Unlocking Entropic Elasticity of Nematic Elastomers Through Light and Dynamic Adhesion

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Nematic liquid crystal elastomers (LCEs) generally show soft elasticity, masking entropic elasticity inherent in crosslinked networks. They macroscopically deform with little stress increase under straining because of the soft shear mode attained by nematic director rotations. Moreover, the nematic interaction in main-chain LCEs can arrest the ergodic response to cycling strain. It manifests hysteresis, slow relaxation, and increased viscosity, which critically affect their mechanical applications such as actuation and adhesion. Here, it is shown that entropic elasticity fully recovers after photo-isomerization of azobenzene units incorporated in a nematic LCE. With the light-induced bent cis-isomers at room temperature, the degree of soft elasticity, viscosity, and adhesion are tangibly lowered. Mechanical responses rationalize that cis isomers unlock the frozen configurational degree of freedom by reducing nematic order in the same manner observed upon temperature increase. The present results not only unveil how the nematic interaction suppresses entropic elasticity leading to the soft state, but also offer a guide to tuning viscoelasticity toward dynamic mechanical applications.

1. Introduction

Liquid crystal elastomers (LCEs)\textsuperscript{[5]} are weakly crosslinked polymer networks with molecular units often called “mesogens” that induce liquid crystal (LC) phases. In the case of nematic LCEs, the attractive interactions\textsuperscript{[4]} between mesogens tend to align their long molecular axes with each other without entering a crystal or glassy amorphous state. Because the network is crosslinked, the molecular units are immobile unlike a low molecular weight (M\textsubscript{n}) nematic LC. Instead, the nematic tensor order parameter couples to the strain field through the polymer network, leading to novel actuation and morphing applications.\textsuperscript{[1–4]}

Moreover, nematic LCEs\textsuperscript{[7]} exhibit unique mechanical properties, such as a higher viscoelasticity and a soft elasticity, by which the materials can deform under little increase in stress. The ability to reversibly switch them to a classic rubber elasticity, which is attained in an isotropic state by increasing the temperature (T), or light irradiation,\textsuperscript{[8–11]} can further provide an LCE with a dynamic nature in terms of mechanical damping,\textsuperscript{[12–14]} adhesion,\textsuperscript{[15,16]} and friction.\textsuperscript{[17]} Although their applicability as dynamic functional units has been well demonstrated in these systems, the changes to the underpinning mechanical properties, for example, stress–strain and viscoelastic responses associated with the phase transition, remain largely unexplored. Such a fundamental understanding will also help in material optimization for fine tuning of their functions. Thus, the present experimental study focuses on uncovering the correlation between the local nematic scalar order parameter Q and the basic mechanical properties by exploiting the non-glasy photo-responsive nematic LCE with azobenzene units\textsuperscript{[8–10,18]} in the main chain.

A polydomain nematic LCE was investigated as a simple system that has no macroscopic anisotropy as in an aligned monodomain system.\textsuperscript{[19]} Polydomain LCEs are obtained by crosslinking monomer components in their isotropic state, and are often called “isotropic-genesis” LCEs. If they are crosslinked under a nematic state with a long-range nematic order, they are called “nematic-genesis.”\textsuperscript{[20]} The nematic-genesis LCE can show Schlieren textures\textsuperscript{[2,21]} as in the low-M\textsubscript{n} nematic LC because they are simply frozen and memorized by crosslinking. By contrast, the isotropic-genesis polydomain LCE typically shows a mosaic of small randomly oriented birefringent nematic domains when the system enters the nematic phase. Although each nematic domain attempts to grow under the nematic mean field, the randomly frozen network topology, which operates as a random disorder,\textsuperscript{[22–24]} disturbs the domain coarsening. As a result, each nematic domain typically shows a characteristic length of ~1 μm with a unique relative orientational correlation,\textsuperscript{[25]} which displays a Maltese cross pattern under depolarized light scattering (DPLS).\textsuperscript{[7,26]}

To the naked eye, polydomain LCEs appear to be opaque under visible light because of the size of the scattering centers, that is, nematic domains, which in an isotropic phase become...
transparent and lose their birefringence. Although a similar opaque or turbid appearance is known for a low-$M_w$ nematic LC owing to the spatio-temporal fluctuation of nematic directors, note that the nematic LCE shows only a spatial fluctuation, that is, a polydomain texture, without a temporal change. The cross-links suppress the director and translational fluctuations. For an LCE in an isotropic phase at a higher $T$, thermal isotropic motion of the chain strands is allowed as in conventional rubber.[27] Therefore, the orientational degree of freedom of the molecular strands of LCEs in a nematic phase is greatly reduced compared to that in an isotropic phase. In other words, the nematic interaction masks the entropy related to the chain orientation.

The last point becomes more important when considering soft elasticity[1] upon mechanical stretching tests. Upon slow uniaxial stretching of the non-glassy polydomain LCE, the nematic alignment direction of each domain merely rotates[28–31] there is no change in the nematic order, and thus, of the internal energy $U$. Because the macroscopic shape of the elastic body changes by rotating the chain distribution at a constant shape of the network chains (through a coupled director–shear soft mode)[31] the applied strain is accommodated without reducing the chain entropy $S$, normally at the root of the rubber elastic response.[1] The overall change in the free energy density, $\Delta F = \Delta U - T \Delta S$, is zero. Because the stress is the strain derivative of $\Delta F$, the LCE can be soft. Note that $\Delta F$ may transiently increase at a finite strain rate owing to the rotational viscosity and other internal constraints[7] in the main-chain nematic LCE. It also appears as a slow stress relaxation.[32–34] These features, that is, soft elasticity and higher viscoelasticity, in a nematic phase differ remarkably from those of conventional rubbers with entropic elasticity and low viscoelasticity. The soft elastic response ends when the director rotation maximally aligns with the applied strain, after which $\Delta S$ starts decreasing and obeys the universal rubber-elastic energy scale, $\mu \approx k_B T \rho$, where $\mu$ is the modulus, $k_B$ is Boltzmann’s constant, and $\rho$ is proportional to the cross-link density.

As the phase changes when the temperature of a nematic LCE passes through $T_{NI}$, which is the nematic–isotropic transition temperature, the mechanical properties also change. Phenomenologically, the Landau-de-Gennes model[15] explains the phase transition through the $T$-dependent parameter $Q(T)$. Here, $Q(T)$ controls the phase; when $Q = 0$ or $\neq 0$, the system is in an isotropic or nematic phase. For practical applications, the spatiotemporal control of $Q$ by light irradiation instead of changing $T$ has been widely explored.[8–10,18,36] Utilizing photoresponsive molecular units such as the azobenzene moiety,[17] when conventional azobenzene units adsorb light, they undergo a trans–cis isomerization, whereupon they bend.[18,19] The cis state is energetically unfavorable and thermally relaxes back to a trans state in the absence of lock-in mechanisms.[69] Nevertheless, it is possible to investigate the cis-rich state within a certain period less than the lifetime after ultraviolet, UV, irradiation. The bent units, which are believed to act as impurities in the nematic mean field, leave the nematic distribution.[23] As a result, $Q$ can be reduced or controlled; thus, the LCE phase can be switched by light.

A number of previously reported azobenzene-LCE systems have shown a certain light-induced reduction of $Q$, which induces changes in shape.[8–10,41–46] However, no experimental systems have been developed that show the landscape regarding the stress–strain curves through a straining cycle including viscoelasticity, thereby clearly characterizing and differentiating the basic mechanical properties of the nematic and cis-isomer-induced isotropic phases. Only a few studies on glassy or smectic LCEs have reported their modulus changes upon/after light irradiation, by which the softening or hardening of materials was evaluated within the small strain regime.[16,47,48] Various actuation modes have been demonstrated for LCE with alignment controls, such as monodomain and hybrid patterns.[8–10,41–45,49,50] By contrast, non-glassy polydomain LCEs with azobenzene units have yet to be studied. Moreover, in application-oriented studies on azobenzene-based actuation and shape-morphing, photothermal[51] and photoisomerization effects have yet to be separately analyzed.

Herein, we study the pure effects of photo-isomerized molecular units on the mechanical properties of a main-chain non-glassy nematic LCE prepared through the thiol-ene reaction.[52,53] The polydomain LCE formed in a trans azobenzene state is used as a reference to investigate the strain–rate–dependent stress–strain (SS) curves before and after light irradiation. A clear reduction in the soft elasticity and a less viscous nature are observed in a cis-rich state. Owing to the relatively long lifetime of the cis state, the SS curves are collected at different cis-to-trans ratios under ambient $T$. It is demonstrated that the cis-concentration-dependent changes in the SS curves are qualitatively identical to those observed for a temperature-dependent change, showing that the entropic elasticity is unlocked in the cis state. Example applications based on the present photo-controlled mechanical properties associated with the phase change, the generation of photo-stress related to the actuator property, and the speed- and contact-duel-time-dependent dynamic adhesion are also shown.

2. Results and Discussion

2.1. Basic Thermal Properties of LCE

The present photoresponsive LCE is composed of monomers, as shown in Figure 1a. Two nematic LCEs, LC8-Az2 and LC9-Az1 (Figure 1b and Experimental Section), were used owing to their favorable photoresponses. The red curve in Figure 2a shows a heating DSC thermograph of LC8-Az2 in a trans state, which appears as a thermodynamically stable state upon the second heating of the initially UV-irradiated sample. The glass transition appears at $\approx -35 \degree C$ and $T_{NI} = 43 \degree C$, which are similar to those of the previously reported LCE analogue[7] without Azo. LC9-Az1 in a trans state also shows an almost identical DSC curve (Figure S1, Supporting Information, red curve). The polydomain texture with a characteristic length scale of $\approx 1 \mu m$ at room $T = 20 \degree C$ is confirmed from both the polarized optical microscopy (POM) image (Figure 2b, inset) and the Maltese cross pattern of the DPLS (Figure 2c, left), which corresponds to a POM image in the reciprocal space.[7,25,54] Based on these appearances and the diffuse halo shown in wide-angle X-ray scattering (WAXS) (Figure 2d; Figure S2, Supporting Information), the nematic phase at $20 \degree C$ is reconfirmed for both
Figure 1. Main-chain nematic LCE. a) Chemical formulae of components. b) Schematic of a nominal polymer unit for LC9-Az1 and LC8-Az2.

Figure 2. a) DSC curves upon the first and second heating of UV-irradiated LC8-Az2. Initially, LCE is in a cis-rich state, showing no endothermic $T_{NI}$ peak at 40 °C, and instead showing a broad exothermic peak at 80 °C during the thermal cis-to-trans isomerization. Defining the cis content at 100% before isomerization, the enthalpy change is estimated to be 72.1 kJ mol$^{-1}$. Upon the second heating, a $T_{NI}$ peak appears at 43 °C. b) A thin sample of LC8-Az2 (~7 µm) observed with POM (530 nm) at 20 °C. $Q$ versus $T$, where $Q \propto I_{POM}$ and $I_{POM}$ is the mean transmission intensity. (Inset) POM image of polydomain LCE. Bright parts indicate the nematic domains with directors ±45° from the directions of the polarizers. (bar: 2 µm). c) DPLS (632.8 nm) patterns of LC8-Azo2 at 20 °C and 60 °C. d) WAXS of LC8-Azo2 at 20 °C (Cu Kα radiation). (Insets) WAXS patterns with or without uniaxial strain indicated by the black arrow.
LC8-Az2 and LC9-Az1. At $T > T_{NI}$, the birefringent polydomain textures and Maltese cross patterns disappear (Figure 2c right; Figure S3, Supporting Information). The change in $Q$ estimated from the intensity of the POM image,[54] which is the degree of birefringence, shows a diffuse phase transition characteristic typical of main-chain nematic LCEs (Figure 2b).

2.2. Effect of Light Irradiation on Nematic Order $Q$

The light absorption spectrum of LC8-Az2 changes after ultraviolet (UV) light irradiation (365 nm, 50 mW cm$^{-2}$ for 5 min), where the $\pi-\pi^*$ transition band at $\approx 365$ nm decreases and gradually recovers the original band of the trans state (Figure 3a). The time constant of the relaxation, at which the cis ratio reduces 1/2.718, becomes $\approx 100$ min assuming first-order kinetics overcoming an activation energy barrier between isomers (Figure 3a, inset). Defining cis% $= 100$ at $t = 1$ min, the data show that $\approx 70\%$ of azobenzene remains in a cis state at $\approx 10$ min. POM images before and after UV irradiation of a specific region are shown in Figure 3b. The irradiated part initially appears dark at $t = 1$ min, suggesting an isotropic state without birefringence. The initial polydomain pattern gradually recovers over time.

From the temporal change in the POM intensity, the time evolution of $Q$ is obtained and plotted with that of cis% obtained from the absorption spectrum in Figure 3c. Regarding $Q$, the initial state mostly recovers after $\approx 200$ min of relaxation.
in the dark. In comparison with the corresponding cis%, the result suggests that \(50-\)cis% can completely obliterate the nematic order, where bent cis moieties operate as impurities in a nematic state. Because 100 cis% in LC8-Az2 roughly corresponds to the azobenzene concentration in the sample of \(\approx 2 \times 10^{-4}\) mol g\(^{-1}\) (the upper bound), the critical concentration, \(c_{cr} \approx 10^{-4}\) mol g\(^{-1}\), of cis azobenzenes is required to make the system isotropic without a thermal effect at room \(T\). Considering that perfect trans-to-cis photoconversion is not expected, this estimation may overestimate the value of \(c_{cr}\). Nevertheless, it is possible to discuss the result by comparing to that of LC9-Az1, in which the total azobenzene concentration is half that of LC8-Az2.

For LC9-Az1, the upper limit of the cis concentration is approximately equal to \(c_{cr}\) because of its low AZO composition. Thus, the actual cis concentration after cessation of UV irradiation should always be lower than \(c_{cr}\) owing to spontaneous back isomerization. This suggests that the isotropic phase can never be attained on LC9-Az1 purely through photo-isomerization (i.e., non-thermally). Indeed, the DSC heating curve after UV irradiation of LC9-Az1 (Figure S1, Supporting Information, blue) still shows an endothermic broad peak at approximately \(T_{NI}\), suggesting that the system is in a nematic phase. By contrast, in the DSC heating curve after UV irradiation of LC8-Az2 (Figure 2a, blue) no such peak exists, indicating that LC8-Az2 is in an isotropic phase with an adequate amount of bent cis azobenzenes higher than \(c_{cr}\). Thus, the following mechanical characterization is mainly conducted on LC8-Az2, which can reach the isotropic state, \(Q = 0\), isothermally by light.

It should also be noted that the trans-rich state easily recovers upon visible light (e.g., at a wavelength of 460 nm) irradiation or thermal annealing. The former is confirmed through the reappearance of the Maltese cross DPLS pattern after blue light irradiation (Figures 3d; Figure S3, Supporting Information). The latter is also traced on the DCS curves (Figure 2a) based on the broad exothermic peak at \(\approx 80 ^\circ\)C, which corresponds to the heat generated by cis-to-trans isomerization and disappears upon second heating.

### 2.3. Effect of Light Irradiation on Stress–Strain Curves

As we are interested in how the azobenzene state affects the soft elasticity and viscoelasticity, the SS curves are investigated at different strain rates, \(\dot{e}\), at room \(T\). This simple mechanical test is chosen rather than using a continuously oscillating strain, such as a dynamic mechanical apparatus, by which the mechanical properties within the large strain range are difficult to characterize. Figure 4a shows the SS curves in the trans state, showing typical soft elasticity with a stress plateau up to a strain

![Figure 4. Responses to mechanical strain at room T. Strain rate, \(\dot{e}\),-dependent SS curves on a) trans and b) cis-rich states. c) Stress relaxation curves of trans and UV-light-irradiated cis-rich states at \(\dot{e} = 0.4\). d) Stress at \(\dot{e} = 0.4\) versus \(e\). e) Hysteresis through a strain cycle, \(\dot{e} = 0 \rightarrow 1 \rightarrow 0\) versus \(\dot{e}\), corresponding to each closed area of each SS curve. f) Partially-UV-light-irradiated LCE strip after a strain cycle. DPLS pattern evolutions upon a strain cycle of g) trans and h) cis-rich states. Note that the residual (final) strain of the trans state is \(\approx 0.7\).](image-url)
Mechanical features of the main-chain nematic LCEs. These soft elastic and viscoelastic responses are typical stress relaxation of the trans state at a stress release. The black curve in Figure 4c shows the typical pattern (Figure 2d inset). The stress plateau value increases with cis% and trans-rich states, stress plots at cis% = 0.6. The sample is in the nematic phase without any strain-induced crystallization as confirmed through the WAXS pattern (Figure 2d inset). The stress plateau value increases with cis% reaching zero after ≈220 s. The heating rate was 10 °C min⁻¹ on average. d) Thickness effects on SS curves at 22 °C taken after UV irradiation on LC8-Az2 to induce a cis-rich state.

2.4. cis%- and T-Dependent Stress–Strain Curves

To elucidate how the SS curve shapes change with Q in the two cases, Q(cis%) (Figure 3c) and Q(T) (Figure 2b) are investigated at a specific strain rate ε = 0.0042 s⁻¹ (Figure 5a,b). Upon increasing the cis% at room T, the SS curves gradually lose the soft elastic range with decreasing the plateau stress (Figure 5a). Because the upper strain bound of the soft elastic range is related to the average chain anisotropy Q(T), which should become isotropic with Q = 0, both curves capture well how entropic elasticity recovers expelling the soft elasticity as Q decreases. Most interestingly, changes in the SS curve shapes are almost indistinguishable from those with a decreasing T (Figure 5b).

The difference in the final macroscopic shape between the trans and cis-rich states can be recognized by the shape after a strain cycle (Figure 4f). The cis-rich part of the sample strip, which was partially irradiated through UV, fully recovers its original width. The narrow trans part shows the residual strain along the longer axis. The microscopic nematic domains in the nematic phase, that is, the trans-azobenzene state, should gradually rotate their directors toward strain direction upon stretching, which is captured by the change in the DPLS patterns (Figure 4g). By contrast, the cis-rich state shows no change in the DPLS patterns (Figure 4h), suggesting that the system is in an isotropic phase throughout the strain cycle.
The slopes of SS curves of equilibrated data in Figure 4a,b;[55] The data extracted from Figure 4e.

Supporting Information. Although the changing trend of the curve shapes is similar to that of LC8-Az2, the entropic elasticity with the monotonic SS response is not attained at room T. This result corresponds well with the DSC results with the existence of the TNI peak even after UV irradiation (Figure S1, Supporting Information, blue) and originates from the lower effective cis concentration than ccr required to destroy the nematic order.

Figure 5c shows the uniaxial tensile strain on increasing T under a small load of 10 kPa at a different cis% after thermal annealing for different periods of time. The temperature T with the steepest slope suggests TNI under each condition. The estimated TNI is ≈42 °C for the trans state corresponding to that obtained by DSC (Figure 2a, red curve), decreases with an increase in cis%[55] and finally disappears from the present T range. This further suggests that the cis-rich state has no T range assigned to the nematic phase. This is strongly supported by the fact that no TNI peak appears on the DSC curve between the glass transition and the cis→trans isomerization peak at ≈80 °C (Figure 2a, blue curve).

The overall data shown in Figures 4 and 5, and Table 1 clearly demonstrate that the cis-rich state of LC8-Az2 after sufficient UV irradiation is in an isotropic phase with the entropic elasticity recovered in the same manner as observed upon an increase in T. Herein, we investigate the main-chain nematic LCEs, where the mesogens are incorporated into the main chains of the polymer network (Figure 1b). Moreover, azobenzene is also incorporated in the main chain. Thus, the bent cis azobenzenes can directly reduce the nematic order of the main chains by increasing the degree of their effective orientational fluctuation, and can unlock the entropic elasticity by exciting the thermal main-chain dynamics that occur upon an increase in T.

2.5. Generation of Photo-Stress and Thickness Limitation

According to the confirmed photo-induced change in the mechanical properties, the generation of photo-stress should also be possible as in the previous studies on LCE with azobenzene units.[8–10,18,36] The stress monitored at a constant strain ε of ≈0.4 (Figure 6a) shows switchable isothermal stress values between zero and ≈70 kPa by UV or blue light irradiation. Upon light irradiation at both wavelengths, that is, UV and blue light, the stress increases owing to the photothermal effect, which reduces Q depending on the light intensity (Figure 6b,c). If a monodomain LCE is prepared with LC8-Az2, light-induced reversible actuation is expected.

Because light irradiation on LCE inevitably causes a spatial distribution of the light absorbed azobenzene units along the thickness direction, there should be an upper limit of the thickness to attain an isotropic state with the entropic elasticity as a whole sample. SS curves of LC8-Az2 with different thicknesses after UV irradiation (365 nm, 50 mW cm−2 for 5 min) are shown in Figure 6d. The sample with a thickness of 0.6 mm never reaches the homogeneous cis state (even after 24 h UV irradiation), showing a trace of the soft response with a finite slope up to an ε of ≈0.6. The finite slope indicates that the system is roughly modeled using trans- and cis-rich layers combined in parallel according to the cis% distribution, where UV light cannot reach the trans-rich layer on the inner side. This result suggests that a sample with a thickness of less than 170 μm should be applied to reach the full entropic elasticity of the present LC8-Az2 through UV light irradiation. Although the condition should change depending on the mol% of AZO

| Table 1. Summary of azobenzene-state dependent mechanical properties. |
|-----------------|-----------------|-----------------|
|                | Soft elasticity | Tensile modulus | Hysteresis |
|                | (MPa)           | (MPa)           | (MPa)     |
| Trans          | Yes (up to 0.6) | 0.01            | 0.02      |
| Cis            | No              | 0.11            | 0.02      |

[a] The slopes of SS curves of equilibrated data in Figure 4a, b. [55] The data extracted from Figure 4e.

Figure 6. Effects of light irradiation under stress at a constant strain. a) After a sample of LC8-Az2 (5 × 10 × 0.1 mm) is strained at 0.0042 s−1 to ε = 0.4 at 20 °C, the stress relaxes over time. Relaxation curves of trans and UV-light-irradiated cis-rich states are shown. In addition, a curve under UV-light-irradiation is shown. (Inset) Long-term data. Note that the UV-light-irradiated curve relaxes to zero within ≈60 000 s because of the thermal cis-to-trans back isomerization in the dark. By contrast, under light-irradiation, no relaxation occurs (a photo-stationary state). b) Repeatable photo-induced stress generation with UV and blue lights. Upon UV or blue light irradiation, the surface T increases by 13 °C or 5 °C, respectively. Thus, upon switching-off the light, the stress first decreases rapidly owing to a decrease in T and becomes stable there. In this case, photo-isomerization is incomplete, leading to the reduced stress difference of ≈30 kPa < 70 kPa for the optimal value in (a). c) A change in photo-induced stress upon milder light-irradiation with an increase in T of the surface of less than 5 °C. With this lower light intensity, the stress changes slowly owing to the slower isomerization rate.
and other monomer amounts, this characterization method may also be useful for optimizing other actuation modes, for example, bending.[36,48]

2.6. Time-Dependent Dynamic Adhesion

In addition to the change in the SS curve shape that can generate stress, the viscoelasticity modulated by light can affect the adhesion property,[15,16,56] which is characterized based on, for example, a probe tack test (Figure 7a). The adhesion force, \( F_{ad} \), can be measured as the maximum force before detachment of a probe from the sample surface upon pulling the probe at a constant speed, \( v \), after a certain duel time of contact, \( t_{duel} \) (Figure 7b). Considering the difference in the stress relaxation property shown in Figure 4c, the effect of the duel time on the adhesion is first evaluated (Figure 7b, inset). In contrast to the slight \( t_{duel} \)-dependence for the cis-elastic state, the gradual increase in \( F_{ad} \) over a period of 1000 min is observed for the trans, that is, a nematic, state. In a nematic state, the stress gradually relaxes to zero leaving the residual strain owing to the coupled director-shear soft mode[41] and the arrested state.[7] During the duel time of contact, the true contact area may gradually increase owing to a stress relaxation, which can increase \( F_{ad} \). By contrast, the cis-elastic state relaxes after several tens of seconds retaining the entropic-elasticity-based stress (Figure 4c, black), which prevents a slow growth of the true contact area, and thus, results in little \( t_{duel} \)-dependence.

Figure 7c shows the \( v \)-dependent \( F_{ad} \), in which higher \( F_{ad} \) values for the trans state are recognized. The curves show a good correlation with those of the \( t_{duel} \)-dependent hysteresis of the SS curves (Figure 4e), which is also a qualitatively similar trend as those obtained previously.[15,16] The present results suggest that the kinetic properties of the adhesion are particularly controlled by cis% using the present LCE. By combining this tunability with previously reported systems of switchable adhesion,[57-62] further material optimization regarding their spatio-temporal tunability may be possible in the future.

3. Conclusion

This study presented a comprehensive characterization of the mechanical property changes of azobenzene-based nematic LCEs before and after light irradiation. It was demonstrated that our polydomain main-chain LCE with AZO exhibits a clear phase transition between the nematic and isotropic phases isothermally through photoisomerization of azobenzenes on the network strands. The photo-induced phase transition is associated with drastic mechanical property changes; the soft elasticity with viscoelastic property in the nematic phase disappears in the isotropic phase, which recovers the entropic elasticity with little hysteresis. The accompanying transformation of SS curves also has profound implications for how the nematic order masks entropic elasticity. As a consequence of the changes in the mechanical properties, the photo-induced stress generation was confirmed and the ability to modulate the time-dependent kinetic adhesion properties through light irradiation was exemplified. The present fundamental knowledge allows an establishment of the relationship between the phases and mechanical properties necessary to finely tune the photo-induced dynamic actuation, morphing, damping materials, friction, and adhesion.

4. Experimental Section

Materials and Preparation of LCE: For preparation of LCE, the authors slightly modified the methods reported previously,[7,15,52,63,64] in which single-step crosslinking reaction of a thiol-acrylate Michael addition was used. The diacrylate monomer, 1,4-bis[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (RM82), was purchased from Wilshire Technologies. The diacrylate spacer, tri(propylene glycol) diacrylate (TPGDA, isomer mixture), and two thiol monomers: 2,2’-(ethylenedioxy) diethanethiol (EDDET) and pentaerythritol tetakis (3-mercaptopropionate) (PETMP), were purchased from Sigma–Aldrich. The azobenzene monomer, 4,4’-Bis(9- (acryloyloxy)nonyloxy)azobenzene (AZO), was purchased from Synthon. Triethylyamine (TEA, Sigma–Aldrich) was used as the reaction catalyst. As the radical scavenger, butylated hydroxytoluene (BHT, from Sigma–Aldrich) was used to suppress the unwanted reaction between acrylates.
Toluene (Sigma–Aldrich) was used as the solvent. All chemicals were used in their as-received condition with no purification.

At the specific molar ratio of functional groups shown below, RM82, TPGDA, EDDE, AZO, and PETMP were weighed, BHT was added (0.5 wt%), and toluene was added (30 wt%).

\[(\text{RM82}:\text{TPGDA}:\text{EDDE}:\text{AZO}:\text{PETMP}) = (31.17:12.99:44.16:7.79:3.90)\]

for LC8-Az2, (35.06:12.93:44.16:9.03:3.90) for LC9-Az1 in the molar ratio. After the mixture was gently mixed at elevated T = 70 °C for 10 min, TEA was added (≈2% w/w) to start reaction between thiol and acrylate groups. The mixture was kept between two glass slides with the spacer at various thicknesses at 75 °C (isotropic phase) overnight. For thin sample for POM, a wedge cell was used with the spacer of 7.5 µm. Every sample was then placed in a vacuum oven at 75 °C at least 12 h to ensure the solvent evaporation prior to the characterization.

**Optical Microscopy:** The authors observed LC alignment using a transmitted polarizing optical microscope (POM) (BX-51P, Olympus) under crossed-nicols conditions. The light source was monochromatic (530 nm) light. Temperature, T, at the sample was controlled on a temperature-controlled setup.

**Depolarized Light Scattering (DPLS):** For DPLS measurement, a He–Ne laser (wavelength of 632.8 nm, 1 mW, Melles Griot 05-LHP-111) was used. The sample was placed between a set of polarizers under crossed-nicols condition, which is often called as the HV mode. The laser light diameter was ≈0.6 mm. The scattering pattern on a paper screen placed around the observation point. T was changed at the rate less than ≈0.01 °C s⁻¹. The local order parameter Q of the LCE was estimated using POM images of thin sample being based on the birefringence of the sample. In brief, \(Q = \sqrt{P_{\text{OM}}^\ast M_{\text{OM}}}\), where \(P_{\text{OM}}\) is the total transmittance intensity.

**Dynamic Scanning Calorimetry (DSC):** For differential scanning calorimetry (DSC, DSC6100 SII Nanotechnology), samples with ≈15 mg were loaded into standard aluminum DSC pans. The samples, which had been UV (365 nm)-irradiated for 10 min at 50 mW cm⁻², were cooled to −60 °C at −5 °C min⁻¹ and heated to 110 °C at 5 °C min⁻¹ to acquire the first heating data. Then, the sample was cooled to −60 °C and heated again to acquire the second heating data. The glass transition was identified as that with the baseline shift at lower T range. The broad isothermal peak ≈80 °C on the first heating was due to the thermal cis-to-trans isomerization event. The nematic–isotropic transition peak could be found at a local minimum of the endothermic peak on the second heating.

**Stress–Strain Response:** The stress–strain curves for LCE films on the tensile mode were obtained using a commercial instrument (EMX1000, IMADA). The sample width, and effective length were, 0.05–0.17 mm, 30 mm, respectively. T was controlled using a custom-made chamber with the multiple thermocouples around the sample. At least three samples from different sample batches were used and the results showed little difference qualitatively, for example, of the soft elastic range, and quantitatively, for example, of the stress values (within the error of ≈10%).

**Wide Angle X-Ray Scattering (WAXS):** The phase of the present LCE at RT was characterized using a Rigaku type 4037 diffractometer using graded d-space elliptical side-by-side multilayer optics, monochromated Cu Kα radiation (wavelength 0.1542 Å, 40 kV, 30 mA), and a flat camera with an imaging plate (R-Axis IV, Rigaku) with T control unit (FP82HT, Mettler). The exposure time was 5 min with a 150 mm sample-to-camera length.

**Light Irradiation:** UV (365 nm) and blue (460 nm) lights were irradiated using light-emitting diodes light sources (HLV-24UV365 and HLV2-22BL, CCS) with the light power monitored (Optical power meter 3664, Hioki).

**Adhesion Measurement:** For measurement of adhesion, the probe–tack test was conducted. A LCE film (≈15 × 15 × 0.1 mm³) was fixed to a glass slide. On the frontside, a flat surface of the spherical stainless-steel probe (with the radius of 5 mm) with a certain weight (w = 30 g) was first placed to exert preload 0.3 N and the state was held for a duel time, t₀. Then, the probe was pulled at a certain speed, v, monitoring the force during the detachment (EMX1000, IMADA). The maximum force at detachment was defined as adhesion forces F₀ and three data were averaged for each condition. Ambient T was 22 °C and relative humidity was ≈30%.

**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**

T.O. conceived the central idea and performed the main experiments. H.M and T.O. performed WAXS experiments. The results were analyzed by T.O., E.K., and Y.N. T.O. wrote the manuscript, and all authors discussed the results and the manuscript.

**Data Availability Statement**

Data available on request from the authors.

**Keywords**

adhesion, azobenzene, entropic elasticity, hysteresis, liquid crystal elastomers, soft elasticity

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