

Optical recording of stable holographic grating in a low T_g statistical copolymer covalently functionalized with an azo-dye



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ABSTRACT

A novel photoaddressable copolymer with low glass transition temperature was synthesised and its optical properties were studied. The photoresponsive material was obtained from chemical modification of a poly(styrene-co-acrylic acid) copolymer. A holographic polarization grating was recorded in the material and was monitored by measuring its diffraction efficiency. It is shown that the holographic grating stored in the material is highly stable in time, despite the fact that the polymer glass transition temperature is near room temperature. This stability is a consequence of electrostatic interactions between the azo-groups and the carboxylic substituent group of the main polymer chain.

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1. Introduction

Holographic data recording devices promise to be the next generation of high-density ultra-fast storage memories [1]. Much research has been devoted both to the study of the optical reconstruction of a hologram and to the development of photosensitive materials capable of storing the information. A number of requirements need to be met by these photosensitive materials [1,2] and nowadays a wide range of different photosensitive materials are being studied. Holographic memories are being investigated because they offer the possibility of storing a higher density of data in comparison with the more conventional media such as CDs, DVDs or Blue-ray disks. Furthermore, holographic media can store whole pages of information in the entire volume of the material, whereas the other widespread options store them bitwise and on the surface. The possibility of storing in the volume of the material further increases the storage capability. For instance, a substantial amount of data can be registered in the same material. Many materials are known where holographic data can be stored. In particular, azobenzene containing polymers have been shown to be appropriate candidates for storage media [3–6].

The photochemistry of azobenzene is well-known [7–9]. The molecule in the thermodynamically stable trans state upon

absorption of a linearly polarized photon of an absorbing wavelength isomerizes into the cis form changing its morphology and its dipole moment [10]. The back transformation can also be caused by absorption of another photon or by thermal relaxation in a timescale several orders of magnitude higher than its optical counterpart [11]. The multiple *trans*–*cis*–*trans* photoisomerization process produces a statistical excess of molecules aligned in a direction perpendicular to the polarization axis of the actinic light. The molecular reorientation that occurs due to the polarization of light is also dependent on the intensity of the actinic beam. The sensitivity to the light polarization is maintained when the dye is immersed in a polymer. The macroscopic electric susceptibility of the bulk material changes as a consequence of the nanoscopic alignment of the molecules, and therefore birefringence [12,13] can be induced in the material. Another effect that could be observed in these materials is the modulation of the surface due to a macroscopic mass-transport of the polymeric chains as a consequence of the photoinduced orientation of the chromophores [14–17].

There are many ways to introduce the azobenzene molecule in the polymeric matrix. Simple mixing presents the advantage that it is easily prepared [18]. However, the recorded information is rapidly erased due to thermal randomization of the oriented azo-dyes [1], provided the working temperature is near the glass transition temperature of the sample [18].

By covalently attaching the chromophore to the polymer, materials with high and low T_g can be obtained [19,20]. If the T_g

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is high above room temperature optical stability can be obtained [19]. However, in this case it is expected that when working at temperatures near the T_g of the photosensitive material, after a relatively short period of time, the recorded information is erased due to thermal randomisation. In contrast, in the case of the polymer being covalently bonded to the chromophore, it is expected that the material will need more energy to lose the generated orientation. Moreover, the stability of azo functionalized polymers at temperatures near to their T_g also depends on the pending groups chosen to covalently attach the polymer to the dye.

Furthermore, in order to achieve the required optical demands, the polymeric matrix must be transparent in the visible region of the spectrum [1]. Poly(methyl methacrylate) and poly(styrene) are thus widely used because of their transparency in the visible wavelength range. However, all these polymers have high glass transition temperatures (T_g), and, at room temperature, they are found in the more rigid glassy state. A materials T_g signals the change from a glassy to a rubber behavior. For many targeted applications it is highly desirable that the photoaddressable polymer is found in the rubber state at room temperature. For instance, fabrication and processing of flexible holographic films at room temperature requires polymers with glass transition temperature near or below room temperature. It was recently shown, that diffraction gratings could be induced in low T_g azopolymers [20]. In that work it was demonstrated that thin azo-polysiloxane films with additional nitrophenyl or naphthyl groups could be used as flexible materials where diffraction gratings could be recorded. The authors presented that whereas the naphthalene substituted azo-polysiloxane showed high diffraction grating stability, the nitrobenzene diffraction efficiency plummeted almost instantaneously. It was shown that the naphthyl substituted azo-polysiloxane showed high diffraction stability, even though its T_g lay around 40 °C. The authors proposed that an interaction between the photo-oriented naphthyl groups through aromatic stacking was responsible for the inhibited relaxation.

The development of holographic memories requires highly stable materials where the information could be stored for prolonged time intervals [1,2,21]. In order to achieve high-density storage capabilities, the intrinsic mass transport usually found in a wide variety of azopolymers upon grating inscription [8,15,22–27] must be avoided [1,28]. It is already known [28,29] that certain polymer architectures favor or hinder the mass transport in azopolymers.

In view of this, the development of a material satisfying the following requirements: having a stable photoinduced anisotropy, being in the flexible rubber state at room temperature and where chiefly birefringence modulation arises, was the main motivation for this work.

Regarding the generation of a material with stable photoinduced anisotropy, some considerations must be taken into account. When an azopolymer is illuminated with a polarized writing beam both dipole moment of *trans* and *cis* isomers are aligned perpendicular to the light polarization. Given that the *trans* isomer is thermally stable, the stability loss of the photoinduced anisotropy is associated to the relaxation of the photo-oriented *cis* configuration. An interaction (electrostatic, h-bonding, etc.) between the dye *cis* configuration and some groups of the copolymer can inhibit its relaxation contributing to the photoinduced stability of the material.

Considering these points, a new photoresponsive copolymer with low T_g was obtained from chemical modification (nitration, reduction, diazotisation and copulation with β -naphthol) from commercial poly(styrene-co-acrylic acid).

Poly(styrene-co-acrylic acid) is a widely used copolymer in the painting industry to disperse dyes, because its acrylic group can interact with the dye polar groups. Besides, these dyes can be

obtained through conventional and consecutive chemical modifications on the aromatic ring of the styrene repeating unit. The modification degree of these reactions can be easily controlled and, thus, a statistical copolymer can be obtained. The key to stabilize the photo-oriented *cis* configuration is the proper choice of the azo substituent group. It must be able to interact electrostatically with the pendant groups of the copolymer and, thus, the relaxation of the grating can be inhibited, rendering the diffraction grating more durable.

2. Experimental

2.1. Materials

Acrylic acid and styrene (Sigma–Aldrich) were purified by distillation. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallised from methanol. 3-Nitrotoluene, sulfamic acid, 2-naphthol and tin powder were purchased from Sigma–Aldrich. Other chemicals used in this study were commercially purchased and used without further purification.

2.1.1. Synthesis of poly(styrene-co-acrylic acid) (PSA)

The synthesis of PSA was carried out by solution radical polymerization using AIBN as the initiator and dioxane as solvent. The reaction was performed at 70 °C for 24 h following a previously reported procedure [30]. The polymer was precipitated in diethyl ether and dried under vacuum until constant weight. (yield: 91%).

2.1.2. Synthesis of PSA-azo

PSA-azo was prepared from PSA by subsequent styrene units nitration, reduction, diazotization and copulation as follows.

2.1.2.1. Nitration. First, PSA (1 g) was dissolved in 3-nitrotoluene (10 mL), which was kept at 15 °C. Nitric acid (8 mL, 65%) and sulfuric acid (2 mL, 98%) were added dropwise into the PSA solution under vigorous stirring. The nitration reaction was carried out at 30 °C during 72 h and then the obtained mixture was transferred into a separating funnel. After the phase separation had occurred, the brown oil phase was separated and gradually added into isopropanol (100 mL) under stirring. The yellow precipitate was collected by filtration, repeatedly washed with isopropanol. Purification was completed by dissolving the product in THF (5 mL), added into an excess of petroleum ether (100 mL), filtered and dried under vacuum. This purification process was performed twice to remove residual 3-nitrotoluene. The obtained yellow precipitate was collected by filtration and dried under vacuum at 85 °C for 12 h. (yield: 74%).

2.1.2.2. Reduction. Reduction of *p*-nitrostyrene units of partially nitrated PSA (PSA-NO₂) was performed by using tin powder as catalyst. Tin powder (2 g) was added into hydrochloric acid (c) (11 mL) and refluxed with stirring at 60 °C. A solution of PSA-NO₂ (1 g) in N,N-dimethylformamide (12 mL) was added dropwise into the acid solution under vigorous stirring. The reaction was carried out at 100 °C for 24 h. The mixture was cooled to room temperature and then filtered to separate the insoluble tin salts from the polymer solution.

2.1.2.3. Diazotization. The acid polymer solution was cooled to 0 °C under magnetic stirring. Sodium nitrite (0.41 g, 6 mmol) in water (1.2 mL) was added dropwise into the acid polymer solution. The reaction was carried out at 0 °C with stirring for 5 h. Excess of sodium nitrite was removed by adding sulfamic acid (97.1 mg, 1 mmol).

2.1.2.4. Copulation. A suspension of 2-naphthol (0.72 g, 5 mmol) was prepared in NaOH 2 M (2.8 mL) at 60 °C under magnetic stirring. Once dissolved, the solution was cooled to 15 °C and H₂O (25 mL) and HCl (c) (0.5 mL) was added to reach a pH value of 9. Finally, the copulation reaction was performed by adding the polymer solution dropwise to the 2-naphthol suspension. The pH was adjusted to 9 by adding NaOH 2.5 M. The reaction was completed at 80 °C for 1 h. The colored product was filtered, washed with distilled water, dissolved in THF (5 mL) and added into an excess of petroleum ether (100 mL). The purple precipitate was collected by filtration and dried under vacuum at 85 °C for 12 h. (yield: 68%).

The synthetic pathway of PSA-azo is outlined in Fig. 1.

2.1.3. Characterization of PSA-azo

The obtained polymers were characterized by the following techniques.

2.1.3.1. Nuclear Magnetic Resonance (NMR). ¹H NMR spectra were recorded on a Bruker AC-200 spectrometer operating at 200 MHz. All spectra were performed using DMSO-d₆ as solvent. All areas used in the ¹H NMR analysis were normalized to the methylene and methine protons of the polymer backbone, which were chosen as reference peaks.

The nitration degree (n_D) of styrene units in PSA-NO₂ was determined by considering the presence of three aliphatic hydrogens and, on average, $(5 - n_D/100)$ aromatic hydrogens per styrene repeating unit. Therefore n_D was calculated from:

$$n = 100 \times \left[5 - 3 \frac{\sum I_{\text{aromatic}}}{\sum I_{\text{aliphatic}}} \right], \quad (1)$$

where $\sum I_{\text{aromatic}}$ and $\sum I_{\text{aliphatic}}$ are the sums of the peak areas corresponding to aromatic and aliphatic protons of styrene repeating units, respectively.

2.1.3.2. Size Exclusion Chromatography (SEC). Molecular weight distributions and polydispersity indices of the polymers were determined using SEC. Samples were prepared at concentrations near 5 mg mL⁻¹ in THF. The instrument operates at 30 °C with a Styragel column (HR-4) from Waters covering the molecular weight range of 5000–600000 g mol⁻¹ at a flow rate of 1.0 mL min⁻¹. Number and weight-average molecular weights were calculated using a universal calibration method using poly(styrene) (PS) standards.

2.1.3.3. Differential Scanning Calorimetry (DSC). Calorimetric measurements were made on a TA Q20 differential scanning calorimeter under a dry nitrogen atmosphere. Indium standard was used for calibration. Samples of 5–10 mg were placed in the DSC pan. Dynamic experiments to measure the T_g values of PSA, PSA-NO₂ and PSA-azo samples were equilibrated at 20 °C, heated to 150 °C at 20 °C min⁻¹ and held at that temperature for 10 min to remove the thermal history. Then, samples were cooled to -20 °C held for 10 min, and again heated to 150 °C at 20 °C min⁻¹. All T_g values were taken as the midpoint of the transition in the second heating scan.

2.2. Film preparation and UV-vis spectrum

Thin PSA-azo films were prepared by dissolving 90 mg of the azopolymer powder into 1 mL of THF. The solution was stirred and two 100 μL droplets were spin-coated at a speed of 2200 rpm on a previously cleaned coverslip. The films were finally dried in a vacuum oven for 12 h at 60 °C. The film thickness was (0.8 ± 0.1) μm, as measured by scanning electron microscopy (SEM). A UV-vis spectrum of the PSA-azo film was obtained with a Shimadzu UV-1800 spectrophotometer.

2.3. Holographic grating recording setup

In order to record a diffraction grating in the film the Lloyd configuration was used [13,22,31]. Fig. 2 shows the experimental setup used. A solid state LRS-473-TM-50-5 laser operating at 473 nm, hereafter called the writing beam, was spatially filtered and collimated using the microscope objective O, pinhole PH and lens L. The irradiating intensity and the polarization state of the laser beam impinging on the sample was controlled by rotating the half-wave plate (HWP) and the polarized P2. The intensity was measured with a Newport 1918-R calibrated photodetector and fixed at 250 mW cm⁻². The polarization axis of the writing beam was set at +45° with respect to the \hat{y} axis (the axes are defined in Fig. 2). The interference of two orthogonally polarized writing beams (one with its polarization axis at 45° and the other at -45°) gives rise to a polarization holographic grating [13], where the polarization, instead of the intensity, is spatially modulated. In this configuration, the wavefront is divided upon reflection from the mirror M and coherently interferes with the non-reflected beam. As a result, an interference pattern appears in the plane

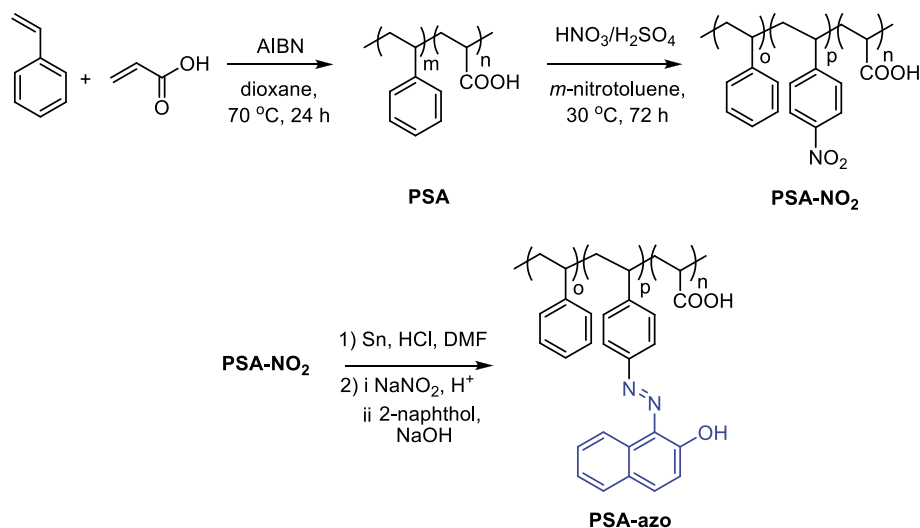


Fig. 1. Synthetic scheme of poly(styrene-co-acrylic acid) (PSA) with azoaromatic moieties (PSA-azo).

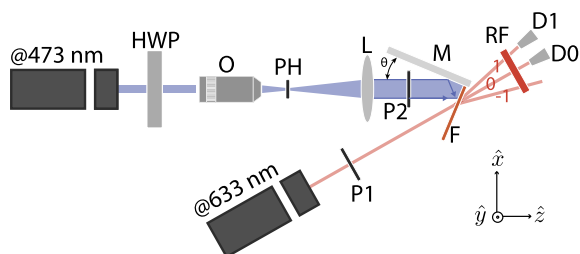


Fig. 2. Experimental setup used to record a holographic grating on the film. The intensity of the first and zeroth order were measured and used to calculate the diffraction efficiency of the recorded grating. HWP: half-wave plate. O: objective. PH: pinhole. L: lens. P1, P2: polarizers. M: mirror. RF: red-filter. D0, D1: photodetectors. F: film.

perpendicular to the mirror, where the film sample F is located. The period Λ of the pattern can be expressed as a function of the angle θ between the beam and the mirror using Bragg's condition:

$$\Lambda = \frac{\lambda_w}{2 \sin \theta}, \quad (2)$$

where $\lambda_w = 473$ nm is the wavelength of the writing beam. In this work a period of about 3 μm was used.

A He–Ne laser operating at 633 nm was used as the reading beam to probe the sample and polarized at $+45^\circ$ with respect to the \hat{y} axis with polariser P1. If a diffraction grating is successfully recorded on the material the reading beam should diffract into many diffraction orders: the 0th, ± 1 st, ± 2 nd, etc. Photodiode D0 was used to measure the intensity of the 0th order, while photodiode D1 measured the intensity of the ± 1 st order. In practice, only the ± 1 st orders are usually observed. The red filter (RF) was used to prevent any spurious light from the writing beam to be measured. A global parameter usually used to quantify the success of the grating inscription is obtained by taking the intensity of either ± 1 st order relative to the 0th order. This parameter is called the 1st order diffraction efficiency and is usually defined [25,28] as follows:

$$\eta = \frac{I_1}{I_0}, \quad (3)$$

where η is the 1st order diffraction efficiency, I_1 the intensity of the 1st diffracted order and I_0 that of the 0th order. In order to investigate whether an SRG could be recorded in the material, AFM measurements were performed operating in soft tapping mode with a scanning probe microscope (Nanoscope IIIa, Multimode from Digital Instruments). Finally, all measurements related to the optical characterization were done at room temperature.

3. Results and discussion

3.1. Chemical characterization of PSA-azo

Fig. 3 shows the ^1H NMR spectra of PSA, together with PSA- NO_2 and PSA-azo. The PSA copolymer composition was calculated from ^1H NMR spectroscopy by comparing the peak area of the aromatic protons of styrene at about 6.7–7.2 ppm (protons in position 4, 5, 6, 7, 8) with the peak area of methylene and methine protons of acrylic repeating units at about 0.5–2.2 ppm (protons in position 9, 10) that deducts the contribution of the styrene backbone protons (protons in position 1, 2). From this analysis it was obtained a copolymer composition styrene:acrylic acid of $\sim 1:1$.

For product PSA- NO_2 the ^1H NMR spectrum exhibited two peaks in the aromatic region characteristic of the *para*-substitution of styrene repeating units with nitro groups [32]. Signal at $\delta = 8.0$ ppm corresponds to protons in position 5', 7' and signal

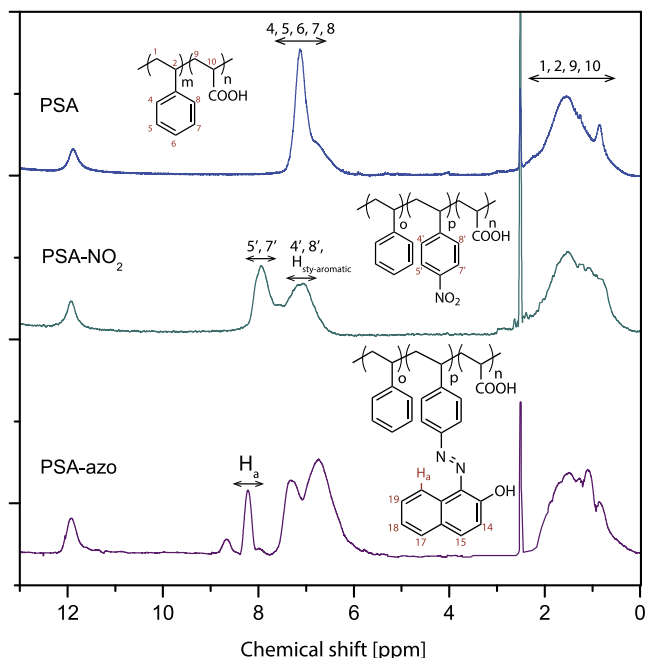


Fig. 3. ^1H NMR spectra of PSA, PSA- NO_2 and PSA-azo.

Table 1

Molecular weights and thermal properties of PSA, PSA- NO_2 and PSA-azo copolymers.

Polymer	M_w (g mol $^{-1}$)	M_n (g mol $^{-1}$)	PDI	T_g ($^\circ\text{C}$)
PSA	13000	8125	1.6	130
PSA- NO_2	11200	8000	1.4	137
PSA-azo	15300	11300	1.5	28

at $\delta = 7.0$ ppm corresponds to protons in position 4', 8', as well as the aromatic protons of the unmodified styrene repeating units ($H_{\text{sty-aromatic}}$). A nitration degree of 90% was obtained from Eq. (1) for PSA- NO_2 , which is consistent with previously reported PS nitration degrees by a similar nitration procedure [32].

For product PSA-azo the ^1H NMR spectrum exhibited new signals in the aromatic region between 6.0 and 7.8 ppm corresponding to the contribution of aromatic protons of the 2-naphthol substituent (protons in position 14, 15, 17, 18, 19), aromatic protons of the *para*-substituted styrene repeating unit and the non-substituted styrene repeating unit. Moreover, the new signal at 8.3 ppm was attributed to the aromatic proton H_a (shown in Fig. 3) of the 2-naphthol substituent with a characteristic higher chemical shift [33]. By comparing the integral of H_a with the signal of aromatic protons between 6.0 and 7.8 ppm, the degree of azo-coupling reaction from PSA- NO_2 was calculated to be 100% which is in agreement with the disappearance of the aromatic proton signal of PSA- NO_2 at 8.0 ppm.

Table 1 shows the mean molecular weight of PSA, PSA- NO_2 and PSA-azo copolymers determined by SEC. All copolymers showed unimodal distributions (data not shown) which indicated uniform chemical modifications in this study. Moreover, cross-linking or degradation reactions did not occur by the functionalization strategy performed in the current work. It was found that nitration of PSA conducted to a higher elution volume than the original PSA, which is likely due to interactions between $-\text{NO}_2$ and $-\text{COOH}$ groups and therefore lower hydrodynamic volume. For the case of PSA-azo, a single broad peak was observed at lower elution volume than PSA, indicating a larger hydrodynamic volume due to the effect of the bulky azoaromatic groups incorporated in the modification strategy.

Table 1 also shows T_g values measured for PSA, PSA-NO₂ and PSA-azo. It was evidenced that nitration of PSA conducted to a slight increase in T_g , which reflects a higher chain stiffness and cohesive density of the polymer respect to PSA. On the contrary, the T_g for PSA-azo (28 °C) was found to be considerably lower than that for PSA, which is likely due to an increase in free volume given by the bulky incorporated azoaromatic moiety.

3.2. UV-vis spectroscopy

Fig. 4 shows the obtained normalized spectrum, where a strong peak centered at 525 nm can be observed. negligible absorbance is obtained around 633 nm. This justifies the choice of the writing and reading beams, whose wavelengths were 473 nm and 633 nm, respectively. The material has strong absorption near the wavelength of the first laser, but, in contrast, it is mostly transparent to the latter.

3.3. Holographic grating recording

Fig. 5 shows the time development of the first-order diffraction efficiency η as a function of the recording time. The writing beam is turned on at time $t = 0$. As time progresses a continuous increase of the diffraction efficiency was observed. After 2 h of irradiation, the writing beam was turned off, as is indicated by the arrow in the same figure. Assuming an exponential decay from the off position, the asymptotic value of the efficiency can be obtained as $0.139 \pm 0.005\%$. After 72 h the efficiency was measured again and the obtained value was 0.14%, thus rendering the grating temporally stable.

Two processes are usually attributed to the recording of the diffraction grating. One of them, a volume effect, due to the modulation of the index of refraction caused by the nanoscopic angular reorientation of the chromophores. The other one, a modulation of the surface of the sample (SRG), driven by a macroscopic rearrangement of the polymeric chains interacting with the oriented chromophores. The latter are known to produce more stable and efficient gratings [17]. However, no SRG could be observed in the surface of the film, as indicated by AFM measurements (data not shown). The diffraction grating could be linked chiefly with a modulation of the birefringence of the material.

Usually, the decrease in the diffraction efficiency can be explained as a thermal randomization of the chromophores [1,15]. Upon irradiation at the appropriate wavelength (corresponding to the $\pi - \pi^*$ transition band), where the *trans* isomer

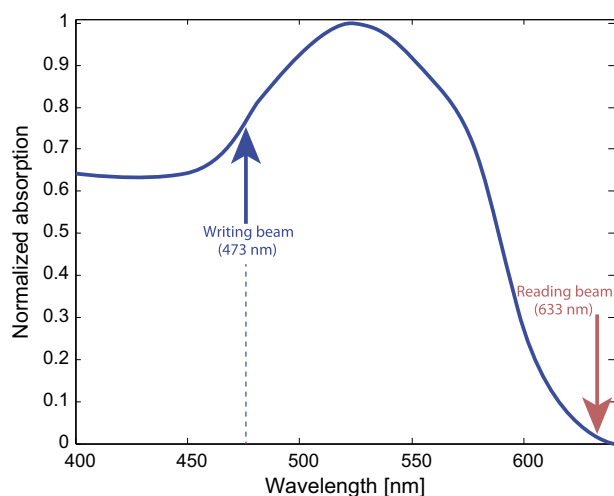


Fig. 4. Absorption spectrum of the PSA-azo film.

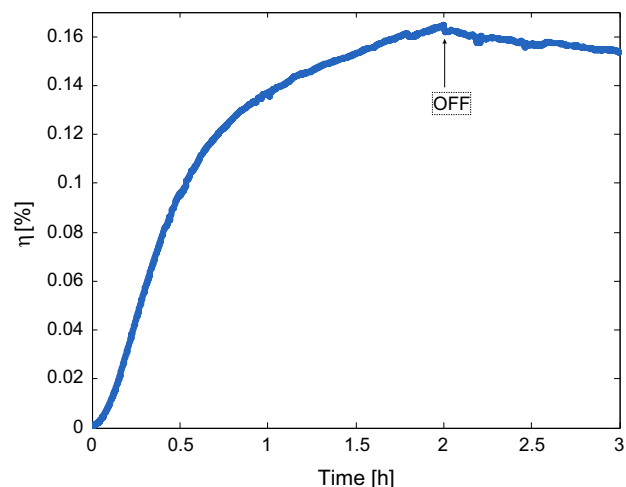


Fig. 5. Evolution of the first order diffraction efficiency at a writing power of 250 mW cm^{-2} .

absorbs more strongly [15], the stationary macroscopic state is composed of a mixture of oriented *trans* and *cis* isomers. When the laser is turned off, the back isomerization of the meta-stable *cis* molecules to the *trans* state is achieved through thermal isotropization. In general, the remnant birefringence and, thus, diffraction efficiency, can be attributed to the oriented *trans* isomers. In contrast, the *cis* species relax to the thermodynamically stable *trans* isomer and end up oriented randomly, incapable of contributing to the overall birefringence/diffraction efficiency whatsoever. However, if other interactions of the *cis* isomer with the polymer occur this randomization could be inhibited. For example, in some azo-containing polymers the chromophores are tethered to the polymer chains, and are thus incapable of moving provided they lack the needed free volume to photoisomerize [2,15,34]. This could explain why such azopolymers present high remnant diffraction efficiencies.

In the case of the developed material presented in this work, some similar effects can occur. In fact, given that the material has a low T_g , the free volume is enough to let the molecules thermally relax at room temperature in a few minutes. It is interesting to note that the first and second orders of the diffraction grating are easily visible even after two months of the first inscription. The sample was stored in a dry place, at room temperature and atmospheric pressure, meaning that no special care must be taken to preserve the grating.

It was recently shown [20] that holographic gratings could be recorded in low- T_g materials. In that work, the stability of the recorded grating depended on the pendant groups of the polymer. In particular, it was shown that the π -stacking interaction between the naphthyl groups and the azophenyl rings hindered the decrease in the diffraction efficiency. In contrast, in the case of incorporating nitrophenyl groups to the polymer backbone, the diffraction efficiency rapidly decreases when the laser is turned off, due to thermal isotropization. In this sense, a stable diffraction grating unaffected by thermal randomization could be obtained through proper substitution.

In the case of PSA-azo, upon absorption of photons of the writing beam, the azo-substituents isomerize back and forth between the stable *trans* state and the meta-stable *cis* state. The photostationary state can be described by an excess of *cis* isomers [35] with its dipole moment oriented perpendicular to the axis of polarization of the writing beam [11]. In this case the polarization is modulated throughout the sample [13] because the interference pattern was obtained by mixing two orthogonally polarized waves.

Following a reasoning similar to that previously described by Luca et al. [20], the overall stability encountered for PSA-azo in this work can be explained as a result of electrostatic inter- and/or intra-chain interactions that stabilize the bent and optically oriented *cis* state, avoiding thermal randomization.

4. Conclusions

A novel photoaddressable copolymer with low T_g was developed. A holographic polarization grating could be successfully recorded. It was also demonstrated that the diffraction grating resulted highly stable, even though the polymer T_g was near room temperature. This stability was attributed to electrostatic interactions between the azo group and the carboxylic acid group substituents of the main polymer chain, which could help stabilize the otherwise thermally unstable recorded diffraction grating at room temperature. This chemical architecture could inspire the application of more flexible photoaddressable polymers as candidates for optical memories operating at room temperature, with negligible data loss due to thermal randomisation.

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References

- [1] F.K. Bruder, H. Rainer, T. Rölle, M.S. Weiser, T. Fäcke, From the surface to volume: concepts for the next generation of optical-holographic data-storage materials, *Angew. Chem. Int. Ed.* 50 (2011) 4552–4573.
- [2] T. Bieringer, Photoaddressable polymers, in: H.J. Coufal, D. Psaltis, G.T. Sincerbox (Eds.), *Holographic Data Storage*, Springer Series in Optical Sciences, Springer-Verlag, 2000, pp. 209–230.
- [3] Y. Zhao, T. Ikeda, *Smart Light-responsive Materials*, Wiley, 2009.
- [4] X. Pan, C. Wang, C. Wang, X. Zhang, Image storage based on circular-polarization holography in an azobenzene side-chain liquid-crystalline polymer, *Appl. Opt.* 47 (1) (2008) 93–98.
- [5] H. Ono, K. Suzuki, T. Sasaki, T. Iwato, A. Emoto, T. Shioda, N. Kawatsuki, Reconstruction of polarized optical images in two- and three-dimensional vector holograms, *J. App. Phys.* 106 (2009).
- [6] T. Sasaki, M. Izawa, K. Noda, E. Nishioka, N. Kawatsuki, H. Ono, Temporal formation of optical anisotropy and surface relief during polarization holographic recording in polymethylmethacrylate with azobenzene side groups, *Appl. Phys. B* 114 (3) (2014) 373–380.
- [7] H. Rau, Photoisomerization of azobenzenes, in: J.F. Rabek (Ed.), *Photochemistry and Photophysics*, CRC Press, 1990, pp. 3–47 (Chapter 1).
- [8] O.N.J. Oliveira, D.S. dos Santos Jr., D.T. Balogh, V. Zucolotto, C. Mendonça, Optical storage and surface-relief gratings in azobenzene-containing nanostructured films, *Adv. Colloid Interface Sci.* 116 (2005) 179–192.
- [9] H.M. Dhammika Bandara, S.C. Burdette, Photoisomerization in different classes of azobenzene, *Chem. Soc. Rev.* 41 (2012) 1809–1825.
- [10] N.S. Allen (Ed.), *Handbook of Photochemistry and Photophysics of Polymer Materials*, Wiley, 2010.
- [11] Z. Mahimwalla, K.G. Yager, J. Mamiya, A. Shishido, A. Priimagi, C.J. Barrett, Azobenzene photomechanics: prospects and potential applications, *Polym. Bull.* 69 (2012) 967–1006.
- [12] T. Todorov, L. Nikolova, N. Tomova, Polarization holography. 1: a new high-efficiency organic material with reversible photoinduced birefringence, *Appl. Opt.* 23 (1984) 4309–4312.
- [13] P.S. Ramanujam, L. Nikolova, *Polarization Holography*, 1st ed., Cambridge Univ. Press, 2009.
- [14] D.Y. Kim, S.K. Tripathy, L. Li, J. Kumar, Laser-induced holographic surface relief gratings on nonlinear optical polymer films, *Appl. Phys. Lett.* 66 (10) (1995) 1166–1168.
- [15] N.K. Viswanathan, D.Y. Kim, S. Bian, J. Williams, W. Liu, L. Li, L. Samuelson, J. Kumar, S.K. Tripathy, Surface relief structures on azo polymer films, *J. Mater. Chem.* 9 (1999) 1941–1955.
- [16] B.M. Schultz, M.R. Huber, T. Bieringer, G. Krausch, S.J. Zilker, Length-scale dependence of surface relief gratings in azobenzene side-chain polymers, *Syn. Metals* 124 (2001) 155–157.
- [17] J.E. Koskela, J. Vapaavuori, J. Hautala, A. Priimagi, C.F.J. Faul, M. Kaivola, R.H.A. Ras, Surface-relief gratings and stable birefringence inscribed using light of broad spectral range in supramolecular polymer-bisazobenzene complexes, *J. Phys. Chem. C* 116 (2012) 2363–2370.
- [18] G. Díaz Costanzo, L. Ribba, S. Goyanes, S. Ledesma, Enhancement of the optical response in a biodegradable polymer/azo-dye film by the addition of carbon nanotubes, *J. Phys. D: Appl. Phys.* 47 (13) (2014) 135103.
- [19] X. Wu, T.T. Ngan Nguyen, L.-R.L. C.T. Nguyen, N.D. Lai, Optically accelerated formation of one- and two-dimensional holographic surface relief gratings on dr1/pmma , in: *Holography – Basic Principles and Contemporary Applications*, InTech, 2013, pp. 147–170.
- [20] A.R. Luca, I.A. Moleavin, N. Hurdud, M. Hamel, L. Rocha, Mass transport in low T_g azo-polymers: effect on the surface relief grating induction and stability of additional side chain groups able to generate physical interactions, *Appl. Surface Sci.* 290 (2014) 172–179.
- [21] S. Hvilsted, C. Sánchez, R. Alcalá, The volume holographic optical storage potential in azobenzene containing polymers, *J. Mat. Chem.* 19 (2009) 6641–6648.
- [22] F. Lagugné-Labarthe, T. Buffeteau, C. Sourisseau, Azopolymer holographic diffraction gratings: time dependent analyses of the diffraction efficiency, birefringence, and surface modulation induced by two linearly polarized interfering beams, *J. Phys. Chem. B* 103 (1999) 6690–6699.
- [23] A. Sobolewska, A. Miniewicz, Analysis of the kinetics of diffraction efficiency during the holographic grating recording in azobenzene functionalized polymers, *J. Phys. Chem. B* 111 (2007) 1536–1544.
- [24] H. Audorff, R. Walker, L. Kador, H. Schmidt, Polarization dependence of the formation of surface relief gratings in azobenzene-containing molecular glasses, *J. Phys. Chem. B* 113 (2009) 3379–3384.
- [25] A. Sobolewska, S. Bratkiewicz, A. Miniewicz, E. Schab-Balcerzak, Polarization dependence of holographic grating recording in azobenzene-functionalized polymers monitored by visible and infrared light, *J. Phys. Chem. B* 114 (2010) 9751–9760.
- [26] H.S. Kang, S. Lee, J.-K. Park, Monolithic, hierarchical surface reliefs by holographic photofluidization of azopolymer arrays, direct visualization of polymeric flows, *Adv. Funct. Mater.* 21 (2011) 4412–4422.
- [27] A. Kravchenko, A. Shevchenko, P. Grah, V. Ovchinnikov, M. Kaivola, Photolithographic period patterning of gold using azobenzene-functionalized polymers, *Thin Solid Films* 540 (2013) 162–167.
- [28] H. Audorff, K. Kreger, R. Walker, D. Haarer, L. Kador, H. Schmidt, Holographic gratings and data storage in azobenzene-containing block copolymers and molecular glasses, *Adv. Polym. Sci.* 228 (2010) 59–121.
- [29] C. Frenz, A. Fuchs, H. Schmidt, U. Theissen, D. Haarer, Diblock copolymers with azobenzene side-groups and polystyrene matrix, synthesis, characterization and photoaddressing, *Macromol. Chem. Phys.* 205 (2004) 1346–1358.
- [30] B.L. Rivas, S.A. Pooley, F. Brovelli, E. Pereira, L. Basaez, F. Osorio, J.-C. Moutet, E. Saint-Aman, Synthesis and properties of polymer film modified electrodes to detect metal ions, *J. Appl. Polym. Sci.* 98 (2005) 1192–1197.
- [31] P. Rochon, E. Batalla, A. Natansohn, Optically induced surface gratings on azoaromatic polymer films, *Appl. Phys. Lett.* 66 (2) (1995) 136–138.
- [32] A. Piliplipides, P. Budd, C. Price, A. Cuncliffe, The nitration of polystyrene, *Polymer* 34 (1993) 3509–3513.
- [33] L. Racané, Z. Mihalić, H. Cerić, J. Popović, V. Tralić-Kulenović, Synthesis, structure and tautomerism of two benzothiazolyl azo derivatives of 2-naphthol: a crystallographic, nmr and computational study, *Dyes Pigments* 96 (3) (2013) 672–678.
- [34] E. Heydari, E. Mohajerani, A. Shams, All optical switching in azo-polymer planar waveguide, *Opt. Commun.* 284 (2011) 1208–1212.
- [35] Y.J. Liu, H.T. Dai, X.W. Sun, Holographic fabrication of azo-dye-functionalized photonic structures, *J. Mat. Chem.* 21 (2011) 2982–2986.