Bonding and molecular environment effects on photoorientation in epoxy-based polymers having azobenzene units

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ABSTRACT

An azo prepolymer (TAZ) was synthesized by reaction between Disperse Orange 3 (DO3) and diglycidyl ether of bisphenol A (DGEBA). The resulting TAZ was blended with DGEBA and two different monoamines, one aliphatic and one aromatic, benzylamine (BA) and m-toluidine (MT), to prepare various azo copolymers with different azo contents. In addition, two guest–host systems were prepared: 5.16% by weight of DO3 in DGEBA-BA and in DGEBA-MT polymers. Their reversible optical storage properties were studied and compared. The maximum obtainable birefringence increases linearly with TAZ weight fraction, independently of the power of the writing beam, the environment in which the azo moiety is located, and the bonding between the dye and the matrix. It was found that, in BA-based copolymers, with lower T_g, the fraction of birefringence conserved after relaxation is smaller and the writing rates are higher than in MT-based copolymers. The film thickness dependence of the birefringence signal is also analyzed.

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1. Introduction

The demand for advanced materials with better properties to meet new requirements or to replace existing materials is incessantly increasing. Among them, epoxy resins are one of the most important classes of thermosetting polymers. The crosslinked networks have many desirable properties, which include high modulus, excellent chemical and corrosion resistance, good dimensional stability and high working temperatures. They are extensively used in many applications such as coatings, adhesives, laminates and matrices for composite materials and structural components.

On the other hand, photoresponsive polymers containing azobenzene moieties have been extensively investigated because of their promising and diversified applicabilities in optical data storage, optical switching, and optoelectronics [1–3]. To increase chromophore load-

ing and alignment stability, researchers have investigated covalent attachment of the chromophore to the polymer as either pendant group [4,5] or a comonomer [6,7], or crosslinking the active moiety into the polymer system [8].

The generation of optical anisotropy induced by the excitation of azobenzenes incorporated in polymer matrices with linearly polarized light takes place as the result of repeated photoisomerization processes. The photoisomerization is only activated when the chromophore's transition dipole moment axis has a component parallel to the light polarization. The direction perpendicular to the light polarization is excluded from optical activation and will become enriched in chromophores. The concentration of the chromophores aligned perpendicular to the light polarization steadily increases under illumination with polarized light, until saturation level is attained. The net result of this process is an excess of azobenzene groups aligned perpendicular to the laser polarization. The resulting anisotropy can be erased by irradiation with circularly polarized light.

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The non-centrosymmetric alignment of the azo chromophores that results from the photoinduced process is not in a state of thermodynamic equilibrium. Therefore, the alignment would relax to a random configuration in the absence of irradiation. To prevent the randomization of the orientated molecules, the azo chromophores are usually incorporated in a polymer which has a high glass transition temperature (T_g). This is due to the fact that the molecular orientational motion is closely associated with the T_g of the polymer.

In this context, in a previous a study, we reported the synthesis and characterization of two epoxy-based copolymers prepared with the same azobenzene monomer [9]. In this study, we investigate two strategies for incorporation of an azo dye into polymers for reversible optical storage: (a) covalent attachment of the dye to the polymer as a comonomer; and (b) solution mixing of the dye as a guest in the polymer host. We present the results of absorbance and induced anisotropy measurements on two series of epoxy-based copolymers and two guest–host systems under light irradiation. We show the benefits of covalent dye–polymer attachment, and we analyze the influence of different main-chain segments on the molecular reorientation. The time to achieve birefringence, as well as the time to randomize the orientation, depends on a series of factors which we wanted to investigate. Light intensity is one of these factors. The more photons a sample absorb, the faster the writing or erasing process [10]. The influence of film thickness is another factor to take into account. We have also measured the effects of varying azobenzene groups concentration.

2. Experimental section

2.1. Materials and samples preparation

The host polymers and the epoxy-based copolymers containing variable azo units content and different main-chain segments were synthesized and its procedure described elsewhere [9]. An azo prepolymer (TAZ) was synthesized by reaction between Disperse Orange 3 (DO3, Aldrich), and diglycidyl ether of bisphenol A (DGEBA, DER 332 from Dow). The resulting TAZ was blended with DGEBA and two different monoamines, one aliphatic and one aromatic, benzylamine (BA, Aldrich) and *m*-toluidine (MT, Aldrich), to prepare various azo copolymers. Fig. 1 shows the structural units of the compared copolymers, *p* and *q* are the degrees of polymerization of the TAZ and DGEBA-BA/MT blocks, respectively. In addition, two guest–host systems were prepared: 5.16% by weight of DO3 in DGEBA-BA (BA-DO3) and 5.16% by weight of DO3 in DGEBA-MT (MT-DO3). The concentration of DO3 in the guest–host systems is comparable to the copolymers having 20 wt% TAZ.

Tetrahydrofuran (THF) was purchased from Panreac and used without further purification.

Films were prepared by spin-coating using a P6700 spin-coater from 5 wt% polymer solutions in THF, onto clean glass slides. The spinner cycle program was as follows: 200–1000 rpm (depending on the required thickness) for 30 s, 4000 rpm for 10 s, and 8000 rpm for 20 s.

The films were heated above the T_g of the polymer and subsequently stored at room temperature. Relatively homogeneous thin films of variable thicknesses were obtained by this procedure.

2.2. Measurements

The molecular weights of polymers were determined by Size Exclusion Chromatography (SEC) with THF as eluent and polystyrene standards as calibration standards.

The experimental setup used in the optical storage experiments is similar to that previously reported [9]. Anisotropy was induced in the film using a linearly polarized (LP) argon continuous laser operating at 488 nm (writing beam) with a polarization angle of 45° with respect to the polarization direction of the reading beam. The power of the writing beam used in the experiments was varied (between 6 and 20 mW) on a spot of 0.4 mm². The change in the transmission of a low power He–Ne laser (reading beam) operating at 633 nm, which passes through two crossed polarizers and the sample, was measured with a photodiode. All measurements were performed at room temperature.

UV–visible spectra have been recorded in a THF solution and in films on a Milton Roy Spectronic Genesys 5 spectrophotometer fitted with polarizing optics. The films were exposed to LP argon laser beam at 488 nm (6 mW) for enough time to reach saturation, and UV–visible spectra of films, for light polarized parallel and perpendicular to the writing polarization direction were recorded. The dichroism ratio of the films, *D*, was calculated from the measured absorbance at maximum wavelength (λ_{max}) parallel ($A_\parallel$) and perpendicular ($A_\perp$) to the electric vector of the incident light (Eq. (1)).

$$D = A_\perp / A_\parallel \tag{1}$$

3. Results and discussion

The azo polymer systems that were studied possess the general structure presented in Fig. 1. A brief account of their compositions and thermal properties can be found in Table 1.

Fig. 2 shows the UV–visible spectra of the azo chromophore, DO3, and the azo prepolymer, TAZ, in THF solution. The maximum absorption wavelength (λ_{max}) of DO3 (broken line) is 440 nm. The strong $\pi \rightarrow \pi^*$ and weak $n \rightarrow \pi^*$ transitions are overlapped. The *trans* isomer is thermodynamically more stable than the *cis* isomer, and thus dominates the absorption spectrum. The lifetime of *cis*-aminoazobenzene is on the order of microseconds, and therefore most of the *cis* isomer is thermally converted to the *trans* isomer at room temperature [11]. In agreement with several reports [12,13], after being bonded to the polymer chain, the maximum absorption wavelength of the chromophore moieties was red-shifted from 440 nm for DO3 to 475 nm for TAZ. We could explain this red-shift as follows: DO3 has a donor group (–NH₂) and an acceptor group (–NO₂) at separated positions. If a new chemical bound (–CH₂–N–CHOH–) is produced, the structural
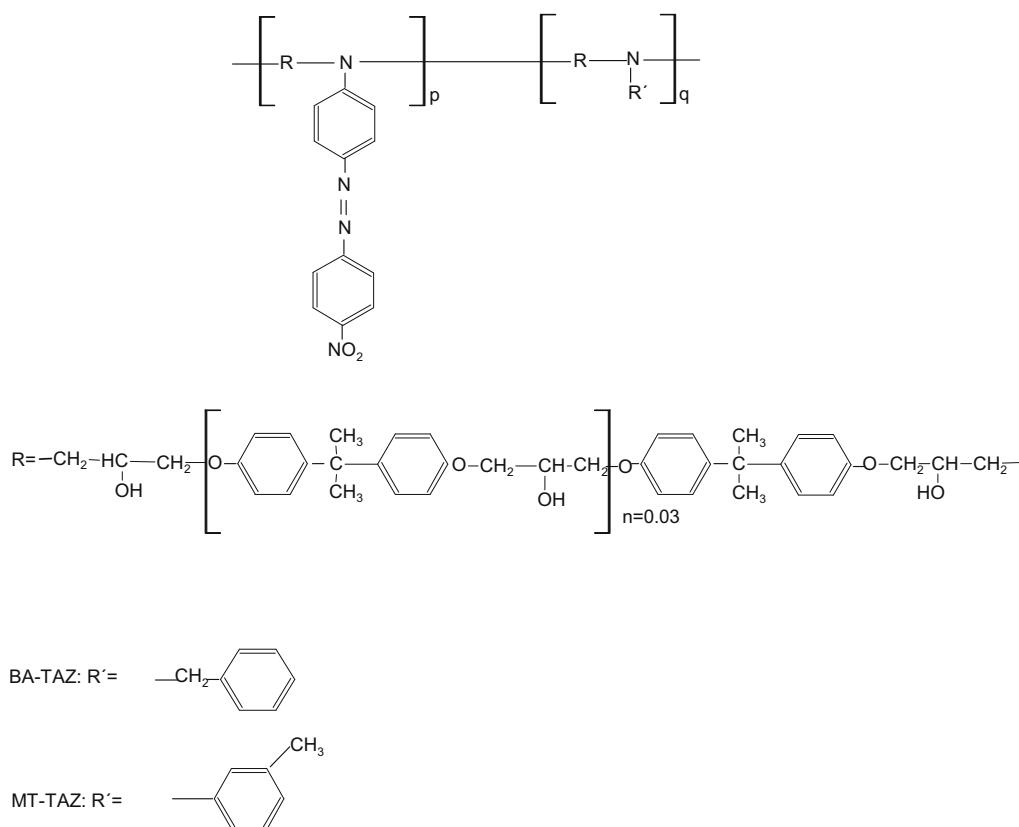
Fig. 1. Chemical structures of the copolymers used in this study.

Table 1
Structure and thermal properties of the polymers.

Polymer code	Copolymer composition (wt% TAZ)	T_g (°C)	Mw	Mw/Mn
BA-DO3[a]		59	12,300	1.79
BA-10TAZ	10	58	11,900	1.70
BA-20TAZ	20	58	10,300	1.66
BA-50TAZ	50	59	10,400	1.81
MT-DO3[a]	–	85	11,600	1.73
MT-10TAZ	10	79	11,200	1.60
MT-20TAZ	20	85	12,000	1.63
MT-50TAZ	50	76	9500	1.51

[a] Guest–host system containing 5.16 wt% DO3 dispersed.

Fig. 2. UV–visible spectra of: azo chromophore, DO3, and the azo prepolymer, TAZ, in THF solution.

change of the donor decreases the electron-release behaviour and will change the resonance absorption peak as a result. It is important to note that the shape of DO3 and TAZ spectra is similar; confirming that the azo dye left in the cured sample has not degraded during the curing cycle.

The photochemical properties of the present polymers are summarized in Table 2. All the copolymers exhibit nearly the same maximum absorption wavelengths which would ensure the comparison of their photoinduced properties at the same level. This means that the presence of different main-chain segments and/or the amount of dye content is changed do not influence the electronic properties of the chromophore moieties. The UV–visible spectra of all spin-coated films were red-shifted compared to the
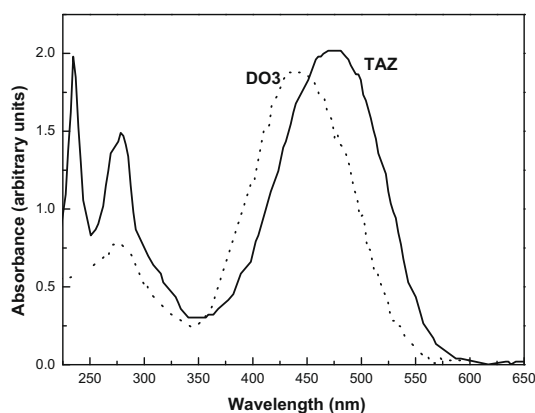
UV–visible spectra of the same polymer in solution (Table 2). The shift can be ascribed to an increased interaction between the azo groups within the polymer matrix [14]. For DO3 in DGEBA-BA (BA-DO3) and DGEBA-MT (MT-DO3), similar shifts in absorption maxima to longer wavelength are observed in UV–visible spectra (see Table 2) when comparing with λ_{max} of DO3 in THF solution. The observed red-shifts are the same order of magnitude for both matrices, suggesting similar local matrix polarities. Tawa et al.

Table 2
Photochemical properties of the polymers.

Polymer code	λ_{max} (nm)		Dichroism (D) at λ_{max}
	Solution[a]	Film	
TAZ	475	477	1.20
BA-DO3[b]	–	448	1.12
BA-10TAZ	470	477	1.19
BA-20TAZ	470	477	1.27
BA-50TAZ	470	477	1.31
MT-DO3[b]	–	448	1.17
MT-10TAZ	465	477	1.19
MT-20TAZ	465	477	1.29
MT-50TAZ	465	477	1.35

[a] THF.
[b] Guest–host system containing 5.16 wt% DO3 dispersed.

[15] have studied the dynamics of DO3 in different matrices, and found that the maximum absorption wavelength of DO3 depends on the local polarity surrounding the chromophore.

Typical examples of the optically induced dichroism are presented in Fig. 3, where the polarized UV–visible absorption spectra of BA-TAZ and MT-TAZ films are shown. The absorption coefficient for light polarized parallel to the writing direction is substantially less than that for light polarized in the perpendicular direction. The spectra of written films (parallel and perpendicular) and unwritten ones (not shown) do not show significant shape and λ_{max} differences, indicating that the mechanism responsible for the dichroism is a reorientation of the *trans* azobenzene moiety. The irradiation of the polymer films containing variable azo content induced a small dichroism D, of about 1.31 (BA-TAZ) and 1.35 (MT-TAZ) for TAZ content up to 50 wt% (Table 2). The values of dichroism achieved for both copolymers containing the same TAZ content are the same order of magnitude. Concerning the guest–host systems, BA-DO3 and MT-DO3, the dichroism ratios are lower compared with the ones obtained for copolymers with the same chromophore content (BA-20TAZ and MT-20TAZ). This behaviour was the expected one considering that DO3 molecules have high mobility in the polymer matrices, as they are simply physically mixed with the polymers. In return, copolymers have the chromophore chemically linked to the polymer chain which limits its mobility, and consequently, increments the thermal stability of the azopolymers.

The T_g range of the copolymers is from 58 to 85 °C (see Table 1), as found by DSC, which should favour a good orientational temporal stability of the photoactive chromophores of great interest for applications in optoelectronics when more stable photoinduced birefringence is required at ambient and slightly elevated temperatures.

Representative writing–erasing curves of optically induced and subsequently eliminated birefringence for BA-50TAZ and MT-50TAZ are shown in Fig. 4. Films were illuminated by a linearly polarized light from a He–Ne laser at 633 nm. As seen from Fig. 3a, there should be no absorption in the films at this wavelength. At the beginning of the experiment, no light is transmitted through the analyzer as the azo compound is randomly oriented. At point A, the LP writing laser beam is engaged and the photoin-
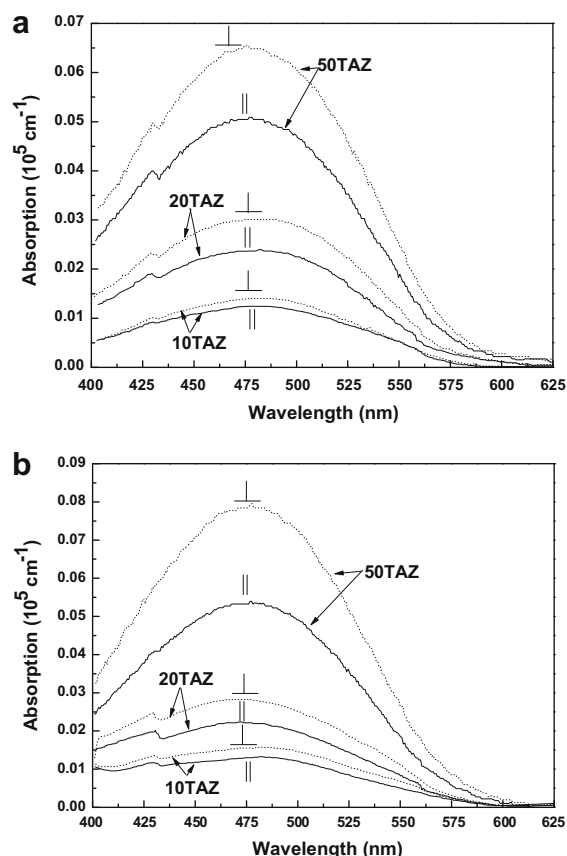

Fig. 3. UV–visible spectral changes of copolymers films with variable azo content irradiated with LP 488 nm light at 6 mW: (a) BA-TAZ and (b) MT-TAZ. Solid and dotted lines are of spectra taken by probe light with the electric vectors parallel to ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to that of the writing beam, respectively.
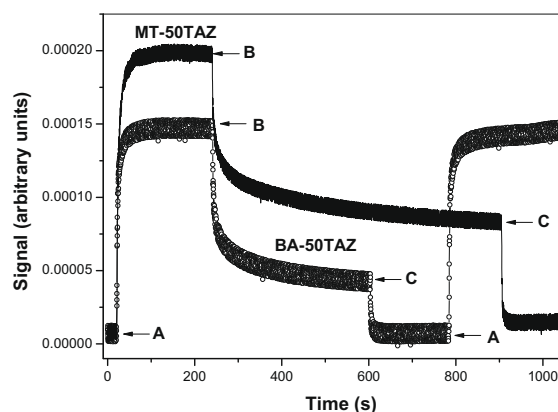

Fig. 4. Typical writing and erasing curves for copolymers containing 50 wt% TAZ: (a) BA-TAZ, 970 nm thickness; (b) MT-TAZ, 850 nm thickness. The pump beam (6 mW) is on at point A and off at B. Circularly polarized light was introduced at point C.

duced birefringence is rapidly built up to the saturation level. When the excitation light is turned off (point B in the figure), the signal starts to drop to a relaxed level where the rate of change of anisotropy is very small. To remove
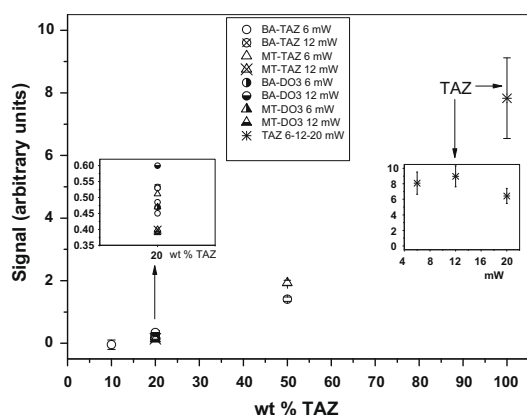
Fig. 5. Maximum induced birefringence values measured at 6 and 12 mW for the homopolymer, the two copolymers series and the guest–host systems, plotted as a function of TAZ weight fraction. The inset on the left shows a magnification in the region of 20 wt% TAZ. The inset on the right shows the dependence of the maximum signal achievable for TAZ homopolymer with the writing beam power.

the remaining birefringence, circularly polarized light is introduced at point C.

The maximum achieved birefringence for each copolymer is plotted as a function of TAZ weight fraction in Fig. 5 for different powers of the writing beam. All the films have comparable thickness values, on the order of 1000 (±100 nm). As expected, birefringence values increase with TAZ concentration. Since the birefringence is due to the anisotropy and photoinduced orientation of the azo units, a higher value of birefringence should appear when the azo content increases. The birefringence increases linearly with TAZ weight fraction up to 50 wt% TAZ, independently of the power of the writing beam, the environment in which the azo moiety is located, and the bonding between the dye and the matrix. The TAZ homopolymer achieved higher birefringence than the copolymers.

The maximum induced birefringence is independent on the laser power of the writing beam for the copolymers. This means that at a power of 6 mW, saturation is reached for all the systems analyzed. Concerning TAZ hompolymer, the influence of the writing beam power on its response is shown in the inset on the right of Fig. 5. The intensity of transmitted probe beam slightly increases with the laser power up to 12 mW, and then decrease. The first slight increase in the birefringence extents with the writing beam power is mainly caused by the reorientation mechanism, and indicates that saturation was not reached at 6 mW. As the writing beam power increased further, the thermal effect cannot be neglected in the case of TAZ since the heat from irradiation of writing beam was enough to increase the temperature around the irradiating point. This sample heating counteracts the process of orientation, causing the decrease in birefringence extent and therefore the decrease in transmitted intensity of probe beam. The different behaviour of TAZ when is compared to the copolymers is related to its low T_g value (T_g TAZ = 28 °C).

It can also be seen from Fig. 5 that for guest–host systems the reached photoinduced optical anisotropy is comparable with the values observed for the copolymers,

confirms that the azo moieties bonded to the copolymer have the sufficient mobility to be aligned.

The writing process is associated with the *trans–cis–trans* isomerization rates, quantum yields, and the local mobility of the azo group. Since the same chromophore is used in all the polymers analyzed, and the energy absorbed by the polymer films at the irradiation wavelength is the same (see Table 2), it is expected that the writing process should be affected by TAZ concentration, on the laser excitation intensity, and molecular weight and T_g of the polymer sample. We have investigated all these factors dependence on the growth of the birefringence signal. Most of the polymers possess molecular weight in the same range, which would perhaps facilitate the comparison of their properties on the same level. We analyzed the averaged time-derivative of the optically induced birefringence for achieving a quantitative representation for the photoorientation kinetics. The analysis was performed for the copolymers (BA-TAZ, MT-TAZ) and guest–host systems (BA-DO3, MT-DO3), for the time to achieve 80% of the saturation value. To compare the rate of writing, it is essential that films of comparable thickness be used; polymer films thicknesses were uniform, on the order of 1000 nm with ±100 nm variation. The derivative at each point was numerically calculated by averaging the slopes of two adjacent data points; the average of all values up to 80% of saturation was calculated for each sample. Slower writing times are reflected by lower values of the curve slope. These results are summarized in Table 3. We found that increasing TAZ concentration provoked an increment in the writing kinetics. It is clear that the kinetics of photoorientation depends on the molecular arrangement of the environment. This was expected since the reorientation of the azo chromophore around its short molecular axis induced by photoinduced isomerization cycles is dependent on the local free volume distribution.

The glass transition temperature can be a guide to predict the relative size of the free volumes. The rotational motion of *trans* isomers is considered to be restricted into a small free volume. During irradiation, slope values in BA-TAZ copolymers and BA-DO3 guest–host are much higher compared with those in MT-based systems. These results are an indication that the *trans* isomers rotate more easily

Table 3
Power of the writing beam and matrix effects on the writing dynamics.

Polymer code	Thickness (nm)	Writing slope ($\times 10^{-5}$)	
		6 mW	20 mW
BA-DO3	1000	1.48	
	1100		2.96
BA-20TAZ	950	0.267	
	1000		0.825
BA-50TAZ	970	2.25	
	970		5.71
MT-DO3	1030	0.234	
	1050		0.616
MT-20TAZ	980	0.055	
	950		0.097
MT-50TAZ	850	1.28	
	900		2.95

in polymers with lower T_g (see Table 1). The magnitude of the writing slope in BA-based copolymers is five times larger than the MT-based copolymers for samples with 20 wt% TAZ. The copolymers compared have a difference in T_g values of 27 °C ($T_{gBA20TAZ}$ = 58 °C, $T_{gMT20TAZ}$ = 85 °C). However, for 50 wt% TAZ content, the difference in T_g of the copolymers is smaller ($T_{gBA50TAZ}$ = 59 °C, $T_{gMT50TAZ}$ = 76 °C), i.e., 17 °C. The writing slope is only two times greater in BA-based copolymer than in MT-based copolymer, consistent with the smaller free volume differences indicated by measured T_g values. Also of interest is the fact that guest–host systems exhibit faster writing response (five times) compared with the copolymers containing the same DO3 concentration (20 wt% TAZ). Another interesting result that can be extracted from Table 3 is that the growth rate depends on the laser power of the writing beam. The efficiency of alignment is seen to be directly proportional to the number of photons involved in the writing process, confirming the statistical nature of the process.

On turning off the laser beam at point B in Fig. 4, the birefringence of the copolymers decreases nearly 50% for MT-TAZ and 60% for BA-TAZ, independent of film thickness, TAZ concentration and intensity of the writing beam. This stable birefringence pattern corresponds to the "store" step. In the case of the guest–host systems, the transmission signal decreased to 65% for MT-DO3 and 75% for BA-DO3 of the maximum. This low residual signal is characteristic of guest–host films because the azo moiety has a high mobility since the azo chromophores are not functionalized into the polymer backbone. Part of the decrease is associated with 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. The copolymers used in this work have a relatively low molecular weight, increasing the concentration of chain ends, allowing for extensive motion. Depending on the mobility of azobenzene chains in matrices, different relaxations were observed. Then, according to the different T_g of the polymers analyzed, the remnant birefringence in MT-based polymers is greater than that in BA-based polymers. The lower the T_g value, the higher the molecular mobility and lower the remnant birefringence. No power dependence of the decay of the birefringence signal was found. This was expected as the writing laser is already off.

Concerning the effect of the film thickness, we have investigated this variable on the maximum birefringence obtainable. A series of curves of BA-TAZ and MT-TAZ films of different thicknesses, containing 20 wt% TAZ, is shown in Fig. 6. Over the sample thickness range studied, the maximum signal obtainable increases with the thickness of the film. These results are consistent with the ones obtained by Song et al. [16]. They observed greater photoinduced birefringence for thicker films for a guest–host system. As the sample thickness increases the writing intensity can vary substantially throughout the sample. As a consequence, the effective writing time to reach saturation increases dramatically (see Fig. 6). For thick samples,
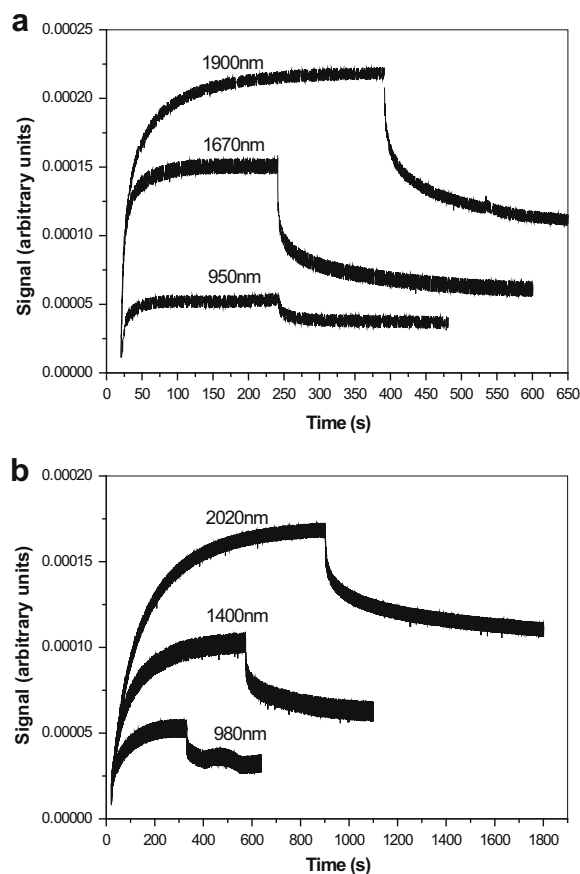

Fig. 6. Film thickness dependence of the photoinduced birefringence measured at 6 mW of: (a) BA-TAZ, and (b) MT-TAZ films. The copolymers contain 20 wt% TAZ.

complete saturation is not achieved in the finite experimental time. This effect is more evident for MT-TAZ copolymers (Fig. 6b).

At point C in Fig. 4 the erasing laser beam is turned on. This is the same writing beam, but its polarization is now circular instead of planar. Its effect is to randomize the orientation of the azobenzene groups. This randomization is achieved very fast on all the films compared to that of the writing process. The time to remove the remaining birefringence seems to be independent of the nature of the copolymer, TAZ concentration, power of the beam, and film thickness. One could try to erase a written sample by heating. The written information is stable below the T_g of the copolymer. For amorphous polymers it is enough to reach T_g and restore complete disorder in the film [17]. The overall thermal stability of the induced reorientation is very important. It is clear that heating of a written sample destroys the induced orientation, and as one gets closer to the T_g, all reorientation is lost. For this reason, it is important to synthesize polymers with high T_g to be used in reversible optical storage process.

In Fig. 4 the writing beam is again turned on (second point A in BA-50TAZ) and its effect is to produce the same level of birefringence in the same amount of time as for the

first writing on the same spot. The writing–erasing cycle can be repeated many times on the same spot on the polymer film, achieving the same level of birefringence with the same rate.

4. Conclusions

We have investigated the growth and decay processes of the optically induced birefringence in two azobenzene-functionalized epoxy-based copolymers and a homopolymer, and have contrasted the results with two guest–host systems.

The highest levels of induced birefringence are obtained for the homopolymer. When utilizing copolymers and guest–host systems, the maximum obtainable birefringence increases linearly with TAZ weight fraction. It was found that the maximum response is independent of the power of the writing beam, the environment in which the azo moiety is located, and the bonding between the dye and the matrix.

In an azobenzene-functionalized copolymer, if the birefringence is not erased by circularly polarized light, the decay segment of the signal does not reach the initial level within the time of the experiment. It was found that the free volume provides a dominant effect for remnant anisotropy. In BA-based polymers, with lower T_g and larger free volume, the remnant birefringence was found to be smaller than in MT-based polymers. Covalent attachment is seen to be an effective means to obtain remnant birefringence when irradiation is interrupted.

Concerning the writing dynamics, BA-based polymers show much higher growth slopes because of easier rotation of azobenzene groups. A study on the effect of light intensity on alignment behaviour indicated that a higher writing rate can be obtained by using irradiation light at higher intensity.

Concerning the film thickness effect, the maximum birefringence obtained increases with the thickness of the sample. An even more critical consequence of the film thickness is the significant increase in writing times for thick films resulting from the decrease in intensity of the writing beam as it penetrates into the sample.

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