

Optimization of azopolymer films for optical memory applications by using ethylene glycol as a free-volume generator

Optimización de films de azopolímero para aplicaciones de memoria óptica, usando etilenglicol como generador de volumen libre

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ABSTRACT: Azopolymers are well known for their photo-induced properties, in particular, the photoinduced birefringence. Improving their performance has been of great interest in recent years for the development of applications as, for example, polarization holography, lithography and optical storage. In this work, we present the optimization of the azopolymer for optical memory applications by using ethylene glycol as a free-volume generator. Thin films were fabricated with Poly[1-[4-(3-carboxy-4-hydroxyphenyl-azo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) and ethylene glycol at different % w/w concentrations. Samples were characterized by measuring the birefringence during recording, relaxation and erase cycles. The measured glass transition temperature (T_g) showed a minimum for the concentration 40 %w/w, at which the degree of decay, $D = 1 - \Delta n_{REM} / \Delta n_{MAX}$, reaches a maximum. Birefringence was also simulated using a stochastic model that includes the key factors involved in the recording process. We show that the material can be optimized for optical memories storage applications by balancing the free volume with the azobenzene concentration. This causes a decrease in the amount of azobenzenes while maintaining the efficiency of the samples.

Key words: Azopolymer, Birefringence, Free Volume, Optical Memories

RESUMEN: Los azopolímeros son conocidos por sus propiedades ópticas, en particular la birrefringencia fotoinducida. Mejorar su rendimiento ha sido de gran interés en los últimos años para el desarrollo de aplicaciones que van desde memorias ópticas hasta litografía. En este trabajo, presentamos la optimización del azopolímero para aplicaciones de memoria óptica, utilizando etilenglicol como generador de volumen libre. Se fabricaron láminas delgadas compuestas por Poly[1-[4-(3-carboxy-4-hydroxyphenyl-azo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO) y etilenglicol a diferentes concentraciones % w/w. Las muestras fueron caracterizadas midiendo la fotoinducción de birrefringencia durante los procesos de grabado, relajación y borrado. La temperatura de transición vítrea (T_g) alcanzó un mínimo para una concentración de 40 %w/w, correspondiente a un máximo en el grado de decaimiento, $D = 1 - \Delta n_{REM} / \Delta n_{MAX}$. Además, se simuló la birrefringencia inducida utilizando un modelo estocástico que tiene en consideración los factores clave en la generación del proceso de grabado. Mostramos que el material puede ser optimizado para aplicaciones en memorias ópticas al balancear el volumen libre con la concentración de azobenceno. Esto corresponde una disminución de azobencenos, manteniendo la eficiencia de las muestras.

Palabras clave: Azopolímero, Birrefringencia, Volumen Libre, Memorias Ópticas

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1. Introduction

Azobenzene-functionalized polymers (azopolymers) have been of great interest in the last years because their photosensitive response leads to a wide range of applications, for example, polarization holography, optical storage, lithography and as actuators of nanoscale objects [1-7].

Azobenzene *trans-cis* isomerization is a photochemical process that leads to the main photo-induced properties of azopolymers. By absorbing photons at a particular wavelength, the azobenzene undergoes a continuous cycle between two conformational states: the fundamental (*trans*) and the excited (*cis*) state.

The main photo-induced properties that are observed when azopolymers are illuminated with polarized light are the induced birefringence and mass transport. The first one results from a combination of the rapid stochastic movements of the azobenzene molecule and the photon absorption probability. This probability is proportional to the square cosine of the angle (Ω) between the incident electric field (\vec{E}) and the transition dipole moment of the molecule (\vec{p}), which is approximately parallel to the long axis of the azobenzene [8]. During photoisomerization, the conformational change leads to a random reorientation of the azobenzene transition dipole moment. This reorientation will occur continuously while the molecule absorbs photons until its transition dipole moment is perpendicular to the incident electric field, where the absorption probability becomes zero. This means that although the rotation of the long axis of the azobenzene is random, after some time, the resultant effect is an accumulation of *trans* azobenzene molecules in the direction with the lower absorption probability (perpendicular to \vec{E}). Because of this photo-selective orientation, the azopolymer becomes optically anisotropic (birefringent).

The second photo-induced property that some azopolymers exhibit, occurs when they are illuminated with a spatial distribution of intensity, phase, or polarization. The mass migrates from the highly illuminated areas on the sample to the darker ones, with higher efficiency when the polarization is parallel to the intensity gradient [9]. When the sample is illuminated by an interference pattern, this phenomenon produces a surface relief grating (SRG), which had been broadly studied in previous works [6,10-12].

Many factors affect the photo-induced birefringence, such as temperature, chemical structure of the azobenzenes derivatives and free volume in the polymer matrix [13-15]. In particular, the free volume plays a fundamental role in photo-induced birefringence recording efficiency, since azobenzene molecules need a minimum free volume to isomerize. The free volume of a polymer can be increased by artificially expanding the distance between the polymer chains. It has been shown that the addition of nanoparticles or plasticizers [11,16-18] can be used as nanospacers of the polymer chains, therefore increasing the free volume.

Different models have been developed to describe and characterize photo-induced anisotropy. For example, Sekkat *et al.* [19] modelled the angular redistribution by the definition of rate equations and the use of Legendre polynomials. Palto *et al.* [20] made a simulation of the reorientation of azobenzene molecules based on the excitation-driven rotational diffusion of the molecules in the potential of their neighbours. Ebralidze *et al.* [21] proposed a model where the anisotropy in azo dye-coloured films is attributed to the generation of anisotropic grains. The photo-induced anisotropy in azopolymers has also been simulated using a Monte Carlo approach [22,23]. In that case, a set of probabilities is assigned to the



photoisomerization and thermal diffusion processes. After several iterations, the final orientation of the azobenzene molecules determines the anisotropy in the system.

In this work, we study the effect of the free volume on the photo-induced birefringence in an azopolymer film, both by experimentation and simulations. We show that the material can be optimized for optical memory storage applications by balancing the free volume with the azobenzene concentration. This causes a decrease in the amount of azobenzenes while maintaining the efficiency of the samples. A reduction of the azobenzene molecules is beneficial because they are not environmentally friendly, and they are toxic to humans. Also, the final cost of the film is reduced since the relative cost of the PAZO with respect to the other components of the film is high. In section 2 we present numerical results of photo-induced anisotropy in an azopolymer, using a stochastic model where photoisomerization, rotational diffusion and free volume are considered. In section 3, we describe the preparation of azopolymer films, using ethylene glycol as a plasticizer with the goal of increasing the free volume. A description of the experimental setup used to measure the induced birefringence is also provided and the measurements and results are presented. At last, in section 4, we present the conclusion of this work.

2. Optical induced anisotropy simulations

To describe the azobenzene orientation under a uniform illumination, we developed a Monte Carlo model that captures the main characteristics of the photo-induced birefringence dynamics. In this model, a set of probabilities are defined to take into account the relevant processes involved in the photo-induced birefringence: the probability that an azobenzene photoisomerizes, the probability that there is enough free volume to isomerize and the probability that the azobenzene orientation changes due to thermal diffusion (rotational diffusion). Fig.1 shows a typical scheme of an azobenzene molecule in *trans* state, where the vector \vec{d} represents the long axis direction of the molecule, and consequently its transition dipole moment.

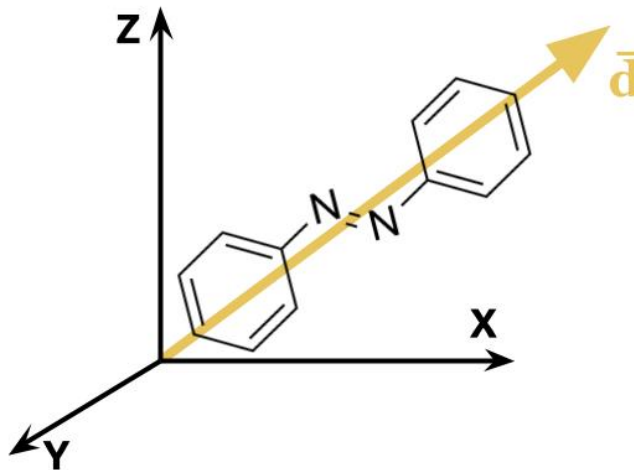


Fig.1. Scheme of an azobenzene molecule in *trans* state, where the vector \vec{d} corresponds to the long-axis direction.

Without illumination, the most probable state of the azobenzenes is the *trans* state with their long axis randomly oriented, therefore the azopolymer is isotropic. To simulate this initial condition, we generate $N=5000$ azobenzenes randomly oriented (N vectors \vec{d} with random orientations), located in an equally spaced mesh. This is schematized in Fig. 2(a), where the green arrows correspond to the \vec{d} vectors and the electric field (\vec{E}) is shown in the \hat{x} direction.

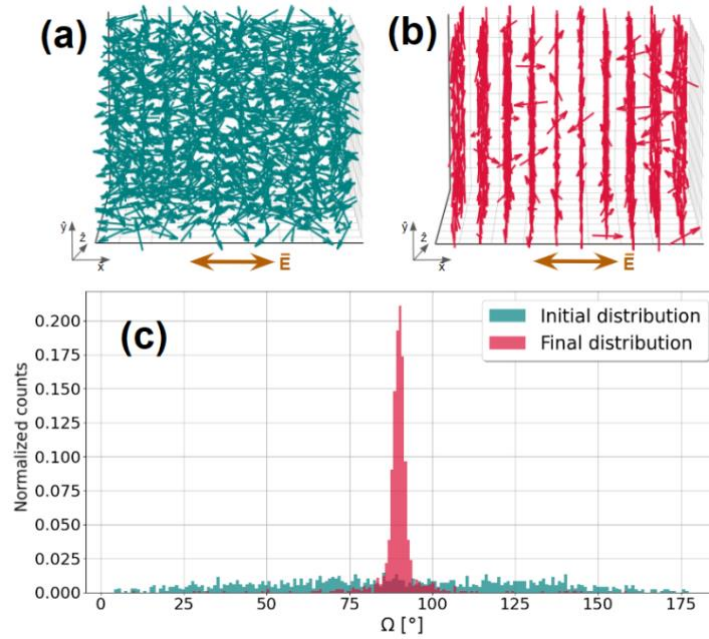


Fig.2. The initial (a) and final (b) orientation of the azobenzene molecules simulated with the probabilistic model. Also, an histogram of the angle Ω for the initial (green) and final (red) configurations.

In each iteration, an azobenzene molecule has a probability of having enough free volume to isomerize (P_{FV}), and a probability of photoisomerization (P_w) given that it absorbed a photon. These two probabilities are key for the azobenzene photoorientation. However, thermal processes such as diffusion (specifically rotational diffusion) compete with ordering processes such as photo-selective orientation. As it was explained before, after many photoisomerization cycles, the molecules tend to align perpendicular to the electric field, therefore making the bulk material anisotropic. This is schematized in Fig. 2(b), where most of the azobenzenes, represented as red arrows, are orientated perpendicular to the electric field in the final step of the simulation. The apparent organization is an artifact of the simulation that arises from the fact that the original positions are equally spaced instead of being randomly oriented. In Fig. 2(c), the distribution of Ω at the initial and final step of the simulation is shown. An increase in the concentration of azobenzenes at an angle Ω around 90° (perpendicular to \vec{E}) is archived. Consequently, we can define an order parameter (Δ_o) which is a measurement of the anisotropy, as the difference between the projection of \vec{d} in the directions parallel (d_{\parallel}) and perpendicular (d_{\perp}) to the electric field, as

$$\Delta_o = \frac{\sum^{N_T} d_{\perp} - \sum^{N_T} d_{\parallel}}{N_T} \quad (1)$$

where N_T is the number of *trans* azobenzenes and the modulus of \vec{d} is arbitrary set to 1. Because the *cis* azobenzene has spherical symmetry, its contribution to the order parameter can be neglected [22].

When the azobenzene photoisomerizes, a rotation of the azo group (-N=N-) occurs producing a conformational change. The probability of photoisomerization, P_w , depends on the illumination intensity on the molecule I and the angle between the electric field and the molecules transition dipole moment, Ω , as [19]

$$P_w = \gamma_w \cos^2(\Omega) I, \quad (2)$$

where γ_w includes the quantum yield and the absorption cross section of the azobenzene molecule. This factor can be different if the transition is from the state *trans* to *cis* (γ_{TC}) or the other way, from *cis* to *trans*

(γ_{CT}). Also, in the case of the transition *cis* to *trans*, P_w does not depend on $\cos^2(\Omega)$. In the simulations performed in this work, we fix $\gamma_{TC} = \gamma_{CT} = 0.5$ and $I = 1$.

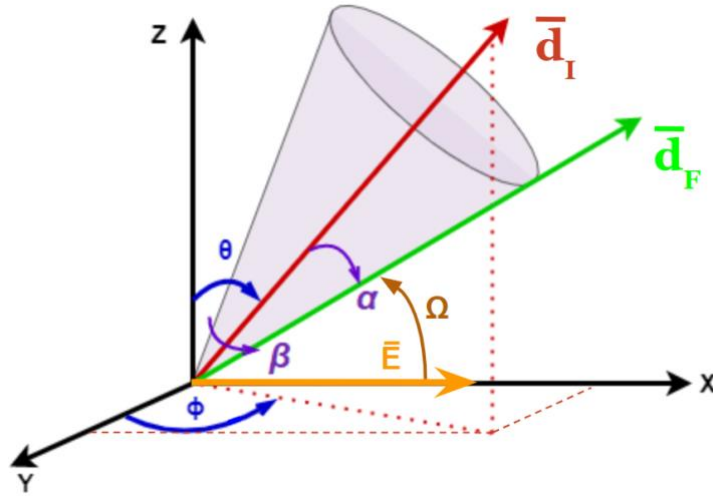


Fig.3. Coordinate system used to describe the rotation of the azobenzene molecule, where β is an angle between $[0, 2\pi)$, and α depends on the reorientation process. The red (\bar{d}_I) and green (\bar{d}_F) arrows are the initial and final orientation, respectively. The direction of the electric field (\bar{E}) in \hat{x} is also shown.

Fig. 3 schematizes the coordinate system used to describe the rotation of the azobenzene molecule. First consider that the long axis of the azobenzene, defined by the vector \bar{d}_I (red arrow in Fig. 3), is oriented at an angle Ω with respect to the electric field $\bar{E} = E \hat{x}$. Since its modulus is arbitrarily set to 1, \bar{d}_I is only determined by its orientation in spherical coordinates, then, by the angles θ and ϕ . When the molecule photoisomerizes, its long axis rotates to a new orientation (green arrow, \bar{d}_F , in Fig. 3). This reorientation is a composition of two rotations in three dimensions. The first one is a clockwise rotation at an angle α in $[0, \pi]$ on the plane defined by \bar{d}_I and \bar{E} . The second one is a rotation at an angle β in $[0, 2\pi)$ respect the initial orientation axis, \bar{d}_I . In the simulations, β will always be a random angle between 0 and 2π , while the angle α will be different if the rotation is due to photoisomerization or rotational diffusion. For the photoisomerization process, the angle α will be fixed at 56.7° [24].

The other phenomenon we take into consideration is rotational diffusion, a random rotation due to thermal agitation. We will assume the shape of the *trans* azobenzene as an ellipsoid of volume V , with a the length of two of its semiaxis and b the length of the longer axis [22]. The shape of the *cis* azobenzene will be considered as a sphere of radius R [22]. Using the Einstein-Stokes theory, the diffusion coefficients of the azobenzenes are, $D_{rot}^{Sph} = \frac{k_B T}{8 \pi \eta R}$ and $D_{rot}^{Ell} = \frac{k_B T}{6 \eta V G(\phi)}$ [25], for the *cis* and *trans* isomers respectively, where k_B is the Boltzmann's constant, T the temperature and η the viscosity. The function $G(\phi)$ is defined as

$$G(\phi) = \frac{2}{3} \frac{\phi^4 - 1}{\phi \left[\frac{2\phi^2 - 1}{\sqrt{\phi^2 - 1}} \ln(\phi + \sqrt{\phi^2 - 1}) - \phi \right]} \quad (3)$$

with $\phi = a/b$. The reorientation of the dipole moment due to rotational diffusion occurs in each iteration. In the simulations, α will be a random angle taken from a Gaussian distribution with a variance determined by the diffusion coefficients, $a = 0.7$ nm, $b = 1.5$ nm, $\eta = 0,01$ Pa s and $T = 300^\circ$ K.

In order for the azobenzene to perform the fast movements that occur during photoisomerization and reorientation, a certain free volume in the polymer matrix should be available [16]. The larger the free volume, the easier for molecules to diffuse through the polymer. Increasing the size and number of the free-

volume elements would allow faster diffusive rotation, reorientation and photoisomerization, and a higher number of allowed azobenzene available to photoisomerize.

If the mean free volume (V_M) in the polymer is less than the critical volume (V_C), the azobenzenes will not be able to photoisomerize. We will assume that the volume of the free-volume elements follows a Gaussian distribution with mean V_M and variance ΔV . The probability that the azobenzene has the necessary volume in its surroundings to be able to photoisomerize, is the cumulative probability that results from integrating the probability distribution for volumes higher than V_C [15],

$$P_{FV} = \frac{1}{2} \operatorname{erfc} \left(\frac{1 - \frac{V_M}{V_C}}{\Delta V_O} \right), \quad (4)$$

where $\Delta V = \Delta V_O T$, with ΔV_O a thermal fluctuation coefficient and erfc is the complementary error function. This probability determines, at the beginning of each simulation, the number of azobenzene molecules that are allowed to photoisomerize. The thermal fluctuation coefficient will be fixed as $\Delta V_O = 0.004$ [15] and $V_C = 1$.

Fig. 4 shows Δ_o for different values of V_M . As it can be expected, the higher V_M , the higher the number of azobenzenes that are allowed to photoisomerize and then the higher the maximum asymptotic value of Δ_o .

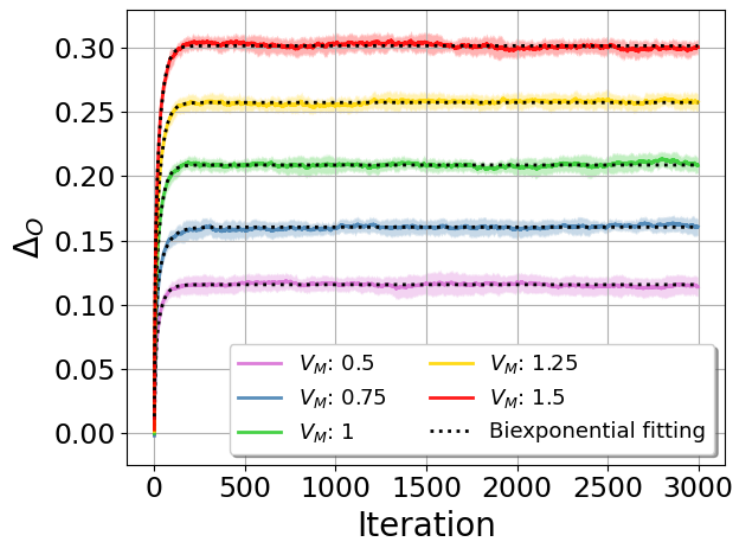


Fig.4. Δ_o anisotropy curves for different V_M parameter simulations. The shadowed area corresponds to the standard deviation.

In general, the growth of the induced birefringence in time can be fitted by an empirical model that consist of the addition of two exponential functions (biexponential model) [11],

$$\Delta n_{\uparrow}(t) = A \left(1 - e^{-\frac{t}{t_A}} \right) + B \left(1 - e^{-\frac{t}{t_B}} \right) + C, \quad (5)$$

Fig. 4 also shows that the simulated Δ_o can be fitted correctly using this model (dashed lines). This means that this model correctly captures the behaviour of the induced birefringence when the main process involved are the photoisomerization, free volume and rotational diffusion.

3. Experiment

We study experimentally the effect of the free volume on the induced birefringence, by measuring the recording-relaxation cycles on samples prepared with different concentrations of ethylene glycol. The ethylene glycol, normally used as plasticizer, is expected to increase the free volume and the photo-induced anisotropy.

3.a. Azopolymer Films Preparation and characterization

Azopolymer-ethylene glycol films were fabricated at different percent weight to weight (%w/w, mass of solute in a given mass of solution). The azopolymer used was the Poly[1-[4-(3-carboxy-4-hydroxyphenyl-azo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] (PAZO), which is available at Sigma Aldrich. The chemical structure and the absorbance spectrum of PAZO is shown in Fig. 5(a), with a peak absorbance at 360 nm.

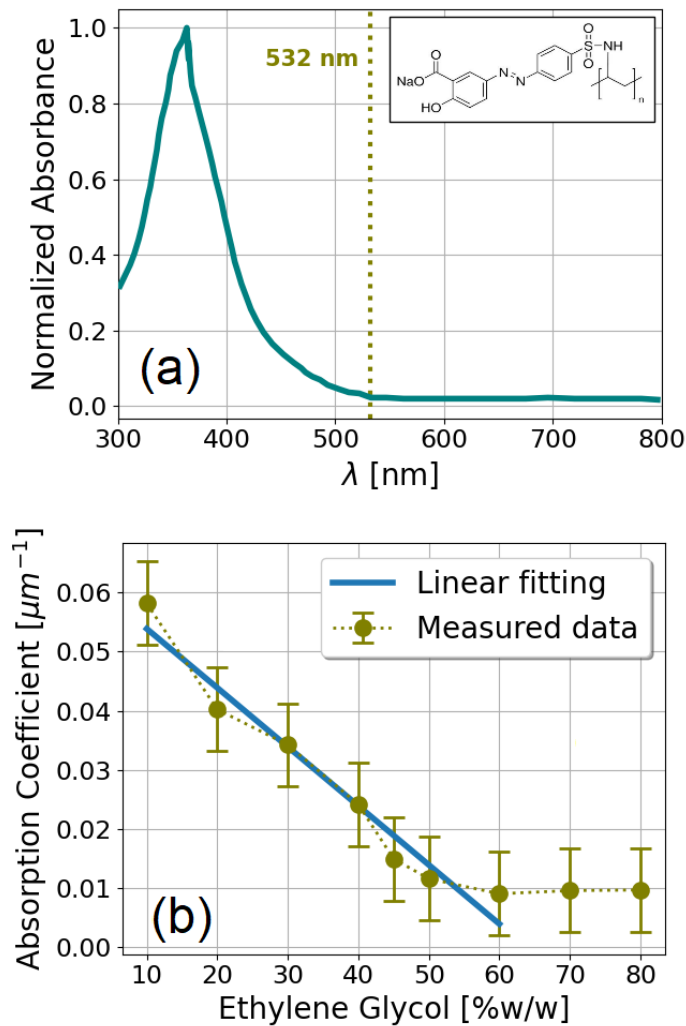


Fig.5. Chemical structure of the PAZO polymer and absorbance curve of PAZO (a) and absorption coefficient at $\lambda = 532\text{nm}$ (c) for different concentrations. Dashed lines are only for visual help.

PAZO and ethylene glycol were dissolved in methanol in an ultrasonic bath. Films were prepared by spin coating on a 22x22 mm coverslip glass. Different numbers of 100 μl drops were spin coated at 1800 rpm to control the thickness of the films. Finally, the films were baked under a vacuum for 17 hours with a stepped rising temperature (12 hours at 30°C and three 1-hour steps at 40°C, 50°C and 60°C, and finally 2 hours at 80°C). The thickness of each sample was measured from the images of their cryogenic fractures using a scanning electron microscope (SEM). Samples with thickness in the order of 1 μm , within a 10% error were

selected. Fig. 5(b) shows the absorption coefficient for different %w/w concentrations at $\lambda=532$ nm. According to Beer-Lambert law, the absorption coefficient is linearly related to the concentration, so a linear fitting was done up to 60 %w/w with a $r^2=0.96$. For higher concentrations, the resolution limit was reached resulting in a constant value.

The glass transition (T_g) for each sample was determined from Differential Scanning Calorimetry (DSC) measurements, as is shown in Fig.6. As was explained before, the addition of ethylene glycol should produce an increase in the free volume. Then, a decrease of the T_g with the addition of plasticizer is expected since the free volume depends inversely on the experimental T_g [26]. As is observed in Fig. 6, the T_g decreases linearly as ethylene glycol increases up to 40 %w/w, where T_g reaches a minimum. A linear fit with $r^2=0.96$ is also shown. This linearly decrease is expected, as it has already been reported in Ref. [27].

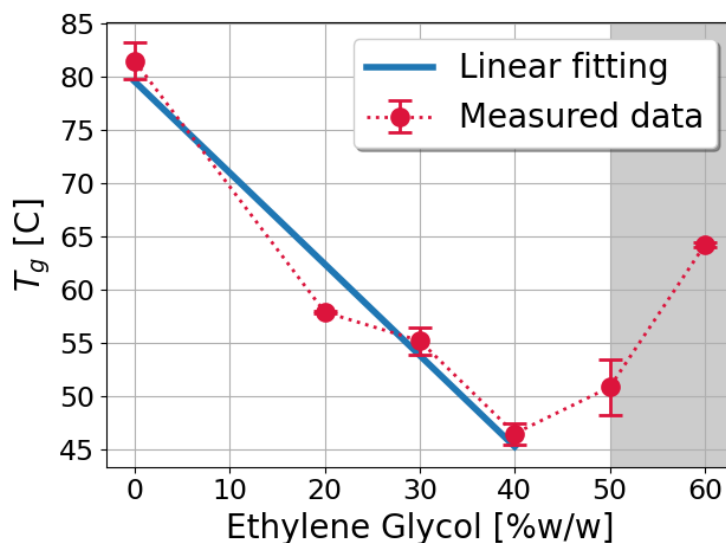


Fig.6. T_g as a function of the %w/w Ethylene Glycol concentrations. A linear fit up to 40 %w/w is also shown, with a $r^2=0.96$. Dashed lines are only for visual help.

Samples with concentrations equal or greater than 70 %w/w, might not form a homogeneous film due to the high ethylene glycol content, making the identification of T_g in the DSC curves impossible. It is expected that for a system with high plasticizer concentration, 50 % w/w and more (grey shadow in Fig.6), the linear behavior is no longer observed. For these concentrations, the ethylene glycol does not act as a plasticizer as the molecular interaction cannot be neglected [28]. Despite the high ethylene glycol percentages, the PAZO continues giving the solid structure for the films.

3.b. Birefringence characterization

The induced birefringence was induced by illuminating the sample with a linear polarized 473 nm laser (writing beam), while the measurement of the induced birefringence was done by using a 633 nm linearly polarized laser (reading beam). Both lasers were chosen considering the absorption spectra of the azopolymer (see Fig. 5(b)). The experimental setup is shown in Fig. 7. The 473 nm laser beam was spatial filtered and then amplified by using a telescope (L1 and L2) and a pinhole (PH). A linear polarizer (P1) was used to configure the polarization of the beam in the direction \hat{x} . The sample (A) was illuminated at normal incidence. The angular position of the half-wave plate (WP1) optical axis was chosen to achieve a maximum intensity over the sample. The sample was illuminated with a 25 mW beam over a 2.5 mm diameter area.

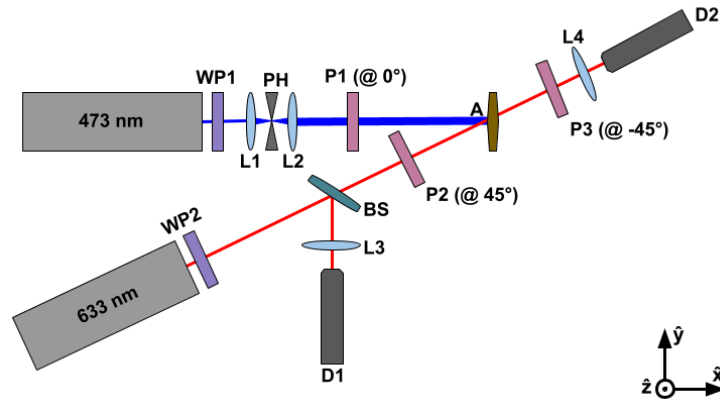


Fig.7. Schematic of the optical system used to induce and measure the induced birefringence: WP, half-wave plate; P, polarizer; L, lens; PH, pin-hole; A, azopolymer sample; BS, beam-splitter; D, detector.

In order to compensate for possible fluctuations in the reading intensity, the 633 nm laser beam was divided into two paths using a beam-splitter (BS). In the first one, the beam was focused by a lens (L3) on a photodiode (D1) to measure an intensity proportional to the laser intensity (I_L). The azopolymer film was positioned on the second path between two cross polarizers (P2 and P3). A half-wave plate (WP2) was used to increase the transmission of the laser beam through P2. The transmission axis of P2 was placed at 45° from the transmission axis of P1. Then, the reading beam was focused by a lens (L4) in a photodiode (D2) to measure the transmitted intensity through P3 ($I(t)$).

In Fig.8 an example of the writing, relaxation and erase processes on the sample is shown. Before the writing beam is switched on, the sample is isotropic, meaning that the polarization of the reading beam is not affected by the film. Because the transmission axis of P2 and P3 are perpendicular to each other, no intensity is measured by D2. When the writing beam is switched on, the azopolymer film becomes anisotropic so it can change the polarization state of the reading beam. As the azobenzene molecules orient perpendicular to the writing beam polarization, the transmitted intensity through P3 increases until it reaches an asymptotic value, known as maximum birefringence (Δn_{MAX}). The birefringence (Δn) is related to the measured intensity by [29]

$$I(t) = I_o \sin^2 \left(\frac{\pi \Delta n(t) d}{\lambda} \right), \quad (6)$$

where d is the thickness of the sample, λ the reading wavelength (633 nm) and I_o the intensity on D2 measured without the sample and with the transmission axes of P2 and P3 parallel. Absorption and reflection coefficients of the different optical elements were taken into consideration to properly calibrate the intensity on D2 to measure I_o . The inhomogeneities in the azopolymer are averaged in the illuminated area by the reading beam.

When the illumination is switched off, some azobenzenes change their orientation due to thermal relaxation. The measured intensity by D2 starts to decrease until it reaches a constant value, known as the remanent birefringence (Δn_{REM}). Finally, the sample is erased using circular polarized light, by adding a quarter-wave plate after P1, with its fast axis at 45° from the transmission axis of P1. As was mentioned in section 2, the evolution of the induced birefringence while the sample is illuminated is usually fitted by a biexponential function. However, we observed that a triexponential function such as

$$\Delta n_{\uparrow}(t) = A(1 - e^{-\frac{t}{t_A}}) + B(1 - e^{-\frac{t}{t_B}}) + C(1 - e^{-\frac{t}{t_C}}) + D, \quad (7)$$

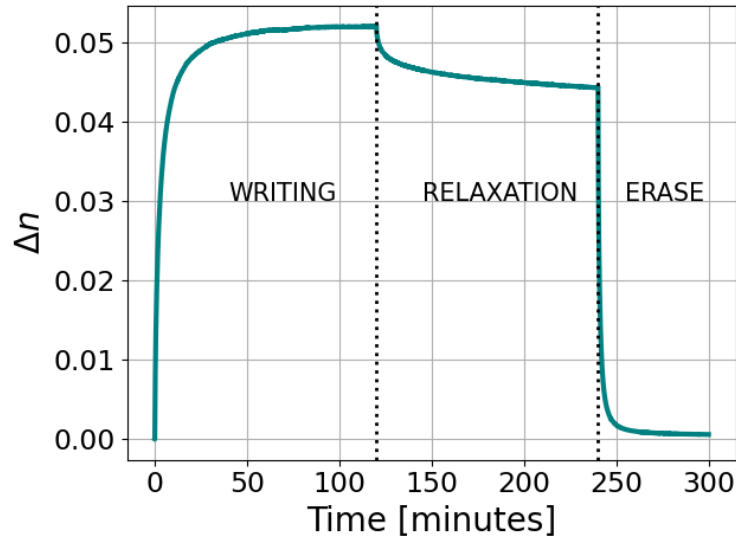


Fig.8. Photo-induced birefringence during writing, relaxation and erasing, for a sample with a 50 % w/w concentration and a thickness of $0.93 \pm 0.05 \mu\text{m}$.

fits better the measurements. This implies that there is another process involved which was not considered neither in the anisotropy simulations nor in the biexponential phenomenological model. Further study of this phenomenon will be done in future works. Regarding the relaxation process, the measurements still fit correctly with a biexponential function [11],

$$\Delta n_{\perp}(t) = E e^{-\frac{t}{t_E}} + F e^{-\frac{t}{t_F}} + G, \quad (8)$$

In both cases, the constants A, B, C, D, E, G are fitting parameters, as well for their correspondent's characteristic times t_k . The sum (A+B+C+D) corresponds to the maxima of the induced birefringence, Δn_{MAX} , and G to the remanent birefringence, Δn_{REM} . In Fig. 9, Δn_{MAX} and Δn_{REM} are shown for different %w/w concentrations. As it can be seen on the figure, the effect of the free volume is not observed since the birefringence is constant within the experimental errors of the order of 10%.

The performance of the material as an optical memory is characterized by the degree of decay $D = 1 - \Delta n_{REM} / \Delta n_{MAX}$, a factor independent of the sample thickness. In Fig. 9(b), the factor D is shown for different %w/w concentrations. As explained in section 3.a, the free volume in a polymer is inversely proportional to the experimental T_g , and consequently, T_g is inversely proportional to the ethylene glycol concentration (Fig.6). In Fig.9(b) an inverse behavior to the T_g is also observed: the factor D increases until it reaches a maximum at 45 %w/w, meaning that the changes in D are caused by the free volume in the sample. The low fluctuation of the values up to 30 % w/w, means that the decrease in azobenzene concentration is compensating for the increase in the free volume. Consequently, it is possible to produce a material with the same performance as an optical memory with a reduced amount of azobenzenes. For higher concentrations, the increase in free volume results in a higher difference between Δn_{MAX} and Δn_{REM} , meaning that the material is not optimized for optical memories. Even though an increase of the free volume can produce bigger values of Δn_{MAX} , it also allows for higher mobility of the azobenzenes, further reducing Δn_{REM} . The factor D decreases from 45 % w/w to 60 %w/w, and for concentrations higher than 60 %w/w, it has similar values than the ones observed up to 30 %w/w. However, as was already mentioned, for concentrations higher than 50%w/w, ethylene glycol no longer acts as a plasticizer, as it increases the molecular interactions, restricting the mobility of the polymer.

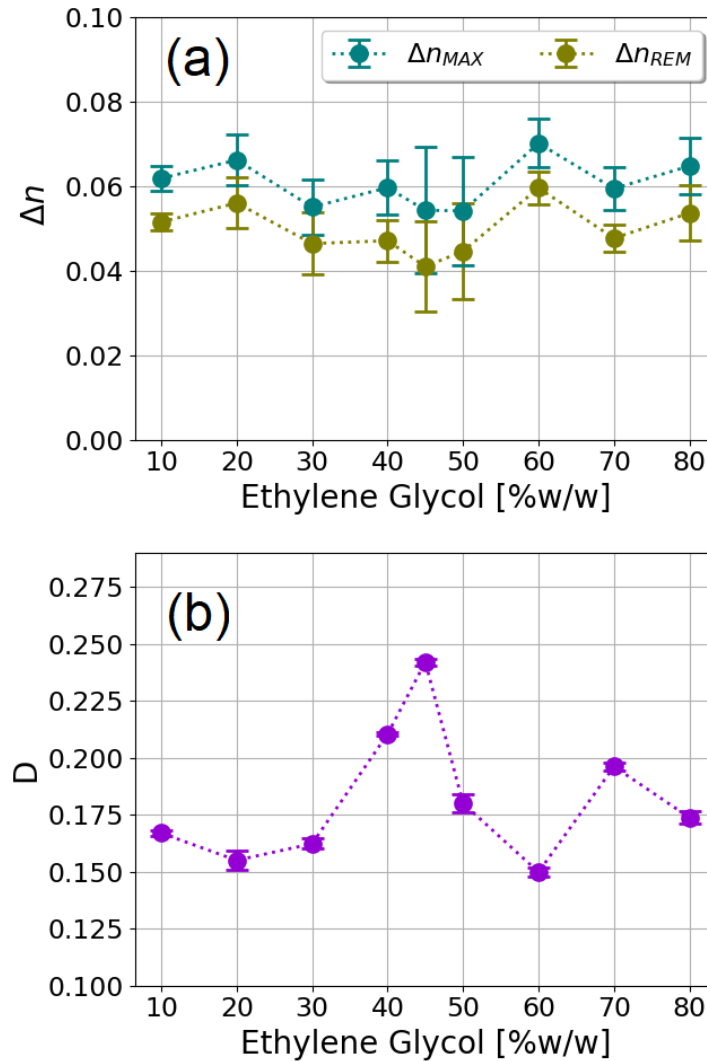


Fig.9. Δn_{MAX} and Δn_{REM} (a) and the and the $\Delta n_{MAX} / \Delta n_{REM}$ ratio (b) for different PAZO - Ethylene Glycol concentrations. Dashed lines are only for visual help.

4. Conclusions

In this work we used ethylene glycol as a free-volume generator in PAZO films. Thin films of azopolymer were fabricated with PAZO and ethylene glycol at different %w/w concentrations. DSC measurements showed a decreasing T_g up to 40 %w/w, that means that the free volume increases up to the same concentration. We show that as a consequence, the induced birefringence degree of decay increases with the ethylene glycol concentration up to a measured concentration of 45 %w/w.

Stochastic simulations were performed by considering the key factors in the photoinduced anisotropy. The simulations agree with the biexponential empirical model, however, the evolution of the induced birefringence under illumination behaved as a triexponential. This implies that there is another process that is not taken into account neither in the anisotropy simulations nor in the biexponential empirical model. Further study of this phenomenon will be performed in future works.

We observed that the increase in the free volume does not affect the performance of the azopolymer for optical memory usage up to 30 % w/w. In fact, free volume can compensate for the decrease in azobenzene concentration allowing the same performance as optical memory with a smaller number of chromophores.

For concentrations around 45%w/w, the material is not optimized for optical memories, as the degree of decay factor is higher, meaning that the difference between the maximum and remanent birefringence increases. For concentrations greater than 60 %w/w the degree of decay becomes similar to the ones observed up to 30 %w/w. Nevertheless, the ethylene glycol acts as a plasticizer up to the 50 %w/w concentration.

As a consequence, plasticizers can be used as free-volume generators, and their effect can be balanced with the number of chromophores to produce materials with optimal performance as optical memory storage but minimizing the azobenzene concentration.

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