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Communication

Photomechanical Solid Polymers: Model for Pressure and Strain Induced by Photoisomerization and Photo-Orientation

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Abstract: Photoactive polymers are important for fundamental studies and applications in several area of photonics such as data storage and holography and nonlinear optics and photomechanics. The latter is perhaps one of the most important applications of such materials, since they act as light to mechanical energy transducers and move under light action. For example, azo-polymers irradiated by inhomogeneous resonant ultra-violet or visible light undergo molecular and macroscopic motion, at sub-glass transition temperatures by photoisomerization of the azo dyes. Our recent research in this field highlighted the fundamentals of mobility enhancement by light, including light-induced viscosity change and acceleration of relaxation times, and photomechanics, encompassing motions in gradients of actinic light leading to surface structuring and actuation. In this paper, we present an original model which predicts the creation of mechanical pressure, i.e., motion, by a photo-induced change in the occupied volume and length of anisometric isomers, and we give simple analytical expressions describing the dynamics of volume as well as strain change upon polarized light irradiation of photomechanic samples.

Keywords: azobenzenes; photoisomerization; polymers; viscosity; relaxation times; molecular and matter motion; photosoftening; photomechanics; surface structuring

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1. Introduction

Photoactive polymers have been studied intensively over the past few years for important uses in photonics, including applications as photoresponsive smart materials with properties controllable by light. Manipulation of molecular mobility by photoisomerization is of central importance in the observation of many of the photo-induced effects in photoisomerizable materials [1]. Indeed, light absorption enhances the mobility of molecules and influences relaxation times in glass-forming materials due to free volume change by photoisomerization at sub-glass transition temperatures (T_g) [2]. A spectacular increase in mobility, up to viscous regimes, occurs in polymers due to chromophore photoisomerization [3–6]. Viscoelastic functions of polymers strongly depend on T_g [7]. Their change is spectacular when the operating temperature approaches T_g, and segmental motion is frozen below T_g. Photoisomerization enhances molecular mobility well below T_g, leading to applications in, for example, nonlinear optics (NLO) [8,9] and holography [10] as well as other photonic applications, including optical birefringence [8] and data storage [11–13] and surface structuring, i.e., surface relief gratings (SRGs) [6,14,15], and photomechanics [16–21]. Photosoftening of the polymers is required for the creation of surface structuring and actuation.

Photo-induced actuation of azo-polymers offers the possibility of direct conversion of visible light into mechanical energy, as well as applications in transport and locomotion at miniature scales. Recent reviews summarize applications of photomechanics in azo-polymers [1,16,17,22]. The latter (both amorphous and liquid crystalline, LC) are known for

their ability to undergo photomechanical motions and deformations at nano-scales, and they hold promise for the creation of useful nano-machines [23]. Our recently published works discussed photochemical tweezing and photomechanics, including mobility enhancement and control of viscosity and relaxation times by photoisomerization [1,2], and in this paper we present an original theoretical model for polymers deformable by photoisomerization. That is, we show that the change in the volume and length of the azobenzene chromophore creates mechanical pressure and motion. We will go on to discuss the model.

Material motion is fueled by light absorption and mechanical motion of tiny molecules, i.e., azobenzene derivatives. The latter switch, i.e., change shape, in a few picoseconds, between an elongated trans isomer and a more globular cis isomer by light absorption [24], and the energy u which fuels the motion of the dye is given by the total energy absorbed by the molecules [25]. In photochemical tweezing, the force $\boldsymbol{F}$ that moves the polymer derives from u, i.e., it is the spatial derivative of u ($\boldsymbol{F} = -\nabla u$). The detailed mathematical formalism of the photoisomerization force and the related motion of photoreactive units in intensity gradients and vectorial fields can be found in [25,26], including numerical simulations [27], which discuss the concept of photochemical tweezing in vectorial fields and light-induced diffusion in solid polymers. An appreciable decrease in viscosity η by photoisomerization was observed in solutions [28,29], and substantial enhancement of mobility, termed athermal photofluidity, was observed in solid films of azo-polymers [3–5]. A theoretical model was developed in [2] for viscosity decrease and acceleration of relaxation times induced by photoisomerization. Here, we discuss a material's shape change by photoisomerization.

2. Model for Pressure and Strain Induced by Photoisomerization

2.1. Dynamics of Volume Change and Pressure Build-up

Several theoretical models were developed and theoretical studies carried out to describe the role played by photoisomerization in the control of the optical response of LC and amorphous photomechanical materials (see, for example, [30–33]). Molecular mobility in glass-forming materials, depends, in any temperature and pressure conditions, primarily on the polymer's free volume V_f with $V_f = V - V_\infty$, and V is the specific volume, and V_∞ an occupied volume. V_∞ includes the volume of the molecules and the volumes corresponding to their rotational and vibrational motions. Next, we discuss an original model, albeit an extreme case model, of the photomechanical response of azo-polymers where the occupied volume of the molecules is nearly equal to the specific volume, i.e., negligible free volume, and no extra free volume is created by photoisomerization, i.e., negligible photoexpansion. In other words, the model assumes that the chromophores are interacting, i.e., not isolated, like in LC materials [34,35], and the space, i.e., volume, occupied by nonphotoisomerizable matter remains unchanged and follows the motion of the light-activated chromophores. The total concentration N of the chromophores is equal to the initial concentration of the trans molecules, and light is assumed to be absorbed throughout the thickness of the sample, i.e., an optically thin sample, irradiated perpendicular to its plane and with an average absorbed intensity I_A. Assuming that each isomer has an occupied volume which includes the volume needed for isomerization, i.e., v_c for the cis isomer and v_t for the trans isomer, the volume fractions of the azo-polymer film, occupied by the trans and cis populations, are given by $(1-\alpha)Nv_t$ and $\alpha N v_c$, respectively (vide infra). N is the total density of the chromophores, and it is equal to the reciprocal of the specific volume ($N = 1/V$), and α is the extent of the cis isomers.

The total volume occupied by the isomers is $V = V_c + V_t$ where V_c (V_t) is the volume occupied by the total cis (trans) population n_c (n_t). Noting that, $n_c = VN_c$ and $n_t = VN_t$ with N_c and N_t as the respective concentrations of the cis and trans populations, and using $V = n_c v_c + n_t v_t$, we obtain $1 = \alpha N v_c + (1-\alpha)Nv_t$; therefore $V = \alpha v_c + (1-\alpha)v_t$. The volumes V, and v_t and v_c are expressed in $cm^3/molecule$. It is useful to express V as $V = \alpha(v_c - v_t) + v_t$ and to introduce a reduced volume $v_R = (V - v_t)/(v_c - v_t) = \alpha$. An all-cis sample may be achieved for photoreactions where only the trans isomer absorbs actinic light, such as ultra-violet (UV) light excitation of trans-azobenzene [36]; for light

excitations absorbed by both isomers, the photostationary state (pss) is a balance between the cis and trans isomers [37]. For one-way trans→cis photoisomerization, α varies between zero at time t and one for t going to infinity. In other words, the volumes occupied by the azo-polymer at the initial time and infinity are given by the volumes occupied by the trans and cis isomers, respectively. In all cases, for a given absorbed irradiation intensity, I_A, at a given wavelength, λ, the time evolution of the irradiated volume of the azo-polymer is identically given by the evolution of the extent of the cis isomer, which in turn is defined by the absorption cross section of the isomers σ and the isomerization quantum yields ϕ (vide infra) [36,37].

Note, from the expression of the reduced volume, v_R, that no volume change in the irradiated sample is possible if the volume of the azobenzene molecule remains unchanged upon trans and cis isomerization, i.e., $V = v_t$, and the difference in the occupied volume and the volume of the trans isomer is proportional to the difference in volumes of the two isomers, that is $(V - v_t) = \alpha\,(v_c - v_t)$. Even though this model ignores free volume and expansion, both of which could be introduced into the equations of a more elaborate model, it does, however, describe reversible volume change in the material, and, more importantly, it shows that the differing volumes of the isomers build a mechanical pressure inside the material *(vide infra)*, and it preserves the physics and simplifies the discussion.

Many of the azo-polymers studied for photomechanical properties contain the azobenzene molecule of which the trans and cis isomers are spectrally distinguishable. Trans-azobenzene (t-AB) presents an absorption band in the UV region of the spectrum around 360 nm, and cis-azobenzene (c-AB) in the visible region around 450 nm. In addition, the lifetime of the c-AB is generally on the order of hours, depending on the polarity of the host material. Therefore, c-AB can be considered stable on a time scale of minutes, i.e., the time scale of the experiments. In such systems, the dynamics of $trans \rightarrow cis$ photoisomerization and photo-orientation under polarized UV light irradiation are described by double exponentials for both the population, i.e., α, and the order parameter of A_2^t and A_2^c of t-AB and c-AB, respectively [36]. To describe the intermolecular interaction of the azobenzene molecules in LC materials, one may assume a Maier–Saupe type potential and introduce it into the rate equations of photo-orientation of azobenzenes under polarized UV light.

Assuming linearly polarized irradiation and t-AB as a rodlike molecule, and the rates of the cis→trans thermal reaction and the diffusion, i.e., stochastic thermally activated molecular motion, in the cis and trans forms small, a feature which is true in solid polymers, and if the irradiating light is turned on at the time $t = 0$, α and v_R of irradiated samples are given by [36]

$$v_R = \alpha \cong \left(1 - \frac{1}{2}\{0.66exp(-k_2 t) + 1.22exp(-k_0 t)\}\right), \quad (1)$$

$$k_2 = 2.23\, I_A \phi_{tc} \sigma_t, \quad (2)$$

and

$$k_0 = 0.35\, I_A \phi_{tc} \sigma_t \quad (3)$$

$k_{0,2}$ and t are expressed in units of s^{-1} and s, respectively. This equation is obtained by substituting the expression of α in V, where I_A is the absorbed irradiation intensity, and ϕ_{tc} is the isomerization quantum yield of the trans→cis photoisomerization, and σ_t is the absorption cross section of t-AB. Both σ_t and ϕ_{tc} are at the irradiation wavelength. Equation 1 shows analytically that the volume of the sample evolves with two time constants that mainly depend on the absorbed irradiation light intensity and the parameters of $trans \rightarrow cis$ photoisomerization. Assuming an isotropic volume change, we have $P = K\,(\Delta V/V)$ [38], with ΔV as the volume change of the material upon irradiation, e.g., the volume at irradiation minus the initial volume, P is the optical pressure, and K the bulk modulus of the polymer. So, using the expression of V, the pressure reads

$$P = K(V - v_t)/v_t = K(v_c/v_t - 1)\alpha \quad (4)$$

The pressure builds in the azo-polymer as the content of the cis isomer increases, and the larger the volume change in the chromophore, upon trans→cis isomerization, the larger the pressure (Figure 1). It is noteworthy that volume expansion of film samples was experimentally observed in glassy polymers by different authors using ellipsometry [39] as well as actuation [40]. The slope of P at the early time evolution, for a given irradiation intensity, and its value at the photostationary state ($\alpha_{PSS} \sim 1$) yield the values of the bulk modulus of the polymer, and the relative ratio of the volumes of the trans isomer to that of the cis isomer, e.g., (v_c/v_t), knowing the photoisomerization parameters of the chromophores, e.g., ϕ_{tc} and σ_t. Note the intuitive behavior that the larger the bulk modulus, the larger the pressure. The photomechanical activity scales with the bulk modulus and it depends on the polymer studied.

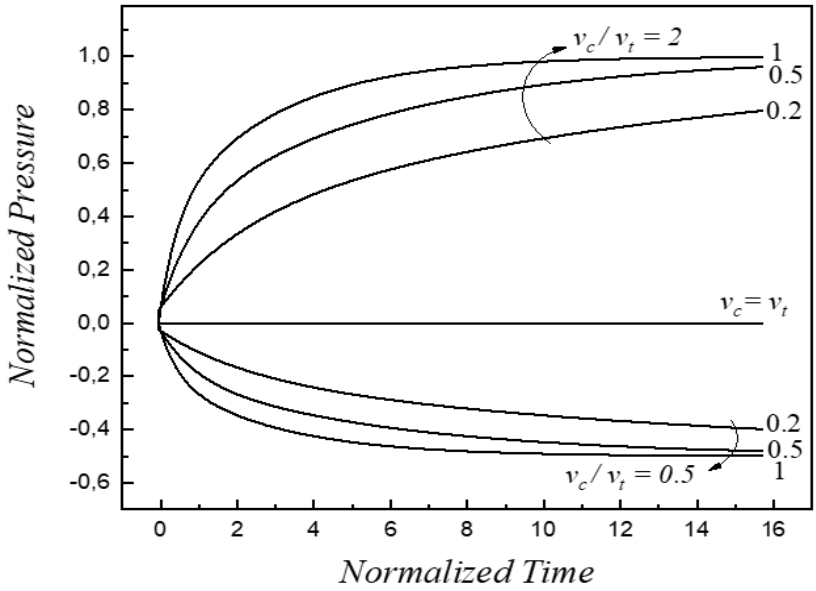

Figure 1. Theoretical simulation of the time evolution of the pressure P, normalized by K, using Equations (1) and (2), for different normalized pump intensities, i.e., in units of $I = I_A\phi_{tc}\sigma_t$: 0.2, 0.5, and 1.0, and for different ratios of the occupied volumes of the isomers: $v_c/v_t = 0.5$, 1.0, 2.0. Note that when $v_c/v_t = 1$, no pressure occurs, i.e., no isomeric volume change. Negative (positive) pressure occurs for $v_c/v_t < 1$ $(v_c/v_t > 1)$ and the larger the pump intensity, the faster the pressure build-up.

This model holds for unpolarized light, propagating perpendicular to the sample's plane, and uniformly irradiating the sample surface; the irradiated volume is given by the irradiating spot size at the sample surface times the penetration depth of the light into the sample, which is given by the thickness of optically thin samples.

2.2. Strain Induced by Photo-Orientation

Next, we assume that the isomers are uniformly distributed in the irradiated volume, and that linearly polarized light, say along a direction denoted by $\|$, uniformly irradiates the sample. $\perp$ refers to a direction perpendicular to $\|$. Photo-orientation occurs and it influences the deformation process. Indeed, $N_{t,c,\|}$ and $N_{t,c,\perp}$ denote the concentration distribution, and $A_2^{t,c}$ the geometrical order parameters of the isomers in the $\|$ and $\perp$ directions, respectively. The lengths of the sample in $\|$ and $\perp$ directions are given by

$$L_{\|,\perp} = N_{t,\|,\perp} l_t + N_{c,\|,\perp} l_c \tag{5}$$

$$N_{t,c,\|} = (1 + 2\mathbf{A_2^{t,c}}) N_{t,c} \tag{6}$$

$$N_{t,c,\perp} = (1 - \mathbf{A_2^{t,c}}) N_{t,c} \tag{7}$$

$$A_2^t = \frac{1}{5}\{exp(-k_2 t) - exp(-k_0 t)\}; A_2^c = -P_2^{tc} A_2^t \quad (8)$$

The expressions of $A_2^{t,c}$ are developed in [36]. $l_{t,c}$ is the average length per molecule for an all-trans (all-cis) sample. The subscripts c and t refer to cis and trans, respectively. After rearrangement, the strains $\epsilon_{\parallel,\perp} = \left(L_{\parallel,\perp} - L\right)/L$, with L the length of the sample prior to irradiation, are

$$\epsilon_{\parallel} = (l_c/l_t - 1)\alpha + 2\left(1 - P_2^{tc} l_c/l_t\right) A_2^t \quad (9)$$

$$\epsilon_{\perp} = (l_c/l_t - 1)\alpha - \left(1 - P_2^{tc} l_c/l_t\right) A_2^t \quad (10)$$

$$\epsilon_{\parallel} - \epsilon_{\perp} = 3\left(1 - P_2^{tc} l_c/l_t\right) A_2^t \quad (11)$$

P_2^{tc} is a parameter that characterizes the change in the orientation of the azobenzene molecule after trans→cis isomerization, and its absolute value is between zero and one. A_2^t is always negative and so is $\epsilon_{\parallel}$; if $l_{t,c}$ are assigned to the lengths of the long axis of the trans and cis isomers, i.e., 9 and 5.5 Å, respectively, the length of the sample in the direction parallel to the irradiation light polarization $L_{\parallel}$ is smaller than L, a feature which is indicative of the shrinkage of the sample in the direction of the irradiating light polarization. $\epsilon_{\perp}$ is also negative and the absolute value of $\epsilon_{\parallel}$ is larger than that of $\epsilon_{\perp}$ at any time, indicating that the sample also shrinks in the perpendicular direction but the amount of shrinkage in the parallel direction is larger than that in the perpendicular one (Figure 2). At saturation, e.g., at pss ($\alpha_{PSS} \sim 1$), photo-orientation disappears, e.g., $A_2^t \sim 0$, and $\epsilon_{\parallel} = \epsilon_{\perp} = \epsilon_{pss}$ is independent of light intensity, and it only depends on the relative difference between the lengths of the long axis of the trans and cis isomers. The system saturates at large irradiation doses, because even molecules that are oriented perpendicular to the irradiation light polarization present an appreciable probability of being photoisomerized, and the model of isotropic volume change holds. The orientation of mesogens in liquid crystalline films influences the bending direction of macroscopic samples. Indeed, when a homeotropic sample is irradiated, perpendicularly to its front surface, mesogens at that surface reorient, and the average length per molecule increases parallel to the front surface, producing expansion of that surface and the film bends away from the light source [41]. The depletion of photo-orientation of azo-polymer films near pss was reported for an optically thin self-assembled monolayer containing the azobenzene molecule [42], and reversal of bending at long irradiation times was observed for azo-polymer cantilevers [43]. In nematic liquid crystal elastomers (LCEs), photoisomerization disrupts the orientational order of the liquid crystal, and it is well known that the extent of cis isomer influences the shape of LCEs by the change in the nematic order parameter [44]. Furthermore, LCE samples irradiated with linearly polarized UV light bend in the direction of light polarization, towards the light source, indicating an appreciable strain in the direction parallel to the UV polarization ($\epsilon_{\parallel} > \epsilon_{\perp}$) [34]; a finding predicted by Figure 2 for intermediate irradiation times, i.e., not in the photostationary state. Indeed, it would be interesting, as suggested by the results in Figure 2, to observe the anisotropic strain near the pss to assess the effect of photo-orientation on anisotropic strain at long irradiation times or high irradiation intensities or both. The effect of photo-orientation on actuation was studied in LC polymer films, and bi-directional bending was observed by rotating the irradiation light polarization between two orthogonal directions, and it was shown that reorientation of the azo-chromophores perpendicular to light polarization results in expansion (contraction) of the front surface of the sample and its bending away from (towards) the laser source for the parallel (perpendicular) configuration [45].

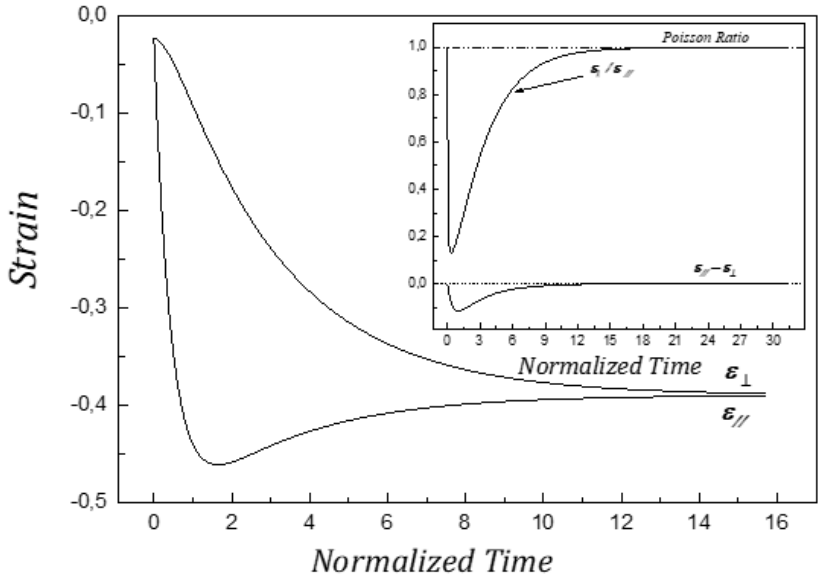

Figure 2. Theoretical simulations of the time evolution of anisotropic stain based on Equations 1, 3, and 4. The parameters used for the simulation are $I = 1$, $P_2^{tc} = -0.05$, corresponding to cis orientation compared to trans orientation [36], and $l_c/l_t \cong 0.61$, corresponding to $l_t = 9$ and $l_c = 5.5$. The inset shows the transient of Poisson's ratio $\left(\epsilon_\perp/\epsilon_\parallel\right)$ and $(\epsilon_\parallel - \epsilon_\perp)$. Note that at saturation, the sample deforms equally in $\epsilon_\parallel$ and $\epsilon_\perp$ directions, i.e., $\epsilon_\parallel = \epsilon_\perp$.

3. Conclusions

Photomobile materials convert light energy to mechanical energy by the action of photosensitive units, i.e., by the mechanical shape change in the isomers. For example, azobenzene derivatives confer to polymers their photoactivity, and are at the center of the observed motions in photomechanical polymers. Here, we present a model showing that pressure is built up in materials by the change in the volume occupied by the isomers. Polarization effects on photomechanics are also discussed via a photo-orientation model showing that both the change in the length of the chromophores and their orientation contribute to strain build-up in the material. The model predicts that future research could be both theoretical and experimental. Theoretically, it is possible to include in the formalism of the actual model the free volume change by photoisomerization, to account for expansion by photo-induced free volume increase, and liquid crystalline molecular interaction, to account for its contribution to the photo-induced order and anisotropic strain in the material. In addition, the model could be sophisticated by introducing the cis→trans back photoisomerization, and its effect on the material's volume and directional strain. Experimentally, it is interesting to test, for example, both amorphous and LC materials containing chromophores with anisometric isomers having different lengths and volumes, to study their effect on the photomechanical properties of the material. Understanding of the material–property relationship will allow for the development of new photoactive materials with properties tailored for specific applications, and we believe that much is yet to come in photoactive matter-related technological development.

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