Optical storage in azobenzene-containing epoxy polymers processed as Langmuir Blodgett films

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ABSTRACT

In this study, azocopolymers containing different main-chain segments have been synthesized with diglycidyl ether of bisphenol A (DGEBA, DER 332, $n = 0.03$) and the azochromophore Disperse Orange 3 (DO3) cured with two monoamines, viz. benzylamine (BA) and m-toluidine (MT). The photoinduced birefringence was investigated in films produced with these azopolymers using the spin coating (SC) and Langmuir Blodgett (LB) techniques. In the LB films, birefringence increased with the content of azochromophore and the film thickness, as expected. The nanostructured nature of the LB films led to an enhanced birefringence and faster dynamics in the writing process, compared to the SC films. In summary, the combination of azocopolymers and the LB method may allow materials with tuned properties for various optical applications, including in biological systems were photoisomerization may be used to trigger actions such as drug delivery.

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1. Introduction

The photoisomerization of azobenzene-containing materials has been known for several years but only recently has this process been applied to biological systems. The fundamental challenge of coupling the photoisomerization process to a large functional change in a biomolecule has been fulfilled in many instances, and it appears that the effective photocontrol of biomolecules might be possible [1,2]. Several new possibilities can be envisaged with photoisomerization in biologically-relevant systems, including the use of photocontrol for drug delivery. In all such applications, in addition to the search for novel materials displaying the required optical properties, one important issue is related to the degree of control over molecular architecture, which is not offered by the conventional casting and/or spin coating fabrication methods of polymeric films. Higher degree of molecular control can be reached with film fabrication techniques where the polymer chains may be deposited in a layer-by-layer fashion, as in the case of Langmuir Blodgett (LB) films or electrostatically assembled layer-by-layer (LbL) films [3–8]. These techniques allow for control at the molecular level, yielding nanostructured films with controllable thickness and architecture. LB films built with conventional amphiphilics may be highly organized with a structure comprising layers with crystalline order, but those obtained from polymers have no order in the plane. In this case, organization is mainly caused by the layer-by-layer nature of the films [9].

For optical storage, for example, higher birefringences are normally reached with thin LB films owing to their layered nature. To reach the orientation responsible for the birefringence, azobenzene chromophores have to move cooperatively, and their motion depends on the neighboring molecules. The presence of the substrate (for monolayers especially) has a significant influence on the motion of the molecules directly in contact [10]. In the LB method, an insoluble layer of the material spread on an aqueous subphase is transferred onto a solid substrate by dipping the substrate vertically across the film at the air/water interface. Repeated dipping cycles of the same substrate lead to multilayer films. The photoinduced birefringence has been found to decrease with the number of layers in the LB film because some order is lost when certain number of layers is exceeded [9]. The difference in behavior of these materials and their films is given by the difference in packing.

In a previous publication [11] we synthesized epoxy polymers containing azo groups covalently linked, with the amines benzylamine (BA) and m-toluidine (TA) used as hardeners. Materials with different chemical structures and azo group concentrations were prepared and characterized. With regard to their optical storage properties, the maximum birefringence obtained increased linearly with the weight fraction of the azo groups, regardless of the power of the writing beam and of the interactions between the dyes and their environment [11,12]. The residual birefringence after relaxation was smaller in

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BA-based copolymers with lower Tg, in comparison with MT-based copolymers. In this study, the azobenzene-containing epoxy polymers were processed as thin films by spin coating or with the LB technique. The aim was to evaluate improvements in the optical storage properties of the polymer caused by manipulation in nanostructured films, which could be useful in producing optical memories or other optical devices.

2. Experimental

2.1. Materials

A difunctional epoxy resin, diglycidyl ether of bisphenol A (DGEBA, DER 332, $n = 0.03$), with an epoxy equivalent of 175 g/eq, kindly provided by Dow Chemical, was used. The azochromophore Disperse Orange 3 (DO3) was supplied by Aldrich and tetrahydrofuran (THF) was purchased from Panreac. The reactants and solvent were used as received with no further purification. The epoxy-based azocopolymers were synthesized following the procedure described elsewhere [11]. First, a thermoplastic precursor modified with azobenzene groups (TAZ) was synthesized through reacting DO3 and DGEBA. A stoichiometric ratio DO3 eq/DGEBA eq = 0.5 was used to generate a reaction product with epoxy groups at the end of the chains. A selected amount of the resulting TAZ, with a chromophore concentration per weight relative to the polymer backbone of 26 wt.%, was blended with the same amount of DGEBA and benzylamine (BA, Fluka) or m-toluidine (MT, Fluka). A total epoxy/amine stoichiometric relation r = 1 was selected in order to prepare two azocopolymers containing different side chains segments (TAZ50/DGEBA/BA and TAZ50/DGEBA/MT). The chemical structures of the reactants and the final properties of the polymers were reported in previous works [11,12].

2.2. Fabrication of spin coated and Langmuir Blodgett films

Spin coated (SC) films were prepared with a P6700 spin coater from Specialty Coating System Inc. from 5 wt.% azocopolymer solutions in THF onto clean glass slides, following a method previously described [12]. Langmuir films were prepared in a Langmuir trough model KSV5000 from KSV Instruments (Finland). A typical solution concentration was 1 mg/mL, and ca. of 100 μL were spread at the air–water interface. After chloroform evaporation, the films were compressed with movable barriers at 20 mm/min. Surface pressure-area (π-A) isotherms were measured using a Wilhelmy plate made of filter paper and the curve was computer-recorded. Pure water provided by a Milli-Q purifier, with a resistivity of 18.3 MΩ·cm, was used as subphase. All the isotherms were measured inside a class 10,000 clean room, with the temperature controlled at 21 ± 1 °C.

The pre-formed Langmuir monolayers of TAZ and the azocopolymers were transferred onto solid substrates in the form of Langmuir Blodgett films (LB). The BK7 glass slides used as substrates were cleaned with a 2% ethanolic KOH solution diluted with 10% of water. The deposition pressure was 30 mN/m in most cases, with only a few depositions being conducted at 20 mN/m. The dipper speed for downstrokes and upstrokes was continuously tuned in the range between 2 and 5 mm/min in order to obtain a transfer ratio around 1. LB films with several numbers of layers were produced for each material. The film thickness of LB films was obtained with ellipsometry using a Semilab Sopra GES-5E ellipsometer from Telstar, leading to values from 112 ± 3.1 to 170 ± 4.5 nm. Homogeneous thin films were obtained by spin coating, with typical thickness of 500 ± 100 nm, determined with atomic force microscopy (AFM) using a Nanoscope IIIa scanning probe microscope (Multimode™, Digital Instruments). The thickness was obtained from the topographic AFM images of scratched films, from the difference in height between a flat area of the sample and the surface of the clean glass slide. The images were taken in the tapping mode in air using an integrated tip/cantilever (125 μm in length with ca. 300 kHz resonant frequency and spring constant of ca. 40 N/m). Typical scan rates during recording were 0.7–1 line·s^{-1} using a scan head with a maximum range of 50×50 μm.

2.3. Optical measurements

Optical storage experiments were carried out at room temperature and under ambient conditions, using the experimental setup described in Ref. [11]. The irradiation process was performed using a linearly polarized argon laser operating at 488 nm (writing beam) with a polarization angle of 45° with respect to the polarization direction of a low power He–Ne laser operating at 632.8 nm (reading beam). The power of the writing beam used in the experiments was varied between 6 and 18 mW on a spot of 0.4 mm^2. The change in the transmission of the reading beam, which passed through the sample between two crossed polarizers, was measured with a photodiode. The induced optical birefringence (Δn) was determined by measuring the reading beam transmission ($T = I/I_0$) using:

$$\Delta n = (\lambda/\pi d) \sin^{-1} (I/I_0)^{1/2} \tag{1}$$

where λ is the wavelength of the reading beam, d is film thickness, I is the intensity of the reading beam after the second polarizer, and I_0 is the transmitted intensity of the reading beam between parallel polarizers in absence of anisotropy. In order to remove the photoinduced birefringence, a circularly polarized argon laser operating at 488 nm (erasing beam) was used.

3. Results and discussion

3.1. Langmuir and Langmuir Blodgett films

The precursor TAZ and its copolymers with DGEBA and two monoamines were spread as Langmuir monolayers onto an ultrapure water subphase, whose surface pressure-area (π-A) isotherms are shown in Fig. 1. Mean molecular area values were calculated based on the average molecular weight of the repeating units, which were estimated by the molar ratio of each material in the feed mixture for copolymerizations. The monolayers were stable, with small changes in area per molecule when the pressure π was kept at 30 mN/m. The collapse pressures were ca. 58 mN/m for TAZ and ca. 63 mN/m for TAZ50/DGEBA/BA and TAZ50/DGEBA/MT. These film features make them adequate for Langmuir Blodgett depositions, as discussed later.

The isotherm for TAZ exhibits a plateau-like region, which is typical of phase transitions, such as the liquid-expanded to liquid-condensed transition in phospholipids [13]. The extrapolated area to zero pressure
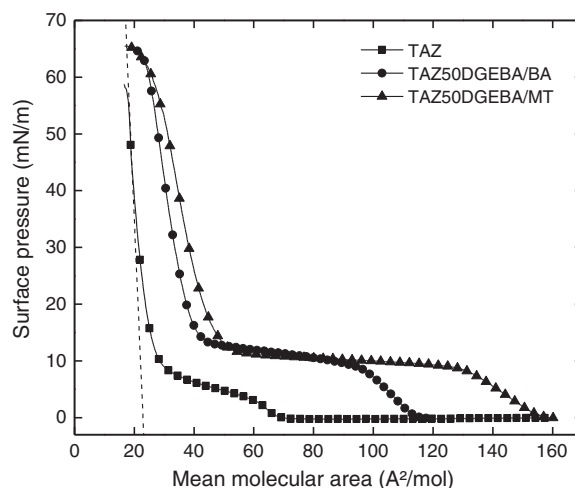

Fig. 1. Surface pressure-area (π-A) isotherms for Langmuir monolayers of the precursor TAZ and the copolymers TAZ50/DGEBA/BA and TAZ50/DGEBA/MT.

for the condensed phase of the monolayer was 23 Å^2/mol, as marked by a dashed line in Fig. 1, which corresponds approximately to the area occupied by the repeating unit of the copolymer. The shape of the curves for the copolymers TAZ50/DGEBA/BA and TAZ50/DGEBA/MT was similar to that for TAZ, but with a longer, better-defined plateau and a larger area per molecule. Stable films could not be produced with DGEBA owing to its small amphiphilic character. The plateau in the isotherms is believed to be due to some reorganization of the DGEBA moiety that is present in all the copolymers. This hypothesis is supported by the observation of longer plateaus for the copolymers that have higher proportions of DGEBA. Nevertheless, a definitive conclusion can only be reached upon using spectroscopic methods, such as the polarization-modulated infrared reflection absorption spectroscopy (PM-IRRAS) for Langmuir monolayers, with which one may determine the orientation of molecular groups.

The slope of the π-A curves in the liquid-condensed phase is not as steep as for traditional amphiphiles such as fatty acids and phospholipids, being however typical of polymeric materials. The extrapolated areas to zero pressure were 43 and 48 Å^2/mol for TAZ50/DGEBA/BA and TAZ50/DGEBA/MT, respectively. Therefore, the repeating unit of these copolymers occupies a larger area than the repeating unit of TAZ, probably because the incorporation of monoamines BA and MT caused an increased anchoring of the molecule on the water surface. These amine groups would share the surface with the polar regions of the azodyes.

Langmuir Blodgett films with up to 100 layers could be transferred onto glass substrates. The transfer ratio, obtained by dividing the decrease in area of the monolayer on the trough by the area of the substrate crossing the interface, was close to 1 in all depositions, thus indicating good transfer in the up and downstrokes (Y-type LB films). The uniform growth was further confirmed by UV–vis spectroscopy, in which the absorbance maximum at 480 nm increased almost linearly with the number of deposited layers. An example of such kind of plot is shown in Fig. 2 for TAZ50/DGEBA/MT, while similar plots were observed for all the other materials (results not shown).

3.2. Optical properties

To analyze the influence of the film structure over the induced anisotropy, films of TAZ50/DGEBA/BA prepared with SC and LB techniques were used in optical storage experiments. The thickness of the SC film was 512 nm, while the 100-layer LB film was 129 nm thick. Fig. 3 shows the optical storage curves with the writing beam (6 mW) turned on at point A and turned off at point B. Optical anisotropy was induced in the SC film as well as in the LB film upon switching the writing laser at
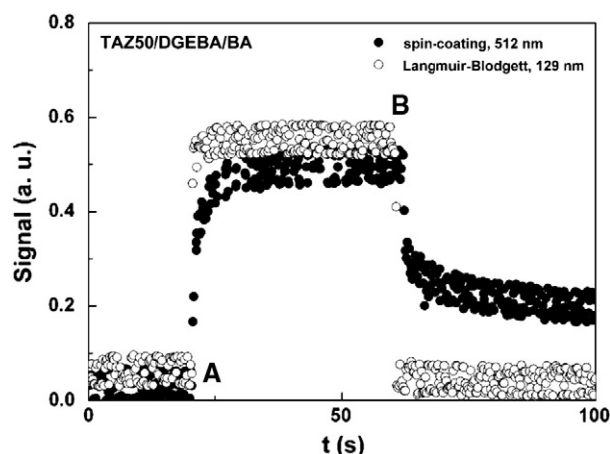

Fig. 3. Comparison of the optical behavior of TAZ50/DGEBA/BA in spin coated and Langmuir Blodgett films. The various points for the same time of writing (open and closed circles) represent distinct measurements with the same sample.

point A. The increase in the signal was faster for the LB film, with the time necessary to reach 80% of the maximum anisotropy (t_{80}) being 172 ms, much shorter than the 1980 ms for the SC film. So, the ability to reorient for the chromophores in the nanostructured LB film is much higher, and optical memories should be 10 times faster with this kind of film. Furthermore, the maximum signal was a little higher for the LB film, in spite of its much smaller thickness. The photo-induced birefringence was $\Delta n = 1.3 \cdot 10^{-2}$ and $8.2 \cdot 10^{-2}$ for the SC and LB films, respectively. The six-fold increase in birefringence for the LB film is consistent with the higher birefringence reported for azopolymers in the form of LB films in comparison to spin coated films [9,14]. The increase in birefringence has been attributed to the layered nature of the LB films, although the azochromophores appeared to be randomly oriented in the layer plane [9]. This can be assigned to the ordered packing in LB films which increases the induced anisotropy [15].

Upon turning the writing laser off at point B, the signal decayed to almost zero for the LB film, while for the SC film some remnant birefringence was observed. This result was not expected based on the literature, as the remnant birefringence is normally higher for LB films owing to the close packing of the azochromophores attached as side groups [16]. It seems that for the present results, the same factors inducing high mobility in LB films, leading to faster writing processes and higher birefringence, allow for a complete randomization of the azochromophores after the laser was turned off.

The influence of the polymer structure and azochromophore concentration over the optical properties was evaluated for 100-layer LB films of different azopolymers, and compared with values for SC films of similar thicknesses. The data are shown in Fig. 4 and Table 1. The birefringence Δn increased with the azobenzene concentration in SC films, as expected [12], with higher values for TAZ (26 wt.% DO3, $\Delta n = 2.8 \cdot 10^{-2}$) than for the azocopolymers (13 wt.% DO3, $\Delta n = 1.3–1.5 \cdot 10^{-2}$). A different behavior was observed for LB films from the azocopolymers ($\Delta n = 8 \cdot 10^{-2}$) in which the birefringence was higher than in TAZ ($\Delta n = 4.5 \cdot 10^{-2}$) even having a lower DO3 content. It is also remarkable that only the TAZ LB films had a non-zero remnant birefringence, analogously to the SC films. One possible explanation for this different behavior is the larger thickness of the LB TAZ film (170 nm) than for the azocopolymer films (110–130 nm), probably because the polymeric chains with functional groups in the chain ends had a larger volume. It is known that as the LB films become thicker, their properties asymptote those of SC films owing to the loss in organization, as reported for LB films of HPDR13 and cadmium stearate [17]. Moreover, TAZ molecules are probably more closely packed due to the LB processing (see the lowest extrapolated
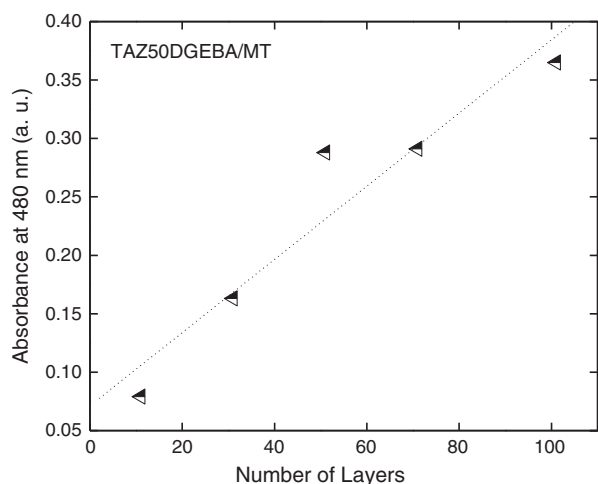

Fig. 2. UV–vis absorbance at 480 nm vs. the number of layers for LB films of TAZ50/DGEBA/MT.
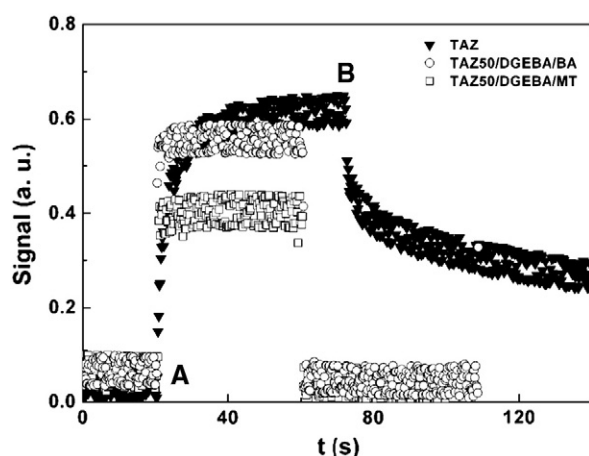
Fig. 4. Optical storage curves for 100-layer LB films of TAZ, TAZ50/DGEBA/BA, and TAZ50/DGEBA/MT.

Fig. 5. Writing sequence for TAZ LB films (100 layers) irradiated at different laser powers.

area of TAZ in Fig. 1), which may imply a lower free volume available for the azo groups to isomerize.

In a previous paper [12], the maximum induced birefringence was shown to be independent of the laser power of the writing beam for SC films of azopolymers, with maximum birefringence saturating when the laser power reached 6 mW. In the case of LB films, the same behavior versus beam power as the SC films is observed for the TAZ films, as shown in Fig. 5. In contrast, Fig. 6 shows that for TAZ50/DGEBA/BA LB films the dependence on the power beam is seen up to 18 mW, the same applying to TAZ50/DGEBA/MT LB films (results not shown). These dependences are better illustrated in Fig. 7, where the maximum transmitted signal of the reading laser increased with the laser power of the writing beam for an azocopolymer LB film.

Fig. 8 shows an increased transmitted signal with the number of layers in the LB film for the TAZ50/DGEBA/MT copolymer, which should be attributed to the increased thickness, as was the case of SC films [12]. The dependence of the photoisomerization process on the thickness of LB films from azopolymers has been investigated by Haro et al. [18], where the efficiency of the process was assumed to depend on the balance between the stress arising from the larger cross-section of cis-isomers and their interaction with neighboring molecules. Furthermore, the cis-trans isomerization was faster in well-packed azobenzene layers in the LB films, while the slowest isomerization process took place for a 35-layer LB film, which was presumably less ordered [18]. It is clear therefore that for this copolymer system up to 100 layers the film thickness is still not sufficient for a decrease in the order which would lead to lower birefringence.

The mechanisms responsible for the photoinduced birefringence in all the results reported here are essentially the same as extensively described in the literature (see Ref. [9] for a review). Information is written by reorienting chromophores after several photoinduced trans-cis-trans isomerization cycles, since after a given cycle the chromophores oriented perpendicularly to the polarization direction of the writing laser beam no longer suffer isomerization. Therefore, birefringence is photoinduced with an increasingly larger fraction of
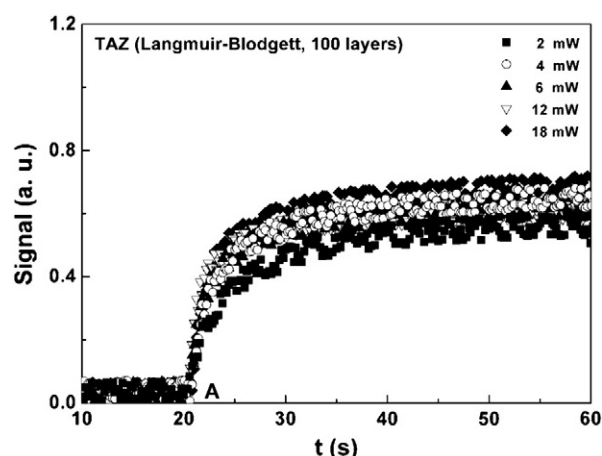
these perpendicularly oriented chromophores until saturation occurs. The writing rate and the maximum birefringence achieved depend on various factors, especially on the concentration of azochromophores in the polymer system and on the free volume available for each chromophore to isomerize. When the writing beam is switched off, relaxation takes place reducing the birefringence to an extent that depends on the environment of the chromophores. For the LB films reported here, it seems that the azochromophores in the copolymers had a larger free volume for isomerization, thus leading to enhanced optical properties.

The importance of the free volume for the photoisomerization processes has been demonstrated in various types of work in the literature (see [19]). The role of several parameters governing the final photoisomerization results being discussed in a review paper by Natansohn and Rochon [10 and references therein]. The minimum volume required for the photoisomerization of an azopolyester was determined with measurements at high pressures [20], while the free volume requirement has also been proven essential for the photomechanical effects in azopolymer films studied with neutron reflectometry [21]. Significantly, changes in the free volume were shown to affect the mechanical properties of azopolymer films too [22]. The dependence on the free volume has been treated quantitatively with theoretical models, such as the one proposed by Mita et al. [23] and extended by Dallagnol et al. [24]. The latter was based on two assumptions involving size distributions of cavities which suffered thermal fluctuations. The first assumption was that the volumes of the cavities were described by a Gaussian function centered at an average
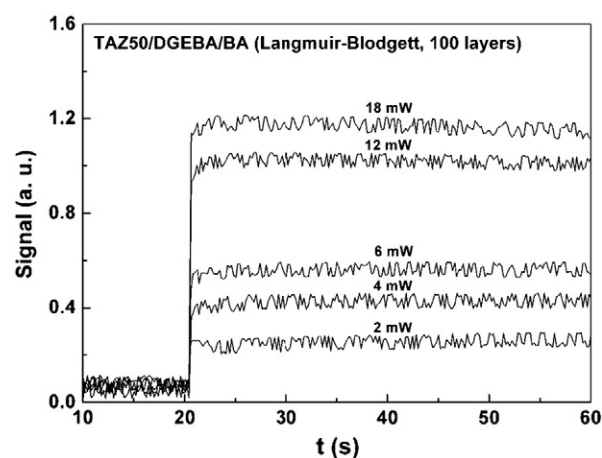
Table 1
Induced optical anisotropy for LB films of TAZ, TAZ50/DGEBA/BA and TAZ50/DGEBA/MT with 100 layers. The thickness of each LB film is also shown, and Δn for spin coated (SC) films with similar thickness of LB films are given as references.

Sample	Thickness (nm)	Δn (10^{-2})	
	LB	SC	LB
TAZ, 100 layers	170 ± 4.5	2.8 ± 0.12	4.5 ± 0.11
TAZ50/DGEBA/BA, 100 layers	129 ± 2.6	1.3 ± 0.14	8.1 ± 0.16
TAZ50/DGEBA/MT, 100 layers	112 ± 3.1	1.5 ± 0.03	7.6 ± 0.20

Fig. 6. Writing sequence for TAZ/DGEBA/BA LB films (100 layers) irradiated at different laser powers.
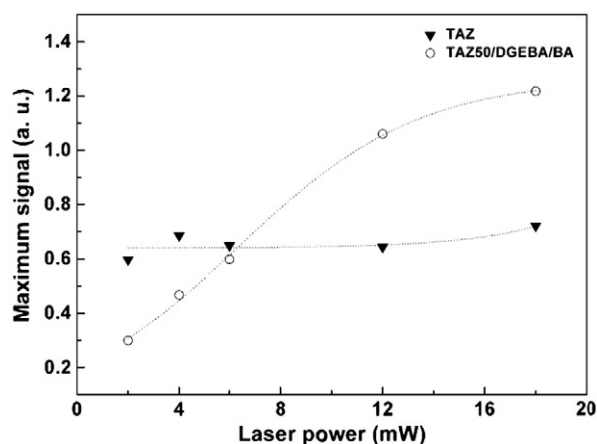
Fig. 7. Influence of the writing laser power over the maximum photoinduced birefrigence for TAZ, and TAZ50/DGEBA/BA LB films.

volume, while in the second assumption azobenzenic molecules were uniformly distributed in the cavities. The model explains the photoinduced birefringence as a function of time, temperature and the initial free volume state, in which the photoreorientation obeyed the model proposed by Sekkat et al. [25] where the kinetics of the photoinduced mechanisms was explained by biexponential functions.

The application of theoretical models to treat photoisomerization data quantitatively is not straightforward owing to several parameters that need to be known. Weidner et al. [26] showed that the free volume for the chromophores to isomerize depends on the molecular geometry of the azomolecules used for producing self-assembled monolayers (SAMs), and indeed a strategy to create free volume in SAMs was developed by incorporating a bulky group in the monolayer-forming molecules [27]. The kinetics of isomerization was also found to depend strongly on the packing of mixed LB films containing polyions [6].

4. Conclusions

Azo-containing epoxy copolymers were processed in LB films and had their photoinduced birefringence studied, with results being compared to the optical storage for spin coated films studied previously [12]. Particular emphasis was given to the influence of factors such as polymer structure, azo concentration, writing laser power, and number of layers in the LB films. The higher birefringence and faster kinetics in the writing process for the LB films pointed to an increased ability to orient for the chromophores in comparison with the spin coated films. While spin coated films exhibited no influence of the laser power over the transmitted signal, the signal increased with the writing power in azocopolymers LB

films. As expected, the maximum transmitted signal increased with the number of layers in LB films owing to the increased film thickness. For spin coated films, the copolymer architecture caused a decrease in the maximum birefringence from $2.8 \cdot 10^{-2}$ to 1.3–$1.5 \cdot 10^{-2}$ (see Table 1), which is attributed to a dilution of the azo monomer concentration in the chain. However, when the same copolymers were deposited as LB films they displayed enhanced optical storage characteristics in comparison with the precursor TAZ ($\Delta n = 8 \cdot 10^{-2}$ for the copolymers and $4.5 \cdot 10^{-2}$ for TAZ). The latter is probably a consequence of the larger area occupied by these copolymers in the Langmuir film on the water surface, which confers a larger free volume for isomerization of the azochromophores.

An important contribution in this work was to show that LB films are promising for optical applications of azo-containing epoxy polymers, since the improved mechanical properties arising from the epoxy network [12] do not reflect in a poorer optical performance after film processing, unlike the case of spin coated films. This opens new avenues for research and development in various areas, including for biological applications. Indeed, fundamental studies on photoisomerization of azodyes have been proven relevant in various recent endeavors. For example, azobenzene molecules were attached inside 3 nm pore channels of mesoporous silica nanoparticles which served as drug delivery carriers [28] in a single living cell, where the release was photodriven by isomerizing the azogroups. Isomerization of a photoresponsive surfactant was used to control the reversible folding-refolding of the protein lysozyme [29]. The mechanisms and potential applications of photoswitching in biomolecules driven by isomerization of azobenzene-containing materials have been reviewed by Beharry and Woolley [1], where functional changes in peptides, proteins, nucleic acids, lipids and carbohydrates are discussed. More specifically, a synthetic optical switch was proposed for the ionotropic glutamate receptor, which is an important ligand-gated ion channel for neurosciences [30]. The channel conductance could be controlled with the photoisomerization of an azobenzene moiety attached to the receptor, in a device that – according to the authors [30] – could be used in biology as well as in bioelectronics and nanotechnology.

Fig. 8. Influence of the number of layers over optical behavior for TAZ/DGEBA/MT LB films.

References

[1] A.A. Beharry, G.A. Woolley, Chem. Soc. Rev. 40 (2011) 4422–4437.
[2] A. Emoto, E. Uchida, T. Fukuda, Polymers 4 (2012) 150–186.
[3] A. Ulman, Organic thin films, Academic Press, San Diego, 1995..
[4] S. Dante, R. Advincula, C.W. Frank, P. Stroeve, Langmuir 15 (1999) 193–201.
[5] H.R. Hafiz, F. Nakanishi, Nanotechnology 14 (2003) 649–654.
[6] M. Takahashi, T. Okuhara, T. Yokohari, K. Kobayashi, J. Colloid Interface Sci. 296 (2006) 212–219.
[7] M. Haro, J. del Barrio, A. Villares, L. Oriol, P. Cea, M.C. López, Langmuir 24 (2008) 10196–10203.
[8] J. Han, D. Yan, W. Shi, J. Ma, H. Yan, M. Wei, D.G. Evans, X. Duan, J. Phys. Chem. B 114 (2010) 5678–5685.
[9] O.N. Oliveira Jr., D.S. Dos Santos Jr., D.T. Balogh, V. Zucolotto, C.R. Mendonça, Adv. Colloid Interface Sci. 116 (2005) 179–192.
[10] A. Natansohn, P. Rochon, Chem. Rev. 102 (2002) 4139–4176.
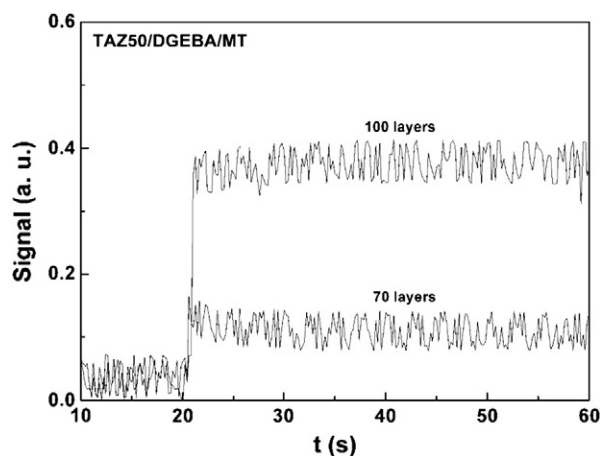[11] R. Fernández, I. Mondragon, P. Oyanguren, M.J. Galante, React. Funct. Polym. 68 (2008) 70–76.

[12] R. Fernández, I. Mondragon, M.J. Galante, P.A. Oyanguren, Eur. Polym. J. 45 (2009) 788–794.
[13] V.M. Kaganer, H. Möhwald, P. Dutta, Rev. Mod. Phys. 71 (1999) 779–819.
[14] A. Dhanabalan, C.R. Mendonça, D.T. Balogh, L. Misoguti, C.J. Constantino, J.A. Giacometti, Macromolecules 32 (1999) 5277–5284.
[15] C.R. Mendonça, A. Dhanabalan, D.T. Balogh, L. Misoguti, D.S. dos Santos Jr., M.A. Pereira-da-Silva, J.A. Giacometti, S.C. Zilio, O.N. Oliveira Jr., Macromolecules 32 (1999) 1493–1499.
[16] L.F. Ceridorio, D.T. Balogh, L. Caseli, M.R. Cardoso, T. Viitala, C.R. Mendonça, O.N. Oliveira Jr., J. Colloid Interface Sci. 346 (2010) 87–95.
[17] F.J. Pavinatto, J.Y. Barletta, R.C. Sanfelice, M.R. Cardoso, D.T. Balogh, C.R. Mendonça, O.N. Oliveira Jr., Polymer 50 (2009) 491–498.
[18] M. Haro, A. Villares, I. Gascon, S. Martin, L. Oriol, P. Cea, Curr. Appl. Phys. 10 (2010) 874–879.
[19] Z. Sekkat, C.S. Kang, E.F. Aust, G. Wegner, W. Knoll, Chem. Mater. 7 (1995) 142–147.
[20] Z. Sekkat, G. Kleideiter, W. Knoll, J. Opt. Soc. Am. B 18 (2001) 1854–1857.
[21] K.G. Yager, O.M. Tanchak, C. Godbout, H. Fritzche, C.J. Barrett, Macromolecules 39 (2006) 9311–9319.
[22] N. Mechau, M. Saphiannikova, D. Neher, Macromolecules 38 (2005) 3894–3902.
[23] I. Mita, K. Horie, K. Hirao, Macromolecules 22 (1989) 558–563.
[24] F.F. Dall'agnol, O.N. Oliveira Jr., J.A. Giacometti, Macromolecules 39 (2006) 4914–4919.
[25] Z. Sekkat, J. Wood, W. Knoll, J. Phys. Chem. 99 (1995) 17226–17234.
[26] T. Weidner, F. Bretthauer, N. Ballav, H. Motschmann, H. Orendi, C. Bruhn, U. Siemeling, M. Zharnikov, Langmuir 24 (2008) 11691–11700.
[27] M. Ito, T.X. Wei, P.L. Chen, H. Akiyama, M. Matsumoto, K. Tamada, Y. Yamamoto, J. Mater. Chem. 15 (2005) 478–483.
[28] Y.A. Lau, B.L. Henderson, J. Lu, D.P. Ferris, F. Tamanoi, J.I. Zink, Nanoscale 4 (2012) 3482–3489.
[29] S.C. Wang, P. Mirarefi, A. Faraone, C.T. Lee, Biochemistry 50 (2011) 8150–8162.
[30] M. Volgraf, P. Gorostiza, R. Numano, R.H. Kramer, E.Y. Isacoff, D. Trauner, Nat. Chem. Biol. 2 (2006) 47–52.