Epoxy-Based Azopolymers with Enhanced Photoresponsive Properties Obtained by Cationic Homopolymerization

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Azopolymers are highly versatile materials due to their unique photoresponsive properties. In this contribution, a novel azo-modified epoxy network is synthesized by cationic homopolymerization with boron trifluoride monoethylamine (BF$_3$.MEA) complex as initiator. The effect of the addition of a fixed content of amino-functionalized azo chromophore, Disperse Orange 3, into the polymer matrix is studied in detail. First of all, the thermal curing cycle is optimized by means of differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) measurements. Then, the resulting bulk azo-modified epoxy networks are characterized by means of thermogravimetric analysis (TGA), FTIR, DSC, UV–vis spectroscopy, and rheological measurements. Finally, the optical response of thin films of these materials is determined. The results evidence that azo-modified epoxy networks obtained by cationic polymerization with optimized curing cycle display high T_g values, high maximum photoinduced birefringence, fast writing speed, and exceptionally high remnant anisotropy. Therefore, this material is a promising candidate to be used for optical storage applications.

1. Introduction

In the past few decades, polymers containing azobenzene units, commonly named azopolymers, have been extensively investigated for their unique photoresponsive properties related to photoinduced trans–cis–trans isomerization of the azo chromophores.[1] Due to these properties, azopolymers can be used for several applications in the fields of data storage, optical sensors, photonic devices, and photoprocessing among others.[2–6]

It is known that the photoresponsive properties of azopolymers are affected by the mobility of the azobenzene groups in the polymer matrix. Recent studies on photo-orientation in amorphous polymers have demonstrated the role of several polymer structural features (such as main chain rigidity, T_g, nature of the connection of the chromophore to the main chain, and free volume around the azo moiety) on the photoinduced anisotropy. In general, better optical responses are obtained for materials with higher T_g values.[7] Furthermore, it was reported that in high-T_g polymers, crosslinking or formation of interpenetrating polymer networks improve even more the stability of the photoinduced orientation.[7]

Epoxy networks are intensively used in a wide range of technological applications due to their excellent thermal and mechanical properties.[8] Currently, there are few published studies on the development of photoresponsive azo-modified epoxy networks with different optical properties.[9–11] We have previously reported the synthesis and characterization of azo-modified epoxy systems obtained by different polymer growth mechanisms: step growth polymerization, by epoxy-amine[1] and epoxy-isocyanate[12] reactions, and anionic homopolymerization initiated by different amines.[1] It was demonstrated that the photoresponsive properties are strongly influenced by the molecular weight between cross-linking points of the network (M_c). Higher M_c is reflected in shorter relaxation times and lower remaining birefringence.

In recent years, considerable attention has been given to the study of cationic initiators as curing agents for epoxy monomers.[8,13–15] Boron trifluoride complexes, and complex aromatic salts of Lewis acids such as diaryliodonium and triarylsulfonium have been reported as effective thermal initiators for cationic polymerization of different epoxy monomers.[16] It was demonstrated that depending on both the type of cationic initiator and the chemical structure of the epoxy monomer a variety of products can be obtained, from low-T_g rubbers to very high-T_g materials.[8] For instance, the cationic homopolymerization of diglycidyl ether of bisphenol A (DGEBA) initiated by boron trifluoride complexes results in densely crosslinked networks with relatively high values of glass transition temperature (between 160 and 180 °C).[17] These are suitable features for the development of photoresponsive azo-modified networks, as previously stated. To our knowledge, studies

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on photoresponsive behavior of azo-modified epoxy systems obtained by cationic homopolymerization have not been reported in the literature yet.

The aim of this study is to develop novel azo-modified epoxy networks by cationic polymerization, based on the idea of maximizing the photoresponsive behavior of the material. The selected epoxy monomer was based on DGEBA with boron trifluoride monoethylamine (BF$_3$•MEA) complex as thermal initiator of the crosslinking reaction. To fully understand the structure–property relationship of the developed azo-modified epoxy networks, their chemical, thermal, and optical properties were analyzed in detail and compared with azo-modified epoxy systems obtained by different polymer growth mechanisms.

2. Experimental Section

2.1. Materials

A push–pull azo dye, 4-(4-nitrophenylazo)aniline (Disperse Orange 3, DO3, Aldrich; $T_m = 200 °C$), was selected as the photosensitive molecule. The difunctional epoxy resin employed was high purity DGEBA (Sigma-Aldrich, DER 332) with a mass per mole of epoxy groups equal to 174 g mol^{-1}. Boron trifluoride monoethylamine complex (BF$_3$.MEA, Aldrich) was selected as thermal initiator. All reactants were used as received and their chemical structures are shown in **Figure 1**.

An azo-containing epoxy thermoplastic precursor (TPAZO) was synthesized from the bulk reaction between DO3 and DGEBA with an amine (NH$_2$)/epoxy stoichiometric ratio equal to 0.5 to obtain products with epoxy groups at the chain ends.[18] The reaction mixture was prepared by mixing the required amount of monomers at ≈200 °C (above T_m of DO3 crystals), and cured in a convection oven at 180 °C for 1 h to avoid polyetherification reaction, which would lead to the formation of an azo-network. Under the selected synthesis conditions, there were no free amino groups of DO3 after the reaction with DGEBA, as demonstrated in a previous publication.[18] Thus, the proposed structure of TPAZO is shown in **Figure 2**. The resulting material was completely amorphous with a T_g of 22 °C.

2.2. Synthesis of Azo Networks

2.2.1. DGEBA/BF$_3$•MEA Networks

DGEBA/BF$_3$•MEA samples were prepared by melt-mixing the selected initiator in the corresponding amount of DGEBA at 80 °C, until it becomes a homogeneous optically clear mixture. According to the literature, 0.096 mol of BF$_3$•MEA per mol of DGEBA were added.[19] Different curing cycles were tried to optimize it in order to reach complete epoxy conversion.

2.2.2. DGEBA/BF$_3$•MEA/TPAZO Networks

Epoxy networks with azobenzene moieties were obtained. Samples were prepared in the appropriate stoichiometry to obtain a 10 wt% of DO3 in the polymer network. On the one hand, the TPAZO, with a concentration of 25.8 wt% of DO3, was dissolved in a small amount of tetrahydrofuran (THF, Biopack, 99%) at room temperature and half the DGEBA resin was incorporated. Then, the THF was removed by evaporation at 65 °C. Furthermore, BF$_3$•MEA was dissolved in the remaining amount of DGEBA resin at 80 °C for 15 min. Finally, both mixtures were blended and homogenized by hand. The resulting mixture was placed for 1 h in a vacuum oven at 60 °C to remove volatiles. Different curing cycles were tried to optimize it in order to reach complete epoxy conversion.

2.3. Film Deposition

DGEBA/BF$_3$•MEA/TPAZO reactive mixtures were dissolved in THF at a concentration of 10–15 wt%. Films were prepared by spin coating the solutions over previously cleaned glass slides according to the standard RCA method,[20] 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 thicknesses of the films were varied in the range of 200–300 nm by adjusting the concentration of the solution. Once prepared, the reactive mixtures were subjected to thermal treatment in a convection oven during the time required to attain complete conversion
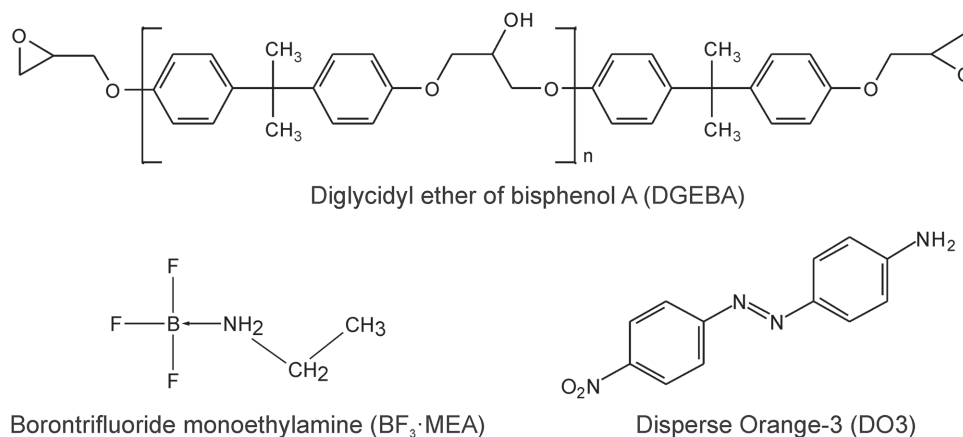

Diglycidyl ether of bisphenol A (DGEBA)

Borontrifluoride monoethylamine (BF$_3$·MEA)

Disperse Orange-3 (DO3)

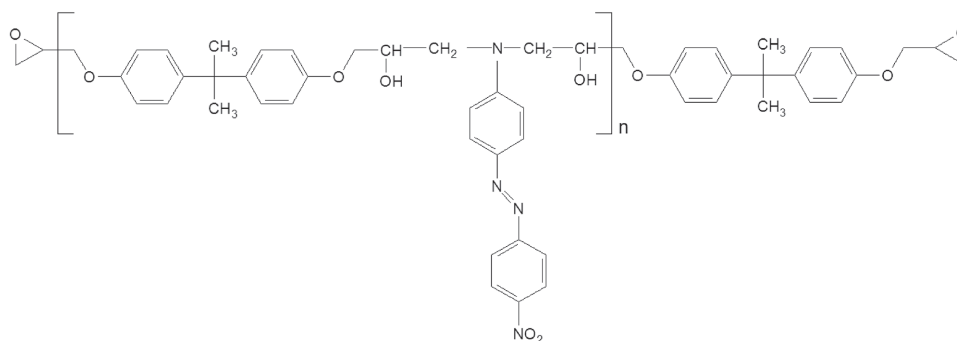**Figure 1.** Chemical structures of reactants.

Figure 2. Chemical structure of TPAZO prepolymer.

of epoxy monomer. Samples were subsequently stored at room temperature.

2.4. Characterization Techniques

Differential scanning calorimetry (DSC) was conducted using a PerkinElmer Pyris 1 device. Small sample quantities of the degassed reactive mixtures were placed in aluminum pans and dynamic scans were performed from room temperature to 300 °C at 10 °C min^{-1}, under nitrogen flow.

Fourier transform infrared spectroscopy (FTIR) was performed using a Thermo Scientific Nicolet 6700 Spectrometer with 32 coadded scans at 4 cm^{-1} resolution. Near-infrared spectroscopy (NIR) was used to monitor the curing process of DGEBA in the presence of BF$_3$•MEA with and without TPAZO at different temperatures. A heated transmission cell (HT-32 Spectra Tech) and a programmable temperature controller (CAL 9500P, Spectra Tech, $\Delta T \pm 0.1$ °C) were employed. Reactive mixtures were placed between two glass covers separated by about 2 mm. The height of the epoxy absorption peak at 4530 cm^{-1} was followed as a function of reaction time and the peak located at 4623 cm^{-1}, which is characteristic of the benzene ring, was selected as reference.[21] In addition, mid-infrared spectroscopy (MIR) was performed in ATR mode over the range 400–4000 cm^{-1} from 32 coadded scans at 4 cm^{-1} resolution.

Thermogravimetric analysis (TGA) was carried out in a TGA-50 Shimadzu Thermogravimetric Analyzer. About 10 mg samples were put in an aluminum pan and heated from room temperature to 700 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. Also, isothermal scans were performed at 180 °C and 210 °C.

Rheological measurements were carried out using an Anton Paar Physica MCR 301 rheometer equipped with a CTD 600 thermo chamber. Rheological characterization of reactive mixtures was performed to monitor the cure process from the liquid monomer to the solid thermoset stage. Measurements were performed in disposable aluminum parallel plates system (25 mm diameter, 1 mm gap) in oscillatory mode with 1% amplitude at a frequency of 1 Hz. Isothermal scans were carried out at 160 °C for the neat epoxy system, whereas the DO3-modified epoxy system was tested at 180 °C. Moreover, dynamic mechanical analysis (DMA) tests were performed at a heating rate of 5 °C min^{-1} from 20 to 260 °C with a fixed frequency

of 1 Hz. Rectangular specimens (10 mm × 20 mm × 1.3 mm) were tested under torsion mode with a distance between clamps equal to 20 mm. The storage modulus (G'), loss modulus (G) and the mechanical loss factor (tan $\delta = G''/G'$) were determined. The T_g was reported as the temperature at which tan δ reached a maximum value in the tested temperature range.

UV–vis spectra were acquired with an Agilent 8453 diode array spectrophotometer. Glass-supported sample films were directly irradiated.

Photoinduced birefringence measurements were carried out under ambient conditions at room temperature. The optical configuration of the equipment has been previously reported.[1] Each sample was placed between two crossed linear polarizers. A semiconductor laser at 488 nm (Coherent Sapphire TM 488-20 OEM Laser Optically Pumped Semiconductor Laser) was used as writing beam to induce optical anisotropy in the polymer film. Another semiconductor laser at 635 nm (laser diode, model I-R-5-P) was used as reading beam to measure the power 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 films were irradiated with 4 mW mm^{-2} of the writing laser. Each photo-orientation experiment was done on a different previously nonirradiated spot so as to avoid influences of irradiation history. The change in the transmission of the reading beam ($T = I/I_0$), which passed through the sample between the crossed polarizers, was measured with a photodiode. The induced optical birefringence (Δn) was determined according to Equation (1)

$$\Delta n = \left(\frac{\lambda}{\pi d}\right)\sin^{-1}\left(\frac{I}{I_0}\right)^{\frac{1}{2}} \qquad (1)$$

where λ is the wavelength of the reading beam, d is the 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 erase the photoinduced birefringence, a removable quarter-wave plate was used to induce circular polarization in the argon laser (erasing beam). Film thicknesses were determined with a perfilometer Tencor D100 by sensing the height difference between each film and the glass substrate, across a scratch made in the sample. Each optical measurement was performed on a different sample.
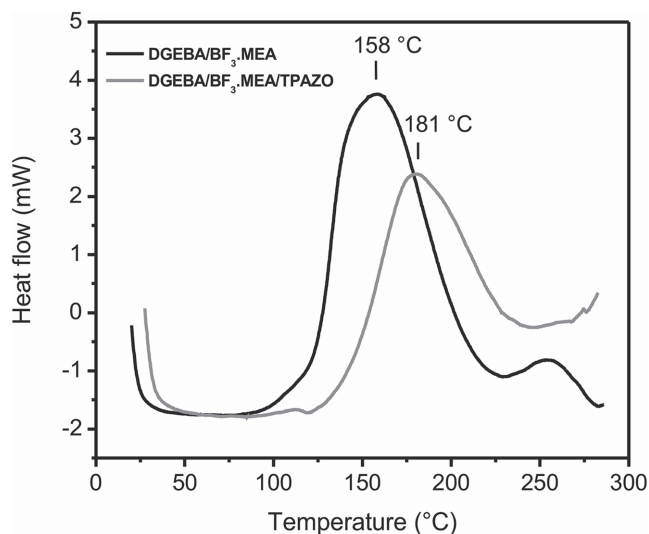
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Figure 3. Comparison of DSC thermograms of dynamic curing of neat (DGEBA/BF₃.MEA) and TPAZO-modified epoxy (DGEBA/BF₃.MEA/TPAZO) reactive mixtures.

3. Results and Discussion

3.1. Polymerization Kinetics of Neat and Azo-Modified Epoxy Networks

In the literature, results concerning the cationic polymerization of DGEBA initiated by BF₃-amine complexes are not abundant.[17,22–26] The kinetics of polymerization of neat and TPAZO-modified epoxy systems were monitored by DSC and FTIR, and then compared. **Figure 3** shows DSC thermograms in dynamic scans, from room temperature to 300 °C, of neat and TPAZO-modified epoxy reactive mixtures. For the pure polymer, the maximum reaction rate was developed ≈160 °C while a secondary reaction peak appeared at ≈250 °C, which can be ascribed to intra- and intermolecular transfer reactions among ether and remaining oxonium groups, which have a higher activation energy than the propagation reactions, as demonstrated by Pascault and co-workers.[17,22] The main reaction peak was clearly shifted to higher temperatures, from
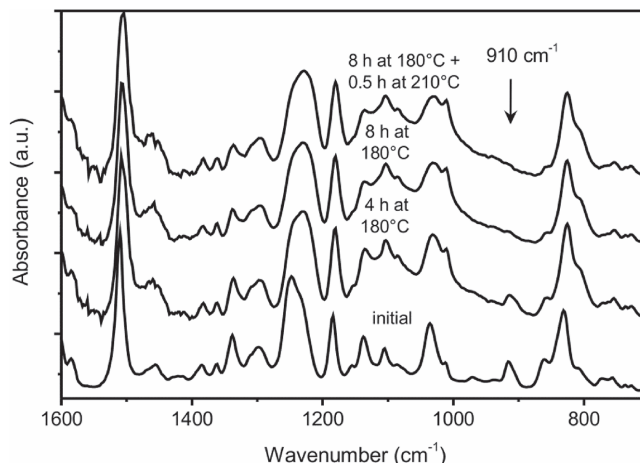

Figure 5. MIR spectra of bulk polymers for DGEBA/BF₃.MEA/TPAZO system, at different times of curing and postcuring.

158 to 181 °C, for the TPAZO-modified system, indicating a decrease in the reaction rate in this dynamic cure due to the presence of the precursor containing azo chromophores. From kinetic studies of cationic polymerization of epoxides,[17] it is known that chain-propagation steps are slow compared to the initiation reactions. On the basis of this argument, we interpret that the polymerization rate of DGEBA decreased with the TPAZO content as the effective concentration of epoxy groups decreased.

Conversion versus time curves obtained by FTIR at different reaction temperatures, appear in **Figure 4**. In agreement with DSC results, they showed that the addition of TPAZO markedly reduced the conversion rate of epoxy groups, also when the curing reaction was isothermal. For example, it is clearly seen that after 3 h at 160 °C, the reaction reached ≈95% conversion for the pure matrix. Meanwhile, only 60% of the epoxy groups have reacted for the TPAZO-modified system. As can be seen, 8 h at 180 °C were necessary to reach around 95% conversion in the modified system.

Figure 5 exhibits FTIR spectra in the NIR zone obtained after different curing periods for the TPAZO-modified system. During reaction, the maximum conversion in these highly
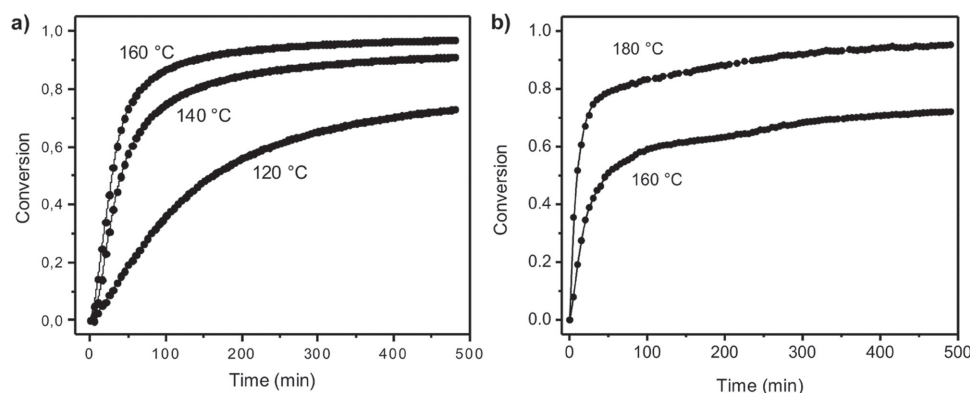

Figure 4. Conversion as a function of reaction time at different temperatures for: a) DGEBA/BF₃.MEA system (at 120 °C, 140 °C, and 160 °C); b) DGEBA/BF₃.MEA/TPAZO system (at 160 °C and 180 °C).
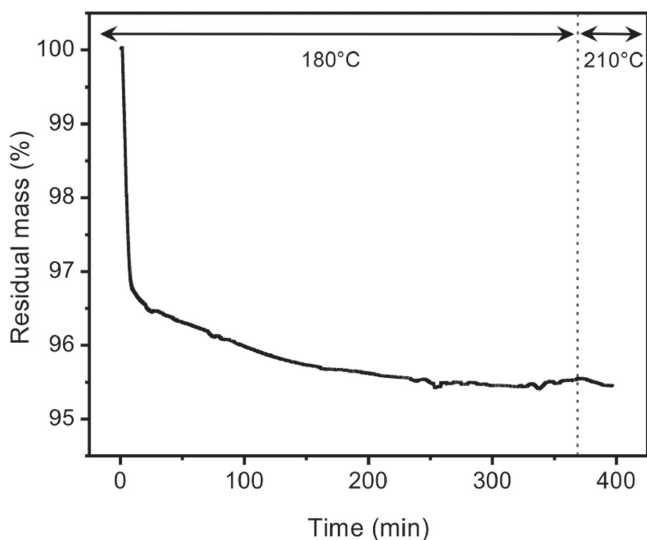
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Figure 6. Thermogravimetric behavior during isothermal cure at 180 °C and postcure at 210 °C.

Figure 7. Evolution of the storage (*G′*, black line) and loss modulus (*G″*, gray line) for DGEBA/BF₃.MEA/TPAZO system at 180 °C.

crosslinked matrices approached, but did not reach, 100% due to the limited mobility and restricted diffusion in these systems. As can be seen, a postcuring treatment at 210 °C for 30 min was required for the complete disappearance of the epoxy signal at 910 cm⁻¹.

To select the appropriate curing conditions, the thermal stability of DGEBA/BF₃·MEA/TPAZO mixtures was also evaluated during the curing and postcuring processes using TGA (**Figure 6**). The curve displays an initial drop (3.5%), corresponding to loss of physically adsorbed water,[27] and then a very subtle weight loss (around 1%) during the rest of the process, which would be attributed to some small thermal degradation during the postcuring stage.

Considering all the arguments exposed above, 8 h at 180 °C followed by 30 min at 210 °C was selected as curing and postcuring cycle, in order to obtain complete conversion without significantly losing properties.

Gelation is a critical transition that takes place during the formation of the polymer network and corresponds to the generation of a giant macromolecular structure that percolates the reaction medium. At that point, rigidity of the network starts to develop with a corresponding increase in the elastic modulus of the solid. Rheometry is a versatile technique for quantitatively measuring gelation of a crosslinking system. The crossover point of the dynamic storage modulus (*G′*) and loss modulus (*G″*) evolution during polymerization is one of the generally accepted criteria used to determine the gel point (a precise determination of the gel point would require to obtain the condition where tan δ = *G″*/*G′* becomes independent of frequency; however, this point must be close to the crossover of *G′* and *G″*).[27] **Figure 7** reflects the evolution of the storage (*G′*) and loss modulus (*G″*) of the TPAZO-modified system during reaction at 180 °C. At the gelation stage, *G′* steeply increases and becomes greater than *G″* with the onset of network formation. A crossover of both moduli was observed after only 81 s of reaction, indicating the early gelation ($X_{gel} \approx 0.2$) produced during the cationic polymerization. This result is in accord
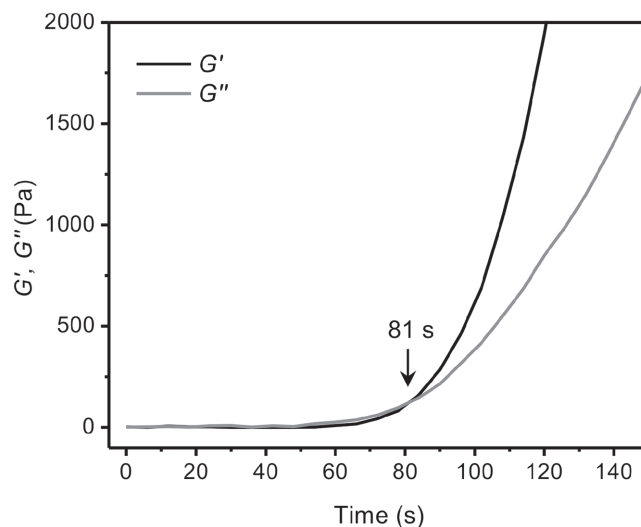
with Matejka et al.[17] who have demonstrated that gelation of this kind of systems is characterized by low conversion of the epoxy groups (X_{gel} = 0.20–0.45) and depends on initiator concentration.

3.2. Thermomechanical Characterization of Bulk Polymers

To have more information about the molecular structure of the resulting networks, DMA measurements as function of temperature were performed. **Figure 8** shows the variation of the dynamic of *G′*, *G″*, and tan δ as a function of temperature for the neat and TPAZO-modified networks. All tan δ profiles showed the occurrence of one α-relaxation (corresponding to T_g), indicating single-phase network structure. This fact was expected, since all the samples were found homogeneous and visually transparent after curing and postcuring processes.

The crosslinking density of the epoxy networks can be calculated with Equation (2), by applying the principles of rubber elasticity[28]

$$\rho = \frac{G'}{RT} \tag{2}$$

where ρ is the crosslinking density expressed in moles of elastically effective network chains per 1 L of sample, *G′* is the storage modulus in Pa in the rubbery region at a temperature well above the T_g (recorded at T_g + 50 °C), *R* is the universal gas constant and *T* is the absolute temperature at which the experimental modulus is selected. **Table 1** summarizes the DMA results, and calculated values of crosslinking density, for neat and TPAZO-modified epoxy networks. As expected, an increase in crosslinking density (and consequently in T_g) was obtained after subjecting both neat and modified epoxy networks to an additional postcuring treatment (at 210 °C for 30 min).
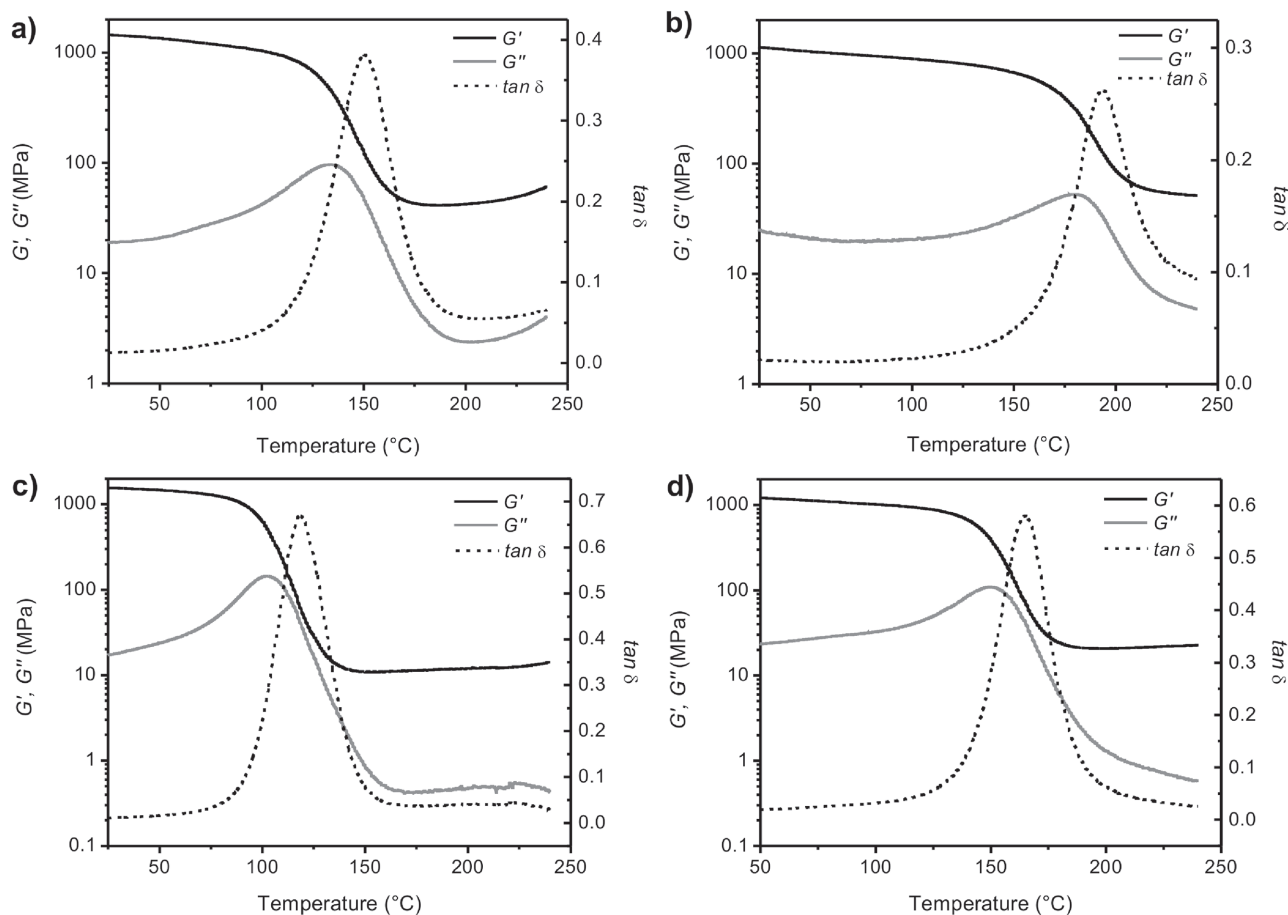
Figure 8. G', G'', and tan δ measurements as a function of temperature for: a) Neat epoxy matrix previously cured at 160 °C for 3 h; b) Neat epoxy matrix previously cured at 160 °C for 3 h, postcured 30 min at 210 °C; c) DGEBA/BF$_3$.MEA/TPAZO network previously cured at 180 °C for 8 h; d) DGEBA/BF$_3$.MEA/TPAZO network previously cured at 180 °C for 8 h, postcured 30 min at 210 °C.

Clearly, this effect was due to the formation of new bonds by conversion of residual free epoxy groups. It also can be seen that the crosslinking density of the network decreased upon TPAZO loading. TPAZO has a higher epoxy equivalent weight than DGEBA. Therefore, a replacement of DGEBA by TPAZO results in a decrease of the effective concentration of epoxy groups in the system, and consequently in a lowering of the crosslinking density of the network.

Table 1. Dynamic viscoelastic properties and crosslinking densities of neat and TPAZO-modified epoxy networks.

System	T_g [°C]	G' (at 25 °C) [MPa]	G' (at T_g + 50 °C) [MPa]	ρ [mol L^{-1}]
Cured DGEBA/BF$_3$.MEA	146 ± 7	1410 ± 57	3 ± 8	9 ± 2
Postcured DGEBA/BF$_3$.MEA	187 ± 5	1110 ± 42	46 ± 7	11 ± 2
Cured DGEBA/BF$_3$.MEA/TPAZO	115 ± 6	1515 ± 64	15 ± 5	3 ± 0
Postcured DGEBA/BF$_3$.MEA/TPAZO	161 ± 5	1220 ± 57	27 ± 8	7 ± 2

3.3. Optical Behavior of Polymeric Films

UV–vis spectra of the same DGEBA/BF$_3$.MEA/TPAZO film before and after curing and postcuring cycles are depicted in **Figure 9**. It is important to note that the thickness of the film did not change along the curing and postcuring cycles.

The absorption spectra exhibited a peak between 484 and 472 nm. As it was reported in the literature and in our own previous work,[29,30] the maximum absorption wavelength of the chromophore moieties was red-shifted (from 440 nm for DO3) after bonded to the TPAZO prepolymer. An additional shift, to lower wavelengths, together with a decrease in the intensity of the signal, was observed during reaction. Tawa et al.[31] analyzed the behavior of DO3 in different local environments, and have postulated that the maximum absorption wavelength of DO3 depends on the local polarity of the media surrounding the chromophore. They also show that a blue-shift occurs in less polar media, as occurred during the course of this cationic polymerization.[32] It should also be considered that the basic strength of the azobenzene units favors the protonation of azo groups during the cationic polymerization. In fact, protonation of azo groups could also contribute to the blue-shift observed during polymerization, as it has been demonstrated.[33]
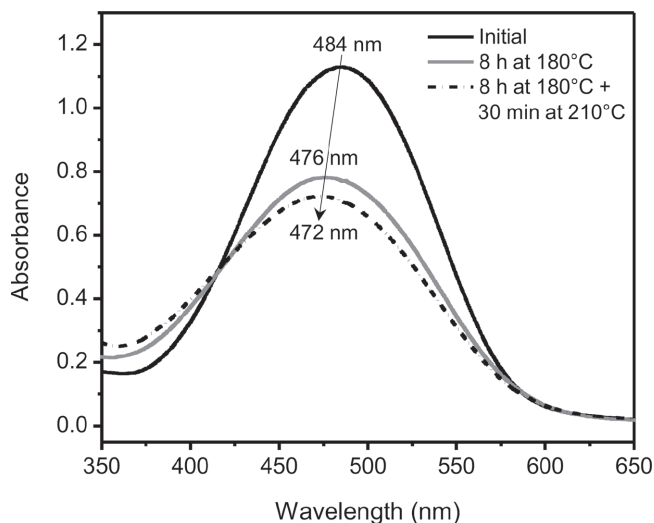
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Figure 9. UV–vis spectra of DGEBA/BF$_3$.MEA/TPAZO polymer films before and after curing and postcuring.

The optical behavior of the obtained films was also analyzed. Illumination of an azo-containing material with linearly polarized light leads to the buildup of photoinduced anisotropy, leaving the initially isotropic materials birefringent. **Figure 10** shows the photoinduced birefringence curves for the TPAZO-modified epoxy networks prepared using different curing cycles. The results of these measurements are summarized in **Table 2**.

First, the maximum birefringence induced in the samples (Δn_{max}) was evaluated. Birefringence is due to the anisotropy and photoinduced orientation of the azo moieties. As it is known, an enhancement in birefringence values is expected when the azo content increases. In our case, identical low azo contents led to analogous and high Δn_{max} values for all the curing schedules. A slight decrease in Δn_{max} was observed after postcuring the samples, probably as a consequence of some
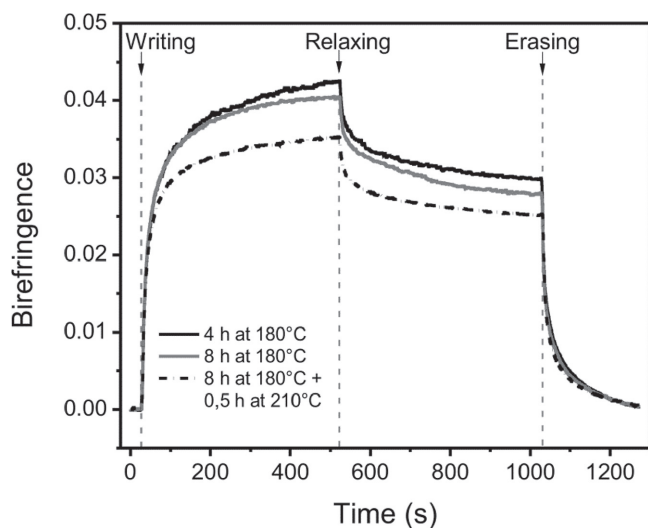
Table 2. Optical properties of TPAZO-modified epoxy networks and other similar chemical systems.

Curing cycle	Chromophore content [wt %]	Thickness [nm]	T_g [°C]	Δn_{max}	RB [%]	$t_{80\%}$ [s]
4 h at 180 °C	10	313	106 ± 1	0.0426	70	78
8 h a 180 °C	10	289	115 ± 6	0.0406	70	62
8 h at 180 °C + 0.5 h at 210 °C	10	258	161 ± 5	0.0353	72	52
CrossTPAZO[18]	25.8	–	116	0.060	72	74
DGEBA/DMAP/ DR13 [1]	10	–	108	0.016	57	329

thermal degradation of a small fraction of azo groups at 210 °C, as it was shown in Figure 6.

The study was also focused on the rate of growth of birefringence. The time required to achieve 80% of saturated birefringence level ($t_{80\%}$) is also shown in Table 2. The developed fast writing speed was expected due to the high mobility of the chromophore pending on the polymer chain. In addition, an increase in the writing rate was noticed upon curing treatment. In a previous work, we had concluded that the photoorientation of the azo chromophores is not influenced by the crosslinking itself but that it depends rather on the local free volume distribution around the chromophores.[34] As the azo chromophore was not forming part of the bridges between the polymer chains, it had a rather high mobility in the free volume of the azo network. Similar results were obtained for crosslinkable polymethacrylates containing azobenzene and acrylic groups on separate side chains in order to maintain an adequate azo mobility in the networks.[35]

The remaining birefringence (RB) once the writing laser is turned off is other of great importance analyzed parameter. The drop in the measured birefringence when irradiation ceased was due to the thermal randomization of the anisotropic molecular alignment that tends to restore the disordered state. It has been reported that this parameter is influenced by the glass transition temperature and cooperative interactions among azobenzene groups that may cause relaxation processes.[12] Table 2 shows the percentage of remaining birefringence after 250 s of turning off the writing beam. No great changes in the stored information were developed after curing or postcuring. This was an unexpected fact, as it would be waited that the higher the T_g value, the lower the molecular mobility, and the higher the remnant birefringence. Crosslinking should also restrain the mobility of oriented azo groups for randomization, thus providing stability to the chromophores orientation and contributing to an increase in the stored information.[30] A fast writing speed was observed due to high mobility of the chromophores. The decrease in $t_{80\%}$ with increasing crosslinking density suggests that the movement is not affected by crosslinks, moreover it seems to be favored by them.

To evaluate the optical behavior, obtained parameters were compared to the values previously reported for two different systems: neat crosslinked TPAZO,[18] and an anionic homopolymerized epoxy system with 4-(dimethylamine)pyridine (DMAP) as initiator and Disperse Red 13 (DR13) as azo chromophore (Table 2).[1] As can be seen, the cationic polymerized material

Figure 10. Writing, relaxing, and erasing curves of DGEBA/BF$_3$.MEA/TPAZO thin films with different curing cycles.

displayed a higher T_g value and much better optical properties than the anionic polymerized one. Both anionic and cationic epoxy homopolymerizations are complex reactions exhibiting high rate of chain-transfer reactions.[8] These reactions reduce both the length of primary chains and the glass transition temperature of polymer networks. Based on the obtained results, this effect seems to have been less marked during the cationic homopolymerization under the conditions tested. As shown in Table 2, the optical properties of the cationic homopolymerized material were comparable to those obtained for a neat crosslinked TPAZO, which had much higher azo chromophore content (25.8 wt%). Therefore, the azo-modified epoxy system obtained by cationic polymerization results a very interesting material to be used for optical storage applications due to its high maximum anisotropy, fast writing speed and very high remnant birefringence.

4. Conclusions

We have analyzed the synthesis and characterization of new azo-modified epoxy materials obtained by a cationic homopolymerization reaction. First, an azo-modified linear polymer was synthesized (TPAZO). Then, the resulting polymer was added to DGEBA and polymerized by cationic homopolymerization using a boron trifluoride monoethylamine (BF$_3$·MEA) complex as thermal initiator. Different cycles were used to prepare networks with a fixed content of azo chromophore. Polymerization kinetics was monitored employing DSC and FTIR techniques. The polymerization rate of DGEBA decreased with the TPAZO addition as the effective concentration of epoxy groups decreased. Thermomechanical and optical characterization of the resulting materials was performed. High T_g polymers were obtained after 8 h at 180 °C and 30 min at 210 °C. The presence of only one T_g value indicated that TPAZO was homogeneously incorporated to the network. Concerning optical behavior, excellent values of maximum birefringence, remnant anisotropy and writing times were obtained. In conclusion, we have satisfactorily prepared a new type of azo-modified epoxy networks by the way of cationic homopolymerization. The resulting networks are promising materials for optical storage applications.

Conflict of Interest

The authors declare no conflict of interest.

[1] L. M. Sáiz, A. B. Orofino, M. M. Ruzzo, G. F. Arenas, P. A. Oyanguren, M. J. Galante, *Polym. Int.* **2011**, *60*, 1053.
[2] S. Lee, H. S. Kang, J.-K. Park, *Adv. Mater.* **2012**, *24*, 2069.
[3] D. Wang, X. Wang, *Prog. Polym. Sci.* **2013**, *38*, 271.
[4] H. Yu, *J. Mater. Chem. C* **2014**, *2*, 3047.
[5] S. Nagano, Y. Koizuka, T. Murase, M. Sano, Y. Shinohara, Y. Amemiya, T. Seki, *Angew. Chem., Int. Ed.* **2012**, *51*, 5884.
[6] F. A. Jerca, V. V. Jerca, D. F. Anghel, G. Stinga, G. Marton, D. S. Vasilescu, D. M. Vuluga, *J. Phys. Chem. C* **2015**, *119*, 10538.
[7] H. Takase, A. Natansohn, P. Rochon, *Polymer* **2003**, *44*, 7345.
[8] J.-P. Pascault, R. J. Williams, *Epoxy Polymers: New Materials and Innovations*, Wiley-VCH Verlag GmbH & Co, Weinheim **2009**.
[9] E. Schab-Balcerzak, H. Janeczek, B. Kaczmarczyk, H. Bednarski, D. Sęk, A. Miniewicz, *Polymer* **2004**, *45*, 2483.
[10] Y. Wang, Y. He, X. Wang, *Polym. Bull.* **2012**, *68*, 1731.
[11] Y. He, X. Wang, Q. Zhou, *Polymer* **2002**, *43*, 7325.
[12] L. M. Sáiz, P. A. Oyanguren, M. J. Galante, *React. Funct. Polym.* **2012**, *72*, 478.
[13] J. V. Crivello, S. Liu, *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 389.
[14] U. Bulut, J. V. Crivello, *Macromolecules* **2005**, *38*, 3584.
[15] I. E. dell'Erba, G. F. Arenas, W. F. Schroeder, *Polymer* **2016**, *83*, 172.
[16] T. Vidil, F. Tournilhac, S. Musso, A. Robisson, L. Leibler, *Prog. Polym. Sci.* **2016**, *62*, 126.
[17] L. Matějka, P. Chabanne, L. Tighzert, J. Pascault, *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1447.
[18] A. B. Orofino, G. Arenas, I. Zucchi, M. J. Galante, P. A. Oyanguren, *Polymer* **2013**, *54*, 6184.
[19] L. González, X. Ramis, J. M. Salla, A. Mantecón, A. Serra, *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 6869.
[20] W. Kern, *Semicond. Int.* **1984**, *7*, 94.
[21] R. Fernández, M. Blanco, M. J. Galante, P. A. Oyanguren, I. Mondragon, *J. Appl. Polym. Sci.* **2009**, *112*, 2999.
[22] N. Bouillon, J. P. Pascault, L. Tighzert, *Makromol. Chem.* **1990**, *191*, 1417.
[23] P. Chabanne, L. Tighzert, J. P. Pascault, B. Bonnetot, *J. Appl. Polym. Sci.* **1993**, *49*, 685.
[24] C. O. Bounds, R. Goetter, J. A. Pojman, M. Vandersall, *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 409.
[25] T. Vidil, F. Tournilhac, L. Leibler, *Polym. Chem.* **2013**, *4*, 1323.
[26] T. Vidil, F. Tournilhac, *Macromolecules* **2013**, *46*, 9240.
[27] J.-P. Pascault, H. Sautereau, J. Verdu, R. J. Williams, *Thermosetting Polymers*, Taylor & Francis, New York **2002**.
[28] L. E. Nielsen, *J. Macromol. Sci., Polym. Rev.* **1969**, *3*, 69.
[29] X. Wang, J. Kumar, S. K. Tripathy, L. Li, J.-I. Chen, S. Marturunkakul, *Macromolecules* **1997**, *30*, 219.
[30] M. Victorel, L. M. Sáiz, M. J. Galante, P. A. Oyanguren, *Eur. Polym. J.* **2016**, *76*, 256.
[31] K. Tawa, K. Kamada, T. Sakaguchi, K. Ohta, *Polymer* **2000**, *41*, 3235.
[32] G. Svatos, C. Curran, J. Quagliano, *J. Am. Chem. Soc.* **1955**, *77*, 6159.
[33] M. Hoefnagel, A. van Veen, B. Wepster, *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 562.
[34] R. Fernández, I. Mondragon, M. Galante, P. Oyanguren, *J. Polym. Sci., Part B: Polym. Phys.* **2009**, *47*, 1004.
[35] H. Takase, A. Natansohn, P. Rochon, *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 1686.