Mean-Field Theory of Photoinduced Molecular Reorientation in Azobenzene Liquid Crystalline Side-Chain Polymers

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A novel mean-field theory of photoinduced reorientation and optical anisotropy in liquid crystalline side-chain polymers is presented and compared with experiments. The reorientation mechanism is based on photoinduced $trans \leftrightarrow cis$ isomerization and a multidomain model of the material is introduced. The theory provides an explanation for the high long-term stability of the photoinduced anisotropy as well as a theoretical prediction of the temporal behavior of photoinduced birefringence. The theoretical results agree favorably with measurements in the entire range of writing intensities used experimentally. [S0031-9007(97)04104-5]

Photoinduced reorientation of molecules in liquid crystals is a fascinating example of structural changes in a material upon illumination. In particular, the observation of photoinduced birefringence [1] and collective rotation of molecules by a circularly polarized beam [2] in nematic films demonstrates the versatility of light-matter interactions in materials with strong cooperativity between molecules. Recently, similar effects have been observed in liquid crystalline azobenzene side-chain polymers [3–5]. Even though these materials share many features with ordinary liquid crystals, the origin of photoinduced reorientation in these materials is quite different in nature. In the case of ordinary (nonabsorbing) liquid crystals, reorientation occurs as a result of the electromagnetic torque exerted by the optical field. Because of the relatively long time scale of the reorientation process, the optical field is practically equivalent to a static field and, hence, a Fréedericksz transition is observed [1]. Conversely, in azobenzene compounds optical absorption plays a dominating role in the reorientation process [3–6]. Furthermore, the photoinduced birefringence has extremely high long-term stability and holograms recorded in both liquid crystalline [3–5] and glassy [6] polymers exist for several years without any sign of degradation. This property has made azobenzene compounds very promising candidates for optical data storage technology.

So far the details of the reorientation process in liquid crystalline azobenzene side-chain polymers have not been clarified. It is generally accepted that reorientation following photoinduced $trans \leftrightarrow cis$ isomerization is the dominating mechanism in the storage process [3–5]. Any attempt to model the polymer material as a collection of independent mesogenic molecules undergoing $trans \leftrightarrow cis$ isomerization will fail to explain the long-term stability, however. Clearly, even a minimal diffusion would be noticeable on a time scale of several years. Alternatively, Palto *et al.* [7,8] have shown that a multidomain model in which the molecules are subject to an ordering mean-field potential is capable of ac-

counting for the long-term stability. In addition, the intermolecular cooperativity within the individual domains provides an explanation for the intricate intensity dependence of the photoinduced anisotropy. Such a mechanism is hard to realize in a model with independent molecules as the anisotropy simply reflects the number of absorbed photons. In Refs. [7,8] the framework of Palto *et al.* was applied to Langmuir-Blodgett films irradiated in the electronic absorption band where isomerization cannot account for the observed effects. In cases where $trans \leftrightarrow cis$ isomerization is the dominating source of photoinduced anisotropy, a similar model should be applicable, however, provided a few modifications are made. In this manner, the highly attractive features of the model by Palto *et al.* can be combined with the photoinduced $trans \leftrightarrow cis$ mechanism responsible for the optical storage process. In this Letter such a new mean-field theory of photoinduced anisotropy is constructed and compared with the experimental results [9] for the azobenzene side-chain polyester P6a12 described in Refs. [5,9–11].

The essential quantity describing the anisotropic properties of a liquid crystalline film is the angular distribution of the mesogenic molecules, i.e., side-chain chromophores in the present discussion. From the temporal evolution of the angular distribution the optical birefringence can be calculated as a function of illumination time and compared with experiments. Initially, the films are prepared in a macroscopically isotropic state. In a multidomain model this is equivalent to saying that the domain directors are uniformly distributed. Furthermore, in a particular domain the angular distribution of chromophores will be symmetric around the director. During illumination by a linearly polarized laser beam, though, the probability of a chromophore to absorb a photon is proportional to $\cos^2 \theta$, where θ is the angle between the transition dipole moment of the chromophore and the laser polarization. If, upon absorption, the chromophore undergoes $trans \rightarrow cis$ or $cis \rightarrow trans$ isomerization, it will in general change direction, say from (θ', φ') to (θ, φ), in order to

accommodate the structural change. The crucial point in the present context is that these events occur with a nonuniform probability of absorption proportional to $\cos^2 \theta$. In a "frictionless" mean-field picture, the probability distribution $p(\theta, \varphi)$ for finding a particular chromophore in a small solid angle $d\Omega$ around an angular position (θ, φ) after isomerization is simply given by the equilibrium distribution [7,8]

$$p(\theta, \varphi) = Ae^{-W(\theta, \varphi)}, \qquad (1)$$

where $W(\theta, \varphi)$ is the mean-field potential and A is a normalization constant. Therefore, the nonuniform probability of absorption depletes the small $-\theta$ tail of the angular distribution and reorients the chromophores according to Eq. (1). In turn, the asymmetry caused by the deficit of chromophores in the small $-\theta$ tail is counteracted by thermal relaxation processes trying to restore equilibrium. It is important to note that in the process of equilibrating an asymmetric distribution the domain director is rotated towards the region with an excess of chromophores. In this manner a "torque" is exerted on the entire domain via the restoring force. Consequently, after illumination the distribution of domain directors is uniaxial rather than uniform and as a result the *macroscopic* equilibrium state has become anisotropic. The new mean-field theory that follows from this simple physical picture then provides an explanation for the origin as well as the long-term stability of the storage process. The lifetime of the macroscopic order can be estimated from the relaxation time $\tilde{\tau}$ of domain rotation. Because of the collective nature of this process it is assumed that $\tilde{\tau}$ is related to the relaxation time of a single chromophore τ via $\tilde{\tau} = n^\alpha \tau$, where n is the number of chromophores in the domain and α is of the order of unity ($\alpha = 1$ in case of mass-proportional relaxation). Typically, for a 1 μm^3 domain $n \approx 10^9$ and $\tau \approx 10$ s (see below) and so $\tilde{\tau} \approx 300$ yr in accordance with the observed stability.

Now, since we deal with a mixture of *trans* and *cis* forms, which generally have widely different absorption cross sections, we have to introduce two distinct angular distribution functions denoted $f_T(\theta, \varphi)$ and $f_C(\theta, \varphi)$, respectively. The temporal evolution of these distributions will involve two different processes: (i) photoinduced reorientation reactions of the type $f_T(\theta', \varphi') \to f_C(\theta, \varphi)$ or $f_C(\theta', \varphi') \to f_T(\theta, \varphi)$ and (ii) thermal relaxation processes $f_T(\theta, \varphi) \to p(\theta, \varphi)$ or $f_C(\theta, \varphi) \to p(\theta, \varphi)$ that serve to restore equilibrium. Hence, the balance between these fundamental processes is described by the following set of equations:

$$\frac{d}{dt} f_T(\theta, \varphi) = A_{CT} I p(\theta, \varphi) \int f_C(\theta, \varphi) \cos^2 \theta \, d\Omega$$
$$- A_{TC} I f_T(\theta, \varphi) \cos^2 \theta$$
$$+ \frac{1}{\tau} [N_T p(\theta, \varphi) - f_T(\theta, \varphi)], \qquad (2)$$

and

$$\frac{d}{dt} f_C(\theta, \varphi) = A_{TC} I p(\theta, \varphi) \int f_T(\theta, \varphi) \cos^2 \theta \, d\Omega$$
$$- A_{CT} I f_C(\theta, \varphi) \cos^2 \theta$$
$$+ \frac{1}{\tau} [N_C p(\theta, \varphi) - f_C(\theta, \varphi)]. \qquad (3)$$

The various terms in these expressions are interpreted as follows: Focusing on the rate of change of the *trans* distribution, the first and second terms in Eq. (2) are the rates at which photoinduced $cis \to trans$ and $trans \to cis$ isomerization occurs, respectively. Reorientation following $cis \to trans$ isomerization is taken into account through the integration over solid angle in the first term. In addition, the $cis \to trans$ rate is proportional to $A_{CT} I \cos^2 \theta$, where I is the incident intensity, and the transition coefficient $A_{CT} = (\hbar \omega)^{-1} \sigma_{CT} \phi_{CT}$ is the product of the absorption cross section σ_{CT} and the quantum efficiency ϕ_{CT} divided by the photon energy $\hbar \omega$. Similarly, the $trans \to cis$ rate is proportional to A_{TC}. Finally, the thermal relaxation is represented by the third term, and the rate of this process is determined by the relaxation time τ. In this term, N_T denotes the total fraction of *trans* chromophores, and this factor has been included to ensure that the thermally induced reorientation leaves the total fraction of *trans* forms unchanged. The various terms in Eq. (3) are perfectly analogous to those in Eq. (2) and their interpretation is therefore straightforward. It is noted that even though the *cis* form is thermally unstable, we have neglected spontaneous $cis \to trans$ transitions in the expressions above since the time scale (several hours) of this process is orders of magnitude longer than the effects studied here.

Initially, practically all chromophores will be in the thermally stable *trans* form and so the polar angle δ_0 of the initial director is identical to the polar angle at which the distribution $f_T(\theta, \varphi)$ is maximum. Experimentally, the $cis \to trans$ transition is quasiresonantly excited [10] and the *trans* fraction will consequently be close to unity at all times. If, furthermore, we assume that the *trans* distribution remains approximately equilibrated, we can simply update the director angle δ by locating the maximum of $f_T(\theta, \varphi)$ at a later time t. In this manner, however, no account is taken of the interaction between domains which in a real material will restrict the rotation of a domain. Physically, such domain-domain interactions may originate from mechanical stress [12] (and, in the case of thin films, substrate anchoring effects may restrict rotation [7]) but at present the specific nature of the interaction is unknown. A transparent way of incorporating this effect is to introduce a threshold intensity [12] I_{th} in the sense that whenever the effective intensity in a particular domain $I \cos^2 \delta$ is less than I_{th}, the direction of the domain is "frozen." In addition, following Refs. [7,8] we can allow for the strength of the mean-field potential to vary via

the order-parameter S, which is a measure of the degree of alignment in a particular domain. For a single-component material [13], S is obtained as the angular average of the second Legendre polynomial $P_2(\cos \beta) = \frac{3}{2} \cos^2 \beta - \frac{1}{2}$, where β is the angle between a molecule and the domain director. Hence, to treat the *trans* and *cis* mixture we will use $S = \langle P_2(\cos \beta) \rangle$, where $\langle \ldots \rangle$ is taken to denote averaging over angles as well as molecular forms.

Once the angular distribution of transition dipole moments in the material is determined, the optical properties can be calculated from basic electrodynamics. With perfectly anisotropic molecules the chromophore polarizability tensor only has a single nonvanishing element (using the principle-axes coordinate system). For the two transitions this element is denoted α_{TC} and α_{CT}, respectively. Accordingly, the refractive index experienced by a probe beam polarized in a certain direction relative to the polarization of the writing beam can be calculated by projecting the polarizability tensors onto this direction. We will assume that the contribution to the refractive index from the polyester backbone n_0 is isotropic. Therefore, for the direction parallel ($\parallel$) and perpendicular ($\perp$) to the polarization of the writing beam we find

$$n_{\parallel}^2 = n_0^2 + \frac{N}{\varepsilon_0} \left\langle \int_0^{2\pi} \int_0^{\pi} [\alpha_{TC} f_T(\theta, \varphi) + \alpha_{CT} f_C(\theta, \varphi)] \right.$$
$$\left. \times \cos^2 \theta \sin \theta \, d\theta \, d\varphi \right\rangle_{\delta_0, \gamma_0} \quad (4)$$

and

$$n_{\perp}^2 = n_0^2 + \frac{N}{\varepsilon_0} \left\langle \int_0^{2\pi} \int_0^{\pi} [\alpha_{TC} f_T(\theta, \varphi) + \alpha_{CT} f_C(\theta, \varphi)] \right.$$
$$\left. \times \cos^2(\varphi + \gamma_0) \sin^3 \theta \, d\theta \, d\varphi \right\rangle_{\delta_0, \gamma_0}. \quad (5)$$

In these expressions, N denotes the density of chromophores, γ_0 is the azimuthal angle of the $\perp$ direction, and $\langle \cdots \rangle_X$ denotes averaging with respect to the parameters X. It can be shown that Eqs. (4) and (5) yield the following simple expression for the phase difference

$$\Delta \phi = \frac{\pi d}{\lambda_P} (n_{\parallel} - n_{\perp}) = \frac{\pi d N}{2 \varepsilon_0 \overline{n} \lambda_P} \langle \alpha_{TC} a_T + \alpha_{CT} a_C \rangle_{\delta_0}, \quad (6)$$

where d is the sample thickness, λ_P is the probe wavelength, $\overline{n} = (n_{\parallel} + n_{\perp})/2$ is the average index (taken as its unperturbed value), and the coefficients a_T and a_C are given by $a_X = \langle f_X(\theta, \varphi) P_2(\cos \theta) \rangle$ with $X = T, C$.

The choice of appropriate mean-field potential is a delicate question. Experimentally, the polyester architecture is known to exhibit several phases and signatures of glass, nematic, smectic, and isotropic phases have been seen [5]. In addition, indications of coexistence between these phases are observed. The simplest mean-field description that includes this effect is that of Maier and Saupe [13]. This model is appropriate for materials with a disordered and an

ordered (nematic) phase which are coexisting in a certain temperature range. The Maier-Saupe potential is of the form $W(\theta, \varphi) = c_0 S \cos^2 \beta + \text{const}$, where c_0 is a constant. With this choice we find the important prediction

$$\left. \frac{d(\Delta \phi)}{dt} \right|_{t=0} = KI,$$

$$K = \frac{\pi d N}{15 \varepsilon_0 \overline{n} \lambda_P} A_{TC} \alpha_{TC} (q S_0^2 - 1), \quad (7)$$

where $q = \alpha_{CT}/\alpha_{TC}$ and S_0 is the initial order parameter. As demonstrated in Fig. 1 this linear intensity dependence has been confirmed experimentally using data from Ref. [9] and, hence, the value of K has been determined. A linear dependence is a unique signature of absorption-induced reorientation and should be compared with the highly nonlinear dependence of ordinary liquid crystals due to the Fréedericksz transition [1]. It is, however, not exclusive to the multidomain model, as is seen by taking $S_0 = 0$ in Eq. (7). In the range $6.73 \leq c_0 \leq 7.5$ the Maier-Saupe potential admits two solutions [13], viz., a disordered one ($S_0 = 0$) and an ordered one ($S_0 \geq 0.32$). Even though the disordered solution strictly speaking represents an isotropic phase, it is assumed that this solution is a reasonable description of poorly ordered phases ($S_0 \approx 0$) as well. We have used the various parameters of the theory as fitting parameters in order to compare experimental phase-difference curves [9] (all obtained at $T = 20\,°C$) with Eq. (6). From this comparison it is found that the case $S_0 \geq 0.32$ cannot reproduce the experimental data whereas for $S_0 = 0.01$ very good agreement between theory and experiment has been obtained. This finding is supported by differential scanning calorimetry and x-ray investigations [11] showing that the initial mesophase is indeed a poorly ordered nematic or smectic. The simulations based on the value $S_0 = 0.01$ are shown in Fig. 2. The best fit has been obtained with the values $c_0 = 6.8$, $A_{TC} = 0.26 \times 10^{-3}$ cm²/mJ, $A_{CT} = 0.96 \times 10^{-3}$ cm²/mJ, $q = 0.20$, $\tau = 10$ s, and
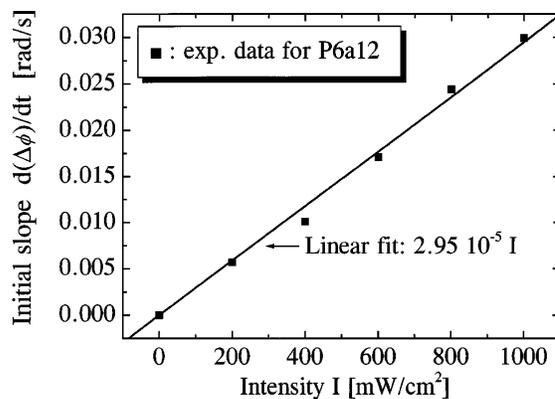

FIG. 1. Experimental values of the initial slope of the photoinduced phase difference as a function of intensity. The solid line is a linear fit to the data.
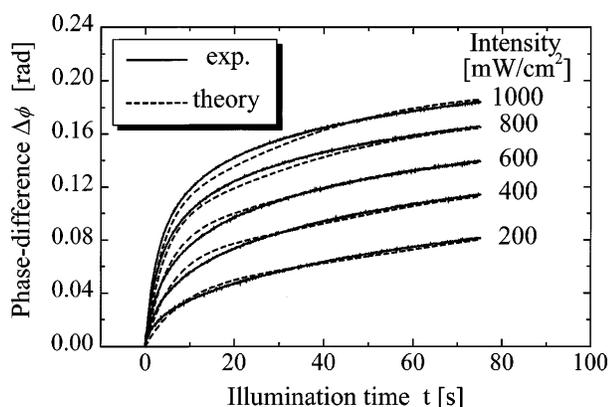
FIG. 2.   The experimental phase-difference curves (solid lines) and theoretical predictions (dashed lines) for five values of the writing intensity.

$I_{\text{th}} = 135$ mW/cm^2. From the experimental absorption spectrum [10] the *trans* $\to$ *cis* absorption cross section can be determined, and together with the above value of A_{TC} this allows us to determine the quantum efficiency ϕ_{TC} with the result $\phi_{TC} = 5\%$. Furthermore, from the values of K and the above parameters the following values of the polarizabilities (using $d = 400$ nm, $\lambda_P = 632.8$ nm, and $\overline{n} = 1.5$) are found: $\alpha_{TC} = 1.2 \times 10^{-34}$ F cm^2 and $\alpha_{CT} = 2.4 \times 10^{-35}$ F cm^2. The quantum efficiency ϕ_{TC} of 5% is of the same order of magnitude as the experimental value for another azobenzene compound, viz., PMMA-DR1 [14], and a ratio of A_{CT} to A_{TC} of approximately 3.7 also seems reasonable, bearing in mind that *cis* $\to$ *trans* isomerization is quasiresonantly excited. The polarizability ratio $\alpha_{CT}/\alpha_{TC} = 0.20$ obtained from the best fit to experiments agrees with the suggestion [14] that the *cis* form is less anisotropic than the *trans* form and, therefore, has a smaller oscillator strength. Also, the value of τ coincides with the decay time found in experiments by observing the decay of the induced anisotropy [5]. Finally, the fitted value of I_{th} is much larger than the value ~ 1 mW/cm^2 reported for hydrophobic azobenzene (HA) dyes [12]. The threshold, however, is determined by the excitation rate, i.e., $I_{\text{th}} \sigma_{TC} \phi_{TC}$, rather than the photon flux, and since the present value of $\sigma_{TC} \phi_{TC}$ is approximately 100 times less than that of HA dyes [7] this suggests a value $I_{\text{th}} \approx 100$ mW/cm^2 in agreement with the fitted result.

In conclusion, we have constructed a novel mean-field theory of photoinduced reorientation in liquid crystalline side-chain polymers which for the first time provides an explanation for several experimental observations including the long-term stability and the intensity dependence of photoinduced anisotropy.

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