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In-situ Monitoring of Photocontrollable Wrinkle Erasure in Azobenzene-based Supramolecular Systems

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In this contribution, dynamic photoinduced wrinkle erasure enabled by photomechanical changes in supramolecular polymer-azo complexes was characterized via confocal microscopy. Different photoactive molecules, disperse yellow 7 (DY7) and 4,4'-dihydroxyazobenzene (DHAB), were compared to 4hydroxy-4'-dimethylaminoazobenzene (OH-azo-DMA). The characteristic erasure times of wrinkles were quickly assessed by using an image processing algorithm. The results confirm that

Introduction

Photo-responsive wrinkle patterns have attracted great interest because photoactive materials can enable dynamic control of surface topographies, leading to broad applications, for instance, in microfabrication, in dynamic templated self-assembly, as well as in smart surfaces with adjustable adhesion, friction, wettability, and optical properties.^[1-6] Furthermore, wrinkled patterns have been advantageous in designing stretchable electronic and advanced optical devices.^[7-10] These patterns can be easily generated by combining a rigid top layer with a soft substrate. When applying external forces, wrinkles form due to the mismatch between the mechanical properties of the two layers.^[11] Azobenzene and its derivatives have been employed to render these wrinkle patterns photo-responsive due to photoisomerization reaction, which can be simply triggered by illumination.^[1,12] Upon illumination, azobenzene and its derivatives can switch between geometrical trans and cis isomers, which results in the conversion of electromagnetic energy into mechanical energy.^[13] The wavelength of the transition depends strongly on the substitution of azobenzene, thus providing options for creating photo-responsive systems over a wide wavelength range.^[14,15] When incorporated into polymer systems, the photomechanical energy conversion has been predicted to modify the mechanical properties of the whole

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the photoinduced movement on the topmost layer can be successfully transferred to the substrate. Furthermore, the chosen supramolecular strategy allows decoupling the effect of molecular weight of the polymer and photochemistry of the chromophore, allowing quantitative comparison of wrinkling erasure efficiency of different materials and providing a facile way to optimize the system for specific applications.

material system,^[16] which has also been experimentally proven both through AFM-based^[17] and FTIR-based^[18] measurements.

To study the conversion of this molecular-level motion into a larger scale, a double-layered system generating wrinkle structures is commonly employed. This system consists of an uppermost layer containing azopolymer and an elastomeric poly(dimethylsiloxane) (PDMS) substrate.[11,19,20] Other than the double-layered structure, the multilayer structure was also reported to lead to controllable hierarchical surface micropatterns.^[21] Within the multilayer structure, the photoinert layers, such as the polystyrene and oxygen plasmainduced SiOx layer, were added between the photo-responsive layer and the elastomeric substrate. In this case, the wrinkle evolution of the multi-layered structure strongly depended on the intermediate photo-inert layers with wrinkle-reinforcing or stress relaxation effects. Furthermore, combining buckling instability and all-optical surface-patterning of the azopolymer was shown to lead to a controllable hierarchical patterned surface with tuneable adhesion and wetting properties,^[22] which opens up opportunities for tissue engineering and biological applications.

Supramolecular design can be simply explained as two molecules held together by non-covalent interactions, including ionic bonding, hydrogen bonding, and halogen bonding.^[23] This material design strategy can be employed to build photoresponsive systems^[24,25] ranging from nanoscale, such as lightdriven molecular motors,^[26,27] to macroscopic level-like photodynamic surfaces.^[28,29] In the literature, supramolecular design has been successfully utilized in the preparation of polymer-azo complexes and in further investigation of the influence of supramolecular interaction,^[30] molecular weight,^[31] and position of azobenzene derivative with respect to the polymer backbone.^[32] An advantage of the supramolecular design is that the ratio of complex components can be easily tuned, directly influencing the rate of pattern evolution at constant illumination intensity. Furthermore, by using a specialized FTIR technique, it has been shown that photomechanical energy can be transferred over supramolecular hydrogen and halogen

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bonds.^[33] Interesting photomechanical effects have also been observed in hydrogen-bonded liquid-crystalline elastomer systems.^[34,35] Considering the dynamic wrinkle erasure in double-layer systems, a simple azopolymer complex between poly(4-vinypyridine) (P4VP) and 4-hydroxy-4'-dimethylaminoazobenzene (OH-azo-DMA) was developed to realize light-induced wrinkle evolution.^[36] With this complex, the lightinduced changes in the surface morphology can be triggered when there is only one chromophore present in every 20 polymer repeat units, thus demonstrating a very efficient way of converting the sub-nanometre photoisomerization reaction into 10 µm scale changes of surface patterns. On the other hand, in another context, 4,4'-dihydroxyazobenzene (DHAB) Backbone and chitosan composite film fabricated through supramolecular interactions has shown the capacity of photomechanical actuation, which can efficiently lift weight over hundreds of cycles by alternatively illuminating the UV and visible light.^[37] In this work, a fluorescent dye was added to the PDMS substrate to deepen the understanding of dynamic photo-

induced wrinkle erasure in a previously reported double-layered model system consisting of P4VP(OH-azo-DMA) and PDMS substrate,^[36] thus enabling the characterization of the erasure of wrinkles in the PDMS substrate by confocal microscopy (Figure 1). With this new method, we were able to show the translation of the movement of the photoactive layer to the passive substrate below in-situ. The influence of various factors, including the amount of sample stretching, the chromophore concentration, and the illumination intensity on the erasure performance was investigated. In addition, by taking advantage of the simple supramolecular material fabrication strategy, other azobenzene derivatives, disperse yellow 7 (DY7) and DHAB, were employed to compare the pattern erasure efficiency with OH-azo-DMA. Furthermore, P4VP with different molecular weights was investigated to show the influence of the polymer backbone on photomechanical properties of supramolecular complexes. The characterization by confocal microscope proved that the movement caused by photoisomerization of azopolymer is successfully transferred from the upper layer to the substrate, which means the two layers were well attached, and the wrinkle evolution happened both horizontally and vertically. Additionally, the confocal microscope imaging was used to analyse the erasure performance quantitatively. Instead of using AFM to measure the wrinkling amplitude,^[38,39] we developed a MATLAB algorithm that correlated the image change in contrast with wrinkles depth, following the dynamics of wrinkles in time. This versatile method that accounts for the gradual photobleaching of fluorescent dye, quickly assesses characteristic erasure times of wrinkles with different complexes. Results indicate that both the chromophore concentration and component significantly influence the wrinkle erasure performance.

Results and Discussion

Influence of Chromophore Concentration and Polymer Backbone

Initially, the previously reported hydrogen-bonded P4VP(OHazo-DMA) complex, the chemical structure of which is shown in Figure 2a, was employed to establish the optimal parameters for further study. To study the fundamental properties, the P4VP-azo complexes were spin-coated on clean glass substrates with the same coating parameters as used when spin-coated on PDMS substrates. The UV-vis absorption, with increasing OHazo-DMA content from 1 mol% to 25 mol% samples, shows no changes in the shape of spectra although demonstrating the increase in absolute absorbance as a function of increasing chromophore content, which indicates that no azobenzeneazobenzene aggregation occurred in prepared samples.^[40] The thickness of P4VP(OH-azo-DMA) films with different azo fractions was measured by the stylus profilometry, as shown in Figure 2b. For practical reasons, the measurement was conducted with the samples coated on glass substrates, which allowed to estimate the azopolymer layer thickness on the PDMS. The thickness with increasing OH-azo-DMA content ranged from 175 nm to 325 nm, whereas the PDMS thickness, measured by a digital vernier caliper, was about 1.6 ± 0.1 mm, being four orders of magnitude thicker than the azopolymer films. Upon stretching, the azopolymer film is not as stretchable as the PDMS, thus, in addition to the formation of surface wrinkles, the film adopted the deformations by slight cracking.

To study the photo-erasure performance in this material system, the wrinkled surfaces were generated upon external stretching, as shown in Figure 1b, due to a mismatch of mechanical properties between the azopolymer layer and PDMS substrate.^[11] These patterned surfaces could be further erased by illumination of 488 nm light. Upon illumination, the



Figure 1. Schematic of azopolymer/PDMS double layer: a) preparation by spin-coating azopolymer on BODIPY-containing PDMS, b) wrinkle generation by external stretching (red arrows), and c) wrinkle erasure by 488 nm laser beam from confocal microscope while stretching.



Figure 2. a) Chemical structure of the P4VP(OH-azo-DMA) supramolecular complex and UV-vis absorption of P4VP(OH-azo-DMA) based on different azo mol fractions, b) thickness of P4VP(OH-azo-DMA) films based on different azo mol fractions.

mechanical energy caused by isomerization of azobenzene is transferred to the polymer chain via the hydrogen bonding,^[33] and the overall photoinduced plasticization of the uppermost film results in the erasure of wrinkles.[36] In this work, confocal microscopy with 488 nm laser was employed to both induce the photoisomerization in the polymer-azo layer and record the wrinkle erasure in the lowermost thick PDMS layer by introducing BODIPY dve into PDMS substrate. This method allows to directly capture the movement that occurred in substrate instead of polymer-azo film. The commonly employed method in literature to record wrinkle erasure has been the optical microscope,^[1,2,12,21,36] which generally captures the overall behaviour of the whole sample from the top view and does not elucidate the movement at the interface of the two materials in the double layer system. By adopting confocal microscopy, both fluorescent and transmitted channels can be simultaneously observed (shown in Figure S4), thus, the movement transfer between photoactive and passive layers can be directly followed.

The 2 cm×1 cm PDMS-azopolymer sample was placed in a custom-built stretcher, whereas the middle 1 cm×1 cm area was effectively stretched to the desired length. To compare the influence of chromophore concentration, all the samples with different OH-azo-DMA contents were stretched to 2 cm and illuminated under 10% intensity of the laser. All the videos were captured under the same magnification combining a 20x objective lens and 1x or 5x zoom, resulting in an image size of 425.10×425.10 μm² or 85.02×85.02 μm². As shown in Figure 3a, with different OH-azo-DMA contents, the periodicity of the wrinkles differs. When the OH-azo-DMA fraction exceeded 5 mol%, the periodicity of wrinkles decreased, and more wrinkles were generated on the surface. Furthermore, it can be observed that upon illumination, the higher the azo fraction is, the faster the wrinkles are erased. For instance, comparing both 1 mol% and 2.5 mol% OH-azo-DMA samples at 0 s and 50 s in Figure 3a, the change of the wrinkles can barely be observed, whereas the higher azo-containing samples had significant erasure of the wrinkles. This observation is constant with previous report^[36] that 5 mol% chromophore content (equalling the nominal occupation of every 20th polymer repeat unit) is a threshold above which the efficient erasure could be easily observed. Furthermore, when compared to photoinduced surface patterning – another process requiring mass transport of the polymers – the lower chromophore content to produce efficient surface patterns was found to be 1 mol%. In addition, during the erasure process, no new cracking was observed, which means the PDMS/azopolymer were well attached, and the movement was successfully transferred from the photoactive layer to the passive substrate.

The sample containing 5 mol% OH-azo-DMA with high molecular weight of P4VP (marked as P4VP_{60k}-DMA) was investigated to compare the performance between different molecular weights of polymer backbone. Compared with low molecular weight polymer backbone, P4VP_{60k}-DMA exhibited longer periodicity of wrinkles and less cracking upon external stretching (shown in Figure S5). A similar wrinkle structure with less cracks was observed by Vapaavuori et al.^[36] with a relatively high molecular weight of P4VP ($M_w = 50$ kDa). This could be attributed to the higher molecular weight polymer, which improved the mechanical properties of the thin film and resisted the cracking due to the mismatch of mechanical properties with PDMS. According to literature, the entanglement molecular weight of P4VP should be similar to polystyrene, which is around 30-40 kg/mol.^[41,42] Both high molecular weight P4VP applied in this work and earlier work reported in literature, was above the entanglement molecular weight, resulting in a stronger polymer film with less cracks upon stretching. However, in this work, we found that the higher molecular weight polymer significantly decreased the efficiency of wrinkle erasure. As shown in Figure S5, the wrinkle structures can still be observed on the surface of P4VP_{60k}-DMA sample after 120 s, whereas in the Figure 3a, the wrinkle of lower molecular weight with the same azo content sample was almost erased at 50 s.

A custom MATLAB code was developed to extract the characteristic erasure time constant from the captured video, further used in comparing the efficiency of photoinduced erasure between different samples. The wrinkling erasure can be visually perceived by the change of the grey colour over time. Periodic lighter and darker grey regions correspond to peaks and valleys of wrinkles. Film cracking also generates a variation of the grey colour, but this variation is not spatially





Figure 3. a) Images of the light-induced wrinkle erasure at different OH-azo-DMA content. As indicated in the figure, the horizontal structures are wrinkles, whereas the vertical structures are cracks generated upon stretching. All the images were captured at the same magnification under 10% laser intensity and 2 cm stretch; b) Erasure time constant analysed from captured videos of OH-azo-DMA samples with different azo contents under 10% laser intensity and 2 cm stretch; c) Erasure time constant analysed from captured videos of OH-azo-DMA samples with different azo contents under different laser intensity and 2 cm stretch.

regular nor changes over time. Upon the irradiation with 488 nm light, both grey regions shift gradually to smoother and uniform grey regions, corresponding to the decrease in the amplitude and subsequent disappearance of wrinkles. Therefore, we extracted a grey intensity profile over a region of wrinkles for each frame – the median value using adjacent pixels was also considered for additional precision of this line

profile. Since photobleaching of the fluorescent dye occurs during the measurements, a cubic smoothing spline interpolation (csaps Matlab's function) of the profile line, with smoothing parameter $p = 1 \times 10^{-7}$, was used as a reference, and then the resulting line was integrated by using the trapezoidal method. The decay of the grey variation over time is fitted to an exponential model (Figure S3). The erasure time constant versus

OH-azo-DMA content is shown in Figure 3b, which supports the direct observation from captured videos. When the OH-azo-DMA content was below 5 mol%, the erasure was observed to be much slower, for example, 1 mol% sample was too slow to be observed in the measured timescale, thus, the erasure time constant couldn't be calculated by MATLAB code.

The erasure was accelerated by increasing the chromophore content, which was observed to be saturated at 25 mol%. This type of increase in the photo-response at low chromophore content of the system has been previously observed in the context of photoinduced surface patterning.^[43] As observed in the literature,^[23] the relationship between the azo/polymer ratio and the photo-response is very material-dependent and not necessarily linear. Here, increasing azo fraction above 10 mol% does not significantly improve the efficiency of the photoinduced erasure. This can be rationalized through the relationship between azobenzene number density and observed change in mechanical properties (photoinduced plasticization) being sublinear and saturating at a certain chromophore content. This can be related to the decrease in the overall photoisomerization events in a polymer system having a high azobenzene number density.^[44] When comparing to other supramolecular polymer-azo systems, analogous saturation in the efficiency of the photoinduced motions, both in terms of photo-orientation and photoinduced-surface patterning has been observed.^[45,46]

With the help of a confocal microscope and the custombuilt stretcher, the effect of laser intensity and stretching state on the wrinkle erasure can be studied. The results of the time constant as a function of different laser intensity is presented in Figure 3c. It can be observed that the time constant decreased when laser intensity increased from 10% to 15%, however, it became saturated at 20%. This behaviour could be attributed to 15% intensity already having reached the upper limitation to promote photoisomerization and thus the erasure efficiency and even higher laser intensity leading to the azopolymer film degrading under illumination. However, the effect of the stretching state on the erasure time constant was not significant (shown in Figure S6), although the stretching state affected the wrinkle generation, wrinkles could barely be observed on the surface when the sample was stretched to shorter than 1.5 cm. This indicates that the buckling only appears when the strain between top and substrate layers reaches a specific threshold value, as predicted in the literature.^[47] However, the absolute amount of wrinkles did not influence the rate of erasure, which renders the comparison of the erasure performance between different chromophore contents possible. The erasure time constant of P4VP_{60k}-DMA shown in Table S1 is 108.3 s, whereas the erasure time constant of the lower molecular weight P4VP sample is 19.7 s under the same characterization parameters. This deceleration of erasure upon increasing molecular weight has been previously reported in the context of photoinduced erasure of surface-relief gratings at the scale of 100 nm.^[31] The authors noted that increased molecular weight was concomitated with increased T_{α} , which resulted in deceleration of the erasure. Especially, the high molecular weight of P4VP was much higher than the entanglement molecular weight, whereas the low molecular weight P4VP was far below it, which resulted in a significant difference in erasure time constant, thus suggesting a more pronounced photoinduced plasticization in a non-entangled small molecular weight system.

To summarize, the developed algorithm allows us to quantitatively compare the effect of different key parameters to the efficiency of the photoinduced wrinkle erasure. This efficiency can be enhanced by changing the initial fabrication parameters of the polymer-azo complexes, by both increasing the relative chromophore concentration as well as decreasing the molecular weight of the P4VP backbone. Out of the external control factors, the illumination laser intensity also has a direct impact on the wrinkle erasure. However, it is important to note that none of these three relationships appears linear – thus indicating the complex cascade of the processes involved in the wrinkle erasure.

Influence of the Chromophore Component

Based on the study of OH-azo-DMA content, 5 mol% azo content was selected for further comparison of the photomechanical performance between different chromophore components, DY7 and DHAB. As mentioned above, 5 mol% is the threshold at which the erasure is more efficient, enabling easy observation (see Figure 3a). Furthermore, taking into account a low molar concentration of the azobenzene, the plasticization effect of azobenzene on the polymer system is expected to be small, which facilitates the comparison. The chemical structures of the two molecules are shown in Figure 4a. Compared with OH-azo-DMA, the DHAB has the second hydroxy group instead of the dimethylamino as the substitution, whereas the DY7 exhibits two functional N=N bonding. In addition, the absorption peak observed from UV-vis spectroscopy, shown in Figure 4b, of three polymer-azo complexes indicates the comparability between the different azobenzene derivatives. DHAB exhibits a symmetric structure, which leads to a similar absorption peak as parent azobenzene. Whereas the OH-azo-



Figure 4. a) Chemical structure of DHAB (red) and DY7 (blue), and b) normalized UV-vis absorption of 5 mol % OH-azo-DMA, DHAB and DY7 complexed with P4VP.



DMA exhibits a dimethylamino group, which leads to a more polar structure, and thus, has a slightly red-shift at the maximum absorption peak. Furthermore, the dimethylamino group also provides an extra nitrogen atom, enhancing the $n\rightarrow\pi^*$ transition, then resulting in the absorption with a longer wavelength.^[30,48] For the DY7, due to the larger conjugated length, the delocalization of π -electrons increases and lowers the energy of the π - π^* transition, thus, exhibiting an absorption at a longer wavelength.^[49] Furthermore, the thickness of 5 mol% DY7 and DHAB films was 163 ± 16 nm and 126 ± 2 nm, respectively, which is similar to OH-azo-DMA film at 193 ± 18 nm.

To compare the impact of different azobenzene derivatives and thus different photoisomerization characteristics on the wrinkling erasure, the above-mentioned characterization was carried out on 5 mol% DY7 and DHAB samples, with the parameters of 2 cm stretching and 10% laser intensity, and the results were shown in Figure 5. Compared with OH-azo-DMA, there were fewer wrinkles generated on DY7 and DHAB surfaces. According to the quantitative analysis result, the



Figure 5. a) Images of the light-induced wrinkle erasure from 5 mol % DY7/ OH-azo-DMA/DHAB complexed with P4VP. The horizontal structures are wrinkles, whereas the vertical structures are cracks generated upon stretching. b) Erasure time constant analysed from captured videos of 5 mol % DY7/OH-azo-DMA/DHAB complexed with P4VP. All the images were captured at the same magnification under 10 % laser intensity and 2 cm stretch.

erasure rate constant of DY7 was similar to OH-azo-DMA, whereas the DHAB exhibited the highest erasure time constant. Combining with the molecular structure shown in Figure 4a, DY7 has one more functional N=N bond responding to the light illumination than OH-azo-DMA, which should lead to a larger photomechanical response^[50] and thus faster erasure. Previous findings of the comparison between monoazobenzene and bisazobenzene indicated that the bisazobenzene exhibited higher performance in photoinduced surface patterning.^[51,52] In this work, although the structures of monoazo (OH-azo-DMA) and bisazo (DY7) were not exactly the same, bisazo still presented a similar performance in the current material system. This is in accordance with the previous work showing that for these types of para-bisazobenzenes, the two azobenzene units couple easily and the yield of reaching cis-cis configuration through two consecutive photoisomerizations is very low.^[53] To realize the full potential of a photomechanical energy transfer, synthetic strategies to decouple the two azobenzene units in bisazobenzenes should be explored. Additionally, the low erasure rate of DHAB results from the double hydroxy groups and the symmetric structure of the chromophore. Two hydroxy groups can both be bonded with P4VP by hydrogen bonding,^[37,54] which makes the whole molecule fixed onto the polymer matrix, potentially resulting in the limitation of the molecular movement. Furthermore, the symmetric structure leads to less polarization of the DHAB molecule, which exhibits a slower response time of the photoisomerization.^[14,50] Combining the UV-Vis absorption result in Figure 4b, the 488 nm laser may not be able to maximize the photoisomerization of DHAB, thus, hindering the wrinkle erasure process. This allows us to conclude that efficient photoisomerization is needed to drive mechanical changes leading to photoinduced wrinkle erasure.

Conclusion

Overall, the previously reported double layer system containing P4VP(OH-azo-DMA) supramolecular complexes and PDMS substrate was employed to study the influence of various factors on the photo-controllable wrinkle erasure. By adding the fluorescent dye into the PDMS substrate, the movement occurring in the substrate can be directly recorded with the help of a confocal microscope. This indicates that the wrinkle erasure caused by photoisomerization of azobenzene was efficiently transferred to the substrates and the wrinkle evolution happened both horizontally and vertically. Furthermore, various chromophore content, ranging from 1 mol% to 25 mol%, the molecular weight of polymer backbone, and chromophore components, DHAB and DY7, were applied in supramolecular complexes. The quantitative analysis of the wrinkle erasure time constant reveals that the erasure efficiency is significantly dependent on the chromophore component, content and molecular weight of the polymer backbone. From 1 mol% to 25 mol%, higher chromophore content leads to a lower erasure time constant which means faster erasure of wrinkles. However, a higher molecular weight of polymer backbone decelerated wrinkle erasure. In addition, the azoben-



zene derivatives exhibit distinct behaviour of the wrinkle erasure due to their structural difference. To sum up, choosing a polar azobenzene molecule, instead of a symmetric one, could promote the efficiency of wrinkle erasure. In conclusion, the approach used in this study provides more comprehensive information about the dynamics of wrinkles erasure, which is important to further applications requiring accurate control.

Experimental Section

Sample Preparation

P4VP (M_w = 3800, Polymer Source[™], Inc.) and OH-azo-DMA (Tokyo Chemical Industries, Inc., Portland, OR) were first weighted to have the desired molar ratio from 1 to 25 mol% of OH-azo-DMA in P4VP. The mixtures were dissolved in dimethylformamide (DMF) (Sigma-Aldrich) to get solutions of 10 wt.% dry content. DY7 (Sigma Aldrich) and DHAB (Beam Co.) were prepared as the same protocol with P4VP(OH-azo-DMA) solution at 5 mol% azo content. High molecular weight P4VP (M_w = 60000, Sigma-Aldrich) was complexed with 5 mol% OH-azo-DMA and marked as P4VP_{60K}-DMA. All chemicals were used as received without further purification.

PDMS (Sylgard[™] 184) was mixed as 10:1 elastomer to hardener ratio, poured into Petri dishes, degassed for 30 min, and then cured at 60 °C for 2 h. Furthermore, a fluorescence dye, BODIPY (493/503), purchased from Sigma-Aldrich, was introduced in elastomer/hardener mixture as 0.1 wt.% before degassing. Before the spin-coating, PDMS substrates were plasma cleaned for 1 min at 50 W power in the HPT-100 Plasma Cleaner (Henniker Plasma). Then the solutions were spin-coated by a Laurell WS-650MZ-23NPPB, at 2000 rpm for 30 s on the PDMS. For measuring the UV-visible spectra and the thickness of the films, the solutions were deposited on the clean glass substrates with the same parameter.

Sample Characterization

The UV-vis spectra were performed by a UV-2600 spectrometer (Shimadzu) with the samples spin-coated on glass substrates. For measuring the thickness, a Dektak 6 M Stylus profilometer (Bruker) was used. The films were scratched, and the thickness was measured by recording the profile of the scratch. For capturing the videos of the wrinkling erasure, a custom-built stretcher was used. Azopolymer/PDMS samples were cut into $2 \text{ cm} \times 1 \text{ cm}$, whereas the middle $1 \text{ cm} \times 1 \text{ cm}$ area was effectively stretched. The upright Zeiss confocal microscope (LSM 710, Axio Examiner) with a $20 \times /0.8$ objective lens was employed to capture the video of the erasure movement for further quantitative analysis. MATLAB code was generated to extract the grey intensity profile over a region of wrinkle from each frame and fit it to an exponential model, which could be further calculated to give the erasure time constant.

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Conflict of Interests

There are no conflicts to declare.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Azo compounds · confocal microscope photocontrollable wrinkle erasure · supramolecular chemistry

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