Enhanced stability of photo-induced anisotropy due to intermolecular interactions in an azo-prepolymer confined in block copolymer

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ABSTRACT

Many efforts in the field of azobenzene-containing polymers are concentrated on exploring new material concepts to obtain efficient and stable photo-induced anisotropy. Here, an easy approach to improve the birefringent properties of an epoxy-based azo-prepolymer is reported. The designed azo-prepolymer was selectively confined in a self-assembled domain of a block copolymer and thanks to the formation of hydrogen bonds a major enhancement of its optical response was achieved. In particular, the resulting material presented double the maximum level of optical anisotropy of the neat azo-prepolymer and nearly 80% of remaining birefringence.

Keywords: Azobenzene Birefringence Block copolymers Epoxy Hydrogen bonding

1. INTRODUCTION

Azobenzene and its derivatives are fascinating molecules due to their unique response to light fields. Key to some of the most intriguing applications of these chromophores is their ability to photo-orientate through optical induced *trans–cis–trans* isomerization cycles. Notably, irradiation by linearly polarized light of appropriate wavelength enables azobenzene molecules to align in the direction perpendicular to the light polarization. This photo-induced orientation gives rise to optical anisotropy or birefringence in polymers doped or functionalized with azobenzene groups [1], [2].

Increasingly, amorphous azobenzene-containing polymers or azo-polymers are being recognized as promising materials for optical data storage applications. Compared to inorganic materials, such polymeric systems have the advantage of being highly processable and versatile. Thus, in these easily processed materials the birefringence is strong, stable, and switchable, making them ideal for optical memories. A single domain could encode one bit by either being isotropic or birefringent, a difference that is easily probed optically. On the negative side, part of the orientation optically generated in the material is lost with time. Hence, both the efficiency of photo-orientation and the amount of remaining birefringence are the main parameters that determine the quality of the obtained material and they highly depend on the structure of the chromophores as well as on their local environment [3], [4], [5].

The incorporation of azobenzene molecules in a polymer matrix can be done in different ways [6]. In the simplest form of amorphous optically active polymer, the azobenzene guest molecules are dispersed in a host polymer matrix. Such guest–host systems are both flexible and cost effective as they only require mixing of the constituents to produce the desired material [7]. However, the effectiveness of conventional guest–host systems is limited by crystallization and aggregation of chromophores, which affects the photo-orientation process. Moreover, in these simple systems the temporal and thermal stabilities of the induced birefringence are typically poor, leading to a decrease in the overall response of the material.

In contrast to guest–host systems, in azo-functionalized polymers the chromophores are covalently linked to the polymer backbone, which can prevent the aggregation of azobenzene units [8]. Nevertheless, from a practical point of view, azo-functionalized polymers are significantly less attractive than guest–host systems, owing to greater

complexity of sample preparation and higher cost of the process. In order to combine the advantages of covalently linked systems and guest–host systems, concepts widely exploited in supramolecular chemistry become useful. In fact, non-covalent interactions offer a new way to link the active molecules to the polymer backbone. Thus, intermolecular interactions between the polymeric matrix and the azobenzene molecules can prevent the aggregation of the chromophores, enhancing the photo-orientation of the active groups and the remaining induced birefringence [9].

Taking above into account, the aim of this work is the design of novel photo-responsive materials with enhanced stability of induced optical anisotropy. In order to achieve this goal, a thermoplastic azo-prepolymer (TAZ) was selectively introduced into one self-assembled phase of a block copolymer (BCP), polystyrene-*b*-poly4-vinylpyridine (PS-*b*-P4VP). Polystyrene is a non-polar polymer, whereas poly4-vinylpyridine is a polar polymer containing a pyridine group that can form hydrogen bonds with the azo-prepolymer. Consequently, novel optically active materials were developed combining the advantages of covalently functionalized polymers and the easy-to-process alternative provided by guest–host systems. Furthermore, the confinement of the azobenzene groups in one of self-assembled block copolymer domains could have effects on the photo-orientation process due to the restriction imposed by a confining geometry on the motion and rearrangement of the azobenzene moieties [10]. Therefore, the influence of covalent bonding and non-covalent intermolecular interactions as well as the effect of chromophores confinement on birefringence were studied.

2. EXPERIMENTAL SECTION

As chromophore, 4-(4-nitrophenylazo)aniline, Disperse Orange 3 (DO3), supplied by Aldrich, was employed. An epoxy resin, diglycidyl ether of bisphenol A (DGEBA), DER 332, $n = 0.03$, with an epoxy equivalent of 175 g eq^{-1}, was kindly provided by Dow Chemical. Linear PS-*b*-P4VP block copolymer with PS ($M_n = 41,000$ g mol^{-1}) and P4VP ($M_n = 24,000$ g mol^{-1}) was purchased from Polymer Source.

TAZ was synthesized in bulk reaction between DO3 and DGEBA in an amine/epoxy ratio equal to 0.5, following a procedure previously described [11], [12], [13]. This functionalization reaction of the epoxy resin with azobenzene groups to obtain TAZ is described in Scheme 1. Then, 5 wt% solutions in dichloroethane of TAZ and guest–host systems of PS-*b*-P4VP containing 15 wt% TAZ or DO3 (TAZ/PS-*b*-P4VP or DO3/PS-

b-P4VP) and PS containing 15 wt% TAZ or DO3 (TAZ/PS or DO3/PS) were prepared. To ensure hydrogen bonds formation, solutions were sonicated during 2 h and kept overnight with magnetic agitation.

Films of all samples were prepared onto clean glass slides by spin-coating using a P6700 spin-coater from Specialty Coating System Inc. Annealed samples were prepared by heating at 80 °C for 24 h in vacuum. Films thickness was calculated from topographic atomic force microscopy (AFM) images of scratched films. Variable thicknesses between 850 nm and 1.8 μm were obtained.

The morphology of the samples was studied by atomic force microscopy. AFM images were obtained with a Nanoscope IIIa scanning probe microscope (Multimode™, Digital Instruments). Tapping mode (TM) in air was employed using an integrated tip/cantilever (125 μm in length with ca 300 kHz resonant frequency and spring constant of ca 40 N/m).

Transmission optical microscopy (TOM) was employed to study the macroscopic separation of samples using a Nikon Eclipse E600 microscope. The objective lens magnification was 1000×.

Infrared spectra were taken using a Nicolet Nexus 670 Fourier transform infrared (FTIR) spectrometer equipped with a single horizontal golden gate attenuated total reflectance cell.

An experimental setup, similar to that previously reported [11], was built to induce birefringence in samples. Optical anisotropy was induced using a linearly polarized argon laser at 488 nm (writing beam) with a polarization angle of 45° with respect to the polarization direction of a He–Ne laser at 632.8 nm (reading beam). The writing beam power was 6 mW on a spot of 0.4 mm^2 and the change in the transmission of the reading beam, which passed through the sample between two crossed polarizers, was measured with a photo-diode. The induced birefringence (Δn) was determined measuring the reading beam transmission according to:

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

where λ is the reading beam wavelength, d is the film thickness, I is the reading beam intensity after the second polarizer and I_0 is the reading beam intensity between parallel polarizers in absence of anisotropy.

3. RESULTS AND DISCUSSION

PS-*b*-P4VP is an excellent BCP host due to the ability of the pyridine group to form hydrogen bonds with chromophores containing hydroxyl groups. In this work, a push–pull azo-amine, DO3, with high dipole moment was selected as chromophore to develop materials with reversible optical storage properties. An azo-prepolymer bearing hydroxyl groups, TAZ, was achieved by one-step bulk reaction between an epoxy resin and the azo-amine.

Firstly, the morphologies of DO3/PS-*b*-P4VP and TAZ/PS-*b*-P4VP binary systems, generated by self-assembly of the BCP, were investigated using TM-AFM (Fig. 1). Both guest–host systems display a self-assembled structure where most microdomains are parallel oriented to the film surface. Two different scale colours can be distinguished: PS blocks appear brighter than P4VP self-assembled domains [14]. In addition, high miscibility of DO3 and TAZ in the BCP was achieved without showing any segregation either with or without annealing treatment. Taken above into account, both the chromophore and azo-prepolymer might be confined in P4VP self-assembled phase as consequence of intermolecular interactions.

To corroborate this assumption, binary systems with PS as host matrix were analyzed. Fig. 2 shows TOM images of TAZ/PS-*b*-P4VP and TAZ/PS. Homogeneity at macroscopic level was reached only in TAZ/PS-*b*-P4VP system, confirming the preferential affinity between TAZ and P4VP. In fact, in our previous work [15], binary systems of DO3 and poly(styrene-*b*-butadiene-*b*-styrene) were studied and it was shown that DO3 aggregates were detected on the BCP surface. Additionally, the formation of hydrogen bonds with pyridine ring was verified by FTIR spectroscopy following the symmetric ring stretching mode of the pyridine group at 993 cm^{-1} (Fig. 3). In the binary systems a new band arose slightly above 1000 cm^{-1}, which can be attributed to hydrogen bonds formation with pyridine ring, as was also reported by other authors [16].

With regard to the optical properties of the designed materials, from the point of view of applications, the maximum birefringence (corresponding to a writing mechanism) and the remaining birefringence (corresponding to a storing mechanism) are the most important parameters. Therefore, our investigation focused primarily on the enhancement of those properties.

Writing-relaxing-erasing sequences obtained for TAZ, TAZ/PS-*b*-P4VP and DO3/PS-*b*-P4VP systems are depicted in Fig. 4. In the beginning there is no transmission of the reading beam, which continuously illuminates the samples, since azobenzene molecules are randomly distributed. At point *A*, the writing beam is turned *ON* and the reading beam is transmitted through the crossed polarizers due to the optically induced anisotropy in the films. As a result, birefringence is rapidly built up to the saturation level. Here it should be pointed out that as Δn values depend on the azobenzene content, for comparative purposes, the birefringence normalized to the chromophore content (Δn_N) was also calculated. When the writing beam is turned *OFF*, at point *B*, the signal begins to drop to a relaxed level where the rate of change of anisotropy is very small. The stable fraction of photo-induced anisotropy is called remaining birefringence. To completely remove that remaining photo-orientation, circularly polarized light is introduced at point *C* using a quarter-wave plate. Noteworthy is the significant increase in Δn_N and remaining birefringence of TAZ when confined in P4VP block copolymer domain.

A summary of the optical characteristics of samples non-annealed and after thermal annealing can be found in Table 1. Similar optical activity was noticed for annealed and non-annealed systems confirming that the thermal treatment employed did not result in chromophore aggregation or hydrogen bonds breakage [17]. As expected, Δn increased as DO3 content was higher since larger number of photo-active units generated higher photo-induced orientation. Nonetheless, when comparing the normalized values, a significant increase of birefringence level was achieved for TAZ/PS-*b*-P4VP. Specifically, Δn_N of TAZ/PS-*b*-P4VP is twice and three times higher than that of TAZ and DO3/PS-*b*-P4VP, respectively. These evidences are a clear consequence of strong non-covalent interactions between the host matrix and the guest azo-prepolymer. The glass transition temperature of TAZ is around 30 °C. Therefore, this azo-prepolymer has molecular mobility at room temperature, which contributes to thermal randomization, counteracting the orientation process and decreasing the saturated level of

birefringence [13]. Hydrogen bonding between the hydroxyl groups of TAZ and pyridine moieties prevented randomization and enhanced the birefringence level.

Concerning the stability of the induced anisotropy, the percentage of remaining birefringence after 60 s of turning *OFF* the writing beam (rem^{60}) was determined. As shown in Table 1, rem^{60} of TAZ increased from 30% to almost 80% when the azo-prepolymer was as guest in the BCP host. Moreover, the remaining birefringence of DO3/PS-*b*-P4VP binary system was slightly higher than that of TAZ. This can be better understood taking into account the presence of hydrogen bonding interactions also between pyridine and DO3 amine groups. These intermolecular interactions seem to be more effective than covalent ones in TAZ to retain the induced photo-orientation. It should be also pointed out that DO3 molecules were confined in self-organized domains of BCP. Such local confinement may restrain the azobenzene mobility due to interactions with the nanodomains wall, which might reduce azobenzene moieties randomization. Consequently, confinement effects exerted by the BCP could also contribute to the stability of the optically induced anisotropy.

Finally, the optical response of binary systems with polystyrene (TAZ/PS and DO3/PS) was also analyzed. However, the lack of interaction with PS matrix resulted in the aggregation of chromophores, leading to poor optical properties: low Δn and total randomization of the induced photo-orientation after turning *OFF* the writing laser.

CONCLUSIONS

We have demonstrated an easy method to improve the optical properties of azobenzene-based materials. An azo-prepolymer bearing hydroxyl groups, TAZ, was achieved by one-step facile reaction between an epoxy resin and an azo-amine. The morphology of binary systems of TAZ and DO3 in PS-*b*-P4VP and PS were studied by AFM and TOM. A microstructure was generated by self-assembly of the block copolymer. In addition, TAZ and DO3 were selectively confined in P4VP block. Furthermore, hydrogen bonding allowed attaching the azo-prepolymer and chromophore to the repeating units of P4VP, thereby suppressing macroscopic phase separation. The maximum and remaining birefringence values of TAZ as well as TAZ/PS-*b*-P4VP and DO3/PS-*b*-P4VP guest–host systems were also evaluated. The intermolecular interactions gave rise to enhanced optical response in samples investigated. The optical activity could also be improved by the confinement effect in BCP. Specifically, Δn of

TAZ/PS-*b*-P4VP, containing just 3.9 wt% of azobenzene, was around 0.8×10^{-2} and its remaining birefringence was almost 80%.

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Figure captions

Scheme 1. Schematic representation of TAZ synthesis.

Fig. 1 TM-AFM phase images of: DO3/PS-*b*-P4VP non-annealed (a) and after annealing at 80 °C for 24 h (b) and TAZ/PS-*b*-P4VP non-annealed (c) and after annealing at 80 °C for 24 h (d) (3 μm × 3 μm).

Fig. 2 TOM images of: (a) TAZ/PS-*b*-P4VP and (b) TAZ/PS.

Fig. 3 FTIR spectra of PS-*b*-P4VP, TAZ/PS-*b*-P4VP and DO3/PS-*b*-P4VP in the range of 1020–950 cm^{-1}.

Fig. 4 Typical writing, relaxing and erasing curves of samples non-annealed.

Table captions

Table 1. Optical features of samples as a function of DO3 content.