

# Light-Induced Deformation of Azobenzene Elastomers: A Regular Cubic Network Model

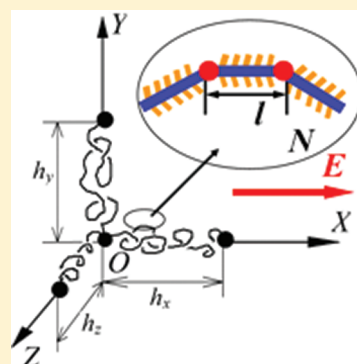
V. Toshchevikov,<sup>†,‡,\*</sup> M. Saphiannikova,<sup>†</sup> and G. Heinrich<sup>†,§</sup>

<sup>†</sup>Leibniz Institute of Polymer Research Dresden, 01069 Dresden, Germany

<sup>‡</sup>Institute of Macromolecular Compounds, 199004 Saint-Petersburg, Russia

<sup>§</sup>Institut für Werkstoffwissenschaft, Technische Universität Dresden, 01069 Dresden, Germany

**ABSTRACT:** We propose a microscopic theory of light-induced deformation of azobenzene elastomers bearing photosensitive azo-moieties in their strands. The theory is based on the orientation approach (Toshchevikov et al. *J. Phys. Chem. B* 2009, 113, 5032), in which the light-induced mechanical stress originates from reorientation of chromophores with respect to the electric vector of the light. A regular cubic network model built from freely jointed polymer chains bearing azobenzene chromophores is used to calculate the light-induced deformation of azobenzene elastomers under homogeneous light illumination. We show that the photomechanical behavior of azobenzene elastomers is very sensitive to their chemical structure: it depends on the orientation distribution of chromophores around the main chains which is defined by the chemical structure of spacers. Depending on the chemical structure, azobenzene elastomers demonstrate either expansion or uniaxial contraction along the electric vector of the light. The magnitude of the light-induced deformation depends on the degree of cross-linking: the larger is the degree of cross-linking, the smaller is the magnitude of deformation. Additionally, we discuss possible bending motions of azobenzene elastomers under inhomogeneous light illumination, when the light intensity changes inside the polymer due to the absorption of the light energy by the material.



## 1. INTRODUCTION

Photosensitive elastomers containing azobenzene chromophores in their structure have been extensively explored recently as highly functional and smart materials which are able to transform the light energy into mechanical stress.<sup>1–13</sup> Since the light stimulus can be controlled rapidly, precisely, and remotely, azobenzene elastomers have a fascinating potential for technical applications serving as artificial muscles, sensors, microrobots, micropumps, and actuators. Moreover, since deformation driven by light requires neither batteries nor controlling equipment on the materials themselves, it should be simple to miniaturize the photosensitive devices based on azobenzene elastomers for micro- and nanoapplications.

Light-induced deformation of azobenzene polymers is caused by the photoisomerization process of azobenzene chromophores under light illumination. 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,<sup>14–16</sup> that leads to the light-induced deformation of azobenzene polymers. By introducing azobenzene chromophores into a polymer network matrix, photodeformable azobenzene elastomers have been synthesized recently demonstrating reversible deformation under light irradiation: either contraction or expansion depending on their chemical structure.<sup>1–6</sup> More recently, by using azobenzene liquid crystalline elastomers (LCEs), not only photocontraction/expansion but also photoinduced bending has been acquired.<sup>7–13</sup> In comparison with contraction/expansion, which is a two-dimensional action, bending is a three-dimensional movement and should be

advantageous for constructing artificial hands and medical micro-robots. For instance, an unusual behavior was observed for an azo-dye doped LCE sample floating on water: the LCE was found to drift away from the illuminated spot resembling the motion of flatfish such as skates or rays.<sup>10</sup>

There exist two types of photodeformable elastomers containing azobenzene moieties. In the systems of the first type,<sup>3–10</sup> azobenzene chromophores are incorporated into anisotropic liquid crystalline (LC) nematic elastomers. The rod-like trans-isomers of azobenzene chromophores stabilize the LC phase, whereas the bent *cis*-isomers destabilize it. Consequently, *trans*–*cis* photoisomerization caused by the ultraviolet illumination induces a transition of the LC-elastomer from the nematic to isotropic state, this transition being accompanied by a contraction of a sample with respect to the LC-director. The theoretical description of the light-induced deformation in materials of such a kind is based on a modification of the theory of phase transitions in nematic elastomers. The temperature of the nematic-to-isotropic phase transition is now a function of the light intensity<sup>4,5</sup> due to the decreasing number of rod-like particles under light illumination.

Photodeformable elastomers of the second type are based on elastomeric matrices which are macroscopically isotropic.<sup>8,11–13</sup> In this case the light-induced deformation is caused by an orientation anisotropy of the chromophores which is induced by the

**Received:** July 5, 2011

**Revised:** November 25, 2011

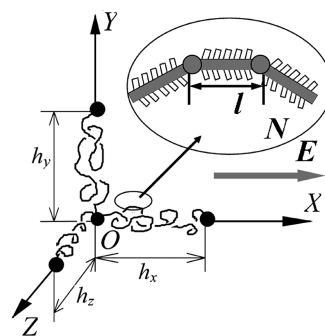
**Published:** December 20, 2011

polarized light. The probability for the photoisomerization process depends on the orientation of the chromophores with respect to the electric vector of the light,  $\mathbf{E}$ . The maximal probability for a transition from the rod-like trans-state to the bent cis-state corresponds to an orientation of the rod-like chromophore parallel to the vector  $\mathbf{E}$ . As a result, the number of rod-like chromophores, which lie along the vector  $\mathbf{E}$ , becomes lower than the number of chromophores, which are oriented in perpendicular direction. This orientation anisotropy leads to a deformation of a sample with respect to the vector  $\mathbf{E}$ . Hence, one obtains a possibility to vary the direction of deformation of a material by rotating the polarizing vector of the light,<sup>8,11–13</sup> whereas the direction of deformation in the azobenzene polymers based on nematic elastomers is restricted by the LC-director.<sup>3–10</sup> Thus, investigation of photodeformable elastomers with varying direction of deformation is of special interest. To our knowledge, there are no theories in the literature which describe light-induced deformation of isotropic azobenzene elastomers along the electric vector of the light.

In order to overcome this drawback, we develop here a theory of light-induced deformation of isotropic photosensitive elastomers bearing azobenzene chromophores in their strands. The theory is based on an orientation approach proposed recently by us for describing the irreversible deformation of glassy azobenzene polymers under light irradiation.<sup>17–19</sup> According to this approach, the light-induced mechanical stress originates from reorientation of chromophores with respect to the electric vector of the polarized light due to multiple trans–cis–trans photoisomerization processes of chromophores under light illumination. The light-induced anisotropy is described by introducing an effective orientation potential which was originally proposed by other authors.<sup>20</sup> We have shown in refs 17–19 that this orientation potential provides values of the light-induced stress comparable or higher than the values of the yield stress typical for glassy polymers,  $\sigma_Y \sim 50$  MPa, at light intensities  $I_p \sim 1$  W/cm<sup>2</sup> that are usually used in experiments. At stresses  $\sigma > \sigma_Y$  a polymer demonstrates an irreversible deformation.

Thus, the orientation approach developed in refs 17–19 allowed us to explain the possibility for inscription of surface relief gratings<sup>21–26</sup> onto glassy azobenzene polymers avoiding the concept of light-induced softening.<sup>27–33</sup> Moreover, the orientation approach<sup>17–19</sup> has illustrated that the photoelastic behavior of azobenzene polymers is very sensitive to their chemical structure, namely to the orientation distribution of chromophores around the main chains. Depending on it, a sample can demonstrate either expansion or uniaxial contraction along the polarization direction of the light. These results are in a qualitative agreement with experiments<sup>34–37</sup> and computer simulations<sup>38–40</sup> and demonstrate a great potential strength of the orientation approach<sup>17–19</sup> for describing the photomechanical properties of azobenzene polymers. In the present paper, we extend the orientation approach developed in refs 17–19 for amorphous uncross-linked azobenzene polymers to azobenzene elastomers taking the chain structure of network strands explicitly into account. We calculate the light-induced elongation of azobenzene elastomers which is caused only by the reorientation of azobenzene chromophores under illumination of the linearly polarized light. The influence of other complex effects, which can amplify the light-induced elongation (orientation interactions between chromophores, presence of LC-phases, etc.), can be topics of further generalizations.

The paper is organized as follows: In section 2, we present a regular cubic network model to be used for calculation of the



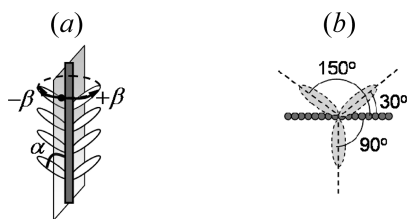
**Figure 1.** Cell of a regular cubic network model built from freely jointed polymer chains bearing azobenzene chromophores in side chains.  $\mathbf{E}$  is the electric vector of the linearly polarized light.

light-induced elongation of azobenzene elastomers under homogeneous illumination of linearly polarized light. The equilibrium elongation is determined from minimizing the free energy, i.e., from a balance between the orientation interaction of chromophores with the linearly polarized light and the entropic elasticity of network strands. In section 3, we consider the photomechanical behavior of azobenzene elastomers under homogeneous light illumination (expansion/contraction) as a function of structural parameters which characterize an orientation distribution of chromophores around the main chains and the degree of cross-linking. In section 4, we discuss possible bending motions of azobenzene elastomers under inhomogeneous light illumination, when the light intensity changes inside a material due to the effects of absorption of the light energy.

## 2. MODEL AND MAIN EQUATIONS

In cross-linked polymers, average components of the end-to-end vectors for polymer chains between network junctions are not equal to zero,<sup>41,42</sup> in contrast to polymer melts. This means that each polymer chain in a cross-linked polymer is effectively stretched between network junctions. In order to describe this effect we use a simplified three-chain network model which has been introduced originally by James and Guth for nonordered rubbers.<sup>43</sup> It has been modified by Jarry and Monnerie<sup>44</sup> and by one of the authors<sup>45,46</sup> for ordered polymer networks. This model represents a cell of a regular cubic network and consists of three identical polymer chains which are stretched along the axes of a rectangular frame of references,  $OX$ ,  $OY$ , and  $OZ$  (Figure 1). Each chain between junctions is built from  $N$  freely jointed rod-like segments (Kuhn segments) of the length  $l$ . Thus, this chain model takes into account the finite extensibility of network strands. For an unstretched isotropic network, the end-to-end distances of the three chains in the cell are identical and assumed to be equal to the average end-to-end distance of network strands in a real elastomer:  $h_x = h_y = h_z \equiv h_0$ . For dense elastomers, we can estimate the value of  $h_0$ , using the freely jointed chain model, as  $h_0 \cong l(N)^{1/2}$ , due to the screening of the excluded volume interactions in dense polymer systems.<sup>42</sup>

In the present paper, we extend the three-chain network model to photosensitive elastomers bearing azobenzene chromophores in their strands. We assume that each Kuhn segment inside the three chains in the network cell contains  $N_{ch}$  rod-like azobenzene chromophores which are covalently attached to the main chain of the segment (Figure 1). The architecture of the chromophores inside the network strands is characterized by the



**Figure 2.** (a) Orientation distribution of chromophores inside a chain segment. (b) Three positions of a chromophore which correspond to the three local minima of the potential of internal rotations for a polyethylene's spacer between the chromophore and the main chain. The condition  $W(\alpha, \beta) = W(180^\circ - \alpha, \beta)$  is fulfilled.

orientation distribution function of the chromophores around the long axis of a Kuhn segment,  $W(\alpha, \beta)$ . Here,  $\alpha$  is the angle between the long axis of a chromophore and the main chain;  $\beta$  is the angle between the plane of symmetry of the segment and the plane formed by the long axis of the chromophore and the main chain (Figure 2a). Thus, the angle  $\beta$  characterizes rotations of chromophores around the main chain. The distribution function  $W(\alpha, \beta)$  is the same for all Kuhn segments. Varying the form of the function  $W(\alpha, \beta)$  we can describe both main-chain azobenzene elastomers (when  $\alpha = 0$  for all chromophores) and the side-chain azobenzene elastomers. In the latter case, the function  $W(\alpha, \beta)$  is defined by the potentials of internal rotations and by the length of spacers connecting the chromophores with the main chain.

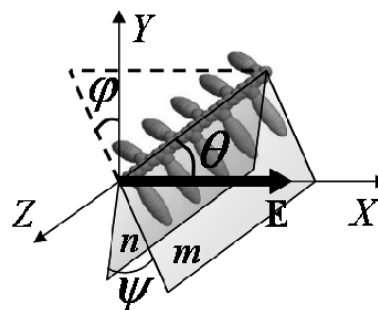
As in refs 17–19, we assume a symmetry of azobenzene macromolecules, which is typical for these compounds. Short azobenzene molecules (oligomers) possess, as a rule, a planar symmetry,<sup>38–40</sup> so that we have for the distribution function:  $W(\alpha, \beta) = W(\alpha, -\beta)$ , where the angle  $\beta$  is measured from the plane of symmetry. Moreover, the condition  $W(\alpha, \beta) = W(180^\circ - \alpha, \beta)$  is satisfied for oligomers having spacers with symmetrical potential of internal rotation (Figure 2b), e.g., for polyethylene's spacers, which are widely used in azobenzene polymers.<sup>3,4,35,36</sup> In our model, such short symmetric oligomers are considered as the Kuhn segments of network strands. Important examples of compounds possessing the symmetry  $W(\alpha, \beta) = W(\alpha, -\beta)$  and  $W(\alpha, \beta) = W(180^\circ - \alpha, \beta)$  are the main-chain azobenzene elastomers ( $\alpha = 0$ ) as well as the side-chain azobenzene elastomers, in which the chromophores are fixed at equiprobable angles  $\beta = \pm\beta^*$  and  $\alpha = 90^\circ$ .

The interaction of chromophores with the linearly polarized light leads to a preferential orientation of chromophores perpendicular to the electric vector of the light,  $\mathbf{E}$ .<sup>14–16</sup> Physically, such an orientation anisotropy of the chromophores is caused by a complicated quantum-mechanical process of multiple trans–cis–trans photoisomerization of chromophores in the field of the light wave. As in previous works,<sup>17–19,38–40</sup> we describe the orientation anisotropy of azobenzene chromophores with respect to the vector  $\mathbf{E}$  of the light by means of an effective orientation potential acting on each chromophore:

$$V(\Theta) = V_0 \cos^2 \Theta \quad (1)$$

Here  $\Theta$  is the angle between the long axis of the chromophore and the polarization vector of the light  $\mathbf{E}$ ;  $V_0$  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<sup>20,47</sup>

$$V_0 = \frac{1}{2} a v \tau I_p \equiv C I_p \quad (2)$$



**Figure 3.** Spatial orientation of a chain segment with respect to the electric vector of the light  $\mathbf{E}$ ;  $\theta$ ,  $\phi$ , and  $\psi$  are the three Euler angles, see text for details. The plane  $n$  is the plane of symmetry of the segment; the plane  $m$  is formed by the vector  $\mathbf{E}$  and the long axis of the segment.

where  $a$  is the absorption coefficient,  $v$  is the volume of azobenzene and  $\tau$  is the effective transition time between two isomer states. The value of the proportionality constant  $C$  at room temperature has been estimated in previous works as  $C \sim 10^{-19} \text{ J} \cdot \text{cm}^2 / \text{W}$ .<sup>20,47</sup>

The reorientation of chromophores under light irradiation results in the reorientation of chain segments with respect to the vector  $\mathbf{E}$  due to the covalent bonding between chromophores and chain segments. The orientation of a Kuhn segment with respect to the vector  $\mathbf{E}$  can be defined by the three Euler angles,  $\theta$ ,  $\phi$ , and  $\psi$  (Figure 3):  $\theta$  is the angle between the long axis of the Kuhn segment and the vector  $\mathbf{E}$ ;  $\phi$  is the angle between the axis OY and the projection of the long axis of the Kuhn segment on the plane YZ;  $\psi$  is the angle between the plane of symmetry of the Kuhn segment (the plane  $n$ ) and the plane  $m$  formed by the long axis of the segment and the vector  $\mathbf{E}$ , see Figure 3. Thus, the angle  $\phi$  determines the rotation of the Kuhn segment around the vector  $\mathbf{E}$  and the angle  $\psi$  defines the rotation of the segment around its long axis. Now, we can introduce an effective potential of a Kuhn segment in the field of the light wave,  $U(\Omega)$ , which represents the sum of potentials of all chromophores in the field of the light wave. Here, we set  $\Omega \equiv (\theta, \phi, \psi)$ . Using eq 1, the potential  $U(\Omega)$  can be written as

$$U(\Omega) = N_{\text{ch}} V_0 u(\Omega) \quad (3)$$

Here,  $N_{\text{ch}}$  is the number of chromophores in each Kuhn segment and

$$u(\Omega) \equiv \langle \cos^2 \Theta(\Omega) \rangle \quad (4)$$

where  $\Theta$  is the angle between a given chromophore and the vector  $\mathbf{E}$ ; averaging runs over all chromophores inside the Kuhn segment, whose orientation is defined by the angles  $\Omega \equiv (\theta, \phi, \psi)$ . The cosine of the angle  $\Theta$  between a given chromophore and the vector  $\mathbf{E}$  as a function of the angles  $\alpha, \beta, \theta, \phi$ , and  $\psi$  (see Figures 2a and 3) is given by:

$$\cos \Theta = \cos \theta \cos \alpha - \sin \theta \sin \alpha \cos(\psi + \beta) \quad (5)$$

Now, from eqs 4 and 5 after averaging with the distribution function  $W(\alpha, \beta)$  and using the symmetry of chain segments,  $W(\alpha, \beta) = W(\alpha, -\beta)$  and  $W(\alpha, \beta) = W(180^\circ - \alpha, \beta)$ , we find the function  $u(\Omega)$  in the following form (cf. with eq (35))



of ref 17):

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

We note that, due to axial symmetry with respect to the vector  $\mathbf{E}$ , the potential  $u(\Omega)$  is independent of the angle  $\varphi$ . Moreover, the potential of a Kuhn segment in the field of the light wave,  $u(\Omega)$ , is determined by the orientation distribution of the chromophores inside the segment and, in particular, it is defined by the moments of the angular distribution,  $\langle \sin^2 \alpha \rangle_W$  and  $\langle \sin^2 \alpha \cos 2\beta \rangle_W$ . Below, these factors are included in our calculations as structural parameters of the theory.

The reorientation of Kuhn segments under light illumination leads to a deformation of an azobenzene elastomer. Using the axial symmetry of the problem with respect to the electric vector of the light  $\mathbf{E}$  we can conclude that an elastomer should demonstrate a uniaxial deformation along the vector  $\mathbf{E}$ . Because of the condition of incompressibility for elastomers<sup>41,42</sup> the end-to-end distances for three chains in the cell satisfy the following conditions:

$$h_x = h_0 \lambda \quad \text{and} \quad h_y = h_z = h_0 / \sqrt{\lambda} \quad (7)$$

where  $\lambda$  is the elongation ratio of the elastomer along the electric vector of the light  $\mathbf{E}$ . The next task is to calculate the light-induced elongation ratio  $\lambda$  as a function of the strength of the potential  $V_0$ . The equilibrium value of the elongation ratio should minimize the free energy. This condition reflects a balance between the light-induced reorientation of the chromophores under light irradiation and the entropic elasticity of polymer chains.

The free energy of a deformed elastomer under light irradiation can be written in the framework of the three-chain network model as follows (free energy per a cell):

$$F = NkT \sum_{\alpha=x,y,z} \int d\Omega f_\alpha(\Omega) \ln f_\alpha(\Omega) + N \sum_{\alpha=x,y,z} \int d\Omega U(\Omega) f_\alpha(\Omega) \quad (8)$$

where  $k$  is the Boltzmann constant,  $T$  is absolute temperature, and  $f_\alpha(\Omega)$  is the orientation distribution function of Kuhn segments in a chain stretched along the  $\alpha$ -axis ( $\alpha = x, y, z$ ). The integral in eq 8 runs over the angles  $\theta, \varphi$ , and  $\psi$ :  $d\Omega = \sin \theta d\theta d\varphi d\psi$ ,  $\theta \in [0, \pi]$ ,  $\varphi \in [0, 2\pi]$ , and  $\psi \in [0, 2\pi]$ . The first term in eq 8 describes the entropic elasticity of the network strands and the second one represents the orientation potential of the chromophores in the field of the light wave.

In order to find the free energy as a function of the elongation ratio  $\lambda$  we have to determine the distribution functions  $f_\alpha(\Omega)$  which should minimize the free energy at given value of  $\lambda$  and satisfy the following normalization conditions:

$$\int d\Omega f_\alpha(\Omega) = 1 \quad (9)$$

$$N \int d\Omega f_\alpha(\Omega) l \cos \theta_\alpha = h_\alpha(\lambda) \quad (10)$$

Condition 10 means that the end-to-end distance of the chain  $h_\alpha$  equals the summarized projection of all Kuhn segments inside the chain on the axis of a chain stretching, i.e. on the  $\alpha$ -axis. The angle  $\theta_\alpha$  in eq 10 is the angle between the long axis of a Kuhn segment

and the  $\alpha$ -axis:  $\cos \theta_x = \cos \theta$ ,  $\cos \theta_y = \sin \theta \cos \varphi$ , and  $\cos \theta_z = \sin \theta \sin \varphi$ . The values  $h_\alpha$  ( $\alpha = x, y, z$ ) as functions of the elongation ratio  $\lambda$  are given by eq 7.

In terms of the variation principle, the conditions for the distribution function  $f_\alpha(\Omega)$ , which provides the minimum of the free energy, can be reformulated as follows. At any variation of the distribution function,  $\delta f_\alpha$ , which satisfies eqs 9 and 10, i.e.

$$\int d\Omega \delta f_\alpha(\Omega) = 0 \quad \text{and} \quad \int d\Omega \delta f_\alpha(\Omega) \cos \theta_\alpha = 0 \quad (11)$$

the equilibrium distribution function  $f_\alpha(\Omega)$  should provide a variation of the free energy equal to zero,  $\delta F = 0$ . Using eq 8, the condition  $\delta F = 0$  can be rewritten as follows:

$$\int d\Omega \delta f_\alpha(\Omega) \left[ 1 + \ln f_\alpha(\Omega) + \frac{N_{ch} V_0}{kT} u(\Omega) \right] = 0 \quad (12)$$

Here, we have used eq 3 for the function  $U(\Omega)$ . According to the Lagrange variation principle, conditions 11 and 12 are satisfied simultaneously when

$$1 + \ln f_\alpha(\Omega) + \frac{N_{ch} V_0}{kT} u(\Omega) = A_\alpha + B_\alpha \cos \theta_\alpha \quad (13)$$

where  $A_\alpha$  and  $B_\alpha$  are the Lagrange multipliers that satisfy eqs 9 and 10 for the function  $f_\alpha(\Omega)$ . From eq 13 we obtain the function  $f_\alpha(\Omega)$  in the following form:

$$f_\alpha(\Omega) = Z_\alpha^{-1} \exp \left[ -\frac{N_{ch} V_0}{kT} u(\Omega) + B_\alpha \cos \theta_\alpha \right] \quad (14)$$

where  $Z_\alpha = Z_\alpha(V_0, \lambda)$  is the partition function which represents a reformulated Lagrange multiplier:  $Z_\alpha^{-1} = \exp(A_\alpha - 1)$ . The normalization condition (9) gives for  $Z_\alpha(V_0, \lambda)$ :

$$Z_\alpha(V_0, \lambda) = \int d\Omega \exp \left[ -\frac{N_{ch} V_0}{kT} u(\Omega) + B_\alpha(V_0, \lambda) \cos \theta_\alpha \right] \quad (15)$$

The term  $B_\alpha \cos \theta_\alpha$  in the exponents of eqs 14 and 15 has a simple physical meaning: It reflects the influence of a stretching force which stretches a polymer chain between network junctions. It is known that the influence of a stretching force on a polymer chain is equivalent to an application of the orientation potential which is proportional to the cosine of the angle  $\theta_\alpha$  between a Kuhn segment and the direction of the stretching force.<sup>42</sup> By this, the Lagrange multiplier  $B_\alpha$  in the exponents has a meaning of the magnitude of the stretching force acting on a polymer chain; it depends on the elongation ratio  $\lambda$  and on the strength of the light-induced potential,  $V_0$ . The dependence  $B_\alpha = B_\alpha(V_0, \lambda)$  is determined by eq 10. Substituting eqs 14 and 15 into the normalization condition (eq 10) we obtain the relationship for the function  $B_\alpha = B_\alpha(V_0, \lambda)$  which can be calculated as a solution of the following equation with respect to the parameter  $B_\alpha$ :

$$\frac{\int d\Omega \exp \left[ -\frac{N_{ch} V_0}{kT} u(\Omega) + B_\alpha \cos \theta_\alpha \right] \cos \theta_\alpha}{\int d\Omega \exp \left[ -\frac{N_{ch} V_0}{kT} u(\Omega) + B_\alpha \cos \theta_\alpha \right]} = \frac{h_\alpha(\lambda)}{Nl} \quad (16)$$

Using eq 7, the parameter  $h_\alpha/Nl$  on the right-hand side of eq 16 can be rewritten as a function of  $\lambda$  in the following form:

$$\frac{h_x}{Nl} = \gamma\lambda \quad \text{and} \quad \frac{h_y}{Nl} = \frac{h_z}{Nl} = \gamma/\sqrt{\lambda} \quad (17)$$

Here, we have introduced a dimensionless parameter

$$\gamma \equiv \frac{h_0}{Nl} \quad (18)$$

where  $h_0$  is the average end-to-end distance of network strands in an isotropic elastomer. The parameter  $\gamma$  characterizes a chain stretching between network junctions and is related to the degree of cross-linking. For elastomers we have  $h_0 \cong l(N)^{1/2}$ ,<sup>41,42</sup> so that

$$\gamma \cong 1/\sqrt{N} \quad (19)$$

On the other hand, the degree of cross-linking  $\nu$  (number of network strands in the unit volume) is related to the parameter  $N$  as follows:  $\nu = c/N$ , where  $c$  is the number of Kuhn segments in the unit volume (density of a polymer). Thus, for dense elastomers, the degree of cross-linking  $\nu$  is a quadratic function of the structural parameter  $\gamma$ :

$$\nu \cong \gamma^2 c \quad (20)$$

The larger is the value of the structural parameter  $\gamma$ , the higher is the degree of cross-linking  $\nu$ . In all further calculations, the factor  $\gamma \cong 1/(N)^{1/2}$  will be included as a parameter of the theory. Varying the values of the parameter  $\gamma$  (or parameter  $N$ ) one can consider the effects of the degree of cross-linking on the photomechanical behavior of azobenzene elastomers.

It is now a simple matter to find the equilibrium elongation  $\lambda$  from the minimum of the free energy,  $\partial F/\partial \lambda = 0$ . Substituting eq 14 into 8 we obtain the free energy as a function of the parameters  $\lambda$  and  $V_0$  in the following form:

$$F(V_0, \lambda) = NkT \sum_{\alpha=x,y,z} [B_\alpha(V_0, \lambda)(h_\alpha/Nl) - \ln Z_\alpha(V_0, \lambda)] \quad (21)$$

Thus, the condition  $\partial F/\partial \lambda = 0$  can be rewritten as follows:

$$\sum_{\alpha=x,y,z} B_\alpha(V_0, \lambda) \partial h_\alpha / \partial \lambda = 0 \quad (22)$$

Here, we have used the relationship  $\partial[\ln Z_\alpha]/\partial \lambda = (h_\alpha/Nl)(\partial B_\alpha/\partial \lambda)$  which follows from eqs 15 and 16. Using the explicit functions  $h_\alpha = h_\alpha(\lambda)$  given by eq 7, the derivatives in the left-hand side of eq 22 are straightforward. Moreover, using the equivalence of the chains stretched along the y- and z- axes (i.e.,  $h_y = h_z$  and  $B_y = B_z$ ) we can rewrite eq 22 finally in the following form:

$$B_x(V_0, \lambda) \lambda^{3/2} = B_y(V_0, \lambda) \quad (23)$$

Equations 16 and 23 define the equilibrium elongation as a function of the strength of the potential,  $\lambda = \lambda(V_0)$ . The solution of eqs 16 and 23 and the dependence  $\lambda = \lambda(V_0)$  as a function of the structural parameters of azobenzene elastomers are discussed in the next section.

### 3. LIGHT-INDUCED ELONGATION OF AZOBENZENE ELASTOMERS AS A FUNCTION OF THEIR STRUCTURAL PARAMETERS

We start this section by noting that the solution of eq 23, which defines the light-induced elongation of an azobenzene elastomer

as a function of the light intensity, can not be expressed in terms of elementary functions, since the factors  $B_\alpha(V_0, \lambda)$  given by eq 16 can not be rewritten in terms of elementary functions. Of course, eq 23 can be solved numerically. On the other hand, for small degrees of chain stretching,  $h_\alpha \ll Nl$ , one can use an expansion into a series with respect to the small parameter  $B_\alpha$  in eq 16. This expansion corresponds to the linear (or so-called Gaussian) regime of deformation, when the degree of chain stretching is proportional to the magnitude of the stretching force:  $h_\alpha/Nl \propto B_\alpha$ .<sup>42,48</sup> In this regime, the finite extensibility of the polymer chain plays almost no role.

It should be noted that the Gaussian regime can cover a broad region of the network elongation, if the network strands are long enough. As it was shown by two of the authors,<sup>48</sup> polymer chains remain in the Gaussian regime at relative deformations  $h_\alpha/Nl < 0.4$ . Using the last relationship as well as eqs 17 and 19 one can see that the Gaussian regime takes place approximately at the following values of the elongation ratio:

$$6.25/N \lesssim \lambda \lesssim 0.4\sqrt{N} \quad (24)$$

For example, at  $N = 100$  the Gaussian region is  $0.06 < \lambda < 4$  and at  $N = 25$  we have  $0.25 < \lambda < 2$ , i.e. the Gaussian regime can hold until several hundreds percents of relative deformation,  $\varepsilon \equiv \lambda - 1$ . Thus, we present below our analysis of the photomechanical behavior of azobenzene elastomers for two situations: (1) the Gaussian regime of deformation, since it can cover a broad region of the network elongation, and (2) the regime of limiting deformations, where the effects of finite extensibility of polymer chains play a major role.

**3.1. Gaussian Regime of Deformation,  $h_\alpha/Nl < 0.4$ .** Expanding the left-hand side of eq 16 into a series with respect to the small parameter  $B_\alpha$  and keeping only the first nonzero terms proportional to  $B_\alpha$  we rewrite eq 16 for the function  $B_\alpha(V_0, \lambda)$  in the following form:

$$B_\alpha(V_0, \lambda) \langle \cos^2 \theta_\alpha \rangle_0 = \frac{h_\alpha(\lambda)}{Nl} \quad (25)$$

where the average  $\langle \cos^2 \theta_\alpha \rangle_0$  for the angle  $\theta_\alpha$  between the long axis of a Kuhn segment and the  $\alpha$ -axis ( $\alpha = x, y, z$ ) is calculated as follows:

$$\langle \cos^2 \theta_\alpha \rangle_0 = \frac{\int d\Omega \cos^2 \theta_\alpha \exp \left[ -\frac{N_{ch} V_0}{kT} u(\Omega) \right]}{\int d\Omega \exp \left[ -\frac{N_{ch} V_0}{kT} u(\Omega) \right]} \quad (26)$$

The expression in the right-hand side of the last equation corresponds to the averaging over separate rod-like oligomers, bearing chromophores, under the influence of the light wave. The averaging over the system of separate oligomers is marked by an index "0" after the angle brackets in eq 26. From eq 6 one can see that the effective potential  $u(\Omega)$  is invariant with respect to the transformations of the coordinate system  $X \rightarrow (-X)$ , or  $Y \rightarrow (-Y)$ , or  $Z \rightarrow (-Z)$ . From such a symmetry, it follows that  $\langle \cos \theta_\alpha \rangle_0 = 0$ . Therefore, the first term, which appears in eq 25 after expansion into a series of the right-hand side of eq 16, contains only the second moments  $\langle \cos^2 \theta_\alpha \rangle_0$ .

It is now a simple matter to find the equilibrium elongation  $\lambda$  for the Gaussian regime as a function of the strength of the potential  $V_0$ . Substituting the functions  $B_x(V_0, \lambda)$  and  $B_y(V_0, \lambda)$

given by eq 25 into eq 23 for the equilibrium elongation and using the explicit functions  $h_\alpha(\lambda)$  given by eq 17 for  $\alpha = x, y, z$  one can obtain the following expression for  $\lambda$ :

$$\lambda = \left[ \frac{\langle \cos^2 \theta_x \rangle_0}{\langle \cos^2 \theta_y \rangle_0} \right]^{1/3} \quad (27)$$

The right-hand side of the last equation depends on the strength of the potential  $V_0$ ; the dependence of  $\langle \cos^2 \theta_x \rangle_0$  on  $V_0$  is given by eq 26. Thus, the light-induced elongation of azobenzene elastomers in the Gaussian regime is independent of the chain length  $N$  and of the degree of cross-linking, since in this regime the finite extensibility of network strands plays almost no role. At the same time, according to eq 27, the deformation of an azobenzene elastomer is determined by the orientation anisotropy in the system of separate rod-like segments bearing chromophores in the side chains. The orientation anisotropy of short oligomers, bearing azobenzene chromophores in the side chains, has been investigated by us in refs 17–19. The uniaxially ordered system of short azobenzene oligomers under light illumination can be characterized by the orientation order parameter,  $S_0$ :

$$S_0(V_0) = \langle P_2(\cos \theta) \rangle_0 \equiv \frac{3\langle \cos^2 \theta \rangle_0 - 1}{2} \quad (28)$$

where  $\theta \equiv \theta_x$  is the angle between the long axis of an oligomer and the electric vector of the light  $\mathbf{E}$ . For an isotropic system one has  $S_0 = 0$ , whereas for a fully oriented system  $S_0 = 1$ . Using the relationships  $\langle \cos^2 \theta_x \rangle_0 = (1 + 2S_0)/3$  and  $\cos^2 \theta_x + \cos^2 \theta_y + \cos^2 \theta_z = 1$ , that gives  $\langle \cos^2 \theta_y \rangle_0 = \langle \cos^2 \theta_z \rangle_0 = (1 - S_0)/3$ , eq 27 can be rewritten in terms of the order parameter  $S_0$  as follows:

$$\lambda(V_0) = \left[ \frac{1 + 2S_0(V_0)}{1 - S_0(V_0)} \right]^{1/3} \quad (29)$$

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 short oligomers, whose chemical structure is the same as the chain segments of the elastomer. In refs 17–19, we used the value of the order parameter  $S_0$  for estimating the relative extension,  $\varepsilon \equiv \lambda - 1$ , of a glassy polymer consisting of short azobenzene oligomers:  $S_0 = \varepsilon/\varepsilon_{\max}$ , where  $\varepsilon_{\max}$  is the maximal relative extension corresponding to a fully oriented sample with  $S_0 = 1$ . For  $\varepsilon_{\max} > 0$  we have found in refs 17–19 several types of photomechanical behavior of glassy azobenzene polymers depending on their chemical structure: (i) expansion along the electric vector of the light  $\mathbf{E}$  ( $\varepsilon > 0$ ,  $S_0 > 0$ ), (ii) contraction along the vector  $\mathbf{E}$  ( $\varepsilon < 0$ ,  $S_0 < 0$ ), and (iii) nonmonotonic behavior of the deformation with the light intensity (expansion at small light intensities and contraction at large light intensities). These types of photomechanical behavior of azobenzene polymers built from short oligomers have been observed experimentally<sup>34–37</sup> and have been found in computer simulation studies.<sup>38–40</sup>

Using eq 29 we can extend now the findings obtained in refs 17–19 for azobenzene polymers consisting of short oligomers to cross-linked azobenzene elastomers built from long chains. From eq 29 we can conclude that an azobenzene elastomer should demonstrate the same photomechanical behavior (expansion/contraction) as its low-molecular-weight analogue. For instance, an azobenzene elastomer displays a uniaxial expansion along the electric vector of the light  $\mathbf{E}$  ( $\lambda > 1$ ), if its low-molecular-weight analogue demonstrates the expansion along

the vector  $\mathbf{E}$  ( $\varepsilon > 0$  and  $S_0 > 0$ ), and vice versa:  $\lambda < 1$ , if  $\varepsilon < 0$  and  $S_0 < 0$ . To understand how the photomechanical behavior of azobenzene elastomers depends on their chemical structure, one can analyze the order parameter  $S_0$  as a function of the structural parameters  $\langle \sin^2 \alpha \rangle_W$  and  $\langle \sin^2 \alpha \cos 2\beta \rangle_W$ . This analysis is presented in the next subsection.

**3.2. Effects of the Chemical Structure of Network Strands on the Photo-Mechanical Behavior of Azobenzene Elastomers.** In order to establish the structure–property relationships for azobenzene elastomers, one can consider the dependence  $S_0(V_0)$  separately for small and large values of the strength of the potential  $V_0$ . Expanding the right-hand side of eq 26 into a series with respect to the small parameter  $N_{\text{ch}}V_0/kT$  and keeping only the first terms proportional to  $N_{\text{ch}}V_0/kT$  that come from both numerator and denominator in eq 26, we obtain for  $\theta \equiv \theta_x$ :

$$\langle \cos^2 \theta \rangle_0 \approx \frac{1}{3} + \frac{N_{\text{ch}}V_0}{3kT} \int \frac{d\Omega}{8\pi^2} u(\Omega) [1 - 3 \cos^2 \theta] \quad \text{at} \quad \frac{N_{\text{ch}}V_0}{kT} \ll 1 \quad (30)$$

Here, we have used that  $\int d\Omega = 8\pi^2$  and  $(8\pi^2)^{-1} \int d\Omega \cos^2 \theta = 1/3$ . Using eq 6 for the potential  $u(\Omega)$ , the integral in the right-hand side of eq 30 can be calculated as:

$$\int \frac{d\Omega}{8\pi^2} u(\Omega) [1 - 3 \cos^2 \theta] = \frac{3}{2} C_1 \int \frac{d\Omega}{8\pi^2} \sin^2 \theta [1 - 3 \cos^2 \theta] = \frac{2}{5} C_1 \quad (31)$$

where

$$C_1 = \langle \sin^2 \alpha \rangle_W - 2/3 \quad (32)$$

Note that the term  $\langle \sin^2 \alpha \cos 2\beta \rangle_W$  disappears in eq 31, since it is multiplied by the factor  $\cos 2\psi$  (see eq 6), which disappears after integration:  $\int_0^{2\pi} \cos 2\psi \, d\psi = 0$ . As a result, we obtain from eqs 28, 30, and 31 that the order parameter at small strengths of the potential is independent of the azimuthal distribution of chromophores with respect to the angle  $\beta$  and depends only on the orientation distribution of the chromophores with respect to the angle  $\alpha$ :

$$S_0(V_0) \approx [\langle \sin^2 \alpha \rangle_W - 2/3] \frac{N_{\text{ch}}V_0}{5kT} \quad \text{at} \quad \frac{N_{\text{ch}}V_0}{kT} \ll 1 \quad (33)$$

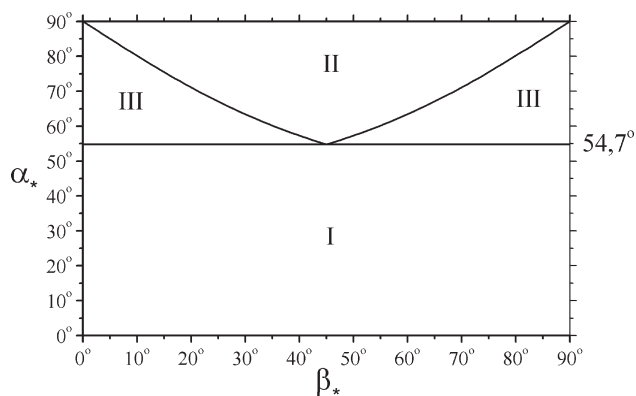
Thus, the sign of deformation at small field strengths coincides with the sign of the factor  $C_1$ . If  $C_1 > 0$ , an azobenzene elastomer demonstrates a uniaxial expansion ( $S_0 > 0$  and  $\lambda > 1$ ), whereas, if  $C_1 < 0$ , it shows a uniaxial contraction ( $S_0 < 0$  and  $\lambda < 1$ ) at  $N_{\text{ch}}V_0/kT \ll 1$ .

In contrast to small values of  $N_{\text{ch}}V_0/kT$ , the photomechanical behavior of azobenzene elastomers at high strengths of the potential  $V_0$  depends on the orientation distribution of the chromophores with respect to both angles  $\alpha$  and  $\beta$ . This difference is caused by the fact that the light-induced elongation of azobenzene elastomers at small values of  $V_0$  is determined by averaged values of the potential,  $\langle u(\Omega) \rangle_\Omega$ , see eq 30, whereas the photomechanical behavior at high values of  $V_0$  is controlled by the minima of the potential  $u(\Omega)$ . One can see from eq 6 that the positions of minima for  $u(\Omega)$  are determined by the sign of the parameter  $C_2$ , which depends on both factors  $\langle \sin^2 \alpha \rangle_W$  and  $\langle \sin^2 \alpha \cos 2\beta \rangle_W$ :

$$C_2 = \frac{3}{2} [\langle \sin^2 \alpha \rangle_W - 2/3] - \frac{1}{2} \langle \sin^2 \alpha \cos 2\beta \rangle_W \quad (34)$$

If  $C_2 > 0$ , the prefactor before  $\sin^2 \theta$  in eq 6 for  $u(\Omega)$  is positive at any values of  $\psi$  and, hence, the minimum of  $u(\Omega)$  is achieved at  $\theta = 0$ .





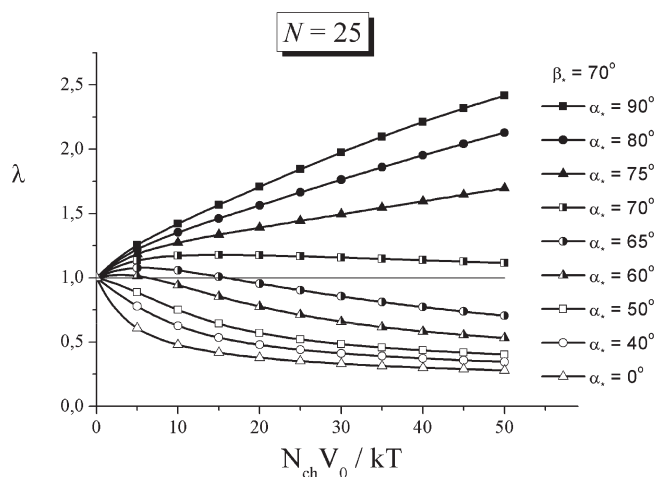
**Figure 4.** Three areas of the structural angles  $\alpha_*$  and  $\beta_*$  for three types of photomechanical behavior of azobenzene elastomers.

Therefore, if  $C_2 > 0$ , the orientation distribution function of the chain segments for  $N_{\text{ch}}V_0/kT \gg 1$  has a narrow peak at  $\theta = 0$  that corresponds to  $S_0 = 1$  according to eq 28. Thus, if  $C_2 > 0$ , an azobenzene elastomer demonstrates a uniaxial expansion along the electric vector of the light  $\mathbf{E}$  ( $S_0 > 0$  and  $\lambda > 1$ ) at  $N_{\text{ch}}V_0/kT \gg 1$ . On the other hand, if  $C_2 < 0$ , there exist values  $\psi$ , for which the prefactor before  $\sin^2 \theta$  in eq 6 for  $u(\Omega)$  is negative. Hence, in this case, the global minimum of  $u(\Omega)$  is achieved at  $\theta = 90^\circ$  which corresponds to a planar orientation of the segments with  $S_0 = -0.5$ , according to eq 28. Thus, if  $C_2 < 0$ , an azobenzene elastomer demonstrates a uniaxial contraction along the electric vector of the light  $\mathbf{E}$  ( $S_0 < 0$  and  $\lambda < 1$ ) at  $N_{\text{ch}}V_0/kT \gg 1$ .

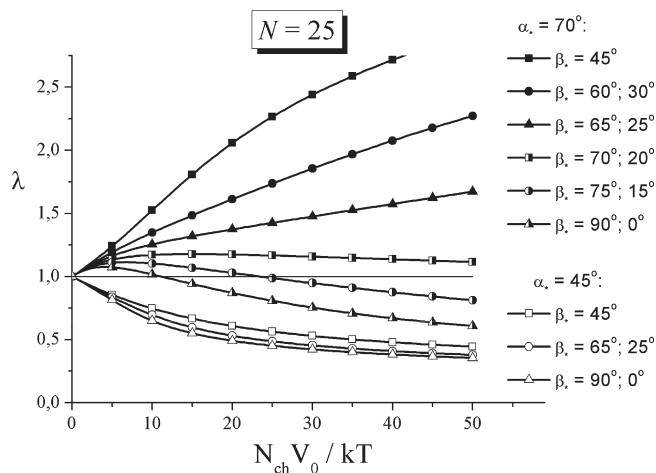
Summarizing the results for  $\lambda(V_0)$  at small and large strengths of the potential, one can distinguish three types of photomechanical behavior of azobenzene elastomers depending on their structure. (I) If  $C_1 < 0$ , then we automatically obtain  $C_2 < 0$  according to eq 34 and in this case an azobenzene elastomer demonstrates a uniaxial contraction ( $S_0 < 0$  and  $\lambda < 1$ ) both at small and at large strengths of the potential. (II) If  $C_2 > 0$ , then we get  $C_1 > 0$  according to eq 34 and an azobenzene elastomer shows a uniaxial expansion ( $S_0 > 0$  and  $\lambda > 1$ ) both at small and at large strengths of the potential. (III) In the intermediate case, when  $C_1 > 0$  and  $C_2 < 0$ , an azobenzene elastomer demonstrates a non-monotonic deformation as a function of the strength of the potential: a uniaxial expansion at  $N_{\text{ch}}V_0/kT \ll 1$  and a uniaxial contraction at  $N_{\text{ch}}V_0/kT \gg 1$ .

To demonstrate the structure-dependent photomechanical behavior of azobenzene elastomers, we have calculated the dependences  $\lambda(V_0)$  for elastomers, whose structural angles  $\alpha$  and  $\beta$  are fixed at equiprobable values  $\beta = \pm \beta_*$  and  $\alpha = \alpha_*$ ,  $180^\circ - \alpha_*$ , the values  $\alpha_*$  and  $\beta_*$  being varied. Note that such specific structures are chosen only for the visualization of the results and this choice does not restrict the generality of our considerations, since the light-induced orientation potential  $u(\Omega)$  depends on the chemical structure of the network strands only through the parameters  $\langle \sin^2 \alpha \rangle_W$  and  $\langle \sin^2 \alpha \cos 2\beta \rangle_W$ , see eq 6. Therefore, any azobenzene elastomer, whose distribution of chromophores around the main chains is characterized by the values  $\langle \sin^2 \alpha \rangle_W = \sin^2 \alpha_*$  and  $\langle \sin^2 \alpha \cos 2\beta \rangle_W = \sin^2 \alpha_* \cos 2\beta_*$ , should demonstrate the same photomechanical behavior as an elastomer, whose structural angles  $\alpha$  and  $\beta$  are fixed at the values  $\beta = \pm \beta_*$  and  $\alpha = \alpha_*$ ,  $180^\circ - \alpha_*$ .

Figure 4 shows the diagram for values of the parameters  $\alpha_*$  and  $\beta_*$ , at which three types of photomechanical behavior take place for azobenzene elastomers: (I) monotonic contraction, (II)



**Figure 5.** Dependence of the elongation ratio  $\lambda$  on the reduced strength of the potential,  $N_{\text{ch}}V_0/kT$ , at fixed value of the structural angle  $\beta_* = 70^\circ$  and at varying values of the structural angle  $\alpha_*$ ; the strand length is  $N = 25$ .



**Figure 6.** Same as Figure 5 but at fixed values of the structural angle  $\alpha_* = 70^\circ$ ,  $\alpha_* = 50^\circ$  and at varying values of the structural angle  $\beta_*$ ; the strand length is  $N = 25$ .

monotonic expansion, and (III) nonmonotonic deformation of the elastomer with increasing light intensity (expansion at small light intensities and contraction at high light intensities). The boundary between the areas I and III are given by the condition  $C_1 = 0$ , which reads  $\sin^2 \alpha_* = 2/3$ , i.e.,  $\alpha_* \approx 54.7^\circ$ . The boundary between the areas II and III are given by the condition  $C_2 = 0$  which can be rewritten as follows:

$$\alpha_* = A(\beta_*) \equiv \arcsin \sqrt{\frac{2}{3 - |\cos 2\beta_*|}} \quad (35)$$

Note that the diagram presented in Figure 4 for azobenzene elastomers is the same as it was obtained by us in ref 17 for azobenzene polymers built from short oligomers, since azobenzene elastomers and their low-molecular-weight analogues are characterized by the same photomechanical behavior (expansion/contraction) as it was discussed above.

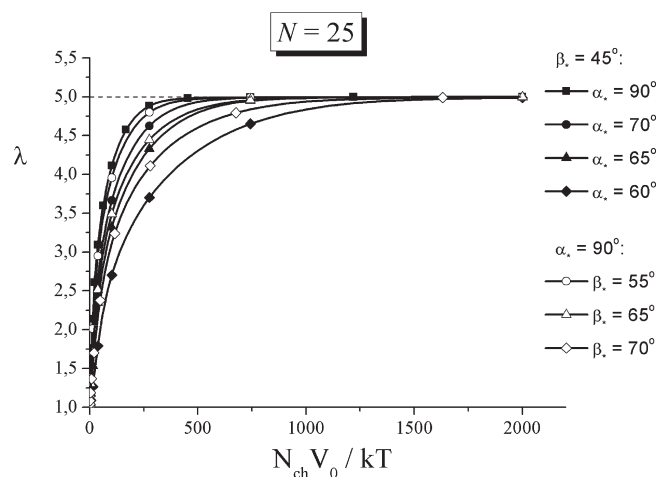
Figures 5 and 6 show the dependences  $\lambda(V_0)$  for different values of  $\alpha_*$  and  $\beta_*$  belonging to the areas I, II, and III presented

in Figure 4 and at fixed value of the strand length,  $N = 25$ . In Figure 5, the parameter  $\alpha_*$  is varied at fixed value  $\beta_* = 70^\circ$ ; in Figure 6, the parameter  $\beta_*$  is varied at two fixed values  $\alpha_* = 70^\circ$  and  $\alpha_* = 45^\circ$ . The dependences  $\lambda(V_0)$  have been calculated by means of numerical solutions of eqs 16 and 23. Thus, these dependences are not restricted by the Gaussian regime but provide exact values of the elongation ratio  $\lambda$  at any value of  $V_0$ . The results of numerical calculations show three types of photomechanical behavior of azobenzene elastomers in accordance with the qualitative considerations presented above.

- I When  $\alpha_* < 54.7^\circ$  (the area I in Figure 4), the chromophores lie preferably along the main chains of the network strands. Their orientation perpendicular to the electric field  $\mathbf{E}$  of the light results in the same orientation for the Kuhn segments and is accompanied by a uniaxial contraction of an azobenzene elastomer with respect to the vector  $\mathbf{E}$  ( $\lambda < 1$ ). In this case, the elongation ratio  $\lambda$  decreases monotonically with increasing value of  $V_0$  (open symbols in Figures 5 and 6).
- II When  $A(\beta_*) < \alpha_* < 90^\circ$  (the area II in Figure 5), the chromophores preferably lie perpendicular to the main chains of the network strands. The orientation of the chromophores perpendicular to the electric vector  $\mathbf{E}$  under light illumination leads to the orientation of the chain segments parallel to the vector  $\mathbf{E}$  and is accompanied by a uniaxial expansion of an azobenzene elastomer along the vector  $\mathbf{E}$  ( $\lambda > 1$ ). In this case,  $\lambda(V_0)$  is a monotonically increasing function (filled symbols in Figures 5 and 6).
- III The values of structural angles  $54.7^\circ < \alpha_* < A(\beta_*)$  (the area III in Figure 5) correspond to the structures with non-monotonic dependence of the elongation ratio  $\lambda$  on the field strength  $V_0$ :  $\lambda(V_0)$  is an increasing function at small values of  $V_0$  and a decreasing one at large field strengths (semiopen symbols in Figures 5 and 6).

In accordance with eq 33 the initial slope of  $\lambda(V_0)$  is independent of the azimuthal distribution with respect to the angle  $\beta$  (see Figure 6). This slope increases with increasing parameter  $\langle \sin^2 \alpha \rangle_W = \sin^2 \alpha_*$ , i.e., when the structural angle  $\alpha_*$  increases (see Figure 5). Moreover, at increasing value of the angle  $\alpha_*$  from  $\alpha_* = 0$  to  $\alpha_* = 90^\circ$ , the elongation ratio  $\lambda$  increases at any fixed values of  $\beta_*$  and  $V_0$  and thus, the function  $\lambda(V_0)$  demonstrates sequentially the I, III, II—types of photomechanical behavior, see Figure 5. Furthermore, one can see from Figure 6 that at increasing values of the angle  $\beta_*$  from  $\beta_* = 0$  to  $\beta_* = 45^\circ$  as well as at decreasing  $\beta_*$  from  $\beta_* = 90^\circ$  to  $\beta_* = 45^\circ$ , the elongation ratio  $\lambda$  increases at any fixed values of  $\alpha_*$  and  $V_0$ .

We conclude the present subsection by noting that the findings concerning the three types of the photomechanical behavior discussed above hold not only for the Gaussian regime of elongation but also for any values of the light intensity, including the limiting deformations of azobenzene elastomers. In other words, the diagram presented in Figure 4 for the photomechanical behavior (expansion/contraction) is independent of the length of network strands  $N$  and of the degree of cross-linking. This diagram is determined only by the chemical structure of the network strands, namely, by the orientation distribution of the chromophores around the main chains. The length of the network strands  $N$  determines the photomechanical behavior of azobenzene elastomers only at limiting elongations, where eq 29 for the Gaussian regime does not hold anymore. Instead of the unlimited elongation  $\lambda \rightarrow \infty$  (if  $S_0 \rightarrow 1$ ) and unlimited contraction  $\lambda \rightarrow 0$



**Figure 7.** Dependence of the elongation ratio  $\lambda$  on the reduced strength of the potential,  $N_{\text{ch}}V_0/kT$ , in the region of limiting elongation of azobenzene elastomers with  $N = 25$  ( $\lambda_{\text{max}} = 5$ ) and at varying values of the structural angles  $\alpha_*$  and  $\beta_*$ .

(if  $S_0 \rightarrow -0.5$ ), which are provided by eq 29 at  $V_0 \rightarrow \infty$ , the effects of finite extensibility of the network strands result in the limiting elongations of azobenzene elastomers at  $V_0 \rightarrow \infty$ . The values of limiting elongation of azobenzene elastomers depend on the length of the network strands and on the degree of cross-linking, as we will show in the next subsection.

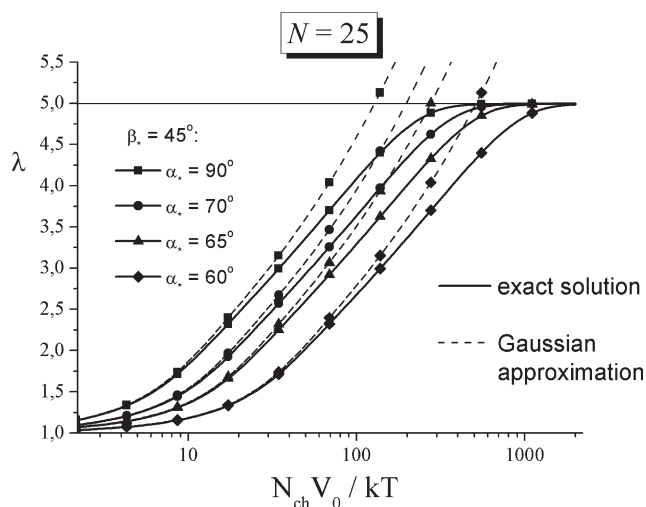
**3.3. Limiting Deformations of Azobenzene Elastomers,  $0.4 < h_a/Nl < 1$ . Effects of the Degree of Cross-Linking on the Photo-Mechanical Behavior of Azobenzene Elastomers.** The limiting elongation of a polymer network is determined by the finite extensibility of the networks strands. In our model, the maximal,  $\lambda_{\text{max}}$  and minimal,  $\lambda_{\text{min}}$ , elongation ratios correspond to such deformations of the network cell, when  $h_x = Nl$  or  $h_y = Nl$ , respectively. Using the last two relationships and eqs 17–19 we find:

$$\lambda_{\text{max}} = \gamma^{-1} \cong \sqrt{N} \quad \text{and} \quad \lambda_{\text{min}} = \gamma^2 \cong 1/N \quad (36)$$

where  $N$  is the number of Kuhn segments in a network strand and the parameter  $\gamma = h_0/Nl$  defines the average degree of chain stretching between network junctions;  $\gamma$  is related to the degree of cross-linking; see eq 20. Thus, one can see from eq 36 that the limiting values of the elongation ratio depend only on the parameter  $\gamma$  (or  $N$ ) and is independent of the orientation distribution of the chromophores around the main chains.

Figure 7 illustrates the dependences  $\lambda(V_0)$  at fixed value  $N = 25$  (when  $\lambda_{\text{max}} = 5$ ) and at varying values of the parameters  $\alpha_*$  and  $\beta_*$  for the case, when an azobenzene elastomer demonstrates a uniaxial expansion under light illumination (the area II in Figure 4). Figure 8 shows the dependences  $\lambda(V_0)$  in the logarithmic scale in order to compare the photomechanical behavior at small and large strengths of the potential for  $N = 25$  and at varying values of  $\alpha_*$ . The solid lines in Figure 8 illustrate exact results for  $\lambda(V_0)$  calculated by means of the numerical solution of eq 23; dashed lines show the dependences  $\lambda(V_0)$  given by eq 29 for the Gaussian approximation. One can see from Figure 8 that at elongations that satisfy eq 24 for the Gaussian regime (i.e., at  $\lambda < 2$  for  $N = 25$ ) the exact function  $\lambda(V_0)$  is well described by the Gaussian approximation. At higher values of  $V_0$  the Gaussian approach fails, and each dependence  $\lambda(V_0)$  tends to the limiting





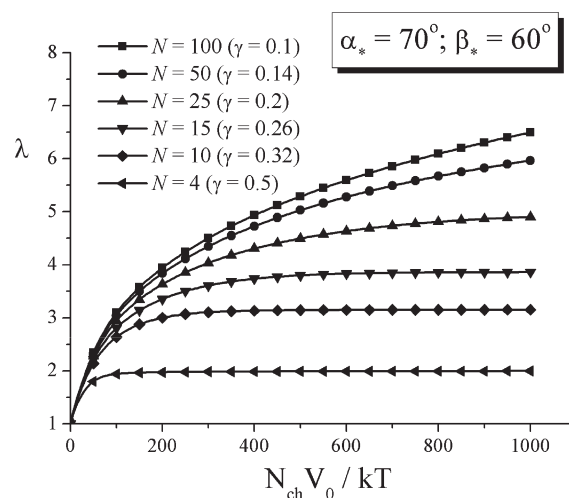
**Figure 8.** Same as Figure 7 but plotted on logarithmic scale. Solid lines illustrate the results for the exact solution of eq 23; dashed ones show  $\lambda$  calculated in the framework of the Gaussian approximation given by eq 29.

value, this limiting value being independent of the parameters  $\alpha_*$  and  $\beta_*$ ; see Figures 7 and 8, and being determined only by the parameter  $N$ , e.g.,  $\lambda_{\max} = 5$  for  $N = 25$ . The independence of the limiting deformation on the values  $\alpha_*$  and  $\beta_*$  takes place for azobenzene elastomers with all three types of photomechanical behavior given in Figure 4.

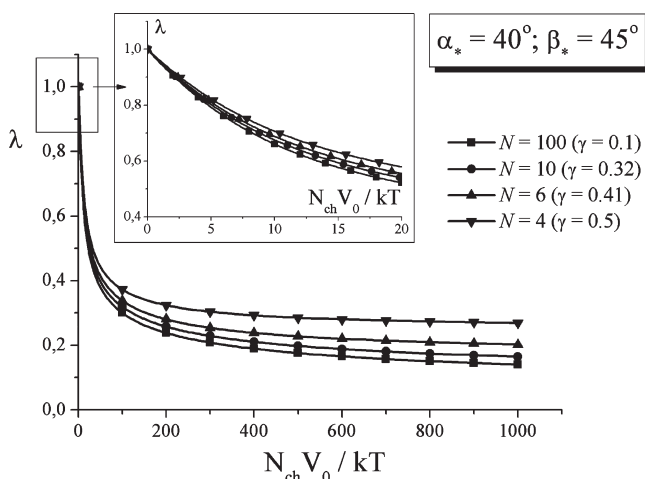
We note, however, that the limiting elongation is reached at an exact limit  $V_0 \rightarrow \infty$ . But at finite strengths of the potential  $V_0$  (i.e., at finite light intensities available in experiments) the values of the elongation ratio  $\lambda$  can significantly differ for elastomers with different values of the parameters  $\alpha_*$  and  $\beta_*$ , although the values of  $N$  are the same for these elastomers, see Figures 5–8. Thus, the maximal values of the elongation ratio, which are reachable in experiments, can strongly depend on the parameters  $\alpha_*$  and  $\beta_*$  (for given  $N$ ), since maximal light intensities available in experiments can be not enough to reach the limiting elongations of azobenzene elastomers.

Furthermore, eq 36 allows us to study the effects of the degree of cross-linking on the photomechanical behavior of azobenzene elastomers. The degree of cross-linking (i.e., the number of network strands in the unite volume,  $\nu$ ) is directly proportional to the parameter  $\gamma^2$ , see eq 20. Thus, one can see from eq 36 that the increase of the degree of cross-linking is accompanied by the decrease of the magnitude of the limiting deformation, namely,  $\lambda_{\max}$  decreases for uniaxially stretched elastomers and  $\lambda_{\min}$  increases for elastomers which demonstrate uniaxial contraction. Figures 9–11 show the dependences  $\lambda(V_0)$  at varying values of the parameter  $\gamma$  and for fixed values of the structural parameters  $\alpha_*$  and  $\beta_*$ , for which azobenzene elastomers demonstrate a uniaxial expansion (Figure 9), a uniaxial contraction (Figure 10), and a nonmonotonic photomechanical behavior (Figure 11). One can see that the larger is the degree of cross-linking  $\gamma$  (i.e., the smaller is the chain length  $N$ ), the smaller is the magnitude of the light-induced deformation. This tendency is caused by the fact that the initial stretching of shorter chains is higher ( $\gamma \approx 1/(N)^{1/2}$ ). As a result, the deformation of azobenzene elastomers built from shorter chains is smaller.

One can see from Figures 9–11 that the effects of the degree of cross-linking on the photomechanical behavior is much stronger for elastomers, which demonstrate a monotonic expansion along

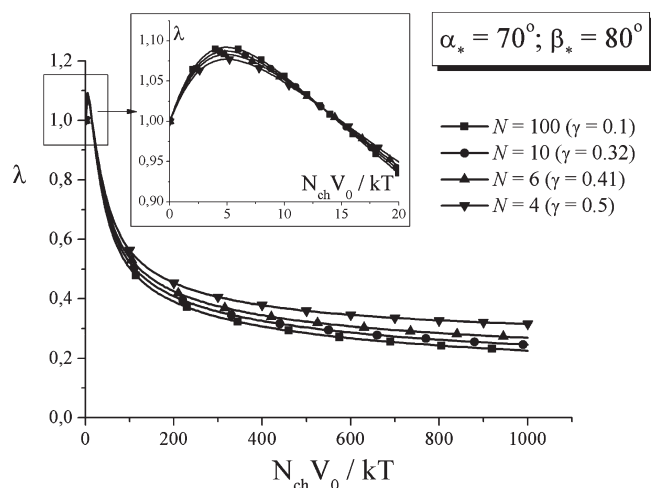


**Figure 9.** Dependence of the elongation ratio  $\lambda$  on the reduced strength of the potential,  $N_{\text{ch}} V_0 / kT$ , at varying values of the chain length  $N$  for azobenzene elastomers which demonstrate light-induced uniaxial expansion (the area II in Figure 4).  $\alpha_* = 70^\circ$  and  $\beta_* = 60^\circ$ .



**Figure 10.** Same as Figure 9 but for azobenzene elastomers which demonstrate light-induced uniaxial contraction (the area I in Figure 4).  $\alpha_* = 40^\circ$  and  $\beta_* = 45^\circ$ .

the electric vector of the light (Figure 9), than for elastomers, which show a uniaxial contraction at large strengths of the potential  $V_0$  (Figure 10 and 11). For example, at varying values of  $N$  from 100 to 10, the light-induced deformation changes only slightly for elastomers which show a contraction at large  $V_0$  (see Figure 10 and 11). At the same time, the differences in the light-induced elongations for elastomers, which demonstrate monotonic expansion, are significant at varying values of  $N$  from 100 to 10 (see Figure 9). These results are explained by the fact that the rate of chain stretching is higher for elastomers, which demonstrate expansion along the electric vector of the light, than for elastomers, which show a uniaxial contraction at large  $V_0$ . Indeed, in the former case, the extension takes place for chains, which lie along the vector  $\mathbf{E}$ , and is characterized by the linear dependence on  $\lambda$ :  $h_x/Nl \approx \gamma\lambda$ ; whereas in the latter case, the extension takes place for chains, which lie perpendicular to the vector  $\mathbf{E}$ , and their relative extension is described by a slower dependence on



**Figure 11.** Same as Figure 9 but for azobenzene elastomers which demonstrate a nonmonotonic photomechanical behavior (the area III in Figure 4).  $\alpha_* = 70^\circ$  and  $\beta_* = 80^\circ$ .

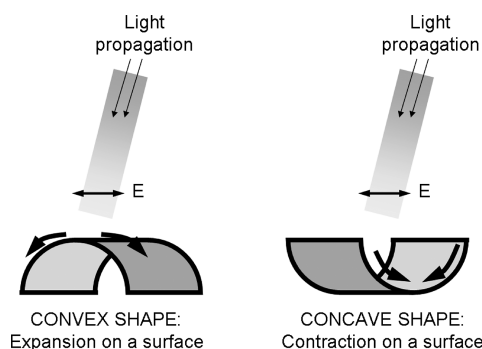
$\lambda: h_y/Nl \cong \gamma/(\lambda)^{1/2}$ . As a result, under light-induced elongation, the non-Gaussian regime appears earlier for uniaxially stretched elastomers than for compressed ones and, therefore, the effects of the finite extensibility of the network strands and of the degree of cross-linking are stronger in the former case than in the latter one.

#### 4. DISCUSSION

In the previous sections, we have considered the light-induced deformation (expansion or contraction) of azobenzene elastomers under homogeneous light irradiation, when the light intensity is constant inside a polymer. On the other hand, in reality the light intensity can change its value from layer to layer deep down a polymer film due to absorption of the light energy inside the polymer. As a result, a gradient of the light intensity should lead to a gradient of mechanical stress inside a polymer film and result in the appearance of a torsion force which can bend a film. Note that the light-induced bend deformation of photosensitive materials has been observed in many experiments.<sup>7–13</sup> Bending is a three-dimensional movement and is of a special interest for different technical applications.

Using our findings for the light-induced deformation under homogeneous light illumination, we can describe qualitatively bending movements of photosensitive elastomers. The light intensity decreases from layer to layer deep down inside a polymer film due to absorption of photons by the chromophores. Thus, the maximal intensity of the light and the maximal magnitude of light-induced deformation are expected at the surface of a polymer film. It is now important to point out that depending on the chemical structure, a photosensitive polymer can display either expansion or contraction at the surface. This means that a polymer film as a whole can demonstrate either convex or concave shape with respect to the direction of the light propagation, see Figure 12. Such a variety of bend deformations of photosensitive polymer films follows immediately from our findings presented in the previous section.

Photosensitive polymers, which are uniaxially compressed under homogeneous light illumination (the area I in Figure 4), should demonstrate a concave bending movement with respect to the direction of the light propagation, see Figure 12. At the same time, photosensitive polymers, which are stretched under



**Figure 12.** Bend deformation of an azobenzene elastomer (convex or concave shape) depending on the direction of deformation of a film on the surface (expansion/contraction).

homogeneous light illumination (the area II in Figure 4), should display a convex bending movement with respect to the light propagation, see Figure 12. Nontrivial photomechanical behavior is expected for structures, which correspond to the area III in Figure 4: they should demonstrate a convex bend deformation at small light intensities and a concave bending at high ones. For these structures, a more complicated behavior can take place at certain intensities of the external light irradiation: torsion forces appearing in different domains inside a sample can have opposite directions due to nonmonotonic photomechanical response of the domains on the light stimulus, whose intensity is varied inside the sample. In this case, the overall deformation of the sample seems to be a result of a nontrivial interplay between torsion forces of opposite directions inside the sample.

Calculation of the magnitude of the bend deformation as a function of the light intensity is a special problem which can be a topic of further generalizations. The magnitude of deformation can be determined from the balance between the mechanical stresses appearing in neighboring layers inside a polymer film. The stresses in neighboring layers can be calculated using an orientation approach as presented here. Note that this approach provides typical values of macroscopically visible deformation ( $\lambda \sim 1.2$  or  $\lambda \sim 0.8$ ) at strengths of the potential  $N_{ch}V_0/kT \sim 5$  (see Figures 5–11). Using eq 2, the light intensity corresponding to the value  $N_{ch}V_0/kT \sim 5$  at room temperature and for  $N_{ch} \sim 10$  can be estimated as  $I_p \sim 20 \text{ mW/cm}^2$ . The last value belongs to a typical region of the light intensities  $1 \text{ mW/cm}^2 < I_p < 1 \text{ W/cm}^2$  that were used in experiments on light-induced bend deformation of azobenzene elastomers.<sup>7–13</sup> To conclude, the results presented in the paper demonstrate a great potential strength of the proposed orientation approach which can be generalized for describing other complex phenomena in photosensitive polymers (e.g., bend deformation, effects of LC-order, dynamic behavior, etc.) in the future.

#### CONCLUSIONS

We have proposed a theory of light-induced deformation of azobenzene elastomers under illumination with uniform and linearly polarized light. The theory is based on the statistical approach developed recently by us<sup>17–19</sup> for amorphous uncross-linked azobenzene polymers built from short rigid oligomers bearing azobenzene chromophores. According to this approach, the photoinduced mechanical stress originates from the preferable reorientation of the azobenzene chromophores perpendicular to the electric vector of the light. In the present work,

we have extended the theory<sup>17–19</sup> to azobenzene elastomers taking the chain structure of the network strands explicitly into account. A regular cubic network model built from identical freely jointed polymer chains bearing azobenzene chromophores has been used. Different orientation distributions of chromophores around the main chains have been considered. We have shown that the photoelastic behavior of azobenzene elastomers is very sensitive to their chemical structure. Azobenzene elastomers can demonstrate uniaxial contraction/expansion along the polarization vector of the light, if the chromophores have their preferable orientation parallel/perpendicular to the main chains. For intermediate chemical structures, the elongation of a sample displays a nonmonotonic behavior with the light intensity and can even change its sign: a stretched sample starts to be uniaxially compressed. Increase of the degree of cross-linking results in a decrease of the magnitude of the photoinduced deformation at fixed light intensity. We have shown that the direction of the light-induced elongation of an azobenzene elastomer (expansion/contraction) coincides with the direction of deformation for its low-molecular-weight analogue, i.e. for the system of short oligomers, whose chemical structure is the same as for the chain segments of the elastomer. Thereby, we generalize the results of the theory<sup>17–19</sup> given for uncross-linked amorphous azobenzene polymers to azobenzene elastomers.

The structure–property relationships established in the present study for azobenzene elastomers under uniform light irradiation can be extended for describing the bend deformation of these materials under the influence of inhomogeneous light illumination, when the light intensity changes from layer to layer inside a polymer film due to absorption of photons by the material. In this case, depending on the chemical structure of a material, an azobenzene elastomer can demonstrate either convex or concave shape with respect to the light propagation. These theoretical findings seem to be useful for designing photosensitive smart materials of specific properties that can be used in technical devices to transform the light energy into mechanical forces with exactly controllable directions.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: toshchevikov@ipfdd.de.

## ACKNOWLEDGMENT

The financial support of the DFG with Grant GR 3725/2-1 is gratefully acknowledged.

## REFERENCES

- (1) Eisenbach, C. D. *Polymer* **1980**, *21*, 1175–1179.
- (2) Xie, S.; Natansohn, A.; Rochon, A. P. *Chem. Mater.* **1993**, *5*, 403–411.
- (3) Finkelmann, H.; Nishikawa, E.; Pereira, G. G.; Warner, M. *Phys. Rev. Lett.* **2001**, *87*, 015501.
- (4) Hogan, P. M.; Tajbakhsh, A. R.; Terentjev, E. M. *Phys. Rev. E* **2002**, *65*, 041720.
- (5) Warner, M.; Terentjev, E. *Macromol. Symp.* **2003**, *200*, 81–92.
- (6) Li, M.-H.; Keller, P.; Li, B.; Wang, X.; Brunet, M. *Adv. Mater.* **2003**, *15*, 569–572.
- (7) Ikeda, T.; Nakano, M.; Yu, Y.; Tsutsumi, O.; Kanazawa, A. *Adv. Mater.* **2003**, *15*, 201–205.
- (8) Yu, Y.; Nakano, M.; Ikeda, T. *Pure Appl. Chem.* **2004**, *76*, 1467–1477.
- (9) Yu, Y.; Nakano, M.; Shishido, A.; Shiono, T.; Ikeda, T. *Chem. Mater.* **2004**, *16*, 1637–1643.
- (10) Camacho-Lopez, M.; Finkelmann, H.; Palfy-Muhoray, P.; Shelley, M. *Nat. Mater.* **2004**, *3*, 307–310.
- (11) Yu, Y.; Nakano, M.; Ikeda, T. *Nature* **2003**, *425*, 145.
- (12) Yu, Y.; Ikeda, T. *Macromol. Chem. Phys.* **2005**, *206*, 1705–1708.
- (13) Jiang, H.; Kelch, S.; Lendlein, A. *Adv. Mater.* **2006**, *18*, 1471–1475.
- (14) Geue, T.; Ziegler, A.; Stumpe, J. *Macromolecules* **1997**, *30*, 5729–5738.
- (15) Jung, C. C.; Rosenhauer, R.; Rutloh, M.; Kempe, C.; Stumpe, J. *Macromolecules* **2005**, *38*, 4324–4330.
- (16) Kullina, C.; Hvilsted, S.; Hendann, C.; Siesler, H. W.; Ramanujam, P. S. *Macromolecules* **1998**, *31*, 2141–2151.
- (17) Toshchevikov, V.; Saphiannikova, M.; Heinrich, G. *J. Phys. Chem. B* **2009**, *113*, 5032–5045.
- (18) Toshchevikov, V.; Saphiannikova, M.; Heinrich, G. Theory of light-induced deformations in azobenzene polymers: structure-property relationship. In *Proceedings of SPIE "Optical Materials in Defence Systems Technology VI"*; Society of Photo-Optical Instrumentation Engineers: Washington, DC, 2009; Vol. 7487, pp 74870B.1–12.
- (19) Saphiannikova, M.; Toshchevikov, V.; Ilnytskyi, J. *Nonlinear Opt., Quantum Opt.* **2010**, *41*, 27–57.
- (20) Chigrinov, V.; Pikin, S.; Verevochnikov, A.; Kozenkov, V.; Khazimullin, M.; Ho, J.; Huang, D. D.; Kwok, H. S. *Phys. Rev. E* **2004**, *69*, 061713.
- (21) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136–138.
- (22) Kim, D. Y.; Tripathy, S. K.; Li, L.; Kumar, J. *Appl. Phys. Lett.* **1995**, *66*, 1166–1168.
- (23) Grenzer, M. Photoinduced material transport in amorphous azobenzene polymer films. Habilitation thesis, Potsdam University: Potsdam, Germany, 2007.
- (24) Mechau, N.; Saphiannikova, M.; Neher, D. *Macromolecules* **2005**, *38*, 3894–3902.
- (25) Mechau, N.; Saphiannikova, M.; Neher, D. *Appl. Phys. Lett.* **2006**, *89*, 251902.
- (26) Yager, K. G.; Barrett, C. J. *Macromolecules* **2006**, *39*, 9320–9326.
- (27) Barrett, C. J.; Rochon, P. L.; Natansohn, A. L. *J. Chem. Phys.* **1998**, *109*, 1505–1516.
- (28) Kumar, J.; Li, L.; Jiang, X. L.; Kim, D.-Y.; Lee, T. S.; Tripathy, S. *Appl. Phys. Lett.* **1998**, *72*, 2096–2098.
- (29) Lefin, P.; Fiorini, C.; Nunzi, J.-M. *Pure Appl. Opt.* **1998**, *7*, 71–82.
- (30) Pedersen, T. G.; Johansen, P. M.; Holme, N. C. R.; Ramanujam, P. S.; Hvilsted, S. *Phys. Rev. Lett.* **1998**, *80*, 89–92.
- (31) Baldus, O.; Zilker, S. J. *Appl. Phys. B: Laser Opt.* **2001**, *72*, 425–427.
- (32) Gaididei, Y. B.; Christiansen, P. L.; Ramanujam, P. S. *Appl. Phys. B: Laser Opt.* **2002**, *74*, 139–146.
- (33) Lee, J. D.; Kim, M. J.; Nakayama, T. *Langmuir* **2008**, *24*, 4260–4264.
- (34) Bubblitz, D.; Helgert, M.; Fleck, B.; Wenke, L.; Hvilsted, S.; Ramanujam, P. S. *Appl. Phys. B: Laser Opt.* **2000**, *70*, 863–865.
- (35) Bian, S.; Williams, J. M.; Kim, D. Y.; Li, L.; Balasubramanian, S.; Kumar, J.; Tripathy, S. J. *Appl. Phys.* **1999**, *86*, 4498–4508.
- (36) Fukuda, T.; Matsuda, H.; Shiraga, T.; Kimura, T.; Kato, M.; Viswanathan, N. K.; Kumar, J.; Tripathy, S. K. *Macromolecules* **2000**, *33*, 4220–4225.
- (37) Fabbri, F.; Garrot, D.; Lahlil, K.; Boilot, J. P.; Lassailly, Y.; Peretti, J. J. *Phys. Chem. B* **2011**, *115*, 1363–1367.
- (38) Ilnytskyi, J.; Saphiannikova, M.; Neher, D. *Cond. Matter Phys.* **2006**, *9*, 87–94.
- (39) Ilnytskyi, J.; Neher, D.; Saphiannikova, M.; Wilson, M. R.; Stimson, L. *Mol. Cryst. Liq. Cryst.* **2008**, *496*, 186–201.
- (40) Ilnytskyi, J.; Neher, D.; Saphiannikova, M. *J. Chem. Phys.* **2011**, *135*, 044901.
- (41) Treloar, L. R. G. *The Physics of Rubber Elasticity*, 2nd ed., Clarendon press: Oxford, U.K., 1958; p 343.



- (42) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon: Oxford, U.K., 1986.
- (43) James, H. M.; Guth, E. J. *Chem. Phys.* **1943**, *11*, 455–481.
- (44) Jarry, J. P.; Monnerie, L. *Macromolecules* **1979**, *12*, 316–320.
- (45) Gotlib, Yu. Ya.; Torchinskii, I. A.; Toshchevnikov, V. P. *Macromol. Theory Simul.* **2002**, *11*, 898–912.
- (46) Gotlib, Yu. Ya.; Torchinskii, I. A.; Toshchevnikov, V. P. *Macromol. Theory Simul.* **2004**, *13*, 303–317.
- (47) Veer, P. U.; Pietsch, U.; Rochon, P. L.; Saphiannikova, M. *Mol. Cryst. Liq. Cryst.* **2008**, *486*, 1108–1120.
- (48) Toshchevnikov, V. P.; Heinrich, G.; Gotlib, Yu. Ya. *Macromol. Theory Simul.* **2010**, *19*, 195–209.