. The molecularly engineered soft robots can serve as a triggered model to overcome current challenges limiting untethered soft robotic systems, such as difficulties driving on a rough terrain as well as slow-paced and inconsistent motility.

4. Experimental Section

Synthesis of Molecularly Engineered Azobenzene: Phenol (>99.5%), 4-aminophenol (>98%), 2-bromopropanol (>95%), 3-bromopropanol (>93%), 4-bromobutanol (>80%), 5-bromopentanol (>90%), 6-bromohexanol (>95%), 7-bromohexanolate (>88%), and 8-bromoacetate (>90%) were purchased from TCI (Tokyo, Japan) and used as received.

1H and 13C NMR spectra were recorded on Bruker AVANCE III at 400 and 100 MHz, respectively, using CDCl3 as the solvent for all synthesized compounds. As a representative synthesis of Azo-n, the synthesis method of Azo-5 is briefly described. (E)-1,2-diazadienediybis(4,1-phenyleneoxy-5,1-pentanediy) bisacrylate (Azo-5) was synthesized in the same procedure in previous researches.[45, 46] Azo-5 was synthesized with synthesized 4,4’-[(E)-1,2-diazadienediy]diphenol and 5-bromopentyl acrylate. Detailed synthetic procedures for two building units are described in Supporting Information. To a stirred solution of 4,4’-[(E)-1,2-diazadienediy]diphenol (0.5 g, 2.33 mmol) in dimethylformamide (10 mL) were added 5-bromopentyl acrylate (1.1 g, 5.14 mmol) and K2CO3 (0.97 g, 7.10 mmol). The reaction mixture was stirred at 80 °C for 4 h and quenched with water. The resulting solid was then filtered and dried under vacuum. The product was purified by column chromatography using ethyl acetate/n-hexane (20:80 v/v) to give a yellow solid (0.55 g, yield = 48%).

1H NMR (CDCl3, 400 MHz): δ 7.9 (d, 4H), 7.1 (d, 4H), 6.5 (d, 2H), 6.2 (m, 2H), 5.9 (d, 2H), 4.3 (m, 4H), 4.1 (m, 4H), 1.9 (m, 4H), 1.8 (m, 4H), 1.6 (m, 4H). 13C NMR (CDCl3, 100 MHz): δ 166.28, 161.19, 146.75, 140.68, 130.59, 128.56, 124.47, 119.71, 64.38, 28.85, 28.41, 22.62.

Synthesis of Azobenzene LCNs: The modified Azo-n LCNs were synthesized by copolymerization with 88.4 wt% of 1,4-bis(4-(3-acryloyloxypropoxy) benzoyloxy)-2-methylbenzene (RM257) and 10 wt% of Azo-n. For equivalent chirality control, 0.1 wt% chiral dopant (R1011) was mixed. The polymerization was initiated by 1.5 wt% photoinitiator Irgacure 784 (1:784, Ciba). The mixture was heated to 130 °C for homogeneous mixing in an isotropic state and drawn by capillary action into Elvamid (Du Pont)-coated rubbed glass cells. The aligning layer on the glass cells had 90° alignment difference between the top and bottom, to form a TN geometry. The LCN film thickness was varied by inorganic spacers ranging from 9 to 14 µm. For photocuring, the mixture was cooled down to 75 °C at the rate of 10 °C min-1 for the nematic state and photopolymerized by 50 mW cm-2 of 512 nm light for 60 min. After photocuring, the films were removed from the glass substrates and cut with various film geometries and TN offset angles.

Phase Behavior Analysis: The melting (Tm) and nematic-to-isotropic transition temperature (TNI) of the modified azobenzene and liquid crystalline mixtures were determined by DSC (Jade DSC, Perkin Elmer)
and circular-POL (Nikon) equipped with a hot stage (FP82/HT, Mettler Toledo) as a temperature-control unit.

Relation between Structure and Optomechanical Properties: The thermo-mechanical properties of the TN LCN samples of dimensions 9 mm (L) × 3 mm (W) × 14 μm (T) were determined by dynamic mechanical analysis (TA Instrument Q800) at a frequency of 1 Hz and a heating rate of 3 °C min⁻¹ in air atmosphere. The Tg was taken from the maximum of the tan δ curve. The cross-link density was determined from the thermo-mechanical data using Flory’s rubber elasticity theory. Thermal contraction of azo-LCNs was measured under 0.1 N preload and heated at 3 °C min⁻¹. The photogenerated stress of azo-LCNs was measured upon 0.4 W cm⁻² exposure of the broad-spectrum UV–vis light (320–500 nm), creep experiment under 1 MPa stress, exposure until stress plateau.

The absorbance of Azo-n LCNs at 365 nm was measured by UV–vis spectra (Evolution 350, ThermoFisher) to reveal the cis concentration under the broad-spectrum light (0.4 W cm⁻²) exposure with time. The low concentration of azobenzene (2 mol%) with RM257 (97.6 mol%) and low film thickness (4 μm) were used to avoid the effect of intensity decay through the thickness direction. Photomotility Analysis: The modified azo-LCNs were cut from the harvested film in various geometries with a tuning aspect ratio of a stripe-shaped film from the control sample length with dimensions of 1 mm (W) × 14 μm (T) and 15° offset angle and had various offset angles of 0° to 90° in intervals of 15° with dimensions of 15 mm (L) × 1 mm (W) × 14 μm (T). The photomotility of the polymer film was initiated with 0.36 ± 0.03 W cm⁻² of the broad-spectrum UV–vis irradiation (320–500 nm). Light irradiation was generated using a Mercury bulb (OmniCure, S2000), and ultraviolet (365 nm) and visible light at 410 nm (purple) and 442 nm (blue). The polymer temperature was varied under the photothermal effect of irradiation and heating the plate under the paper substrate. The thermal effects were monitored using a forward-looking infrared (FLIR, E4) camera.

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

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Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
J.G.K. and J.J. performed experiments and data analysis; J.J.W. conceived the idea and designed the research; R.S. synthesized Azo-n monomers; J.G.L. performed the simulation of rolling motility of a light-fueled soft robot; M.C., J.H.Y., and J.J.W. directed the project; J.G.K., J.L., M.C., and J.J.W. wrote the manuscript and all authors provided feedback.

Data Availability Statement
Research data are not shared.

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