Light switchable surface topographies
Liu, Ling

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Enhanced Deformation of Azobenzene-modified Liquid Crystal Polymers under Dual Wavelength Exposure: A Photophysical Model

Abstract

Azobenzene-embedded liquid crystal polymers can undergo mechanical deformation in response to ultra-violet (UV) light. The natural rod-like trans state azobenzene absorbs UV light and isomerizes to a bent-like cis state, which disturbs the order of the polymer network, leading to an anisotropic deformation. The current consensus is that the magnitude of the photo-induced deformation is related to the statistical building up of molecules in the cis state. However, in a recent experimental study \cite{175}, it was shown that a drastic (4-fold) increase of the photo-induced deformation can be generated by exposing the samples simultaneously to 365 nm (UV) and 455 nm (visible) light. To elucidate the physical mechanism that drives this increase, we developed a two-light attenuation model and an opto-mechanical constitutive relation that not only accounts for the statistical accumulation of cis azobenzenes, but also for the dynamic trans-cis-trans oscillatory isomerization process. Our experimentally-calibrated model predicts that the optimal single-wavelength exposure is 395 nm light, a pronounced shift towards the visible spectrum. In addition, we have identified a range of optimal combinations of two-wavelength lights that generate a favorable response for a given amount of injected energy. Our model provides mechanistic insight in the different (multi)wavelength exposures used in experiments and, at the same time, opens new avenues towards enhanced, multi-wavelength opto-mechanical behavior.

Keywords: Liquid crystal polymers, photophysics, azobenzene, isomerization, oscillation, light-activated system.

This chapter is based on the publication:
5.1 Introduction

Responsive polymers now serve as new building blocks to create soft actuators. Light-activated systems are especially advantageous for remote control as their application does not require built-in electrodes and heating devices as in electrically or thermally actuated materials. The probably most-studied light responsive systems are liquid crystal (LC) polymers copolymerized with azobenzene \[18, 67, 168, 205, 274\]. Azobenzene functions as a photoisomerizable molecule that is covalently embedded in the LC polymeric skeleton and absorbs ultra-violet (UV) light leading to a transition from a rod-like trans state into a bent-like cis state. This process affects the orientational order of the neighboring LC network, producing an opto-mechanical response, thus transforming optical energy into elastic mechanical work. The deformation is anisotropic, with a contraction along the director (i.e., the average orientation of the local LC molecules) and an expansion in the two perpendicular directions, accompanied by density changes. This actuation can be reversed by exposing the material to visible (VIS) light or heat, which accelerate the cis azobenzenes to fall back to the trans state. The current consensus in experimental \[20, 33, 158, 174, 205, 286\] and theoretical studies \[34, 284, 287, 288, 344\] is that the amplitude of the photo-induced deformation is related to the volume fraction of azobenzene molecules in the cis-state. The molecular mechanism that is at the base of this relation is the statistical building up of molecules in the cis-state and the ensuing disturbance of the local orientational order of the neighboring LC molecules. However, a recent experimental study \[175\] has revealed that this is only one side of the story. By exposing azobenzene-modified LC polymer (LC-Azo) samples to two LEDs emitting 365 nm UV light and 455 nm visible light, the largest mechanical response was found to occur under a combination of the two wavelengths, boosting the volume increase by a factor of 4 for intensities in the range of 100-300 mW/cm\(^2\).

To explain this phenomenon, we developed a two-wavelength light penetration model to predict the trans-to-cis and cis-to-trans conversions under mixed 365 nm and 455 nm exposure. A new constitutive relation is proposed that not only includes photo-induced deformations due to the statistical accumulation of cis isomers but also due to the dynamic trans-cis-trans isomerization cycles. By combining this relation with the double-wavelength attenuation model, it will be demonstrated that our numerical simulations are able to reproduce and elucidate the experimental results and to predict optimal wavelengths under one and two light exposures.

5.2 Photophysics model

A two-lights nonlinear penetration model is developed based on previous theoretical studies \[34, 406\]. In Ref. \[406\], a two-lights model was proposed in which one light only activates the trans-to-cis forward-reaction and the other only the cis-to-trans back-reaction, thus accounting for two reactions during isomerization. Here we extend our single-light illumination model \[34\] to double wavelength exposure by accounting for the trans-to-cis forward reaction and the cis-to-trans back-reaction for both lights and the thermally-activated spontaneous back-reaction, thus accounting for five reactions in total. We consider a LC-Azo coating with thickness \(w\), subject to two light sources with wavelengths of 365 nm and 455 nm and intensities \(I_{0,1}\) and \(I_{0,2}\), respectively. We
5.2: Photophysics model

define a z-axis pointing upwards, with the top of the coating at \( z = w \) and the bottom at \( z = 0 \). The incident lights are propagating towards the negative z-direction. \( I_1(z,t) \) and \( I_2(z,t) = I_1(z,t)/I_{0,1} \) denote the local light intensity and reduced light intensity inside the medium for the 365 nm light and \( I_2(z,t) \) and \( I_2(z,t) = I_2(z,t)/I_{0,2} \) for the 455 nm light. The conversion rates between the two isomers consist of five parts: the two photo-induced trans-to-cis forward-reactions due to the 365 nm and 455 nm lights, the two photo-induced cis-to-trans back-reactions by the two lights and the thermal spontaneous back-reaction with a characteristic time of \( \tau \). The conversion rate of the azobenzene isomers and the attenuation of the light intensities can be written as

\[
\frac{\partial n_t}{\partial t} = -\eta_1 \Gamma_{t1} \zeta I_1(z,t) n_t(z,t) - \eta_2 \Gamma_{t2} \zeta I_2(z,t) n_t(z,t) + \eta_1 \Gamma_{c1} \zeta I_1(z,t) n_c(z,t) + \eta_2 \Gamma_{c2} \zeta I_2(z,t) n_c(z,t) + \frac{1}{\tau} n_c(z,t),
\]

\[
\frac{\partial I_1}{\partial z} = \gamma_1 \Gamma_{t1} \zeta I_1(z,t) n_t(z,t) + \gamma_1 \Gamma_{c1} \zeta I_1(z,t) n_c(z,t),
\]

\[
\frac{\partial I_2}{\partial z} = \gamma_2 \Gamma_{t2} \zeta I_2(z,t) n_t(z,t) + \gamma_2 \Gamma_{c2} \zeta I_2(z,t) n_c(z,t),
\]

where \( n_t \) and \( n_c = 1 - n_t \) are the volume fractions of the trans and the cis azobenzenes, \( \eta_i \) and \( \eta_c \) \((i = 1, 2)\) are the quantum efficiencies and the \( \Gamma_i \) and \( \Gamma_c \) are the cross-section absorption coefficients (see also [34]). The parameter \( \zeta \) is the polarization coefficient which describes the probability of the azobenzene molecules to absorb energy from the incoming light. It depends on the director alignment and the order parameter of the network, \( S \). Here we follow the experiments\(^{[175]}\) and a diffuse light source is used so that \( \zeta = [1 - SP_2(\cos \phi)]/3 \), where \( \phi \) is the angle between the director and the propagating direction of the light, and \( P_2(x) = (3x^2 - 1)/2 \)\(^{[34]}\). The constants \( \gamma_i = \hbar \omega_i \rho_0 \delta \) \((i = 1, 2)\), depend on the Planck constant \( \hbar \), the frequencies of the incident light \( \omega_i \) and the absolute number density of the chromophores \( \rho_0 \delta \) (\( \rho_0 \) is the total concentration of all mesogenic molecules before illumination and \( \delta \) is the molar fraction of azobenzene dyes).

We use the dimensionless parameters \( \alpha \) and \( \beta \) to quantify the magnitude of the source incident intensities relative to the internal material properties:

\[
\alpha_1 = \eta_1 \Gamma_{t1} I_{0,1}, \quad \alpha_2 = \eta_2 \Gamma_{t2} I_{0,2}, \quad \beta_1 = \eta_1 \Gamma_{c1} I_{0,1}, \quad \beta_2 = \eta_2 \Gamma_{c2} I_{0,2},
\]

for the wavelength \( \lambda_1 = 365 \text{ nm} \) (\( \alpha_1, \beta_1 \)) and \( \lambda_2 = 455 \text{ nm} \) (\( \alpha_2, \beta_2 \)), and we define the attenuation lengths

\[
d_{t1} = 1/\gamma_1 \Gamma_{t1}, \quad d_{t1} = 1/\gamma_1 \Gamma_{c1}, \quad d_{c2} = 1/\gamma_2 \Gamma_{c2},
\]

for the trans (\( d_{t1}, d_{t2} \)) and the cis (\( d_{c1}, d_{c2} \)) azobenzenes. The attenuation lengths are related to \( \alpha_i \) and \( \beta_i \) by

\[
\frac{d_{t1}}{d_{c1}} = \frac{\beta_1}{\alpha_1} \eta_1, \quad \frac{d_{t2}}{d_{c2}} = \frac{\beta_2}{\alpha_2} \eta_2,
\]
where the two quantum efficiency ratios are defined as
\[
\eta_1 = \frac{n_1}{n_{c1}}, \quad \eta_2 = \frac{n_2}{n_{c2}}.
\]

Now, by substituting Eqs. (5.4) and (5.5) into Eqs. (5.1)-(5.3) and dividing the light attenuation equations by the corresponding original intensities \(I_{0,i}\), we obtain

\[
\tau \frac{\partial n_t}{\partial t} = 1 + \beta_1 \zeta I_1(z,t) + \beta_2 \zeta I_2(z,t)
\]
\[
- (1 + (\alpha_1 + \beta_1) \zeta I_1(z,t)) + (\alpha_2 + \beta_2) \zeta I_2(z,t) n_t(z,t),
\]
\[
\frac{\partial I_1}{\partial z} = \left[ \left( \frac{1}{d_{t1}} - \frac{1}{d_{c1}} \right) n_t(z,t) + \frac{1}{d_{c1}} \right] \zeta I_1(z,t),
\]
\[
\frac{\partial I_2}{\partial z} = \left[ \left( \frac{1}{d_{t2}} - \frac{1}{d_{c2}} \right) n_t(z,t) + \frac{1}{d_{c2}} \right] \zeta I_2(z,t).
\]

We solve the problem in the photo-stationary state by setting the right-hand side of Eq. (5.8) equal to zero, which yields the stable volume fractions for the two states:

\[
n_t(z) = \frac{1 + \beta_1 \zeta I_1(z) + \beta_2 \zeta I_2(z)}{1 + (\alpha_1 + \beta_1) \zeta I_1(z) + (\alpha_2 + \beta_2) \zeta I_2(z)},
\]
\[
n_c(z) = \frac{\alpha_1 \zeta I_1(z) + \alpha_2 \zeta I_2(z)}{1 + (\alpha_1 + \beta_1) \zeta I_1(z) + (\alpha_2 + \beta_2) \zeta I_2(z)}.
\]

By substituting Eq. (5.11) into Eqs. (5.9) and (5.10) we obtain two coupled non-linear ordinary differential equations which can be solved for the reduced intensities \(I_1(z)\) and \(I_2(z)\) through the thickness. The volume fractions \(n_t(z)\) and \(n_c(z)\) follow by substituting the intensities into Eqs. (5.11) and (5.12).

The solutions for \(I_1(z)\), \(I_2(z)\), \(n_t(z)\) and \(n_c(z)\) depend on eight system parameters, i.e., the dimensionless parameters \(\alpha_i\) and \(\beta_i\) and the attenuation lengths for \(t\) and \(c\) light, \(i = 1, 2\). To parameterize these values we use the experimental absorbance spectra of the \(c\) and \(t\) isomers (i.e., \(A_{t1}, A_{t2}, A_{c1}\) and \(A_{c2}\) in Fig. 5.1(a)) in addition to the \(c\) conversion measurements for mixed UV-VIS exposure at 100 mW/cm² UV intensity (see the red triangles in Fig. 5.1(b)). In Fig. 5.1(b), only the data for 100 mW/cm² are used for parametrization; the results for 200 and 300 mW/cm² are predictions of the model. The parameterized coefficients are listed in Table 5.1. Details of the parametrization can be found in the Appendix 5.A. In the parameterization process, we reduce the number of the to-be-fitted parameters down to four, i.e., \(\alpha, d_{ti}, \eta_2/\eta_1\) and \(\eta_2/\eta_c\) by making use of the light absorption spectra of \(t\) and \(c\) azobenzenes (see Fig. 5.1(a)).

The experimentally measured \(^{[175]}\) and the predicted \(c\) conversion under various exposure configuration are plotted in Fig. 5.1(b). For pure UV exposure, the conversion from \(t\) to \(c\) is maximal compared to the other scenarios where 455 nm light is added (see Fig. 5.1(b)). This is due to the fact that the additional 455 nm light accelerates the photo-induced back-reaction so that at the photo-stationary state a lower volume fraction of \(c\) is reached. To illustrate the effect of adding 455 nm light (based on the obtained light parameters from Table 5.1) we take the measured data...
point $I_0|_{\lambda=365\text{nm}} = 100 \text{ mW/cm}^2$ and $I_0|_{\lambda=455\text{nm}} = 50 \text{ mW/cm}^2$ as an example (so that the ratio is equal to 0.5 in Fig. 5.1(b)). The light attenuation and the corresponding cis conversion through the thickness are presented in Fig. 5.2(b), together with the results for a pure UV illumination case in Fig. 5.2(a). For pure 365 nm exposure, the photo-triggered forward-reaction is strong compared to the other two back-reactions (thermally and optically) and a high cis volume is achieved along the thickness (see FIG.5.2(a)). The attenuation of the UV light is much lower than in the Beer-Lambert limit, because once the trans azobenzenes isomerize to the cis state, the cis azobenzenes absorb UV light much less, so that the light can penetrate fur-

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**Figure 5.1** – (a) Measured absorbance spectra for the trans and cis azobenzenes. The inset is a schematic representing the assumed mechanism for UV-responsive LC-Azo networks. The inserted table lists the absorbance value of trans and cis azobenzenes under 365 nm and 455 nm exposure. (b) The numerical results (lines) and the experimental data (symbols) for the averaged cis concentration as a function of the ratio between the intensities of the 455 nm and the 365 nm wavelengths under dual wavelength illumination for three UV input intensities. The experimental data are taken from Ref. [175] (copyright NPG).
Table 5.1 – The values for the light parameters used to calculate the cis conversion levels in Fig. 5.1(b). The four independent parameterized variables are $\alpha_1$, $d_{t1}$, $\eta_{t2}/\eta_{t1}$ and $\eta_{t2}/\eta_{c2}$; all other variables follow from Eqs. (5.21a)-(5.21f) in Appendix 5.A.

<table>
<thead>
<tr>
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<th>Wavelength</th>
<th>365 nm ($i = 1$)</th>
<th>455 nm ($i = 2$)</th>
</tr>
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<tbody>
<tr>
<td>$\alpha_i$ (for 100mW/cm$^2$)</td>
<td></td>
<td>66.28</td>
<td>0.21</td>
</tr>
<tr>
<td>$\beta_i$ (for 100mW/cm$^2$)</td>
<td></td>
<td>1.14</td>
<td>14.08</td>
</tr>
<tr>
<td>$d_{t1}/w$</td>
<td></td>
<td>0.0281</td>
<td>0.5413</td>
</tr>
<tr>
<td>$d_{c1}/w$</td>
<td></td>
<td>0.5409</td>
<td>0.2707</td>
</tr>
<tr>
<td>$\eta_{ti}/\eta_{t1}$</td>
<td></td>
<td>1</td>
<td>0.049</td>
</tr>
<tr>
<td>$\eta_i = \eta_{t1}/\eta_{ti}$</td>
<td></td>
<td>3 [34, 287]</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Figure 5.2 – The cis volume fraction (left axis) and the reduced light intensities (right axis) through the thickness for (a) single 365 nm light exposure with intensity $I_0 = 100$ mW/cm$^2$, and (b) double beam exposure with 365 nm light of $I_0 = 100$ mW/cm$^2$ and 455 nm light of $I_0 = 50$ mW/cm$^2$. The addition of the 455 nm light increases the cis-to-trans transition so that at large depth more azobenzenes are in the trans state and thus the 365 nm light gets more attenuated.

Table 5.1 – The values for the light parameters used to calculate the cis conversion levels in Fig. 5.1(b). The four independent parameterized variables are $\alpha_1$, $d_{t1}$, $\eta_{t2}/\eta_{t1}$ and $\eta_{t2}/\eta_{c2}$; all other variables follow from Eqs. (5.21a)-(5.21f) in Appendix 5.A.

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<tr>
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<td>0.03</td>
</tr>
</tbody>
</table>

Figure 5.2 – The cis volume fraction (left axis) and the reduced light intensities (right axis) through the thickness for (a) single 365 nm light exposure with intensity $I_0 = 100$ mW/cm$^2$, and (b) double beam exposure with 365 nm light of $I_0 = 100$ mW/cm$^2$ and 455 nm light of $I_0 = 50$ mW/cm$^2$. The addition of the 455 nm light increases the cis-to-trans transition so that at large depth more azobenzenes are in the trans state and thus the 365 nm light gets more attenuated.

ther, resulting in a large uniform cis concentration. With the addition of 455 nm light (see FIG.5.2(b)), it can be observed that the 455 nm light can penetrate much deeper than the 365 nm light because of the low absorbance of 455 nm light by both trans and cis molecules. As a result, at large depth the 455 nm light dominates, resulting in a pronounced back-reaction to trans and thus a low cis concentration.

5.3 Photo-mechanical response

In many previous theoretical studies, the photo-induced strain was commonly assumed to be linearly proportional to the cis volume fraction [34, 158, 284], or non-linear but monotonously increasing [287, 407, 408]. However, the measured density decrease [175] (Fig. 5.3) shows that the largest response ensues when a small amount of 455 nm is added, for which the corresponding cis is not the highest (Fig. 5.1(b)). Clearly, it is insufficient to only consider the order reduction due to the statistical cis accumulation and ignore the fact that all active isomers are enduring cyclic trans-to-
cis and cis-to-trans conversions at high speed, which generates free volumes at the regions traveled by the oscillating isomers.

Here we propose a new constitutive relation in which we explicitly take the dynamic trans-cis-trans conversions into account. The strain tensor components in the local coordinate system read

\[ \varepsilon_{ij}^{\text{ph}}(z) = P_{ij} n_c(z) + D_{ij} f(z), \]  

(5.13)

where the first term on the right hand side is the conventional static contribution (see e.g. Ref. [34]) and the second term is a new dynamic term added to describe the effect of the continuous trans-cis-trans isomerization cycles. The subscripts in Eq.(5.13), \( i \) and \( j \), refer to the local Cartesian reference system. The \( P_{ij} \) are the components of the photo-responsivity tensor \([34]\), which macroscopically link the cis accumulation to a decrease in the order parameter leading to a spontaneous deformation. The \( D_{ij} \) have a similar interpretation as the \( P_{ij} \) but account for the free volume generation due to the dynamics of the isomers. The function \( f \) is phenomenological, resembling a continuous probability density function \([409]\):

\[ f = n_\tau(z)(A + B\frac{\sum \alpha_k I_k}{\sum(\alpha_k I_k + \beta_k I_k)} - C)^2)^{-3}, \]  

(5.14)

where \( A, B \) and \( C \) are constants and subscript \( k \) refers to the two lights with wavelength \( \lambda_k \) \((k = 1, 2)\). The probability feature of \( f \) captures the appearance and magnitude of free volume generation favored by the polymer skeleton. The driving force for the dynamic contribution to deformation is

\[ n_\tau = 1 + \beta_1 \zeta I_1(z) + \beta_2 \zeta I_2(z), \]  

(5.15)

the volume fraction of azobenzenes undergoing backward cis-to-trans transitions during the time \( \tau \) (see Eq. (5.8)). Since the forward rate equals the backward rate in the photo-stationary state, \( n_\tau \) also represents the volume fraction of trans-to-cis transitions during time \( \tau \), so that a large \( n_\tau \) corresponds to a large dynamic trans-to-cis-to-trans cycling rate.

The density decrease (equal to the volume increase) of a sample can be obtained by calculating the averaged volumetric strain through the thickness \( \int_0^w \varepsilon_{\text{vol}}^{\text{ph}}(z)dz/w \), where \( \varepsilon_{\text{vol}}^{\text{ph}}(z) \) is equal to the trace of the strain tensor given in Eq.(5.13).

We conduct a parameterization process to obtain the values of all unknown constants, i.e., the material responsivity parameters \( P_{ii} \) and \( D_{ii} \) (with \( i = 1, 2, 3 \)), as well as \( A, B \), and \( C \) in the function \( f \), based on measured density decrease data \([175]\) and the light parameters used in Fig. 5.1(b) (listed in Table 5.1). The numerical results are shown in Fig. 5.3 with all the obtained parameters for different light intensities listed in Table 5.2.

The power exponents in the probability-density-function-like Eq. (5.14) might be not unique. Other exponents with different sets of parameterized constants \( (P_{ii}, D_{ii}, A, B \text{ and } C) \) might still give good fitting for the optimal response under dual light exposure (i.e., Fig. 5.3). The physical meaning of \( n_\tau \) represents the volume fraction of azobenzenes undergoing trans-to-cis-to-trans cycling during the time of \( \tau \). Other time constants might also be applicable (i.e., \( \tau/2 \)), and produce similar results with different sets of fitted constants.
From Fig. 5.3 we observe that the dynamic effect only occurs under specific intensity combinations of the 365 nm and the 455 nm light. Outside those ranges, such as the pure 365 nm illumination or a mixed exposure with comparatively large 455 nm intensity (ratios larger than 0.5), the dynamic effects are small and almost all the deformations are attributed solely to the cis accumulation. One possible explanation for this limitation is that it needs a special energy input that can simultaneously boost trans-to-cis and cis-to-trans transitions to an appropriate level to sustain the generated free volumes, which cannot be realized by purely exposing either 365 nm or 455 nm light. The dynamic contribution increases with light intensity. For the 100 mW/cm$^2$ 365 nm light illumination, the static $n_c$ contribution is comparable to the dynamic contribution, but for the 300 mW/cm$^2$ intensity, even with an increase of the cis concentration (Fig. 5.1(b)), the $n_c$ contribution is much lower than the dynamic counterpart.

According to parameterized constants (Table 5.2), consistencies are found at different input intensities for the responsivity parameters $P_{ii}$ and $D_{ii}$, and the constant $A$, which influences the amplitude of the dynamic effect, indicating they are material properties independent of illumination conditions. The $B$, characterizing the range of effective combinations of the two lights for the dynamic contribution, is consistent for the 100 and 200 mW/cm$^2$ UV intensity, but dramatically decreases for the 300 mW/cm$^2$ case, which represents the corresponding wide effective range found in the experiments. The $C$ imparts the most effective configuration for the dimensionless light parameters $\alpha_k$ and $\beta_k$. $C$ decreases for increasing intensity, indicating a higher ratio of the intensity of the 455 nm light to the 365 nm is required and the density decrease curves shift to the right with increasing intensity input. Here no effort has been done to further formulate an expression for $C$. The origin of the varying optimal intensity ratio of the visible light and UV light is a target of future studies. but it is believed that, when the UV intensity is increased, a VIS/UV ratio increase can help to maintain the ratio between the two intensities through the sample and let the two lights contribute together to trigger a cooperative dynamic effect in the bulk material.

Good to note there that, here we ignore the volume changes resulting from mechanical stresses and assume that all the density changes are attributed solely to the opto-mechanical response. This is partially due to the significantly-increased computation cost when the finite element package is incorporated during the iterative least squares fitting procedure. In addition, the director configuration used in the experiment [175] is a uniform cholesteric phase under localized exposure, which is found that the final volume increase is larger than the pure photo-induced volume.

<table>
<thead>
<tr>
<th>Intensity(mW/cm$^2$)</th>
<th>100</th>
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<th>300</th>
</tr>
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<tbody>
<tr>
<td>$P_{ii}$</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>$D_{ii}$</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>$A$</td>
<td>0.92</td>
<td>0.92</td>
<td>0.92</td>
</tr>
<tr>
<td>$B$</td>
<td>12000</td>
<td>12000</td>
<td>400</td>
</tr>
<tr>
<td>$C$</td>
<td>0.9710</td>
<td>0.9675</td>
<td>0.9524</td>
</tr>
</tbody>
</table>
5.3: Photo-mechanical response

The amount of the increased volume depends on the in-plane dimension and thickness of the films, and the anisotropies of the elastic and photo-responsivity properties of the LC material. The analysis presented in this chapter mainly focuses to distinguish the static and dynamic con-

![Graph](image)

**Figure 5.3** – The numerical (solid lines) and experimentally measured [175] (circles) density decrease for various input intensities of the 365 nm light: $I_{365} =$ (a) 100, (b) 200 and (c) 300 mW/cm$^2$. The red curves show the total density changes (numerical results) and the other two colors show the two contributions, i.e., the effect due to the cis isomer accumulation (blue) and the dynamic trans-cis-trans oscillation cycles (green).
Chapter 5: Topographical enhancement via double-light exposure

Figure 5.4 – Photo-isomerizations of crosslinker azobenzenes (a) and pendant-type azobenzenes (b) in liquid crystal glassy networks under illumination: azobenzenes (yellow rods) and liquid crystal molecules (blue rods). The double connections of the crosslinker azobenzenes attaching to the polymer skeleton transfer the molecular dynamic isomerizations to the whole network, whereas the isomerizations of the pendant azobenzenes are decoupled from the network. (c) The softening of the measured Young’s modulus (lines, left axis) and the measured temperatures (dots, right axis) under a mixed UV-VIS exposure: \( I_{365} = 300 \text{ mW/cm}^2 \) with \( I_{455} = 4.8, 18, 48, 99, 198 \text{ mW/cm}^2 \) from step A to E, respectively. (Figure (a)-(b) from [175], copyright NPG; Figure (c) from [294], copyright RSC)

The origin of the boosted opto-responses and the special conditions needed to trigger the enhancement (see the UV/VIS intensity ratio for the optimal response in Fig. 5.3) are worth further discussion. For the glassy network fabricated in the experiments [175], azobenzenes are attached to the polymer skeleton at both ends, as shown in Fig. 5.4(a). In a reference experiment, networks with crosslinker azobenzenes have a similar magnitude of deformation in comparison to networks containing pendant-type of azobenzenes (attaching to the polymer by only one end, see Fig. 5.4(b)) under pure UV light illumination. This indicates a comparable decrease of the order parameter in the two networks. Under mixed UV-VIS illumination, the response of the network with pendant azobenzenes shows no enhancement. Thus crosslinker-type azobenzenes are essential to trigger a larger opto-response. It is believed that the full connection between the oscillating azobenzenes and the polymer main chain manages to pass the isomerization dynamics to the neighboring LC chain so that the skeleton is continuously being distorted by the cycling azobenzenes, leading to a cooperative network deformation. It is again worthwhile to emphasize that a special VIS/UV intensity ratio is needed to trigger a boosted response. It was found that excessive oscillation dynamics of azobenzenes under larger visible and UV light intensities soften the material dramatically, leading to three orders of magnitude decrease in Young’s modulus [294], see Fig. 5.4(c). Therefore the oscillating level of the co-polymerized azobenzene is key to explain the enlarged response. The probability
5.4 Optimal wavelength

The discrepancy between the cis conversion level and the opto-mechanical response under double wavelengths illumination brings in a new question: if a single light exposure is used, which wavelength is optimal? To answer this question, one needs to obtain the light parameters for an arbitrary wavelength $\lambda_i$ ($365 \text{ nm} \leq \lambda_i \leq 455 \text{ nm}$), i.e., the dimensionless parameters $\alpha_i$ and $\beta_i$, the attenuation length for trans $d_i$, and the quantum efficiency ratio $\eta_i = \eta_{ti}/\eta_{ci}$. Here we follow the same procedure as in the parameterization step for the two wavelength illumination, but now applied for one wavelength only. To obtain all the necessary input parameters for $\lambda_i$, we assume the quantum efficiencies $\eta_{ti}$ and $\eta_{ci}$ follow an S-shaped variation between the quantum efficiencies of the 365 nm and 455 nm wavelengths and make use of the absorbance spectra $A_{ti}$ and $A_{ci}$ from Fig. 5.1(a) (see the Appendix 5.B for details). The prediction for the density decrease under single wavelength exposure is given in Fig. 5.5 for three different input intensities. Interesting, the optimal wavelength for single LED illumination undergoes a pronounced shift of 30 nm towards the visible regime. The optimal wavelength does not only generate a high cis conversion level, it also triggers a considerable dynamic effect with the help of the enhanced cis absorbance. This result corroborates recent experiments in which not a UV but a higher wavelength light source was selected to trigger azobenzene embedded systems, such as the usage of blue-green light [176, 286, 410] and other illumination scenarios [274, 411–413].

![Figure 5.5](image)

**Figure 5.5** – Predicted density decrease as a function of wavelength for single light illumination for three source intensities.

Next we ask the question: “What is the optimal combination of wavelengths for a two-light illumination system?”. The optimization parameters are the two wavelengths $\lambda_1$ and $\lambda_2$, and their intensities. We assume the total input energy of the two wavelengths together is 300 mW/cm$^2$, thus addressing the question which system...
features an optimal efficiency for a given energy input. The result is shown in Fig. 5.6 by a three-dimensional contour plot for the density decrease as a function of the two wavelengths and their intensities. Clearly, for every energy distribution, there always exists a wavelength selection for comparatively large responses in which the dynamic effect can be exploited. A general approach to maximize the double-wavelength response is to choose near-UV light emitting at the largest intensity and to let the other wavelength be close to the effective cis absorbance range, which leads to a relatively high cis conversion and simultaneously a large dynamic trans-cis-trans cycling rate. This result quantitatively matches the light-induced motion of azobenzene crystal plates [342], in which a mixed 200 mW/cm$^2$ 365 nm and 60 mW/cm$^2$ 465 nm light exposure generates the most favorable deformation.

This study might help to explain a recent founding that liquid crystal glassy polymers have largest deformation and volume expansion when they are excited under a certain oscillation frequency under electric actuation [163]. The “resonance frequency” of liquid crystal polymers indicated in Ref. [163] is similar to the method presented in this study.

The above single and double wavelength approaches can be extended to more than two light sources and their corresponding intensity distribution, such as LC actuators containing Azo-derivatives exposed to light sources emitting multiple wavelength peaks, like mercury light [153, 366] and actinic light [20, 174, 364, 414]. This would allow to filter out those wavelengths that have small contributions to the overall actuation
response, leading to a higher system efficiency.

It should be noted that our analysis assumes isothermal conditions, so that the predictions are valid for exposure scenarios in which temperature changes are limited. For systems undergoing a considerable temperature increase under strong light intensities \cite{294,366}, one needs to take the self-heating into account since the characteristic fall-back time of the cis azobenzene, $\tau$, decreases with temperature, leading to reduced light parameters $\alpha$ and $\beta$ (see Eq. 5.4), and thus affects the light attenuation and the constants in Eq. (5.14).

### 5.5 Conclusion

In short, we have developed a double-wavelength attenuation model that accurately describes the trans and cis distributions in films of azobenzene-embedded LC polymers. In addition, we have formulated an experimentally-calibrated photo-mechanical constitutive relation that is able to differentiate between strains resulting from the statistical accumulation of cis and the dynamic trans-cis-trans isomerization cycles. Our results show that the optimal single wavelength light for the studied system is not UV light, but 395 nm light, a considerable shift towards the visible spectrum. Our model provides fundamental mechanistic insight on the different wavelength exposures used in experiments \cite{175,176,274} and opens the possibility to explore the maximal opto-mechanical response under various multi-wavelength illumination configurations.

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chapter 5: Topographical enhancement via double-light exposure
5.A Light attenuation parameterization

To parameterize all eight necessary optical parameters $\alpha_i$, $\beta_i$, $d_{ti}$ and $d_{ci}$ ($i = 1, 2$), we first make use of the absorbance spectra for the trans and cis azobenzenes, given in Fig. 5.1(a). The absorbance, $A$, of a specific wavelength is defined as the common logarithm of the ratio of the incident ($I_0$) to the transmitted intensity ($I_t$) through a sample with a certain thickness, and is given by

$$A = \log_{10} \left( \frac{I_0}{I_t} \right) = - \log_{10} T, \quad (5.16)$$

where $T$ is the transmittance of the light, $T = I_t/I_0$. Then, the transmittance of the trans state of azobenzene at wavelength $\lambda_i$, i.e., $T_{ti} \equiv T_{ti}\mid_{\lambda=\lambda_i}$ is related to the absorbance $A_{ti} \equiv A_{ti}\mid_{\lambda=\lambda_i}$ by

$$T_{ti} = 10^{-A_{ti}}. \quad (5.17)$$

By definition, the transmittance is equal to the reduced intensity at the bottom surface, $T_{ti} = I_{ti}(z = 0) = I_i(z = 0)/I_{0i}$. Now, by assuming the light attenuation of the probing light to follow the Beer-Lambert law \cite{175} (ignoring photo-induced isomerization conversion because the probe intensity is low), we can write

$$T_{ti} = e^{-w/d_{ti}}, \quad (5.18)$$

where $w$ is the sample thickness and $d_{ti}$ the attenuation length of trans at wavelength $\lambda_i$. By combining Eqs. (5.17) and (5.18) we can write the relation between the attenuation length and its corresponding absorbance as

$$\frac{d_{ti}}{w} = -\frac{1}{\ln 10^{-A_{ti}}}. \quad (5.19)$$
By using the absorbance spectrum of the trans state, the ratio of the attenuation lengths for different wavelengths can be obtained, i.e.,

$$\frac{d_t|\lambda=365\text{nm}}{d_t|\lambda=455\text{nm}} = \frac{\ln 10^{-A_t|\lambda=455\text{nm}}}{\ln 10^{-A_t|\lambda=365\text{nm}}} = \frac{A_t|\lambda=455\text{nm}}{A_t|\lambda=365\text{nm}}. \quad (5.20)$$

The last equation clearly shows that a higher absorbance is correlated to a smaller attenuation length.

The next step is to maximally decrease the number of the unknown independent variables for dual wavelength exposure. For the quantum efficiency ratio of the 365 nm light, we use the value adopted from the literature [34, 156, 287], \(\eta_1 = 3\). However, there is no reported measurement or numerically fitted value for the quantum efficiency ratio of the 455 nm light. Here we aim to parameterize the following four independent variables: the dimensionless parameter \(\alpha_1\), the attenuation length for trans \(d_t\), the ratio between the quantum efficiencies of the two wavelengths for trans \(\eta_2/\eta_1\) and the quantum efficiency ratio for the 455 nm light \(\eta_2 = \eta_{t2}/\eta_{c2}\). All other light parameters can be related to these independent variables via the ratio of absorbances and Eqs. (5.4)-(5.7):

\[
\begin{align*}
\beta_1 &= \frac{A_{c1} 1}{A_{t1} \eta_1}, \\
\alpha_2 &= \frac{A_{t2} \omega_1 \eta_2}{A_{t1} \omega_2 \eta_1}, \\
\beta_2 &= \frac{A_{c2} 1}{A_{t2} \eta_2}, \\
d_t &= \frac{A_{t1}}{A_{t2}}, \\
d_c &= \frac{A_{t1}}{A_{t2}}.
\end{align*}
\]

Here, \(\omega_1\) and \(\omega_2\) are the frequencies of the 365 nm and 455 nm light, \(A_{t1}\) and \(A_{t2}\) are the absorbances of trans at wavelength 365 nm and 455 nm, respectively, and \(A_{c1}\) and \(A_{c2}\) are the corresponding absorbances of cis (see Fig. 5.1(a)).

By fitting the predicted averaged cis concentrations through the film thickness, \(\int_0^w n_c(z)dz/w\), at the photo-stationary state to the measured data as a function of the ratio of the 455 nm to 365 nm light, the remaining four independent parameters can be found. The order parameter \(S\) takes a typical value for LC nematic glassy polymers, \(S = 0.6\) [34, 416]. Here we ignore the effect of the order decrease in the evaluation of \(\zeta\) since the reduction of the order parameter in heavily-crosslinked, glassy LC polymer is usually small [34, 147]. The tested LC-Azo samples are in the cholesteric phase [175] so that the angle between the director and the propagating direction of the two lights is uniform through the thickness: \(\phi = 90^\circ\), giving a value of \(\zeta = 0.433\) in Eqs. (8)-(12). Only the data for the 100 mW/cm² intensity exposure in Fig. 5.1(b) are used for parametrization and the obtained parameter values are listed in Table 5.1. Then the parameters are used to predict the experimental results.
for the 200 and 300 mW/cm\(^2\) intensities in Fig. 5.1(b), showing good agreement. It is good to note here that the values of \(\alpha_i\) and \(\beta_i\) given in Table 5.1 are for a light intensity of 100 mW/cm\(^2\). For the other intensities, the dimensionless parameters \(\alpha\) and \(\beta\) are enhanced in proportion to the source intensity (see Eq. (5.4)).

### 5.B Optimal wavelength

To predict the optimal wavelength for single light illumination, one needs the light parameters for an arbitrary wavelength \(\lambda\). We still apply the relations for the light parameters between two different wavelengths, Eqs. (5.21c)-(5.21f), to acquire the necessary inputs. To the best of our knowledge, there is no previously reported data for the quantum efficiency of the wavelengths between 365 nm and 455 nm. Here we assume a monotonic and gradual variation of the two ratios between quantum efficiency ratios, \(\eta_t/\eta_{t1}\) and \(\eta_c/\eta_{t1}\), as shown in FIG.5.7(a), for the wavelength \(\lambda\) and \(\lambda_1 = 365\) nm. Two distinct variation schemes are tested here. One is an S-shaped variation (solid line in Fig. 5.5(a)), assuming the slopes on both ends to be close to zero. The other tested variation is exponentially decreasing from the maximal point and the slope at the other end is assumed to be zero (dashed line in FIG.5.7(a)).

All the resulting light input parameters, calculated from the assumed quantum efficiencies, the absorbance spectra of azobenzene (Fig. 5.1(a)) and the parameterized results for the 365 nm light (Table 5.1), are shown in Fig. 5.5(b) for all wavelengths between 365 nm and 455 nm. The attenuation length \(d_c\) at nearly 400 nm wavelength is the highest since the corresponding cis absorbance is the lowest. Due to the continuous decline of the trans absorbance in the tested wavelength range, the \(d_t\) always rises. It should be noted that the two attenuation lengths only depend on the absorbances and are independent of the quantum efficiencies. For light with wavelengths approaching 455 nm, the photo-induced forward-reaction capacity, characterized by \(\alpha\), deceases dramatically and the capacity for the back-reactions, indicated by \(\beta\), increases gradually, as expected.

Results of the averaged cis conversion and the density decrease for both the S-shape and the exponential quantum efficiencies are shown in Fig. 5.7(c)-(d), respectively. We observe that if only a single LED light source is used for actuation, a wavelength between 380 nm and 400 nm is predicted to be preferable. Light inside this wavelength range can be effectively absorbed by both trans and cis azobenzenes, but the absorbance by trans is still large enough to trigger the dynamic contribution in addition to a sufficiently large cis conversion.

In comparison to Fig. 5.3, the density decrease for the 100 mW/cm\(^2\) single wavelength exposure can reach a similar value as the dual light counterpart (see FIG. 5.7(d) and FIG. 2 in the main text). But for the higher intensities, the single illumination results are lower than those of the dual lights. According to the definition of the function \(f_i\), Eq. (5.14), successfully triggering a large dynamic contribution requires two things. The first is a boosted dynamic trans-cis-trans oscillation, described by \(n_T\). The second requires an appropriate combination of the forward- and backward reaction capacities all the way through the bulk sample (which leads to the value of the item after \(B\) in Eq. (5.14) close to zero through the thickness and thus the
averaged bulk response throughout can be maximized).

For mixed UV-VIS illumination, the $n_τ$ continuously increases with increasing ratio $I_{455}/I_{365}$ since the 455 nm light has a maximal back-reaction triggering capacity, as shown in Fig. 5.8(a). But the value of $n_τ$ for an arbitrary wavelength $λ$ for single light illumination is small until the wavelength enters the effective cis absorbance region, as in Fig. 5.8(b). When the light input intensity is small (i.e., 100 mW/cm$^2$), the $n_τ$ for the single light illumination is slightly smaller than the two lights case at the optimal wavelength range. But the single-light illumination has an overall larger deformation response compared to the mixed UV-VIS cases since the former is able to generates a larger bulk contribution from the dynamic trans-cis-trans cycling response throughout the thickness. For the larger intensity input, the $n_τ$ for the dual wavelength exposure is considerably larger than that for the one light exposure, so that the mixed UV-VIS exposure has a higher density decrease than the single-wavelength exposure.

It is good to note that, due to the limited availability of quantum efficiency data,
5.B: Optimal wavelength

**Figure 5.8** – (a) The variations of the averaged $n_\tau$ as a function of the input light ratio $I_{455}/I_{365}$ for different UV input intensities under mixed 365 nm and 455 nm illumination. (b) The variations of the averaged $n_\tau$ as a function of wavelength under single-LED illumination for different intensities. The solid lines correspond to the results using the S-shape quantum efficiency assumption and the dashed lines correspond to the exponential assumption in Fig. 5.7(a).

only an interpolation within the 365 nm and 455 nm range is possible and therefore we only predict a single-wavelength exposure response inside this range. The assumptions for the monotonous variations of the quantum efficiencies are not unique, and therefore only serve to explore qualitative trends.