Photochromic properties of azo dye polymer thin films: evidence of an additional reversible mechanism of molecular behaviour

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Photoinduced refractive index and absorption anisotropies in thin films of an azo dye polymer have been carried out by pump-probe experiments. A refractive index change of Δn=-0.04 was obtained by independently measuring the two indices, parallel and perpendicular to pump light polarization. A long-term stability of the induced birefringence and a reversible photoinduced memory effect have been observed. The experimental results cannot be completely explained by the proposed photoisomerization models to describe the process involved.

Keywords: Photochromic polymers; optical waveguides; photoinduced refractive index.

Mediante experimentos de sonda-bombeo, hemos registrado anisotropías fotoinducidas en películas delgadas de un polímero azoaromático. Las mediciones se llevaron a cabo determinando independientemente los índices de refracción en las direcciones paralela y perpendicular a la dirección de polarización del haz de bombeo. Reportamos la variación del índice de refracción, Δn=-0.04. Así como también la estabilidad temporal de la birrefringencia inducida y la reversibilidad del efecto de memoria fotoinducido. Los resultados experimentales no pueden ser totalmente explicados por los modelos de fotoisomerización que describen los fenómenos involucrados.

Descriptores: Polímeros fotocromáticos; guías de onda; índice de refracción fotoinducido.

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1. Introduction

Photosensitive organic polymers have potential applications in novel high-performance and low-cost optoelectronic devices. Due to reversible control of the refractive index and birefringence [1,2] they can be applied not only to optical storage[3], dynamic holographic recording [4] but also to optical control of integrated optical devices [5].

One of the principal advantages of these photochromic materials is the large refractive index variation (up to Δn=0.1) compared to that obtained by electro-optical Pockels effects.

Molecular orientation or angular hole burning through molecular photo-isomerization processes constitutes the mechanism acknowledged to be at the origin of reversible refractive index changes [6]. Azo-dye molecules in their fundamental "trans" state exhibit strongly anisotropic dipolar transition moment tensor: photon absorption mainly occurs when the light is polarized along the molecular axis. Thus, under light illumination and after multiple trans-cis-trans isomerization cycles, molecules tend to rotate toward the perpendicular direction with respect to the pump polarization, leading to refractive index changes and optical anisotropy. This model is in agreement with the experimental work of Rochon *et al.* [2], where the birefringence is induced by linearly polarized light and the refractive index is decreased in the direction parallel to light polarization. Birefringence can then be erased by circularly polarized light.

Although the photoinduced birefringence, $\Delta n = n_{//} - n_{\perp}$, has been measured before in these kinds of polymer films [1,2,7], there are reports of the time evolution of the two refractive indices $n_{//}$ and $n_{\perp}$.

In this letter we report the measurements of photoinduced optical anisotropy in thin-films of poly(methyl methacrylate) (PMMA) functionalized with Disperse Red 1 (DR1). We have not only measured the birefringence, Δn, but also the independent time evolution of the two indices $n_{//}$ and $n_{\perp}$. In this way, further information is obtained. In particular, in contradiction with what is usually accepted, we found experimental evidence that molecular orientation is not able to explain all the observed results.

2. Experimental

The refractive index variations were measured by an attenuated total reflection setup [8] in the grating configuration. The grating geometry is shown in Fig. 1. The polymer film is deposited by the spin-coating technique on a silica substrate in which a grating (period Λ=0.7μm and depth 0.15μm) has been previously etched. The guided wave is excited through the first diffracted order of the grating coupler.

The spin-coating technique widely used in microelectronic technology allows us even to obtain films of thickness $0.2\mu m$ [9,10,11] from these kinds of polymer films, depending on both the viscosity of the deposited material and the acceleration of the spinner system. In this work, the polymer film of PMMA, functionalized with DR1 at 35% molar concentration, was deposited with a thickness $e = 0.635\mu m \pm 2 \cdot 10^{-3}$, measured by a scan step with a resolution of $20A^{\circ}$.

This polymer film supports two TE and two TM modes at the probe wavelength λ= 632.8 nm. We can assume that the x, y and z-axis constitute the principal axis of the refractive index ellipsoid. From the measurements of the effective indices of these 4 modes, it is possible to deduce the refractive indices n_x, n_y, n_z of the polymer film as well as its thickness e. After deposition, the polymer film is heated to 120°C and allowed to cool.

The four effective indices are recorded using the experimental setup shown in Fig. 2. The probe beam, a low intensity cw He-Ne laser (10μW) at wavelength λ_s=632.8 nm, is focused on the sample with the correct angle of incidence to excite guided modes. Birefringence is photo-induced by a pump beam emitted from the green line (λ_p=514nm) of an argon laser linearly polarized along y. This pump beam is directed at the sample at normal incidence, and is large enough to ensure a uniform irradiance throughout the site of the probe beam. The guided modes are detected by the dark lines, which are visible in the transmitted beam profile (probe). The angular positions θ_m of these dark lines (M-lines) are automatically detected with a computer-controlled CCD acquisition system. The measurements of these M-line positions lead directly to the effective indices n^m_{eff} of the guided modes, expressed by the transmission grating equation [12]:

$$\sin(\theta_m) + p\frac{\lambda_s}{\Lambda} = n^m_{eff}, \qquad (1)$$

where Λ is the grating period and p is an integer, numbering the transmitted orders. Throughout pump illumination, M-lines, positions are moving, which allows us to monitor variations in the polymer film refractive indices.

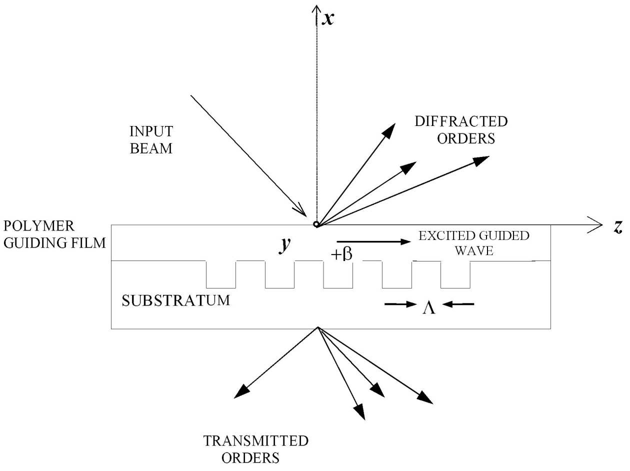

FIGURE 1. Schematic representation of the grating coupler configuration.

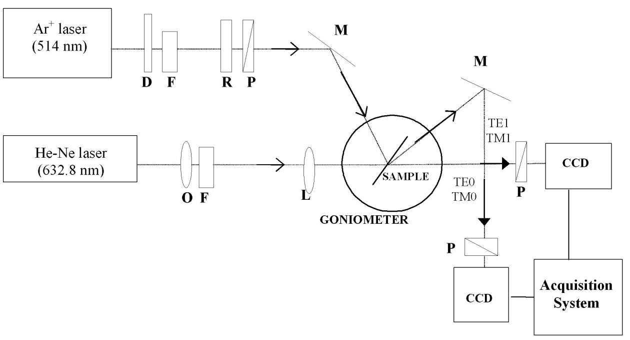

FIGURE 2. ATR configuration for pump-probe experiments. M1, M2: mirrors; F: filters; L: lens; P: linear polarizers; R: quarter-wave plate; C: CCD camera; D: dispersive plate; O: objective.

3. Results and discussion

3.1. Refractive index variation

The results presented in Fig. 3 were obtained using a y-polarized incident pump beam with an incident irradiance of 20.1 mW/cm^2. While a strong decrease ($\Delta n \approx -0.04$) of the refractive index along the pump polarization (n_y) is observed in Fig. 3a, the diminution of the refractive index along the perpendicular axis (n_x) is only 0.002, as we can see in Fig. 3b.

The technique used to measure the index variations does not allow us to derive precisely the refractive index n_z along the propagation axis since, in TE polarization, only n_y is probed while in TM polarization, the electric field is almost parallel to n_x. However, based on symmetry properties of the pumping sequence, x and z-axes are equivalent, so Δn_z=Δn_x.

These results indicate, on the one hand, that by the end of the pumping period, the refractive indices relax to a stationary level. That is, the material does not return to its initial state even after a long stay in darkness. Therefore, a memory effect is obtained. On the other hand, after relaxation, the average refractive index, $\bar{n} = (n_x + n_y + n_z)/3 = (n_y + 2n_x)/3$ does not return to its initial value. A net variation $\Delta\bar{n} \approx -0.025$ is observed.

Besides the index variations, the long-term stability of the refractive index change has been tested. This is proven by the experimental results presented in Fig. 4. During the pumping period, the initial value (A) of the refractive index n_y decreases just to reach point (B). Soon after the pumping period (C), in several minutes, it reaches a quasi-stationary level, which represents 57% of the maximum refractive index change (D). By the end of 24 hours, 39% of the maximum refractive index change remains (E).

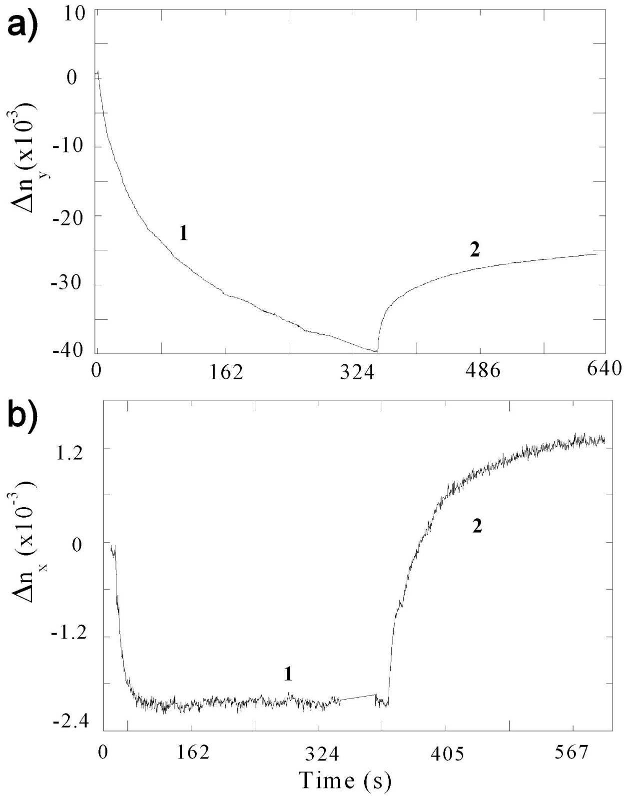

FIGURE 3. Evolution of the photoinduced birefringence in a polymeric thin film, PMMA/DR1 of thickness e=0,635 μm: (**1**) under the pump-on period, (**2**) under relaxation period.

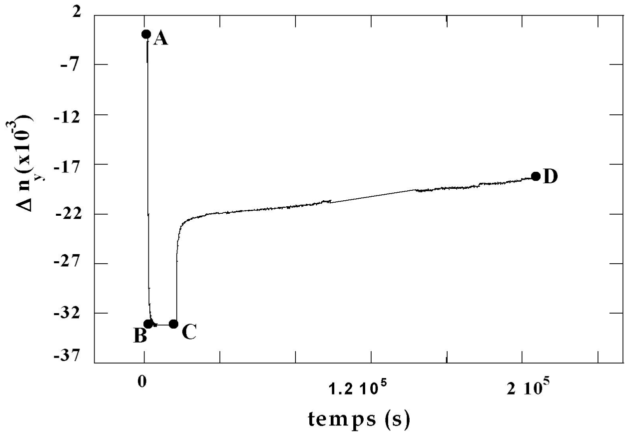

FIGURE 5. Stability of the photo induced birefringence. (A) pump on, (B) minimal index refraction value, (C) pump off, (D) quasi-stationary level, (E) 39% of the maximum refractive index change remains.

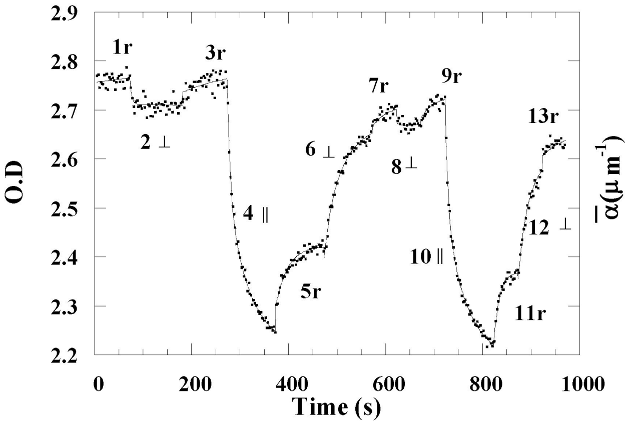

FIGURE 6. Optical density (dotted line) and average absorption (stright line) of a spin-coated polymeric PMMA/DR1 film. Reversal of the photoinduced anisotropy: (||) pump beam parallel to the probe beam. (⊥) pump beam perpendicular to the probe beam. (***r***) relax.

When the homogeneous polymer film is exposed to the linearly polarized pump beam, the film becomes birefringent due to the photo-isomerization of the azo group that occurs almost exclusively for molecules oriented parallel to the pump beam. Based on the observed experimental results, we assume that throughout the pump-on period, the photoinduced birefringence is principally caused by the angular hole burning. Even after the pump-on period, the molecular reorientation seems not to play an important role. Currently admitted models assume that all optically excited molecules rapidly relax to the fundamental "trans" state. According to this model, molecular reorientation should be the only physical mechanism at the origin of photo-induced birefringence. However, molecular rotation cannot modify the average index of the material, and in this case $\bar{n}$ should return to its initial value. Clearly, this is in contradiction with what we have observed. Therefore, our findings indicate that a "permanent" change in molecular state is the main phenomenon at the origin of the observed photo-induced birefringence. Yet, we cannot exclude the possibility that some molecular reorientation process may exist in addition to permanent molecular modification.

3.2. Absorption measurements

The results of the birefringence measured were confirmed by absorption spectra, which were recorded under parallel and perpendicular polarization of the probe and pump beams. These measurements were carried out with the white light emitted from a halogen lamp as the probe, and an Ar$^+$ laser beam of 0.5mW/cm^2 as the pump. While the parallel absorption coefficient undergoes a decrease of nearly 15% of its initial value, the change in the perpendicular absorption coefficient is almost negligible. Like the photoinduced birefringence, the anisotropy in dichroism remains after a long stay of the device in darkness.

It is important to note that the persistent induced anisotropy does not correspond to an irreversible bleaching of the sample. This is proven by the experimental results presented in Fig. 5. This plot shows the change in optical absorption of a probe beam linearly polarized along y (equivalent to n_y measurements). The record shows the response to a sequence of 13 pumping conditions, alternatively "relax" (darkness) and y/z pumping polarizations. The first z pumping (event # 2) does not significantly affect $\bar{\alpha}_y$ in agreement with the results previously shown in this paper. The second pumping (event # 4) is applied along y and induces a strong $\bar{\alpha}_y$ decrease, as was expected. However, the next z pumping (event # 6) roughly restores $\bar{\alpha}_y$ to its initial value. Clearly, the change in absorption (or refractive index) is fully reversible and no molecular destruction or permanent irreversible change is observed.

4. Conclusions

In conclusion, a reversible photoinduced memory effect has been reported in polymeric thin-films of PMMA functionalized with DRI. The results are in good agreement with the previous experiments reported [2,7], and they suggest that a circularly polarized pump erases birefringence but it should induce a decrease in both $n_x$and n_y. The independent index measurements n_x(or $\bar{\alpha}_x)$ and n_y(or $\bar{\alpha}_y)$ permit us to derive new results which can give a new insight into the underlying physical mechanisms responsible for photo-induced anisotropy.

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