Dielectric and Mechanical Properties of Azobenzene Polymer Layers under Visible and Ultraviolet Irradiation

Norman Mechau, Marina Saphiannikova,* and Dieter Neher

Institute of Physics, University of Potsdam, Am Neuen Palais 10, 14469 Potsdam, Germany

Received October 7, 2004; Revised Manuscript Received February 23, 2005

ABSTRACT: Photoinduced changes in the mechanical and dielectric properties of azobenzene polymer films were measured utilizing the method of electromechanical spectroscopy. The measurements revealed a strong correlation between the time-dependent behavior of the plate compliance and the dielectric constant under irradiation. Actinic light causes a light softening of the film that also manifests itself in the increase of the dielectric constant, whereas ultraviolet irradiation results in an initial plasticization of the film followed by its hardening. The latter is accompanied by decrease of the dielectric constant. A semiquantitative model based on the kinetics of the photoisomerization process in azobenzene polymers is proposed. We assume that both visible and ultraviolet irradiation increase the free volume in the layer due to photoisomerization. Additionally, ultraviolet light increases the modulus of the polymer matrix due to the presence of a high density of azobenzene moieties in the cis state. These assumptions allowed us to reproduce the time-dependent behavior of the bulk compliance as well as the dielectric constant at different irradiation intensities, for both visible and ultraviolet light, with only two adjustable parameters.

Introduction

The first inscriptions of surface relief gratings (SRGs) on azobenzene polymer films were reported independently in 1995 by two research groups.[1,2] Inscription was done by exposing the sample to a periodic intensity or polarization pattern that resulted from the interference of two polarized laser beams. The wavelength of the laser was in the absorption region associated with the cyclic trans−cis−trans isomerizations of the azo dye. Most important, the absorption of light on this wavelength induced material flow over micrometer distances even at room temperature, which is well below the glass transition temperature, T_g, of the investigated polymers.

Several models[3−8] have been proposed to explain the origin of the inscribing force (see review in ref 9), but none of them describe satisfactorily the light-induced motion of the azobenzene polymers at a molecular level.[10] In all models, to explain the mass transport over micrometer distances during irradiation at room temperature, it is necessary to assume a considerable degree of photoinduced plasticization, at least comparable with that at the glass transition. For example, it has been proposed, in a linear viscoelastic analysis of the dynamics of SRG formation, that the Young's modulus of the azobenzene polymer film must be reduced by 3 orders of magnitude under illumination with actinic light.[10,11] However, only very weak plasticization has been found in mechanical experiments performed recently in our group.[12,13] At room temperature, a less than 10% increase of the plate compliance upon homogeneous illumination with actinic light was observed. This is far below the degree of "softening" induced by heating the same layer above T_g. These results suggest that illumination of an azobenzene polymer layer with actinic light cannot induce a transition into a macroscopic low-viscosity melt.

Presently, there is no doubt that multiple trans−cis and cis−trans photoisomerizations of the azobenzene moieties are involved in the light-induced material flow. In many studies the softening effect was attributed to this rapid cycling between two conformations of the azobenzene moieties. Interestingly, using low-intensity ultraviolet light, Srikhirin et al.[12] observed an opposite effect: the film compliance decreased by a few percent. The authors argued that cis isomers somehow harden the material when illuminated with ultraviolet light.

Until now, photoinduced mechanical changes in azobenzene polymers have been explained empirically.[12,13] The reason is that neither photoisomerization rates nor cis fractions were estimated in the polymer film used for particular mechanical experiment. In this study we combine, for the first time, transient absorption data with the results of electromechanical and dielectric spectroscopy to gain insight into the intrinsic relationship between photokinetics and mechanical processes in the layer. Moreover, we propose a model that is capable of describing quantatively the transient behavior of the plate compliance as well as the dielectric constant under illumination at different intensities with actinic and ultraviolet light. This model seems to prove the validity of intuitive assumptions proposed previously by different authors.[12,14]

Experiment

The material investigated was an amorphous azobenzene side chain polymer, poly(2-hydroxyethyl)methacrylate-*co*-(2-(4-(4-cyanophenylazo)phenoxy)acetyl)methacrylate) (see Figure 1), with a molecular weight of 86 000 g/mol, an azo content of 52%, and a glass transition temperature $T_g = 99$ °C. Layers for transient absorption measurements were prepared from a solution of the polymer in tetrahydrofuran (2.5 wt %), which was spun at 1000 rpm onto a glass substrate. The layer thickness was 150 nm in all cases. Films for electromechanical and dielectric experiments were coated on glass slides covered with ca. 100 nm thick transparent indium−tin oxide bottom electrodes. The layer thickness was measured with a Dektak II depth profiler to be about 500 nm. After drying and annealing, several equally spaced 4 mm wide aluminum strip top electrodes (80 nm) were deposited onto the film surface by thermal evaporation.

In the electromechanical and dielectric experiments, the sample was irradiated with visible (VIS) or ultraviolet (UV) light: $\lambda_{VIS} = 488$ nm and $\lambda_{UV} = 365$ nm. In both cases a xenon lamp was used as a light source with an appropriate interfer-

10.1021/ma0479316 CCC: $30.25

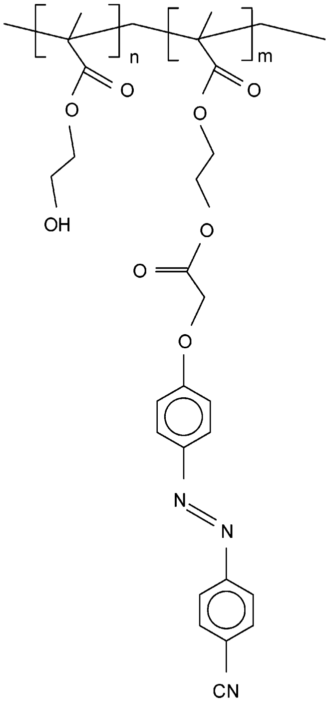

Figure 1. Chemical formula of the statistical copolymer poly(2-hydroxyethyl)methacrylate-*co*-(2-(4-(4-cyanophenylazo)phenoxy)acetyl)methacrylate). Here $n = 48\%$ and $m = 52\%$.

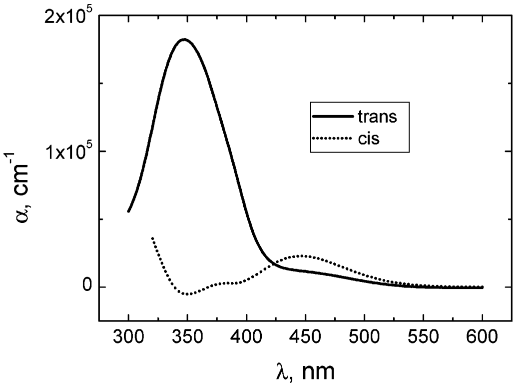

Figure 2. Absorption spectra of the investigated polymer when all chromophores are in the trans or in the cis state. The latter was calculated using the procedure described in ref 15.

ence filter. The light was unpolarized to diminish photoorientational effects. Figure 2 shows absorption spectra of the investigated polymer when all chromophores are in the trans or in the cis state. The latter was calculated from the absorption spectra of a 150 nm thick layer, using the procedure proposed in ref 15. One can see that at $\lambda_{UV} = 365$ nm mainly the trans isomers absorb the light, while at $\lambda_{VIS} = 488$ nm both isomers have comparable absorption coefficients and, thus, a cyclic trans–cis–trans isomerization takes place.

Transient absorption experiments were performed with the help of the lock-in technique. Samples were illuminated with homogeneous light of either $\lambda_{UV} = 365$ nm or $\lambda_{VIS} = 488$. The intensity at the sample was varied from 1 to 10 mW/cm^2 (for UV irradiation) and from 1 mW/cm^2 to 1 W/cm^2 (for VIS irradiation). The absorption of the polymer layer at 365 nm was probed by simultaneously illuminating the sample at $\lambda = 365$ nm with a beam of about 1 μW/cm^2. This intensity was sufficiently small to avoid any influence on the transient absorption experiment. The probing beam was chopped to create a reference signal for the lock-in detection. Its light intensity was measured using a large-area Si diode.

The photoinduced changes in the mechanical and dielectric properties of the thin azobenzene polymer films were measured by means of electromechanical spectroscopy.[16] This method utilizes the electrostriction effect, i.e., the change in thickness, Δh, of a thin polymer layer sandwiched between two electrodes upon application of the alternating electric field

$$\Delta h = QE_0^{\,2}h \tag{1}$$

Here, h is the initial layer thickness, E_0 is the field amplitude, and Q is the electrostriction coefficient, which is proportional to the plate compliance, β_{zz}

$$Q = -\frac{\epsilon_{\mathrm{vac}}\beta_{zz}}{6}(3\epsilon' + (\epsilon' - 1)(\epsilon' + 2)) \tag{2}$$

where ϵ_{vac} is the vacuum susceptibility and ϵ' is the real part of the dielectric constant. The Claussius–Mosotti formula $\partial\epsilon'/\partial h = -(\epsilon' - 1)(\epsilon' + 2)/(3h)$ has been used in the derivation of eq 2.[16] This formula is valid for an isotropic material subjected to hydrostatic pressure,[17] and thus, eq 2 is an approximation for thin polymer layers.

The frequency of the alternating electric field in the electromechanical measurements was 2.5 kHz, which caused a periodic variation in layer thickness of ca. 10 pm at a frequency of 5 kHz. This thickness modulation was measured interferometrically by analyzing the field-induced phase shift of a beam from a He–Ne laser reflected at the aluminum top electrodes. Real and imaginary parts of the dielectric constant were recorded simultaneously at 2.5 kHz with a home-built setup.

Results

Plate Compliance. The plate compliance is defined by the relative change in layer thickness, $\delta h \equiv \Delta h/h$, upon application of a stress σ_{zz} normal to the layer plane

$$\delta h = \beta_{zz}\sigma_{zz} \tag{3}$$

Since, in the ideal case, the polymer layer cannot expand parallel to the substrate, β_{zz} differs from the bulk compliance β_{bulk}[18,19]

$$\beta_{zz} = \frac{1 + \nu}{3(1 - \nu)}\beta_{\mathrm{bulk}} \tag{4}$$

with ν being Poisson's ratio. In the following, we assume that ν does not change under illumination, and thus, the relative change of bulk compliance is equal to the relative change of β_{zz}

$$\delta\beta_{zz} = \frac{\beta_{zz}(t) - \beta_{zz}(0)}{\beta_{zz}(0)} = \delta\beta_{\mathrm{bulk}} \tag{5}$$

Here $\beta_{zz}(0)$ is the plate compliance in the dark, before the light is turned on. The value of the plate compliance was calculated from the electrostriction coefficient Q according to eq 2 utilizing the in-situ measured real part of the dielectric constant.

Figure 3 shows relative changes of the plate compliance $\delta\beta_{zz}$ under VIS and UV irradiation. When VIS light with an intensity of 1 mW/cm^2 is switched on, $\delta\beta_{zz}$ rapidly increases to a value of 0.06 and stays at this level during further irradiation. After switching off the light, $\delta\beta_{zz}$ quickly returns to its initial value in the dark. As it was already mentioned in the Introduction, UV illumination causes a complicated response. When UV light with an intensity of 1 mW/cm^2 is switched on, $\delta\beta_{zz}$ first increases rapidly but then starts to decrease gradually. After switching off the light, one observes an initial abrupt drop of $\delta\beta_{zz}$, followed by its gradual increase to the initial value in the dark.

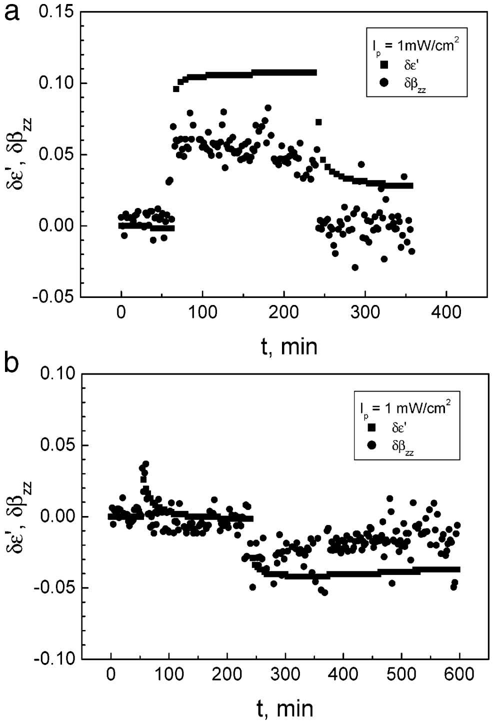

Figure 3. Time dependencies of the relative dielectric constant, $\delta\epsilon'$, and the relative plate compliance, $\delta\beta_{zz}$, under VIS (a) and UV (b) irradiation with 1 mW/cm^2.

Although these measurements of the plate compliance give a characteristic qualitative result, they can be hardly used to develop a quantitative model for two reasons. First, it is impossible to follow very rapid mechanical changes at the moments when the light is switched on or off (it takes about 2 min to measure the plate compliance). Second, the data are usually very noisy when we record changes in the film thickness that are less than 10 pm and thus are very sensitive to any vibrations.

Dielectric Constant. Fortunately, we have found a strong correlation between the time-dependent behavior of the plate compliance and the dielectric constant, under VIS as well as under UV irradiation (Figure 3). Contrary to the plate compliance, the dielectric constant can be measured with a very high accuracy and with a time resolution of about 10 s.

Figure 3 shows relative changes of the dielectric constant

$$\delta\epsilon'(t) = \frac{\epsilon'(t) - \epsilon'(0)}{\epsilon'(0) - \epsilon_\infty} \tag{6}$$

under VIS and UV irradiation. Here $\epsilon'(0)$ is the initial value of dielectric constant in the dark, and ϵ_∞ is the susceptibility at an infinitely high frequency. $\epsilon'(0)$ slightly varies from sample to sample, being about 3.2 ± 0.1. ϵ_∞ can be approximated by n^2, where n is the refractive index of polymer. In this study, n was determined by means of ellipsometry to be equal to 1.60 at 632 nm, which gives $\epsilon_\infty = 2.56$.

When VIS light with an intensity of 1 mW/cm^2 is switched on, $\delta\epsilon'$ increases within a few minutes to a value of 0.1 and stays at this level during further irradiation. After switching off the light, $\delta\epsilon'$ slowly returns to its initial value in the dark. When UV light with an intensity of 1 mW/cm^2 is switched on, $\delta\epsilon'$ first increases rapidly but then starts to decrease, approaching its value in the dark. After switching off the light, one observes an abrupt drop of the dielectric constant followed by its very slow increase to the initial value in the dark.

As it was already mentioned, relative changes of the dielectric constant and plate compliance demonstrate very similar qualitative behavior under VIS and UV irradiation (Figure 3). We suspect that the reason for these changes is common in both cases and is related to the photoisomerization process in the polymer layer. Direct light-induced heating of the layer can be excluded, since illumination with VIS and UV light causes very different behavior. Light-induced changes in the layer thickness, $\Delta h(t)$, can be also excluded as a possible source for the observed effects. For illumination with either VIS or UV light, we could not detect any change in thickness by atomic force microscopy within the resolution of ca. 1 nm (limited by the layer roughness of ca. 1 nm). Such small light-induced changes in thickness would cause only negligible variations in β and ϵ', in comparison to those found in this study.

An essential difference in the time-dependent behavior of the dielectric constant and the plate compliance can be observed after the light is switched off: the dielectric constant returns to its initial value much slower than the plate compliance. Such slow relaxation of the dielectric constant is probably caused by orientational effects, even though we tried to avoid these effects by illuminating the sample with unpolarized light. However, a certain degree of photoinduced alignment of the azobenzenes molecules in the direction perpendicular to the film surface is still possible. Therefore, when the light is switched off, the chromophores might relax back to an isotropic orientational distribution, which results in a slow change of the dielectric constant.

Theoretical Approach

Photoisomerization Kinetics. To understand transient electromechanical properties, one should first consider configurational changes of the azobenzene chromophore which take place in the polymer film under irradiation. Before the light is turned on, all chromophores are in the trans state. Under illumination with VIS or UV light, photoisomerization takes place, and the number density of trans isomers, $n_T(t)$, decreases according to the following differential equation:

$$\frac{\mathrm{d}n_T(t)}{\mathrm{d}t} = -k_{TC}I_p n_T(t) + k_{CT}I_p n_C(t) + \gamma n_C(t) \tag{7}$$

Here, $n_C(t)$ is the number density of cis isomers, k_{TC} is the rate constant of the trans−cis photoisomerization, k_{TC} is the rate constant of the reverse cis−trans photoisomerization, I_p is the intensity of the light in W/cm^2, and γ is the rate of the cis−trans thermal back-relaxation. If we define the cis fraction as $f_C(t) = n_C(t)/N$, where N is the total number density of chromophores, then eq 7 can be rewritten for the cis fraction as

$$\frac{\mathrm{d}f_C(t)}{\mathrm{d}t} = -\tau_p^{-1} f_C(t) + k_{TC}I_p \tag{8}$$

Here, we have introduced $\tau_p = [(k_{TC} + k_{CT})I_p + \gamma]^{-1}$ as the characteristic time of the isomerization process. For

Table 1. Rate Constants and Absorption Coefficients for VIS and UV Illumination

	k_{TC}, cm^2/J	k_{CT}, cm^2/J	γ, s^{-1}	α, cm^{-1}
VIS	0.41 ± 0.05	2.9 ± 0.4	$(3.0 \pm 0.1) \times 10^{-5}$	6.6×10^3
UV	3.2 ± 0.3	2.9 ± 0.3	$(3.0 \pm 0.1) \times 10^{-5}$	1.6×10^5

the situation where light is switched on at $t = 0$, eq 8 can be easily solved, resulting in

$$f_C(t) = k_{TC} I_p \tau_p (1 - \exp(-t/\tau_p)) \tag{9}$$

On the other hand, the isomerization rate, $\dot{f}_{iso} \equiv df_{iso}/dt$, is given by

$$\dot{f}_{iso}(t) = [(k_{CT} - k_{TC}) I_p + \gamma] f_C(t) + k_{TC} I_p \tag{10}$$

Thus, we define $\dot{f}_{iso}$ as the number of all isomerization events per unit of time, accounting for both trans−cis and cis−trans isomerizations. When the photostationary state is reached ($t = \infty$), the following two relations are obtained

$$f_{C,\infty} = k_{TC} I_p \tau_p \qquad \dot{f}_{iso,\infty} = 2 f_{C,\infty} {\tau_C}^{-1} \tag{11}$$

where $\tau_C = [k_{CT} I_p + \gamma]^{-1}$ is the effective lifetime of cis isomer under illumination.

From transient absorption measurements it is possible to determine all rate constants (see Appendix and Table 1) and calculate $f_C(t)$ and $\dot{f}_{iso}(t)$ for a given light intensity for VIS and UV irradiation. Since the studied layers were quite thick (ca. 500 nm), we took into account that the light intensity is not constant throughout the film but decreases with the penetration depth, z, according to the Lambert−Beer law

$$I_p(z) = I_p \exp(-\alpha z) \tag{12}$$

where α is the absorption coefficient at a particular wavelength (shown in Table 1) and z-axis points toward the substrate. Therefore, in eqs 9−11 an average intensity $I_p(1 - \exp(-\alpha h))/\alpha h$ was used instead of I_p. It should be noticed that α does not stay constant during VIS or UV illumination but slightly varies with time. However, in this paper we do not account for this variation because it is the second-order correction and does not affect the outcome of our approach. Comparing $f_C(t)$ and $\dot{f}_{iso}(t)$ curves calculated with the experimental parameters (see Table 1) at the same light intensity (Figure 4), two main differences between photoisomerization at VIS and UV can be noticed: (1) At λ_{VIS}, the cis fraction in the steady state is relatively small, about 0.1, while at λ_{UV}, the cis fraction is relatively high, about 0.3 at $I_p = 1$ mW/cm^2 and 0.5 at $I_p \geq 10$ mW/cm^2. (2) At λ_{VIS}, the isomerization rate is significantly higher than at λ_{UV} for $I_p \geq 10$ mW/cm^2. These two differences motivated us to introduce a two-component mechanical model which is capable of explaining the time dependences of the plate compliance and the dielectric constant under visible and ultraviolet irradiation.

Two-Component Mechanical Model. Let us consider an azobenzene polymer layer as a two-component system, consisting of the polymer matrix and free volume (the latter can be visualized as small voids embedded into the polymer matrix). Then, in the linear approximation, the bulk modulus of the layer, K, can be defined as

$$K = K_0(1 - a\phi) \tag{13}$$

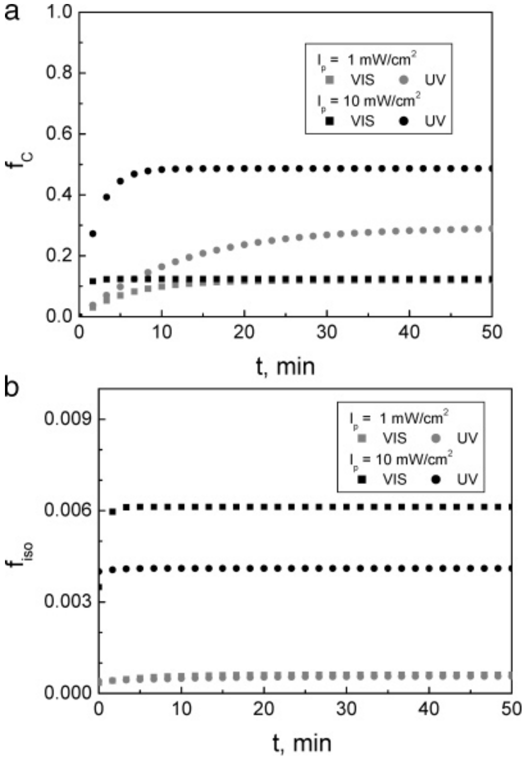

Figure 4. Time dependencies of cis fraction, f_C, (a) and isomerization rate, $\dot{f}_{iso}$, (b) under VIS and UV irradiation with 1 and 10 mW/cm^2. These dependencies were calculated from eqs 9 and 10, using parameters extracted from transient absorption experiments (see Appendix).

where K_0 is the mechanical modulus of the polymer matrix at room temperature in the dark, ϕ is the amount of the free volume, and a is the positive coefficient of proportionality. Any free volume present in the layer in the dark is included into K_0.

We now assume that photoisomerization of the azobenzene molecules generates a certain number of small voids in the frozen amorphous polymer environment. Therefore, because of irradiation with the VIS light, the bulk modulus of the layer will decrease according to eq 13, and hence, the bulk compliance, $\beta = 1/K$, will increase. Taking into account that $a\phi \ll 1$, relative changes of the bulk compliance (and hence of the plate compliance, see eq 5) will be proportional to the free volume

$$\delta\beta_{bulk}(t) = a\phi(t) \tag{14}$$

It is clear that using eq 14, we can readily explain the qualitative changes of the plate compliance under VIS irradiation (Figure 3a). Multiple photoisomerization cycles create free volume in the azobenzene polymer film which manifests itself as a softening of the layer. When the light is switched off, photoisomerization stops immediately, the free volume gradually disappears, and $\delta\beta_{zz}$ returns to its initial value in the dark.

To explain the complicated response of the azobenzene polymer layer to UV irradiation, we have to consider an additional phenomenon. As it was noticed previously by Srikhirin et al.[12] and confirmed by our own experiment (see Figure 3b), hardening of the polymer layer apparently correlates with the increase of the cis concentration. This can be explained if we assume that interactions of azobenzene chromophores in the cis state with their nearest environment are stronger than those in the trans state. Therefore, the modulus of the polymer matrix is expected to increase with the concentration of cis isomers. Thus, in the first linear approximation, eq 13 can be rewritten as

$$K = K_0(1 + bf_C)(1 - a\phi) \tag{15}$$

Here, b is a coefficient of proportionality, which is positive. Taking into account that $bf_C \gg 1$, the relative change of the bulk compliance is given by

$$\delta\beta_{\text{bulk}}(t) = a\phi(t) - bf_C(t) \tag{16}$$

Interestingly, we did not observe that the layer hardens in the presence of cis isomers in the VIS experiments. This difference in behavior between VIS and UV can be explained if we assume that only a large fraction of cis isomers is able to harden the matrix.

Light-Induced Changes of the Dielectric Constant. The real part of the dielectric constant for a system with a single relaxation time, τ, is given by

$$\epsilon' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (\omega\tau)^2} \tag{17}$$

Here, ϵ_0 is the static susceptibility, ϵ_∞ is the susceptibility at an infinitely high frequency, and ω is the angular frequency. In the Kirkwood–Fröhlich approach,[20] which takes into account intermolecular interactions and hindered rotation

$$\epsilon_0 - \epsilon_\infty = \frac{4\pi}{3k_BT}\frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty}\left(\frac{\epsilon_\infty + 2}{3}\right)^2\langle\delta M^2\rangle \tag{18}$$

where k_B is the Boltzmann constant and T is the absolute temperature. In this equation $\langle\delta M^2\rangle$ represents fluctuations of the total dipole moment, M, which for a real chain is equal to[21]

$$\langle\delta M^2\rangle = gN\mu^2 \tag{19}$$

Here, $N\mu^2$ is the value of $\langle\delta M^2\rangle$ for a system composed from freely rotating dipole units, with N being the number of dipole groups per unit volume and μ being the dipole moment of a given group. g is the so-called correlation factor which depends on the strength of statistical correlations between dipoles and on their interactions with the polymer matrix. To understand the meaning of the correlation factor, it is instructive to consider two limiting cases: (1) $g = 1$, dipoles rotate freely and $\langle\delta M^2\rangle = N\mu^2$; (2) $g = 0$, dipoles are totally frozen in the polymer matrix and, thus, cannot rotate at all.

It was reported previously that the increase of ϵ' under VIS irradiation could be explained by the increase of the dipole moment of azobenzene when it isomerizes from the trans to the cis state.[22] However, this change would be detectable, only if fluctuations of the long axis or rotation of the azobenzene dye around this axis were possible at (or faster than) the measurement frequency of 2.5 kHz at room temperature. Recent dielectric spectroscopy studies[23] on different azobenzene side chain polymers showed that only the γ-relaxation process and the high-frequency tail of the β-relaxation process contribute to the dielectric constant at these conditions. The γ-relaxation process was assigned to the rotational fluctuations of the methyl groups and the β-relaxation process to the local fluctuations of the ester groups. In contrast, the relaxation frequency of the azobenzene moieties was significantly lower (about 1–10 Hz). This allows us to argue that ϵ' changes under irradiation mainly due to the change in g rather than due to the change in the dipole moment of azobenzene. This interpretation is supported by relating the predicted change in dipole moment of our chromophore, which is 5.2 D in the cis state compared to 6.8 D in the trans state (the quantum chemistry calculations were carried out by using a commercial software product "Gaussian 98") to the observed change in dielectric constant. Despite the presence of cis isomers with smaller dipole moment, we observe a well-pronounced increase of ϵ' in the VIS-illuminated sample.

Consequently, keeping μ constant and using eqs 17–19, it is easy to show that the relative change of the dielectric constant is equal to the relative change of the correlation factor

$$\delta\epsilon'(t) = \frac{\epsilon'(t) - \epsilon'(0)}{\epsilon'(0) - \epsilon_\infty} = \delta g(t) \tag{20}$$

Furthermore, one can show that in the absence of statistical correlations between dipoles the relative change of the correlation factor is also given by eqs 14 and 16 (the coefficients can of course take other values). First, it is obvious that the presence of the free volume increases the rotational freedom of the dipoles. Second, the presence of cis isomers leads to an increase of the strength of intramolecular interactions in the polymer matrix which results in decrease of rotational freedom of dipoles. This means that whenever the azobenzene polymer film undergoes changes of its mechanical properties—softens or hardens—this is reflected by an appropriate change in ϵ'.

Let us show that our model is able to reproduce the time-dependent behavior of the dielectric constant under irradiation with visible light. In our model, $\delta\epsilon'$ is equal to the relative change in the correlation factor and, therefore, is proportional to the amount of the free volume accumulated in the azobenzene polymer layer from the moment $t = 0$, at which the light is switched on, until the moment t

$$\delta g_{\text{VIS}}(t) = c\int_0^t \dot{\phi}(t')\exp[-(t - t')/\tau_m]\,dt' \tag{21}$$

Here $\dot{\phi}(t')$ is the additional free volume produced per one unit at time t' due to multiple photoisomerization cycles. Relaxation of ϕ after this moment is described by the exponential decay with the characteristic time τ_m. The coefficient of proportionality c can be estimated from the dependence of the relative dielectric constant on temperature. We have determined $c \approx 215$ by measuring $\delta\epsilon'$ at the glass transition temperature ($\delta\epsilon' \approx 5.4$) and using a literature value of $\phi \approx 0.025$.[20]

Let us first assume that $\dot{\phi}$ is strictly proportional to the isomerization rate

$$\dot{\phi}(t') = a_0\dot{f}_{\text{iso}}(t') \tag{22}$$

This gives

$$\delta g_{\text{VIS}}(t) = \delta g_{\text{VIS},\infty}\begin{cases}[1 - \exp(-t/\tau_m)] & \text{light is on at } t = 0\\ \exp[-(t - t_{\text{off}})/\tau_m] & \text{light is off at } t = t_{\text{off}}\end{cases} \tag{23}$$

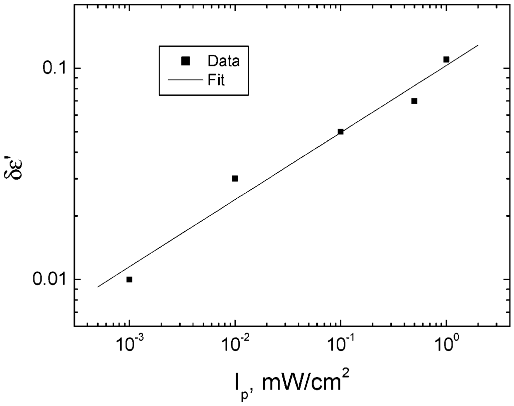

Figure 5. Intensity dependence of the relative dielectric constant, $\delta\epsilon'$, under VIS irradiation.

with

$$\delta g_{\mathrm{VIS},\infty}(I_{\mathrm{p}}) = a_0 c\dot{f}_{\mathrm{iso},\infty}\tau_{\mathrm{m}} \approx 2a_0 c\,\frac{k_{\mathrm{TC}}\,k_{\mathrm{CT}}}{k_{\mathrm{TC}} + k_{\mathrm{CT}}}\,\tau_{\mathrm{m}} I_{\mathrm{p}} \qquad (24)$$

By deriving this equation, we took into account that γ is negligibly small compared to $k_{\mathrm{TC}}I_{\mathrm{p}}$ and $k_{\mathrm{CT}}I_{\mathrm{p}}$. Actual values of τ_{m} were determined from the initial exponential decrease of the relative dielectric constant after switching the light off. They were found to be independent of I_{p}, and thus, eq 24 predicts a linear increase of the relative dielectric constant with the light intensity in the stationary state. However, the experimentally measured $\delta\epsilon'$ curve increases with the light intensity nonlinearly, as demonstrated in Figure 5. This curve can be fitted using a power-law dependence

$$\delta g_{\mathrm{VIS},\infty}(I_{\mathrm{p}}) = a_1 I_{\mathrm{p}}^{\,a_2} \quad \mathrm{W\ m^{-2}} \qquad (25)$$

with $a_1 = 0.050 \pm 0.004$ and $a_2 = 0.32 \pm 0.03$. The nonlinear behavior can be understood as follows: when the light intensity reaches a critical value, chromophores can reutilize free volume which has been generated by an earlier isomerization event.[13] As result, the additional free volume is not anymore proportional to the isomerization rate. This has been taken into account by introducing a nonlinear dependence of $\dot{\phi}$ on the isomerization rate

$$\dot{\phi}(t') = [a_0\,\dot{f}_{\mathrm{iso}}(t')]^{a_2} \qquad (26)$$

This assumption does not change the principal form of the time-dependent solution given by eq 23, but $\delta g_{\mathrm{VIS},\infty}$ is now defined by eq 25 with

$$a_1 \approx c(a_0 k_{\mathrm{TC}})^{a_2}\left[1 + a_2\,\frac{k_{\mathrm{CT}} - k_{\mathrm{TC}}}{k_{\mathrm{TC}} + k_{\mathrm{CT}}}\right]\tau_{\mathrm{m}} \qquad (27)$$

Taking $\tau_{\mathrm{m}} = 200$ s, we can reasonably well reproduce the time dependencies of the relative dielectric constant at different intensities of visible light (Figure 6a). However, when the light is switched off, $\delta\epsilon'$ relaxes much slower than δg as predicted by eq 23. We already mentioned that orientational effects (neglected in our model) might be a reason for this discrepancy between the experimental data and the model prediction.

To describe the time-dependent behavior of the dielectric constant under irradiation with ultraviolet light, we introduce an additional term in eq 21

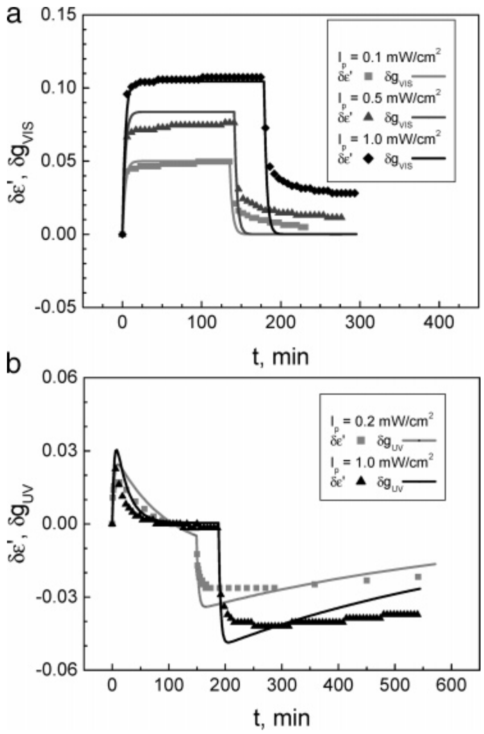

Figure 6. Time dependencies of the relative dielectric constant, $\delta\epsilon'$, under VIS (a) and UV (b) at different intensities. Lines show the relative correlation factor, δg, as predicted by eqs 21 and 28.

$$\delta g_{\mathrm{UV}}(t) = \int_0^t \dot{\phi}(t')\exp[-(t - t')/\tau_{\mathrm{m}}]\,\mathrm{d}t' - bf_{\mathrm{C}}(t) \qquad (28)$$

Here b is a free parameter which correlates the relative hardening to the fraction of cis isomers. This equation, with $\tau_{\mathrm{m}} = 200$ s and $b = 0.1$, satisfactorily describes transient experiments under irradiation with UV light (Figure 6b). When UV radiation is switched off, the cyclic photoisomerization immediately stops, i.e., the first term in eq 28 disappears, and one observes a sharp drop in the dielectric constant. Interestingly, we could use the same power law (see eq 25 for VIS light) to describe the response at different intensities of UV light. Note that there is a significant discrepancy between the model predictions and the measured data at longer times after the UV light is switched off.

In contrast to the dielectric constant, the bulk compliance should not (or only weakly) depend on orientational effects. This explains why using the same eqs 21 and 28 (but with different values of the fitting parameters) we managed to describe satisfactorily the time dependence of $\delta\beta_{zz}$ not only under irradiation but also at longer times after the VIS or UV light has been switched off (Figure 7). Despite significant noise in the data, one can clearly see that, in the case of UV irradiation, the gradual recovery of the bulk compliance to its initial value in the dark is reproduced much better than that of the dielectric constant (Figure 7a). In the case of VIS irradiation, both the model predictions and the measured data exhibit an immediate drop of $\delta\beta_{zz}$ to zero after the light is switched off (Figure 7b).

Equipped with the formalism described above, we are also able to reproduce the complicated time dependence of the dielectric constant under multiple illumination with VIS and UV (Figure 8). During the first two cycles

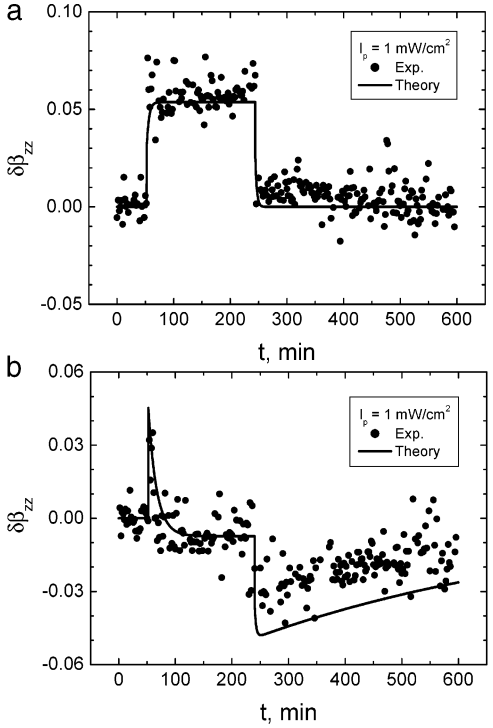

Figure 7. Time dependencies of the relative plate compliance, $\delta\beta_{zz}$, under VIS (a) and UV (b) irradiation with 1 mW/cm^2. Lines show a model prediction as described by eqs 21 and 28.

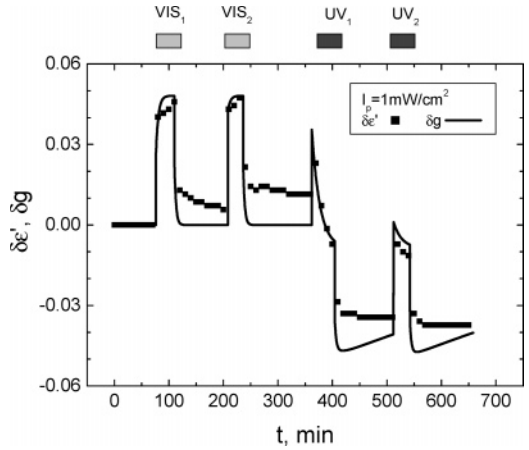

Figure 8. Time dependencies of the relative dielectric constant, $\delta\epsilon'$, under multiple irradiation with VIS and UV light. The relative correlation factor, δg, as predicted by eqs 21 and 28, is also shown.

the film is illuminated with VIS light. Because of the fast cyclic photoisomerization the layer undergoes slight softening, leading to an increase of $\delta\epsilon'$ to a value of 0.05. When the VIS light is switched off, photoisomerization stops immediately and ϵ' slowly relaxes to its initial value in the dark. Note that the height of the plateau in the second VIS illumination step is comparable to that in the first step. In the subsequent two cycles, the film was illuminated with UV light. At the beginning of every illumination cycle, the layer slightly softens due to photoisomerization but then gradually hardens due to the increase of the cis fraction. When the UV light is switched off, photoisomerization abruptly stops, but the remaining cis content leads to the sudden drop of ϵ'. This results in an effective "hardening" of the layer compared to the nonilluminated material, which slowly relaxes back to the initial value in the dark. The characteristic time of the relaxation process is comparable to the lifetime of the cis isomers $1/\gamma \sim 10$ h. This is in agreement to our model prediction that the recovery of ϵ' correlates with the thermal back-relaxation of the cis fraction. Because the dark pause between the two UV illumination steps is less than 2 h, the cis content is still very high at the beginning of the second UV cycle. Therefore, the maximum of $\delta\epsilon'$ in the second UV illumination step is considerably lower than that measured during the earlier illumination cycles.

Discussion and Conclusions

In this study we have developed a semiquantitative model that is capable to describe the time and intensity dependence of the electromechanical and dielectric properties of an azobenzene polymer layer measured at two particular wavelengths: $\lambda_{\mathrm{VIS}} = 488$ nm and $\lambda_{\mathrm{UV}} = 365$ nm. This two-phase model is based on two assumptions: (1) Cyclic photoisomerization creates additional free volume in the polymer layer that results in a softening of the layer. This process does not change the mechanical modulus of the polymer matrix. (2) In addition, in the case of UV irradiation, a high population of the cis fraction slightly increases the modulus of the polymer matrix. This effect can be explained if cis isomers have stronger interactions with the surrounding matrix than trans isomers.

To support the model presented here, we plan to measure changes in mechanical and dielectric properties of the film when irradiated at intermediate wavelengths. Such measurements will hopefully clarify the question why we do not observe an abrupt hardening after switching the light off in the film previously irradiated with VIS light. Note that only 10% of azobenzene chromophores are in the cis state at $\lambda_{\mathrm{VIS}} = 488$ nm. Presently, we assume that the matrix only hardens when the cis fraction reaches some critical value, which is far above 10%. Another possible explanation is that different isomerization mechanisms—inversion at VIS and rotation at UV—could be responsible for the different matrix response when illuminated at 365 and 488 nm.

With respect to the formation of SRG under nonhomogeneous illumination, the data presented here support our earlier interpretation that light-induced changes in the polymer film (either VIS or UV illumination) are very different from those caused by simple heating.[13] Most important, all data can be explained by a model that is continuous with respect to time and intensity. This excludes that illumination under conditions described here induces a phase transition. Nevertheless, the data suggest that a certain fraction of free volume is introduced into the layer by the photoisomerization process and that this additional volume remains within the layer for a considerable amount of time (ca. 5 min). Therefore, the experiments strongly suggest that the light-induced free volume must redistribute itself differently (with time and/or spatially) than the free volume introduced by simple heating, which allows the otherwise still hard material to flow in response to a light-driven force (still unknown). Such a difference is expected since one isomerization event consumes ca. 2 eV in energy in the range of picoseconds, and this energy can be then gradually converted into a considerable molecular rearrangement—reorientation of azobenzene moieties, presumably followed by a change of main chain conformation.

Interestingly, recent studies on the inscription of the surface relief gratings revealed that the diffraction efficiency decreases with increasing temperature.[24] When the temperature exceeded 50 °C, it was impossible to induce any changes of the layer topography. This result appears to be totally unexpected since the bulk compliance of azobenzene polymers slightly increases with temperature. Therefore, any flow of material in response to the external force is expected to be faster at higher temperatures. Our experiments allow us to speculate that the main reason behind such puzzling behavior could be the faster relaxation of the light-induced free volume at higher temperatures, caused by an increase in local chain dynamics. In this case, we indeed expect that the formation of SRGs at higher temperatures is less effective compared to SRGs formed at room temperature.

Acknowledgment. V. Börger and H. Menzel (University of Braunschweig) are gratefully acknowledged for supplying the polymers. We, further, acknowledge Dr. Stumpe (IAP Golm) for many fruitful discussions. We also thank Dr. K. Morawetz for the ellipsometric measurements and B. Stiller for performing the AFM experiments under illumination. This work was financially supported by the DFG under Grant NE410/6-2.

Appendix. Transient Absorption

The time dependence of absorption coefficient was probed at $\lambda_{UV} = 365$ nm with concurrent illumination of the layer at 365 and 488 nm. From these data, the time-dependent normalized absorption was calculated

$$\delta A(t) \equiv \frac{A_\infty - A(t)}{A_\infty - A_0} \tag{A1}$$

where A_0 and A_∞ are the absorbance in the dark and in the photostationary state, respectively. Here, we did not take into account the photoorientation of azobenzene moieties because after switching the light off we have observed a full recovery of the absorbance to its initial value in the dark (this process correlates with the thermal back-relaxation of the cis fraction). In the case if photoorientation effects in the investigated polymer will be pronounced, we would not expect a full recovery of the absorbance value.

Figure 9 shows the time dependencies of $-\ln(\delta A)$ at different intensities of VIS and UV light. The slope of the curves gives $\tau_p^{-1} = (k_{TC} + k_{CT})I_p + \gamma$, which depends linearly on I_p. Plotting the linear dependence of τ_p^{-1} on I_p yields its slope, S, which is equal to the sum of the rate constants k_{TC} and k_{CT}.

Further, the photostationary value of the cis fraction increases with the light intensity as

$$f_{C,\infty} = \frac{k_{TC} I_p}{S I_p + \gamma} \tag{A2}$$

and saturates at high intensities to

$$f_{C,\infty} = \frac{k_{TC}}{S} = 1 - \frac{A_\infty}{A_0} \tag{A3}$$

For our polymer, $f_{C,\infty}$ is 0.12 at VIS and 0.55 under UV illumination. Knowing S and measuring $f_{C,\infty}$, we were able to separate k_{TC} and k_{CT}. Additionally, we have measured the rate of the cis−trans thermal back-relaxation, γ, following recovery of the normalized film absorbance after switching off the light. 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.[25] Therefore, the value of γ, relevant to the time scale of our experiments, was estimated after the first 3 min, when a much slower monoexponential decay of absorption was already established.

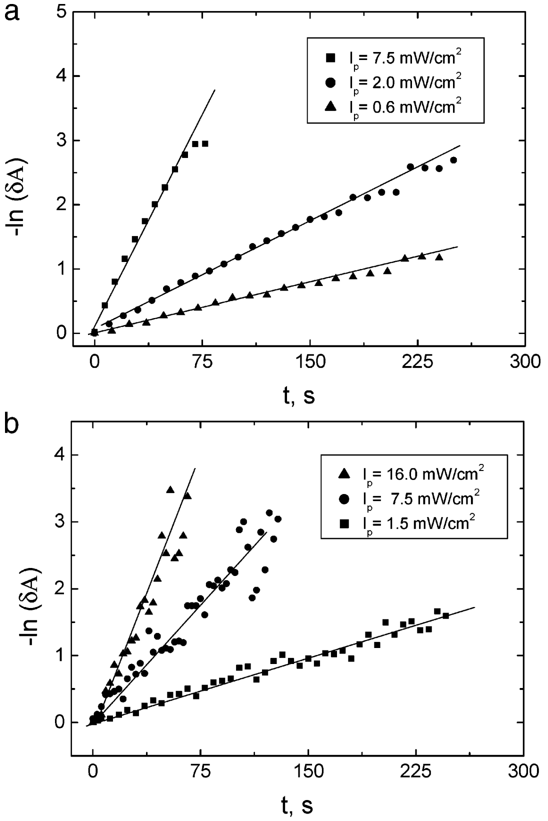

Figure 9. Time dependencies of $-\ln(\delta A)$ measured at different intensities of VIS (a) and UV (b) light.

The values determined from transient absorption experiment, for illumination with VIS and UV, are summarized in Table 1.

References and Notes

(1) Rochon, P.; Batalla, E.; Natansohn, A. *Appl. Phys. Lett.* **1995**, *66*, 136.
(2) Kim, D. Y.; Li, L.; Jiang, X. L.; Shivshankar, V.; Kumar, J.; Tripathy, S. K. *Macromolecules* **1995**, *28*, 8835−8839.
(3) Barrett, C. J.; Rochon, P. L.; Natansohn, A. L. *J. Chem. Phys.* **1998**, *109*, 1505.
(4) Kumar, J.; Li, L.; Jiang, X. L.; Kim, D.-Y.; Lee, T. S.; Tripathy, S. *Appl. Phys. Lett.* **1998**, *72*, 2096.
(5) Baldus, O.; Zilker, S. J. *Appl. Phys. B: Laser Opt.* **2001**, *72*, 425.
(6) Lefin, P.; Fiorini, C.; Nunzi, J.-M. *Pure Appl. Opt.* **1968**, *7*, 71.
(7) Pedersen, T. G.; Johansen, P. M.; Holme, N. C. R.; Ramanujam, P. S.; Hvilsted, S. *Phys. Rev. Lett.* **1998**, *80*, 89.
(8) Bublitz, D.; Fleck, B.; Wenke, L. *Appl. Phys. B: Laser Opt.* **2001**, *72*, 931.
(9) Oliveira, O. N., Jr.; Kumar, J.; Li, L.; Tripathy, S. K. In *Photoreactive Organic Thin Films*; Sekkat, Z., Knoll, W., Eds.; Elsevier Science: Amsterdam, 2002; p 560.
(10) Saphiannikova, M.; Geue, T. M.; Henneberg, O.; Morawetz, K.; Pietsch, U. *J. Chem. Phys.* **2004**, *120*, 4039−4045.
(11) Geue, T.; Saphiannikova, M.; Henneberg, O.; Pietsch, U.; Rochon, P.; Natansohn, A. *Phys. Rev. E.* **2002**, *65*, 052801.
(12) Srikhirin, T.; Laschitsch, A.; Neher, D.; Johannsmann, D. *Appl. Phys. Lett.* **2000**, *77*, 963−965.

(13) Mechau, N.; Neher, D.; Börger, V.; Menzel, H.; Urajama, K. *Appl. Phys. Lett.* **2002**, *81*, 4715−4717.
(14) Viswanathan, N. K.; Kim, D. Y.; Bian, S.; Williams, J.; Liu, W.; Li, L.; Samuelson, L.; Kumar, J.; Tripathy, S. K. *J. Mater. Chem.* **1999**, *9*, 1941−1955.
(15) Fischer, E. *J. Phys. Chem.* **1967**, *71*, 3704.
(16) Winkelhahn, H. J.; Pakula, T.; Neher, D. *Macromolecules* **1996**, *29*, 6865.
(17) Osman, A. E.; Dumont, M. *Opt. Commun.* **1999**, *164*, 277.
(18) Landau, L. D.; Lifshitz, E. M. *Theory of Elasticity*, 2nd ed.; Elsevier Science Ltd.: Amsterdam, 1981.
(19) Ferry, J. D. *Viscoelastic Properties of Polymers*; John Wiley & Sons: New York, 1980.
(20) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover Publications: New York, 1967.
(21) Saphiannikova, M. G.; Lukasheva, N. V.; Darinskii, A. A.; Gotlib, Y. Y.; Brickmann, J. *Macromolecules* **2000**, *33*, 606−612.
(22) Fritz, A. *Korrelation optischer und dielektrischer Untersuchungen an photochromen Copolymeren mit Azobenzolderivaten in der Seitengruppe*; Mensch & Buch Verlag: Berlin, 2000.
(23) Fritz, A.; Schönhals, A.; Sapich, B.; Stumpe, J. *Macromol. Chem. Phys.* **1999**, *200*, 2213−2220.
(24) Henneberg, O. *In-situ Untersuchungen zur Entstehung von Oberflächengittern in Polymeren*; Potsdam University: Potsdam, 2004.
(25) Barrett, C.; Natansohn, A.; Rochon, P. *Chem. Mater.* **1995**, *7*, 899.

MA0479316