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Synthesis and characterization of epoxy polymers containing azobenzene groups that exhibit optical birefringence

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Abstract

A push–pull azo dye (DO3) was used as photosensitive substance to satisfactorily synthesize new epoxy polymers containing azo groups covalently linked. Three different amines BA, TA and MXDA were used as hardeners. Materials with different chemical structure and azo group concentration were prepared. The polymerization kinetics was followed using SEC, FTIR and DSC. It was observed that polymerization rate increases with the azo chromophore incorporation and with the photosensitive component concentration in the reaction precursors. The photoinduced birefringence of the obtained films has been analyzed. A completely reversible optical orientation was reached.
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1. Introduction

Many years ago, Todorov et al. [1] demonstrated that azo dyes in polymeric matrices could give rise to optical birefringence when excited by polarized light. The mechanism of this process involves repeated *trans–cis* photoisomerization of azobenzene groups and thermal *cis–trans* relaxation, resulting in the alignment of azobenzene groups in the direction perpendicular to the polarization of the incident light, when light in the blue or green region

is employed [2,3]. This photoinduced *trans–cis* isomerization of azobenzene and its derivative has been studied in solution and in doped and functionalized glassy polymers [4] in order to produce materials that could be used for electrooptical devices, polarization holographic grating, and nonlinear optics [5].

This type of photoinduced isomerization process is also of particular interest because the induced changes in molecular orientation can be transferred to the surrounding molecules [6]. The kinetic studies of the *trans–cis* isomerization of the azo groups have provided information on the structure morphology and segmental mobility of the azo polymers. For example, the azo labels on different sites of polymers

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were used as molecular probes to detect the free volume distribution and physical aging of the polymers. The influence of the polymer properties on the photochemical and thermal isomerization has been demonstrated by kinetic studies on different azo polymers and the rate of isomerization of the azo groups attached covalently to the polymers depends on the structural properties of the polymer matrix [7]. As the relaxation of the orientation is related to the free volume in the polymer, it is interesting to increase the T_g to freeze almost all molecular movement of polymer segments at room temperature. The problem is that photoisomerization can also be hindered and become so slow that any photoinduced anisotropy is prevented [8].

New azo polymers including polymers containing aliphatic azo groups and crosslinked polymers were synthesized [9,10]. In this last group, epoxy composites find new and new possibilities of applications, when azobenzene chromophores are introduced in epoxy systems [11].

Based on that knowledge, the principal objective of this work is to synthesize and characterize epoxy polymers with diverse chemical structure that contain azo groups covalently linked and could exhibit optical anisotropy when are excited with polarized laser light in the blue region. Their optical behaviour will be analyzed in detail in a subsequent publication.

2. Experimental

2.1. Materials and samples preparation

A push–pull azo dye, $NO_2—C_6H_4—N=N—C_6H_4—NH_2$ (Disperse Orange 3, DO3, Aldrich, AZ), $T_m = 200 \,°C$ was selected as photosensitive molecule. An azo prepolymer (TAZ) was synthesized by reaction between DO3 and a diglycidyl ether of bisphenol A (DGEBA, Der 332 Dow), with an epoxy equivalent of 174 g eq^{-1}. It was prepared in a stoichiometric relation $r = eq\ AZ/eq\ DGEBA = 0.5$, to generate reaction products with epoxy groups in the extreme of chains. The samples were prepared mixing DGEBA and the required amount of DO3 at 200 °C, in an oil bath during 2 min in order to obtain a homogeneous solution. Then, polymerization was carried out in an oil bath at 180 °C.

The resulting TAZ was blended with DGEBA and two different monoamines (MA), one aliphatic and one aromatic, benzylamine (BA, Aldrich) and

m-toluidine (TA, Aldrich), to prepare azo-modified thermoplastics. TAZ, MA and the quantity of DGEBA necessary to have a stoichiometric ratio $r' = eq\ MA/eq\ epoxy\ (TAZ + DGEBA) = 1$ were mixed at room temperature adding some tetrahydrofuran (THF) drops to homogenize the sample. After that, THF was removed by evaporation at room temperature. Reactions were performed during 120 min at 60 °C for BA and 140 min at 100 °C for TA.

Along with the monoamines, an aliphatic diamine (*m*-xylilendiamine, MXDA, Aldrich) was utilized as hardener with the aim of developing crosslinked polymer. In this case, reaction was carried out at 100 °C for about 60 min.

2.2. Measurements

AZ/DGEBA reaction was followed in an oil bath at 180 °C, using a set of vacuum sealed tubes. Each tube was removed at different times and quenched in ice. Then, size exclusion chromatography (SEC) was run. A Perking–Elmer chromatograph equipped with a binary pump and a refractive index detector (RI) was used. The mobile phase was THF with an elution rate of 1 mL/min; the separation was carried out with three styragel columns packed with 5 μm particle gel with nominal pore sizes of 100 Å, 500 Å, 104 Å.

Near infrared spectroscopy (NIR) was used to determine the polymerization kinetics. An FITR Instrument, Nicolet Nexus 670/870 was employed. NIR data have been obtained using a calcium fluoride beam splitter, a white light source and a MCT/A detector cooled with liquid nitrogen. The epoxy and primary amine group conversions were calculated following the area of the absorptions band at 4530 cm^{-1} and 5078 cm^{-1} with respect to the area of the reference band at 4623 cm^{-1}.

Differential scanning calorimetry (DSC) was performed using a DSC Mettler Toledo 822 device. The reaction heat (area under the reaction peak) and glass transition temperature (T_g) (defined as the onset of the change in specific heat) were determined from the thermograms obtained in heating scans at 1 °C/min and 10 °C/min, respectively.

Films of systems polymerized using MA were obtained by spin-coating THF solutions of the resulting polymers onto clean glass slides. In the case of systems cured with MXDA, the appropriate amount of precursors was directly cured over clean glass slides. Homogeneous films of similar thickness
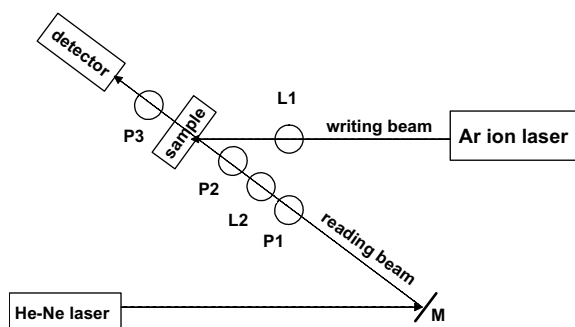
Fig. 1. Schematic illustration of the experimental set up for the measurement of the photoinduced orientation of azo compounds. Optical components: P, polarizer; L, quarter wave plate; M, mirror.

were obtained by these procedures. Photoinduced birefringence of the resulting films was determined using the experimental set up described in Fig. 1. Birefringence was measured by placing the sample between two crossed linear polarizers (P2 and P3). An Ar^+ laser was used as writing beam to induce optical anisotropy in the polymer film, and a He–Ne laser at 633 nm was used as reading beam to measure the power that is transmitted through this optical setup. To achieve maximum signal, the polarization vector of the writing beam was set to 45° with respect to the polarization vector of the reading beam. All measurements were performed at room temperature and all the films were irradiated with 20 mW/mm^2 of the writing laser.

3. Results and discussion

Reactions taking place during the azo dye–epoxy polymerization carried out at 180 °C were analyzed. Fig. 2 shows SEC chromatograms of the reagents, DGEBA and AZ, and a DGEBA/AZ blend, $r = 0.5$, prior to reaction ($t = 0$). SEC chromatograms obtained for samples reacted up to different times are shown in Fig. 3. The chromatograms took at different intervals show, together with the decrease in the main peak at 28 min that is assigned to the overlapped peaks of DGEBA and AZ, the appearance and evolution of higher molar mass peaks arising from DGEBA/AZ reaction products.

FTIR spectra in the NIR region (4000–10,000 cm^{-1}) were also obtained. The evolution of the absorbance peaks during reaction is plotted in Fig. 4. The 4530 cm^{-1} band, assigned to the combined tension and torsion vibrations of epoxy groups, decreased progressively during reaction.
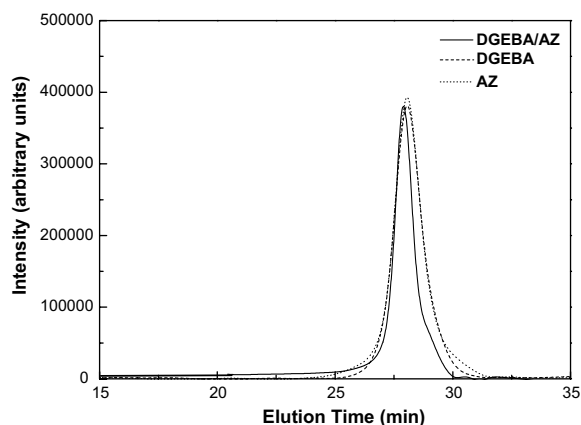

Fig. 2. SEC chromatograms of DGEBA, AZ and a DGEBA/AZ blend, $r = 0.5$ ($t = 0$).
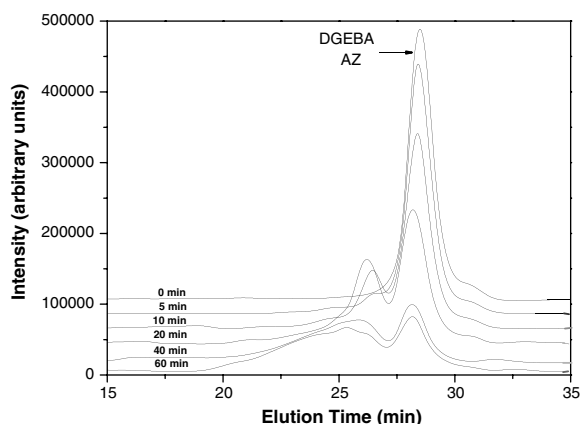

Fig. 3. SEC chromatograms as a function of reaction time for a DGEBA/AZ blend, $r = 0.5$, polymerized at $T = 180$ °C.

The peak at 5078 cm^{-1} arising from the combined tension and torsion vibrations of primary amine also diminished, indicating that the primary amine reacted with epoxy to be completely converted in a secondary amine. The development of the peak at 7000 cm^{-1} corresponding to the hydroxyl groups generated as product of the epoxy–amine reaction also confirmed that condensation took place.

Conversion vs. time curves obtained by NIR for epoxy and primary amine groups are plotted in Fig. 5. As the samples were prepared mixing DGEBA and AZ at high temperature, a NIR spectrum of DGEBA at 180 °C was carried out to determine how much they reacted during mixing. It was considered that the area of the peak at 4530 cm^{-1} of the DGEBA spectrum corresponded to conversion
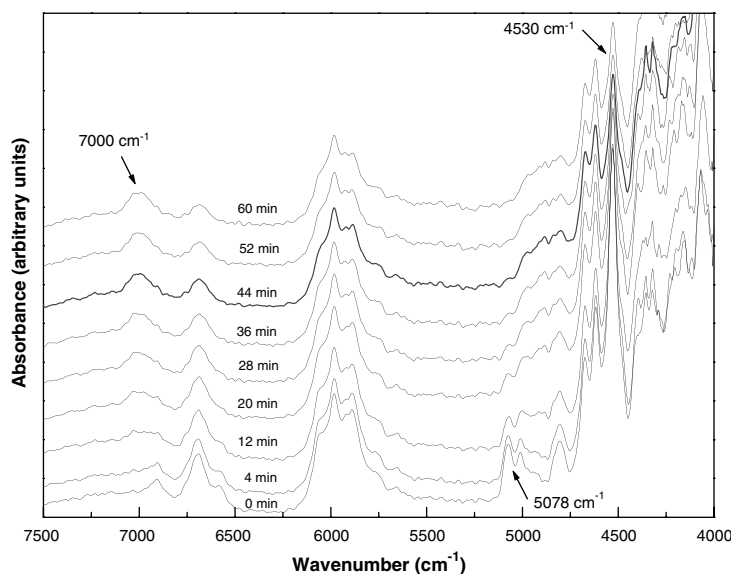
Fig. 4. NIR spectra of a DGEBA/AZ formulation with $r = 0.5$, during polymerization at $T = 180\,°C$ at different reaction times.
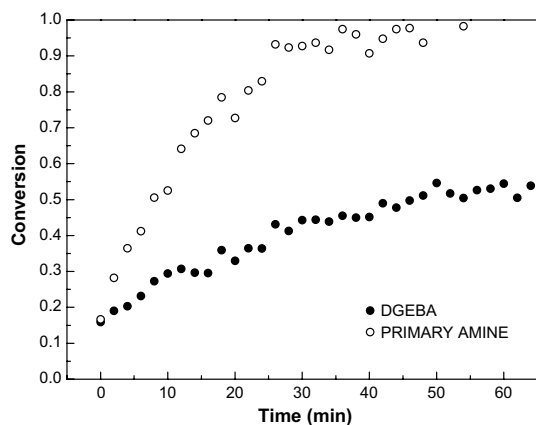

Fig. 5. Conversion as a function of time for DGEBA/AZ at 180 °C, determined by NIR: epoxy conversion (●); primary amine conversion (○).

$X = 0$. According to this, it was determined that at the beginning of the kinetic study (0 min), the epoxy conversion was $X = 0.16$. The primary amine is completely converted in secondary amine after approximately 50 min. The epoxy conversion after 1 h is $X = 0.50$, which is the maximum theoretical value considering that there were used two epoxy equivalents per equivalent of amine. In consequence, 1 h was selected as polymerization time with the purpose of obtaining a prepolymer (TAZ) that subsequently will be dissolved in the epoxy–amine mixtures in order to prepare final materials.

The resulting TAZ was, then, reacted with two different MA, BA and TA, and DGEBA. The samples were prepared with different TAZ concentrations (10, 20 and 50 wt%) and DGEBA was added in the proportion necessary to obtain a stoichiometric ratio between total epoxy (i.e. unreacted epoxy in TAZ plus DGEBA) and amine, as was explained above. TAZ was also reacted in a similar manner with an aliphatic diamine (MXDA) to obtain a crosslinked azo-modified polymer.

Dynamic DSC scans were utilized to calculate reaction heats (ΔH_r) and glass transition temperatures (T_g) of samples with different TAZ composition. ΔH_r was in the order of 100 kJ/eq for all the precursors. This is the expected reaction enthalpy value for a typical epoxy/amine blend. T_g values are listed in Table 1. In addition, 20 wt% azo thermograms (TAZ20) were compared to the pure DGEBA/amine systems, for both, reaction rates and T_g (Figs. 6–8). From the previous results, it is clearly deduced that even though there is no significant influence of TAZ over ΔH_r and T_g values, the reaction is accelerated when TAZ participates in the reaction, as it is demonstrated by the shift of the exothermic peak to lower temperatures in the TAZ20 sample for all the amines. Moreover, the reaction rate increased with the increase in the TAZ content in the initial mixture as is exemplified in Fig. 9 for TAZ/DGEBA/TA. It is also observed a broadening of these exothermic peaks when the TAZ content is increased. This fact can be due to

Table 1
Glass transition temperatures for the different samples used

Blend	T_g (°C)
DGEBA/BA	59
TAZ10/DGEBA/BA	58
TAZ20/DGEBA/BA	58
TAZ50/DGEBA/BA	59
DGEBA/TA	85
TAZ10/DGEBA/TA	79
TAZ20/DGEBA/TA	85
TAZ50/DGEBA/TA	76
DGEBA/MXDA	113
TAZ10/DGEBA/MXDA	106
TAZ20/DGEBA/MXDA	106
TAZ50/DGEBA/MXDA	93
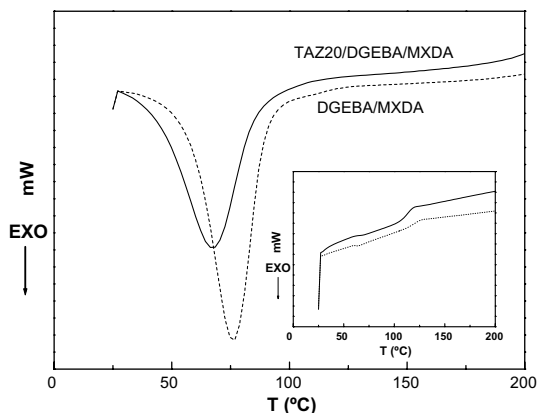
Fig. 8. DSC response in dynamic mode for DGEBA/MXDA and TAZ20/DGEBA/MXDA. First scan heating rate: 1 °C/min; second scan (inner graph) heating rate: 10 °C/min.
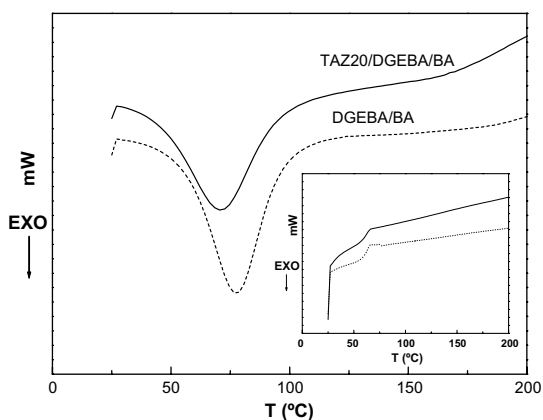

Fig. 6. DSC response in dynamic mode for DGEBA/BA and TAZ20/DGEBA/BA. First scan heating rate: 1 °C/min; second scan (inner graph) heating rate: 10 °C/min.
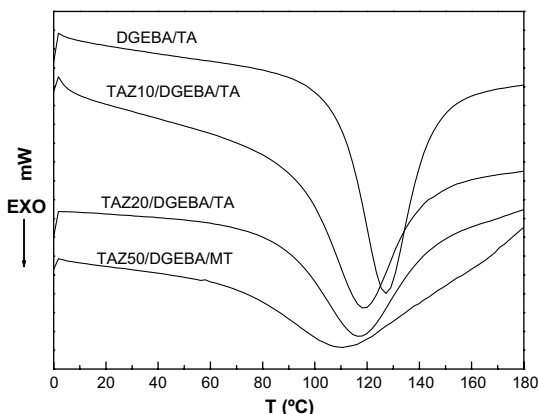

Fig. 9. DSC response in dynamic mode for DGEBA/TA and TAZ/DGEBA/TA samples with several TAZ contents. Heating rate: 1 °C/min.
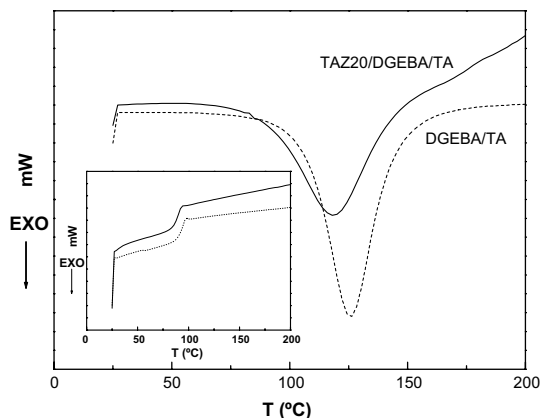
a viscosity increase of the reactive mixtures with the increase in TAZ content, which might delay the diffusion process of reactive chains.

Isothermal polymerization kinetics was evaluated following the evolution of epoxy conversion with time for azo-modified systems using FTIR. Conversion vs. time curves for samples containing 20 wt% AZ were compared to the neat systems (Fig. 10a–c). As we previously showed for the samples analyzed in dynamic scans, polymerization rate increases with AZ addition.

The optical behaviour of the obtained films has been analyzed for thermoplastic films synthesized with BA and TA and thermoset films obtained with MXDA. Typical writing sequences are presented in

Fig. 7. DSC response in dynamic mode for DGEBA/TA and TAZ20/DGEBA/TA. First scan heating rate: 1 °C/min; second scan (inner graph) heating rate: 10 °C/min.
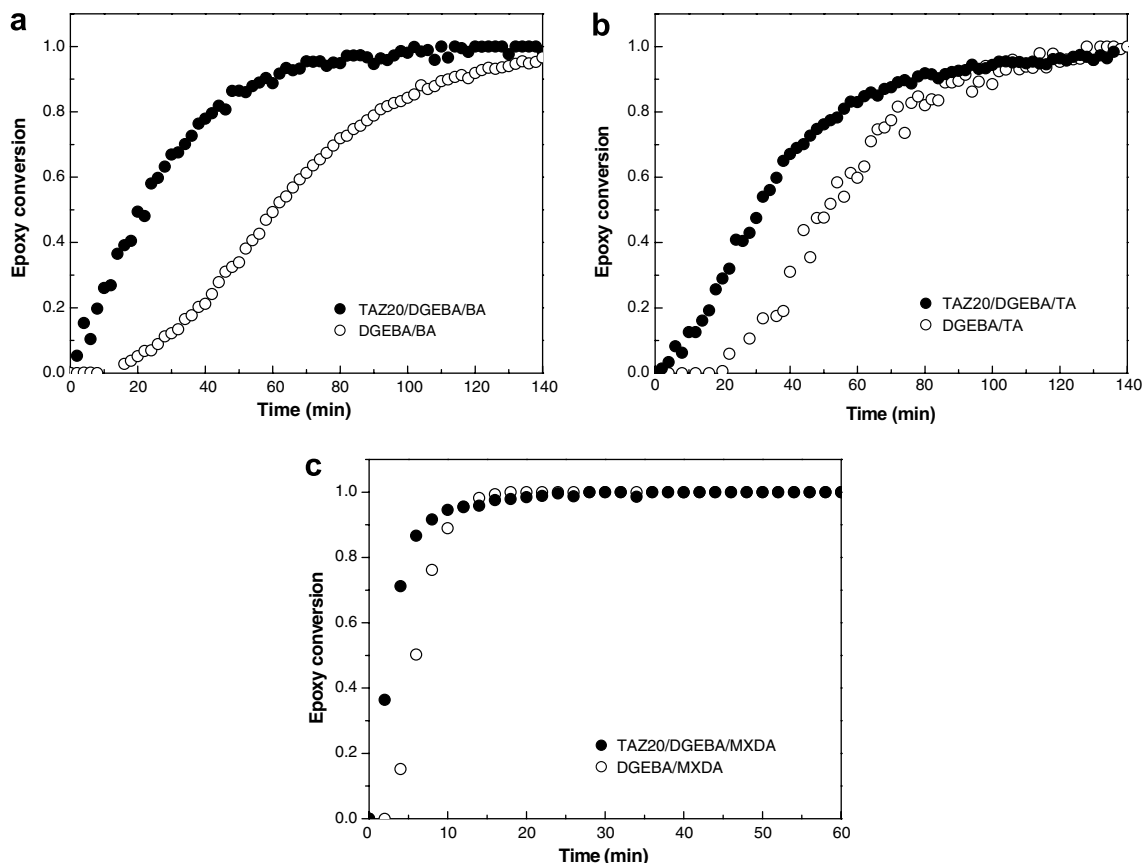
Fig. 10. Conversion as a function of time determined by NIR: (a) DGEBA/BA (○), TAZ20/DGEBA/BA (●); (b) DGEBA/TA (○), TAZ20/DGEBA/TA (●); (c) DGEBA/MXDA (○), TAZ20/DGEBA/MXDA (●).
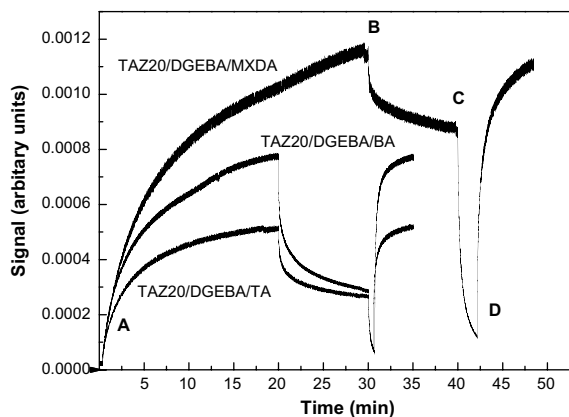

Fig. 11. Writing and erasing tests on azo-functionalized polymers containing 20 wt% TAZ: (A) writing beam is turned on; (B) writing beam is turned off; (C) erasing beam is turned on; (D) writing beam is turned on again on the same spot of the film.

Fig. 11. When the experiment starts, no light is transmitted through the analyzer, due to the azo compounds are randomly oriented. As the polarized Ar$^+$ laser radiation is introduced (marked A in Fig. 11), an anisotropic orientation distribution is created as consequence of the accumulation of *cis* and *trans* isomers that are oriented perpendicular to the polarization vector of the writing beam. Light is thus transmitted through the analyzer due to the onset of birefringence. When the excitation light is turned off (B in Fig. 11), the signal starts to decrease. Part of this decrease has been associated to the thermal reorientation of some azobenzene groups. This thermal reorientation tends to restore the thermodynamically favoured disordered state and is probably made possible by some local heat associated with the laser light which is dissipated through the film when the laser is turned off. At a third stage in the writing sequence (C in Fig. 11), the optically induced birefringence is "erased" by overwriting the test spot with circularly polarized Ar$^+$ beam. Its effect is to randomize back the orientations of the azobenzene groups. Finally, when the

writing beam is turned on again (D in Fig. 11), reorientation occurs. This is the fastest process in all the cases. It seems like samples would have "memory" and "remember" their previous orientation. However, it is necessary to take into account, firstly that before performing the experiments, the films were not heated up to a temperature above T_g to eliminate possible previous orientations that could be one responsible of the deceleration in the recording in the first cycle. And second, a photoinduced plasticization is assumed.

Fig. 11 shows that the maximum level of birefringence is reached by the thermoset polymer indicating that the optical behaviour of azo-modified epoxy polymers depends on the environment in which azo moiety exists. Samples with the same TAZ concentration have been irradiated with the same power of the pump laser. Thus, to account for these results, architecture parameters of the polymer matrix have to be analyzed. For thermoplastic polymers the maximum level of birefringence obtainable decreases greatly when the aromatic amine (TA) is employed instead of the aliphatic one (BA). However, when the writing laser is switched off there is a certain relaxation process which eventually leaves about 37% and 50% of the signal intact in about 10 min for systems polymerized with BA and TA, respectively. Therefore, in the epoxy matrix obtained with BA it is much easier for azo compounds to move on the isomerization processes than in the epoxy matrix obtained with TA. Concerning the azo thermoset prepared with an aliphatic diamine (MXDA), experimental results indicate that azo compounds have good mobility into the network, which also contributes to reach high induced optical birefringence.

The influence of the azo dye concentration, film thickness and laser power over the optical anisotropy of the resulting materials as well as a more deeply analysis of the chemical structure of the polymer is the object of a manuscript in preparation.

4. Conclusions

Several azo-functionalized thermoplastics and thermosets with variable azo content were satisfactorily synthesized and characterized. Reaction rate is accelerated by the presence of the azo compound. A wholly reversible optical anisotropy was developed. Birefringence measurements indicated that these polymers are promising materials to be employed in optical information storage, information processing, optical switching devices, among others.

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