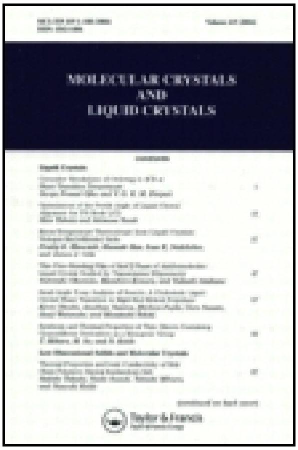

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ON THE NATURE OF PHOTOINDUCED OPTICAL ANISOTROPY IN DIACETYLENE LANGMUIR-BLODGETT FILMS

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Abstract For the first time photoinduced molecular reorientation has been observed in diacetylene Langmuir-Blodgett films. The compound does not show photochemical reactions of *trans-cis* isomerisation, and the observed phenomenon of photoinduced optical anisotropy (POA) cannot be associated with photoinduced *trans-cis* transitions as it is usually considered in viscous dye solutions and polymer films. A change in an interaction energy for excited molecules and local recrystallization as possible reasons of the photoinduced molecular reorientation are discussed.

INTRODUCTION

The effect of photoinduction of optical anisotropy is known for many molecular systems such as solutions[1], polycrystalline films[2], polymer films[3,4] and Langmuir-Blodgett (LB) films.[5-10] An essence of the photoinduced optical anisotropy (POA) effect is that under illumination of a system consisted of molecules with linear oscillators in its absorption band an optical axis of a larger absorption and birefringence perpendicular to the light polarization vector is induced. The detailed study of POA in viscous dye solutions[1] allowed to make the model based on photochemical reactions of *trans-cis* isomerisation under illumination of dye molecules into their absorption band. From that time the *trans-cis* isomerisation is considered as a main reason of POA effect.[2,4] The molecular reorientation is explained by transitions of molecules to *cis*-form and successive relaxation to more stable *trans*-state but with different angular positions. It results in that, at random, the molecules, whose absorption oscillators are perpendicular to the light polarization vector, leave the excitation process and they preserve their angular positions.

Recently the peculiarity of POA in azodye Langmuir Blodgett films forced us to make a new approach in explanation of the effect.[9-11] It was found that POA in LB films can be explained only if molecular interaction is taken into account. The induction of the macroscopic optical axis is explained in detail by rotation of microscopic optical axes of small domains the films consist of.[11] In frame of the model such rotation is possible because of an interaction of excited molecules with a mean molecular field and a substrate. Three reasons responsible for POA have been proposed there, namely changes in the excited state of: (i) molecular conformation, (ii) molecular interaction and (iii) collision rate. Despite the molecules of investigated azocompounds show a high dipole moment change under light excitation[10], they can also show reactions of *trans-cis* isomerisation. Thus it was difficult to decide which of these contributions is more significant.

In this paper we report on the observation of POA in a diacetylene compound, which does not show the reactions of *trans-cis* isomerisation. As we know it is the first example when the light induced reorientation under illumination in the compound's absorption band cannot be explained by photoinduced change in a molecular conformation. Here we discuss a role of both a change in an interaction energy for excited molecules and local recrystallization as a possible reasons of the photoinduced molecular reorientation.

EXPERIMENTAL

To prepare the molecular films we have used a diacetylene compound of structure formula shown in Figure 1.

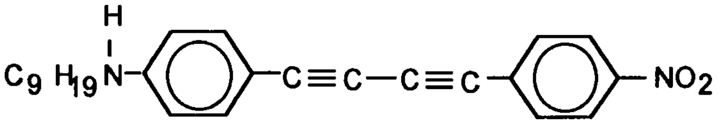

FIGURE 1 The structure formula of the diacetylene molecule.

The most homogeneous films were prepared by Langmuir Schaefer technique[12] at rather low surface pressure of 5 dyn/cm. The dependence of the surface pressure versus the molecular area is shown in Figure 2.

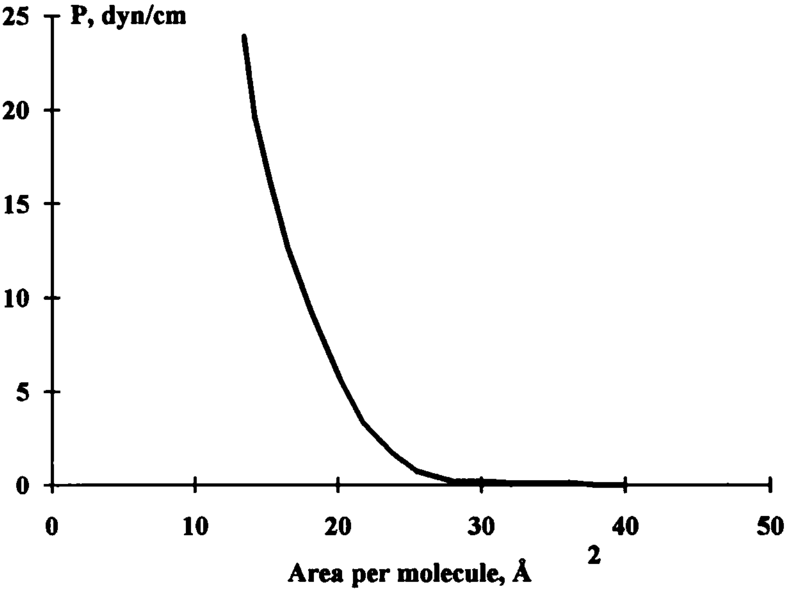

FIGURE 2 The surface pressure versus an area occupied by a molecule (p-A curve) measured for the diacetylene monolayer at the temperature of 20 °C.

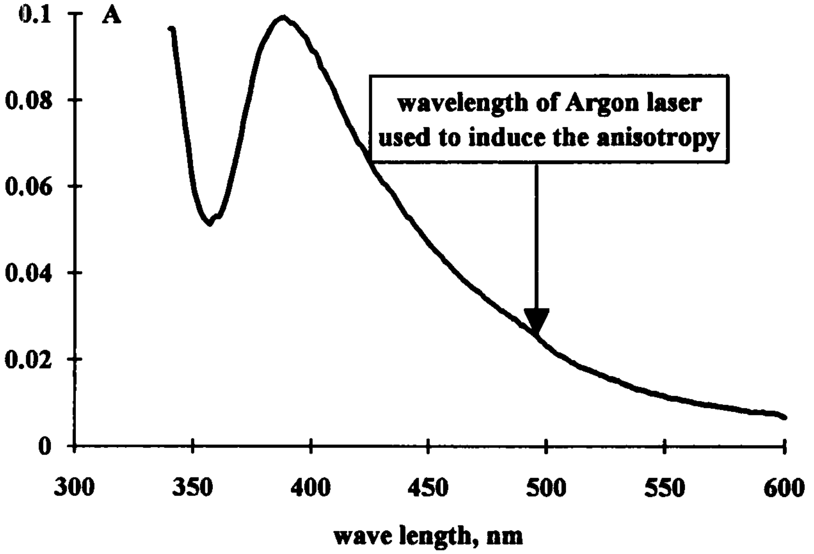

FIGURE 3 The absorption spectrum of 15-layer diacetylene film.

One can see that at the pressure used in the preparation procedure the molecule occupies an area of about 20Å^2. Taking into account a molecular model of the compound and the tilt angle of chromofores of 45° we have estimated the monolayer thickness of about 22Å. The results presented in this paper are obtained for 15 layer films. The films show a micro domain structure that is easily observed in a polarized microscope.

The absorption spectrum of 15 layer film is shown in Figure 3. We use the argon laser illumination of 489 nm wavelength and power of 2 mW to induce the optical anisotropy. We make focusing the laser beam in a spot of 0.2 mm in size. Despite we produce illumination in the spectral region of rather poor film's absorption, after 10 minutes in the place of illumination using a polarizing microscope one can easily see a birefringent spot. The value of the optical path difference due to the birefringence is measured by a standard technique using a polarizing microscope with a 3λ-compensator. The film thickness of 33 nm we used in the calculation of the birefringence was evaluated by simple multiplying the number of monolayers by its estimated thickness of 2.2 nm. We also made the film between two Al electrodes to estimate the thickness by measuring the electrical capacity . From these measurements assuming the dielectric constant to be of 2.5 we found the film thickness of 36 nm, which is quite close to the mentioned value of 33 nm.

After illumination of the films by polarized light of the argon laser we found the main optical axis to be perpendicular to the light polarization vector. The values of induced birefringence versus illumination time are shown in Figure 4. They have been multiplied by 2 to take into account the 45° tilt, to represent the maximum molecular birefringence. The highest induced birefringence $\Delta n \approx 0.4$ is found after 10 minutes of illumination. This value is rather high. For comparison the value of the birefringence measured independently in the nematic phase (at temperature 120 C) is 0.3. Such high value can be explained both an extremely high molecular order parameter in microdomains and perfect reorientation of domains optical axes under polarized illumination of the argon laser. More illumination decreases the value of the induced birefringence. The last result can be explained in two ways: (i) out-of-plane rotation of microdomain axes as explained in [11]; (ii) photochemical process that results in either "decomposition" of the diacetylene molecules or their polymerisation.

In Figure 5 the measurements of changes in absorption of illuminated film for two polarizations (parallel and perpendicular to the inducing polarization vector) are shown. These measurements have been performed during the anisotropy induction using the same Argon laser beam. To measure the dichroism keeping the measuring spot exactly at the same illuminated place, the measuring polarization was changed to 90° by λ/2 plate.

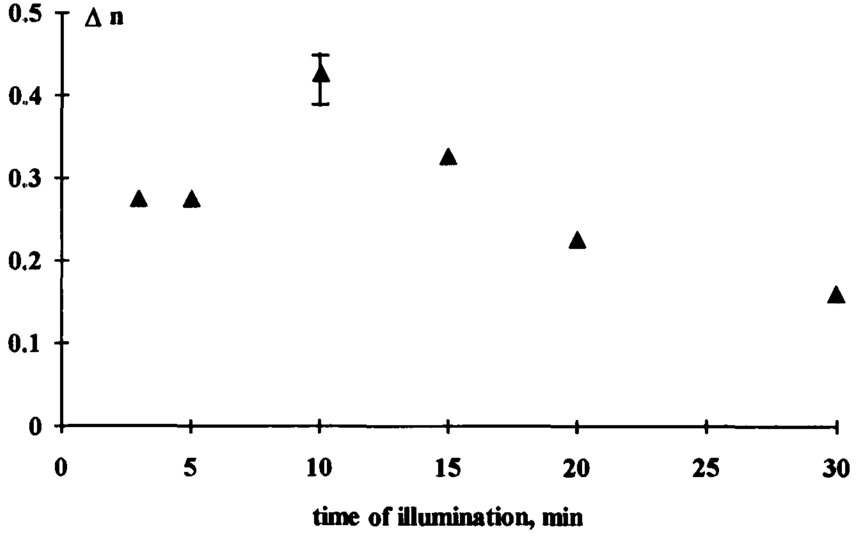

FIGURE 4 The induced birefringence versus illumination time.

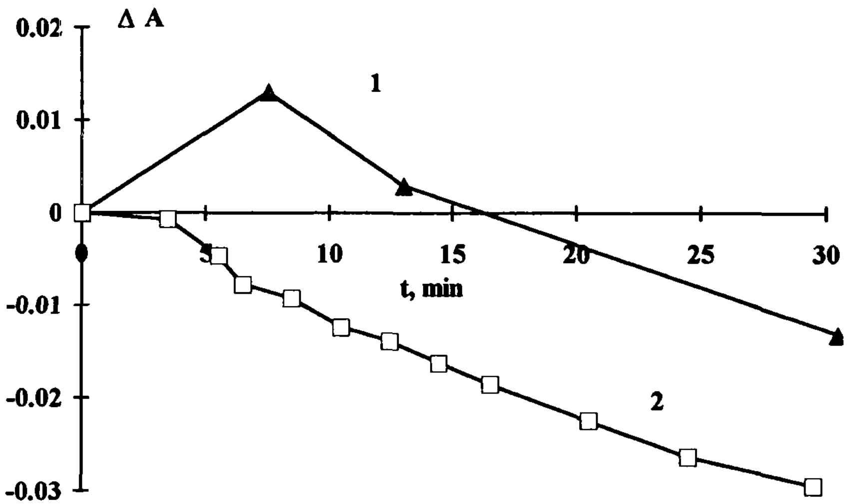

FIGURE 5 The induced optical dichroism versus illumination time. The absorption is measured during the anisotropy induction at λ=489 nm for two polarisations of the measuring beam: 1- polarization is perpendicular to the polarization of the inducing light, 2- polarization is the same as the polarisation of the inducing light.

From the data in Figure 2 one can see that the decrease in the absorption for the polarization parallel to the inducing polarization is exactly compensated by an increase of the absorption in the perpendicular direction for the illumination time up to 8 min. It agrees with the measurements of the induced birefringence versus illumination time and proves that at least for illumination time less than 8 minutes destructive photochemical processes are not significant and the induced axis is associated with a molecular reorientation without loss of material.

DISCUSSION

We explain the observed result of molecular reorientation in frame of the model published in.[11] To introduce a reader to the basic idea, here we remind some aspects of the model assuming an homogeneous material. A crucial point in the described model is that it was introduced a "friction" between molecules and the substrate, which is different for excited and non excited molecules. The Figure 6 explains qualitatively the occurrence of rotation of a domain director under illumination by polarized light. At thermal equilibrium under the influence of the mean molecular field, the molecules in the domain are represented by the initial distribution function $f(\psi)$ (curve 1) with a maximum corresponding to an arbitrary angle ψ_0 with respect to the light polarization vector. An interaction of the molecules with light produces excitations in the initial distribution function. Because the molecule chromophores behave like linear oscillators, the shape of these excitations (curve 2) is proportional to the product $f(\psi)cos^2(\psi)$. It results in asymmetry in the distribution function of ground-state molecules (curve 3). At start moment the sum of curves 2 and 3 gives the initial distribution function (curve 1). Because the excited molecules are in the molecular field they are redistributed to the shape (curve 4) defined by the interaction of the excited molecules with the molecular field. We assume that for the excited molecules the friction with the substrate is much less than for molecules in the ground state. The last assumption is based on the fact that under the excitation the molecule can change its conformation and the energy of the interaction with the mean molecular field. As a result the rate of collisions with the substrate, which defines the friction, will be different for the excited molecules. Thus, during the time while the redistribution of excited molecules takes place (shift to the centre with minimum molecular potential, from curve 2 to curve 4), the ground distribution (curve 3) is still unchanged. Now we can see that the sum of curves 3 and 4 gives the new distribution function (curve 5) shifted with respect to the initial one in the direction of higher ψ. The domain molecules "escape" the absorption of the light. Because the maximum of the distribution

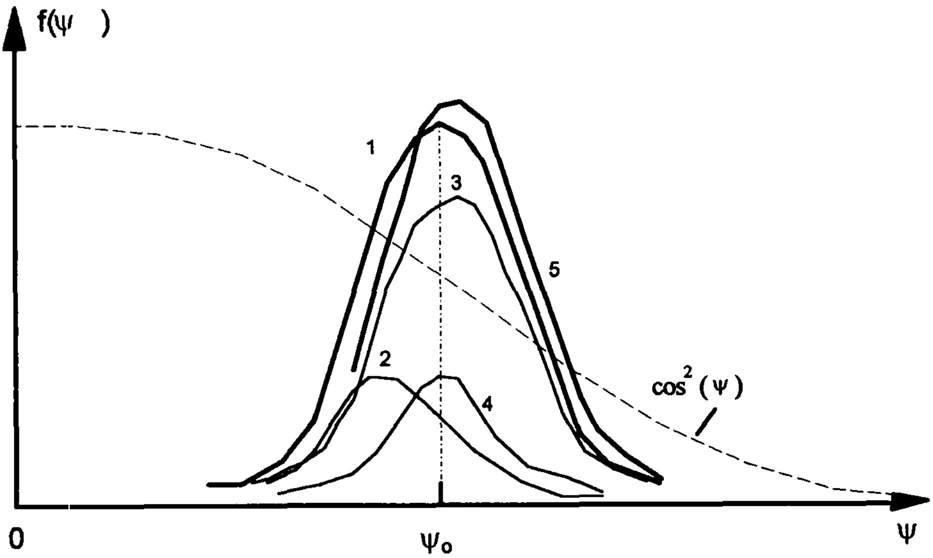

FIGURE 6 Demonstration of the director rotation for a molecular domain. 1- initial molecular distribution function; 2- shape for molecular excitations under polarized illumination (orientation of the light polarization vector is at $\psi=0$); 3- distribution of unexcited part of molecules; 4- equilibrium distribution for excited molecules; 5-new distribution function (sum of curves 3 and 4).

function is shifted, the direction of the molecular field is shifted too, so the redistribution of unexcited molecules takes place as well. At continuous illumination it gives the result of the domain director rotation. The detailed consideration written in [11] gives the following relationship for the angular speed of the domain axis :

$$\Omega = -\frac{\tau_c}{J}\Gamma_a, \tag{1}$$

where

$$\Gamma_a = \frac{I\sigma\tau_e}{2h\nu}W_0\left(1-\frac{\eta}{\eta^*}\right)\sin(2\psi_0)\Delta^2, \tag{2}$$

$$\eta = \frac{J}{W_0\tau_c}\ ,\ \eta^* = \frac{J^*}{W_0^*\tau_c^*}\ , \tag{3}$$

J is the moment of inertia with respect to the axis perpendicular to the longitudinal molecular axis, *Wo* is the amplitude of molecular interaction energy, τ_c is molecular collision time, τ_e is lifetime of the excited state, σ is absorption cross-section, Δ is halfwidth of the distribution function, I is the light intensity, hν is the photon energy. The superscript "*" anywhere is related to an excited molecule and omitted for an unexcited one. Equation (1) defines an "apparent" torque Γ_a acting on the domain molecules. Applying equipartition energy to estimate the thermal average of Γ_a, we have obviously the relationship:

$$\left\langle \frac{1}{2} W_0 \Delta^2 \right\rangle = \frac{1}{2} kT. \tag{4}$$

Formula (2) becomes:

$$\Gamma_a = \frac{I\sigma\tau_e}{2h\nu}\left(1 - \frac{\eta}{\eta^*}\right)\sin(2\psi_0)kT \tag{5}$$

The fact that the apparent torque depend only on temperature is natural because the origin of the rotation is pure dissipative process.

The torque appears only if η and η^* are different. Its sign is related to the sign of $\eta^*-\eta$. For $\eta^*<\eta$, the molecules tend to "escape" from the light polarization orientation. For $\eta^*>\eta$, they would orient along the light polarization vector. In all cases, the rotation induced on molecules obeys the friction law defined by the Equation (1), which expresses that the mean angular velocity of the distribution is proportional to the apparent torque. The final stable equilibrium angle ψ is zero or 90°, depending on the sign of $\eta-\eta^*$.

Now let us discuss the reasons, which can lead to non-zero value of $\eta-\eta^*$. According to Equation (3) one can consider three cases:

(i) change in the moment of inertia; (ii)- change in the interaction energy; (iii)-change in collision time.

(i) The moment of inertia can be changed, for instance, if the molecules can show the photochemical reactions of *trans-cis* isomerization. In our case, for the diacetylene molecules, the *trans-cis* isomerization is excluded and this process is probably not very efficient.

(ii) The change of interaction energy can take place if molecular parameters such as the polarizability and the dipole moment are different in the excited state from those in the ground state. It is well known, that diacetylene compounds do show nonlinear optical properties. It points out that a change in an interaction energy upon excitation can be quite significant to be a reason of the observed POA. Let us try to estimate the value $1-\eta/\eta^*$ in Equation (5) that agrees with the experiment. To do this we take the following values for the parameters: $J=10^{-42}$ kg m^2 (estimated from the molecular model), $\tau_c=10^{-13}$ (typical time for molecular vibrations), $\tau_e=10^{-10}$ (typical lifetime of an excited state for organic dyes), $\sigma=8\times10^{-22}$ m^2 (found from the absorption at λ=489nm), $I=5\times10^4$ W/m^2, T=300K . If we put all mentioned values into Equation (5) one can find that the experimentally observed angular speed $\Omega\approx0.003$ s^{-1} is realised at $(1-\eta/\eta^*)=3\times10^{-3}$. The last value is quite reasonable, so the small change in molecular interaction can do explain the observed POA.

(iii) At low intensities, when heating is small, there is no reason to expect any difference in the collision time if we are far from a phase transition (to nematic or isotropic phase, for instance). Our estimation of temperature change in illuminated spot gives $\Delta T=10^{-3}$ K Nevertheless in multidomain films, the transition temperature can be lower in the vicinity of domain walls, where the molecular distribution has a higher disorder. In this case we can have a change in collision time (which was attributed to angular "recrystallization" in previous papers[8-11]) as a result of a very small heating. Thus the mechanism of recrystallization can not be excluded but needs additional theoretical consideration. We also believe that the systematic investigation of the correlation between change of molecular parameters upon excitation and ability to show POA for different compounds can clarify a role of two mentioned contributions in photoinduced reorientation for the compounds which do not show *trans-cis* isomerisation.

In nonhomogeneous systems, the described model gives rise to new interesting phenomena. For instance, there could exist a difference in torque density Γ_a from place to place, which means the appearance of a force density ~**curl** Γ_a, which could lead to mass transfer. Such a transfer has indeed been observed recently.[13]

There could also exist other nonhomogeneous processes of reorientation. For instance, let us imagin that one photon is absorbed on one well defined molecule. The large energy (2 eV) can be enough to melt localy the orientational ordering. The thermal relaxation leads to a localized angular recrystallization, with an orientation different from the initial one. The rest of the system will readjust elastically to adapt to a new orientation. Statistically, the whole system escapes the direction of maximum absorption with an analoguous behavior to the one a cis-trans transitions in isotrope solutions.

CONCLUSION

To conclude, we have observed photoinduced molecular reorientation in diacetylene Langmuir-Blodgett films. The compound does not show photochemical reactions of *trans-cis* isomerisation, and the observed phenomenon POA can not be associate with photoinduced *trans-cis* transitions as it is usually considered in viscous dye solutions and polymer films. We show and discuss two reasons, which can be responsible for the observed phenomenon: (i) a change in an interaction energy for excited molecules and (ii) local recrystallization.

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