Nonlinear Effects during Inscription of Azobenzene Surface Relief Gratings

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Surface relief gratings were inscribed on azobenzene polymer films using a pulselike exposure of an Ar^+ laser. The inscription process was initiated by a sequence of short pulses followed by much longer relaxation pauses. The development of the surface relief grating was probed by a He−Ne laser measuring the scattering intensity of the first-order grating peak. The growth time of the surface relief grating was found to be larger than the length of the pulses used. This unusual behavior can be considered as a nonlinear material response associated with the trans−cis isomerization of azobenzene moieties. In this study the polymer stress was assumed to be proportional to the number of cis-isomers. One-dimensional viscoelastic analysis was used to derive the polymer deformation. The rate of trans−cis isomerization increases with the intensity of the inscribing light; in the dark it is equal to the rate of thermal cis−trans isomerization. The respective relaxation times were estimated by fitting theoretical deformation curves to experimental data.

Introduction

The first inscriptions of surface relief gratings (SRGs) on azobenzene polymer films were performed independently in 1995 by Rochon et al.[1] and Kim et al.[2] Several models have been proposed to explain the origin of the inscribing force,[3−8] but none of them describes satisfactory the mass polymer transport at a molecular level. The most promising model is based on the interaction of induced electric dipoles with an inhomogeneous electric field.[4] This model explains the magnitude of SRGs obtained for different combinations of polarization states of the inscribing beams. However, the force density estimated for conventional lasers is 2 orders of magnitude smaller than that of the gravitational force (10^4 N/m^3) and, thus, too small to be of influential importance.[9] Besides, this electric force cannot explain the experiment described in the present study. Here we have chosen a pulselike illumination to resolve the time evolution of SRG formation and found that the grating amplitude continues to grow after switching off the pumping laser. This experiment clearly indicates that the inscribing light provides a momentum that is partially maintained in the dark and is able to push polymer molecules over distances that are comparable with the molecular length.

Presently, there is no doubt that multiple trans−cis and cis−trans photoisomerizations of the azobenzene moieties are the trigger of the inscription process. However, both photoisomerization processes stop immediately when the inscribing laser is switched off. The only process that is still continuing in the absence of irradiation is a much slower cis−trans thermal relaxation. The rate constants depend mostly on the type of chromophore and the type of its attachment to the polymer backbone.[10] Relaxation times between 10 s and 12 h have been estimated for a variety of azobenzene polymers.[10−12] In the present study we explain the maintaining growth process in the dark by this slow cis−trans thermal relaxation and determine its relaxation time by fitting an appropriate model to experi-mental data. The proposed model is an adaptation of our recent viscoelastic approach[9] to the case of short time exposures.

Experiment

For the present investigations we used an azobenzene side-chain homopolymer pDR1M (poly{(4-nitrophenyl)[4-[[2-(meth-acryloyloxy)ethyl]ethylamino]phenyl]diazene}). This amorphous polymer was dissolved in tetrahydrofurane (5 mass %) and then spun on a clean glass substrate at spins of 1500−2000 rpm. The film thickness was measured with a Dektak II depth profiler to be about 500 nm.

SRGs were inscribed onto the polymer films using the interference pattern of two plane waves. They were produced by contracircularly polarized beams from an Ar^+ laser operating at the wavelength of 488 nm and at a power density of 0.1−2.5 W/cm^2 on the film surface. The angle between the beams was chosen to be 30°. At this angle intensity, modulations and a slight ellipticity of the resulting polarization in the interference pattern can be neglected.[13] Thus, the pattern can be considered as a linear polarization pattern with a resulting vector of the electric field rotating along the grating vector.

A sequence of short pulses followed by much longer relaxation pauses was utilized for the inscription process (Figure 1). Hereby we do not expect a local heating of our samples. Recent measurements using an electromechanical spectroscopy method[14] have revealed that the softening temperature for a thin azobenzene film reduces only by 12 K under homogeneous illumination with 2.4 W/cm^2. On the other hand, a temperature modeling study[15] predicts a temperature rise of about 1 K during short time irradiation (1 s at 1 W/cm^2). Even if we use this overestimate but consider very long pauses between pulses (10 s at power densities above 1 W/cm^2), it becomes clear that the local heating of samples can be neglected in the present investigations. Also we did not observe photobleaching of the
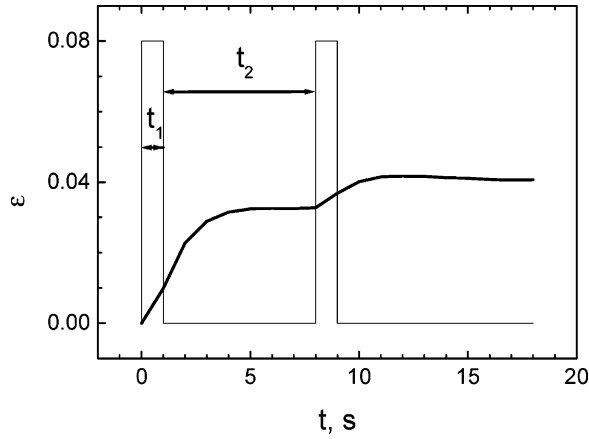
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Figure 1. Dependence of the relative deformation $\epsilon(t)$ on the inscription time t: only the first two pulses are shown (thick line). The thin line represents a pulse sequence with the pulse length $t_1 = 1$ s and the pause between pulses $t_2 = 7$ s. $I_p = 1.25$ W/cm^2.

illuminated area at high power densities, because the exposed dose was always very low and did not exceed 25 J/cm^2.

The gradual development of the SRG was probed in situ by a He−Ne laser. After inscription, the film was scanned with an atomic force microscope. This measurement revealed SRGs with a minimum amplitude of about 10 nm. In this study we neglect birefringence effects which were observed for a functionalized polymer in the few first seconds of illumination.[16] These effects are responsible for a strong increase of the diffraction intensity at the very beginning of illumination. However, birefringence only appears under illumination, it cannot explain that the grating amplitude continues to grow after switching the light off. Neglecting the birefringence grating, the first-order scattering intensity is proportional to the Bessel function of the first order

$$I_1 = J_1^2(\Delta\psi)I_0 \tag{1}$$

where I_0 is the specular intensity, $\Delta\psi = \pi n_p A/\lambda_{red}$, $n_p = 1.66$ is the refractive index of the azobenzene polymer, A is the amplitude of the SRG, and $\lambda_{red} = 633$ nm is the wavelength of the probing He−Ne laser. The relative deformation, $\epsilon(t) = A(t)/L$, caused by a sequence of very short pulses is small. Thus, $I_1/I_0 \approx \Delta\psi^2/4$, and relative deformations can be calculated from measured intensities as follows

$$\epsilon(t) = 2(I_1/I_0)^{0.5}\frac{\lambda_{red}}{\pi n_p L} \tag{2}$$

where $L \approx 500$ nm is the sample thickness.

Theoretical Approach

Generally the polymer deformation can be described by[17]

$$\epsilon(t) = \int_0^t J(t - u)\frac{d\sigma(u)}{du}\,du \tag{3}$$

where $\sigma(t)$ is the stress at the time t and $J(t)$ is the creep compliance of the material obtained from a simple single step loading creep test. It was calculated previously for a model with one, two, and three relaxation times.[9] The choice between two latter models will not affect the outcome of our approach qualitatively. Therefore, to keep the number of fit parameters small we only consider a model with two relaxation times, τ_1

and τ_2. In this model the stress relaxation modulus consists of two components

$$G(t) = G_1 e^{-t/\tau_1} + G_2 e^{-t/\tau_2} \tag{4}$$

and the creep compliance is defined by

$$J(t) = \frac{1}{G_0}\left[\frac{t}{g_0} + \frac{g_1}{g_0} + C\exp(-\omega_0 t)\right] \tag{5}$$

where $G_0 = G_1 + G_2$, $g_0 = G_1\tau_1 + G_2\tau_2$, $g_1 = G_1\tau_1^2 + G_2\tau_2^2$, $\omega_0 = g_0/\tau_1\tau_2$, and $C = (-\omega_0 + \tau_1^{-1})(-\omega_0 + \tau_2^{-1})/\omega_0^2$.

To solve eq 3 we have to define the relation between polymer stress and the pulse sequence used. It was already proposed by Barrett et al.[3] that the origin of the pressure experienced in the material is due to the excess free volume required for isomerization from the compact trans isomer to the bulkier cis isomer. To take into account polarization effects, this model assumes that pressure is proportional not only to the cis isomer population but also to a polarization activity factor which changes along the grating vector. In our one-dimensional approach, we follow a similar hypothesis assuming that the polymer stress, σ, averaged over one grating period is proportional to the molecular density of cis isomers, n.

By use of a hole-burning model[18,19] n can be expressed as follows (see Appendix)

$$\frac{\partial n(t)}{\partial t} = -(5k_T I_p + \tau_c^{-1})n(t) + k_T I_p N \tag{6}$$

where N is the total density of chromophores, I_p is the intensity of the pumping beam in W/cm^2, and $k_T = \Phi_{TC}\sigma_T$. Here Φ_{TC} is the quantum yield of the direct trans−cis isomerization and σ_T is the average cross section of the trans isomers. τ_c^{-1} is the rate of the cis−trans thermal back relaxation. In the presence of the pumping beam the molecular density changes according to

$$n_1(1,t) = n_{sat}(1 - e^{-t/\tau_p})$$

for the first pumping cycle

$$n_1(i,t) = (n_2(i-1,t_2) - n_{sat})e^{-t/\tau_p} + n_{sat} \tag{7}$$

for the ith pumping cycle, and in absence of the pumping beam it changes to

$$n_2(i,t) = n_1(i,t_1)e^{-t/\tau_c}$$

for the ith pumping cycle. Here $n_{sat} = k_T I_p N\tau_p$ is the molecular density of cis isomers at the saturation limit for a given intensity of the inscribing laser, $\tau_p^{-1} = 5k_T I_p + \tau_c^{-1}$ where τ_p^{-1} is the rate of the trans−cis isomerization, t_1 is the pulse length, and t_2 is the pause between two pulses. It is obvious that in the absence of the pumping beam, the maximum value of τ_p is equal to τ_c and it decreases with the intensity of the pumping beam.

The stress derivative in eq 3 can be expressed as

$$\frac{d\sigma(t)}{dt} = \frac{dn_k(i,t)}{dt} = p_i^k e^{-(t-u_i^k)/\tau_k} \tag{8}$$

where $p_1^1 = n_{sat}/\tau_p$, $p_i^1 = (n_{sat} - n_2(i-1,u_i^1))/\tau_p$, and $p_i^2 = -n_1(i,u_i^2)/\tau_c$. Here $u_i^1 = T(i - 1)$ and $u_i^2 = u_i^1 + t_1$, $T = t_1 +$
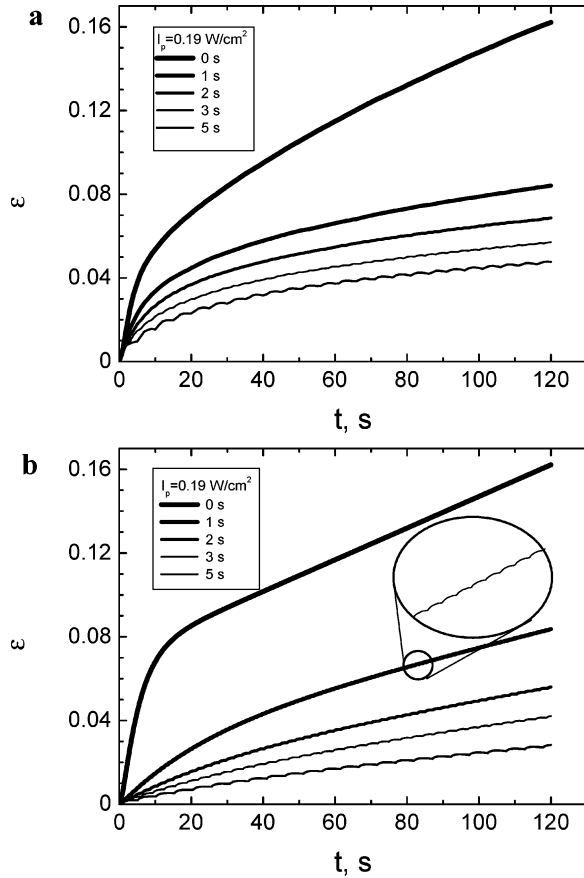
Figure 2. Dependence of the relative deformation $\epsilon(t)$ on the inscription time t: (a) experiment and (b) theory. Pulse length: $t_1 = 0.125$ s. Pause between pulses: $t_2 = 0$ s (continuous exposure), 1, 2, 3, and 5 s. $I_p = 0.19$ W/cm^2.

Figure 3. Dependence of the relative deformation $\epsilon(t)$ on the inscription time t: (a) experiment and (b) theory. Pulse length: $t_1 = 0.125$ s. Pause between pulses: $t_2 = 1$ s, 2, 3, and 4 s. $I_p = 0.315$ W/cm^2.

t_2. Together with the Boltzmann superposition principle[17] eq 3 gives

$$\epsilon(t) = \sum_{i=1}^{N} \begin{bmatrix} \int_{T(i-1)}^{T(i-1)+t_1} J(t-u)p_i^1 e^{-u/\tau_p}\, du + \\ \int_{T(i-1)+t_1}^{Ti} J(t-u)p_i^2 e^{-u/\tau_c}\, du + \\ + \int_{Ti}^{t} J(t-u)p_{i+1}^1 e^{-u/\tau_p}\, du, \qquad 0 \le t \le t_1 \\ + \int_{Ti}^{Ti+t_1} J(t-u)p_{i+1}^1 e^{-u/\tau_p}\, du + \\ \int_{Ti+t_1}^{t} J(t-u)p_{i+1}^2 e^{-u/\tau_c}\, du, \qquad t_1 \le t \le t_2 \end{bmatrix}$$

$$(9)$$

Substitution of eq 5 in eq 9 leads to a final solution which was solved numerically using a recursive Fortran program.

Results

Our experimental data can be divided into two groups.

In the first group the pulse length, t_1, was kept constant but the pause between pulses, t_2, was gradually increased. Experimental data for $t_1 = 0.125$ s and $I_p = 0.19$ W/cm^2 are presented in Figure 2a. For $t_2 = 5$ s moments of time when the inscribing laser is switched on can be recognized as local minima on the $\epsilon(t)$ curve. The SRG grows continuously far beyond the length of the pulse. Therefore, it becomes difficult to distinguish between subsequent pulses if the pause between them is smaller than 3 s. For shorter pauses between pulses (1 and 2 s) the
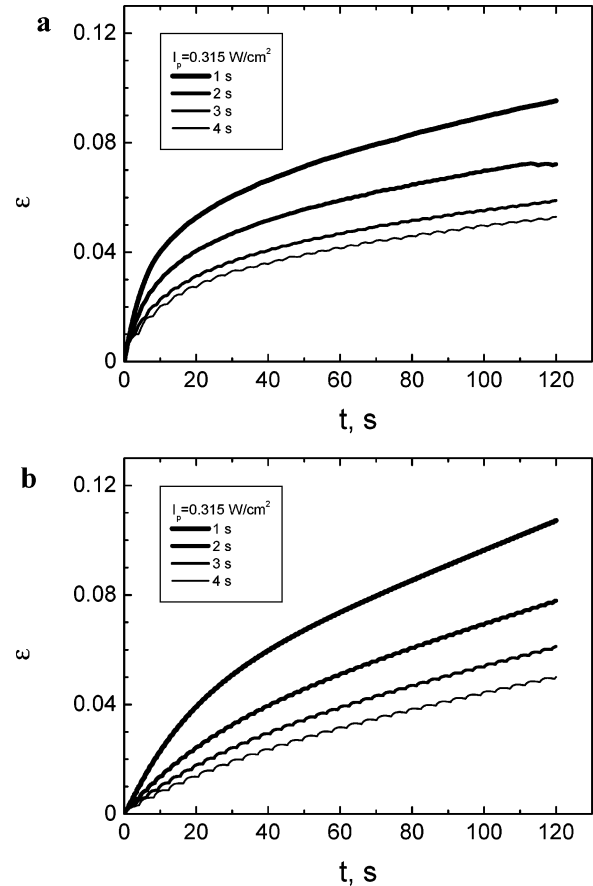
deformation curves are very smooth. They appear to be similar to the curve obtained under continuous inscription. The relative deformations accumulated after a long series of pulses are approximately half of the value achieved under continuous inscription. A qualitatively similar behavior was observed for $t_1 = 0.125$ s and $I_p = 0.315$ W/cm^2 (Figure 3a). Pulses can be usually recognized if the pause between them is 3 or 4 s. Again, shorter pauses provide smooth deformation curves.

In the second group of experiments the pulse length, t_1, was gradually decreased but the pause between pulses, t_2, was kept constant. The typical behavior is shown for $t_2 = 10$ s and $I_p = 1.25$ W/cm^2 (Figure 4a). The lowest curve corresponds to the shortest pulse length, $t_1 = 0.125$ s, and the highest one to the longest pulse length, $t_1 = 1$ s. However, differences in shape between the deformation curves are small. The inscription part is nearly as long as the relaxation part: about 3 s for the shortest pulse and about 5 s for the longest one. This unusual behavior can be considered as a nonlinear material response. In a linear case we would expect that the length of the relaxation part is equal to the length of a pause between pulses. We observed linear behavior at much lower powers of the inscription laser.[9]

The inscription part of the deformation curve can be slightly reduced if pulses become ultrashort. An example of such reduction is presented for $t_2 = 10$ s and $I_p = 2.5$ W/cm^2 (Figure 5a). The lowest curve corresponds to the shortest pulse length, $t_1 = 0.005$ s; the inscription part is about 1 s. The highest curve corresponds to the longest pulse length, $t_1 = 0.125$ s; the inscription part is about 5 s.

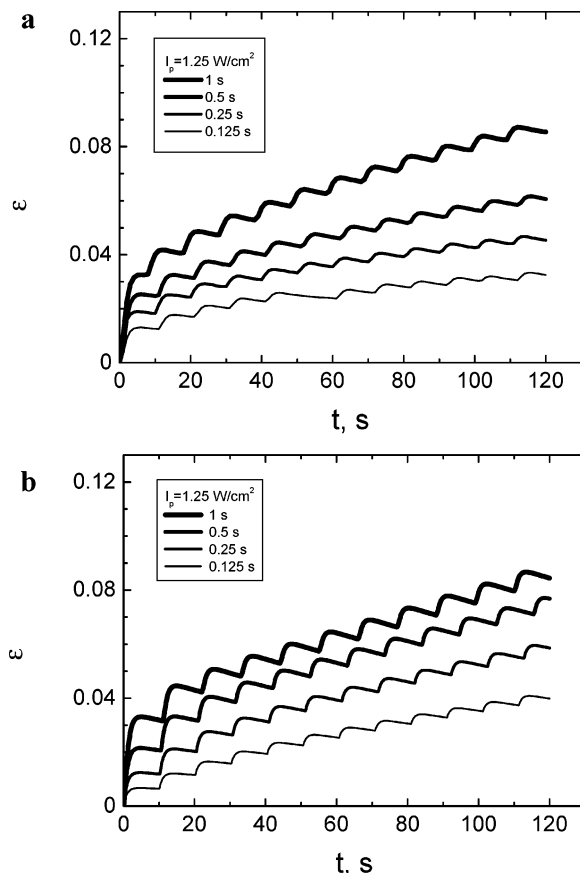The nonlinear behavior of the deformation curves can be reproduced using the theory presented in the Theoretical

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Figure 4. Dependence of the relative deformation $\epsilon(t)$ on the inscription time t: (a) experiment and (b) theory. Pulse length: $t_1 = 1, 0.5, 0.25$, and 0.125 s. Pause between pulses: $t_2 = 10$ s. $I_p = 1.25$ W/cm². The longer plateau in the lowest curve of part a of the figure is an experimental error.

Approach. After multiple fitting the following set of parameters was chosen for the description of the experimental data:

$$\tau_c = 50 \text{ s}, \qquad k_T = 0.2 \text{ cm}^2/\text{J}$$
$$G_1/G_0 = 0.9, \qquad G_2/G_0 = 0.1$$
$$\tau_1 = 0.1 \text{ s}, \qquad \tau_2 = 100 \text{ s}$$

Corresponding fitting results are presented in Figures 2−5b. The theory reproduces quite satisfactory the form of the deformation curves for all intensities of the pumping beam. However, it underestimates their initial slopes due to neglect of birefringence effects. On the other hand, it is known that the cis−trans thermal back relaxation is not strictly monoexponential but exhibits an anomalous fast component for the first few seconds.[10] The hole-burning model utilized in this study, however, assumes a monoexponential decay in the absence of irradiation. This can also lead to some discrepancies between experimental and calculated data.

Discussion

In this study we assume that the polymer stress is proportional to the number of cis isomers, $n(t)$. Hence, a saturation value of stress will be achieved when $n(t) = n_{sat}$. The fraction of cis isomers, $f = n_{sat}/N$, increases with the inscription intensity (see also Figure 6)

$$f = \frac{1}{5 + (k_T I_p \tau_c)^{-1}} \qquad (10)$$
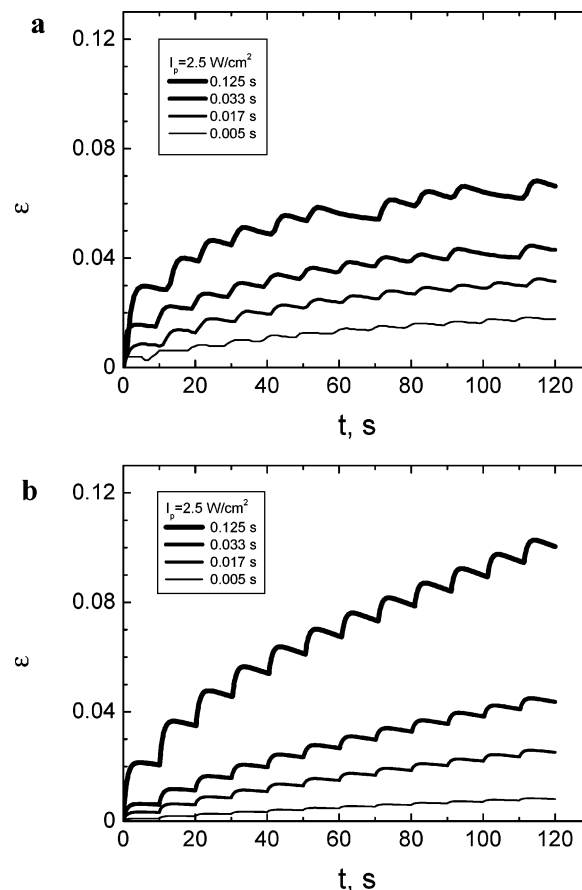

Figure 5. Dependence of the relative deformation $\epsilon(t)$ on the inscription time t: (a) experiment and (b) theory. Pulse length: $t_1 = 0.125, 0.033, 0.017$, and 0.005 s. Pause between pulses: $t_2 = 10$ s. $I_p = 2.5$ W/cm². The longer plateaus in the upper curve of part a of the figure are an experimental error.
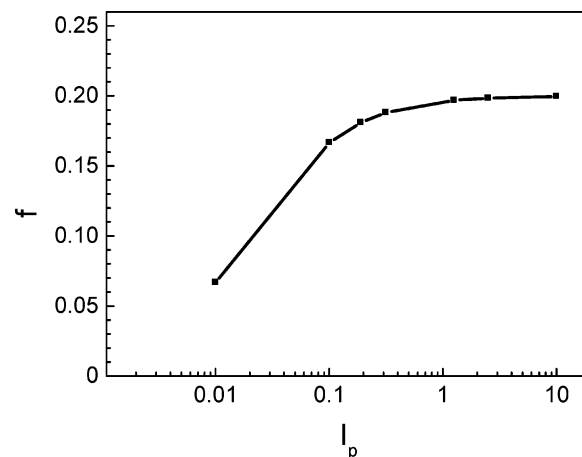

Figure 6. Dependence of the cis isomer fraction f on the inscription intensity I_p.

At high inscription intensities f saturates to about 0.2. This saturation value is entirely defined by the ratio $k_C/k_T = 4$ (see Appendix). A smaller ratio of k_C/k_T will not affect the time dependencies, but the estimated fraction of cis isomers will become larger (for example, $f = 0.25$ follows from $k_C/k_T = 3$). Our saturation value is in fairly good agreement with ref 12 for poly[4-[2-(methacryloyloxy)ethyl]azobenzene], where a saturation value of 0.19 was obtained. The authors also used a hole-burning model but did not consider the cis−trans thermal back relaxation. Therefore, in their study f did not depend on the inscription intensity.
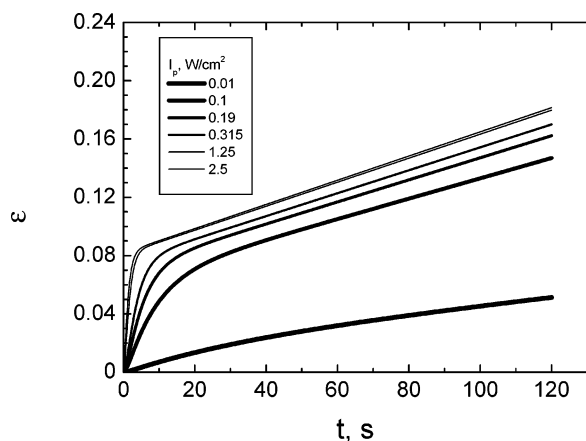
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Figure 7. Theoretical dependence of the relative deformation $\epsilon(t)$ on the inscription time t. Continuous exposure. $I_p = 0.01$, 0.1, 0.19, 0.315, 1.25, and 2.5 W/cm².

How fast $n(t)$ will reach its saturation value depends on the rate of trans–cis isomerization, $\tau_p^{-1} = 5k_T I_p + \tau_c^{-1}$. Thus, τ_p is also a function of the inscription intensity. In our case it is equal to 4.8 s for $I_p = 0.19$ W/cm², 3.0 s for $I_p = 0.315$ W/cm², 0.8 s for $I_p = 1.25$ W/cm², and 0.4 s for $I_p = 2.5$ W/cm².

The theory presented utilizes a nonlinear force model: the force is saturated at high intensities of the inscription laser. For illustration purposes we calculated deformation curves under continuous exposure for different intensities (Figure 7). Polymer deformation (achieved after 120 s) can be significantly enhanced by increasing I_p as far as $I_p < 0.1$ W/cm². At higher inscription intensities the number of cis-isomers starts to saturate (see also Figure 6). As a result of increasing I_p from 0.1 to 2.5 W/cm², the polymer deformation can be enhanced only by a few percent. The curves for $I_p = 1.25$ W/cm² and $I_p = 2.5$ W/cm² are nearly undistinguishable. This result correlates with the intensity dependence of SRG formation measured for a number of azobenzene-functionalized polymers.[20] The inscription rate was saturated at a power of about 0.01 W/cm² and was found to be independent of either the degree of azo functionalization or chemical structure. In all cases, Disperse Red 1 (DR-1) was used as the chromophore which led the authors to conclusion that only the photoisomerization dynamics of DR-1 defines the saturation intensity. The polymer used in our study is also functionalized with DR-1; however we obtained a higher estimate of the saturation intensity.

To fit the theoretical model to the experimental data, we have used $\tau_c = 50$ s. From absorption measurements for pDR1M τ_c was found to be about 10 s.[10] Thus, our estimation of the cis–trans thermal relaxation time has the same order of magnitude as this experimental value. The remaining quantitative discrepancy can be again assigned to model simplifications discussed above.

Appendix. Hole-Burning Model

The hole-burning model is described in detail in ref 12. According to this model the number density of trans isomers,

$n_T(t)$, is connected with the number density of cis isomers, $n_C(t)$, via the differential equation

$$\frac{\partial n_T(\theta)}{\partial t} = -\Phi_{TC} P_T(\theta) n_T(\theta) + \Phi_{CT} P_C(\theta) n_C(\theta) + \gamma n_C(\theta) \tag{A1}$$

where Φ_{TC} and Φ_{CT} are the quantum yields of the direct trans–cis and reverse cis–trans isomerization, respectively, P_T and P_C are the probabilities of the absorption of a photon by a molecule in the trans and cis state, respectively, and $\gamma = \tau_c^{-1}$ is the rate of the cis–trans thermal back relaxation.

For linear polarized light the probability of absorption is given by

$$P_J(\theta) = I\sigma_J[1 + 2e_J P_2(\cos\theta)] \tag{A2}$$

where σ_J and e_J are the average absorption cross section and the molecular anisotropy of trans ($J = T$) and cis ($J = C$) isomers, respectively. At the beginning of the inscription process, the number of cis isomers is negligible and trans isomers are distributed randomly in the polymer matrix. Further, we assume that a sequence of very short pulses followed by much longer relaxation pauses does not result in any preferential orientation of the isomers

$$\begin{cases} n_C(\theta,t) = n(t) & t > 0 \\ n(t) = 0 & t = 0 \end{cases}$$

and

$$n_T(\theta,t) = \frac{N}{2} - n(t) \tag{A3}$$

where N is the total molecular density of chromophores.

Upon integrating eq A2 over θ, the probability of absorption can be expressed

$$P_J(\theta) = 2I\sigma_J \tag{A4}$$

since

$$\int_0^\pi P_2(\cos\theta) \sin\theta \, d\theta = 0$$

and eq A1 can be transformed into

$$\frac{\partial n(t)}{\partial t} = -(\Phi_{TC}\sigma_T I + \Phi_{CT}\sigma_C I + \gamma)n(t) + \Phi_{TC}\sigma_T IN \tag{A5}$$

This equation can be further simplified considering values of the average absorption cross section and the quantum yield of the direct and reverse photoisomerization at $\lambda_{blue} = 488$ nm (the wavelength of the Ar inscribing laser)[21]

$$\sigma_C/\sigma_T = 0.51, \quad \Phi_{CT} = 0.7 \pm 0.1, \quad \Phi_{TC} = 0.11 \pm 0.03 \tag{A6}$$

Introducing $k_T = \Phi_{TC}\sigma_T$ and $k_C = \Phi_{CT}\sigma_C$, one receives $k_C/k_T = 3.3 \pm 1.4$. If we choose $k_C = 4k_T$, then eq A5 can be rewritten as follows

$$\frac{\partial n(t)}{\partial t} = -(5k_T I + \gamma)n(t) + k_T IN \tag{A7}$$

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