



Effects of physical crosslinks on the photoresponse of epoxy-based polymers

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ABSTRACT

The influence of physical crosslinks on the photoinduced anisotropy in epoxy linear polymers with azobenzene and alkyl side groups was studied. Two series of linear epoxy-based polymers were synthesized by reaction between diglycidyl ether of bisphenol A (DGEBA), Disperse Orange-3 (DO3), and dodecylamine (DA). Two strategies of synthesis were employed in order to analyse the optical behavior of the polymers with their architecture. As a result, a polymer with randomly distributed amine groups (one-step polymerization), and another with both amines forming blocks (two-step polymerization) were synthesized. The experimental evidence derived from different techniques confirmed that isothermal annealing at several temperatures produced association of DA alkyl chains. The rate of this physical gelation process could be varied with the annealing temperature and the polymer architecture. The association strength of the alkyl chains was higher for the block polymer. The rate of the physical gelation process increased as the annealing temperature did. UV–visible spectroscopy showed interactions between the azo groups and aggregated alkyl chains only for the polymer prepared in two steps. For the same chromophore content, block polymers yielded higher birefringence than random ones did. The increment in the information stored (remnant birefringence) for annealed samples was considerable only for block polymers. This study demonstrates the importance of the polymer architecture and the presence of domains of alkyl chains on its potential photo responsiveness.

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1. Introduction

Azobenzene derivatives are very attractive for light-driven experiments, due to their easy *trans*–*cis* isomerization, which is one of the cleanest photochemical processes known to date [1]. Unlike other stimuli, temperature, electric fields, or solution composition, light offers many advantages as a primary energy source, particularly, its fast, clean, precise and remotely-controlled application. Linearly polarized light is known to induce a reorientation of azobenzene groups in the glassy state of amorphous polymers. After optical irradiation for a sufficiently long time, the materials are characterized by a preferential chromophore orientation perpendicular to the polarization direction of the light. Such polymers have been considered for applications in the area of digital and holographic reversible optical storage [2].

The nature of the polymer matrix plays a crucial role, mainly due to its power to enable or restrict the chromophores motion. We have previously reported the generation of photosensitive crosslinked coatings characterized by very high

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thermal, optical, and mechanical stability [3]. It was demonstrated that the presence of chemical crosslinks had a key part in the stability of photoinduced orientation.

Hydrophobic interactions among alkyl chains are important in the formation of many kinds of self-assembled polymer aggregates and gels. Examples of the role of van der Waals interactions between long alkyl chains in the self-assembly of metal thiolates [4] and organic–inorganic hybrid materials [5,6] can be encountered. Zucchi et al. showed that linear amphiphilic epoxy polymers synthesized by the polyaddition of diglycidyl ether of bisphenol A with dodecylamine could undergo a physical gelation process through the tail-to-tail association of dodecyl chains [7].

Photoinduced motions in azopolymers are dictated by the properties of the photoactive units and their interactions with the local environment. In this study, epoxy linear polymers with azobenzene and alkyl side groups were prepared and their photoinduced optical response was investigated. The azobenzene groups contribute to light response while alkyl chains form strong physical crosslinks by tail-to-tail associations among them, and exhibit the behavior of a physical network. Synthesized linear polymers with a hydrophilic main chain and some hydrophobic pendant chains are also known as amphiphilic polymers. As the polar polymer backbone does not have chemical affinity with the hydrophobic side chains, a phase separation tendency may be expected between the main chain parts of the polymers and the alkyl side chain parts, generating domains of associated side chains. The presence of domains of aggregated alkyl chains are an attractive alternative for optimizing chromophore motions. In order to explore the way in which the polymer architecture influences the degree of physical gelation, two strategies of synthesis were employed and compared. The aim of the present study was to analyze the effects of polymer architecture and physical crosslinks on the photoinduced anisotropy.

2. Experimental

2.1. Chemicals

The chemical reagents used in this study are shown in Fig. 1. The diepoxy monomer was based on the diglycidyl ether of bisphenol A (DGEBA, DER 332, Aldrich) with a mass per mole of epoxy groups equal to 174.3 g mol^{-1} ($n = 0.03$). The comonomers used were two different monoamines: Disperse Orange-3 (DO3, Aldrich) with a melting temperature of $200 \text{ }^\circ\text{C}$, and dodecylamine (DA, 98 wt%, Fluka), respectively.

2.2. Synthesis of linear polymers

Two series of photoresponsive epoxy-based linear polymers with pendant alkyl chains were synthesized by the bulk reaction between monomers, varying amines ratio. The reaction between DGEBA and DO3 has been previously described [8]. The syntheses were performed in a stoichiometric ratio = eq amine/eq epoxy = 1, using variable $r = \text{DO3/DA}$ ratios: 0.33 (0.25/0.75), 1 (0.50/0.50), and 3 (0.75/0.25). One of the series was prepared in one step by mixing DGEBA and the required DA amount at $60 \text{ }^\circ\text{C}$. Then DO3 was incorporated at $200 \text{ }^\circ\text{C}$ in order to obtain a homogeneous solution. Polymerization was carried out in a convection oven at $180 \text{ }^\circ\text{C}$ for specified times depending on the DO3/DA ratio (75 min for $r = 0.33$, 60 min for $r = 1$ and 45 min for $r = 3$). The other series was polymerized in two steps, as follows: DGEBA and the required DA amount were mixed and polymerized in bulk at $100 \text{ }^\circ\text{C}$ for 60 min. DO3 was then dissolved at $200 \text{ }^\circ\text{C}$ and reacted at $180 \text{ }^\circ\text{C}$ for specified times depending on the DO3/DA ratio. Curing reaction was carried out for 60 min ($r = 0.33$), 45 min ($r = 1$), and 35 min ($r = 3$). The use of larger curing times favours the etherification reaction, an undesirable side reaction [3]. For each

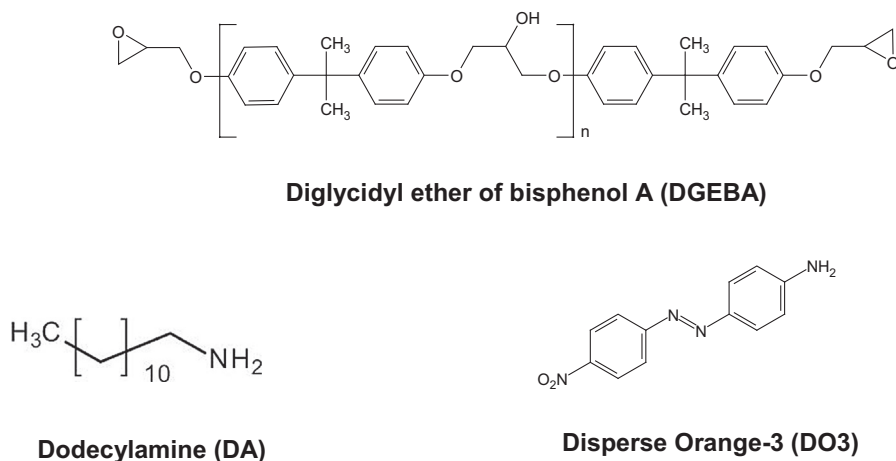


Fig. 1. Chemical structure of the reagents.

formulation and type of synthesis, optimum polymerization times were determined via FTIR spectroscopy in the NIR region ($4000\text{--}10,000\text{ cm}^{-1}$). The assignment of relevant peaks of epoxy and amine is listed in Table 1. The 4530 cm^{-1} band, assigned to the combined tension and torsion vibrations of epoxy groups, decreased progressively during reaction until its disappearance. The reference band was 4623 cm^{-1} [9]. For example, Fig. 2 illustrates two spectra taken initially ($t = 0$) and at the end of the reaction for the formulation with $\text{DO3/DA} = 0.33$ cured in one step.

To arrest subsequent structuration processes, polymers were stored at $-5\text{ }^\circ\text{C}$, a temperature that is below their glass transition temperatures.

Samples were then annealed at 60 or $100\text{ }^\circ\text{C}$ for specific intervals to favor the association of dodecyl chains. Gel fractions (weight of insoluble dried sample/initial sample weight) were determined gravimetrically from samples cut in squared pieces of approximately $1 \times 1 \times 0.2\text{ cm}^3$. The gel fraction content was estimated by weighing the insoluble portion obtained after extraction in tetrahydrofuran (THF, Biopack, 99%) for 24 h at room temperature.

2.3. Characterization techniques

All linear polymers were dissolved in THF at a concentration of 2–5 wt% and then filtered. Films were prepared by spin coating the solutions over previously cleaned glass slides, using a single wafer spin processor (model WS-400E-6NPP-lite, by Laurell) and a spinner cycle program of 3000 rpm for 60 s. The films thicknesses were varied (in the range of 100–200 nm) by adjusting the solution concentration. They were determined with a profilometer Tencor D100, sensing the height difference between the film and the glass substrate across a scratch made in the sample.

The molar mass distribution of the linear epoxy polymers obtained was analyzed by size exclusion chromatography (SEC). SEC was carried out using a Knauer chromatograph equipped with a separate sample injection camera, HPLC pump (K-501, Knauer), two columns packed with $5\text{ }\mu\text{m}$ styrene–divinylbenzene copolymer particles (Phenomenex Phenogel 50 and 103, nominal pore sizes of 50 and 103 \AA) and a refractive index detector (K-2301, Knauer). The mobile phase was THF with an elution rate of 0.35 mL min^{-1} . All scans were performed at room temperature and determined by polystyrene standards as calibration standards.

Fourier transform infrared spectroscopy (FTIR) was employed to characterize reaction products and to determine optimum polymerization times for all formulations. Measurements were taken using a Thermo Scientific Nicolet 6700 Spectrometer (4 cm^{-1} resolution), provided with a heated transmission cell (HT-32, Spectra Tech) and a programmable temperature controller (CAL 9500P, Spectra Tech, $\Delta T = \pm 0.1\text{ }^\circ\text{C}$). Samples were placed between two glass covers separated by 2 mm.

$^1\text{H-NMR}$ spectra were measured with a Bruker Avance II 500 MHz NMR spectrometer using deuterated chloroform.

Differential scanning calorimetry (DSC, Pyris 1 Perkin Elmer) was used to determine thermal transitions. Dynamic scans were performed under nitrogen flow at $10\text{ }^\circ\text{C min}^{-1}$, and the glass transition temperature (T_g) was defined at the onset of the change in specific heat.

The variation of the storage (G') and loss modulus (G'') with temperature was followed using an Anton Paar rheometer (model Physica MCR-301), equipped with a CTD 600 thermo chamber. Isothermal scans were performed at $100\text{ }^\circ\text{C}$, and dynamic scans were conducted at $1\text{ }^\circ\text{C min}^{-1}$. A parallel-plate configuration (diameter $D = 25\text{ mm}$, gap $H \approx 1\text{ mm}$) was used in oscillatory mode with a 1% amplitude at a frequency of 1 Hz.

Small-angle X-ray scattering (SAXS) measurements were performed in a XEUSS 1.0 HR (XENOCs, Grenoble) equipped with a microfocus X-ray source and a Pilatus 100 K detector (Dectris, Switzerland). The scattering intensity (in arbitrary units) was recorded as a function of the scattering vector $q = (4\pi/\lambda) \sin \theta$, where λ is the radiation wavelength (1.5419 \AA) and 2θ the scattering angle. SAXS spectra were recorded at room temperature.

Table 1
FTIR assignments of the relevant absorption bands of DGEBA/DO3:DA samples.

Wavenumber (cm^{-1})	Band assignment
4530	Epoxy combination peak (stretching and bending)
4623	CH stretching of benzene ring
4800–4900	OH combination peak
4947–5078	Primary amine combination peak (stretching and bending)
6080	Epoxy stretching (first overtone)
6530–6687	Primary and secondary amine stretching
7000	OH stretching (first overtone)
3600–3200	OH stretching
3000–2800	C–H stretching of aliphatic bonds
1603	C=C stretching of aromatic rings
1509	NO_2 asymmetric stretching
1462	N=N stretching
1338	NO_2 symmetric stretching
1338–1302	C–N stretching
1238	C–O–C stretching of aromatic groups
1130	C–O–C stretching of aliphatic groups

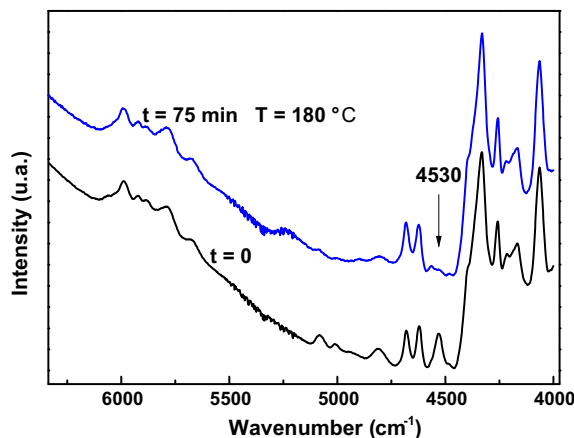


Fig. 2. FTIR spectra in the near region of a formulation cured in one step with DO3/DA = 0.33: initially ($t = 0$) and after polymerization at 180 °C during 75 min.

UV–visible spectra of films were recorded with an Agilent 8453 diode array spectrophotometer. The substrates for the films were 1 mm thick glass slides.

The photoinduced birefringence of the resulting films was determined using the experimental setup described in Fig. 3. Birefringence was measured by placing the samples between two crossed linear polarizers. A semiconductor laser at 488 nm (Coherent Sapphire™ 488-20 OEM Laser) was used as a writing beam to induce optical anisotropy in the polymer film, and another semiconductor laser at 635 nm (laser diode, model I-R-5-P) was used as a reading beam, measuring the power that is transmitted through this optical setup with a photodiode. To achieve the 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 4 mW mm⁻² of the writing laser.

3. Results and discussions

3.1. Polymerization and association of alkyl chains

Two series of photoresponsive epoxy-based linear polymers with pendant alkyl chains were synthesized using two different strategies of synthesis by bulk reaction between monomers, varying the DO3/DA ratio. Despite the chemical differences in molecular structure and reactivity between the two amines (DA or DO3), it is expected that the polymer prepared in one step consists in a linear chain structure with a randomly sequence distribution of both amines. The architecture of the polymer prepared in two steps would basically consist in DGEBA-DA oligomers containing some DO3 units as connectors of the polymer chains. The final products were characterized by FTIR, ¹H-NMR and DSC.

The chain structure of the polymers was confirmed by FTIR in the mid region (Table 1), as depicted in Fig. 4. The hydroxyl groups generated as product of the epoxy–amine reaction was observed between 3600 and 3200 cm⁻¹. The absorption bands corresponding to the aliphatic CH₂ and CH appeared between 3000 and 2800 cm⁻¹. The band resulting from the stretching

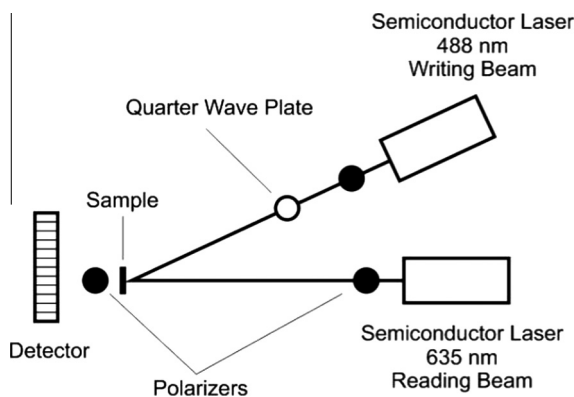


Fig. 3. Experimental setup to measure photoinduced birefringence.

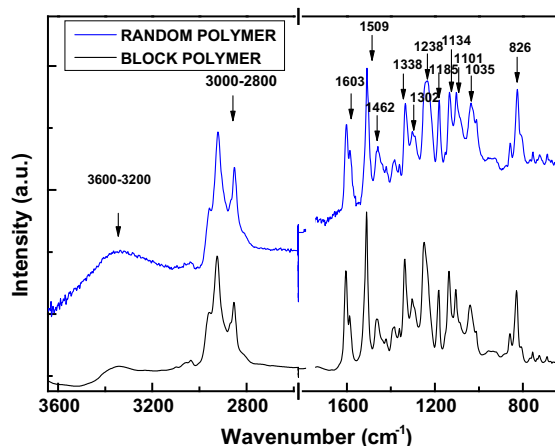


Fig. 4. FTIR spectra in the mid region of block and random polymers for the formulation with DO3/DA = 0.33.

vibration of the C=C aromatic ring of the DGEBA appeared at 1603 cm^{-1} . The peaks at 1509 and 1338 cm^{-1} were attributed to the asymmetric and symmetric vibrations of NO_2 groups, respectively, and the band at 1462 cm^{-1} to the tension vibration of the =N linkage. The vibration of the C–N linkage resulted in a peak that can be observed in the region between 1338 and 1302 cm^{-1} . The bands at 1238 cm^{-1} and 1130 cm^{-1} correspond to the stretching vibration of the aromatic and aliphatic ether group, respectively. No evident differences were observed between the spectra corresponding to both methods of synthesis.

For each series, all formulations exhibited the same pattern in ^1H NMR spectra. For instance, for the formulation DGEBA/DO3:DA with $r = 0.33$ prepared in one step (random polymer): $0.88\text{--}0.91\text{ ppm}$ ($-\text{CH}_3$ from DA); $1.25\text{--}1.3\text{ ppm}$ ($-\text{CH}_2$ from DA); $1.64\text{--}1.66\text{ ppm}$ ($-\text{CH}_2$ from DGEBA); $2.6\text{--}2.64\text{ ppm}$ ($-\text{CH}_2$ from DA); $2.7\text{--}3.67\text{ ppm}$ ($-\text{CH}$ and $-\text{CH}_2$ from DGEBA); $3.93\text{--}4.26\text{ ppm}$ ($-\text{O}-\text{CH}_2$ from DGEBA); $6.8\text{--}7.29$ ($-\text{H}$ aromatic from DGEBA); $7.88\text{--}8.38$ ($-\text{H}$ aromatic from DO3). For the same formulation prepared in two steps (block polymer): $0.89\text{--}0.91\text{ ppm}$ ($-\text{CH}_3$ from DA); $1.22\text{--}1.3\text{ ppm}$ ($-\text{CH}_2$ from DA); $1.64\text{--}1.66\text{ ppm}$ ($-\text{CH}_2$ from DGEBA); $2.59\text{--}2.64\text{ ppm}$ ($-\text{CH}_2$ from DA); $2.78\text{--}3.67\text{ ppm}$ ($-\text{CH}$ and $-\text{CH}_2$ from DGEBA); $3.95\text{--}4.15\text{ ppm}$ ($-\text{O}-\text{CH}_2$ from DGEBA); $6.7\text{--}7.3$ ($-\text{H}$ aromatic from DGEBA); $7.87\text{--}8.37$ ($-\text{H}$ aromatic from DO3).

The reaction between epoxy groups of DGEBA and amine groups of DO3 and DA results in a linear polymer. The mass-average molar masses obtained by SEC are reported in Table 2 for both series of linear polymers.

The glass transition temperatures of the polymers obtained from DSC measurements are listed in Table 3. Tg dependence on amines ratio increases constantly whenever DO3 concentration increases for both series.

The tail-to-tail association of alkyl chains in the course of polymerization have already been reported for a DGEBA-DA formulation [10]. The experimental evidence of the structuration occurring in the polymers analyzed here was obtained by rheometry and SAXS.

Fig. 5 reflects the evolution of the storage (G') and loss modulus (G'') of the formulations prepared with $r = 0.33$, though using different synthesis strategies, during prolonged heating at $100\text{ }^\circ\text{C}$. A crossover of both moduli was observed after 7.5 h (block polymer), and 11 h (random polymer), indicating the formation of physical gels with crosslinks produced by a tail-to-tail association of alkyl chains. As expected, the polymer structure plays a very important role on the physical gelation process. The time necessary for the formation of a physical gel is longer for a random polymer. The block polymer with the same chromophore concentration but annealed at $60\text{ }^\circ\text{C}$ showed the crossover of both moduli after 24 h (not shown), 17 h later compared with $100\text{ }^\circ\text{C}$. This behavior indicates a lower rate of association as annealing temperature decreases. In summary, the rate of the physical gelation process could be varied with the polymer architecture and/or the annealing temperature.

Additional experimental evidence of the structuration occurring in these systems can be obtained by SAXS. For example, Fig. 6 shows SAXS spectra obtained at $22\text{ }^\circ\text{C}$ for DGEBA-DO3/DA random polymer with DO3/DA = 0.33 after 24 h of annealing at $100\text{ }^\circ\text{C}$. Also the spectrum of DGEBA/DA is provided as a reference. A broad interference peak with a maximum at $q = 0.266\text{ \AA}^{-1}$ was observed, corresponding to a characteristic length $d = 2\pi/q = 2.36\text{ nm}$. This distance corresponds to the tail-to-tail association of two partially coiled (or interdigitated) alkyl chains [10].

Physical gels were also examined by solubility tests in THF. Samples were kept at $60\text{ }^\circ\text{C}$ for different periods of time, cooled to room temperature, and immersed in THF for 24 h . Fig. 7 illustrates the evolution of the gel fraction with annealing time at $60\text{ }^\circ\text{C}$ for the different prepared polymers. For all the compositions analyzed, DGEBA-DO3/DA block polymers exhibited high gel fractions reaching values from 70% to 100% after 24 h of annealing. Conversely, regarding random polymers, only the composition with the highest DA content, $r = 0.33$, attained a maximum gel fraction of 70%. Lower concentrations of alkyl chains generated poor tail-to-tail associations among them. For $r = 1$, gel fraction was only 40%, while for the composition with the lowest DA content, $r = 3$, no physical gel was generated.

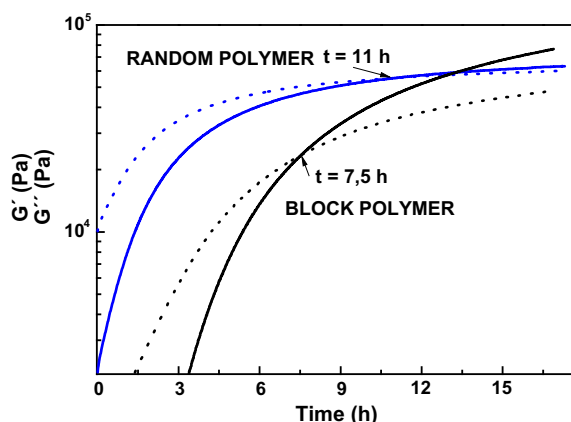
Table 2
Mass-average molar masses of both series of linear polymers.

Formulation	Mw (g mol ⁻¹) Block polymer	Mw (g mol ⁻¹) Random polymer
<i>r</i> = 0.33	2569	3811
<i>r</i> = 1	2516	3687
<i>r</i> = 3	2123	3542

Table 3

Thermal, photochemical and optical properties of DGEBA-DO3/DA films before and after association of alkyl chains.

DO3/DA ratio	% DO3 (wt)	λ_{\max} (nm)		Bulk Tg (°C)		Δn^a		% RB ^b	
		Before	After	Before	After	Before	After	Before	After
<i>Random polymers</i>									
0.33	11.0	471	471	25	31	0.016	0.021	20	45
1	21.5	466	466	44	48	0.036	0.043	55	55
3	31.5	466	464	69	69	0.043	0.052	35	42
<i>Block polymers</i>									
0.33	11.0	476	480	16	35	0.005	0.015	0	45
1	21.5	471	475	19	48	0.013	0.026	4	51
3	31.5	465	468	34	56	0.025	0.032	37	58

^a Birefringence.^b Remnant birefringence.**Fig. 5.** Evolution of the storage (G' , solid lines) and loss modulus (G'' , dashed lines) for DGEBA-DO3/DA polymers with DO3/DA = 0.33 during prolonged heating at 100 °C. Block polymer (black lines), random polymer (blue lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The association among dodecyl chains also produced an increase in the glass transition temperature of the materials (Table 3). After 24 h of annealing at 60 °C, a significant increment in Tg for block polymers was observed. Tg values increased more than 20 °C. By contrast, the change in Tg for random polymers was negligible.

3.2. UV-visible spectroscopy and photo-orientation

The photochemical properties of the present polymers are summarized in Table 3. The absorption spectra of all the polymers exhibited a peak between 466 and 480 nm. In agreement with several reports [11], after being bonded to the polymer chain, the maximum absorption wavelength of the chromophore moieties was red-shifted from 440 nm for pure DO3. The spectra of random polymers did not show any difference before and after physical gelation. In contrast, block polymers displayed a systematic shift of the absorption maxima to shorter wavelength as the azo concentration increased. Fig. 8 depicts UV-vis absorption spectra of block polymers films, before and after association among dodecyl chains. The spectra of all annealed films were red-shifted as compared to the UV-visible spectra of the same polymer but without association between dodecyl chains. The shift can be ascribed to an increased interaction between the azo groups and aggregated alkyl chains. The observed red-shifts are of the same order of magnitude for all the compositions, thus suggesting similar local matrix polarities. Tawa et al. [12] studied the dynamics of DO3 in different matrices, and postulated that the maximum absorption wavelength of DO3 depends on the local polarity surrounding the chromophore. It is known that the blue-

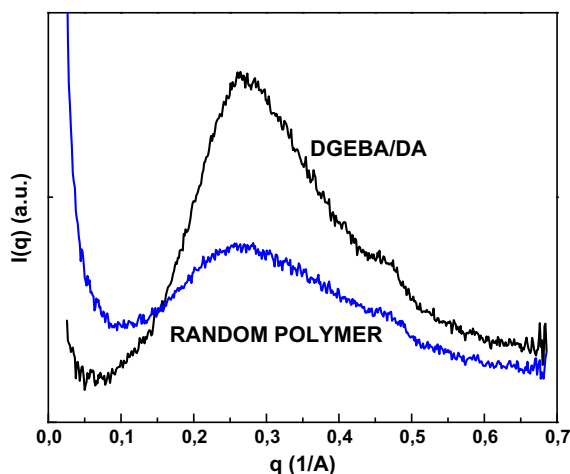


Fig. 6. SAXS spectra of a DGEBA/DA sample reference and DGEBA/DO3:DA with $r = 0.33$ heated for 24 h at 100 °C and recorded at room temperature.

shift of λ_{\max} occurs in less polar solvents given the weak interaction between the DO3 molecules and the solvents [13]. The red-shift observed in the present case may also suggest that local polarity surrounding DO3 increases when alkyl chains form domains.

Illuminating an azo containing material with linearly polarized light leads to the buildup of photoinduced anisotropy, rendering the initially isotropic materials birefringent. Fig. 9 presents the photoinduced birefringence as a function of time, the relaxation of the induced orientation after turning off the illumination (500 s), and the re-randomization of the molecular order under circularly polarized pump (1000 s) for polymers before and after annealing at 60 °C.

From the results provided in Fig. 9 and Table 3, several observations should be highlighted. With the same chromophore content, random polymers achieve higher birefringence than block ones do. In other words, a random set of chromophores contributes better to anisotropy. The same result has been observed for polymers after physical gelation. Random polymers yielded higher birefringence values; the increase was in the order of 0.005–0.007 (if compared to the same polymer without alkyl chains association). As regards block polymers, it is noted that the increment in the maximum birefringence is higher as DA concentration increases. For example, the composition with the highest DA content, $r = 0.33$, showed an increment of more than 3-fold the maximum birefringence after annealing. The compositions with $r = 1$ and 3 exhibited increments of 2- and 1.3-fold, respectively. Optical properties for all the systems under study are summarized in Table 3. Maximum birefringence remains practically constant with annealing time after reaching the maximum value (approximately 24 h). Fig. 10 illustrates this fact for block polymers.

The presence of alkyl chains domains did not slow down photoorientation kinetics. The dynamic response of the annealed and the as-prepared samples was practically the same. This fast writing speed was expected due to the high mobility of the

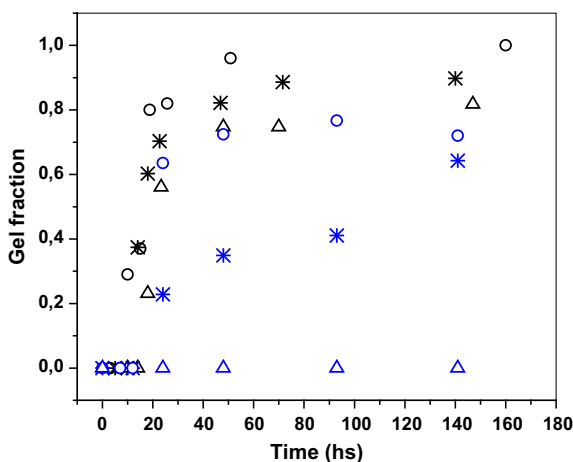


Fig. 7. Gel fractions of DGEBA-DO3/DA physical gels with a variable DO3/DA ratio: 0.33 (circles), 1 (asterisks), 3 (triangles) after annealing for different times at 60 °C. Block polymers (black symbols), random polymers (blue symbols). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

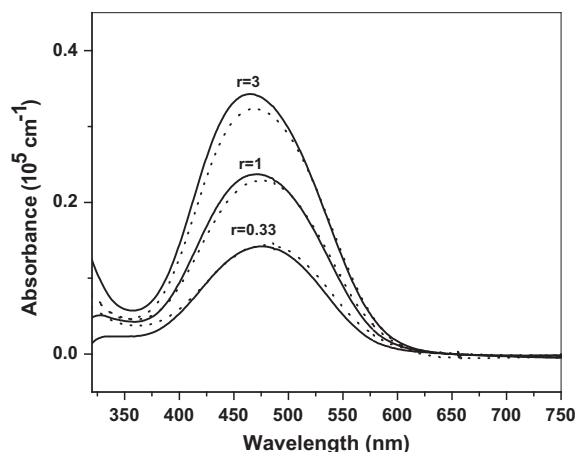


Fig. 8. UV-vis absorption spectra block polymers with a variable DO3/DA ratio, before (solid lines) and after annealing (dotted lines).

chromophore. This observation suggests that the movement of the azobenzene units is not affected by the physical crosslinks.

The drop in the measured birefringence when irradiation ceased (500 s in Fig. 9) was due to the thermal randomization of the anisotropic molecular alignment that tends to restore the disordered state. This stable birefringence pattern corresponds to the “store” step. The increment in the stored information (remnant birefringence, RB) for annealed samples was considerable only for block polymers. The greater the increase, the higher the content of alkyl chains. After alkyl chains association, the increase was approximately 45% for $r = 0.33$ and 1, decreasing to 20% for $r = 3$. Random polymers showed an improvement of 20% in RB only for the formulation with higher levels of DA, $r = 0.33$.

The magnitude of the stored information is related to the mobility of the azo chromophore. The lower the T_g value, the higher the molecular mobility and the lower the remnant birefringence. Crosslinking restrains the mobility of oriented azo groups for randomization, thus providing stability to the photoinduced orientation. Both effects, high T_g and physical crosslinks, contributed to an increase in the stored information by stabilizing chromophores orientation. For example, the T_g of the block polymer prepared with $r = 0.33$ was 35 °C after annealing, while the one for the system with $r = 3$ was 34 °C as prepared. Both T_g values were similar, however, as it can be seen in Table 3, the corresponding RB values are 45% ($r = 0.33$) and 37% ($r = 3$). The presence of physical crosslinks led to an increase in the stored information by stabilizing chromophores orientation. Samples with similar T_g values and alkyl domains showed no changes in the stored anisotropy. For instance, for the composition with $r = 1$, both strategies of synthesis generated materials with the same T_g (49 °C) and similar RB values (55% one step, 51% two steps of synthesis). If the attained RB for materials with different T_g values is compared, it is surprising to realize that the sample with lower T_g but with physical crosslinks presents higher RB percentages. As shown in Table 3, the polymers synthesized with the lowest concentration of DA, DO3/DA = 3, exhibit different T_g values after heat treatment. The

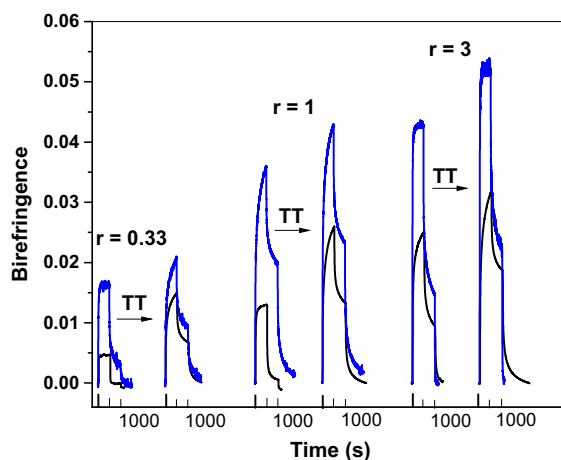


Fig. 9. Time evolution of the photoinduced birefringence showing typical writing-relaxing-erasing cycles for DGEBA-DO3/DA polymers with a variable DO3/DA ratio, before and after annealing for 24 h at 60 °C (TT). Block polymers (black lines), random polymers (blue lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

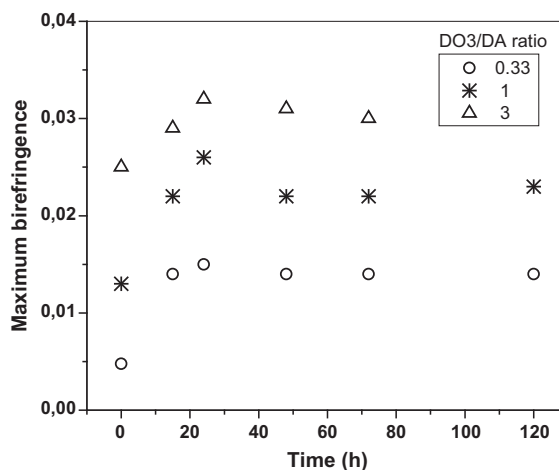


Fig. 10. Extent of maximum birefringence as a function of annealing time at 60 °C for block polymers with a variable DO3/DA ratio.

random polymer had a T_g of 69 °C, while the block polymer exhibited a T_g of 56 °C. However, the RB value for the polymer with lower T_g was much higher: 58% (compared with 42%). This result is not surprising due to the fact that the random polymer did not form physical crosslinks, while the block polymer achieved a high percentage of associated alkyl chains. These results denote the part that physical crosslinks play in the stability of the stored birefringence.

4. Conclusions

We have shown that it is possible to obtain epoxy-based polymers with widely tunable optical properties by combining polymer architecture and physical crosslinks. Photoresponsive linear epoxy polymers containing alkyl chains were synthesized by the bulk polyaddition reaction of stoichiometric amounts of DGEBA with two monoamines: dodecylamine (DA) and Disperse Orange-3 (DO3), respectively. The syntheses were performed in a stoichiometric ratio = eq amine/eq epoxy = 1 using variable $r = \text{DO3/DA}$ ratios: 0.33, 1, and 3. Two strategies of synthesis were employed to analyse the optical behavior with the polymers architecture. As a result, polymers with randomly distributed amines (random polymers) and polymers with both amines forming blocks (block polymers) were synthesized. Isothermal annealing at different temperatures produced tail-to-tail association of alkyl chains. The rate of the physical gelation process, defined by the crossover between the storage and loss moduli, could be varied with the annealing temperature and the polymer architecture. The strength of associations of alkyl chains varied in the order block polymer > random polymer. For all the compositions analyzed, block polymers exhibited high gel fractions attaining values ranging from 70% to 100%, after annealing. In contrast, regarding random polymers, only the composition with the highest DA content, $r = 0.33$, attained a gel fraction of 70% after thermal treatment. For $r = 1$, gel fraction was only 40%, while for the composition with the lowest DA content, $r = 3$, no physical gel was generated.

UV-visible spectra of annealed films were red-shifted, as compared to the same polymer, though with no association between dodecyl chains, only for block polymers. The shift can be ascribed to an increased interaction between the azo groups and domains of alkyl chains.

For the same chromophore content, the random polymer yielded higher birefringence than the block polymer did. That is, a random set of chromophores contributed better to the anisotropy of the material. The increment in the stored information (remnant birefringence) for annealed samples was considerable only for block polymers. The greater the increase, the higher the content of alkyl chains. The motion of the azo group, and thus its orientation, could be affected by the crosslinking of its molecular environment. Hence, it can be concluded that the presence of domains of aggregated alkyl chains results in an increment in the rigidity of the system, that facilitates the birefringence extent, does not affect the mobility of the azobenzene units, and confers better stability upon induced anisotropy after the light is turned off.

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