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Phenomenological analysis of the light intensity dependence of the photoalignment process in azo-containing polymeric films

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A phenomenological model is proposed to analyze the influence of the incident light intensity on the photoinduced anisotropy of an azobenzene-containing polymer film. The optical anisotropy was generated in the films by the incidence of linearly polarized light and monitored by transmittance measurements.

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I. INTRODUCTION

Azobenzene-containing polymers have been reported as active materials for opto-electronics and photonics applications such as in waveguiding, optical switching [1,2], data storage [3,4], and fabrication of surface-relief gratings (SRGs) [5–7]. The photoalignment features of these materials have also been proposed as promising in the orientation of liquid crystals [8–10]. The orientational changes of the photochromic molecules promoted by incident light lead to remarkable changes in the orientation direction of the liquid crystal molecules. The mechanism of photoreorientation is not well understood despite the great number of investigations [11–14]. The current explanation is that after absorbing a photon, an azobenzene molecule can adopt the unstable *cis* conformation, and is subsequently induced back to the stable *trans* conformation upon heating and illumination. After the *cis-trans* transition, the molecule can adopt any angular position, including the original one. However, if the adopted orientation is orthogonal to the light polarization direction, the molecule will no longer absorb light and reorientation will not take place anymore. Thus, after several *trans-cis-trans* photoisomerization cycles, there will be a net population of azobenzene molecules oriented in the orthogonal direction to the light polarization and an anisotropy is developed in the media [13,14].

The threshold for obtaining azo-dye photoalignment depends on the particular molecular structure of the polymer as well as on the technique employed for film fabrication, e.g., self-assembly, Langmuir-Blodgett, etc. A theoretical model developed by Sekkat and collaborators was aimed at investigating the process of photoinduced reorientation of azobenzenes in a viscous medium [15], which agrees with experimental observation for organized films, such as Langmuir-Blodgett films. However, there are some aspects related to the photoisomerization process that are not contemplated in this model; such as the free volume (or vacancy) necessary for reorientation, which depends on the amount and how the azo-dye groups are attached to the polymer. Recently, a model was developed [12] to take into account the distribution of vacancies necessary to accommodate the azo-dye groups in the photoisomerization process. Its predictions were compared with experimental results for a system comprising a small amount of dispersed chromophores in the polymeric matrix and for low temperatures.

In this study, we developed a simple phenomenological model to investigate the influence of the incident laser intensity on the photoalignment of a polymer film containing side-chain azo-dye groups (DR-13). It is shown that the transmittance can be described as a competition between two rates, one of alignment and the other of randomization of azobenzene molecules.

II. THEORETICAL CONSIDERATIONS

We will analyze the reorientation of the azo molecules for normal incidence and linear polarized light. The probability of photon absorption is proportional to cosine square of the angle between the molecular dipole moment and the incident electric field. For linear polarized light, the electric field lies in the plane of the film (x-y), therefore the dipoles oriented in the z direction are not concerned in the reorientation process. In addition, in previous results we observed that the photoalignment does not induce a pretilt angle to the liquid crystal molecules, indicating that the chromophores lie at the surface plane [9]. Therefore, let us consider a polymeric film of thickness d containing azobenzene molecules with long axes randomly distributed in a plane parallel to the substrate. It is assumed that the direction of their transition dipole moments coincides with their long axes and that only in-plane angular reorientation is allowed. Furthermore, the electric field of the linearly polarized incident irradiation vibrates in the direction of the x axis. To describe the anisotropy created in the film due to the alignment of azobenzene molecules, let us define a function $A(t)$ as

$$A(t) \equiv \int_{-\pi/2}^{\pi/2} g(\theta,t)\cos^2\theta d\theta, \tag{1}$$

where $g(\theta,t)$ is the number of azobenzene molecules per unit area whose long axis is located between θ and $\theta+d\theta$ in the instant t after the illumination is turned on. The angle θ is relative to the x axis. Note that $g(\theta,t)$ is proportional to the film thickness and azobenzene concentration. The function

$A(t)$, therefore, can be related to the anisotropy created in the film in the instant t due to alignment of the azobenzene molecules. The maximum value assumed by $A(t)$ occurs when the molecules are completely disorganized, i.e., in $t=0$. This value is

$$A(t=0)=\int_{-\pi/2}^{\pi/2}\frac{n_A}{\pi}\cos^2\theta d\theta=\frac{n_A}{2}, \tag{2}$$

where n_A is the number of azobenzene molecules per unit area. Note that due to the initial isotropy we have $g(\theta,t=0)=n_A/\pi$.

As the illumination starts and alignment occurs, $A(t)\rightarrow c<n_A/2$, where c is a constant. The value of this constant depends on the effect from the temperature that randomizes the aligned azobenzene molecules.

To describe the time behavior of $A(t)$, let us write its time variation $dA(t)/dt$ as

$$\frac{dA(t)}{dt}=F[I_{\text{abs}},A(t)], \tag{3}$$

where $F<0$ and I_{abs} is the intensity of light absorbed by the system expressed in W/cm^2. Expanding Eq. (3) in a Taylor series of $A(t)$ and I_{abs} in the neighborhood of the point $(I_0,n_A/2)$, where I_0 is an arbitrary intensity of incident light, we obtain

$$\frac{dA(t)}{dt}=F\left(I_0,\frac{n_A}{2}\right)-k_1[I_{\text{abs}}-I_0]+k_2\left[\frac{n_A}{2}-A(t)\right]+\cdots, \tag{4}$$

where

$$k_1=\left.-\frac{\partial F}{\partial I_{\text{abs}}}\right|_{I_{\text{abs}}=I_0} \tag{5}$$

and

$$k_2=\left.-\frac{\partial F}{\partial A}\right|_{A=n_A/2}. \tag{6}$$

The constants k_1 and k_2 are positive. The first one can be seen as a measure of how fast the function F varies with the absorbed intensity I_{abs}. Similarly, k_2 is the rate at which the function $A(t)$ increases. The constant $F(I_0,n_A/2)$ is the time variation of $A(t)$ in $t=0$ and $I_{\text{abs}}=I_0$. The arbitrary constant I_0 in Eq. (4) can be interpreted as the minimum rate of photon absorption necessary for the alignment. Actually, many systems reported in the literature present a minimum intensity I_0 for the alignment [11,12]. From the experimental results, however, we observed that our system does not present a minimum light intensity and therefore we can set $I_0=0$. In this framework, we can also set $F(n_A/2,I_0)=0$. Yet, with the additional consideration that $I_{\text{abs}}=\alpha IA(t)$, where$\alpha$ is an absorption coefficient of the film, we can write Eq. (4) as

$$\frac{dA(t)}{dt}=-k_1\alpha IA(t)+k_2\left[\frac{n_A}{2}-A(t)\right], \tag{7}$$

which is a linear, first-order differential equation comprising two rates. The first rate is negative and represents a decreasing in the function $A(t)$ due to the alignment promoted by the incident linearly polarized light. The second is a rate of increasing $A(t)$ due to the randomization of the molecules, attributed to temperature effects.

Considering again that $A(t=0)=n_A/2$, the solution of Eq. (7) is

$$A(t)=\frac{k_2n_A}{2K}(1-e^{-Kt})+\frac{n_A}{2}e^{-Kt}, \tag{8}$$

where $K=k_1\alpha I+k_2$. Note that the decreasing in $A(t)$ is due to the alignment of the azobenzene molecules in the direction orthogonal to the incident light polarization. Therefore, a decreasing in $A(t)$ means an increasing in the birefringence Δn of the film. Thus, we can write

$$\frac{d\Delta n(t)}{dt}=-\gamma[A(t)]\frac{dA(t)}{dt}, \tag{9}$$

where γ is a function that accounts for the relation of the probe light and the aligned azobenzene originating the birefringence. Let us assume $\gamma[A(t)]=\beta$, where β is a constant. From Eqs. (8) and (9) we obtain the following expression for the birefringence:

$$\Delta n(t)=\frac{1}{2}\beta n_A\left(1-\frac{k_2}{K}\right)(1-e^{-Kt}). \tag{10}$$

We would like to employ Eq. (10) to describe the normalized transmittance T_N measurements given by $T/T_{\max}$, where $T_{\max}$ is the maximum transmittance and T is the measured one. The relation between the normalized transmittance T_N and the birefringence Δn is given by [16]

$$\Delta\phi=2\arcsin(\sqrt{T_N}), \tag{11}$$

where

$$\Delta\phi=\frac{2\pi}{\lambda}d\Delta n \tag{12}$$

is the optical phase shift of the light and λ is the wavelength of the probe beam. From Eqs. (10)–(12) we can find

$$T_N=\sin^2\left[\frac{1}{2}\beta n_A\pi\left(\frac{d}{\lambda}\right)\left(1-\frac{k_2}{K}\right)(1-e^{-Kt})\right]. \tag{13}$$

If the normalized transmittance T_N is small, the following approximation can be made:

$$T_N\approx\left[\frac{1}{2}\beta n_A\pi\left(\frac{d}{\lambda}\right)\left(1-\frac{k_2}{K}\right)(1-e^{-Kt})\right]^2. \tag{14}$$

As can be seen, the normalized transmittance T_N increases monotonically with the illumination time t until saturation. This saturation can be calculated by making the limit of T_N when $t\rightarrow\infty$ for each intensity I. This limit gives

$$T_{N\max} = \left[\frac{1}{2}\beta n_A \pi\left(\frac{d}{\lambda}\right)\left(1 - \frac{k_2}{k_1\alpha I + k_2}\right)\right]^2. \tag{15}$$

This saturation value, however, depends on the illumination intensity I and on the material properties. Implicit in Eq. (15) is a maximum value for $T_{N\max}$, which occurs at high intensities of the writing beam. With $I \to \infty$ in Eq. (15), we have

$$T_{N\max}(I \to \infty) = \left[\frac{1}{2}\beta n_A \pi\left(\frac{d}{\lambda}\right)\right]^2. \tag{16}$$

This completes the theoretical tool to analyze the experimental behavior.

III. EXPERIMENTAL METHODS

The photopolymer used, p(MMA-DR13), is a random copolymer of methacrylate derivatives [17,18] containing a chromophore covalently attached to the main chain. The concentration of the co-monomer containing the chromophore was determined by ultraviolet-visible (UV-VIS) measurements. We used a series of films containing 9.3% mol. In the visible region of the spectrum the polymer film exhibits a maximum absorption at $\lambda \approx 480$ nm, as shown in Fig. 1, which also contains the polymer structure. Polymeric solutions at 2% in chloroform were prepared and spin-coated onto glass plates. The films were then annealed during ≈2 h at 70 °C for the solvent to evaporate.

The film thickness d was determined by an interference method using white light in an optical microscope. In the double-beam method of Mirau, a beam of light is split into two coherent wavetrains that are made to interfere. One of these wavetrains is reflected by the surface of the object and the other by a reference surface in front of the objective. In these experiments, a portion of the film is removed from the glass plate and the relative displacement of the interference fringes (m), observed at the border of the step, is used to calculated the film thickness using the formula $d = m\lambda/2$ (d), where λ is the wavelength ($\lambda = 546$ nm can be used for a low-voltage filament lamp since this value corresponds to the maximum intensity of the measuring light). We found a mean thickness $d = 150 \pm 30$ nm.

The photoalignment was achieved at room temperature (~23°) upon irradiating the film with a linearly polarized Nd:YAG (yttrium aluminum garnet) laser as excitation beam, operating in the wavelength $\lambda = 532$ nm, at normal incidence. A spatial filter was used to remove the Gaussian profile of the excitation laser beam, in order to guarantee a uniform intensity on the whole illuminated area. The transmittance of the sample was monitored by a He-Ne probe laser (3.0 mW) crossing the sample at near normal incidence. The sample was placed between crossed polarizers oriented in such a way that the photoalignment of the film (induced by the excitation beam) occurs at 45° from the direction of the polarizer and the analyzer. At this condition, no transmittance is expected, $t = 0$, while the excitation beam is turned off. After turning it on, an increasing of the transmittance was observed until the saturation of the signal. The experimental setup is schematically presented in Fig. 2. The intensities of the excitation beam were measured at the sample position with a power meter.

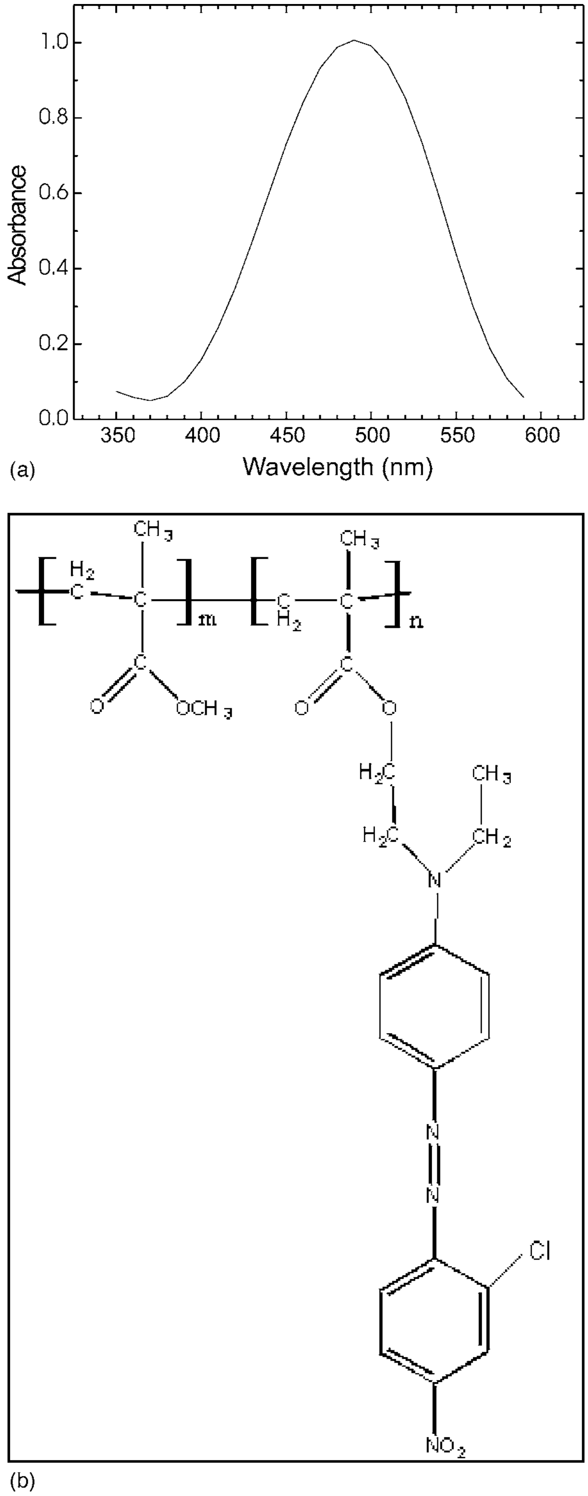

FIG. 1. (a) Absorption spectrum of the polymeric film and (b) schematic representation of the polymeric structure.

IV. RESULTS AND DISCUSSIONS

In Fig. 3, a typical transmittance curve for the p(MMA-DR13) film irradiated with 166.2 mW/cm^2 of light

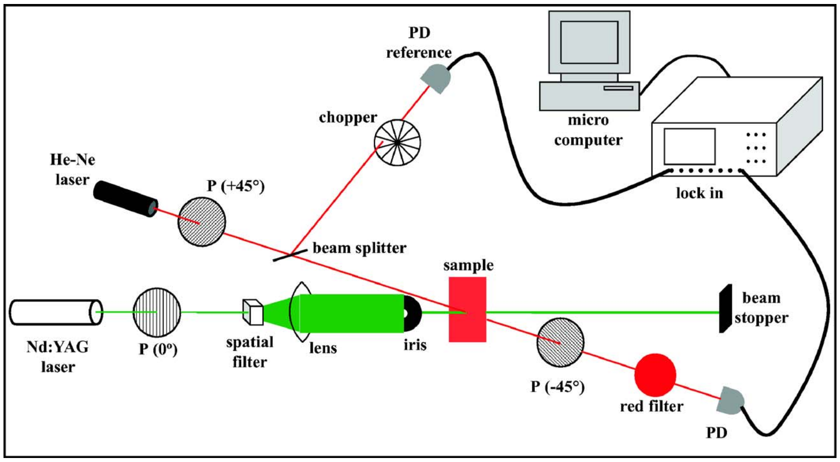

FIG. 2. (Color online) Experimental setup used for the transmittance measurements.

intensity is presented. The sample is initially isotropic (in $t=0$), and after turning on the excitation laser, the azo-dye groups align perpendicularly to the polarization of the excitation beam, resulting in an increasing of the measured transmittance of the sample. After some time of exposure t, a steady state of the photoinduced anisotropy is reached, after which the transmittance remains constant ($T_N = T_{N\max}$). According to the model, this indicates that the rate of alignment due to the illumination is the same as the rate of randomization promoted by temperature. The solid line represents a fit of the experimental curve using Eq. (14).

We performed a series of irradiations with different light intensities. In Fig. 4, the maximum transmittance $T_{N\max}$ as a function of the light intensity I is shown. $T_{N\max}$ monotonically increases with the light intensity until a saturation value of about $T_{N\max}(I \to \infty) = 0.0042$ is attained. According to our model, this saturation is caused by almost all chromophores being aligned, i.e., $A(t)$ assumes its minimum value possible.

As we have said previously, a better unit for n_A and $A(t)$ is the number of azobenzene molecules per unit area; however, in this work we express these quantities in % mol. As a consequence, the parameter β will be expressed in $\%\,\mathrm{mol}^{-1}$ while the constants k_1 and k_2 are not affected. The parameter β can be found from Eq. (16) using the saturation value of $T_{N\max}$ and $n_A = 9.3\%$ mol. We found $\beta = 2.15 \times 10^{-2}\%\,\mathrm{mol}^{-1}$. This value of β can be used to fit the experimental data shown in Fig. 4, together with Eq. (15) to obtain a relation between k_1 and k_2. From this relation it was possible to find their values from the transmittance experimental curves using Eq.(14). The mean values obtained are $k_1 = 1.35 \times 10^{-5}\%\ \mathrm{mol\ W^{-1}\ cm^{3}\ s^{-1}}$ and $k_2 = 2.63 \times 10^{-3}\ \mathrm{s^{-1}}$, where we used $\alpha = 6.9 \times 10^{4}\ \mathrm{cm^{-1}}$ from the absorption spectrum of Fig. 1. The solid line of Fig. 3 was plotted using these parameters.

As a result of the approximation in the series expansion (4), a simple, linear first-order differential equation emerged, which could be solved analytically. The time variation $dA(t)/dt$ can be seen as a competition of two linear terms with the two rates $k_1 \alpha I$ and k_2. The first one can be considered as the rate of the anisotropy is increased by the illumination while k_2 is the rate of randomization of the molecules due to the temperature and other effects. Therefore, k_1 alone can be taken as a proportionality constant that depends on how fast the azobenzene molecules can be aligned. For example, a different k_1 would be expected if the azobenzene molecules of our system were attached to the main chain. Evidently, many systems may not be described in such a simple way. Even the system investigated here may be better described by using higher order in the expansion (4). Studies are now underway to analyze the nonlinear behavior.

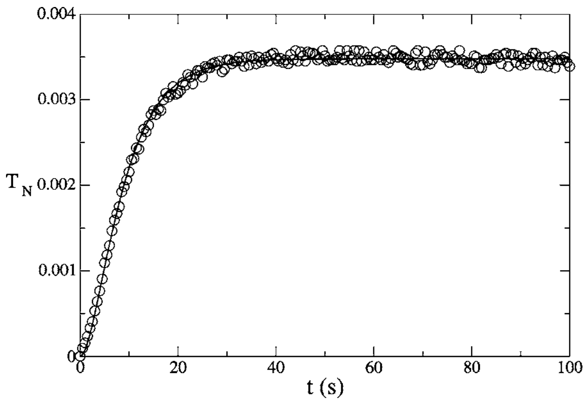

FIG. 3. Typical curve of the normalized transmittance T_N as a function of time t for a film irradiated with 166.2 mW/cm^2. The solid line is a fit made with expression (14).

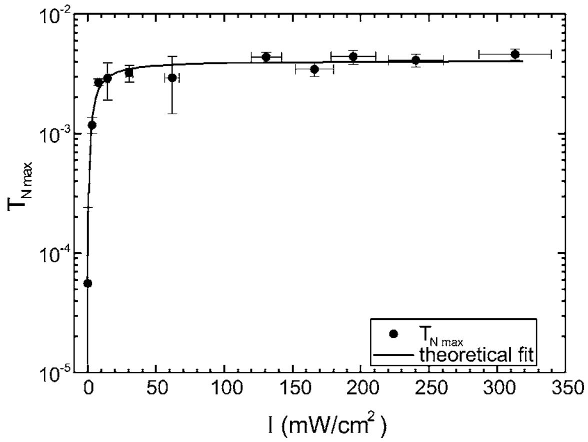

FIG. 4. Maximum normalized transmittance $T_{N\max}$ as a function of light intensity I. The solid line is the fit made with Eq. (15).

V. CONCLUSIONS

A simple phenomenological approach was developed to analyze the normalized transmittance T_N as a function of the incident light intensity I. The model describes the system as a competition between a rate of alignment induced by the excitation light and a rate of randomization of the azobenzene molecules due to the temperature or any other effect. Although very simple, the model offers an analytical resolution and showed good agreement with the experimental data.

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