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Light-induced deformation of polymer networks containing azobenzene chromophores and liquid crystalline mesogens

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Abstract

Two-component polymer networks containing liquid crystalline (LC) mesogens and azobenzene chromophores belong to a class of smart materials which combine uniquely the orientation order of liquid crystals and light-induced deformation of photosensitive polymers. In the present study we develop a theory of light-induced deformation of azobenzene-containing LC networks. It is shown that preferential reorientation of chromophores perpendicular to the polarization direction of the light \mathbf{E} leads to the reorientation of the mesogens due to LC interactions between the components. Reorientation of the chromophores and mesogens results in the light-induced deformation of the polymer network. The sign of deformation (expansion / contraction with respect to the vector \mathbf{E}) depends on the orientation distribution of the mesogens and chromophores inside the network strands. The magnitude of deformation increases with increase of the volume fraction of chromophores and the strength of LC interactions between the components. Influence of the dilution of azobenzene-containing networks by the bent cis-isomers of the chromophores on the light-induced deformation is discussed.

KEYWORDS.

Photo-deformable polymers, polymer networks, liquid crystals, statistical physics.

1. Introduction

Azobenzene-containing polymer networks have been a subject of extensive investigations during the last two decades because of their unique physical properties and ability to change their shape under light illumination.¹⁻¹⁸ Precise and quick control of the light-induced deformation on the macro- and microscopic scales opens up a fascinating potential for the use of these materials as light-controllable sensors, actuators, microrobots, micropumps, artificial muscles, etc.

The light-induced deformation of azobenzene polymers with respect to the polarization direction of the light \mathbf{E} is caused by an anisotropic character of the photoisomerization process of the chromophores. Maximal probability of the transformation of the rodlike trans-isomer to the bent cis-isomer takes place at the parallel orientation of the long axis of the trans-isomer with respect to the vector \mathbf{E} .¹⁹⁻²¹ Thus, after multiple trans-cis-trans isomerization process under visible light irradiation the orientation distribution of the chromophores becomes anisotropic with preferable orientation of the chromophores perpendicular to the vector \mathbf{E} .¹⁹⁻²¹

To describe the light-induced anisotropy, an effective orientation potential, which reorients the chromophores perpendicular to the vector \mathbf{E} , have been introduced independently by Chigrinov et al²² and by one of the authors.²³ The orientation approach, based on this potential, was recently applied to describe the light-induced deformation of azobenzene-containing polymers of different structures, including uncrosslinked amorphous polymers,²⁴⁻²⁶ crosslinked isotropic polymer networks²⁷⁻²⁹ and anisotropic polymer networks with orientation interactions between the chromophores.^{30,31} The proposed theories are able to explain experimental results, as it is summarized briefly below.

(i) The orientation potential provides the mechanical stress, which is enough to deform azobenzene polymers in the glassy state.^{24-26, 32-34} (ii) Depending on the orientation distribution

of chromophores inside polymer chains, which is related to the chemical structure, azo-polymers can demonstrate either expansion or contraction along the polarization vector \mathbf{E} .^{24-31, 35-38} (iii) Light-induced deformation of azobenzene networks depends on the degree of cross-linking and on the concentration of azobenzene chromophores,²⁷⁻²⁹ the theoretically predicted dependences being in a good agreement with experimental data for the light-induced bending deformation of azo-networks.²⁹ (iv) Liquid crystalline (LC) interactions between rodlike chromophores result in the biaxial order and biaxial deformation of azobenzene containing polymers.^{30,31,39-43} The results (ii) and (iv) are confirmed also by computer simulations.⁴⁴⁻⁴⁶ The agreement of the theoretical findings with both experimental results and computer simulations demonstrates a great strength of the proposed orientation approach to describe the photomechanical properties of azobenzene-containing polymers of different structures.

In the present study the orientation approach is used to describe the light-induced deformation of a two-component polymer system consisting of a LC polymer network with included azobenzene chromophores. By this, we develop previous theories,²⁶⁻³¹ which dealt with one-component photosensitive polymers containing only azobenzene chromophores in their structure. At the same time, many experimental works were devoted to the synthesis and investigation of photomechanical properties of two-component azobenzene polymers, which include LC mesogens and azobenzene chromophores.^{3-6,12-17} Below, we will demonstrate that the presence of the two components enriches the photomechanical behavior, which depends on the amount of each component, on the interaction between them and on the distribution of the chromophores and mesogens with respect to the backbones of the polymer chains.

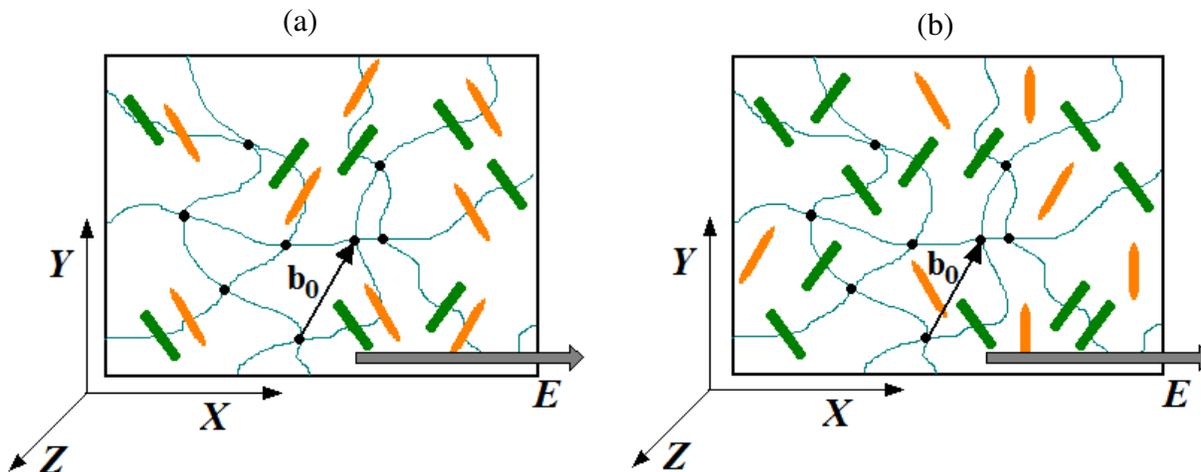


Figure 1. Model of a two-component polymer system consisting of the LC network with included azobenzene chromophores. Chromophores are either chemically attached to network strands (a) or dispersed in the network (b).

2. Model. Main equations

We consider a two-component polymer system, which consists of a LC network with included azobenzene chromophores. The mesogens of the LC network are attached chemically to the network strands (green rods in Figure 1). The chromophores (orange ellipsoids in Figure 1) are either attached chemically to the chains (see Figure 1a) as in refs. 3-5 and 12-17, or dispersed in a network (see Figure 1b), as in ref. 6. Each network strand consists of N freely jointed rod-like Kuhn segments. It is assumed that N_1 Kuhn segments inside a network strand bear N_1 chromophores (a single chromophore per each Kuhn segment) and N_2 Kuhn segments contain N_2 mesogens; $(N - N_1 - N_2)$ Kuhn segments contain neither chromophores nor mesogens. It is obvious that $N_1 = 0$ for LC networks with the chromophores dispersed in the structure.

Orientation distributions of the chromophores and mesogens inside network strands are characterized by the distribution functions $W_1(\alpha_1)$ and $W_2(\alpha_2)$, respectively, where α_1 is the angle between the long axis of a chromophore and a Kuhn segment, α_2 is the angle between the long axis of a mesogen and a Kuhn segment. Functions $W_1(\alpha_1)$ and $W_2(\alpha_2)$ are determined by the

chemical structure and the length of spacers between the main chains and the functional fragments (mesogens and chromophores). Below we will show that the light-induced deformation of azobenzene-containing LC network is very sensitive to the structural parameters which are determined by the second moments of the distribution functions $W_1(\alpha_1)$ and $W_2(\alpha_2)$.

Depending on the amount of rod-like azobenzene chromophores and mesogens, the two-component network can be either in the isotropic state or in the anisotropic state with preferable orientation of the components along the LC-director \mathbf{n}_0 .⁴⁷⁻⁵⁰ Here we study the photomechanical properties of both isotropic and anisotropic networks. In the latter case we consider the geometry when the polarization vector of the light \mathbf{E} is directed along the LC-director: $\mathbf{E} \parallel \mathbf{n}_0$. As we have shown in ref. 31, this geometry provides a largest degree of light-induced deformation.

Application of the linearly polarized visible light to an azobenzene-containing network leads to a multiple trans-cis-trans photo-isomerization process of chromophores. The trans-cis-trans photo-isomerization process is accompanied by alignment of long axes of the chromophores perpendicular to the polarization direction \mathbf{E} of the light.¹⁹⁻²¹ The reorientation of chromophores under light irradiation is described here, as in refs. 22-31, by introducing an orientation potential, which acts on each chromophore:

$$U_{\text{ch}} = V_0 \cos^2 \theta, \quad (1)$$

where θ is the angle between the long axis of a chromophore and the polarization vector \mathbf{E} ; V_0 is the strength of the orientation field, which is proportional to the light intensity, I_p :

$$V_0 = C \cdot I_p. \quad (2)$$

The constant C was estimated as $C \cong 10^{-19} \text{ J} \cdot \text{cm}^2 / \text{W}$.^{22,23,29}

Light-induced ordering of chromophores changes the energy of orientation interactions between the chromophores and mesogens. The energy of orientation interaction between the

components of an azobenzene-containing LC polymer network can be expressed in terms of the mean-field approximation for uniaxial nematic mixtures. According to the scheme of Brochard et al.,⁴⁷ the energy of orientation interactions in a nematic mixture is given by:⁴⁷⁻⁵⁰

$$U_{\text{LC}}(S_1, S_2) = -\frac{1}{2}u_{11}\Phi_1^2S_1^2 - \frac{1}{2}u_{22}\Phi_2^2S_2^2 - u_{12}\Phi_1\Phi_2S_1S_2 \quad (3)$$

where Φ_1 and $\Phi_2 = 1 - \Phi_1$ are volume fractions of the chromophores and the LC network, respectively. Due to the axial symmetry of the potential $U_{\text{ch}}(\theta)$ with respect to the vector \mathbf{E} , the orientation distribution of chromophores and mesogens is assumed to be symmetrical with respect to this vector and determined by the order parameters S_1 and S_2 :

$$S_1 = \int d\Omega f_1(\Omega) \frac{3\cos^2\theta - 1}{2}, \quad (4)$$

$$S_2 = \int d\Omega f_2(\Omega) \frac{3\cos^2\theta - 1}{2}, \quad (5)$$

where $f_1(\Omega)$ and $f_2(\Omega)$ are the orientation distribution functions of the chromophores and the mesogens of the network, respectively, relative to the vector \mathbf{E} ($\mathbf{E} \parallel \mathbf{n}_0$). Integration in Equations (4) and (5) runs over the Euler angles θ and φ : $d\Omega = \sin\theta d\theta d\varphi$, $\theta \in [0, \pi]$ and $\varphi \in [0, 2\pi]$. Here we set $\Omega \equiv (\theta, \varphi)$. Note that at the absence of the light, the angle θ is counted from the LC-director \mathbf{n}_0 in anisotropic networks, whereas in isotropic networks the order parameters counted from any direction are equal to zero: $S_1 = S_2 = 0$.

Parameters u_{ij} in Equation (3) characterize the strengths of the orientation interactions between the components of the azobenzene-containing LC network: between the chromophores (u_{11}), between the mesogens in the network (u_{22}) and between the network and chromophores (u_{12}). The value u_{22} is determined by the structure of a pure LC network and depends on the

number density of the mesogens in the network at the absence of chromophores. The parameters u_{11} and u_{22} are related with the temperatures of the isotropic-to-nematic phase transitions for the pure LC network, $T_{\text{IN}}^{(2)}$ (at $\Phi_2 = 1$), and for a pure dye containing the azobenzene chromophores, $T_{\text{IN}}^{(1)}$ (at $\Phi_1 = 1$): $u_{11} = a_c k T_{\text{IN}}^{(1)}$, $u_{22} = a_c k T_{\text{IN}}^{(2)}$.⁴⁷⁻⁵⁰ Here k is the Boltzmann constant and the prefactor $a_c = 4.542$ corresponds to the critical value of the dimensionless parameter $a = u / kT$, which determines the isotropic-to-nematic phase transition of rod-like objects at the absence of external fields in the classical Maier-Saupe mean field theory.^{48,51} The quantity u_{12} is the parameter of the theory, which changes in the vicinity of the characteristic value $u_{12} \cong \sqrt{u_{11} \cdot u_{22}}$.⁴⁷⁻⁵⁰ Note that for the one-component system (when, e.g., $\Phi_1 = 1$, $\Phi_2 = 0$) the energy U_{LC} given by Equation (3) takes a standard form $\sim u_{11} S_1^2 / 2$ which appears in the classical Maier-Saupe theory.^{48,51}

Equilibrium values of the order parameters S_1 and S_2 are determined by the condition of minimum of the free energy. The part of the free energy which depends on the order parameters S_1 and S_2 is given now by the following equation:

$$F(S_1, S_2) = kT\Phi_1 \int d\Omega f_1(\Omega) \ln f_1(\Omega) + kT\Phi_2 \int d\Omega f_2(\Omega) \ln f_2(\Omega) + U_{\text{LC}}(S_1, S_2) + U_{\text{light}}(S_1) \quad (6)$$

where T is the absolute temperature. The first and second terms in Equation (6) are the orientation entropy of the chromophores and mesogens, respectively. The third term is the energy of the intermolecular LC interaction in the network. The fourth term describes the influence of the light-induced orientation potential V_0 and takes into account the weighted contribution of the chromophores with the volume fraction Φ_1 :

$$U_{\text{light}}(S_1) = \Phi_1 V_0 \int d\Omega f_1(\Omega) \cos^2 \theta = \Phi_1 V_0 \frac{2S_1 + 1}{3} \quad (7)$$

Here we note that the free energy given by Equation (6) neglects the influence of the network deformation on the order parameters. This corresponds to the Gaussian approach,^{29,31} in which the end-to-end distance of network strands is approximated by the Gaussian distribution function and the finite extensibility of network strands is not taken into account. In the Gaussian approach, the influence of the network deformation on the order parameters is very weak and can be neglected. It was shown that the Gaussian approach describes very well the light-induced deformation of azobenzene elastomers built from long enough network strands ($N \gg 1$) in a broad region of deformation, which can reach even 100% of relative deformation.^{29,31} The relative errors of the order parameters and network deformation predicted by the Gaussian approach can be estimated as $\sim N^{-1}$.⁵² Thus, at $N \gg 1$ the influence of the network deformation on the order parameters can be neglected in a good approximation.

The distribution functions $f_1(\Omega)$ and $f_2(\Omega)$ in the framework of the mean-field approach have the following form:^{31,47-50}

$$f_1(\Omega) = Z_1^{-1} \exp(m_1 \cos^2 \theta), \quad (8)$$

$$f_2(\Omega) = Z_2^{-1} \exp(m_2 \cos^2 \theta), \quad (9)$$

where Z_1 and Z_2 are the normalization constants:

$$Z_1 = \int d\Omega \exp(m_1 \cos^2 \theta), \quad (10)$$

$$Z_2 = \int d\Omega \exp(m_2 \cos^2 \theta). \quad (11)$$

Here m_1 and m_2 are the strengths of the molecular self-consistent fields. The field m_1 acts on the chromophores, m_2 influences the mesogens of the network; m_1 and m_2 are functions of S_1 and S_2 according to Equations (4) and (5): $m_1(S_1)$ and $m_2(S_2)$.

Now, substituting Equation (8) and (9) into (6) we find the free energy as a function of the order parameters:

$$\begin{aligned} \frac{F(S_1, S_2)}{kT} = & \Phi_1 \left(-\ln Z_1 + m_1 \frac{2S_1 + 1}{3} \right) + \Phi_2 \left(-\ln Z_2 + m_2 \frac{2S_2 + 1}{3} \right) - \frac{1}{2} a_{11} \Phi_1^2 S_1^2 - \\ & - \frac{1}{2} a_{22} \Phi_2^2 S_2^2 - a_{12} \Phi_1 \Phi_2 S_1 S_2 + \frac{V_0}{kT} \cdot \frac{2S_1 + 1}{3} \Phi_1, \end{aligned} \quad (12)$$

where the reduced strengths of the orientation interactions have been introduced: $a_{11} = u_{11}/kT$; $a_{22} = u_{22}/kT$; $a_{12} = u_{12}/kT$. To obtain Equation (12) we used Equations (4) and (5). The dependence $F=F(S_1, S_2)$ given by Equation (12) contains the strength of the light-induced potential V_0/kT and the strengths of the orientation interactions a_{ij} ($i, j=1, 2$) as parameters. Using Equation (12) we have calculated numerically the values S_1 and S_2 as functions of the parameters V_0/kT , a_{11} , a_{22} , a_{12} from the minima of the free energy. Below, we discuss the results of an analysis of the free energy and present the dependences $S_1(V_0/kT, a_{ij})$ and $S_2(V_0/kT, a_{ij})$, which determine the orientation ordering of chromophores and mesogens under illumination with the light.

3. Light-induced orientation order

Using Equations (10)–(12), the conditions of the extremum for the free energy, $\partial F/\partial S_1 = 0$ and $\partial F/\partial S_2 = 0$, take the following form:

$$\begin{aligned} m_1 = & \frac{3}{2} (a_{11} \Phi_1 S_1 + a_{12} \Phi_2 S_2) - \frac{V_0}{kT}, \\ m_2 = & \frac{3}{2} (a_{22} \Phi_2 S_2 + a_{12} \Phi_1 S_1). \end{aligned} \quad (13)$$

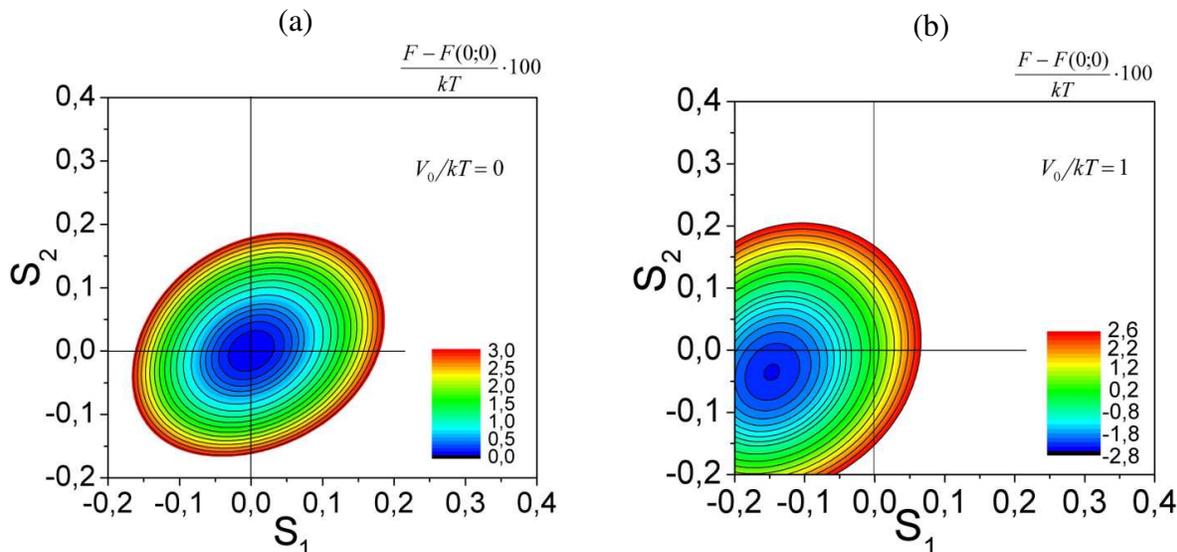


Figure 2. Free energy as a function of S_1 and S_2 at the absence of the light (a) and at the light illumination (b). Weak LC interactions, $a_{ij} < a_c$. $a_{11} = a_{22} = a_{12} = 2$ and $\Phi_1 = \Phi_2 = 50\%$.

One can see that m_l is determined by both the LC interactions and the orientation field V_0 . To find the minimum of the free energy we analyze the map $F(S_1, S_2)$ numerically.

Character of the light-induced ordering of azobenzene chromophores as a function of the light-induced potential V_0/kT is determined by the strengths of the orientation interactions a_{ij} .

One can distinguish two ranges of the values a_{ij} with respect to the critical value $a_c = 4.542$: weak LC interactions ($a_{ij} < a_c$) and strong LC interactions ($a_{ij} > a_c$).

3.1. Weak LC interactions

For polymer networks with weak LC interactions ($a_{ij} < a_c$), the system of Equations (13) at $V_0 = 0$ has only one solution with $S_i = 0$ ($i = 1, 2$). In this case the free energy as a function of S_1 and S_2 has only one minimum at $S_i = 0$, i.e. the network is isotropic (see Figure 2a). At the light illumination ($V_0 > 0$) the minimum of the free energy shifts to negative values of the order parameters ($S_i < 0$) and the network becomes anisotropic (see Figure 2b). Negative values of S_1

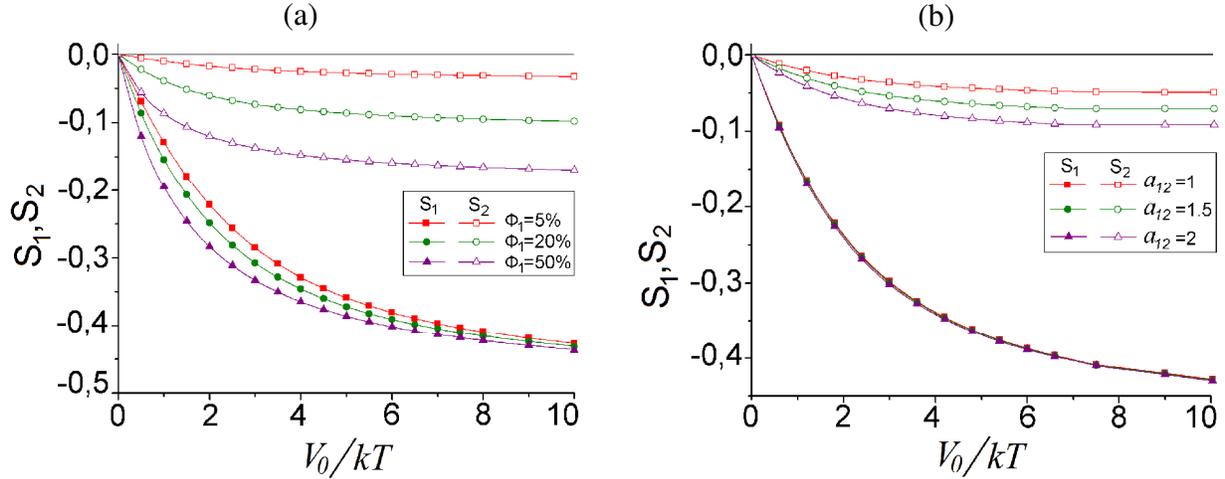


Figure 3. Dependences of the equilibrium order parameters S_1 and S_2 on the reduced strength of the light-induced potential V_0/kT : (a) at varied values Φ_1 , $a_{11} = 3$, $a_{22} = 4$, $a_{12} = \sqrt{a_{11}a_{22}}$; (b) at varied values a_{12} , $\Phi_1 = \Phi_2 = 50\%$, $a_{11} = a_{22} = 2$.

and S_2 reflect a preferable orientation of the chromophores and mesogens perpendicular to the polarization vector \mathbf{E} .

Figure 3 shows the dependences of the equilibrium values of the order parameters S_1 and S_2 on the reduced strength of the light-induced potential V_0/kT . The dependences $S_i(V_0)$ are given at varied values of the volume fraction of chromophores (Figure 3a) and at varied values of the reduced strength of the orientation interaction between mesogens and chromophores a_{12} (Figure 3b). Increase of the volume fraction of chromophores Φ_1 leads to an increase of the magnitudes of the order parameters S_1 and S_2 (see Figure 3a). Increase of the interaction parameter between the chromophores and mesogens a_{12} leads to an increase of the magnitude of the order parameter S_2 (see Figure 3b), but it changes the value of S_1 only slightly.

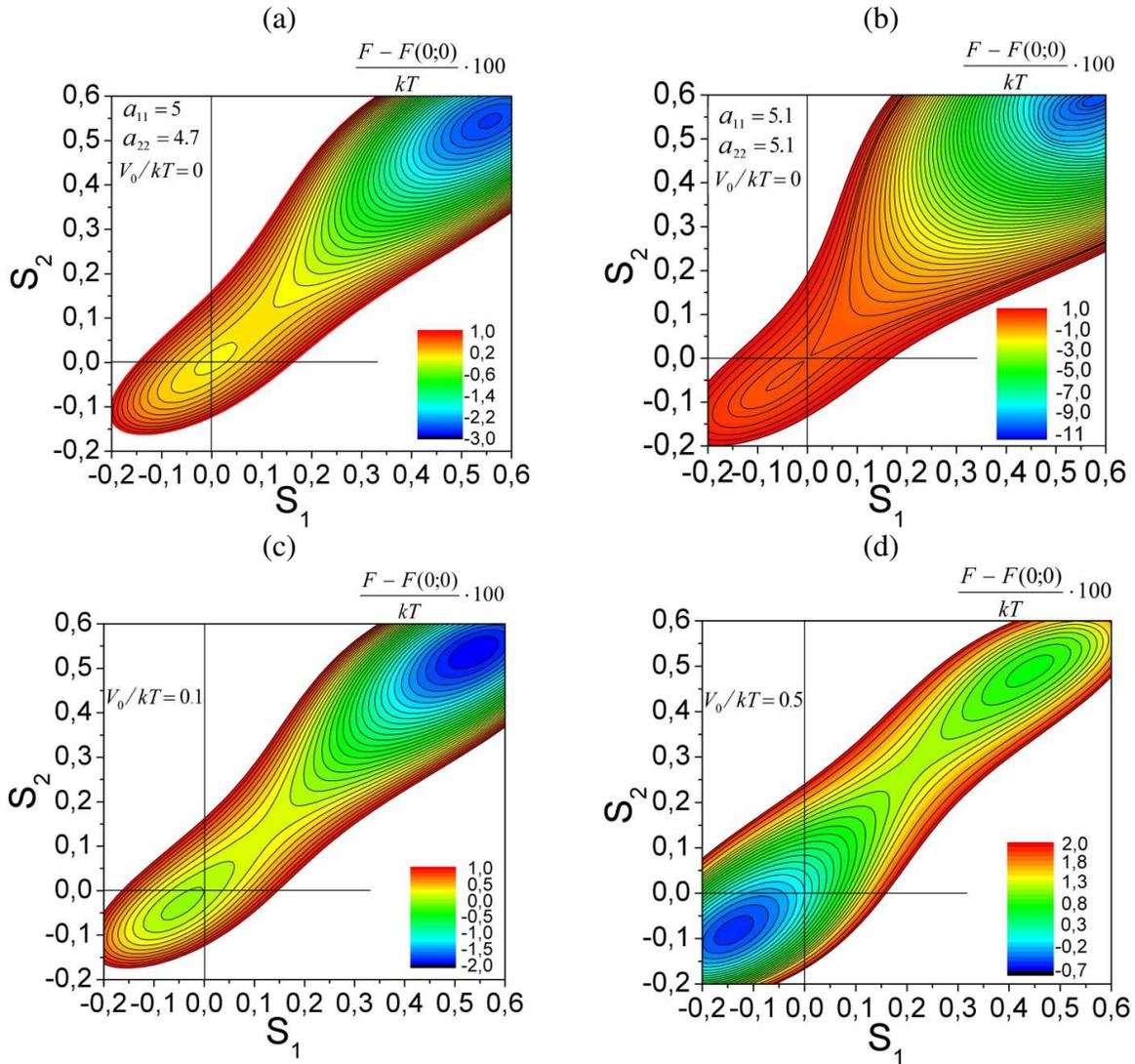


Figure 4. Free energy as a function of S_1 and S_2 at the absence of the light, $V_0 = 0$ (a, b) and under light irradiation, $V_0 > 0$ (c, d). $\Phi_1 = 20\%$ and $\Phi_2 = 80\%$. Strong LC interactions, $a_{ij} > a_c$: $a_{11} = 5$ and $a_{22} = 4.7$ (a, c, d); $a_{11} = a_{22} = 5.1$ (b). $a_{12} = \sqrt{a_{11}a_{22}}$.

3.2. Strong LC interactions

At strong LC interaction ($a_{ij} > a_c$) the free energy at $V_0 = 0$ has two minima. One minimum takes place at $S_i > 0$ ($i = 1, 2$), Figures 4a,b. Position of the second minimum depends on the values a_{ij} : for $a_c < a_{ij} \leq 5$ the minimum is located at $S_i = 0$ (Figure 4a), for $a_{ij} > 5$ it is

located at $S_i < 0$ (see Figure 4b). If $a_{ij} > a_c$, the orientation interactions are so strong, that the minimum at $S_i > 0$ is deeper than the second minimum at $S_i \leq 0$. Thus, at $a_{ij} > a_c$ the non-illuminated system is in the LC state with $S_i > 0$ (Figures 4a,b).

Under light illumination with the polarization direction \mathbf{E} parallel to the LC director \mathbf{n}_0 , the minimum at $S_i > 0$ shifts to smaller values of S_1 and S_2 and the second minimum shifts to the negative values of the order parameters $S_i < 0$ (Figure 4c). Moreover, with increasing V_0 the minimum at $S_i > 0$ raises, whereas the minimum at $S_i < 0$ goes down (Figures 4a and 4c). At critical value $V_0 = V_c$ the two minima at $S_i > 0$ and $S_i < 0$ become to be at the same level. For $V_0 > V_c$ the minimum at $S_i < 0$ becomes deeper than the minimum for positive values of S_i and the network is transformed stepwise into a state with negative values of the order parameters (see Figure 4d). This means that the LC director \mathbf{n}_0 reorients perpendicular to the vector \mathbf{E} .

Figure 5a shows the dependence of equilibrium values of the order parameters of chromophores and mesogens on the light-induced potential V_0/kT at different values of the volume fraction of the chromophores Φ_1 and at fixed value $a_{12} = \sqrt{a_{22}a_{11}}$. One can see that increase of V_0/kT leads to decrease of both values S_1 and S_2 . Note, however, that at small volume fraction of chromophores (e.g., at $\Phi_1=1\%$ in Figure 5a) the influence of the chromophores on the mesogens is relatively weak, so that the order parameter of the mesogens S_2 changes negligibly under light illumination. If the volume fraction of chromophores is large enough, the reorientation of chromophores is able to induce the orientation phase transition: at the critical value $V_0 = V_c$ the order parameters S_1 and S_2 change stepwise from positive ($S_i > 0$) to negative ($S_i < 0$) values. Increase of the volume fraction Φ_1 results in the decrease of the critical value V_c , as well as in the decrease of the order parameter S_1 and S_2 (Figure 5a).

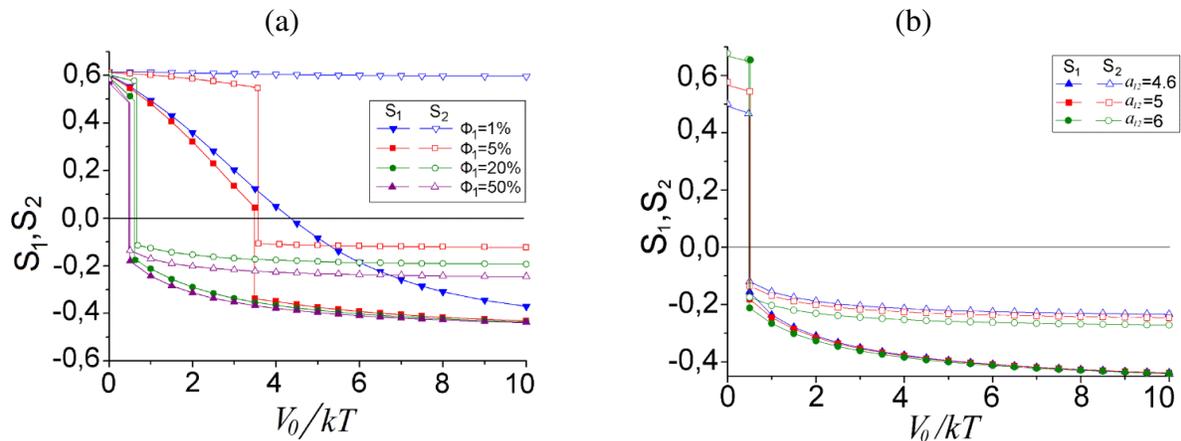


Figure 5. Dependences of the order parameters S_1 and S_2 on the reduced strength of the light-induced potential V_0/kT : (a) at varied values Φ_1 , $a_{11} = 4.7$, $a_{22} = 5$, $a_{12} = \sqrt{a_{11}a_{22}}$; (b) at varied values a_{12} , $\Phi_1 = \Phi_2 = 50\%$, $a_{11} = a_{22} = 4.7$.

Note that in reality the order parameters change continuously in the vicinity of the phase transition.⁴⁸ The mean field approach is not able to describe the pre-transition effects which lead to the continuous change of the order parameters. These effects can be taken into account in the framework of the computer simulations. However, despite its simplicity the mean field approach describes in a very good approximation the main features of the light-induced deformation in one-component LC polymers.³¹ Thus, we expect that this approach is applicable also to the two-component azobenzene-containing LC polymers.

Figure 5b shows the dependences $S_i(V_0/kT)$ at varied values of the interaction parameter between the chromophores and mesogens a_{12} . One can see that the increase of the parameter a_{12} leads to the increase of the magnitudes of the order parameters S_1 and S_2 . However, at strong light-induced orientation field ($V_0/kT > 2$) the order parameter of the chromophores S_1 changes slightly as a function of a_{12} .

Hence, ordering of chromophores induces the orientational order of a polymer network and the presence of the network changes the light-induced phase transition of chromophores. In the next section, we consider the light-induced deformation of azobenzene elastomers.

4. Light-induced deformation of azo-containing LC networks

Reorientation of LC mesogens with respect to the polarization direction \mathbf{E} results in the reorientation of the Kuhn segments with respect to the vector \mathbf{E} due to the mechanical coupling between the mesogens and Kuhn segments. Reorientation of the Kuhn segments leads to network deformation. Thus, under light illumination the network strands change their conformations, and each end-to-end vector \mathbf{b}_0 is transformed into a new vector \mathbf{b} (Figure 1). As in the classical theory of rubber elasticity,^{53,54} we assume that network strands deform affinely with the bulk deformation of the elastomer because of the constraints of the crosslinks:

$$b_x = b_{x,0} \cdot \lambda, b_y = b_{y,0} / \sqrt{\lambda}, \text{ and } b_z = b_{z,0} / \sqrt{\lambda}, \quad (14)$$

where λ is the elongation ratio of the network.

To calculate the elongation ratio as a function of the orientation light-induced field we use the Gaussian approach for the statistics of network strands, as in refs. 29-31. In this approach the distribution of the end-to-end vectors of network strands is approximated by the Gaussian distribution function, neglecting the finite extensibility of the strands.^{55,56} For long enough networks strands ($N > 10$) the Gaussian approach describes very well the photomechanical properties of azobenzene-containing networks in a broad region of deformation, which can reach even 100% of relative deformation.²⁹⁻³¹ In the framework of the Gaussian approach, the distribution of the end-to-end vectors of network strands is given by:^{55,56}

$$P(\mathbf{b}) = P_0 \cdot \exp\left[-\frac{b_x^2}{2\langle b_x^2 \rangle} - \frac{b_y^2}{2\langle b_y^2 \rangle} - \frac{b_z^2}{2\langle b_z^2 \rangle}\right], \quad (15)$$

where P_0 is a normalization constant; $\langle b_x^2 \rangle$, $\langle b_y^2 \rangle$ and $\langle b_z^2 \rangle$ are the mean-square projections of the network strands on the x , y , and z -axes for deformed network under light illumination. The conformational free energy of network strands is defined as:

$$F_{conf} = -kT \cdot \langle \ln P \rangle = kT \cdot \left[\frac{\langle b_{x,0}^2 \rangle \cdot \lambda^2}{2\langle b_x^2 \rangle} + \frac{\langle b_{y,0}^2 \rangle \cdot \lambda^{-1}}{2\langle b_y^2 \rangle} + \frac{\langle b_{z,0}^2 \rangle \cdot \lambda^{-1}}{2\langle b_z^2 \rangle} \right]. \quad (16)$$

Here we used Equation (14) for the relationship between \mathbf{b} and \mathbf{b}_0 . The equilibrium value of the elongation ratio λ is determined from the minimum of the free energy, $\partial F_{conf} / \partial \lambda = 0$, that gives from Equation (16) the following relation for the parameter λ :

$$\left[\lambda \cdot \frac{\langle b_{x,0}^2 \rangle}{\langle b_x^2 \rangle} - \frac{1}{2\lambda^2} \cdot \frac{\langle b_{y,0}^2 \rangle}{\langle b_y^2 \rangle} - \frac{1}{2\lambda^2} \cdot \frac{\langle b_{z,0}^2 \rangle}{\langle b_z^2 \rangle} \right] = 0. \quad (17)$$

Using the axial symmetry around the x -axis, $\langle b_y^2 \rangle = \langle b_z^2 \rangle$ and $\langle b_{y,0}^2 \rangle = \langle b_{z,0}^2 \rangle$, the solution of Equation (17) takes the classical form (cf. with ref. 1):

$$\lambda = \left(\frac{\langle b_{y,0}^2 \rangle \cdot \langle b_x^2 \rangle}{\langle b_y^2 \rangle \cdot \langle b_{x,0}^2 \rangle} \right)^{1/3}. \quad (18)$$

We recall that the influence of the network deformation on the order parameters is neglected in the Gaussian approximation. As it was shown in refs. 29 and 52, this influence would lead to a small decrease of the magnitude of the elongation ratio λ , the relative decrease of λ being estimated as $\sim N^{-1}$. Thus, the shorter are the network strands (e.g., for higher degree of crosslinking), the smaller is the magnitude of λ due to the finite extensibility of network strands.

On the other side, the finite extensibility of network strands does not affect the sign of deformation (extension / contraction) with respect to the electric vector of the light.

Influence of the network deformation on the order parameters can play an important role if the material is affected additionally by external mechanical loading. It is well known that the mechanical stress can induce the orientation phase transition which is accompanied by a significant deformation of a network.⁵⁷ We expect that the deformation of an azobenzene-containing LC polymer under the light illumination and mechanical stress can be determined by a non-trivial interplay between these two stimuli. Very high mechanical stress (above 1.5 GPa) can even completely arrest the trans-cis photoisomerization⁵⁸ and, thus, can prevent the light-induced deformation. Theoretical description of the photomechanical properties of azobenzene-containing networks under external mechanical loading can be a topic of a special work.

The mean-square projections of the network strands $\langle b_\alpha^2 \rangle$ in Equation (18) are related to the projections of the Kuhn segments $\langle l_\alpha^2 \rangle$ on the axes of the frame of references ($\alpha = x, y, z$):

$$\langle b_\alpha^2 \rangle = N_1 \langle l_{1,\alpha}^2 \rangle + N_2 \langle l_{2,\alpha}^2 \rangle + (N - N_1 - N_2) \cdot (l^2 / 3). \quad (19)$$

We recall that N_1 and N_2 are the numbers of the Kuhn segments inside a network strand, which contain the chromophores and mesogens, respectively; $(N - N_1 - N_2)$ is the number of Kuhn segments, which contain neither mesogens nor chromophores. We assume that the network strands are not LC objects and are not influenced by the LC interactions. Thus, the orientation distribution of Kuhn segments bearing neither mesogens nor chromophores is isotropic and their mean-square projections are equal $l^2 / 3$, as it is presented in Equation (19). The quantities $\langle l_{1,\alpha}^2 \rangle$ and $\langle l_{2,\alpha}^2 \rangle$ in Equation (19) are the mean-square projections of the Kuhn segments containing the

chromophores and mesogens, respectively, at the light illumination. Likewise at the absence of the light:

$$\langle b_{\alpha,0}^2 \rangle = N_1 \langle l_{1,\alpha}^2 \rangle_0 + N_2 \langle l_{2,\alpha}^2 \rangle_0 + (N - N_1 - N_2) \cdot (l^2 / 3). \quad (20)$$

Here the brackets $\langle \dots \rangle_0$ mean the averaging with the distribution function at the absence of the light, $V_0 = 0$. In the absence of the light, the relation $\langle b_{x,0}^2 \rangle = \langle b_{y,0}^2 \rangle = \langle b_{z,0}^2 \rangle$ takes place for an isotropic network, whereas $\langle b_{x,0}^2 \rangle \neq \langle b_{y,0}^2 \rangle = \langle b_{z,0}^2 \rangle$ for an anisotropic LC network. Substituting Equations (19) and (20) into (18) and dividing the numerator and denominator by the length of network strand N , one can see that the light-induced deformation depends on the number fractions of chromophores and mesogens attached to the polymer chains: N_1/N and N_2/N .

The averaged quantities $\langle l_{i,\alpha}^2 \rangle$ are related to the order parameters S_i ($i = 1, 2$). To relate the quantities $\langle l_{i,\alpha}^2 \rangle$ with the order parameters S_i we assume that the polar orientation of the long axes of Kuhn segments with respect to the long axes of chromophores and mesogens attached to them is defined by the distribution functions $W_1(\alpha_1)$ and $W_2(\alpha_2)$. We recall that α_1 and α_2 are the angles between the long axis of a Kuhn segment and either chromophore or mesogen, as it was introduced in Section 2. The azimuthal orientation of Kuhn segments is assumed to be random. The latter assumption is trivial for the main-chain liquid crystalline networks; for side-chain LC networks it assumes that network strands are not LC objects and are not influenced by the LC interactions.

Averaging over the orientation of Kuhn segments around the long axes of chromophores and mesogens according to the assumptions given above, we obtain the following relationships:

$$\langle l_{i,x}^2 \rangle = \frac{1 + 2S_i \cdot q_i}{3} \cdot l^2, \quad \langle l_{i,y}^2 \rangle = \langle l_{i,z}^2 \rangle = \frac{1 - S_i \cdot q_i}{3} \cdot l^2. \quad (21)$$

The quantities $\langle I_{1,\alpha}^2 \rangle_0$ are determined by Equation (21) with the order parameters S_i taken at the absence of the light: $S_i = S_i(V_0 = 0)$. The constants q_i in Equation (21) are defined by the chemical structure of an azobenzene elastomer, namely, by the orientation distribution of chromophores and mesogens with respect to the network strands:

$$q_i = \frac{3\langle \cos^2 \alpha_i \rangle - 1}{2}. \quad (22)$$

In the last equation the averaging $\langle \cos^2 \alpha_i \rangle$ is performed with respect to the distribution functions $W_i(\alpha_i)$. The structural parameters q_i can take their values in the range $q_i \in [-0.5; 1]$. The minimal values $q_i = -0.5$ correspond to the chemical structures with a preferable orientation of the chromophores and the mesogens perpendicular to the main chains, whereas the maximal values $q_i = 1$ correspond to the structures with a preferable orientation of the chromophores and the mesogens parallel to the main chains. Thus, according to Equations (18) – (22) the light-induced deformation depends on four structural parameters N_1/N , N_2/N , q_1 and q_2 . Below, we consider the photo-mechanical properties of two particular structures: LC networks with either dispersed chromophores ($N_l = 0$) or with the chromophores attached to the chains ($N_l \neq 0$).

4.1. LC networks with chromophores dispersed in the structure

Reorientation of chromophores dispersed in a LC network does not influence directly the conformations of polymer chains, because the mechanical coupling between the chromophores and the chains is absent. In this case the light-induced deformation is caused by LC interactions between the chromophores and mesogens that lead to a change of chain conformations due to the mechanical coupling between the mesogens and the polymer chains.

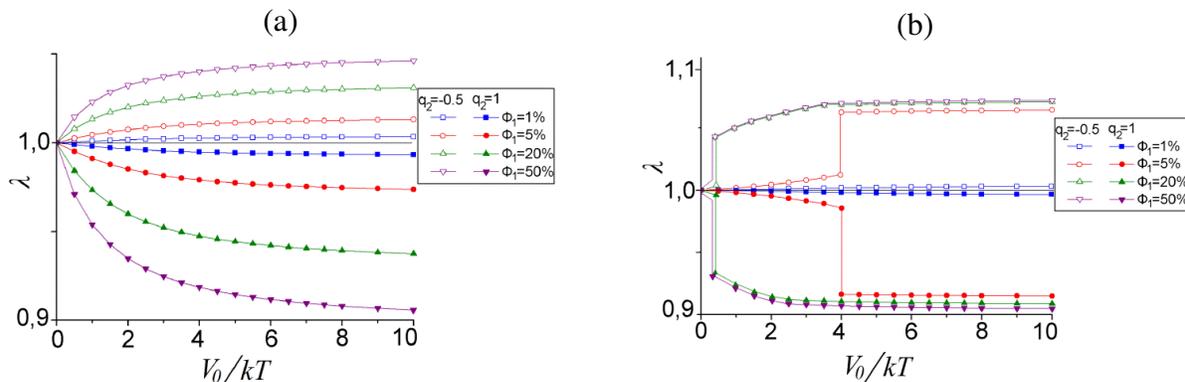


Figure 6. Elongation ratio λ as a function of V_0/kT for LC networks with azobenzene chromophores dispersed in the structure. (a) Weak LC interactions: $a_{11} = 3$, $a_{22} = 4$. (b) Strong LC interactions: $a_{11} = 4.7$, $a_{22} = 5$. $a_{12} = \sqrt{a_{11}a_{22}}$. $N_1/N = 0$, $N_2/N = 0.5$.

Figure 6 illustrates the equilibrium values of the elongation ratios λ as functions of V_0/kT at weak LC interactions ($a_{ij} < a_c$) (Figure 6a) and at strong LC interactions ($a_{ij} > a_c$) (Figure 6b). The results are given for the structures with a preferable orientation of mesogens perpendicular ($q_2 = -0.5$) and parallel ($q_2 = 1$) to the main chains. One can see that at increasing V_0/kT the elongation ratio λ increases for $q_2 = -0.5$ ($\lambda > 1$), while it decreases for $q_2 = 1$ ($\lambda < 1$). Increase of the volume fraction of chromophores Φ_1 results in the increase of the magnitude of the deformation. At weak LC interactions the deformation changes continuously with light irradiation (Figure 6a), whereas at strong LC interactions a light-induced phase transition takes place (Figure 6b). Interestingly, in the latter case the increase of Φ_1 results in the displacement of the phase transition point V_c to the region of smaller values of the parameter V_0 similarly to the behavior of the order parameters given in Figure 5a.

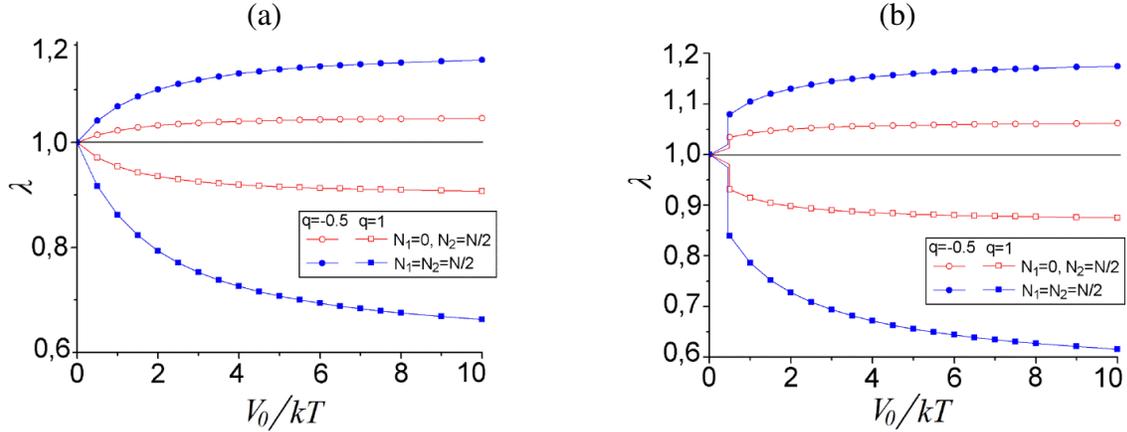


Figure 7. Elongation ratio λ as a function of V_0/kT for LC networks, in which the azochromophores are either attached chemically to the network strands (filled symbols) or dispersed in the network (open symbols). $\Phi_1 = \Phi_2 = 50\%$, $q_1 = q_2 \equiv q$. (a) Weak LC interactions: $a_{11} = 3$, $a_{22} = 4$. (b) Strong LC interactions: $a_{11} = 4.7$, $a_{22} = 5$. $a_{12} = \sqrt{a_{11}a_{22}}$.

4.2. LC networks with chromophores attached to polymer chains

If the chromophores are attached chemically to the network strands, the deformation of the LC network is caused not only by LC interactions between the chromophores and mesogens but also by the mechanical coupling between the chromophores and network strands. Figure 7 illustrates a comparison of the light-induced deformation for polymer networks with the chromophores attached to the polymer chains (filled symbols) and with the chromophores dispersed in the network (open symbols) at fixed volume fraction of the chromophores. As an illustration, the structures with $q_1 = q_2 \equiv q$ are considered.

One can see from Figure 7 that the mechanical coupling between the chromophores and network strands raises considerably the magnitude of the light-induced deformation. The LC network with a preferable orientation of the mesogens and chromophores parallel ($q = 1$) and perpendicular ($q = -0.5$) to the main chains contracts ($\lambda < 1$) and expands ($\lambda > 1$), respectively, along the polarization direction \mathbf{E} . The different sign of light-induced deformation depending on the chemical structure of azo-containing LC networks has been observed experimentally.¹⁵

Moreover, we have found similarly to Section 4.1 that the amplitude of deformation increases with increasing volume fraction of chromophores Φ_1 (not shown here). This result is in agreement with experiments.¹⁸ Uniaxial deformation under uniform light irradiation can be related to the degree of bending deformation which is caused by non-uniform light intensity across a film due to a high absorbance coefficient of azobenzene-containing materials. We have shown that the theoretically predicted bending angle as a function of the amount of azobenzene chromophores can be directly compared with experiments and is in a good agreement with experimental data.²⁹ Thus, the results given in the present section demonstrate that the light-induced deformation of azo-networks is very sensitive to their chemical structure.

5. Effects of the dilution of a LC network by the bent cis-isomers of chromophores

In previous Sections we considered the photo-mechanical behavior of azo-containing LC networks assuming that the concentration of rod-like trans-isomers is constant under light illumination. However, it is well known that under illumination with the visible or UV light, some fraction of the trans-isomers is transformed to the bent cis-isomers and, thus, the number density of trans-isomers decreases. The presence of the bent cis-isomers can result in several effects. For example, the size of a cis-isomer along the polarization vector \mathbf{E} is smaller than this size of the trans-isomer. This effect can lead to a direct change of the sample size along the vector \mathbf{E} . However, as it was shown in ref. 59, reduction in the size of chromophores due to the transition from the trans- to cis- state changes the relative deformation only by $\sim 0.2\%$. Therefore, we can neglect this effect.

We expect that a more pronounced effect is related to the reduction of the LC interactions due to the dilution of the LC-state by the bent cis-isomers, which are not LC objects. The reduction of the strengths of the LC-interactions leads to a change of the order parameters and is accompanied by the change of deformation. In the present Section we consider this dilution effect in detail. Under light illumination, the fractions of trans- (f_T) and cis- (f_C) isomers are given by:⁶⁰

$$\begin{aligned} f_C + f_T &= 1 \\ f_C(I_p) &= k_{TC} I_p \tau_p \end{aligned} \quad (23)$$

where k_{TC} is the rate constant of the trans-cis photoisomerization, I_p is the intensity of the light and τ_p is the characteristic time of the isomerization process:

$$\tau_p = \frac{1}{(k_{TC} + k_{CT}) I_p + \gamma}. \quad (24)$$

Here k_{CT} is the rate constant of the reverse cis-trans photoisomerization and γ is the rate of the cis-trans thermal back-relaxation. At $I_p \rightarrow \infty$ the fraction of the cis-isomers tends to its limiting value, $f_{C,\infty}$:

$$f_{C,\infty} = \frac{k_{TC}}{k_{TC} + k_{CT}}. \quad (25)$$

Note that the value of $f_{C,\infty}$ depends on the wavelengths of the light illumination ranging from 10% for visible light until 50% for UV-light.⁶⁰ In terms of $f_{C,\infty}$ Equation (23) can be rewritten as follows:

$$\Phi_1 = \Phi_1^{(0)} \cdot \left(1 - \frac{f_{C,\infty} \cdot (V_0 / kT)}{\beta + (V_0 / kT)} \right), \quad (26)$$

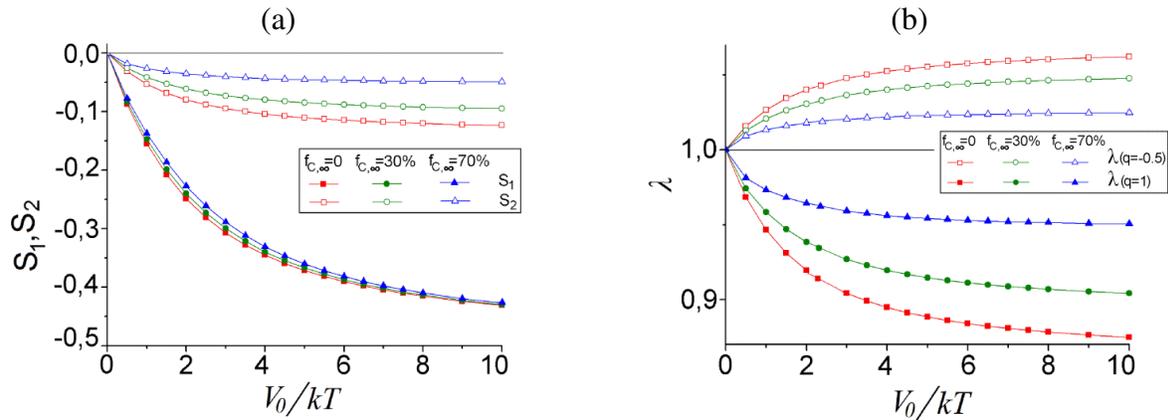


Figure 8. Dependences of the order parameters S_1 and S_2 (a) and of the elongation ratio (b) on the reduced strength of the light-induced potential V_0/kT for two approximations, in which (i) the volume fraction of trans-isomers is assumed to be constant, $f_{C,\infty} = 0$ (squares) and (ii) the dilution by the cis-isomers is taken into account: $f_{C,\infty} = 30\%$ (circles), 70% (triangles). $\Phi_1^{(0)} = 20\%$. Weak LC interactions, $a_{ij} < a_c$: $a_{11} = 3$, $a_{22} = 4$, $a_{12} = \sqrt{a_{11}a_{22}}$.

where $\Phi_1^{(0)}$ is the value of Φ_1 at the absence of the light. The volume fraction of the LC network remains constant, $\Phi_2 = 1 - \Phi_1^{(0)}$. The dimensionless parameter β in Equation (26) is defined as:

$$\beta = \frac{\gamma \cdot C}{kT \cdot (k_{TC} + k_{CT})}. \quad (27)$$

To derive Equations (25) and (26) we used the relationship between I_p and V_0 given by Equation (2). The typical values of the kinetic parameters have been estimated in the literature as follows: $C = 2.7 \times 10^{-19} \text{ J} \cdot \text{cm}^2 / \text{W}$,²⁹ $k_{TC} = 0.41 \text{ cm}^2 / \text{J}$,⁶⁰ $k_{CT} = 2.9 \text{ cm}^2 / \text{J}$.⁶⁰ Depending on the chemical structure, the value γ is ranged between 10^{-5} s^{-1} and 0.5 s^{-1} .⁶⁰⁻⁶³ Using the typical values of C , k_{TC} , k_{CT} and γ , the parameter β can be estimated at room temperature as $2 \cdot 10^{-4} < \beta < 10$. As an illustration, we used in our calculations the value $\beta = 0.5$, which assumes a relatively fast thermal cis-trans isomerization.

Figures 8-10 illustrate a comparison of the order parameters (a-panels) and elongation ratios (b-panels) as functions of V_0/kT for two approximations, in which (i) the volume fraction of trans-isomers is assumed to be unaffected by the light illumination: $\Phi_1 = \Phi_1^{(0)} = \text{const}$ (lines

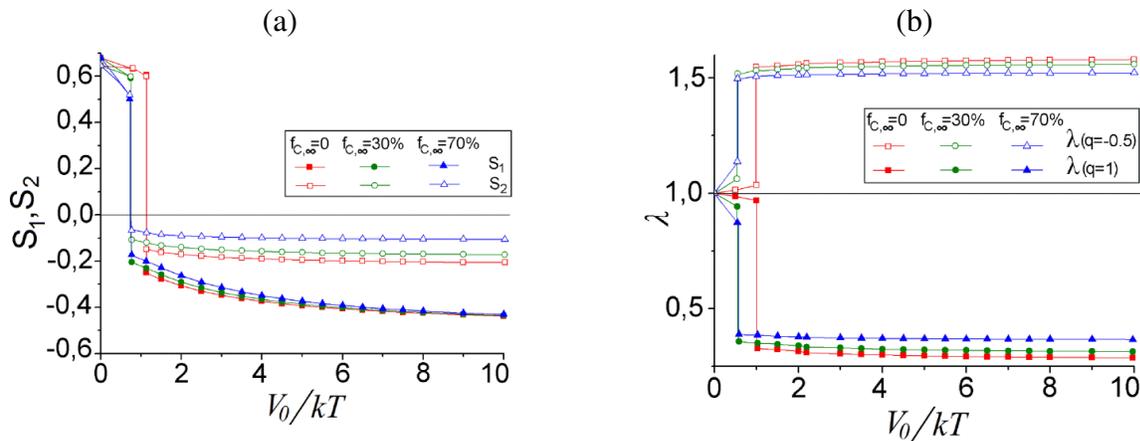


Figure 9. Same as Figure 8 but for strong LC interactions, $a_{ij} > a_c$: $a_{11} = 6$, $a_{22} = 5$.

with squares) or (ii) the dilution by the bent cis-isomers is taken into account according to Equation (26) (lines with circles and triangles). Figure 8 shows the results for weak LC interactions ($a_{ij} < a_c$), whereas Figures 9 and 10 illustrate the results for strong LC interactions ($a_{ij} > a_c$).

One can see from Figure 8 that the dilution effect leads to a decrease of the magnitudes of the order parameters $S_{1,2}$ and elongation ratio λ at weak LC interactions. The higher is the fraction of the cis-isomers, $f_{c,\infty}$, the smaller are the magnitudes of $S_{1,2}$ and λ . Note, however, that the change of the order parameter S_I with the appearance of the cis-isomers is relatively small. This is due to the fact that at weak LC interactions the ordering of the chromophores is caused mainly by the orientation potential of the light and its dependence on the LC interactions is relatively weak. This explains also an observation that the order parameters and elongation ratio change continuously with increasing V_0/kT at weak LC interactions (Figure 8).

At strong LC interactions, the influence of the light is able to induce a phase transition. The phase transition is accompanied by a stepwise change of both order parameters and the elongation ratio as functions of the strength of the light-induced potential V_0 at the transition

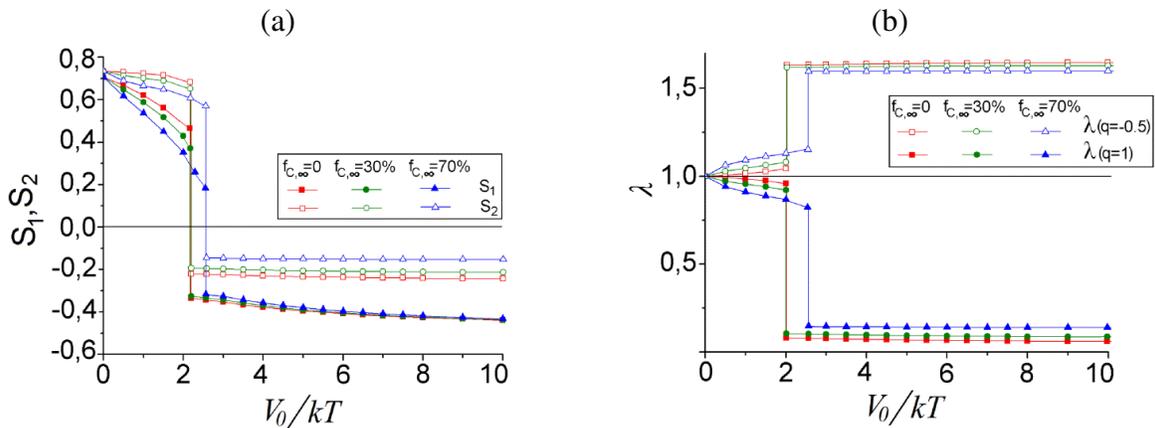


Figure 10. Same as Figure 8 but for strong LC interactions, $a_{ij} > a_c$: $a_{11} = 5$, $a_{22} = 6$.

point V_c (see Figures 9 and 10). The shift of the critical point V_c due to the dilution of the LC network by the bent cis-isomers is determined by two effects: reduction of the LC interactions according to Equation (3) and suppression of the influence of the orientation field V_0 according to Equation (7). If orientation interactions between the chromophores are stronger than these interactions between the mesogens ($a_{11} > a_{22}$), the reduction of the LC interactions provides the main contribution to the free energy. In this case the critical point V_c shifts to smaller values of V_0 , Figure 9. In the opposite case (at $a_{11} < a_{22}$) the suppression of the influence of the light-induced field provides the main contribution to the free energy and the critical point V_c shifts to higher values of V_0 , Figure 10.

Similar to the networks with weak LC interactions, the dilution effect leads to the decrease of the magnitudes of the order parameters $S_{1,2}$ for the networks with strong LC interactions at any values of the strength of the light-induced potential V_0 , Figures 9a and 10a. However, the change of the magnitude of the deformation due to the dilution effect is different at $V_0 < V_c$ and at $V_0 > V_c$. At $V_0 < V_c$ the dilution effects destabilize the LC state and, thus, amplify the light-induced deformation, as can be seen from Figures 9b and 10b. Note that distortion of the LC phase by the bent cis-isomers was used in many experiments in order to produce large-amplitude light-

induced deformation.³⁻⁵ Thus, our theoretical results agree well with the experiments. At $V_0 > V_c$ the dilution effects result in a slight decrease of the magnitude of deformation.

We conclude the present section by noting, that, as in the previous Section, the azobenzene networks with preferable orientation of the mesogens parallel ($q_2 = 1$) and perpendicular ($q_2 = -0.5$) to the main chains demonstrate contraction and expansion, respectively, with respect to the polarization vector \mathbf{E} , see Figures 8-10. Thus, the effect of dilution of an azobenzene network by the bent cis-isomers changes the values of the order parameters, magnitude of the deformation and the critical point V_c . However, it does not influence the main features of the photo-mechanical behavior: continuous and discontinuous change of the order parameters and deformation with increasing V_0/kT at weak and strong LC interactions, respectively, contraction and expansion of the network with respect to the polarization vector of the light \mathbf{E} , depending on the particular chemical structure.

6. Conclusion

The theory of photo-mechanical properties of a two-component polymer system consisting of a LC network with included azobenzene chromophores has been developed. Polymer networks of two types have been investigated, in which the chromophores are either dispersed in the network matrix or included chemically into the network strands.

It has been shown that increase of the volume fraction of the chromophores as well as the increase of the intensity of the orientation interactions between the chromophores and LC mesogens result in the increase of the magnitude of the network deformation. For isotropic networks with weak LC interactions, the deformation changes continuously with intensity of the light, whereas a light-induced phase transition takes place for anisotropic LC networks. The

phase transition is accompanied by the stepwise change of the degree of deformation. Polymer networks with preferable orientation of mesogens parallel / perpendicular to the main chains demonstrate contraction / expansion with respect to the polarization vector of the light. At fixed volume fraction of the chromophores, the magnitude of the light-induced deformation is higher for networks with azobenzene chromophores attached chemically to the network strands as compared to the networks with azobenzene chromophores dispersed in the structure. This effect is caused by the mechanical coupling between the network and chromophores.

The effect of dilution of the network by the bent cis-isomers of azobenzene chromophores leads to a decrease of the magnitudes of the order parameters for azobenzene chromophores and mesogens of the network. For isotropic networks with weak LC interactions, the dilution effect leads to a decrease of the magnitude of deformation. For anisotropic LC networks, the dilution effect results in the increase of the magnitude of deformation at weak light intensities (below the phase transition point) due to distortion of the LC state by the bent cis-isomers. At high light intensities (above the phase transition point), the dilution effect leads to a slight decrease of the magnitude of deformation.

Thus, using an elaborated microscopic model, which reflects a real complexity and variety of azo-containing polymers, we worked out a versatile theoretical approach to description of the photomechanical properties of these fascinating materials depending on their chemical structure and experimental conditions (temperature, wavelength and intensity of the light, etc.). The structure-property relationships obtained in our study can be useful in further practical developments of the light-controllable smart materials based on the LC polymer networks with included azobenzene chromophores.

Acknowledgement

The financial supports of the DFG grant GR 3725/2-2 and the Grant of the President of the Russian Federation for PhD-students are gratefully acknowledged.

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For the Table of Contents

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