Photoinduced Surface Alignment: the Role of Liquid-Crystalline Order

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The optical control of surface alignment was investigated, using azo-dye doped polyimide films as photosensitive material. The kinetics of the realignment of the easy axis was measured in isotropic, nematic and smectic A phases. It is demonstrated that the light-induced realignment of the dye molecules at the polymer-liquid crystal interface is strongly influenced by the presence of the liquid-crystalline order. A simple model is presented, which accounts qualitatively for the experimental observations.

Keywords: photoalignment; dye-doped polymers

INTRODUCTION

The possibility to control the surface alignment of liquid crystals by irradiating polymer films with polarized light, received considerable attention in the past years[1-5]. One method is to incorporate azo dyes into a polymer layer. Upon excitation, azo dyes can reorient within the polymer network. Under the influence of polarized irradiation, the dye molecules are selectively excited with respect to their orientation, consequently the orientational distribution of the dye molecules becomes anisotropic. The anisotropic distribution created in this way, contributes to the azimuthal anchoring energy of the liquid crystal contacting the polymer. The "easy axis" due to the redistribution of the dye mole-

cules is in most cases perpendicular to the polarization direction of the pump beam.

In the present work, we investigate the redistribution process in the presence of a liquid crystal layer. We follow the change of the easy axis at the polymer-liquid crystal interface as a function of irradiation time. We show that the kinetics of reorientation is significantly different in the isotropic, nematic and smectic A phases. The realignment is most effective when irradiation is carried out in the isotropic phase, less effective in the nematic phase and hardly works in the smectic state.

In order to interpret these experimental observations, we adopt an idea put forward earlier by Kósa and Palffy-Muhoray[6], namely that the reorientation probability of the dye molecules at the polymer-liquid crystal interface is influenced by the presence of the liquid crystalline order. We show through a simple model that with this assumption the observed behavior in the three phases can be understood at least qualitatively.

EXPERIMENTAL

We studied the liquid crystals 4-cyano-4'-n-octylbiphenyl (8CB) and 4-cyano-4'-n-octyloxybiphenyl (8OCB) purchased from BDH. The smectic A-nematic phase transitions occur at 32°C and at 67°C; the clearing points are at 39°C and 80°C for the two compounds, respectively. In the experiments the liquid crystals were sandwiched between a reference and a photosensitive plate. The former plate was coated with a polyimide layer (Du Pont PI 2555) and rubbed unidirectionally to assure planar anchoring; the latter one was coated with a

filtered and saturated solution of Disperse Orange 3 (Aldrich Chemicals) azo dye in a polyamic acid solution and subsequently heat treated for 2 hours to complete imidization. The cells were filled in the isotropic phase and cooled to the smectic phase in the presence of a strong magnetic field, parallel to the rubbing direction. This procedure ensured a good initial planar alignment. Photoalignment was induced with an unfocused argon laser beam at 488 nm, at power levels 70 mW. The polarization direction of the pump beam was at 45 degrees from the rubbing direction. The cells were illuminated from the photo-sensitive side. The irradiation was carried out at different temperatures, while the induced twist angle was measured at a fixed temperature within the nematic phase of the liquid crystal. The twist angle was determined with the help of a weak probe beam.

EXPERIMENTAL RESULTS

In Figs. 1 and 2., the photoinduced twist angle is plotted for the two liquid crystals as a function of the irradiation time, at various temperatures. We note that without irradiation the twist angle changed only insignificantly during nematic $\rightarrow$ isotropic $\rightarrow$ nematic thermal cycles. In view of this observation, in nematic and isotropic phases the points belonging to different irradiation times were taken at the same spot. On the other hand, as discussed in an earlier publication[7], in the course of a nematic $\rightarrow$ smectic $\rightarrow$ nematic cycle the twist deformation is reduced, hence for the smectic phase all points were taken at different, unirradiated positions.

The experimental curves presented, clearly show the significance of the liquid crystalline order in the kinetics of the surface reorientation. In spite of the temperature differences, the curves for the isotropic, nematic and smectic phases
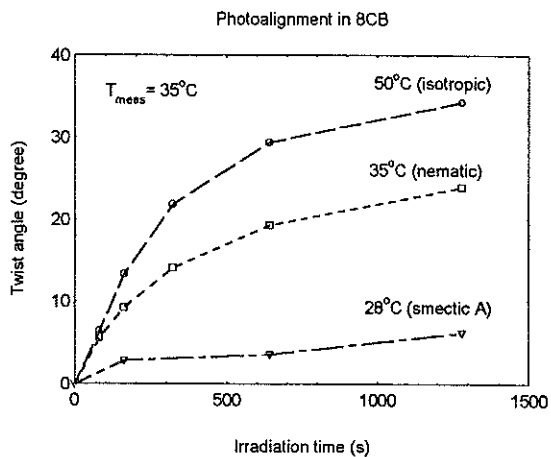
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Photoalignment in 8CB

FIGURE 1. Twist angle as a function of irradiation time at different irradiation temperatures for 8CB.
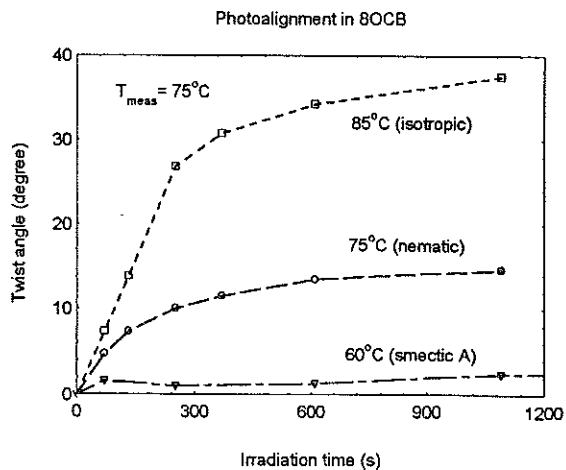
Photoalignment in 8OCB

FIGURE 2. Twist angle as a function of irradiation time at different irradiation temperatures for 8OCB.

are qualitatively similar for the two materials. As a striking example, we may compare the curve taken in the isotropic phase of 8CB at 50°C, to the one taken in the smectic phase of 8OCB at 60°C. Although the photosensitive layer was the same in both cases and the temperature was even lower in the former case, the irradiation was much more effective when the polymer was in contact with the isotropic 8CB rather than the smectic 8OCB.

MODEL

It is a well established fact that dye molecules embedded in a polymer network, can reorient during an excitation process. A detailed theory of light-induced rearrangements of azo dyes in polymers was worked out by Dumont[8]. Here we outline a simplified version of the model, which, nevertheless, retains the basic features of the problem.

We assume that each dye molecule has two stable orientations. Transitions between the two orientations are possible only via the absorption of a photon; the probability of thermal transitions is neglected in the present work. We note that similar models, involving bistable atomic configurations, were successfully applied to describe photoinduced structural changes in chalcogenide glasses[9].

To keep mathematics simple, we deal with a two-dimensional model, i.e. we take into account only dye molecules aligned within the plane of the sample. The orientation of such molecules can be characterized through the azimuthal angle ξ between their long axis and a reference direction, which we choose to be parallel to the rubbing direction. As further simplifications, we suppose that the two stable orientations are orthogonal to each other for every dye molecule, and the transition dipole moment is parallel to the long axis. With these

assumptions, the transition probability per unit time for reorientation from ξ to $\xi+\pi/2$ and for the inverse transition are

$$p_{12} = \Lambda I \cos^2(\xi - \gamma) \ , \quad p_{21} = \Lambda I \sin^2(\xi - \gamma) \tag{1}$$

respectively. Here I is the light intensity, Λ is the product of the absorption cross section and the probability that excitation is followed by a change of orientation; finally γ is the angle between the polarization direction and the rubbing direction.

In order to explain the experimental observations, we take into account the orientational action of the liquid crystal at the interface, in analogy to the guest-host effect in the bulk of nematic or smectic phases. We assume that dye molecules, located near the interface experience a potential of the form

$$U(\xi) = -U_0 \cos^2(\xi - \beta) = -\frac{U_0}{2} - \frac{U_0}{2}\cos 2(\xi - \beta), \tag{2}$$

where β is the azimuthal angle of the director at the photosensitive plate. U_0 is of the same order of magnitude than the liquid crystal mean-field potential, i.e. it is few times kT. For the isotropic phase $U = 0$.

The liquid crystal potential cannot induce in itself transitions, it can, however, influence the light-induced transitions. Obviously, rotations of a dye molecule towards the director are more probable than a rotation in the opposite sense. We include this fact into the model by multiplying the transition probabilities with a Boltzmann factor:

$$\begin{aligned}
p_{12} &= \Lambda \exp\{-\frac{U_0}{2kT}\cos 2(\xi - \beta)\} I \cos^2(\xi - \gamma), \\
p_{21} &= \Lambda \exp\{\frac{U_0}{2kT}\cos 2(\xi - \beta)\} I \sin^2(\xi - \gamma).
\end{aligned} \tag{3}$$

The dye distribution function can be determined from a simple rate equation. Let $x(\xi)$ denote the fraction of dye molecules oriented along ξ. Taking into account that transitions are only possible between orthogonal states, one has $x(\xi+\pi/2)=1-x(\xi)$ and the rate equation reads:

$$dx/dt = (x_s - x)/\tau, \quad \text{with } x_s = p_{21}\tau \quad \text{and} \quad 1/\tau = p_{12} + p_{21}. \qquad (4)$$

The initial condition corresponds to an isotropic distribution of the dye molecules, i.e. at $t=0$, $x(\xi) \equiv 0.5$.

As a next step, we calculate the direction of the easy axis on the photosensitive plate. There are two contributions to the anchoring energy. The first one comes from the dye-liquid crystal interaction and can be given as:

$$W_{dye} = \frac{N}{\pi} \int_0^\pi x(\xi) U(\xi - \beta) d\xi, \qquad (5)$$

where N is the number of dye molecules per unit area at the interface. The second source is the well-known surface memorization effect[10]: at the first cooling cycle, a finite azimuthal anchoring is generated at the unrubbed plate. In our case, this mechanism stabilizes the planar orientation, hence one can write its contribution to the anchoring energy in the form

$$W_{pol} = W_0 \cos^2 \beta. \qquad (6)$$

As shown in Ref.[7], for the case of polyimide, the bulk twist energy in the nematic phase is negligible in comparison with W_{pol}. Consequently, the measured twist angle, β, corresponds to the minimum of the surface anchoring energy. As a simple calculation shows, the minimum of the sum of W_{dye} and W_{pol} has minimum at

$$\beta = \frac{1}{2} \arctan \frac{S}{C + C_0}$$

with

$$S = \int_0^\pi x(\xi) \sin 2\xi \, d\xi, \quad C = \int_0^\pi x(\xi) \cos 2\xi \, d\xi \quad \text{and} \quad C_0 = \frac{W_0}{NU_0}.$$

In Fig. 3, examples of calculated kinetic curves are shown. For the isotropic phase, U_0 was set to zero. In the case of the smectic phase, twist deformation is not allowed, hence we assumed $\beta = 0$ during the entire irradiation time. In the case of the nematic phase, it was taken into account that the director is rotating already during the irradiation. Thus in this case, in the rate equation (Eq. 4), the easy axis was calculated for every time instant and then the transition probabilities were corrected for the new value of β.
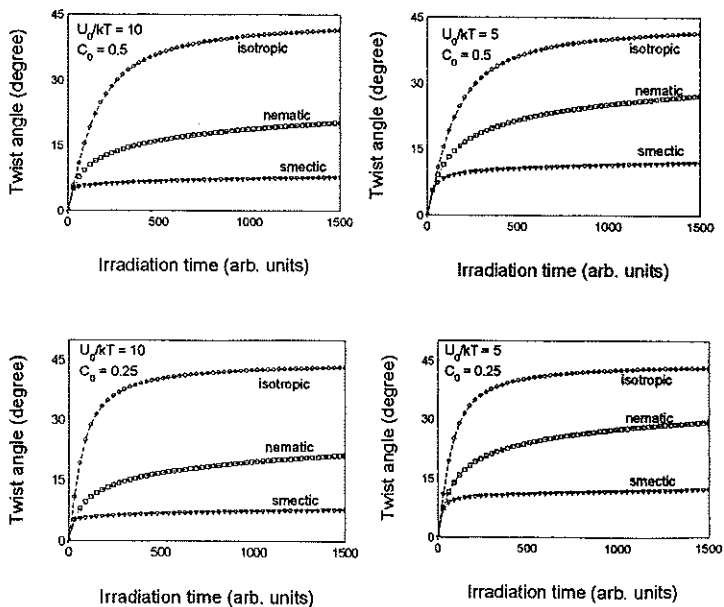

FIGURE 3. Calculated kinetics curves for irradiation in different phases, for different U_0 and C_0 parameters. Polarization direction 45 degrees.

DISCUSSION

According to our considerations, the interaction between the liquid crystal and the dye molecules at the interface leads to a sort of guest-host effect, in the sense that the liquid crystal has an orienting effect on the dye molecules. In the smectic phase, where the director is fixed to the rubbing direction, this orienting effect blocks to a large extent the light-induced rearrangement of the dye molecules at the polymer surface. As a result, the twist angle, induced by irradiation in the smectic phase, is only a fraction of the twist angle obtained after a corresponding irradiation in the isotropic phase.

For the nematic phase, the same mean-field potential is assumed than for the smectic phase. In the former case, however, the director continuously follows the actual easy axis during irradiation and in this way facilitates further rearrangements of the dye molecules. The progress of the twist deformation in nematics is therefore slowed down in comparison to the process in the iso-tropic phase, but much higher twist angles can be induced than in the smectic phase.

The qualitative similarity between the measured and calculated kinetic curves, shown in the figures, is apparent. In view of the simplifications made in our model, we did not try to fit quantitatively the theoretical plots to the experi-mental data. We note, however, that the main features of the calculated curves are retained for a large range of reasonable values of the parameters U_0 and C_0, providing a support of the ideas presented in the paper.

The model discussed here can be generalized to take into account the possibility of thermal transitions of the dye molecules. With this extension, the relaxation processes, observed in other dyed polymer films can be described as well.[11] We suggest furthermore that the coupled rotation of the director and the dye molecules might play a role in director sliding, observed presently on various polymer films[12,13].

Acknowledgments

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