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Light-driven topographical morphing of azobenzene-doped liquid crystal polymer films via tunable photo-polymerization induced diffusion

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ABSTRACT

Photo-polymerization is a convenient way to fabricate azobenzene-doped liquid crystal glassy polymeric networks. During the photo-polymerization process, monomer diffusion is initiated if mesogens with different reactivities are blended in the monomer mixture and the polymerization light intensity is not uniform. Upon the diffusion of liquid crystal monomers and azobenzenes, compositional inhomogeneities are introduced in the polymerized network, leading to stiffness and photo-responsivity gradients. However, the relation between this diffusion process, the resulting compositional gradients and the final light-triggered deformation is not well-understood. Here we developed a computational model to simulate the monomer diffusion and its effect on the mechanics of light-induced topographical switching. By demonstrating light-switchable folding motions and surface transformations of liquid crystal films with various molecular alignments, the photo-responsivity gradient is found to play a major role in modulating the switching performance. Furthermore, the photo-polymerization diffusion can be an effective approach to introduce spatially-varying material properties and to tailor the surface and film deformations by varying the wavelength, illumination area and polarization of the incoming light. The proposed framework can be used to evaluate and control photo-polymerization-induced monomer diffusion to tune light-triggered topographical morphing.

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Foreword: With our contribution to this special issue on the occasion of the 60th birthday of Norman A. Fleck, we touch base with the earlier work that Norman performed on actuators, including (i) actuator classification (Bell et al., 2005; Huber et al., 1997; Zupan et al., 2002), (ii) electrical switching of ferroelectric polycrystals (Huber et al., 1999; Huber and Fleck, 2001; Hwang et al., 1998) and (iii) the actuation of lattice materials (Hutchinson et al., 2003; Symons et al., 2005). In the current paper we discuss a recent actuator material in the realm of soft matter that can be switched by light, i.e., photo-actuated liquid crystal polymers. This new class of soft actuators finds application in friction and wettability control, man-machine interfacing and soft robotics.

1. Introduction

Responsive materials are attractive for a range of applications, including wettability control (Liu et al., 2017; Yao et al., 2011), fluid propulsion (Khaderi et al., 2010; 2011) and soft robotics (Gelebart et al., 2017; Palagi et al., 2016; Park et al.,

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Fig. 1. (a) A schematic denoting the film geometry and representing the diffusion of liquid crystal monomers and azobenzene dyes upon a gradient of the polymerization initiation light, attributed to the absorption of the azobenzenes. A material gradient can be created depending on the final monomer distribution. (b) A schematic of the UV-induced conformational change of azobenzene-modified liquid crystal crosslinked polymers. The LC monomers can be diacrylates with two cross-linking end-sites (in green) or monoacrylates with one crosslinking site to the polymer network (in red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2016). Different active material systems have been developed that can be triggered by heat (Meng and Li, 2013; Ware et al., 2015), pH (Yu et al., 2005), magnetic fields (Khaderi and Onck, 2012; Khaderi et al., 2012), electric fields (Shankar et al., 2007; Wang et al., 2014) and light (Kobatake et al., 2007; Yu et al., 2003). Especially light is attractive, because it features a precise external controllability in both space and time. Different light-responsive materials have been developed recently, including azobenzene-embedded liquid crystal polymers (Liu and Broer, 2014a; White and Broer, 2015). Liquid crystal (LC) polymeric networks doped with light-switchable azobenzene molecules can respond to UV light through a loss-of-order anisotropic deformation when the embedded azobenzenes undergo *trans*-to-*cis* isomerization (see Fig. 1(b)). This deformation can be exploited to induce folding (Harris et al., 2005; Ikeda et al., 2003; van Oosten et al., 2009; White et al., 2008), twisting (Iamsaard et al., 2014; Lee et al., 2011; Wie et al., 2016) and buckling (Gelebart et al., 2017; Skandani et al., 2016) of free-standing films and surface texture changes of substrate-constrained coatings (Hendrikx et al., 2017; Liu et al., 2012a; 2012b; Liu and Broer, 2014b; Liu et al., 2015; Liu and Onck, 2018).

Photo-polymerization is a fast and straightforward technique to fabricate responsive liquid crystal polymer networks. Liquid crystal monomers can be photo-polymerized to form highly ordered, crosslinked glassy polymers (Broer et al., 1995; 1999). The director, defined to be the average orientation of the local liquid crystal molecules ($\vec{n}$ in Fig. 1(b)), can be tuned during the polymerization process via external controls, such as magnetic (Tolbert et al., 1997) and electric fields (Liu et al., 2012b), surface anchoring forces (van Oosten et al., 2009) and photo-alignment layers (de Haan et al., 2012). This enables the molecular design of complex liquid crystal molecule orientations in the polymeric networks, which can trigger significant photo-induced topographical changes that are guided by the imprinted director distribution.

During the process of photo-polymerization, the liquid crystal molecules are subject to diffusion if LC monomers with different reactivities are mixed (Broer et al., 1995; van Nostrum et al., 1998), such as diacrylates and monoacrylates. As schematically shown in Fig. 1(a), diacrylates have higher reactivities than monoacrylates and are therefore depleted faster to form the polymer backbone in regions with higher intensities of the polymerization light. A diffusion process is then initiated between the regions with different light intensities due to monomer concentration gradients. The intensity gradient of the polymerization light can be introduced by adding absorptive dyes (Broer et al., 1995; 1999), masked exposure (van Nostrum et al., 1998; Sánchez et al., 2005) and dichroic photo-initiators (Broer, 2002; Broer et al., 1999) enabling various applications, such as surface grating and embossing (de Gans et al., 2006; Hermans et al., 2007), phase separations (van Nostrum et al., 1998) and optical devices (Broer et al., 1995; van Nostrum et al., 1998).

Also when azobenzene molecules are added to the mixture of LC monomers, polymerization-induced diffusion was found to exist (Aßhoff et al., 2017; ChengChang et al., 2017; Iamsaard et al., 2014; 2016; Lv et al., 2016; van Oosten et al., 2008) as a result of which the local polymer crosslinking density and the azobenzene concentration were found to be spatially varying. This gives rise to gradients of network stiffness and responsivity to light. Materials with such compositional gradients have been a versatile tool to build sophisticated actuators, e.g., by using stiffness gradients to adjust the local load-carrying ability (Bartlett et al., 2015; Ware et al., 2016) and to create specific surface morphologies (Guvendiren and Burdick, 2010; Wang et al., 2016; Yang et al., 2010), and by using responsivity gradients to form topographical textures (Klein et al., 2007; Liu et al., 2013a; 2013b). Compared to the top-down micro-printing technique (Hakan et al., 2016; Truby and Lewis, 2016), such photo-polymerization induced diffusion is an effective tool to introduce material inhomogeneities from the bottom up, while maintaining the pre-designed complex director distributions at micron-scale resolution (Nickmans et al., 2017; 2016; Ware et al., 2015).

Despite its practical and scientific relevance, the process of monomer diffusion during light-induced polymerization is not well understood and its effect on the photo-actuation response has not yet been thoroughly exploited. In this work, we will study the diffusion during photo-polymerization and the subsequent UV actuation of a LC system consisting of three monomers: the bi-functional LC crosslinker diacrylate, the single-reactive-end LC monoacrylate, and the photo-responsive unit azobenzene (see Fig. 1). The wavelength of the polymerization initiation light (λ^p) is selected to be within the effective absorption spectrum of the *trans*-state azobenzene. During polymerization the azobenzene thus functions as an absorptive dye to create a gradient of the polymerization light which then triggers monomer diffusion. We simulate the diffusion process based on the chemical potential equilibrium approach and link the stiffness and photo-responsivity to the concentration ratio of the diacrylate and azobenzene volume fractions, respectively. A nonlinear light attenuation model is used to model the penetration of the actuation light (λ^a) and the *trans*-to-*cis* isomerization process, and we use a photo-mechanical model to predict the topographical changes of various films (free or substrate-constrained) with different director distributions. By studying the one-dimensional diffusion inside films with uniform director alignment, and the multi-dimensional diffusion inside films with non-uniform director distributions, we explore the effect of the diffusion on photo-induced topographical switching and demonstrate the design potential of adjusting the final texture by tuning the monomer diffusion process. Modulations of cantilever bending and twisting motions and manipulations of surface transformations for substrate-constrained films are presented.

The article is organized as follows. The theoretical framework is elaborated in Section 2, related to the diffusion process (2.1), the light penetration process (2.2) and the opto-mechanical constitution of the film (2.3). Results are presented in Section 3 for various film systems, including bending and twisting of cantilever films (3.1), topographical actuation of linearly-patterned coatings (3.2) and wave propagation on LC surfaces (3.3), followed by discussions and conclusions in Section 4.

2. Modelling framework

2.1. Photo-polymerization diffusion model

The volume fractions for all the free monomers, i.e., which have not been polymerized yet and are free to diffuse in the polymer-monomer mixture, are denoted by n_1 , n_2 and n_3 for the diacrylate, monoacrylate and azobenzene molecules, respectively. The Flory-Huggins chemical potential, μ_i , for monomer i is defined as Flory (1953); Leewis et al. (2004a),

$$\mu_i - \mu_i^0 = kT \left[\ln n_i + 1 - \frac{v_i}{v_j} n_j - \frac{v_i}{v_p} n_p + v_i \rho_p \left(\frac{1}{n_p} - \frac{n_p}{2} \right) \right], \quad (1)$$

where the Einstein summation convention is used for repeated indices. μ_i^0 is the chemical potential for an isolated monomer i and the indices i and j run from 1 to 3, denoting the diacrylate, monoacrylate and azobenzene molecules, respectively. The subscript p stands for polymer and n_p is the volume fraction of the overall converted polymer, $n_p = n_{p,1} + n_{p,2} + n_{p,3}$, with $n_{p,i}$ the polymerized portion of the monomer i . The total volume fractions of each monomer are $n_{di} = n_1 + n_{p,1}$ for the diacrylates, $n_{mo} = n_2 + n_{p,2}$ for the monoacrylates and $n_{azo} = n_3 + n_{p,3}$ for the azobenzenes, and $n_1 + n_2 + n_3 + n_p = 1$. The numbers of segments of the monomer and polymer denote their monomeric sizes and are represented by v_i and v_p , respectively. The polymer chain density, ρ_p , is defined to be the weighted average over the three monomer components (Flory, 1953; Leewis et al., 2004a),

$$\rho_p = \frac{1}{n_p} \left(f_1 \frac{n_{p,1}}{v_1} + f_2 \frac{n_{p,2}}{v_2} + f_3 \frac{n_{p,3}}{v_3} \right) \frac{-\ln(1 - n_p) - n_p}{\frac{1}{n_p} - \frac{n_p}{2}}, \quad (2)$$

where f_i corresponds to the polymer network formation ability of each monomer. It was found that Leewis et al. (2004a) by setting $f_i = 1$, there is no swelling and no gross mass transport after the diffusion. For the current studied material system, the mass migration has been found to be small (Liu et al., 2012b; van Nostrum et al., 1998) and thus we take $f_i = 1$ for all the three monomers here. In addition, we take $v_i \ll v_p$ since the number of segments of the three monomers are much less than that of the polymer skeleton.

The diffusion process of the monomers starts once a gradient of one of the chemical potentials is created. The driving mechanism is the difference between the effective reactivities of the monomers in different regions. The effective reactivity of each monomer, R_i^{eff} , is related to the intrinsic polymer chain-addition capacity R_i , the concentration of the photo-initiator, and the local intensity I_p of the light that initiates polymerization. Here we assume a uniform distribution of the photo-initiator during the photo-polymerization process (at a concentration $\leq 1\%$ (Broer et al., 1999; Liu and Broer, 2015; Liu et al., 2015)), and the spatial variation of the light intensity is purely introduced due to the absorption of azobenzenes, which serve as dyes and as photo-triggers. This is verified by checking the extinction coefficients of the photo-initiators (e.g., the Irgacure family (Ahn et al., 2016; Aßhoff et al., 2017; Liu and Broer, 2014a; van Nostrum et al., 1998)), which are two orders of magnitude smaller than those of typical dyes (Broer et al., 1999) and thus we ignore the light absorption of the photo-initiator in our system. Furthermore, complex polymerization light intensity gradients can be constructed using non-uniform director distributions, in which the gradient can be through the thickness direction (Broer, 2002; Broer et al., 1995), as well

as in the plane of the film (Hendrikx et al., 2017; Ware et al., 2015). The polymerization rate was found to be proportional to $(I_p)^a$, in which the exponent a changes from 0.5 at the onset and increases to 1 as the polymerization proceeds (Broer et al., 1999; van Nostrum et al., 1998). To study the effect of diffusion on the final topographical modulation, we take $a = 1$, and $R_i^{\text{eff}} = R_i \mathcal{I}_p$, where $\mathcal{I}_p$ is the local reduced intensity of the polymerization initiating light, see Section 2.2.

A detailed flow diagram for the simulation of polymerization-induced diffusion process is given in Fig. S1. For each polymerization and the sequential diffusion step, we assume that a certain volume of the total free monomers is polymerized, with the ratios between each polymerized component given by

$$\begin{aligned} dn_{p,1} : dn_{p,2} : dn_{p,3} &= R_1^{\text{eff}} n_1 : R_2^{\text{eff}} n_2 : R_3^{\text{eff}} n_3 \\ &= R_1 n_1 : R_2 n_2 : R_3 n_3, \end{aligned} \quad (3)$$

$$dn_{p,1} + dn_{p,2} + dn_{p,3} = dn_p = \Delta_p \mathcal{I}_p. \quad (4)$$

Here Δ_p is a user-defined polymerization conversion step size. After each polymerization step, the current local volume fractions of the free monomers are updated via

$$[n_i]_t = [n_i]_{t-1} - [dn_{p,i}]_t, \quad (5)$$

and the volume fractions of the polymerized monomers are updated by

$$[n_{p,i}]_t = [n_{p,i}]_{t-1} + [dn_{p,i}]_t, \quad (6)$$

$$[n_p]_t = [n_p]_{t-1} + [dn_p]_t. \quad (7)$$

Given a non-uniform light intensity profile and differences between the monomer polymerization rates, the chemical potentials are varying in space. At high intensity regions, monomers with higher reactivities are easier to cross-link to the polymer chain and are depleted faster, leading to a larger decrease in the corresponding chemical potentials. Here we assume that a thermodynamic equilibrium state is reached for every diffusion step and the diffusion is complete when the chemical potentials are uniform throughout the whole mixture. This can be achieved by giving enough time for the photo-polymerization to take place at low intensities (van Nostrum et al., 1998) and by assuming that the dimensions of the film are not too large (Leewis et al., 2004b). This thermodynamic equilibrium of the chemical potential for the three monomers results in the coupled set of equations

$$\frac{[\mu_i]_t - \mu_i^0}{kT} = \frac{\sum_{m=1}^N \left[\frac{[\mu_i]_t - \mu_i^0}{kT} \right]_{\mathbf{x}=\mathbf{x}_m}}{N}, \quad (8)$$

where the right-hand side is the average for all the positions in the mixture and N is the total number of discretized material points. Solving the coupled equations ($i = 1, 2$ and 3 in Eq. (8)) at each material point for all the three monomers with the latest updated $n_{p,i}$ and n_p from Eqs. (6)–(7), leads to a new set of equilibrium volume fractions of the remaining free monomers n_1, n_2 and n_3 . As a result of the chemical potential equilibrium, monomers with larger reactivities diffuse from the low light intensity regions to the high light intensity regions, and monomers with lower reactivities diffuse in the opposite direction. The number of segments v_i also play a role, which represents the size of the monomer and its flow mobility inside the mesogenic blend. Monomers with smaller number of segments feature fast mobility and flow easier.

The whole polymerization and diffusion process can be simulated by starting from the status updated above and repeating equations (3)–(8), in which further portions of the free monomers are converted to the polymer skeleton. This sequential polymerization step depends on the remaining free monomer concentrations, and a further diffusion step follows to reach a new thermodynamic equilibrium. The whole process is summarized in a calculation flow chart (Fig. S1) and (a simple demonstration (Figs. S2–S3) is added for clarity.

The calculation of the photo-polymerization and monomer diffusion are continued step-by-step as described above until a threshold polymer conversion level is reached for the total polymeric fraction n_p (a cut-off of 95% is used here, see Fig. S4), after which all the remaining free monomers are converted into the polymer instantaneously without any further diffusion. The polymer conversion step size Δ_p from Eq. (4), should be sufficiently small to obtain accurate, converged results (see Fig. S4).

It is good to emphasize that the polymerization light intensity profile constantly changes due to the diffusion of the azobenzene. The light is more attenuated at positions where the local azobenzene concentration increases, leading to a steeper intensity gradient (see Section 2.2). This effect is expected to further enhance the diffusion. The light used for the polymerization can be diffuse or polarized and it can be locally or flood exposed. In addition, the wavelength λ^p can be adjusted to accommodate the film geometry, providing multiple ways of tuning the photo-polymerization diffusion process in order to modify the final light-activated topographical changes.

2.2. Light penetration model

The light penetration problem is different for the two types of light used in this study: the actuation UV light which triggers photo-induced surface deformation, and the photo-polymerization initiation light which introduces non-uniform polymerization rates and monomer diffusion.

As for the actuation light, a nonlinear light penetration model developed in our previous work (Liu et al., 2015; Liu and Onck, 2018) based on the work of (Corbett and Warner, 2007; 2008a), which accounts for the photo-bleaching effect due to the *trans*-to-*cis* isomerization, is adopted here and summarized below.

The incoming light with a input intensity of I^0 propagates along the negative direction of the z -axis from the top surface and the governing equations for the evolution of the reduced light intensity, $\mathcal{I} = I/I^0$, where I is the local light intensity, and the azobenzene isomers read

$$\tau \frac{\partial n_t}{\partial t} = (1 + \beta \zeta \mathcal{I}(z, t)) - [1 + (\alpha + \beta) \zeta \mathcal{I}(z, t)] n_t(z, t), \quad (9)$$

$$\frac{\partial \mathcal{I}}{\partial z} = \left[\left(\frac{1}{d_t} - \frac{1}{d_c} \right) n_t(z, t) + \frac{1}{d_c} \right] \zeta \mathcal{I}(z, t), \quad (10)$$

where n_t and $n_c = 1 - n_t$ are the volume fractions of the *trans* and *cis* azobenzene, respectively, and τ is the average lifetime of *cis* which depends on the ambient temperature. The dimensionless coefficients α and β quantify the ability of the incoming light to prompt azobenzene forward *trans*-to-*cis* reactions and *cis*-to-*trans* back-reactions, respectively. Furthermore, d_t and d_c are the attenuation lengths of the *trans* and *cis* molecules, and are related to the ratio of the quantum efficiencies η by $d_t/d_c = \beta\eta/\alpha$. Here, we adopt the previously used value (Knežević et al., 2013; Liu et al., 2015), $\eta = 3$.

The polarization coefficient ζ is defined in Eq. (11) below for polarized light illumination (Corbett and Warner, 2008b; Liu et al., 2018) and in Eq. (12) for diffuse light (Corbett and Warner, 2008b; Liu et al., 2015):

$$\zeta = \frac{1}{3} [2SP_2(\cos \phi) + 1], \quad (11)$$

$$\zeta = \frac{1}{3} [1 - SP_2(\cos \phi)]. \quad (12)$$

The function P_2 is defined as $P_2(x) = (3x^2 - 1)/2$ and ϕ is the angle between the local director and the electric field of the incoming polarized light $\vec{E}$ in Eq. (11) and the angle between the director and the propagating direction of the diffuse light in Eq. (12). S is the scalar order parameter, with typical values for glassy LC polymers between 0.5 and 0.8. (White and Broer, 2015; Zhao and Ikeda, 2009) We assume that the order parameter is not disturbed in the process of diffusion, and we take it is independent of the monomer ratio by choosing $S = 0.8$ in our simulations.

We focus only on the photo-stationary state, where the forward-reaction rate equals that of the back-reaction and the volume fractions of the azobenzene isomers become stable. By assuming a photo-stationary state, we can apply $\partial n_t / \partial t = 0$, and substitute this into Eq. (9) to obtain:

$$n_t(z) = \frac{1 + \beta \zeta \mathcal{I}(z)}{1 + (\alpha + \beta) \zeta \mathcal{I}(z)}. \quad (13)$$

By substituting Eq. (13) back into Eq. (10), a solution for $\mathcal{I}(z)$ is obtained using the boundary condition at the top surface, $\mathcal{I}(w) = 1$. Then n_t can be obtained from Eq. 13 and $n_c = 1 - n_t$.

For the photo-polymerization diffusion process, azobenzene molecules serve as dyes, and the wavelength of the incoming light is chosen inside the effective absorption spectrum of the naturally-stable *trans* azobenzene ($\sim 325 - 410$ nm) (Liu and Broer, 2015). The light intensity is assumed to be low in order to avoid premature isomerization in the polymerization step (Liu et al., 2015; van Oosten et al., 2009; 2008) so that we can ignore the absorption of the photo-initiator azobenzene. The light profile of the polymerization light is considered to be a deteriorated form derived from equations (9)–(10), in which we assume $\alpha \approx 0$ and $\beta \approx 0$ due to the absence of isomerization, and the solution reduces to the Beer-Lambert Law,

$$\mathcal{I}_p = I_p/I_p^0 = e^{\zeta(z-w)/d_p}, \quad (14)$$

where d_p is the attenuation length which depends on the wavelength of the polymerization light.

The two attenuation lengths, d_t and d_p , are dependent on the local concentration of the azobenzene. We assume that they are inversely proportional to the total volume fraction of azobenzene (Marshall and Terentjev, 2013; van Oosten et al., 2008),

$$\frac{d_t}{d_t^0} = \frac{n_{azo}^0}{n_{azo}}, \quad \frac{d_p}{d_p^0} = \frac{n_{azo}^0}{n_{azo}}. \quad (15)$$

Here, d_t^0 and d_p^0 are the attenuation lengths for the original azobenzene concentration without any diffusion, n_{azo}^0 . The local instantaneous azobenzene concentration at each polymerization-diffusion step, $n_{azo} = n_3 + n_{p,3}$, consists of the local free monomeric and polymeric contribution. Due to the diffusion of the azobenzene in each diffusion step, d_p is updated and the intensity field is also updated for the next polymerization step (Eqs. (4) and (14)). The final azobenzene concentration field after the whole polymerization-diffusion process (i.e., when the whole LC mixture is converted to a polymeric solid) affects the local d_t (in Eq. (10)) and influences the local *trans*-to-*cis* isomerization level. Since the polymerization light gradient can be tuned by changing the wavelength λ^p , here we take $d_p^0 = d_t^0$ or $d_p^0 = 2d_t^0$ depending on the tested film thickness in Section 3. The exact attenuation length as a function of the wavelength can be obtained by interpolating experimentally-calibrated values based on the azobenzene absorption spectrum (Liu and Onck, 2017b).

2.3. Constitutive model

The monomer diffusion in Section 2.1 and the UV-triggered azobenzene isomerization in Section 2.2 are employed here to evaluate the material non-homogeneity and predict the topographical switching of polymer films.

The total strain components with respect to the local reference frame (defined by the local director in Fig. 1(b)) can be written as

$$\varepsilon_{ij} = \varepsilon_{ij}^e + \varepsilon_{ij}^{\text{ph}}, \quad (16)$$

with ε_{ij}^e , ε_{ij}^e and $\varepsilon_{ij}^{\text{ph}}$ the elastic strains and the photo-induced spontaneous strains, respectively. The elastic strain tensor is linearly correlated to the stress tensor by assuming a linear elastic response for the glassy LC polymer under UV actuation,

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl}^e = C_{ijkl} (\varepsilon_{kl} - \varepsilon_{kl}^{\text{ph}}), \quad (17)$$

where C_{ijkl} are the components of the elastic stiffness tensor. The liquid crystal polymer is taken as a transversely isotropic material, which has five independent elastic properties: the Young's modulus along the director E_{11} , the transverse moduli $E_{22} = E_{33}$, the Poisson's ratios $\mu_{12} = \mu_{13}$ and μ_{23} , and the shear moduli parallel to the director $G_{12} = G_{13}$.

Gradients of the material elastic properties are introduced if the concentration ratio between the polymerized diacrylate and monoacrylate is varying. Due to the double crosslinking feature of diacrylates, regions with a higher volume fraction of diacrylates have higher moduli (Elias et al., 2006; Lee et al., 2010; 2012; Shimamura et al., 2011). Based on literature values for the change in moduli (see Fig. S5 in SI), we assume that the Young's moduli scale with the concentration of the diacrylates:

$$\frac{E_{11}}{E_{11}^0} = \frac{n_{\text{di}}}{n_{\text{di}}^0}, \quad \frac{E_{22}}{E_{22}^0} = \frac{E_{33}}{E_{33}^0} = \frac{n_{\text{di}}}{n_{\text{di}}^0}, \quad (18)$$

where E_{11}^0 , E_{22}^0 and E_{33}^0 are the Young's moduli at the original diacrylate concentration n_{di}^0 without diffusion. Furthermore, the local n_{di} consists of monomeric and polymeric contributions, $n_{\text{di}} = n_1 + n_{\text{p},1}$. Since only the final polymeric network where diffusion is finished and all monomers are depleted ($[n_1]_{t=t_{\text{end}}} = 0$) is under consideration, $[n_{\text{di}}]_{t=t_{\text{end}}} = [n_{\text{p},1}]_{t=t_{\text{end}}}$ is substituted in Eq. (18) to evaluate the local moduli. An anisotropic $E_{11}^0 = 2E_{22}^0$ is taken as in our previous study (Liu et al., 2015). We assume that the acrylate concentration changes have no effect on the Poisson's ratio and we take $\mu_{12} = \mu_{13} = \mu_{23} = 0.3$ throughout the film (Liu et al., 2015). The independent shear moduli are thus calculated through $G_{12} = G_{13} = E_{11}/(2(1 + \mu_{12}))$. Here we ignore any influence from the diffusion of azobenzenes and assume the stiffness is only dependent on the concentration of acrylates.

The spontaneous photo-induced strains $\varepsilon_{ij}^{\text{ph}}$ are assumed to be linearly proportional to the volume fraction of *cis* molecules as Knežević et al. (2013); Liu et al. (2015); Liu and Onck (2018); van Oosten et al. (2008)

$$\varepsilon_{ij}^{\text{ph}} = P_{ij} n_{\text{c}}. \quad (19)$$

The non-zero components of P_{ij} with respect to the local coordinate axes are P_{11} and $P_{22} = P_{33}$, corresponding to the light-induced contraction and expansions along and perpendicular to the director, respectively.

The photo-induced response of LC polymers is found to be inversely correlated to the crosslinking density (which is assumed to be proportional to the concentration of diacrylates here) in heavily crosslinked systems since a rigid network prohibits cooperative polymer chain movements due to the isomerization of the embedded azobenzenes (Hamed et al., 2017; Lee et al., 2010; 2012; van Oosten et al., 2008). On the other hand, the crosslinking level should not be too small in order to provide sufficient network linkage to transfer the molecular disturbance due to the *trans*-to-*cis* isomerization to the macroscopic polymer deformation (Elias et al., 2006). Also the total concentration of azobenzene molecules affects the photo-responsivity, since a higher concentration triggers an increased absolute amount of *cis* isomers upon isomerization (Lee et al., 2012; van Oosten et al., 2008; Sánchez-Ferrer and Finkelmann, 2013; Van Oosten et al., 2007; Wang et al., 2011; White et al., 2009) (see experimental data in Fig. S6). For the current system, we assume

$$\frac{P_{11}}{P_{11}^0} = \frac{n_{\text{azo}}}{n_{\text{azo}}^0} \frac{n_{\text{di}}^0}{n_{\text{di}}}, \quad \frac{P_{22}}{P_{22}^0} = \frac{P_{33}}{P_{33}^0} = \frac{n_{\text{azo}}}{n_{\text{azo}}^0} \frac{n_{\text{di}}^0}{n_{\text{di}}}, \quad (20)$$

with $P_{11}^0 = -0.2$ and $P_{22}^0 = 0.2$ (Liu et al., 2018).

It should be noted that the linear dependencies of the moduli, Eq. (18), and the photo-responsivities, Eq. (20), upon the variation of monomer concentration are simplified relations for the complex molecular cooperative behavior of the polymer's load-carrying ability and the spontaneous deformations. The final stiffnesses and photo-responsivities feature spatial variations depending on the intrinsic reactivity of each monomer, R_i , the number of monomer segments, ν_i , the selection of the wavelength of the polymerization initiation light which determines d_{p} and the director distribution. The latter two determine the nonuniform light field to prompt different polymerization rates at different locations.

Distinct material gradients can be constructed by assuming different monomer reactivities R_i and monomer size properties ν_i . In addition, various polymerization light intensity gradients can be introduced by choosing different attenuation

Table 1
The reactivity and number of segments of the three monomers.

Case	diacrylate		monoacrylate		azobenzene	
	R_1	ν_1	R_2	ν_2	R_3	ν_3
I	2	1	1	1	2	1
II	2	1	1	1	1	1
III	2	1	1	1	4	1

lengths d_p^0 (see Eqs. (14) and (15)). According to the final effect on the photo-responsivity parameters, several specific scenarios are considered here, as summarized in Table 1. See also Section 3 for details.

The framework above is supplemented by stress equilibrium equations and kinematic equations, and is numerically implemented with various boundary conditions in the commercially available finite element package Abaqus / Standard (Hibbett et al., 1998). Stresses develop during the interplay between the mismatch of spontaneous deformations, the anisotropy of the material and the constraints imposed by the different boundary conditions and will reshape the final topographical texture.

3. Results

Three examples showing the effect of internal material gradients resulting from the diffusion process during polymerization on topographical changes are elaborated in this section: bending and twisting of cantilevers (3.1), topographical undulations (3.2) and travelling waves (3.3). We will use various combinations of film geometries, director distributions, light illumination during polymerization and actuation light configurations. Before going to these examples, we will first look in detail into three characteristic diffusion schemes.

The original monomer concentrations in the LC mesogens blend before polymerization is set as $n_{di}^0 = 0.5$, $n_{mo}^0 = 0.45$ and $n_{azo}^0 = 0.05$, which is a typical composition for light responsive liquid crystal polymers (White and Broer, 2015). Here we ignore the small concentration of the photo-initiator as aforementioned. The reactivity of the diacrylate mesogen is taken to be twice that of the monoacrylate due to the double ends available for cross-linking. The reactivity of the azobenzene depends on the number of reactive ends, i.e., two for the crosslinker-type (e.g., A3MA (Lee et al., 2010; 2011; Liu and Broer, 2015; Liu et al., 2015)), and one for the pendant-type (Cheng et al., 2012; Lee et al., 2012; van Oosten et al., 2009). Moreover, it was found that the bi-functional methacrylate azobenzene features a higher reaction rate than diacrylate LC monomers (van Oosten et al., 2008). Thus in this work, we design several diffusion schemes, from which distinct material gradients are generated, by altering the reactivity of the azobenzene monomer.

As given in Table 1, we focus on several combinations of reactivity and size properties. For Case-I, the reactivities of the diacrylate and azobenzene are assumed to be identical and twice that of the monoacrylate, leading to both the diacrylate and azobenzene molecules diffusing to regions with higher polymerization light intensities. Thus only a stiffness gradient is created (Eq. (18)) and no gradient of the light-responsivity parameter (Eq. (20)) exists despite the monomer concentration gradients. For Case-II and Case-III, the reactivity of azobenzenes is taken as a half of and twice that of the diacrylates, respectively, creating P_{ij} gradients upon diffusion. In Case-II, the diffusion direction of azobenzenes is opposite to that of diacrylates so that regions with higher polymerization light intensities feature higher moduli E_{ij} but have lower responsivities. For Case-III, the diffusion of azobenzenes is stronger than that of diacrylates and regions with higher moduli also have higher responsivities, in contrast to the result of Case-II.

For all the three diffusion schemes above, the size properties are assumed to be the same for all the three monomers and thus the diffusion is purely determined by the difference of the reactivity parameters. However, by fixing the ratios between the reactivities and only varying the sizes, i.e., changing the monomer mobilities, different diffusion states can also be triggered. The sizes of the LC mesogens can be altered, e.g., by changing the spacer length (Liu and Broer, 2014a), or via oligomerization of the concatenated acrylates (McBride et al., 2017). The schemes with varied monomer sizes are found to create similar material property gradients compared to the cases in which only the reactivities are different (as shown by the Case-VI and -V in Table. S1 and the results in Fig. S12 in SI). Thus we mainly focus on the three schemes of Table 1 in this study.

3.1. Bending and twisting of cantilever films

The first example considers liquid crystal polymer folding, which is the most studied topographical switching motion (White and Broer, 2015). Upon light actuation, a deformation gradient is created through the thickness, due to the light penetration and the resulting *trans*-to-*cis* level varying along the thickness, or due to the varying director through the thickness. This folding mechanism can either be pure bending or twisting motions depending on the director orientation with respect to the long-axis of the cantilever. This also affects the folding orientation, i.e., bending towards or away from the light source, and right-handed or left-handed twisting. Here we take a uniform director being parallel to the long-axis for the bending motion and $+15^\circ$ misaligned from the long-axis for the twisting case.

Fig. 2. Through-thickness distributions as a result of polymerization-diffusion (a–d) and actuation (e–f) for films with uniform in-plane director alignment for Cases-I, II and III and for the situation without diffusion. The films are subjected to flood exposure by a diffuse light source.

A diffuse light source is used to create one-dimensional (i.e., through the thickness) material gradients, and the actuation light is also diffuse. We take the thickness of the cantilever $w/d_t^0 = 10$ and the attenuation length of the polymerization light $d_p^0 = 2d_t^0$, meaning that the wavelength of the polymerization light is shifted slightly away from that of the actuation light. For the actuation light parameters, we take $\alpha = 10\beta = 30$ to make a *cis* conversion gradient through the thickness (Liu and Onck, 2018). Note that the monomer diffusion of the cantilevers for bending and twisting motions are identical since their directors are both perpendicular to the propagating direction of the polymerization light.

The gradient of the polymerization light $\mathcal{I}_p = I_p/I_p^0$, and the diffusion of the diacrylate and azobenzene monomers are shown in Figs. 2(a)–(c) for Case-I, II and III together with the case without considering the diffusion. The intensity profiles are different due to the fact that the diffusion of the azobenzenes affects the penetration (Eqs. (14)–(15)). For example, azobenzenes are driven to flow toward the top surface for Case-I and III, leading to a stronger absorption of the polymerization light near the top surface and the fast decrease of the intensity. In contrast, near the bottom region where the azobenzene concentration is smaller, the light is less absorbed and the decrease in intensity is smaller. The stiffness gradient is a direct result of the diffusion of n_{di}/n_{di}^0 in Fig. 2(b), for which the maximal relative concentration change of 30% between the top and bottom corresponds to the measured values in similar systems (van Nostrum et al., 1998; van Oosten et al., 2008). The final effect from the polymerization-induced diffusion on the photo-responsivity parameters is shown in Fig. 2(d). The effects of the diacrylate and azobenzene cancel out for Case-I, and are opposite for Case-II and III: the top region features a higher responsivity in Case-III due to the stronger diffusion of the azobenzenes over that of the diacrylates, while for Case-II this is exactly the other way around (stronger diffusion of diacrylate than that of azobenzene). Figs. 2(e)–(f) show the light penetration of the actuation light and the photo-stationary *cis* conversion level, respectively, which are also influenced by the diffusion of azobenzenes.

For the simulations of cantilever bending, we assume a plane-strain condition along the *y*-axis to suppress the anti-clastic effect (Warner et al., 2010a; 2010b) and take $L/w = 10$. The bending results of the three diffusion schemes are shown in Fig. 3, together with that of the reference case without considering diffusion. The Case-I bending motion, in which only a stiffness gradient is introduced, is found to be close to the situation in which no polymerization diffusion occurs. The photo-induced strain is close to that without diffusion due to the minor difference on n_c field and the unchanged P_{ij} . Despite the stiffness gradient, the generated stress due to the discrepancy between the photo-induced strain and the effective bending strain, which is linear through the thickness, shows only a minor difference compared to the no-diffusion case (see Fig. 4).

The deflections of diffusion Cases-II and III, in which additional gradients of the photo-responsivity are incorporated, are substantially differentiated from that of Case-I in terms of bending magnitude and orientation. The Case-II film bends away from the light source, which correlates with the experimental observation (van Oosten et al., 2008), i.e., the bending curvature $\kappa = -0.034$ (curvature is positive when the beam bends towards to the light source). The increased photo-responsivity near the bottom region gives rise to a larger spontaneous contraction locally (see Fig. 4), overcoming the contraction at the top region, and results in a sign change of the bending curvature. The film of Case-III bends towards the light source more strongly than Case-I ($\kappa = 0.110$), attributed to the collaborative effect of the P_{ij} gradient (Fig. 2(d)) and the stiffness gradient (Fig. 2(b)). Here the former makes the top region contract more and the latter makes the top part stiffer.

Fig. 3. The cantilever bending curves for various diffusion schemes. Here, κ is the bending curvature, which is positive when it bends towards the light source.

Fig. 4. The photo-induced spontaneous strain, the final strain and the final stress along the long-axis direction, (a) $\varepsilon_{xx}^{\text{ph}}$, (b) ε_{xx} and (c) σ_{xx} , through the thickness of the bending films for the diffusion schemes given in Fig. 2.

Fig. 5. The formation of springs of films with the directors $+15^\circ$ misaligned with respect to the cantilever long-axis subject to different diffusion schemes. The result of Case-I is similar to that of the no-diffusion scheme and is not included here. P is the twisting pitch and r is the spring radius.

For the modelling of twisting motions, we take a film of length $L/w = 500$ and a width along the y -axis of $10w$. For the specific photo-responsivity parameters used in this study ($P_{11}^0 = -P_{22}^0 = -0.2$), a $+15^\circ$ misalignment between the director and the cantilever long-axis is chosen to show spring formation (see Fig. 5). For a cantilever with the director $\pm 45^\circ$ misaligned, the film is found to have an axial twisting behavior (see Fig. 6), due to the equal magnitude of the photo-responsivity parameters parallel and perpendicular to the director and thus a pure shear spontaneous strain in the $x - y$ plane. The 3D spring formation of the $+15^\circ$ misaligned samples is shown in Fig. 5, with spring characteristic geometries, the twisting pitch P and the spring radius r (see reference (Enkhbayar et al., 2008) for the algorithm to obtain P and r). Similar to the bending motion, the twist is stronger for the Case-III scheme, featuring a decrease of both the spring radius and pitch. The twist motion of Case-II indicates a change in the sign of the handedness due to the reversed deformation gradient. This

Fig. 6. The formation of axial twisting of free standing films with the director 45° misaligned with respect to the beam long-axis. The twisting formation of Case-I scheme is close to the “no diffusion” scheme and is omitted here.

Fig. 7. Schematics of the unit cells of the two patterned films, (a) the cholesteric/homeotropic film under flood exposure and (b) the uniform cholesteric film under local exposure. Both the polymerization and actuation light sources have similar illumination configurations.

handedness reversion is due to the monomer diffusion and composition change, gives another way to biologically mimic the helix perversion phenomenon in plant tendrils (Godinho et al., 2010; Silva et al., 2017), rather than having director alignment changes located at perversions (Iamsaard et al., 2014).

The above predictions show a considerable effect from the material gradients resulting from the monomer diffusion. The photo-responsivity gradient plays a more significant role than the stiffness gradient in the final morphology modulation. Note that we ignore any light reflection due to the obliquity of the bending (Cheng et al., 2012) or any light blocking (Lee et al., 2011) during the spring formation since the effect of the diffusion-induced material gradients are the focus of the current work.

Other director distributions were selected as well to trigger twisting and bending motions. Beside the uniform director mis-aligned to the long-axis (Lee et al., 2011; Smith et al., 2014; Wang et al., 2012) (as shown in Fig. 5), twisted nematic geometries with their mid-plane directors mis-aligned to the long-axis were fabricated and simulated (Harris et al., 2005; Iamsaard et al., 2014; 2016; Sawa et al., 2011; Wie et al., 2013; 2015; 2016). A twisted nematic configuration with the top surface director aligning along the long-axis and with the bottom surface perpendicular to the long-axis considerably enhances the bending deflection (Harris et al., 2005; Modes et al., 2010; Smith et al., 2014; Van Oosten et al., 2007). The diffusion process in such twisted nematic configurations is the same as in the uniform director film since the directors are all inside the $x - y$ plane. However, the final effect of the diffusion of the twisted nematic films on the bending motion is limited (see Fig. S7), due to the fact that both the top and the bottom regions are contributing together to bend the cantilever towards the light source and a change of the curvature sign is not observed. Similar effects hold for the twisting motion (results not shown).

3.2. Patterned films

The second example is the surface topography change of alternately patterned films. The patterned films were fabricated and found to generate corrugated surface textures (Liu et al., 2012a; 2012b), and were successfully simulated for uniform material properties (Liu and Onck, 2018). The director distribution of the unit cells of the two patterned films studied here are shown in Fig. 7, i.e., the cholesteric/homeotropic film under flood exposure (Liu et al., 2012b) and the uniform cholesteric film under masked exposure (Liu et al., 2012a). The surface texture change of the former film relies on the anisotropy of the photo-induced spontaneous deformation, i.e., expansion along the z -axis for the cholesteric phase and contraction of the homeotropic phase. The latter film relies on the masked illumination to trigger localized expansions.

Fig. 8. Through-thickness distributions as a result of polymerization (a–d) and actuation (e–f) for films with cholesteric (black) and homeotropic (blue) director distributions for Cases-I, II and III and for the situation without diffusion. The films are subjected to flood exposure by a diffuse light source. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

If we assume that the polymerization initiation light follows the configuration of the actuation light, the diffusion process can be triggered not only through the thickness direction in each constituent region but also between the two phases. For the cholesteric/homeotropic film, due to the difference of the effective light absorption by the azo-dyes resulting from the two director alignments, the polymerization light is less attenuated in the homeotropic region and monomers with larger reactivities are expected to flow from the cholesteric part to the homeotropic part. For the uniform cholesteric film, the localized illumination gives rise to diffusion of higher reactivity monomers towards the exposed region. In the experiment (Liu et al., 2012b), the cholesteric/homeotropic film was polymerized via a single-step in situ photo-polymerization, which correlates with the diffusion strategy mentioned above. For the uniform cholesteric film, we assume the exposed region is first polymerized and the diffusion process is complete. A second fast polymerization is given thereupon for the un-exposed region in the first step without introducing any other diffusion.

Here we assume that the flow of the monomers does not affect the director alignment. We ignore the concentration of the chiral dopant, which is responsible for the rotating pattern of the directors in the cholesteric phase. However, the pitch length, L_{pt} (see Fig. 7), defined as the length over which the director makes a full 360° rotation, might be influenced by the diffusion (Broer et al., 1995; 1999). However, we found that (Liu and Onck, 2017a), as long as the number of pitches along the thickness ≥ 4 , the light-triggered surface topography is stable and is independent of the number of pitches and the starting angle at the bottom (Liu and Onck, 2017a; 2018). Therefore, we ignore any change of the pitch length and take $w/L_{pt} = 4$. For the other geometric variables, we take $L/w = 4$ and $L_1 = L_2$. The film thickness is set as $w/d_t^0 = 10$ and $d_p^0 = 2d_t^0$. We take $\alpha = 10\beta = 30$ for the actuation light, and diffuse light sources are used both for the polymerization and actuation. Periodic boundary conditions are applied at all the lateral surfaces of the unit cells, the bottom surface is fixed and the top surface is free of traction.

The results of the polymerization diffusion and the isomerization level of the cholesteric/homeotropic film is shown for the two regions in Fig. 8. Attributed to the polymerization light profile (Fig. 8(a)), the diacrylates flow from the cholesteric to the homeotropic region, and simultaneously flow from the bottom to the top. The flow of the azobenzenes and the relative change of the photo-responsivity parameters depend on the diffusion scheme. A distinct difference between the diffusion of the patterned film, Fig. 8(a)–(d), and that of the uniform director cantilever, Fig. 2(a)–(d), is that the monomer total concentration is no longer conserved inside each phase, indicating the presence of bulk monomer migrations between the two phases. This monomer exchange strongly influences the actuation light penetration and the *cis* conversion (Fig. 8(e)–(f)). For example, the isomerization level inside the bottom region of the cholesteric phase is noticeably smaller for Case-II due to the azobenzenes migration towards this region and thus a decrease of the attenuation length (Eq. (14)).

The light-triggered topographical changes of the two films are shown in Fig. 9. The exchange of monomers and the modification of the photo-responsivity alter the surface profiles. For the cholesteric/homeotropic film, an increase of P_{ij} in one constituent region gives rise to a larger out-of-plane expansion or contraction, at a cost of a decrease of the deformation in the other region. The average effect of Case-II and III diffusion is the change of the position of the mean plane of the deformed surface relative to the no diffusion scheme. As for the uniform cholesteric under localized polymerization and actuation, different surface profile alterations can be achieved by setting the polymerization light exposure pattern to be the

Fig. 9. The normalized surface profiles of (a) the cholesteric/homeotropic film and (b) the uniform cholesteric film. The blues lines in (b) are for the case in which the polymerization light is exposed differently with the actuation light: the polymerization light is exposed onto the left half part while the actuation light is exposed onto the right half part.

Fig. 10. A schematic of a film featuring travelling-wave surface deformations actuated by a rotating polarized light source ($\vec{E}^a$). A similar polarized source is selected for the polymerization ($\vec{E}^p$) and diffusion process to create two-dimensional gradients in material properties. (a)–(b) The directors in the film are uniform throughout the thickness and gradually rotate 180° along the x -axis. (c) The generation of a travelling wave due to a rotating actuation polarized light source. The direction of travelling wave is indicated by the horizontal arrow. The wave is depicted by four consecutive snapshots in time, each corresponding to a specific orientation of the electric field ($\vec{E}^a$) in the plane (right). The figures are adopted and modified from (Liu et al., 2018).

same or opposite to the actuation light configuration. The black lines in Fig. 9(b) corresponds to the surface change when both the polymerization light and actuation light are exposed upon the left half region. While the blue lines are for the results when the polymerization light is still exposed upon the left region but the actuation light is exposed upon the right half. A rougher surface texture can be obtained when the region with a higher photo-responsivity (i.e., the exposed region in the Case-III scheme or the un-exposed region in the Case-II scheme, see Fig.S8 in SI) is actuated. By appropriately designing the polymerization and the actuation configurations and taking advantage of the monomer migrations, an increase of the UV-triggered surface undulation can be achieved. The effect of Case-I diffusion is small, similar to the result in Section 3.1.

3.3. Surface travelling wave

The final example is a film featuring travelling-wave surface deformations (Liu et al., 2018), for which the director distribution of a unit cell is shown in Fig. 10. The directors are gradually rotating in the $x - y$ plane to have a 180° rotation and the film is exposed to a rotating polarized light source (so that the electric field $\vec{E}^a$ rotates in the $x - y$ plane). The regions where the local directors are parallel to the electric field of the actuation light have a maximal *trans*-to-*cis* conversion (see Fig. 11(f), infra vide) and thus have the largest expansion through the thickness. Under a continuous rotation of the polarized actuation light, different regions are sequentially activated most and a travelling surface wave is formed with its propagating direction controlled by the rotation direction of the polarized light, e.g., the wave propagates towards the positive x -axis direction if the actuation light rotation is counter-clockwise in the $x - y$ plane, see Fig. 10.

Fig. 11. (a) Attenuation of the polymerization light intensity at an angle $\psi^p = 90^\circ$. (b)–(d) Distribution of the volume fraction of diacrylate (b), azobenzene (c) and the associated photo-responsivities (d). (e) Attenuation of the actuation light intensity at an angle $\psi^a = 90^\circ$. (f)–(g) Distribution of the volume fraction of isomerized azobenzenes at $\psi^a = 0^\circ$ (f), 45° (g) and 90° (h). These results are based on the Case-II scheme.

Compared to the one-dimensional diffusion (i.e., through the thickness) in Section 3.1 and the bi-phase diffusion in Section 3.2, here the diffusion can be two-dimensional if a polarized light source is used for polymerization. Linear polarized light has been combined with a dichroic radical photoinitiator to generate polarization selective polymerization (Broer et al., 1999; van den Heuvel et al., 2009; Seki, 2016; Van et al., 2014; Yamaoka et al., 2015). By taking advantage of the varying director distribution in the plane of the film, one obtains another handle of tuning the material property gradients. Upon using a polarized polymerization light, the region where the local director is parallel to the electric field $\vec{E}^p$ attenuates the light more strongly, and monomers with higher reactivities are subject to diffusion towards the region with the director being perpendicular to $\vec{E}^p$. By choosing different polarization directions of the polymerization light, one can create a complex diffusion field and two-dimensional gradients in material properties.

A successful generation of the travelling wave relies on a careful selection of the thickness and the input intensity of the actuation light (Liu et al., 2018). Here we follow our previous study and take $\alpha = 10\beta = 5$ and a thickness of $w/d_t^0 = 2$. Such a small thickness and an intermediate light intensity can maximize the difference of the *cis* generation between the regions with orthogonal director and thus maximize the wave amplitude (Liu et al., 2018). The attenuation length of the polymerization light is decreased here (compared to the previous examples), $d_p^0 = d_t^0$, in order to introduce a sufficient intensity gradient for diffusion in this thin film. This means we use 365 nm light for both the polymerization and actuation. The in-plane gradient in director orientation is found to influence the wave formation (Liu et al., 2018); here we follow our previous work and take $L/w = 4$. Periodic boundary conditions are used for all the lateral surfaces of the tested unit cell shown in Fig. 10.

An exemplary two-dimensional diffusion result is shown in Fig. 11(a)–(d) for the Case-II polymerization scheme with the polarized polymerization light oriented along the *y*-axis, $\psi^p = 90^\circ$. Under this polarization status, the center region of the unit cell, in which the director is perpendicular to $\vec{E}^p$, has a higher polymerization light intensity (see Fig. 11), and thus the high-reactivity monomer (i.e., only the diacrylate for Case-II) flows to this region. The azobenzenes flow in the direction opposite to that of diacrylates due to the lower reactivities, which results in a larger P_{ij} at the boundary regions. Due to the continuous change of the angle between the local director and the electric field of the input polarized polymerization light, the monomer concentrations are also gradually changing inside the film in two dimensions.

After the material gradients are imprinted, a rotating polarized actuation light is exposed to trigger travelling waves. The light penetration and the isomerization level for one polarization angle, $\psi^a = 90^\circ$, is shown in Fig. 11(e)–(f), respectively. The corresponding surface deformations under various polarization directions, e.g., $\psi^a = 0^\circ, 45^\circ, 90^\circ, 135^\circ$ and 180° , are plotted

Fig. 12. The normalized surface profiles under a rotating polarized actuation light source for $\psi^a = 0^\circ, 45^\circ, 90^\circ, 135^\circ$ and 180° . (a) Without diffusion, and incorporating Case-II diffusion with (b) $\psi^P = 0^\circ$ and (c) 90° .

Fig. 13. Influence of the material property gradients on the modulation normalized by the thickness of the film for two polarization directions of the polymerization light: $\psi^P = 0^\circ$ and 90° .

in Fig. 12 for the case without diffusion and the Case-II scheme using $\psi^P = 0^\circ$ or 90° . As shown by the movement of the surface protrusion, the travelling wave is successfully formed and guided by the polarized actuation light.

In Fig. 12(a) in which no material gradient exists, the amplitude of the surface change is highest at $\psi^a = 0^\circ$ (or 180°) and lowest at $\psi^a = 90^\circ$. This is attributed to the original stiffness variation along the x -axis. Due to the rotation of the director, the modulus along the x -axis is highest at the center region and lowest at the boundary region. Upon the rotation of $\vec{E}^a$, an identical *cis* conversion level is reached once the local director is perpendicular electric field since there is no diffusion of azobenzenes, and thus the spontaneous deformation is also the same. Therefore the surface deformation is only influenced by the varying modulus, and the lower modulus region is subjected to stronger suppression from the neighboring stiffer regions and thus has a smaller out-of-plane expansion.

We introduce a roughness parameter to quantify the topography. The “modulation” (Liu and Broer, 2014b; Liu and Onck, 2018), which is the vertical distance between the highest and lowest point, is plotted as a function of ψ^a in Fig. 13. The variation of the modulation output indicates a undulatory travelling wave for the no-diffusion condition.

If a material gradient is introduced, the travelling wave characteristics can be tuned by setting different ψ^P . Let us take the Case-II diffusion as an example. If $\psi^P = 0^\circ$, the photo-responsivity is increased at the center region (see the diffusion results in Fig. S9) and dummyTXdummy- its local expansion at $\psi^a = 0^\circ$ is thus enhanced. Moreover, the protrusion height is reduced at $\psi^a = 90^\circ$ (see the blue line in Fig. 12(b)). This leads to a larger modulation variation upon rotation of the actuation polarization angle (Fig. 13). A contrary effect can be reached by setting $\psi^P = 90^\circ$. Thanks to the increased P_{ij} at the boundary region (Fig. 11(d)), the protrusion height at $\psi^a = 90^\circ$ increases and is even larger than that at $\psi^a = 0^\circ$ (Fig. 12(c)). As a result, the dependence of the modulation on the actuation light direction is totally reversed compared to the no diffusion case and the $\psi^P = 0^\circ$ scheme (Fig. 13). This large change of the topographical response indicates that the polarization angle of the polymerization light can be adjusted to make the modulation output constant under rotating polarized light, and the resulting surface wave mimics a perfect peristaltic motion (Kim et al., 2013; Palagi et al., 2016).

For the Case-III scheme, the same effect can be reached by swapping the selection of polymerization polarized light direction, i.e., using $\psi^P = 0^\circ$ (see monomer distributions in Fig. S10) to reverse the dependence of the modulation (like Case-II, $\psi^P = 90^\circ$), and using $\psi^P = 90^\circ$ (see monomer distributions in Fig. S11) to enhance the modulation variation (like Case-II,

$\psi^P = 0^\circ$). This gives flexibility so that no matter which final diffusion scheme is valid for the real monomer composition in the experimental implementation, there is always a feasible method to adjust the modulation output. If only the stiffness gradient is introduced, the effect on the topography is limited, similar to the results in Sections 3.1–3.2.

4. Discussion and conclusions

In this paper, we have demonstrated how to account for diffusion of LC monomers and azobenzene during photo-polymerization of liquid crystal polymers and achieve various topographical modulations. By selecting different combinations of LC monomers and azobenzenes, i.e., diacrylates and monoacrylate LC mesogens, and single-ended or double-ended azobenzenes, the diffusion direction of the monomers can be controlled, resulting in material property gradients throughout the film.

As an illustration, three diffusion schemes that introduce distinct material property gradients are presented. For the Case-I diffusion scheme, diacrylates and azobenzenes diffuse to the region with higher polymerization light intensities and thus only stiffness gradients are created. For the Case-II and Case-III schemes, by selecting different azobenzene molecules with low (Case-II) or high (Case-III) reactivities, gradients of opto-responsivity are embedded: higher opto-responsivity regions are located at areas where there is a higher concentration of azobenzene.

To demonstrate the feasibility of topographical modulations via diffusion, cantilever bending and twisting (Section 3.1), surface changes of substrate-constrained patterned films (Section 3.2) and travelling-wave films (Section 3.3) are analyzed. By introducing diffusion and material gradients, the photo-induced bending curvature and spring helix can either be enhanced or reversed (see Figs. 3 and 5), depending on the diffusion scheme. Also, the actuated corrugation profile of patterned films (see Fig. 9) and travelling wave characteristics (see Fig. 12 and 13) can be tailored by modifying the diffusion scheme.

In addition to selecting monomer concentrations to achieve different diffusion schemes, there are several other ways to make use of polymerization-induced diffusion. For instance, by changing the wavelength of the polymerization light (i.e., changing the attenuation length d_p^0), the level of the polymerization light intensity gradient can be tuned to adjust the level of monomer diffusion. In addition, the illumination area of polymerization light can be controlled, providing additional flexibility (see Fig. 9(b)). The polymerization light source can either be diffuse or polarized, in order to induce complex diffusion patterns in films with non-uniform director distributions (see Section 3.3). Furthermore, the polarization orientation of the polarized polymerization light source can be designed to tune the local responsivity (see Fig. 13).

The results presented in this paper should always be seen in the light of the assumptions made in the model. We therefore review the main model assumptions in the following and assess their limitations. The thermodynamic equilibrium condition used in Eq. (8), for instance, might be difficult to obtain completely if the polymerization reaction rate is of the same order of magnitude as the monomer diffusion rate. The polymerization reaction rate can be increased by increasing the polymerization light intensity or the temperature, possibly leading to polymerization times in the range from minutes (van Oosten et al., 2008) to hours (Iamsaard et al., 2016). Additionally, incomplete diffusion ensues if the film dimensions are too large so that the monomers, driven by the chemical potential gradient, are captured by the polymer network during diffusion (Leewis et al., 2004a). Moreover, the monomer diffusion rate might drop by a few orders of magnitude when the polymer volume fraction increases and the flow mobility of the monomers decreases in the polymer-mesogen mixture (Wopschall and Pampalona, 1972). One can conduct a diffusion-reaction dynamic study to model such an incomplete diffusion process (Leewis et al., 2004a; 2004b; Sutherland et al., 2004), or simply set a large value for Δ_p to emulate a fast polymerization process (see Fig. S4). Such incomplete diffusion is expected to induce less strong material gradients and thus a smaller effect on the final photo-induced topography.

No order parameter variation and phase separation is considered in this work, because the diffusion of acrylates is too slow to trigger a large disturbance in the nematic mixture and to result in a phase transition or separation (Meng et al., 2007; van Nostrum et al., 1998; Sutherland et al., 2004). Evolution of the order parameter might start to play a role if the nematic properties of the diacrylate and monoacrylate (such as their clearing temperature or nematic formation temperature) are drastically different from each other. In that case, the order parameter will change and affect the light attenuation (Eqs. (9)–(10) and (14)), since the azobenzenes follow the alignment order of the LC monomers.

The effect of the Case-I diffusion scheme is found to be small; the influence of the stiffness gradient on topographical switching is limited when a photo-responsivity gradient is absent. Moreover, the prerequisite for the Case-I diffusion scheme (similar diffusion rates for diacrylate and azobenzene and no overall effect on responsivity, see Eq. (20)) might be hard to meet in real experiments.

Since the photo-responsivity evolution is key, it is important to critically evaluate the validity of the relation of P_{ij} as a function of the monomer concentrations, Eq. (20). The used linear relation between P_{ij} and n_{azo}/n_{azo}^0 is based on a linear fit of a limited set of seven experiments (see the references in the caption of Fig. S6 in SI). It might however be the case that the linearity only holds for these specific material systems with certain chemical compositions and processing procedures as well as for a limited range of azobenzene concentrations. Previous experiments (Liu et al., 2012b; Liu and Broer, 2014b) have shown that after a threshold value of the azobenzene concentration, the photo-mechanical response saturates. Other studies (Braun et al., 2016; Cheng et al., 2012; Harris et al., 2005; Kondo et al., 2010) show that an excessive azobenzene concentration even can lead to a decrease of the response, possibly due to reduced penetration depth of the light into the bulk material, increased crosslinking densities (the double-reactive-end azobenzenes are also crosslinkers) and complex

molecular polymer entanglements. To assess the sensitivity of the results on the assumption of linearity, we repeated the simulations for a range of alternative expressions for the photo-responsivity (see the Appendix). These results show that the surface deformations are indeed modified, with the extent of modification being dependent on the specific functional form chosen.

In conclusion, a theoretical framework is established to account for the effect of photo-polymerization-induced diffusion on light-triggered topographical switching. The Flory-Huggins chemical potential is used to describe the monomer-polymer mixture system, consisting of diacrylate and monoacrylate liquid crystal mesogens, and azobenzene molecules. The azobenzene functions as a dye to create light gradients that initiate diffusion in the photo-polymerization process and also as a photo-trigger to induce conformational changes of the LC glassy polymer. Stiffness and photo-responsivity gradients are created throughout the polymer film upon the diffusion-driven redistribution of the diacrylates and azobenzenes. Their effect is simulated via a mechanical framework containing a non-linear UV light penetration model and an opto-mechanical relation by showing topographical texture changes in three different practically-relevant boundary value problems: bending and twisting of cantilevers, topographical modulations of linearly-patterned substrate-constrained coatings and travelling surface waves. From these extensive studies, we conclude that:

1. Mesogens with higher reactivities are found to diffuse to regions with larger polymerization intensities during the process of polymerization and diffusion.
2. The diffusion-induced photo-responsivity adjustment is found to play a dominant role over the stiffness adjustment in the texture modulation of all these problems.
3. By selecting a specific combination of chemical composition, director distributions of the films, the wavelength, exposure area and the polarization status of the polymerization light and actuation light, the light-triggered surface morphing can be tailored and enhanced.

This framework can serve as a method to critically evaluate the influence of diffusion for photo-polymerized liquid crystal mesogenic actuators, and as a predictive tool to tune and optimize the switching performance of soft actuators for applications in optical coatings, friction and wettability control, human-machine interactions and haptics, and soft robotics.

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Sensitivity analysis of the photo-responsivity dependence

In this appendix, we study several alternative relations for the photo-responsivity,

$$\frac{P_{ij}}{P_{ij}^0} = \left(\frac{n_{di}}{n_{di}^0} \right)^{-1} f_i \left(\frac{n_{azo}}{n_{azo}^0} \right), \quad (A1)$$

in which we keep the inverse linear relation between P_{ij} and the concentration of the diacrylates in place and replace the second item in Eq. (20) with a function $f_i(n_{azo}/n_{azo}^0)$. The different functions f_i analyzed are shown in Fig. A1(a)–(b). Besides the previously assumed linear relation (f_1), f_2 represents the case in which the original concentration n_{azo}^0 is already at the convergence plateau (Liu and Broer, 2014b), f_3 represents an exponential increase, and f_4 stands for the systems (Iamsaard et al., 2016; Lee et al., 2012; Wang et al., 2012; White et al., 2009) in which the opto-response starts to increase considerably when the azobenzene concentration reaches n_{azo}^0 . The Gaussian-type relations of f_5 , f_6 and f_7 represent the possible unfavorable effect when the azobenzene concentration is too large (Kondo et al., 2010), with peaks before, at and after n_{azo}^0 , respectively.

We take the reactivity ratios $R_1 : R_2 : R_3 = 2 : 1 : 4$ (i.e., the Case-III scheme, see other schemes in Figs. A2 and A3) and study the new photo-responsivity variation after diffusion for the cholesteric/homeotropic patterned films, as plotted in Fig. A1(c)–(d). We assume that the above material systems have the same opto-mechanical properties, i.e. P_{ij}^0 , before diffusion, and the corresponding normalized surface profiles are shown in Fig. A1(e)–(f). With reference to the diffusion of the diacrylates and azobenzenes in Fig. 8(b)–(c), various possibilities of topographical modulations are shown. For the f_2 case, the effect of the monomer diffusion is limited due to the small change of the photo-responsivity. The homeotropic region has a considerably larger contraction for the f_3 scheme, with a decrease of the expansion in the cholesteric region, due to the large deviation of the responsivity in each phase. A peculiar surface texture enhancement occurs for the f_4 scheme, attributed to the responsivity increase at both regions. For the three normal-distribution(Gaussian)-like schemes, the surface texture is substantially modified. The out-of-plane deformation is decreased considerably at both regions for the f_5 case, and less in the homeotropic or cholesteric region for the f_6 or f_7 scheme, respectively. In summary, the surface deformation is subjected to various modifications based on the assumed relations between the responsivity and azobenzene concentration, and, as expected, can be maximally enhanced for the strong f_4 dependence.

Fig. A1. (a)–(b) Several hypothetical relations between the azobenzene concentration and the photo-responsivity functions $f_i(n_{\text{azo}}/n_{\text{azo}}^0)$. (c)–(d) The corresponding relative changes of the photo-responsivity (black lines: cholesteric phase; blue lines: homeotropic phase) for the Case-III. (e)–(f) The normalized surface profiles (red lines: without diffusion) with various responsivity functions for the Case-III. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. A2. (a)–(b) The corresponding relative changes of the photo-responsivity (black lines: cholesteric phase; blue lines: homeotropic phase) for the Case-I. (c)–(d) The normalized surface profiles (red lines: without diffusion) with various responsivity functions for the Case-I. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. A3. (a)–(b) The corresponding relative changes of the photo-responsivity (black lines: cholesteric phase; blue lines: homeotropic phase) for the Case-II. (c)–(d) The normalized surface profiles (red lines: without diffusion) with various responsivity functions for the Case-II. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.jmps.2018.09.021](https://doi.org/10.1016/j.jmps.2018.09.021).

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