Photo-induced deformation of azobenzene polymers: theory and simulations

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ABSTRACT

A microscopic theory is developed to describe light-induced deformation of azobenzene polymers of different chemical structures: uncross-linked low-molecular-weight azobenzene polymers and cross-linked azobenzene polymers (azobenzene elastomers) bearing azobenzene chromophores in their strands. According to the microscopic theory the light-induced deformation is caused by reorientation of azobenzene chromophores with respect to the electric vector of the linearly polarized light, **E**. Theoretical calculations of the order parameter of short azobenzene molecules (oligomers) affected by the light show that the sign of the light-induced deformation (expansion / contraction along the vector **E**) depends strongly on the chemical structure of the oligomers. The conclusion of the theory about different signs of the light-induced deformation of low-molecular-weight azobenzene polymers is in an agreement with performed series of molecular dynamics simulations. Using the microscopic theory it is shown that cross-linked azobenzene polymers demonstrate the same light-induced deformation (expansion / contraction) as their low-molecular-weight analogues, i.e. polymers consisting of short azobenzene molecules whose chemical structure is the same as chain fragments of the elastomers.

Keywords: azobenzene polymers, light-induced deformation, statistical physics, computer simulations

1. INTRODUCTION

Azobenzene polymers containing azo-moieties in their chemical structure are a class of smart materials which are able to transform the light energy into mechanical stress.[1-19] Since the deformation driven by the light can be controlled rapidly, precisely and remotely, azobenzene polymers have a fascinating potential for micro- and nano-technologies to produce alignment layers for liquid crystalline (LC) fluorescent polymers in the display technology,[1,2] to build waveguides and waveguide couplers,[3,4] to construct data storage media,[5,6] etc. A very hot topic in modern research is design of light-controllable artificial muscles based on azobenzene elastomers.[7-19]

Light-induced deformation of azobenzene polymers is initiated by the photoisomerization of azobenzene chromophores: the chromophores affected by the light of a proper wavelength are able to change their shape from the rod-like trans-state to the bent cis-state.[20-22] The light-induced mechanical force is so large that the light irradiation of the typical intensity $I_p \sim 1$ W/cm^2 can deform azobenzene polymers which are even in the glassy state.[23-28] This feature is used for the inscription of surface relief gratings onto thin azobenzene polymer films.[23-28] To explain the light-induced deformation of glassy azobenzene polymers, some authors have developed a concept of photo-induced softening.[29-35] According to this concept, the light of intensity $I_p \sim 1$ W/cm^2 is able to melt locally a glassy polymer, and such a "molten" polymer can be then irreversibly deformed under weak light-induced mechanical fields. However, as it was shown recently with the help of three different experimental techniques,[25-28] illumination with a visible light does not affect material properties of an azobenzene polymer such as bulk compliance, Young's modulus and viscosity. Therefore, one can claim unambiguously that an azobenzene polymer remains in a glassy state. Hence, the theories which need a concept of photo-induced softening are not able to describe the phenomenon in a correct way.

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Alternative approach to explain photo-mechanical behavior of azobenzene polymers is based on the orientation mechanism: influence of the linearly polarized light leads to orientation anisotropy of chromophores. This anisotropy appears due to anisotropic character of the photoisomerization process: maximal probability of the transition from the rod-like trans-state to the bent cis-state is achieved at such orientation of the rod-like chromophore, when its long axis is parallel to the electric vector of the light **E**.[20-22] As a result, after multiple trans-cis-trans photoisomerization cycles the number of rod-like chromophores, which are arranged parallel to the vector **E**, becomes lower than the number of chromophores which are oriented in perpendicular direction, i.e. orientation anisotropy appears. The light-induced orientation anisotropy can be described by introducing an effective orientation potential acting on each chromophore.[36] Recently, we developed a microscopic theory[37-39] which shows that the orientation potential introduced in ref.[36] provides values of the light-induced stress, σ, comparable and higher than the values of the yield stress, σ_Y, typical for glassy polymers: $\sigma \geq \sigma_Y \sim 50$ MPa at $I_p \sim 1$ W/cm^2. At stresses $\sigma > \sigma_Y$ a glassy polymer demonstrates an irreversible deformation. Thus, the microscopic theory based on the orientation mechanism of azobenzene chromophores is sufficient to explain irreversible light-induced deformation of glassy azobenzene polymers making the concept of photo-induced softening redundant. This demonstrates a great potential strength of the proposed orientation microscopic theory[36-39] for describing photo-mechanical properties of azobenzene polymers of different structures.

Another perspective class of photo-deformable polymers are azobenzene elastomers which display reversible elastic deformations up to tens of percents under light irradiation: uniaxial contraction and expansion depending on their chemical structure[7-12] as well as bending motions.[13-19] One can distinguish two types of photo-deformable azobenzene elastomers. The systems of the first type[9-16] are based on anisotropic liquid crystalline nematic elastomers with incorporated azobenzene chromophores. The rod-like trans-isomers of the chromophores stabilize the LC phase, whereas the bent cis-isomers destabilize it. Consequently, trans-cis photoisomerization caused by an ultraviolet illumination induces a transition of the LC-elastomer from the nematic to isotropic state, this transition being accompanied by a uniaxial deformation of a sample with respect to the LC-director. Theoretical description of the light-induced deformation in the materials of such kind can be based on a modification of the theory of phase transitions in nematic elastomers, with the nematic-to-isotropic phase transition being dependent now on the light intensity.[10,11]

Photo-deformable azobenzene elastomers of the second type are based on elastomeric matrices which are macroscopically isotropic.[14,17-19] Under influence of the linearly polarized light, azobenzene elastomers of this type are deformed along the electric vector of the light **E**. Thus, in contrast to azobenzene polymers based on nematic elastomers whose direction of deformation is restricted by the LC-director,[9-16] the direction of deformation in azobenzene elastomers based on isotropic matrix can be varied by rotating the polarization vector of the light.[14,17-19] Thus, investigation of photo-deformable elastomers with variable direction of deformation is of a special interest. To our knowledge, there are no theories in the literature which describe light-induced deformation of isotropic azobenzene elastomers with variable direction of deformation. In the present paper we develop the microscopic theory[36-39] based on the orientation mechanism of light-induced deformation to describe further the light-induced deformation of isotropic azobenzene elastomers along the electric vector of the light.

The paper is organized as follows. In Section 2.1 we present the microscopic theory of light-induced deformation of uncross-linked low-molecular-weight azobenzene polymers. The theory takes into consideration interactions of azobenzene chromophores with the light wave in the framework of the orientation mechanism[36-39] but does not consider more complex effects, such as excluded volume interactions between molecules, etc. We calculate the orientation order parameter of the oligomers as a function of the light intensity and show that the sign of deformation (expansion / contraction) depends on the chemical structure of the oligomers. Molecular dynamics (MD) simulations, presented in Section 2.2, complement these studies essentially, as far as the interaction potentials used incorporate both short-range repulsive and long-range attractive interactions between chromophores and polymer monomers. The computer simulation study provides a microscopic insight on structure-dependent photo-mechanical properties of low-molecular-weight azobenzene polymers. In Section 3 we extend the microscopic theory developed in Section 2.1 for short azobenzene molecules to cross-linked azobenzene elastomers taking long-chain elasticity of network strands into account.

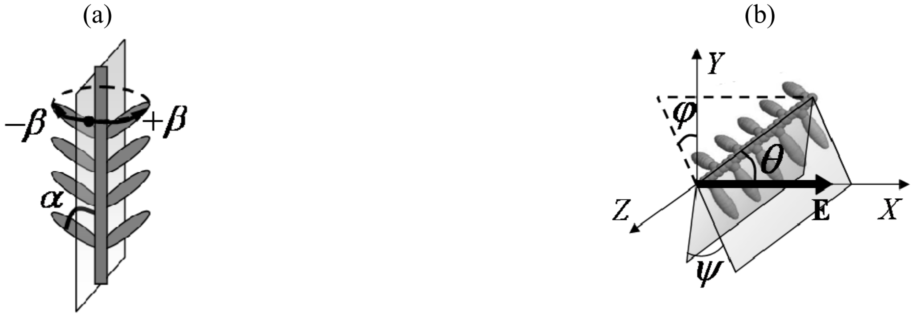

Figure 1. (a) Orientation distribution of chromophores inside an oligomer. (b) Spatial orientation of an oligomer with respect to the electric vector of the light **E**; θ, φ and ψ are the three Euler angles, see the text for details.

2. PHOTO-INDUCED DEFORMATION OF UNCROSS-LINKED LOW-MOLECULAR-WEIGHT AZOBENZENE POLYMERS

2.1 Microscopic theory

In the framework of the approach based on the orientation mechanism[37-39] a photo-induced deformation of azobenzene polymers is initiated by the orientation anisotropy, which is the result of multiple trans-cis-trans isomerization cycles of the chromophores under illumination with the linearly polarized light. Following the previous works,[37-42] we describe the light-induced orientation anisotropy of azobenzene chromophores with respect to the electric vector **E** of the light by means of an effective orientation potential acting on each chromophore:

$$V(\Theta) = V_0 \cos^2 \Theta \ , \tag{1}$$

where Θ is the angle between the long axis of the chromophore and the polarization vector of the light **E**; V_0 is the strength of the potential. The value of V_0 is determined by the intensity of the light I_p and can be estimated as:[36,43]

$$V_0 = \frac{1}{2} a \upsilon \tau \, I_p \equiv C \cdot I_p \ , \tag{2}$$

where a is the absorption coefficient, υ is the volume of an azobenzene and τ is the effective transition time between two isomer states. The value of the proportionality constant C at the room temperature has been estimated in previous works as $\mathrm{C} \approx 10^{-19}\ \mathrm{J{\cdot}cm^2/W}$.[36,43]

Reorientation of chromophores subjected to the potential (1) results in the reorientation of the whole azobenzene-containing polymer molecules due to the covalent bonding between the chromophores and the main chains of the molecules. Short azobenzene molecules (oligomers) are modeled as rigid rods which contain the same number of rod-like azobenzene chromophores rigidly attached to the main chains of the oligomers (Figure 1a). The architecture of chromophores inside oligomers is characterized by the orientation distribution function of chromophores around the main chain, $\mathrm{W}(\alpha,\beta)$. Here α is the angle between the long axis of a chromophore and the main chain; the angle β characterizes an azimuthal rotation of chromophores around the main chain. Azobenzene oligomers possess, as a rule, a planar symmetry;[40-42] the angle β is introduced as the angle between the plane of symmetry of the oligomer and the plane formed by the long axis of the chromophore and the main chain. The function $\mathrm{W}(\alpha,\beta)$ is defined by the potentials of internal rotations and by the length of spacers connecting the chromophores with the main chain. As a rule, one uses the spacers with symmetrical potentials of internal rotation, e.g. polyethylene's spacers.[9,10,44-46] Due to the symmetry of the spacers the orientation distribution of chromophores inside oligomers is symmetrical and obeys the following relations: $\mathrm{W}(\alpha,\beta) = \mathrm{W}(\alpha,-\beta)$ and $\mathrm{W}(\alpha,\beta) = \mathrm{W}(180°-\alpha,\beta)$.

The summarized orientation energy of chromophores inside an oligomer affected by the light can be treated as an effective potential, U, of the oligomer in the field of the light wave. It depends on the orientation of the oligomer in the space and can be written according to Equation (1) in the following form:

$$U(\Omega) = N_{\mathrm{ch}} V_0 u(\Omega) \ , \tag{3}$$

where N_{ch} is the number of chromophores in each oligomer and

$$u(\Omega) \equiv \left\langle \cos^2 \Theta(\Omega) \right\rangle_W \ . \tag{4}$$

The averaging here is performed over all chromophores inside the oligomer with the distribution function $W(\alpha,\beta)$; Ω denotes a set of the three Euler angles which define orientation of the oligomer in the space: $\Omega \equiv (\theta, \varphi, \psi)$, see Figure 1b: θ is the angle between the long axis of the oligomer and the vector **E** which is assumed to be directed along the x-axis; φ is the angle between the y-axis and the projection of the long axis of the oligomer on the plane YZ; ψ is the angle between the plane of symmetry of the oligomer and the plane formed by the long axis of the oligomer and the vector **E**. Thus, the angle φ determines the rotation of the oligomer around the vector **E** and the angle ψ defines the rotation of the oligomer around its long axis.

The value of the cosine of the angle Θ as a function of the angles α, β, θ, φ and ψ is given by:

$$\cos\Theta = \cos\theta\cos\alpha - \sin\theta\sin\alpha\cos(\psi+\beta) \ . \tag{5}$$

Now, from Equation (4) and (5) after averaging with the distribution function $W(\alpha,\beta)$ and using the symmetry of the oligomers, $W(\alpha,\beta) = W(\alpha,-\beta)$ and $W(\alpha,\beta) = W(180°-\alpha,\beta)$, one can find the function $u(\Omega)$ in the following form (cf. with Equation (35) of ref.[37]):

$$u(\Omega) = \frac{1}{2}\left[3\left\langle \sin^2\alpha \right\rangle_W - 2 + \left\langle \sin^2\alpha\cos 2\beta \right\rangle_W \cos 2\psi \right]\sin^2\theta \ . \tag{6}$$

We note that due to axial symmetry with respect to the vector **E**, the potential $u(\Omega)$ is independent of the angle φ. Moreover, the potential of an oligomer in the field of the light wave, $u(\Omega)$, is determined now by the orientation distribution of chromophores inside the oligomer; in particular, it is defined by the moments of the angular distribution of chromophores, $\langle\sin^2\alpha\rangle_W$ and $\langle\sin^2\alpha \cos 2\beta\rangle_W$. Below these factors are used as structural parameters of the theory.

Under influence of the potential (6) the system of azobenzene oligomers becomes uniaxially anisotropic. Uniaxially-ordered system of oligomers can be characterized by the orientation order parameter, S:

$$S(V_0) = \left\langle P_2(\cos\theta) \right\rangle \equiv \frac{3\left\langle \cos^2\theta \right\rangle - 1}{2} \ . \tag{7}$$

For an isotropic system one has $S = 0$, whereas for fully oriented system $S = 1$. In refs.[37-39] the order parameter S has been used for estimating the relative extension, ε, of a glassy polymer consisting of short azobenzene molecules:

$$\varepsilon \cong \varepsilon_{\max} \cdot S \ , \tag{8}$$

where $\varepsilon_{\max} > 0$ is the maximal relative extension corresponding to a fully oriented sample with $S = 1$. In the framework of the approximation given by Equation (8), we have calculated in refs.[37-39] the striction stress σ_{str} which appears at the moment when the light is switched on. The value σ_{str} has been calculated by means of the following equation:

$$\sigma_{\mathrm{str}} = -\left(\partial F / \partial\varepsilon\right)_{\varepsilon=0} \ , \tag{9}$$

where $F = F(\varepsilon, V_0)$ is the free energy of the oligomers in the field of the light wave. The free energy includes three contributions:[37-39] (i) elasticity of a glassy polymer consisting of azobenzene oligomers, (ii) energy of the oligomers in the orientation potential given by Equation (6), and (iii) orientation entropy of the oligomers. It was shown in refs.[37-39] that the striction stress obeys the following asymptotical behavior as a function of V_0:

$$\sigma_{\mathrm{str}}(V_0) \cong \begin{cases} C_1 n_0 V_0 / 3\varepsilon_{\max} & , N_{\mathrm{ch}} V_0 / kT << 1 \\ C_2 n_0 V_0 / 3\varepsilon_{\max} & , N_{\mathrm{ch}} V_0 / kT >> 1 \end{cases} \tag{10}$$

where n_0 is the number of chromophores in the unit volume and the dimensionless coefficients C_1 and C_2 are given by:

$$C_1 = 3\left\langle \sin^2\alpha \right\rangle_W - 2\,, \quad C_2 = 3\left\langle \sin^2\alpha \right\rangle_W - 2 - \left|\left\langle \sin^2\alpha\cos 2\beta \right\rangle_W\right|\,. \tag{11}$$

One can make two important conclusions from Equation (10). First of all, the striction stress estimated from the microscopic theory based on the orientation mechanism is proportional to the intensity of the light I_p: $\sigma_{str} \sim n_0 V_0 = n_0 C I_p$, where $C \approx 10^{-19}$ J·cm^2/W, see Equation (2). Thus, for the laser intensity $I_p \sim 1$ W/cm^2 and for the number density of azobenzenes $n_0 \cong 1.5\cdot 10^{21}$cm^{-3}, which is a typical value for these materials, we obtain $\sigma_{str} \sim n_0 C I_p \approx 100$ MPa. This value is comparable with the values of the yield stress typical for glassy polymers: $\sigma_Y \sim$ 10-100 MPa (e.g., $\sigma_Y \sim 50$ MPa for PMMA). At stresses $\sigma_{str} > \sigma_Y$, a glassy polymer is deformed irreversibly, and the deformation is fixed after the light is switched off. Thus, the microscopic theory is able to explain the possibility of irreversible deformation of glassy azobenzene polymers under light illumination and, consequently, explains the possibility for irreversible inscription of surface relief gratings[23-28] onto glassy azobenzene polymer films avoiding the concept of the light-induced softening.

Furthermore, Equations (10) and (11) show another important result: photo-mechanical behavior of azobenzene polymers depends strongly on their chemical structure, namely, on the orientation distribution of chromophores inside oligomers. In order to illustrate the structure-property relationship for low-molecular-weight azobenzene polymers, we have calculated in the present paper the dependence $S(V_0)$ at different values of the structural parameters $\langle \sin^2\alpha\rangle_W$ and $\langle \sin^2\alpha \cos 2\beta\rangle_W$; the dependence $S(V_0)$ can be used for estimation of the light-induced deformation: $\varepsilon \cong \varepsilon_{max}\cdot S(V_0)$, see Equation (8). The value of the order parameter $S(V_0)$ is calculated by means of Equation (7), where the factor $\langle \cos^2\theta\rangle$ as a function of V_0 is given by:[37]

$$\left\langle \cos^2\theta \right\rangle = \frac{\int d\Omega \;\cos^2\theta \exp\left[-\frac{N_{ch}V_0}{kT}u(\Omega)\right]}{\int d\Omega \exp\left[-\frac{N_{ch}V_0}{kT}u(\Omega)\right]}\;, \tag{12}$$

where k is the Boltzmann constant and T is absolute temperature. From Equations (7) and (12) one can obtain asymptotic behavior for $S(V_0)$ at small and high values of the parameter $N_{ch}V_0/kT$. Expanding into a series the right-hand side of Equation (12) with respect to the small parameter $N_{ch}V_0/kT$ and keeping only the first terms proportional to $N_{ch}V_0/kT$ that come from both numerator and denominator in Equation (12), we obtain for $S(V_0)$ using Equation (7):

$$S_0(V_0) \cong C_1 \frac{N_{ch}V_0}{15kT} \quad \text{at } \frac{N_{ch}V_0}{kT} << 1\;, \tag{13}$$

where the value of C_1 is given by Equation (11). Thus, if $C_1 > 0$, an azobenzene polymer demonstrates a uniaxial expansion ($\varepsilon > 0$), whereas if $C_1 < 0$ it shows a uniaxial contraction ($\varepsilon < 0$) at $N_{ch}V_0/kT << 1$.

At high values $N_{ch}V_0/kT >> 1$ photo-mechanical behavior of low-molecular-weight azobenzene polymers is controlled by the minima of the potential $u(\Omega)$. One can see from Equation (6) that the positions of minima for $u(\Omega)$ are determined by the sign of the parameter C_2 given by Equation (11). If $C_2 > 0$ the prefactor before $\sin^2\theta$ in Equation (6) for $u(\Omega)$ is positive at any values of ψ and, hence, the minimum of $u(\Omega)$ is achieved at $\theta = 0$ that corresponds to $S = 1$ according to Equation (7). Thus, if $C_2 > 0$ an azobenzene polymer demonstrates a uniaxial expansion along the electric vector of the light $\mathbf{E}$ ($S > 0$ and $\varepsilon > 0$) at $N_{ch}V_0/kT >> 1$. On the other side, if $C_2 < 0$ then there exist values ψ, for which the prefactor before $\sin^2\theta$ in Equation (6) for $u(\Omega)$ is negative. Hence, in this case the global minimum of $u(\Omega)$ is achieved at $\theta = 90°$ that corresponds to a planar orientation of the oligomers with $S = -0.5$ according to Equation (7). Thus, if $C_2 < 0$ an azobenzene polymer demonstrates a uniaxial contraction along the electric vector of the light $\mathbf{E}$ ($S < 0$ and $\varepsilon < 0$) at $N_{ch}V_0/kT >> 1$.

Summarizing the results for $S(V_0)$ at small and large strengths of the potential, one can distinguish three types of photo-mechanical behavior of short azobenzene molecules depending on their structure. **(I)** If $C_1 < 0$, then we have automatically that $C_2 < 0$ according to Equation (11), and in this case an azobenzene polymer demonstrates a uniaxial contraction ($S < 0$ and $\varepsilon < 0$) both at small and at large strengths of the potential. **(II)** If $C_2 > 0$, then we have automatically that $C_1 > 0$ according to Equation (11), and an azobenzene polymer shows a uniaxial expansion ($S > 0$ and $\varepsilon > 0$) both at small and at large strengths of the potential. **(III)** In the intermediate case, when $C_1 > 0$ and $C_2 < 0$, an

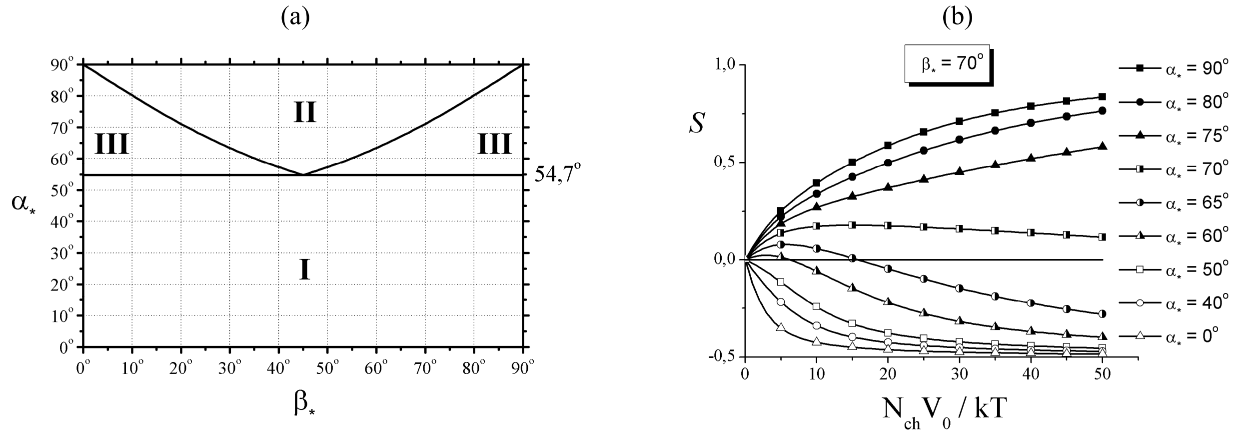

Figure 2. (a) Three areas of the values of the structural angles α_* and β_* for three types of photo-mechanical behavior of azobenzene polymers. (b) Dependences of the order parameter S on the reduced strength of the potential, $V_0 N_{\mathrm{ch}} / kT$, at fixed value of the structural angle $\beta_* = 70°$ and at varied values of the structural angle α_*.

azobenzene polymer demonstrates a non-monotonic deformation as a function of the strength of the potential: a uniaxial expansion at $N_{\mathrm{ch}} V_0 / kT << 1$ and a uniaxial contraction at $N_{\mathrm{ch}} V_0 / kT >> 1$.

To illustrate these three types of photo-mechanical behavior of low-molecular-weight azobenzene polymers, we have calculated the dependences $S(V_0)$ for oligomers, whose structural angles α and β are fixed at equiprobable values $\beta = \pm\beta_*$ and $\alpha = \alpha_*$, $180° - \alpha_*$, the values α_* and β_* being variables. Figure 2a shows the diagram for the values of the parameters α_* and β_*, at which three types of photomechanical behavior take place for azobenzene polymers: (I) monotonic contraction, (II) monotonic expansion, and (III) non-monotonic deformation of the polymer with increasing light intensity. The boundary between the areas (I) and (III) are given by the condition $C_1 = 0$ that reads $\sin^2\alpha_* = 2/3$, i.e. $\alpha_* \approx 54{,}7°$. The boundary between the areas (II) and (III) are given by the condition $C_2 = 0$ that can be rewritten as:

$$\alpha_* = A(\beta_*) \equiv \arcsin\sqrt{\frac{2}{3 - |\cos 2\beta_*|}} \quad . \tag{14}$$

Figure 2b shows the dependences $S(V_0)$ for different values of α_* and β_* belonging to the areas I, II, and III presented in Figure 2a. The dependences $S(V_0)$ have been calculated numerically using Equations (7) and (12). The results of numerical calculations show three types of photo-mechanical behavior of azobenzene polymers in accordance with qualitative considerations presented above.

I. When $\alpha_* < 54{,}7°$ (the area I in Figure 2a), the chromophores lie preferably along the main chains of oligomers. Their orientation perpendicular to the electric field **E** of the light results in the orientation of the oligomers also perpendicular to the vector **E** and is accompanied by a uniaxial contraction of an azobenzene polymer with respect to the vector **E** ($S < 0$ and $\varepsilon < 0$). In this case the function $S(V_0)$ decreases monotonically (open symbols in Figure 2b).

II. When $A(\beta_*) < \alpha_* < 90°$ (the area II in Figure 2a), the chromophores are arranged preferably perpendicular to the main chains of the oligomers. Orientation of the chromophores perpendicular to the electric vector **E** under light illumination leads to the orientation of the long axes of the oligomers parallel to the vector **E** and this is accompanied by a uniaxial expansion of an azobenzene polymer along the vector **E** ($S > 0$ and $\varepsilon > 0$). In this case $S(V_0)$ is a monotonically-increasing function (filled symbols in Figure 2b).

III. The values of structural angles $54{,}7° < \alpha_* < A(\beta_*)$ (the area III in Figure 2b) correspond to the structures with non-monotonic dependence of the order parameter on the field strength V_0: $S(V_0)$ is an increasing function at small values of V_0 and decreasing one at large field strengths (semi-open symbols in Figures 2b). One can see from Figure 2b that at increasing values of the angle α_* from $\alpha_* = 0°$ to $\alpha_* = 90°$ the order parameter S increases at fixed values of β_* and V_0, and the function $S(V_0)$ demonstrates sequentially the I, III, II – types of photo-mechanical behavior.

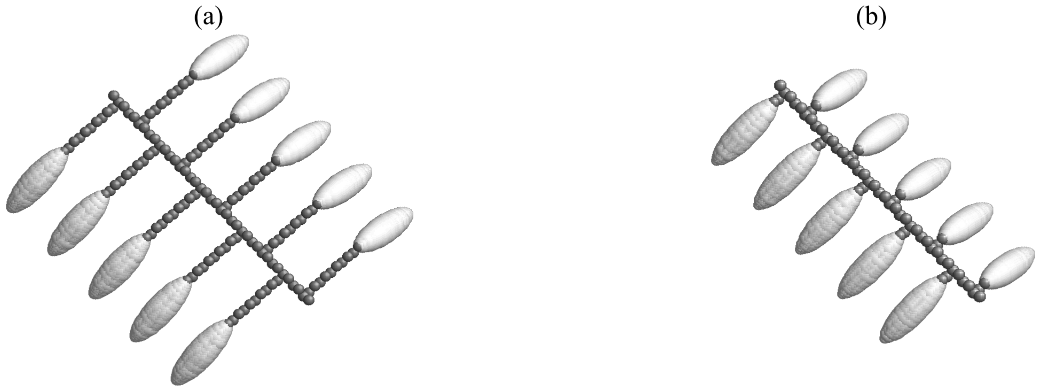

Figure 3. Molecular architecture of the weakly-coupled (a) and strongly-coupled (b) models.

We conclude the present subsection by noting that different signs of light-induced deformation (expansion / contraction) of low-molecular-weight azobenzene polymers of different chemical structures have been observed experimentally[44-47] and have been found in computer simulation studies.[40-42] These results demonstrate a great potential of the proposed microscopic theory based on the orientation mechanism of light-induced deformation for describing the photo-mechanical properties of azobenzene polymers. In the next section we present the results of computer simulation studies which take into account more complex effects on the photo-mechanical behavior of azobenzene polymers, e.g. effects of isotropic and anisotropic excluded volume interactions between azobenzene molecules as well as long-range anisotropic attraction forces that have not been considered in simple theoretical calculations presented above.

2.2 Molecular dynamics simulations

To study the light-induced deformation of uncross-linked low-molecular-weight azobenzene polymers, a series of molecular dynamics simulations has been performed. In the simulations we use a hybrid semi-atomistic modeling,[48] which is efficient for description of the structure, dynamics and phase transformations in LC polymers.[49-51] The polymer beads are represented as Lennard-Jones (LJ) sites and azobenzenes as single-site Gay-Berne[52] particles. Thus, both short-range excluded volume and long range anisotropic attractive interactions are taken into account explicitly. In this way one concentrates on a flexibility of polymer chains and on the ability of mesogens to form LC phases. To reflect a role of the spacer length and the rigidity of the polymer backbone, we construct two models for the side-chain LC polymers. The weakly-coupled model has a flexible backbone and long spacer of 10 LJ sites [40] (Figure 3a), whereas the strongly-coupled one has more rigid backbone and short spacer of two LJ sites[41-42] (Figure 3b). The models are targeted on the description of typical LC azo-polymer (e.g. P6a12) and amorphous azo-polymer (e.g. E1aP), respectively.[44] More details on force-field parameters are given elsewhere.[53]

The MD simulations are performed with the aid of the parallel program GBMOLDD.[54-55] A simulation box with periodic boundary conditions mimics the behavior of the LC polymers within a bulk volume element. We employed the simplified Parrinello-Rahman method, to be referred as $NP_{XX}P_{YY}P_{ZZ}$ ensemble, in which only the diagonal components of stress tensor are constrained[53]. For the integration of the equations of motion we used the leap-frog algorithm, the RATTLE constraint have been applied for the integration of mesogens rotation.[55] The time step $\Delta t = 2\,\mathrm{fs}$ was found to be acceptable for all production runs. The simulation times span from 35 ns to 120 ns and are in the range of 6–20 typical reorientation times for the azobenzene groups, depending on the particular model and its phase.

In both cases of weakly- and strongly-coupled models (representing LC and amorphous azo-polymers, respectively) we concentrate on following properties. The degree of orientational order is measured by the order parameter along certain axis, $S_{\|}$, and via nematic order parameter, S_2:

$$S_{\|} = \left\langle P_2(\mathbf{e}_i \cdot \mathbf{u}) \right\rangle \text{ and } S_2 = \left\langle P_2(\mathbf{e}_i \cdot \mathbf{n}) \right\rangle .$$

Here the unit vector $\mathbf{e}_i$ is defined along the long axis of the i-th elongated object, $\mathbf{u}$ is the unit vector along the axis of interest, $\mathbf{n}$ denotes the nematic director, $P_2(x)$ is the second Legendre polynomial. The elongated object can be either

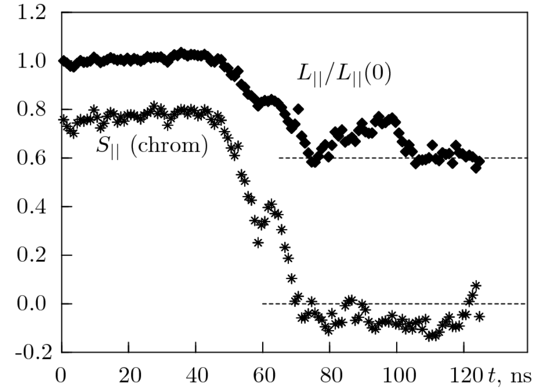

Figure 4. Evolution of the orientation order parameter of azobenzenes $S_{||}$ (asterisks) and of the reduced box dimension along the applied field $L_{||} / L_{||}(0)$ (diamonds) for the monodomain smectic phase at $T = 485\,K$ at reduced field strength $f = 0.005$.

the azobenzene unit or the equivalent ellipsoid of the polymer backbone.[53] Metric properties of polymer backbones are analysed via the components of the gyration tensor.[53] The main emphasize of our study are the microscopic mechanisms responsible for converting reorientational perturbations of the azobenzenes into mechanical deformation of the azo-polymer.

I. Liquid crystalline azo-polymer

We consider the monodomain smectic volume element well equilibrated at $T = 485\,K$, just below the smectic-isotropic transition temperature $T_{SI} \sim 490\,K$.[53] Both the azobenzenes director and applied reorientation field are directed along a certain axis, initial values for both order parameters along this axis are equal to $S_{||} = S_2 \approx 0.75$. With no external field applied the phase is found to be stable for at least 120 ns with minimal fluctuations of the order parameter and of dimensions of the box. With application of the field, this arrangement becomes energetically unfavorable and a torque applied to each chromophore attempts to reorient it perpendicularly to the field. The rate of the reorientation depends on the reduced field strength, f, defined as $V_0 = 1.5 f{\cdot}10^{-20}$ J, where V_0 is the strength of potential in Equation (1). It is also affected by coupling of the chromophores to the polymer matrix.

We found that a weak field with the reduced strength of $f = 0.005 - 0.02$ induces the smectic-isotropic phase transition. In particular, at $f = 0.005$ it takes place during the time interval of $t \sim 45 - 65$ ns, the duration of the transition is approximately 20 ns. The latter does not change with the increase of the field strength to $f = 0.2$ but the transition occurs earlier in time (more details are given elsewhere[42]). One can relate this transition to the so-called photo-chemical transition well known from the numerous experimental studies.[56-57] The transition is accompanied by an essential contraction of the simulation box along the direction of the field, $L_{||}$, as shown in Figure 4. One observes remarkable synchronicity in the behavior of $S_{||}$ and $L_{||}$.

One should stress that these simulations demonstrate that the photo-induced deformations of the LC azo-poymer can be achieved solely due to the reorientation of *trans*-azobenzenes. The deformation is attributed to the fact that the duration of the transition (20 ns) is shorter than the estimated relaxation times for the chromophores reorientations in the equilibrium state, $\tau \approx 43$ ns.[53] As it is shown in Ref. 42, in stronger fields, the smectic-isotropic transition is followed by the isotropic-smectic one, the resulting smectic phase being regrown in such a way that the azobenzenes are perpendicular to the applied field (polarization vector). One should note that no systematic deformation is found during this second transition, this finding is also confirmed by the simulations performed directly in a polydomain isotropic phase.[42] One may conclude that the defining factor in contraction of the volume element of the LC azo-polymer along the field is the “randomization” of the azobenzenes orientations. The spacers are also found to align partially along the nematic director in smectic phase,[42] therefore these also add to the net effect.

To clarify the role of the rearrangements of the backbones we consider the components of their averaged gyration tensor $G_{\alpha,\beta}$ in respect to the direction of the applied field. In the initial smectic phase $G_{||}^{1/2} \approx 2.6\ \mathring{A}$, this value is essentially

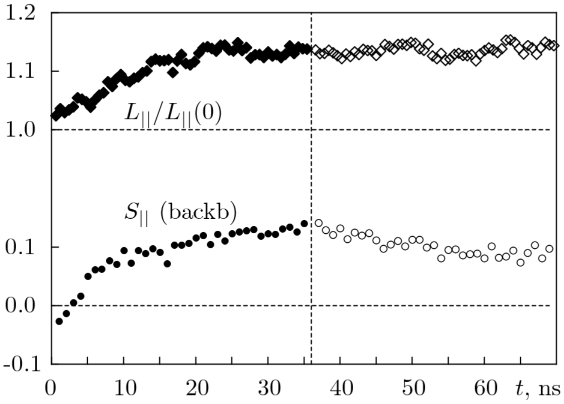

Figure 5. Evolution of the orientational order parameter of polymer backbones $S_{||}$ (circles) and of the reduced box dimension along the applied field $L_{||} / L_{||}(0)$ (diamonds) for the isotropic amorphous phase at $T = 485\,K$ averaged over runs with the reduced field strengths $f = 0.15$, 0.20 and 0.50 .

lower than $G_{\perp}{}^{1/2} \approx 5.5$ Å indicating "sandwiching" backbones in between the azobenzene layers.[53] Upon the field-induced transition, in the isotropic phase, all values are found to be approximately equal to 4.47 Å.[42] Therefore, during the smectic-isotropic transition the component $G_{||}$ increases and this effect "works" towards the extension of the volume element along the field, i.e. in an opposite direction to that of the azobenzenes. The net result is, however, contraction of the volume element, most likely, due to bulkiness of rigid azobenzenes, long spacers and to the flexibility of backbones in this model.

For the polydomain smectic phase no systematic deformation is observed, in contrary to theoretical predictions[32] or experimental results.[17,58] Possible reason behind this result is either modeling (the deformations of opposite sign, related to chromophores and backbones rearrangements, cancel each other) or computational (insufficient system size) issue.

II. Amorphous azo-polymers

The strongly-coupled model is used to represent an amorphous azo-polymer. The initial phase is macroscopically isotropic, therefore we undertake three separate simulations to improve the statistics. In each case the field was directed along *x*-, *y*- and *z*-axis, respectively, and the results over three runs were averaged afterwards. The glass transition temperature T_G for this model is estimated from the density vs temperature plot obtained via step-by-step cooling of the melt within the temperature interval of $T \in [350\,K, 500\,K]$. It is found to be around $450\,K$ (for more details see Ref.[42]).

Most technological applications of such materials are done well below T_G, however, the required time scales are difficult to cover within the MD simulations. We performed a set of simulations at $T = 450\,K \sim T_G$ targeted to reveal certain tendencies for the photo-induced deformations that occur at reduction of the temperature and could be extrapolated further to $T < T_G$ region. The effect of photo-induced deformation was observed in a range of field strength $f \sim 0.1 - 0.7$. All properties of interest are found to behave quite similarly for $f = 0.15$, 0.20 and 0.50 field strengths (here one can ignore small differences in reorientation dynamics in this interval of values of f), and, therefore the results are averaged over these runs to improve statistics.

The behavior of the orientation order parameters for the backbones and of the box dimension along the field are shown in Figure 5. Their values, stabilized after application of the field for $t = 37$ ns, are found to be kept after the field is switched off for at least another 30 ns. This is in a sharp contrast to the case of $T = 500\,K > T_G$, when the order vanishes in about 5 ns after the field is switched off.[42] The same holds true also for the dimension of the volume element along the field $L_{||}$, which changes synchroneously with the orientation order parameter for the backbones.

The results obtained provide an evidence for the following microscopic mechanism for photo-induced deformations in a strongly-coupled model. Due to the strong coupling between chromophores and backbones, the molecules behave

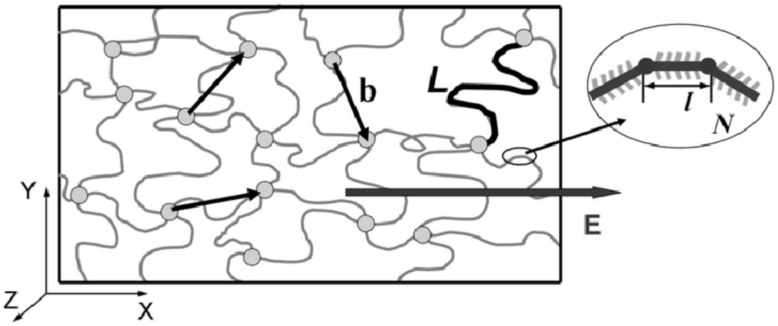

Figure 6. Model of an azobenzene elastomer: each network strand consists of N freely-jointed rod-like Kuhn segments bearing N_{ch} azobenzene chromophores in side chains; $L = Nl$ is the contour length of a network strand.

similarly to rigid bodies (compare with assumption of the microscopic theory in Section 2.1). Given suitable conditions, these massive molecular reorientations lead to the build-up of anisotropic internal stress which causes permanent deformation of the volume element at $T \sim T_G$. The sign of the deformation (extension of the volume element along the field direction) points out on the role of backbone rigidity, as far as the effect of backbones reorientation wins over the effect of chromophores reorientation perpendicularly to the field.

To conclude the present subsection, we note that the molecular dynamics simulations demonstrate unambiguously that opposite photo-induced deformations, observed experimentally on uncross-linked liquid crystalline and amorphous polymers, can be explained solely on the basis of molecular reorientations initiated by application of the effective light-induced orientation potential. For both molecular architectures being considered, chromophores orient perpendicularly and backbones orient parallel in respect to the external field (which direction is associated with the polarization vector). These reorientations compete in terms of volume element deformation, as far as chromophores reorientation promote contraction (prevails for the LC polymers), whereas that of the backbones promotes extension (prevails for the amorphous polymers) along the direction of the field. The final result depends, therefore, on subtle details of molecular architecture.

3. PHOTO-INDUCED DEFORMATION OF CROSS-LINKED AZOBENZENE POLYMERS: EXTENSION OF THE MICROSCOPIC THEORY

By introducing azobenzene chromophores into a polymer network matrix, photo-deformable azobenzene elastomers have been recently synthesized which demonstrate reversible deformation under light irradiation: uniaxial contraction and expansion depending on their chemical structure[7-12] as well as bending motions.[13-19] In the present section we extend the microscopic theory developed in Section 2.1 for uncross-linked azobenzene polymers to cross-linked azobenzene polymers (azobenzene elastomers) bearing azobenzene chromophores in their strands.

An azobenzene elastomer is modeled as an ensemble of polymer chains between network junctions (network strands). Each network strand consists of N freely-jointed rod-like Kuhn segments, see Figure 6. Each Kuhn segment contains N_{ch} azobenzene chromophores which are chemically attached to the main chain of the segment (Figure 6). Architecture of chromophores inside the Kuhn segments is characterized by the orientation distribution function, $W(\alpha,\beta)$, as it was presented in Section 2.1 for short azobenzene molecules (oligomers). Here α is the angle between the long axis of a chromophore and the main chain; β is the angle between the plane of symmetry of the Kuhn segment and the plane formed by the long axis of the chromophore and the main chain (Figure 1a). In other words, short azobenzene molecules which have been modeled in Section 2.1 are considered now as Kuhn segments of network strands in azobenzene elastomers. By this, we extend the formalism presented in Section 2.1 for uncross-linked azobenzene polymers to cross-linked azobenzene polymers taking the chain structure of network strands explicitly into account.

We consider highly elastic azobenzene elastomers whose network strands are long enough ($N >> 1$), so that the distribution of their end-to-end vectors **b** (see Figure 6) obeys the Gaussian statistics. In the absence of any external fields, the end-to-end vector's distribution of network strands is isotropic and can be written in the following form:[59,60]

$$P_0(\mathbf{b}) = C_0 \exp\left[-\frac{3\mathbf{b}^2}{2\left\langle \mathbf{b}^2 \right\rangle}\right] , \tag{15}$$

where the index "0" denotes the distribution of the end-to-end vectors **b** in an isotropic azobenzene elastomer without external fields; C_0 is the normalization constant and $\langle \mathbf{b}^2 \rangle = Nl^2$, where l is the length of the Kuhn segment. We note that the approach given by Equation (15) does not take into account the finite extensibility of network strands, since it allows the network strands to display unrealistic end-to-end distances with $|\mathbf{b}| > Nl$. However, the probability of conformations with $|\mathbf{b}| \geq Nl$ (relative to the probability of the state with $|\mathbf{b}| = 0$) can be estimated as $P_0/C_0 \leq \exp(-3N/2)$ according to Equation (15), i.e. it is negligibly small at $N >> 1$ (e.g., $P_0/C_0 \approx 0.01$ at $N = 3$). Thus, at $N \geq 3$ Equation (15) provides a very good approximation for statistics of network strands (cf. with ref. 61).

Under illumination with the linearly polarized light, each Kuhn segment is affected by the orientation potential given by Equations (3) and (6) due to the interaction of the chromophores with the light wave. Thus, under light illumination the network strands change their conformations, and each end-to-end vector **b** is transformed into a new vector **b′**. As in a classical theory of rubber elasticity,[59,60] we assume that network strands deform affinely with the bulk deformation of the elastomer because of the constraints of the crosslinks. Using the incompressibility of elastomers, one can write the condition of affinity of deformation in the following form:

$$b'_x = b_x \lambda \text{ , } b'_y = b_y / \sqrt{\lambda} \text{ , and } b'_z = b_z / \sqrt{\lambda} \text{ ,} \tag{16}$$

where λ is the elongation ratio of a sample along the x-axis. As in Section 2.1 we assume here that the electric vector of the light **E** is directed along the x-axis.

Below we will use the Gaussian approach also for deformed azobenzene elastomers. Note, that the validity of the Gaussian approach can cover a broad region of deformations λ, if the network strands are long enough ($N >> 1$). To see this, we recall that the Gaussian approach describes very well the statistics of stretched polymer chains if their end-to-end distances are smaller than 40% of their contour lengths, i.e. $|\mathbf{b}'| \leq 0.4Nl$.[61] At $|\mathbf{b}'| > 0.4Nl$ the effects of finite extensibility of polymer chains should be taken into account. Moreover, the main contribution to the statistics of an elastomer comes from network strands whose initial end-to-end distances are given by $\mathbf{b}^2 \leq Nl^2$, according to Equation (15). Thus, the Gaussian approach is applicable to a stretched elastomer, if all strands with initial end-to-end distances $\mathbf{b}^2 \leq Nl^2$ are stretched after deformation of the elastomer not larger than 40% of their contour length, i.e. when the condition $|\mathbf{b}'| \leq 0.4Nl$ is fulfilled at least for the chains with initial elongation $|\mathbf{b}| = N^{1/2}l$. Substituting the condition $|\mathbf{b}'| \leq 0.4Nl$ for $|\mathbf{b}| = N^{1/2}l$ into Equation (16) separately for the chains, which are stretched along the x- and y-axes, we obtain the following conditions for λ in the Gaussian regime: $N^{1/2}l\lambda \leq 0.4Nl$ and $N^{1/2}l / \lambda^{-1/2} \leq 0.4Nl$. The last two conditions can be rewritten as follows:

$$6.25 / N \leq \lambda \leq 0.4\sqrt{N} \text{ .} \tag{17}$$

One can see that the condition (17) for the Gaussian regime can cover a large region of deformation at $N >> 1$. For instance, $0.06 \leq \lambda \leq 4$ at $N = 100$, and $0.25 \leq \lambda \leq 2$ at $N = 25$, i.e. the Gaussian regime can hold until hundreds percents of the relative deformation of the elastomer, $\varepsilon \equiv \lambda - 1$.

Thus, at values λ given by Equation (17), one can use the Gaussian approach for the statistics of network strands. The distribution of the end-to-end vectors **b′** of network strands in a deformed elastomer can be written in the framework of the Gaussian approach as follows:

$$P(\mathbf{b}') = C \exp\left[-\left(\frac{(b'_x)^2}{2\left\langle (b'_x)^2 \right\rangle} + \frac{(b'_y)^2}{2\left\langle (b'_y)^2 \right\rangle} + \frac{(b'_z)^2}{2\left\langle (b'_z)^2 \right\rangle}\right)\right] , \tag{18}$$

where C is a normalization constant. In contrast to an undeformed elastomer which is characterized by an isotropic distribution of the end-to-end vectors of network strands (see Equation (15)), the distribution $P(\mathbf{b}')$ becomes anisotropic, i.e. $\langle (b'_x)^2 \rangle \neq \langle (b'_y)^2 \rangle$ and $\langle (b'_x)^2 \rangle \neq \langle (b'_z)^2 \rangle$ due to reorientation of the Kuhn segments with respect to the vector **E** after the light is switched on. The mean-square sizes of polymer coils $\langle (b'_x)^2 \rangle$, $\langle (b'_y)^2 \rangle$, and $\langle (b'_z)^2 \rangle$ can be expressed in terms of the averaged projections of the Kuhn segments on the x, y, and z-axes:

$$\left\langle (b'_\alpha)^2 \right\rangle = Nl^2 \left\langle \cos^2\theta_\alpha \right\rangle \text{ for } \alpha = x, y, z \; , \tag{19}$$

where θ_α are the angles between the long axis of the Kuhn segment and the x-, y-, and z-axes. The values $\cos\theta_\alpha$ can be rewritten in terms of the Euler angles presented in Figure 1b in the following form: $\cos\theta_x = \cos\theta$, $\cos\theta_y = \sin\theta\cos\varphi$, and $\cos\theta_z = \sin\theta\sin\varphi$. At the absence of the light, we have $\langle\cos^2\theta_x\rangle = \langle\cos^2\theta_y\rangle = \langle\cos^2\theta_z\rangle = 1/3$ and the distribution given by Equation (18) is reduced to Equation (15) for isotropic elastomers. Under light irradiation the polymer coils between network junctions becomes anisotropic: $\langle\cos^2\theta_x\rangle \neq \langle\cos^2\theta_y\rangle = \langle\cos^2\theta_z\rangle$; the equality $\langle\cos^2\theta_y\rangle = \langle\cos^2\theta_z\rangle$ follows from the axial symmetry of the elastomer with respect to the vector **E**.

Now, it is a simple matter to find the light-induced elongation λ as a function of the light intensity using the equation for the free energy F (per the unit volume):

$$F(\lambda) = -ckT\left\langle \ln P(b') \right\rangle_{P_0} \; , \tag{20}$$

where c is the number of network strands in the unit volume, and the averaging runs over all strands, i.e. with the distribution function P_0 given by Equation (15). Substituting Equation (18) into (20) and using the relationship between vectors **b** and **b′** given by Equation (16) we obtain the following expression for $F(\lambda)$ taking into account Equation (19):

$$F(\lambda) = \frac{ckT}{2Nl^2}\left[\frac{\left\langle b_x^2 \right\rangle_{P_0} \lambda^2}{\left\langle \cos^2\theta_x \right\rangle} + \frac{\left\langle b_y^2 \right\rangle_{P_0} \lambda^{-1}}{\left\langle \cos^2\theta_y \right\rangle} + \frac{\left\langle b_z^2 \right\rangle_{P_0} \lambda^{-1}}{\left\langle \cos^2\theta_z \right\rangle} \right] \; . \tag{21}$$

The equilibrium value of the light-induced elongation λ is determined from the minimum of the free energy, $\partial F / \partial\lambda = 0$. Using the fact that $\langle(b_x)^2\rangle_{P_0} = \langle(b_y)^2\rangle_{P_0} = \langle(b_z)^2\rangle_{P_0}$ for an isotropic elastomer as well the equality $\langle\cos^2\theta_y\rangle = \langle\cos^2\theta_z\rangle$ discussed above, we obtain the equilibrium elongation λ from the condition $\partial F / \partial\lambda = 0$ in the following form:

$$\lambda = \left(\frac{\left\langle \cos^2\theta_x \right\rangle}{\left\langle \cos^2\theta_y \right\rangle} \right)^{1/3} \; . \tag{22}$$

The right-hand side of the last equation depends on the strength of the orientation potential V_0 which is proportional to the light intensity I_p, see Equation (2); the dependence of the factors $\langle\cos^2\theta_\alpha\rangle$ on V_0 is given by Equation (12). Thus, the light-induced elongation of azobenzene elastomers in the Gaussian regime is independent of the chain length N, since in this regime the finite extensibility of network strands plays almost no role. At the same time, according to Equation (22) the deformation of an azobenzene elastomer is determined by the orientation anisotropy in the system of separate rod-like Kuhn segments (oligomers) bearing chromophores in side chains. The orientation anisotropy of short azobenzene molecules has been investigated in Section 2.1 in terms of the order parameter S. Now, using the relationships $\langle\cos^2\theta_x\rangle = (1+2S) / 3$ and $\langle\cos^2\theta_y\rangle = \langle\cos^2\theta_z\rangle = (1-S) / 3$, which follow from Equation (7) and from the equality $\cos^2\theta_x + \cos^2\theta_y + \cos^2\theta_z = 1$, Equation (22) can be rewritten in terms of S for oligomers as follows:

$$\lambda(V_0) = \left(\frac{1+2S(V_0)}{1-S(V_0)} \right)^{1/3} \; . \tag{23}$$

The last equation relates the light-induced elongation of an azobenzene elastomer with the light-induced orientation order in its low-molecular-weight analogue, i.e. in the system of oligomers, whose chemical structure is the same as chain segments of the elastomer. Now, using Equation (23) we can extend the results obtained above for uncross-linked low-molecular-weight azobenzene polymers to cross-linked azobenzene polymers. We recall that the order parameter S was used in Section 2.1 for estimating the relative extension ε of glassy polymers consisting of short azobenzene molecules: $\varepsilon = \varepsilon_{\max} S$, see Equation (8). From Equation (23) one can see that an azobenzene elastomer should demonstrate the same photo-mechanical behavior (expansion / contraction) as its low-molecular-weight analogue: the elastomer displays a uniaxial expansion along the electric vector of the light **E** ($\lambda > 1$), if its low-molecular-weight analogue demonstrates the expansion along the vector **E** ($S > 0$, $\varepsilon > 0$), and vice versa: $\lambda < 1$ if $S < 0$, $\varepsilon < 0$. Moreover, as low-molecular-weight azobenzene polymers, azobenzene elastomers should display three types of photo-mechanical behavior depending on the chemical structure of their network strands: (i) contraction along the electric vector of the light **E**,

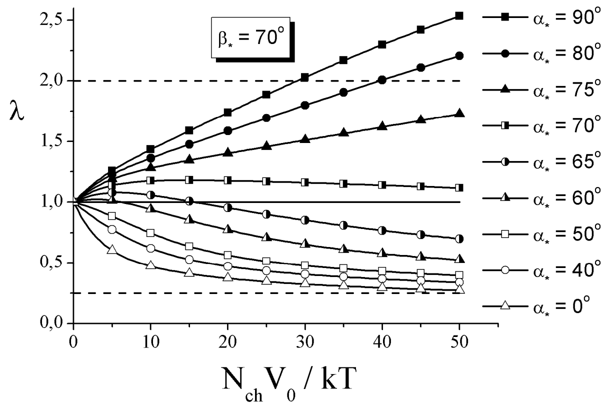

Figure 7. Dependences of the elongation ratio λ on the reduced strength of the potential, V_0N_{ch} / kT , at fixed value of the structural angle $\beta_* = 70°$ and at varying values of the structural angle α_*. The strand length is $N = 25$. Dashed lines show the boundaries of the region where the Gaussian approach is valid according to Equation (17).

(ii) expansion along the vector **E**, and (iii) non-monotonic behavior of the deformation with the light intensity (expansion at small light intensities and contraction at high light intensities).

Figure 7 shows the dependences $\lambda(V_0)$ calculated in the framework of the Gaussian approach given by Equation (23) for azobenzene elastomers, whose structural angles of network strands α and β are fixed at equiprobable values $\beta = \pm\beta_*$ and $\alpha = \alpha_*$, $180° - \alpha_*$; parameters α_* and β_* have been chosen to be of the same values as in Figure 2b for uncross-linked polymers. One can see from Figure 7 three types of photo-mechanical behavior of azobenzene elastomers: (I) monotonic contraction along the electric vector of the light **E** (open symbols), (II) monotonic expansion along the vector **E** (filled symbols), and (III) non-monotonic behavior of λ as a function of V_0 (semi-open symbols). We note that the diagram for the values α_* and β_*, at which three types of photomechanical behavior take place for azobenzene elastomers (I, II, III), is the same as in Figure 2a for uncross-linked polymers due to the connection between photo-mechanical properties of uncross-linked and cross-linked azobenzene polymers discussed above.

Dashed lines in Figure 7 show the boundaries of the region where the Gaussian approach is valid for $N = 25$, as an example, according to Equation (17). One can see that even until the values of the strength of potential $V_0N_{\mathrm{ch}} / kT \sim 30$, the values of the light-induced deformation λ belong to the validity range of the Gaussian regime. For elastomers built from longer chains ($N > 25$) this region is longer according to Equation (17). Using Equation (2), the light intensity corresponding to the characteristic values $V_0N_{\mathrm{ch}} / kT \cong 30$ at the room temperature and for $N_{\mathrm{ch}} = 10$ can be estimated as $I_{\mathrm{p}} \cong 100$ mW/cm^2. The last value belongs to a typical region of the light intensities which are used in experiments on light-induced deformations of azobenzene elastomers.[3-13] Thus, there exists a broad region of the light intensity where the Gaussian approach can be applied for calculation of the light-induced deformation of azobenzene elastomers. We note that at very large degrees of deformation the finite extensibility of network strands can strongly influence the photo-mechanical behavior of azobenzene elastomers. One can expect that at high light intensities the elongation λ tends to its limiting value which depends on the length of network strands: the shorter are the chains between junctions, the smaller is the elongation λ at the same light intensity. More detailed analysis of the effects of finite extensibility of network strands on the photo-mechanical behavior of azobenzene elastomers can be a topic of further generalizations.

4. CONCLUSIONS

In this study we undertake both theoretical and computer simulation studies of the light-induced deformations in azobenzene-containing polymers. Both cases of uncross-linked and cross-linked (elastomeric) systems are considered. Our main assumption is that the reorientation of trans-isomers of azobenzenes perpendicularly to the polarization vector plays the principal role in subsequent molecular rearrangements in the polymer, which, in turn, result in observed deformation of a sample under illumination. This reorientation is modeled in a statistical way, via application of the effective light-induced orientation field. Molecular dynamics simulations of the uncross-linked azobenzene polymers indicate that in the case of the liquid crystalline sample the principal microscopic mechanism is the order-disorder transition, whereas for the amorphous sample it is the rearrangement of stiff polymer backbones parallel to the field. In this way, the rigidity of the backbone and the amount of coupling between the chromophores and backbones are defining factors in a sign of final deformation under illumination. Theoretical studies concentrate on various scenarios for the deformation depending of angular distributions of chromophores in respect to the backbone. We have shown that azobenzene polymers demonstrate uniaxial contraction, uniaxial elongation or in case of some architectures even a non-monotonic dependence of sample deformation on the light intensity. Importantly, it is found in the theoretical studies that the sign of the deformation does not change upon cross-linking of the sample. Hence, it is expected that the microscopic mechanisms observed in the simulations are valid also for the elastomer case. This work is currently in progress.

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