Journal of Polymer Science Part B

Influence of Chromophore Concentration and Network Structure on the Photoorientation Properties of Crosslinked Epoxy-Based Azopolymers

Journal:	*Journal of Polymer Science Part B: Polymer Physics*
Manuscript ID:	08-12-0634.R1
Wiley - Manuscript type:	Original Article
Date Submitted by the Author:	
Complete List of Authors:	FERNANDEZ, RAQUEL; Universidad País Vasco, Chemical & Environmental Engineering, Polytechnic School Mondragon, Inaki; Universidad País Vasco, Chemical & Environmental Engineering, Polytechnic School GALANTE, MARIA; INTEMA, POLYMER DIVISION OYANGUREN, PATRICIA; INTEMA, POLYMER DIVISION
Keywords:	azo polymers, epoxy resin, networks

Influence of Chromophore Concentration and Network Structure on the Photoorientation Properties of Crosslinked Epoxy-Based Azopolymers

R. FERNÁNDEZ [1], I. MONDRAGON [1], M. GALANTE [2], P. OYANGUREN [2] *

[1] 'Materials + Technologies' Group, Department of Chemical & Environmental Engineering, Polytechnic School, Universidad País Vasco/Euskal Herriko Unibertsitatea, Plaza Europa 1, 20018 Donostia-San Sebastián, Spain.

[2] Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J. B. Justo 4302, 7600 Mar del Plata, Argentina.

*Corresponding author: Tel.: +54 223 4816600; fax: + 54 223 4810046

E-mail: oyanguren@intema.gov.ar

ABSTRACT

An azo prepolymer (TAZ) was synthesized by reaction between Disperse Orange-3 (DO3) and diglycidyl ether of bisphenol A (DGEBA). Selected amounts of TAZ were blended with DGEBA and cured with an aliphatic diamine, either meta-xilylenediamine (MXDA) or polyetheramines (Jeffamine D series). The photoinduced anisotropy and optical storage properties in two series of crosslinked epoxy-based azo polymers with different architectures and chromophore contents (from 3 to 24 in weight) have been investigated. Measurements of the birefringence (Δn) induced with linearly polarized 488 nm light show that the Δn values increases with DO3 weight fraction. Networks with the same chromophore concentration but different backbones exhibit similar levels of induced anisotropy under the same irradiation conditions. The remaining birefringence and relaxation times are influenced by the molecular weight between crosslinks ($\overline{Mc}$) of networks. Higher $\overline{Mc}$ is reflected in shorter relaxation times and lower remaining birefringence. In terms of the level of induced dichroism measured on relaxed films, it was found an agreement with the remaining anisotropy.

Keywords: Photoinduced birefringence; Azopolymer; Epoxy networks; Optical storage

INTRODUCTION

Functionalized polymers with azobenzene chromophores covalently attached to the polymer main chain are versatile materials for constructing a variety of optical devices.[1-3] Linearly polarized light is known to induce a reorientation of azobenzene groups in the glassy state of amorphous and liquid-crystalline polymers. After an optical irradiation for a sufficiently long time, the materials are characterized by a preferential chromophore orientation perpendicular to the polarization direction of the light. This anisotropic molecular reorientation induces both birefringence and dichroism properties changing in the materials. Such polymers have been considered for applications in the area of reversible optical storage.[4] Materials that are suitable for such applications are required to display a high thermal and mechanical stability as well as photostability, defined as the ability of a polymer to keep its photoinduced orientation. It is well known that epoxy networks are highly transparent and have excellent mechanical and thermal properties. There are only a few investigations on epoxy resins as photoresponsive polymers mainly focused on amorphous copolymers.[5-11] We have previously studied the reaction kinetics and the optical storage characteristics of two azobenzene-functionalized epoxy-based copolymers and a homopolymer containing Disperse Orange-3, and have contrasted the results with two guest-host systems.[12-14] The question as far as applications in the area of optical storage are concerned arises if a stable photo-orientation can be induced in the polymeric form of the material and if the crosslinks have any influence on the photokinetics of the light-induced process. Moreover, the azo group can be attached in different polymer backbones either in the main-chain or as a side chain, allowing the mechanical and processing properties of conventional polymers to be combined with the optical properties of azo groups.

In an effort to establish materials with the desired optical storage properties, the photoorientation induced via irradiation with linearly polarized light has been investigated in a series of crosslinked epoxy-based azopolymers, each with distinct differences in the molecular structure of the unit building blocks. All the epoxy-based networks analyzed have the chromophore placed in a branch, also called crosslinked side-chain.[15] We discuss to what extent the polymer structure can influence chromophores phoroorientation, and we show that some polymeric epoxy systems provide good results in terms of optical storage and stability. Networks containing variable azobenzene units concentration and different main-chain segments are compared and analyzed.

EXPERIMENTAL

Materials and Samples Preparation

An azo prepolymer (TAZ) was synthesized by reaction between Disperse Orange-3 (DO3, Aldrich) and diglycidyl ether of bisphenol A (DGEBA, DER 332, Dow).[12-13] It was prepared in a stoichiometric ratio r = eq DO3/eq DGEBA = 0.5, to generate reaction products with epoxy groups in the extreme of chains. The resulting TAZ, having a chromophore concentration per weight relative to the polymer backbone of 26 wt %, was attached to networks via the epoxy groups. Selected amounts of TAZ were blended with DGEBA and cured with a diamine, either meta-xilylenediamine (MXDA, Aldrich) or polyetheramines (Jeffamine D series, D230 and D400, Hunstman). The chemical structures of reactants and TAZ are shown in Figure 1. The hardeners were used at a stoichiometric ratio of epoxy to amino-hydrogen groups equal to 1. Curing reaction was carried out at 100°C for MXDA and 140°C for the polyetheramines, for the time necessary to obtain total conversion of the reactants.[14]

Two series of crosslinked epoxy-based azopolymers were synthesized. One of them, TAZ-DGEBA-MXDA, was prepared employing MXDA as curing agent and using variable TAZ content (3-24 wt % DO3). The other series, TAZ-DGEBA-D230/D400, was prepared from the polyetheramines using different compositions (D230/D400 from 100/0 to 40/60). This series has a constant chromophore concentration equal to 13 wt % DO3.

Films were prepared by spin-coating using a P6700 spin-coater from 5 wt % reactive mixture solutions in tetrahydrofuran, onto clean glass slides. Tetrahydrofuran (THF) was purchased from Panreac and used without further purification. The reactive mixture was composed of TAZ, DGEBA and the curing agent. The spinner cycle program was as follows: 1000 rpm for 30 s, 4000 rpm for 10 s, and 8000 rpm for 20 s. Residual THF was removed by evaporation at room temperature. Then, reactive mixture films were cured in an oven at the corresponding temperature, depending on the curing agent employed. After curing, films were heated above the glass transition temperature (Tg) of the network and subsequently, stored at room temperature. Homogeneous thin films were obtained by this procedure. All the films had comparable thickness values, on the order of 700 (±100) nm.

Measurements

Optical storage experiments were carried out at room temperature and under ambient conditions. The experimental setup used in the optical storage experiments was similar to that previously reported.[12] The optical birefringence was induced in the film using a linearly polarized argon continuous laser operating at 488 nm (writing beam) with a polarization angle of 45° with respect to the polarization direction of the probe beam. The power of the writing beam used in the experiments was varied (between 2 and 20 mW) on a spot of 0.4 mm^2, to study the time and amplitude of the optically induced birefringence. The change in the transmission of a low power He-Ne laser (reading beam) operating at 632.8 nm, which passed through two crossed polarizers and the sample, was measured with a photodiode. Each photo-orientation experiment has been done on a different previously nonirradiated spot so as to avoid irradiation history complications. The induced birefringence was determined by measuring the probe beam transmission ($T = I/I_0$) according to:

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

where λ is the wavelength of the incident radiation, d is the film thickness, I_0 is the incident beam intensity and I is the intensity after the second polarizer.

Differential scanning calorimetry (DSC) was performed using a DSC Mettler Toledo 822 device. The glass transition temperature, defined as the onset of the change in specific heat, was determined under nitrogen flow at 10 ºC/min.

UV-visible spectra were recorded in films on a Milton Roy Spectronic Genesys 5 spectrophotometer fitted with polarizing optics. The films were exposed to a linearly polarized 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 on the relaxed films. The dichroism ratio of the films, D, was calculated from the measured absorbance at maximum wavelength (λ_{max}) parallel ($A_{//}$) and perpendicular ($A_{\perp}$) to the electric vector of the incident light (Eq. (2)).

$$D = {}^{A_{\perp}}\!/_{A_{//}} \qquad (2)$$

The theoretical molecular weight between crosslinks ($\overline{Mc}$) was calculated by assuming full conversion by Equation 3, previously employed by Lesser and Crawford.[16]

$$\overline{Mc} = \frac{2\left(Me + \sum_{fa=2}^{\infty} \frac{M_{fa}}{fa}\Phi_{fa}\right)}{\sum_{fa=3}^{\infty}\Phi_{fa}} \qquad (3)$$

where Me is the epoxy equivalent weight of the resin, M_{fa} is the molecular weight of the fa-th functional amine, Φ_{fa} is the mol fraction of amine hydrogens provided by the fa-th functional amine and fa is the amine functionality.

RESULTS AND DISCUSSION

The studies involving the two series of crosslinked epoxy-based azopolymers synthesized pointed to a clear relation between the optical storage properties and the structure of the network to which the azobenzene group is attached. Since the writing and relaxation times for azopolymers are usually in the range of a few seconds, and are basically inherent to the mechanism of orientation, the following discussion will be focused on the maximum and the residual fraction of the induced birefringence. These two parameters are the most important for practical applications. Table 1 summarizes some optical storage features of films from the two series synthesized.

Typical UV-visible spectra of films for the two series are shown in Figure 2. Also shown for comparison is the UV-visible spectrum of TAZ. Notably, the peak maximum is the same for all samples, indicating that the electronic structure of the chromophore was not altered when the dye content was changed and/or different matrices where chromophore was confined were used. These results can be taken as evidence of a negligible aggregation of chromophores, since a significant shift would be expected otherwise. More evidence of the absence of chromophore mutual interaction is shown in the inset of this figure. The absorption coefficient determined at 480 nm is independent of the chromophore content in the films. Figure 2 also shows the wavelength of the writing beam (488 nm), which is within the range of absorption of azobenzene, and the wavelength of the reading beam (633 nm), which is out of this range. All polymers had a maximum absorbance comprised between 476 and 480 nm, very close to the argon laser wavelength. Thus, it is expected an efficient absorption of the writing laser light. This fact could be reflected not only in the level of birefringence reached, but also in the time necessary to achieve it.

The influence of the writing beam power has also been studied for the two series of polymers. Figure 3 shows the maximum intensity of transmitted probe beam for TAZ-DGEBA-D230 films at different writing beam powers. The intensity of transmitted probe beam increased with the laser power up to 6 mW, after which saturation was reached. The saturation curve for TAZ-DGEBA-MXDA series was investigated with the same procedure and similar results as those showed in Figure 3 were obtained. Saturation was reached at approximately 6 mW for all the polymers studied.

To understand the mobility of the azo chromophore in the polymer network and clarify the effect of crosslinking on the orientation behaviour, in-situ birefringence measurements were performed during writing cycles (linearly polarized pump on), relaxation cycles (pump off), and photoinduced erasing processes (circularly polarized pump on). Figure 4a-b shows typical sequences of inducing and erasing birefringence for TAZ and TAZ-DGEBA-MXDA series. No transmission of the probe beam, which passed through two crossed polarizers placed before and after the film was observed, indicating the random orientation of the chromophores. However, when the writing beam was turned on at point A, the transmission increased and reached 80 % of the saturation value in about 10 s. The increase in transmission was directly related to the induced birefringence in the film. When the writing beam was turned off at point B, birefringence levels fall off from the saturation level to a relaxed level (point C). This was probably due to thermally activated dipole reorientation which would tend toward randomization of the anisotropy. The induced birefringence could be optically erased by overwriting the test spot with a circularly polarized laser light that randomized the chromophores orientation, thereby eliminating the macroscopic dipole orientation. This writing-erasing cycle can be repeated many times on the same spot on the polymer film, achieving the same level of birefringence at the same rate.

There are a few important parameters governing the extent and rate of reorientation of the azobenzene groups in an amorphous polymer film. These are the nature of the azo group, the azo group content, and the polymer structure. All polymers compared had a maximum absorbance very close to the writing laser wavelength (Figure 2). As we discuss above, for both series it is expected an efficient absorption of the writing laser light. The other parameters are analyzed in the following sections.

Variable Chromophore Concentration

It is important to determine the relationship between the maximum level of anisotropy that can be induced and the concentration of the chromophores in the polymeric material. Figure 5a, illustrates the birefringence (Δn) of TAZ and TAZ-DGEBA-MXDA samples, as a function of the azo group content (by weight). There was a nonlinear increase in the birefringence level as the azo group content increased. Since Δn is due to the anisotropy and photoinduced orientation of the azo units, a larger number of photoactive chromophores in the polymer chain generated a higher birefringence. The absence of shift of the absorption spectra of networks with variable DO3 content (Figure 2) suggests that it is not expected dipolar interaction among dye groups in this network series. This means that the probability of each dipole being oriented is independent on the proximity of other dipoles. This should lead to a linear relationship between the chromophore concentration and the attainable anisotropy. The results presented in Figure 5a may be related to the increase in the writing beam absorption upon increasing chromophore content, as reported by Dhanabalan et al.[17] The absorption increase induced a sample heating, which counteracted the process of orientation.

The level of maximum birefringence that can be achieved was about 0.03 (for 24 wt % DO3), which is similar to previously published systems, such as the studies of the photo-orientation in melamine networks containing DO3 reported by Stracke et al.[18] There, it was shown that the maximum photoinduced birefringence obtained was 0.034 for materials containing more than 50 wt % chromophore. In a series of papers, Rochon et al.[19-21] demonstrated that for amorphous polymers containing electron-donor substituents on the azobenzene group, the maximum variation in refractive index obtained was 0.08. Most studies were performed on a Disperse Red 1-containing polyacrylate with 85 wt % chromophore. Then, based on the reported values of birefringence levels for amorphous polymers, the birefringence level achieved in the present study is high. The level of Δn achieved for TAZ, shown in Figure 5a, is slightly lower than the ones obtained for networks with comparable chromophore content, indicating that there is no influence of crosslinking on the maximum value attainable. It has to be taken into account that the saturated level of Δn is the result of a combination of two processes: photoselection, which increases birefringence, and thermal randomization, which decreases its level. These two processes reach an equilibrium state while illumination is on, and the preponderance of one or the other determined the saturated level. The possibility for the azo chromophore to move around is great for TAZ which has Tg = 28°C. Consequently, its birefringence level was lower when comparing with networks.

It is important also to know how fast the birefringence can be induced in the film by the polarized laser. The time interval necessary to achieve 80 % of saturated birefringence, $t_{80\%}^{WRITE}$, as a function of chromophore concentration is shown in Figure 5b. For comparison purpose, the corresponding values for TAZ are also incorporated (closed symbols). The results demonstrate that the crosslinks do not cause a slowing down of the kinetics of photo-orientation. On the contrary, similar writing times are observed for networks when comparing with TAZ. For an interpretation of this result we have to conclude that the photo-orientation of the azo chromophores is not influenced by the cross-linking itself but that it depends rather on the local free volume distribution around the chromophores. 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.[22] On the other hand, the order of magnitude of the time to reach the maximum birefringence is in agreement with the ones reported for cast films containing push-pull azo dyes.[23] As shown in Figure 5b, a decrease in the time necessary to reach the maximum birefringence was observed with the increase in DO3 content, independently of the power of the writing beam employed. This behaviour can be understood in terms of a thermal effect. As discussed above, the increase in the sample absorption induced a sample heating as more chromophore was incorporated into the polymer. This sample heating allowed a higher molecular mobility, which results in a faster writing process. In addition, writing dynamics was dependent on the number of photons involved in the writing process. For a given DO3 concentration, writing time was shorter when increasing the power of the writing beam.

When the writing laser beam was turned off, the birefringence decayed to a stable level within 30 s for all the samples analyzed. Part of this decrease can be associated with thermal reorientation of some azobenzene groups.[24] This thermal reorientation tends to restore the thermodynamically favoured disordered state and probably it happens because of some local heat associated with the laser light which is dissipated through the film when the laser is turned off. The birefringence conserved after relaxation for TAZ-DGEBA-MXDA series can be seen in Figure 6. It is interesting to note a slight decrease in the remaining birefringence upon increasing the azo concentration in the networks. This tendency is probably related with the crosslinking density of the polymer matrix. Higher crosslinking restrains the mobility of oriented azo groups for randomization. The prepolymer TAZ exhibited the minimum remaining birefringence = 50 %. Thus, crosslinking plays an important role in the stability of the photoinduced orientation.

Polymer Structural Effects

Recent studies on photo-orientation processes in amorphous polymers have addressed the role of Tg and polymer structural effects, including the main chain rigidity, the nature of the connection of the chromophore to a rigid or semirigid or a flexible main chain, the free volume, the free volume distribution, or a combination of these.[25] The polymer structure and Tg are not the only important parameters for polymers, but the molecular weight and its distribution are also important. In fact, the glass relaxation is characterized by Tg, which is affected by several factors including the molecular weight, swelling, and cross-linking. As was explained in the experimental section, all networks were synthesized employing the same azo-prepolymer (TAZ) in which the chromophore is tethered at both ends to the polymer chain. The connection of TAZ to network precursors is possible thanks to the presence of epoxy groups in the extreme of chains. The difference between the azo-networks is the structure of the diamine employed. The presence of aromatic rings in the backbone of MXDA-cured samples leads to a less flexible chain structure than for TAZ-DGEBA-D230/D400 system. In this section, we discuss to what extent the polymer structure can influence chromophore photo-orientation in the series of epoxy-based networks containing a constant concentration of chromophore.

Figure 7 shows the saturated values of the photoinduced birefringence for TAZ-DGEBA-MXDA (13 wt % DO3) and TAZ-DGEBA-D230/D400 systems against the molecular weight between crosslinks of networks ($\overline{Mc}$). Networks with the same chromophore concentration but different backbones exhibited similar levels of induced anisotropy under the same irradiation conditions. This is an indication that for the networks analyzed here, the maximum induced birefringence is only function of the overall chromophore concentration. These experimental results are consistent with the ones reported by Takase et al.[22] when comparing maximum birefringence of azo-containing polymethacrylate copolymers before and after crosslinking. They found that the maximum value achieved during the linearly polarized laser irradiation is only a function on the azo content.

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, it is expected that the writing process should be affected by the molecular structure and Tg of the polymer sample. During irradiation, $t_{80\%}^{WRITE}$ values decreased as $\overline{Mc}$ increased (or Tg decreased, as the relationship between Tg and $\overline{Mc}$ for both types of networks is lineal for a constant DO3 content). These results are an indication that the *trans* isomers rotate more easily in polymers with lower Tg (see Table 1). Concerning the polymer structural effects on the dynamics of the writing process, we found previously that DO3-doped epoxy-based copolymers exhibit faster writing response (five times) compared with copolymers based on epoxy resin containing the same DO3 concentration (5 wt % DO3), attached covalently as a side chain.[13] The writing dynamics of the azo-network having 5 wt % DO3 content is fifteen times slower when comparing with the guest-host system. That is to say, $t_{80\%}^{WRITE}$ values increase significantly because of the linkage effect. This behaviour is attributed to the restriction of the dynamics of the azo moiety by bonding covalently to a polymer chain and/or the presence of crosslinks between chains.

The influence of the next neighbour on the reorientation of an azo group is also provided by the level of relaxation after the writing laser is turned off. Figure 8 illustrates the remaining birefringence (curve a) as well as the time intervals necessary to achieve 80 % of remnant birefringence, $t_{80\%}^{RELAX}$, (curve b) as a function of the molecular weight between crosslinks of networks. It is worth to note that the movement of azo groups was facilitated in the polymers with higher molecular weight between crosslinks, which was reflected in shorter relaxation times and lower remaining birefringence. This can be due to the smaller Tg values (Table 1) of such polymer systems. The glass transition temperature can be a guide to predict the relative size of the free volumes. The free volume in polymers is considered as one of the polymer matrix effects on polarized light-induced anisotropy, as the rotational motion of *trans* isomers is considered to be restricted into a small volume. Depending on the mobility of azobenzene chains in matrices, different relaxations were observed. The lower the Tg value, the higher the molecular mobility and lower the remnant birefringence. Similar results were obtained by Sekkat et al.[25] when comparing polyurethane polymers, confirming the influence of the polymer structure on photo-orientation.

Typical examples of the optically induced dichroism are presented in Figure 9, where the polarized UV-visible absorption spectra of TAZ-DGEBA-MXDA (13 wt % DO3) and TAZ-DGEBA-D230 films are shown. The absorption coefficient for light polarized parallel to the writing direction was substantially less than that for light polarized in the perpendicular direction. In addition, there appears to be no significant shape difference between written films (parallel and perpendicular) and unwritten ones (see Figure 2a,c), indicating that the mechanism responsible for the dichroism is a reorientation of the trans azo molecule. The dichroic ratios for the different networks are given in Table 1. They were measured on relaxed films and were evaluated from the maximum absorbance recorded with polarized light parallel and perpendicular to the writing direction. As seen from their values, the level of optically induced dichroism stable is in agreement with the remaining anisotropy, as expected.

CONCLUSIONS

In this study we have investigated the photo-induced birefringence and dichroism of azo chromophore in two series of crosslinked epoxy-based azopolymers, each with distinct differences in the molecular structure of the unit building blocks.

Measurements of the birefringence (Δn) induced with linearly polarized 488 nm light show that the Δn values increases with chromophore weight fraction. Networks with the same chromophore concentration but different backbones exhibit similar levels of induced anisotropy under the same irradiation conditions. The remaining birefringence and relaxation times are influenced by the molecular weight between crosslinks of networks. Higher $\overline{Mc}$ is reflected in shorter relaxation times and lower remaining birefringence. In terms of the level of induced dichroism measured on relaxed films, it was found an agreement with the remaining anisotropy.

Azobenzene containing epoxy networks are a class of photosensitive materials which are characterized by a very high thermal, optical, and mechanical stability. Moreover, it has been demonstrated that the presence of crosslinks has no significant influence on the photoorientation process. These properties together with the high values of photoinduced birefringence for low chromophore content, and high remaining birefringence fraction make these materials promising for optical storage applications, waveguides and second harmonic generation.

Acknowledgements: This work was supported by a grant from University of Basque Country (UPV/EHU), Grupo Consolidado IT-365-07, MAT2006-06331-MEC and inanoGUNE projects. The authors also thank the financial support of University of Mar del Plata, CONICET and ANPCyT (Argentina).

REFERENCES

1. Natansohn, A.; Rochon, P. Chem Rev 2002, 102, 4139.

2. Ikeda, T. J Mater Chem 2003, 13, 2037.

3. Yesodha, S.; Pillai, C.; Tsutsumi, N. Prog Polym Sci 2004, 29, 45.

4. Pedersen, T.; Johansen, P.; Pedersen, H. J Opt A: Pure Appl Opt 2000, 2, 272.

5. Schab-Balcerzak, E.; Janeczek, H.; Kaczmarczyk, B.; Bednarski, H.; Sek, D.; Miniewicz, A. Polymer 2004, 45, 2483.

6. Borshch, A.; Brodyn, M.; Lyakhovetsky, V.; Volkov, V.; Kutsenko, A. Opt Comm 2005, 251, 299.

7. He, Y.; Yin, J.; Che, P.; Wang, X. Eur Polym J 2006, 42, 292.

8. Kim, D. Y.; Tripathy S. K.; Li, L.; Kumar, J. Appl Phys Lett 1995, 66, 1166.

9. Viswanathan, N. K.; Balasubramanian, S.; Li, L.; Kumar, J.; Tripathy S. K. J Phys Chem B 1998, 102, 6064.

10. Viswanathan, N. K.; Kim, D. Y.; Bian, S.; Williams, J.; Liu, W.; Li, L.; Samuelson, J.; Kumar, J.; Tripathy S. K. J Mater Chem 1999, 9, 1941.

11. He, Y.; Wang, X.; Zhou, Q. Polymer 2002, 43, 7325.

12. Fernández, R.; Mondragon, I.; Oyanguren, P. A.; Galante, M. J. React Funct Polym 2008, 68, 70.

13. Fernández, R.; Mondragon, I.; Galante, M. J.; Oyanguren, P. A. Eur Polym J 2009, 45, 788.

14. Fernández, R.; Blanco, M.; Galante, M. J.; Oyanguren, P. A.; Mondragon, I. J App Polym Sci, in press.

15. Oliveira Jr., O. N.; dos Santos Jr., D. S.; Balogh, D. T.; Zucolotto, V.; Mendonça, C. R. Adv Coll Interf Sci 2005, 116, 179.

16. Crawford, E. D.; Lesser, A. J. J Polym Sci Part B: Polym Phys 1998, 36, 1371.

17. Dhanabalan, A.; Mendonca, C. R.; Balogh, D. T.; Misoguti, L.; Constantino, C. J. L.; Giacometti, J. A.; Zilio, S. C.; Oliveira Jr., O. N. Macromolecules 1999, 32, 5277.

18. Stracke, A.; Wendorff, J. H.; Maher, J.; Rafler, G. Macromolecules 2000, 33, 2605.

19. Rochon, P.; Gosselin, J.; Natansohn, A.; Xie, S. Appl Phys Lett 1992, 60, 4.

20. Natansohn, A.; Rochon, P.; Gosselin, J.; Xie, S. Macromolecules 1992, 25, 2268.

21. Meng, X.; Natansohn, A.; Rochon, P. J Polym Sci Part B: Polym Phys 1996, 34, 1461.

22. Takase, H.; Natansohn, A.; Rochon, P. J Polym Sci Part B: Polym Phys 2001, 39, 1686.

23. Tawa, K.; Kamada, K.; Ohta, K. J Photochem Photobiol A: Chem 2000, 134, 185.

24. Natansohn, A.; Rochon, P.; Pézolet, M.; Audet, P.; Brown, D.; To, S. Macromolecules 1994, 27, 2580.

25. Sekkat, Z.; Yasumatsu, D.; Kawata, S. J Phys Chem B 2002, 106, 12407 and references there in.

Figure Captions

Figure 1. Chemical structure of the epoxy monomer (DGEBA), amines (MXDA, Jeffamine D230 and D400) and TAZ.

Figure 2. UV-visible spectra of: (a) TAZ-DGEBA-MXDA, 13 wt % DO3, (b) TAZ-DGEBA-D230/D400 (40/60), (c) TAZ-DGEBA-D230, (d) TAZ-DGEBA-MXDA, 24 wt % DO3, (e) TAZ. Also marked in the figure are the wavelengths of the reading and writing beams. The inset shows the UV-visible calibration curve of TAZ-DGEBA-MXDA series.

Figure 3. Extent of birefringence as a function of the power of the writing beam for TAZ-DGEBA-D230 system.

Figure 4. Writing, relaxing and erasing sequences on: (a) TAZ film, and (b) TAZ-DGEBA-MXDA films with variable DO3 content. The power of the writing beam is 6 mW.

Figure 5. (a) Maximum induced birefringence values measured at 6 mW for TAZ-DGEBA-MXDA system; (b) time to achieve 80 % of saturated birefringence at two different powers of the writing beam, plotted as a function of the weight percentage of DO3 in the networks. Also shown are experimental values for TAZ (closed symbols).

Figure 6. Birefringence conserved after relaxation for the TAZ-DGEBA-MXDA series plotted as a function of DO3 weight fraction. The power of the writing beam is 6 mW.

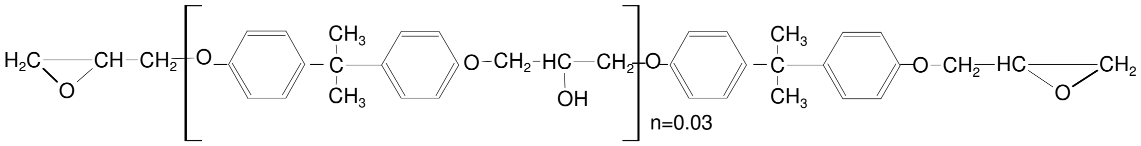
Figure 7. Maximum induced birefringence of networks containing 13 wt % DO3 for TAZ-DGEBA-MXDA (open circles) and TAZ-DGEBA-D230/D400 series (closed circles) measured at 6 mW, as a function of the molecular weight between crosslinks.

Figure 8. (a) Remaining birefringence and (b) relaxation times of networks containing 13 wt % DO3 for TAZ-DGEBA-MXDA (open symbols) and TAZ-DGEBA-D230/D400 series (closed symbols) as a function of the molecular weight between crosslinks.

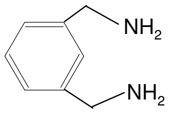
Figure 9. UV-visible spectra of TAZ-DGEBA-MXDA (13 wt % DO3) (solid lines) and TAZ-DGEBA-D230 (dotted lines) for light polarized: (a) perpendicular, and (b) parallel to the writing direction.

Table 1. Optical storage characteristics of films from the series of azo-networks TAZ-DGEBA-MXDA and TAZ-DGEBA-D230/D400. Films were irradiated at 6 mW.

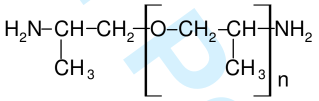
	DO3 (% w/w)	Tg (°C)	$\overline{Mc}$ (g/mol)	Δn	$t_{80\%}^{WRITE}$ (s)	% Rem biref	Dichroism ratio
TAZ-DGEBA-MXDA							
	3	110	472	0.0063	37.5	66	1.243
	5	106	537	0.0113	27.5	66	1.351
	13	101	798	0.0207	9.8	66	1.320
	18	103	1070	0.0246	7.0	64	1.311
	24	103	1680	0.0294	7.8	61	1.258
TAZ-DGEBA-D230/D400							
D230/D400							
100/0	13	85	875	0.0221	7.2	58	1.306
85/15	13	77	897	0.0223	8.1	57	1.295
70/30	13	73	918	0.0234	7.3	56	1.291
55/45	13	68	938	0.0192	4.6	56	1.273
40/60	13	62	958	0.0200	4.3	55	1.251



DGEBA

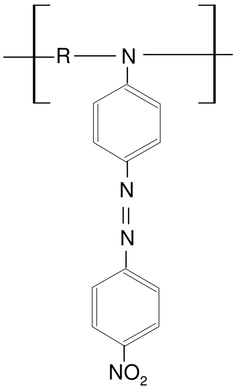


MXDA



D230
n = 2-3

D400
n = 5-6



TAZ

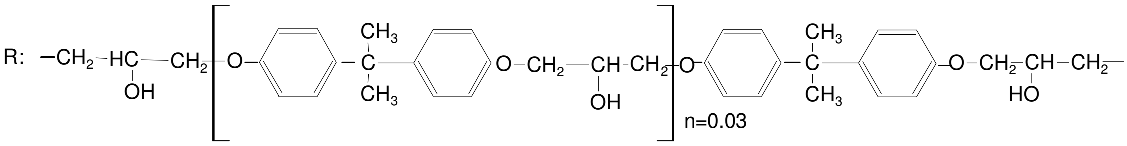


Figure 1

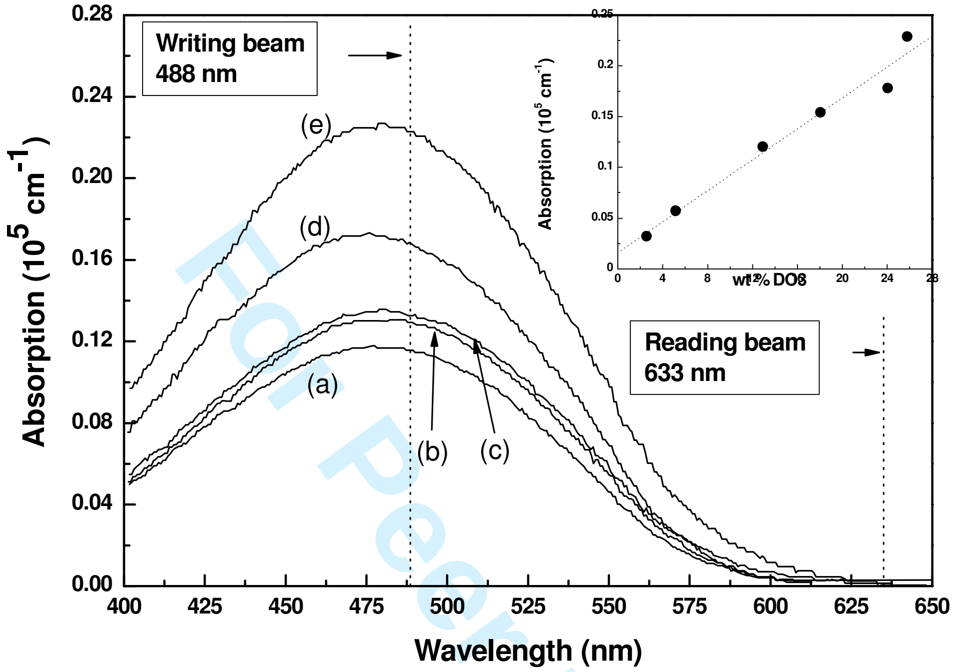

Writing beam
488 nm
Reading beam
633 nm
(a)
(b)
(c)
(d)
(e)
Absorption (10^5 cm^{-1})
0.00
0.04
0.08
0.12
0.16
0.20
0.24
0.28
Wavelength (nm)
400
425
450
475
500
525
550
575
600
625
650
Absorption (10^5 cm^{-1})
0
0.05
0.1
0.15
0.2
0.25
wt % DO3
0
4
8
12
16
20
24
28

Figure 2

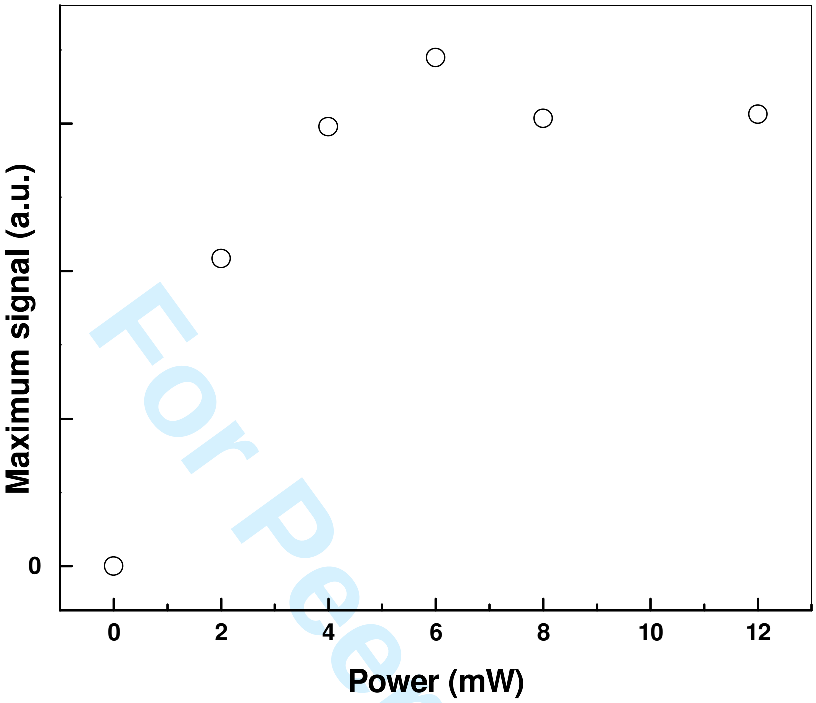


Figure 3

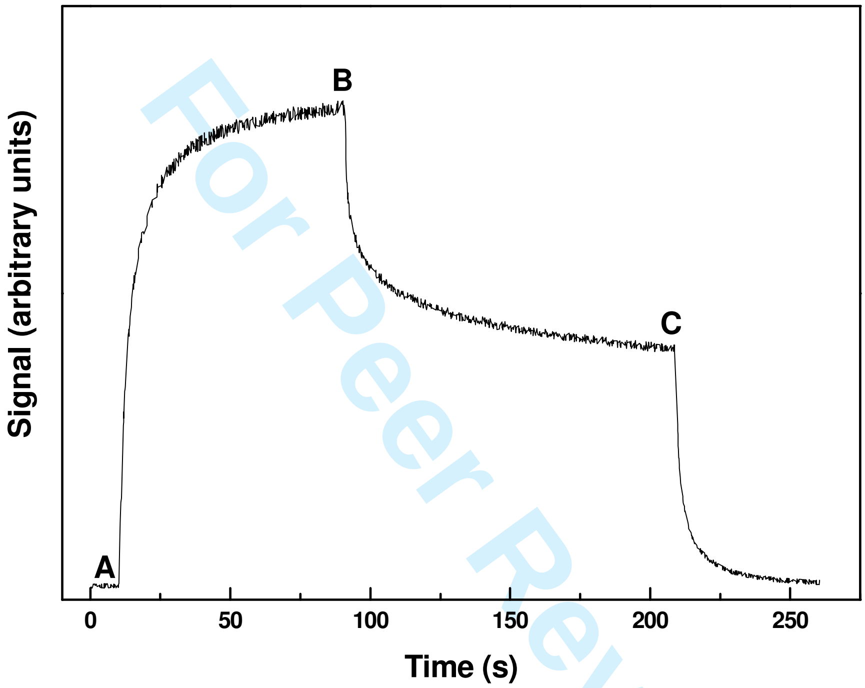


Figure 4a

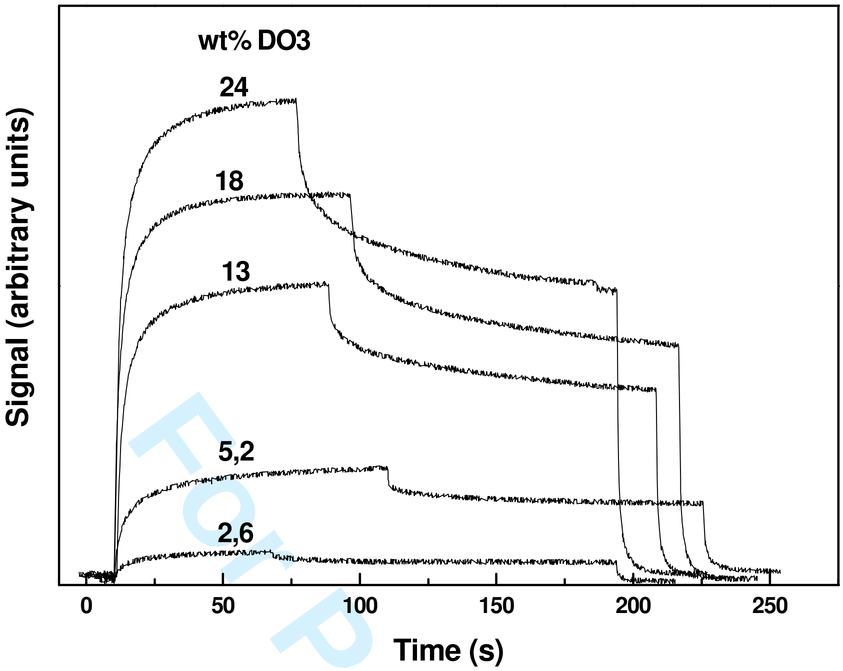

wt% DO3
24
18
13
5,2
2,6
Signal (arbitrary units)
0
50
100
150
200
250
Time (s)

Figure 4b

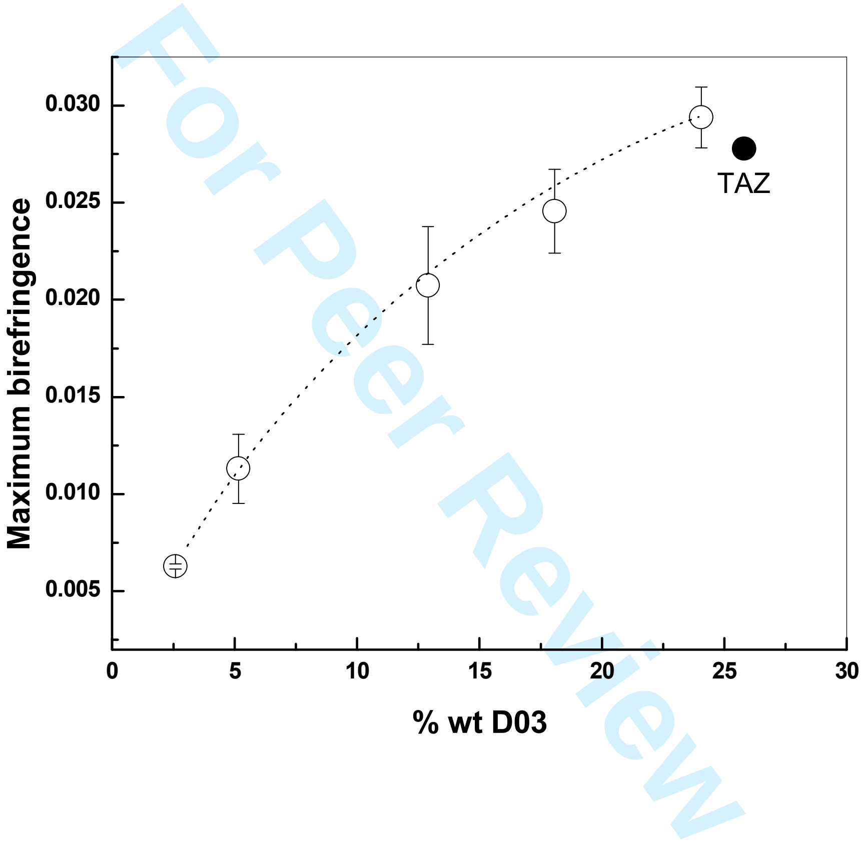

Maximum birefringence
0.005
0.010
0.015
0.020
0.025
0.030
% wt D03
0
5
10
15
20
25
30
TAZ

Figure 5a

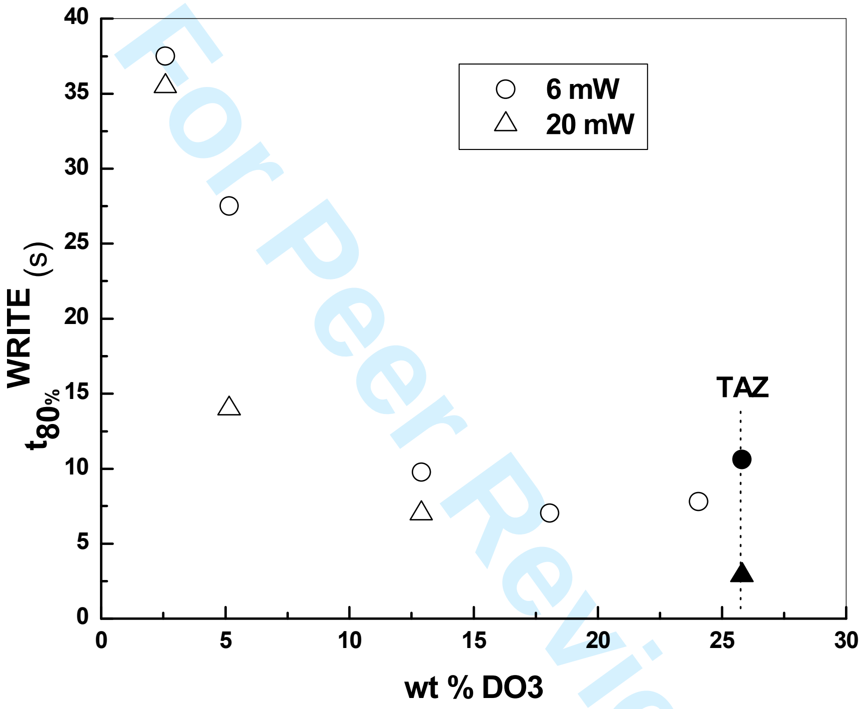

40
35
30
25
20
15
10
5
0
0
5
10
15
20
25
30
$t_{80\%}$ WRITE (s)
wt % DO3
○ 6 mW
△ 20 mW
TAZ

Figure 5b

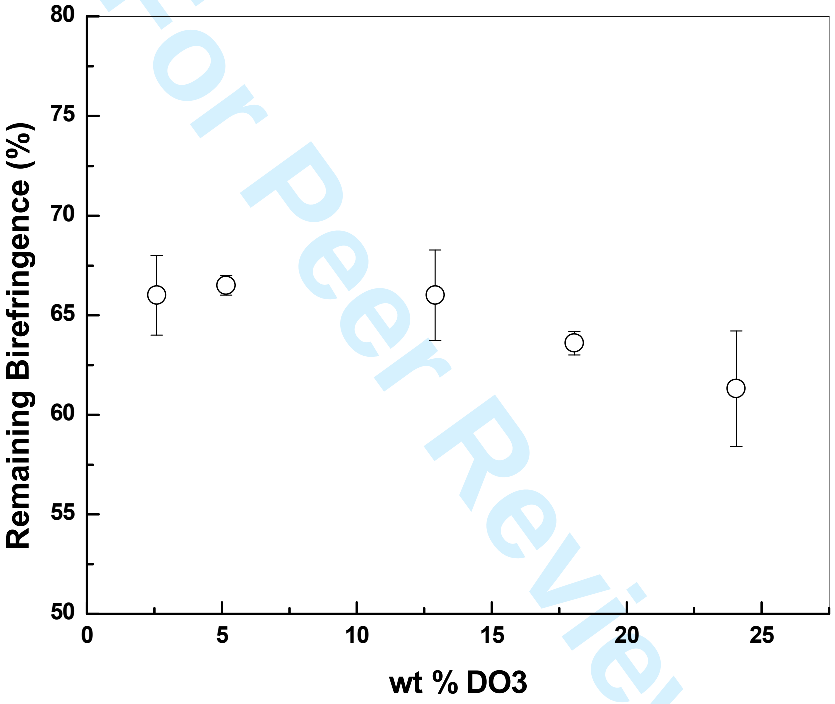

80
75
70
65
60
55
50
Remaining Birefringence (%)
0
5
10
15
20
25
wt % DO3

Figure 6

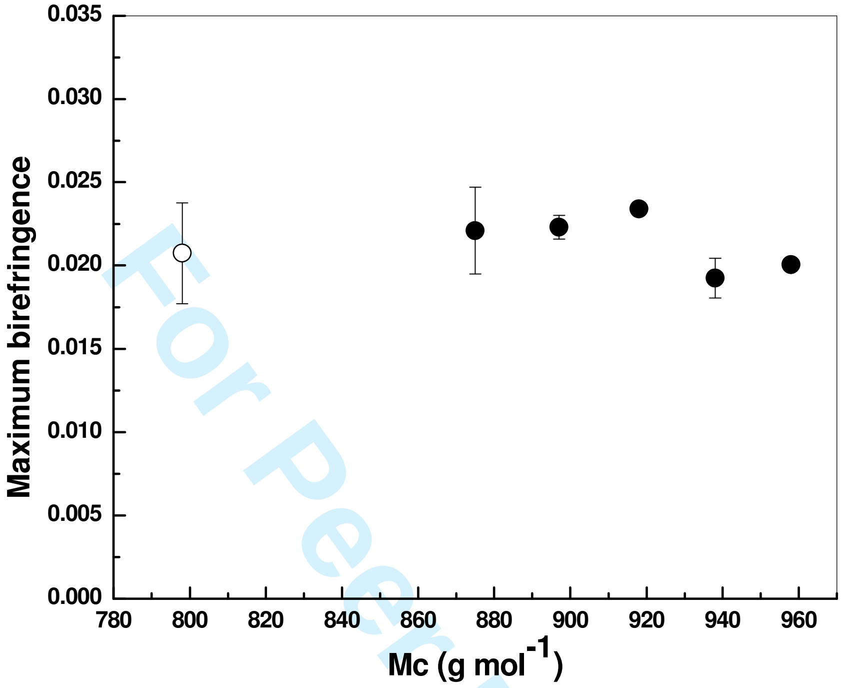

Maximum birefringence
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
780
800
820
840
860
880
900
920
940
960
Mc (g mol^{-1})

Figure 7

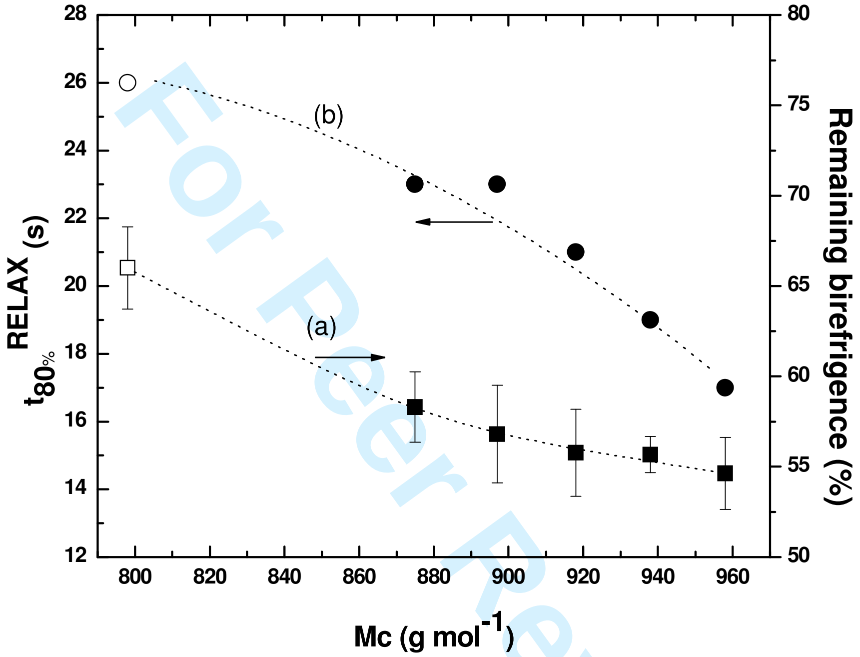

28
26
24
22
20
18
16
14
12
80
75
70
65
60
55
50
800
820
840
860
880
900
920
940
960
$t_{80\%}$ RELAX (s)
Remaining birefrigence (%)
Mc (g mol^{-1})
(a)
(b)

Figure 8

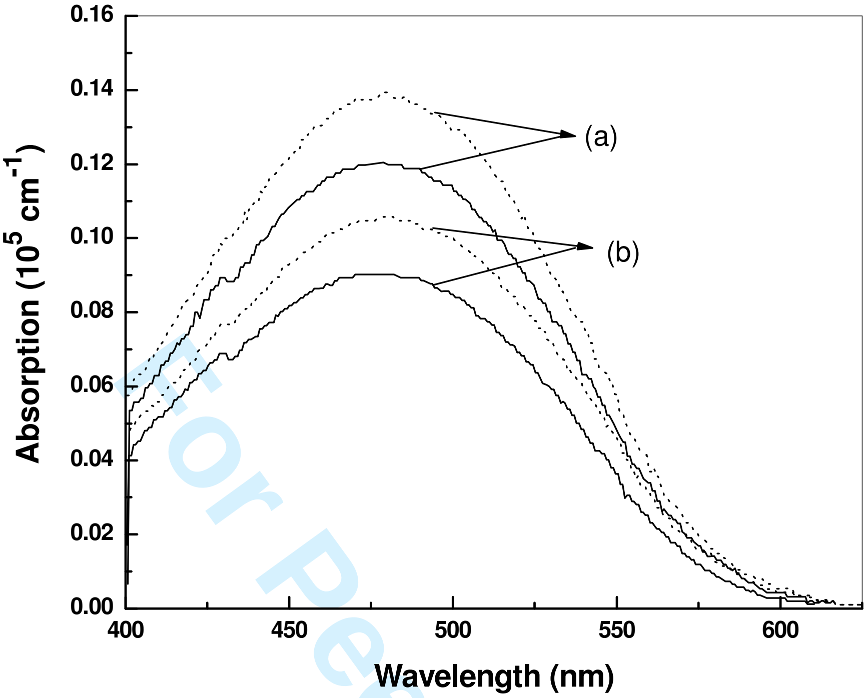

Absorption (10^5 cm^{-1})
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
400
450
500
550
600
Wavelength (nm)
(a)
(b)

Figure 9