



Three-dimensional structures fabricated after laser-induced free radical generation in azoaromatic compounds

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Abstract: Three-dimensional microstructures with selective properties have often been developed for optical and photonic applications. The simplest way to achieve optically active structures is by the functionalization of host matrices using, for instance, organic dyes. Laser fabrication techniques, such as two-photon polymerization, allow manufacturing devices quickly, with high resolution, without shape limitation, among other many advantages. In this work, we demonstrate the fabrication of three-dimensional microstructures via two-photon polymerization, using azobenzene-based dyes as photoinitiator, the compound responsible for absorbing the light and start the polymerization. When a high photoinitiator concentration is used (for instance 1.00 wt%), a significant amount of dye remains unchanged into the final structures, and its optically induced birefringence could be investigated. Therefore, the azobenzene-based dye acts, at the same time, as the photoinitiator and functionalizer.

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1. Introduction

Optical devices need to be built with specific functional materials to achieve selective features aiming for different applications. In the last years, polymer-based devices have been developed using micromachining techniques, such as two-photon polymerization (TPP) [1–3]. An interesting advantage of the polymeric materials is associated with their easy functionalization with different moieties, allowing materials with new physical or chemical properties. Usually, the optical properties of a polymer are changed by mixing with organic dye, which must maintain its original optical properties when added to the polymeric matrix. Several dyes can be used for that purpose, among them, azo dyes based on the azobenzene molecule.

Azoaromatic compounds are often employed in different applications, which are beyond optics and photonics. For instance, azo dyes materials have been used in several biological and medical applications [4,5]. Azobenzene-based dyes having donor and electron acceptor substituents in the aromatic ring (known as push and pull) are often used in optics and photonics applications [6] due to their cis-trans isomerization properties, which can be explored to generate optically induced birefringence and surface relief gratings [7–10]. Their nonlinear optical effects also have been investigated in different works [11–13]. In TPP experiments, azobenzene-based dyes have been used to modify the properties of polymeric matrices and fabricate optically active three-dimensional structures [14,15].

However, upon application of high-intensity light to azobenzene-based dyes, the cleavage of the azo linkage ($N=N$) can occur [16]. Such a feature can be advantageous in TPP experiments to initiate the radical polymerization process if the cleavage is homolytic. In this work, we demonstrate the potential of azobenzene-based dyes as a photoinitiator to generate free radicals

by two-photon absorption and initiate the TPP process, besides evaluating the optically induced birefringence of the fabricated structures, arising from the trans-cis-trans isomerization.

2. Experimental

2.1. Resin preparation and azoaromatic compounds characterization

The samples used in this work are composed of commercial acrylate resins, mixed with distinct azoaromatic compounds, the latter employed as photoinitiator and optically active compound. Two triacrylate monomers, named by *etoxilated(6)trimethylolpropane triacrylate* (SR499 – Sartomer) and *tris(2-hydroxyethyl)isocyanurate triacrylate* (SR368 – Sartomer), are used in equal proportions in weight (% wt), giving mechanical stability for the final structure and avoiding significant shrinkage after the polymerization procedure [17]. In addition, to carry out the photopolymerization, an organic compound known as photoinitiator is added to the resins. A variety of dyes have been used as photoinitiators in polymerization systems [18,19]. In this work, we demonstrate the use of four azobenzene-based dyes as photoinitiators, specifically Sudan Black B (SBB), Disperse Orange 3 (DO3), Disperse Red 1 (DR1) and Disperse Red 13 (DR13). These dyes are soluble in ethanol. We prepared dyes solutions in a concentration of 2.5 mg/mL (SBB), 1.15 mg/mL (DO3), 2 mg/mL (DR1) and 5 mg/mL (DR13), and different volumes are added to the polymeric resin, mixing the compounds until the complete solvent evaporation. To investigate the polymerization threshold, we prepared resins with varying concentrations of dye, ranging from 0.018 until 1.00 wt% (after the ethanol evaporation). Figure 1 shows the absorption spectra for these dyes dissolved in ethanol in a concentration of approximately 10^{-4} mol/L, along with their molecular structure.

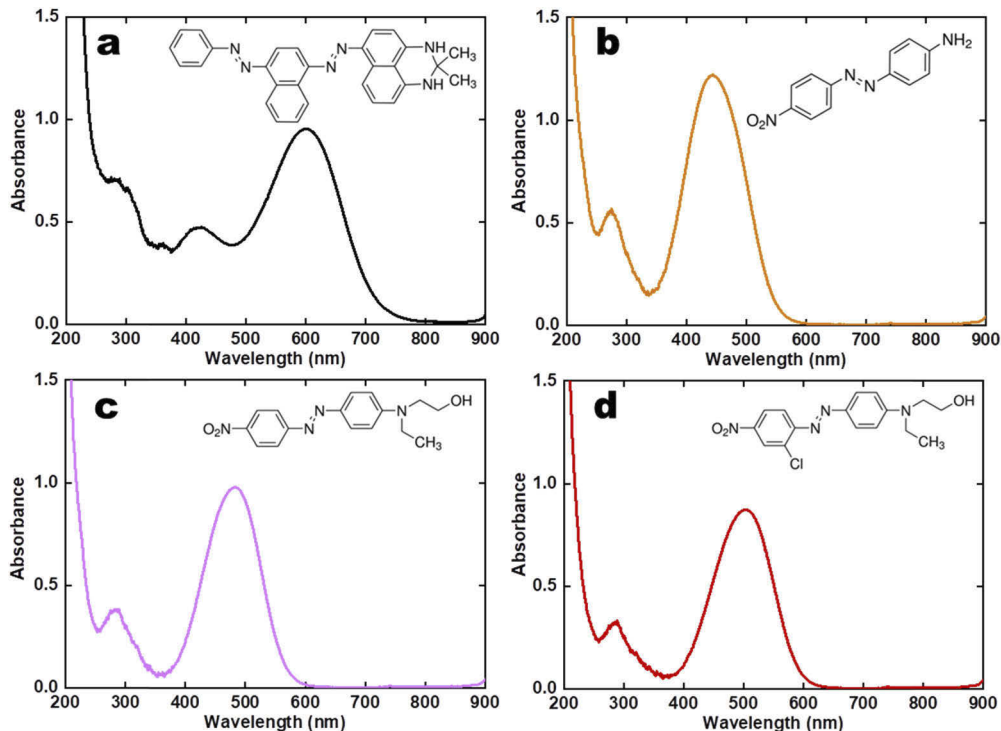


Fig. 1. Absorption spectra of azobenzene-based dyes: (a) Sudan Black B (SBB), (b) Disperse Orange 3 (DO3), (c) Disperse Red 01 (DR1) and Disperse Red 13 (DR13).

As can be seen in Fig. 1, the SBB dye (a) has a broad linear absorption spectrum with its peak centered at 600 nm. For the other dyes, the bands are centered at 445 nm for DO3 (b), 480 nm for DR1 (c), and 503 nm for DR13 (d). It is important to mention, as can be seen in Fig. 1 that none of the compounds used has one-photon absorption at 790 nm, wavelength used for the two-photon polymerization.

2.2. Two-photon absorption measurements

The technique used to quantify the two-photon absorption cross-section (σ_{TPA}) of the azobenzene-based dyes was the open-aperture Z-Scan [20], developed by Sheik-Bahae *et al.* in 1990. The experimental setup consists of a Ti:Sapphire laser amplifier (CPA-2001 system from Clark-MXR Inc.), which provides 150-fs pulses at 775 nm (1 kHz repetition rate), to pump an Optical Parametric Amplifier, which produced 120-fs pulses in the wavelength range from 470–1200 nm. Before the Z-Scan setup, the beam profile is made Gaussian through the use of a spatial filter. In the Z-Scan technique, a sample is translated through the focal plane of a Gaussian beam while its transmittance is measured in the far-field. The Z-scan setup uses a lens with focal length of 13 cm (beam waist radius at focus of approximately 15 μm). The light transmission is acquired using a silicon photodetector connected to a lock-in amplifier.

When a sample presents nonlinear absorption, its total absorption depends on the beam intensity as $\alpha = \alpha_0 + \beta I$ in which α_0 is the linear absorption coefficient, β is the two-photon absorption coefficient, and I is the intensity of the beam. For a Gaussian beam, the transmittance power can be integrated over time for each measured wavelength, giving the normalized transmittance as:

$$T(z) = \frac{1}{\sqrt{\pi}q_0(z, 0)} \int_{-\infty}^{\infty} \ln[1 + q_0(z, 0)e^{-\tau^2}] d\tau \quad (1)$$

in which

$$q_0 = \beta I_0 L \left(1 + \left(\frac{z^2}{z_0^2} \right) \right)^{-1} \quad (2)$$

in which I_0 is the beam intensity, L is the length of the sample, z is the position along the movement axis, and z_0 is the Rayleigh length. From fitting the experimental transmittance curve with Eq. (1), the TPA coefficient β is obtained. It is possible to calculate the σ_{TPA} with the value of β through:

$$\sigma_{\text{TPA}} = \frac{\hbar\omega\beta}{N}, \quad (3)$$

in which ω is the excitation wavelength and N is the number of molecules/ cm^3 . The TPA cross-section is usually presented in Göppert-Meyer units (GM), where 1 GM = $10^{-50} \text{ cm}^4\text{s/photon}$.

All studied dyes were diluted in ethanol with a concentration of 10^{-3} M for the TPA measurements. The samples were placed in a 2 mm glass cuvette to obtain their TPA cross section at 790 nm (which was the wavelength used for the photopolymerization process).

2.3. Two-photon polymerization (TPP) experimental setup

The experimental setup employed here for TPP is described in detail in the Ref. [21]. In summary, the homemade setup uses a femtosecond laser (mode-locked Ti:sapphire oscillator) operating at a repetition rate of 86 MHz, delivering pulses of 100 fs. A small drop of acrylate sample is placed onto a glass substrate with a micrometric spacer and covered by a coverslip. The laser beam, centered at 790 nm, is focused on the resin using a microscope objective (10 \times , NA = 0.85). A pair of galvanometric mirrors can be controlled by dedicated software, allowing the laser scanning through the sample in the x-y plane. The third dimension of the structure is achieved using a translational stage, which holds the sample during the experiment. To control the laser intensity, we use a half-wave plate and a polarizer, positioned before the galvanometric mirrors.

An independent image system composed of a CCD camera, a telescope, and a red LED (whose emission band is far from the linear absorption region of the azobenzene-based dyes) allow following the polymerization process in real-time. The refractive index of the cured resin is higher than the one for the liquid resin [17], which allows observing the photopolymerization. After the microfabrication procedure is finished, the sample is washed by soaking in ethanol heated at 75 °C for 15 min. This washing procedure is repeated for three times.

3. Results and discussion

Before starting the laser fabrication, we performed Z-scan measurements at 790 nm, using a Ti:Sapphire laser amplifier, to determine the σ_{TPA} values of the azobenzene-based dyes employed in this study. The obtained results are summarized in the Table 1. According to Table 1, for SBB, whose linear absorption spectrum ends at approximately 790 nm, the obtained σ_{TPA} value was much higher (one order of magnitude) than the one observed for the other three azoaromatic compounds, which is probably due to the resonant enhancement of the nonlinearity effect. For the other dyes, the σ_{TPA} values are equivalent because they present similar molecular structures and conjugation length.

Table 1. σ_{TPA} at 790 nm.

Azobenzene Dye	σ_{TPA} (GM)
SBB	750 ± 80
DO3	48 ± 5
DR1	47 ± 5
DR13	52 ± 5

After this analysis, we investigate the TPP energy threshold for all prepared samples, using the four azobenzene-based dyes as photoinitiators, in different concentrations. Here, we defined the polymerization threshold value as the minimum energy capable of starting the polymerization reaction, e. g., the minimum energy needed to polymerize a small dot after the laser beam incidence into the sample (fixed point). These values are important to quantify the energy needed to fabricate the microstructures. The obtained results are shown in Fig. 2.

Among all tested dyes, the azoaromatic compound SBB presented the lowest polymerization threshold values in all used concentrations. This result probably is associated with the higher σ_{TPA} value experimentally obtained, which can favor the free radical generation even using low dyes concentrations.

The polymerization threshold curve (Fig. 2) for DO3 and DR1 are very similar. For the DR13 dye, however, the polymerization threshold is significantly lower and too close to the SBB curve. For instance, while the polymerization threshold for a sample containing 1.00 wt% of DO3 (or DR1) is approximately 0.79 nJ, for samples with the same concentration of DR13, the value is around 0.47 nJ, which corresponds to a decrease of ~ 40%. Since the values of the two-photon absorption cross-sections measured for DR1, DR13, and DO3 are similar, the probability of the two-photon absorption process to occur is not the main cause for the differences in the photopolymerization process. Therefore we believe the chemical structures of the compounds are the main key for the differences in the photopolymerization process. The difference in the chemical structures of DR1 and DO3 resides on the substituent in the amino group, two methyl in the DR1, and two hydrogens in DO3. As their thresholds are similar, one can infer that the amino group does not play a significant role in the process. Comparing the structures of DR1 and DR13, the only difference is the presence of the chlorine atom, Cl, localized at the *ortho* position to the azo group in the aromatic ring. Chlorine atom can be electron-withdrawing by induction effects, which reduce the photostability of the DR13 molecules drastically [22], favoring the radical

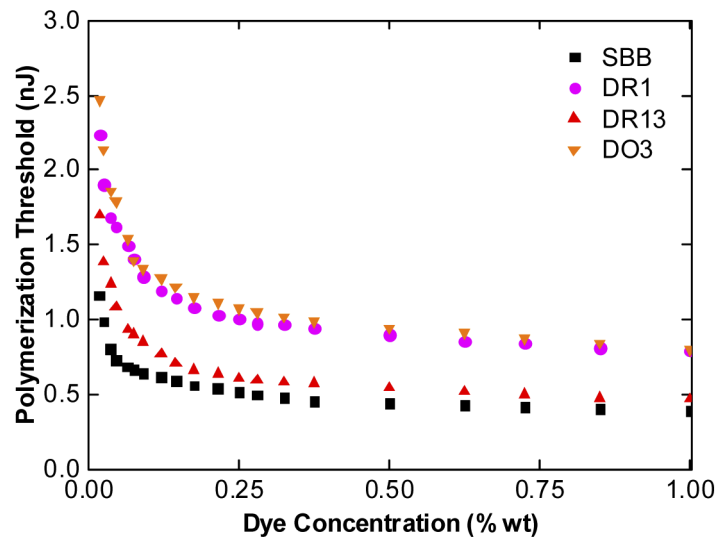


Fig. 2. Polymerization threshold for acrylate samples prepared using azobenzene-based dyes as a photoinitiator.

formation even when low laser intensity is used. A similar experiment using azobenzene (the simplest aryl azo compound), shown that this compound did not start the polymerization even when we employed high laser energy and dye concentration up to 5 wt%, corroborating with our previous hypothesis regarding the influence of the chemical structure in the photopolymerization reactions.

Based on these results, we fabricated several structures using the resins functionalized with the different azobenzene-based dyes. Figure 3 shows optical and scanning electron microscopy images of three-dimensional structures fabricated with 1.00 wt% of the dyes. To collect the optical images, we used an RGB camera coupled in the microscope. Also, in Fig. 3, it is possible to identify delicate details in the structures, as can be seen in the starfishes fabricated with the DR13 dye.

The SEM images of the structures also reveal their good mechanical stability upon microfabrication, even for structures with high aspect ratio, as shown in Fig. 4.

The color of the structures, as observed in the optical microscopy images shown in Figs. 3 and 4 are similar to the ones of the non-polymerized resins (before the photopolymerization is carried out), indicating no significant fading after laser fabrication. These results show that only a small portion of the dye is used to generate free radicals and, consequently, promote the polymerization. Thus, the remaining dye (into the fabricated structure) preserves its original properties, an interesting feature for optics and photonics applications. To evaluating dyes optical properties after laser fabrication, birefringence measurements were carried out on those microstructures. It is important to clarify that no birefringence is observed in samples without the azobenzene dyes. For this purpose, we use an experimental setup as described in the Ref. [15]. Briefly, to evaluate the photoinduced birefringence, we used a low average power He-Ne laser at 632.8 nm (as a reading beam) and an Ar⁺ laser at 514.5 nm (as a writing beam), both linearly polarized. The sample is positioned between two crossed polarizers. The photoinduced birefringence is only stimulated when the writing beam passes through the sample. All signal change is monitored by a CCD camera. To simplify our analysis, we fabricate 3D structures with rectangular geometry (area = 60 μm x 100 μm , height = 60 μm). Figure 5 shows an induced birefringence measurement performed in microstructures functionalized with 1.00 wt% of DR13.

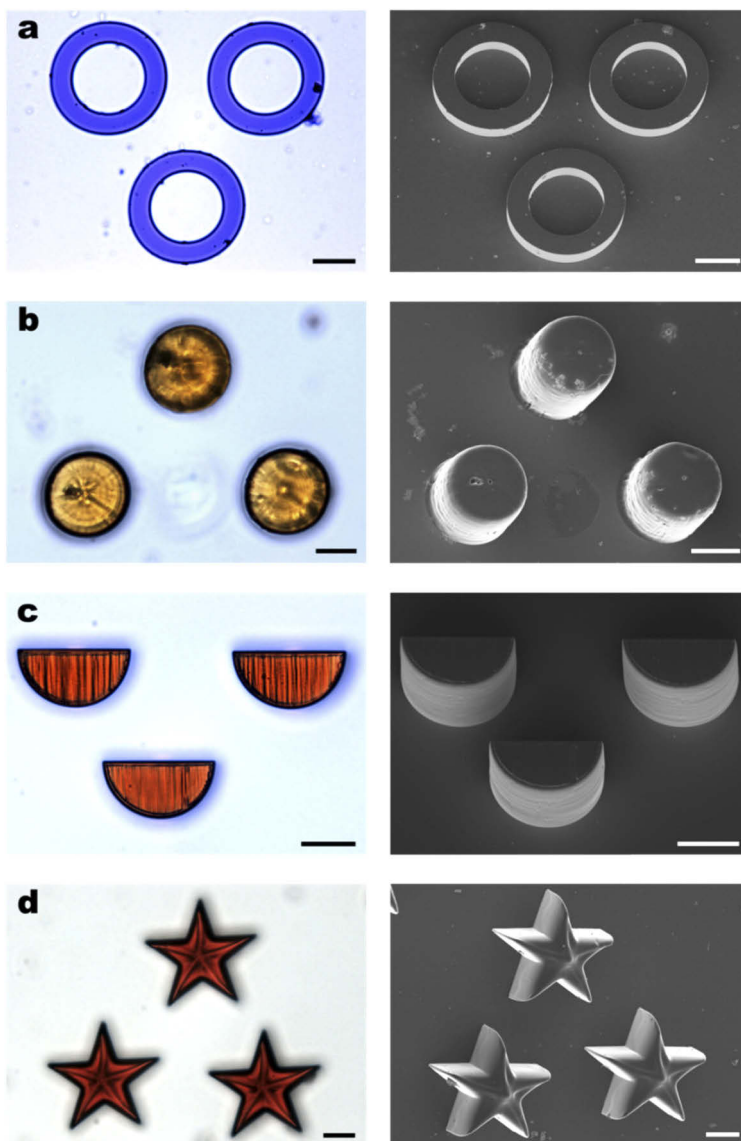


Fig. 3. Optical microscopy (left) and Scanning Electron Microscopy (SEM - right) images of three-dimensional structures fabricated using azobenzene-based dyes as a photoinitiator in a concentration of 1.00 wt%: (a) Sudan Black B (SBB), (b) Disperse Orange 3 (DO3), (c) Disperse Red 1 (DR1) and Disperse Red 13 (DR13). In all images, the scale bar is 30 μm.

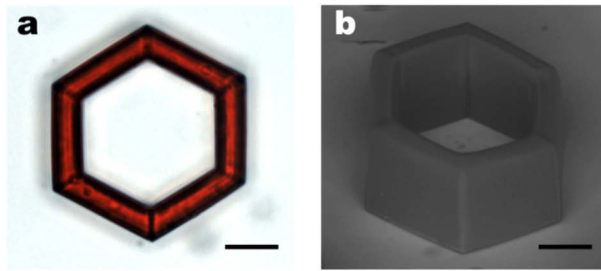


Fig. 4. Optical microscopy (left) and Scanning Electron Microscopy (SEM - right) images of three-dimensional structures fabricated using DR13 as a photoinitiator in a concentration of 1.00 wt%. The mechanical stability is maintained even for structures with a high aspect ratio. In both images, the scale bar is 15 μm .

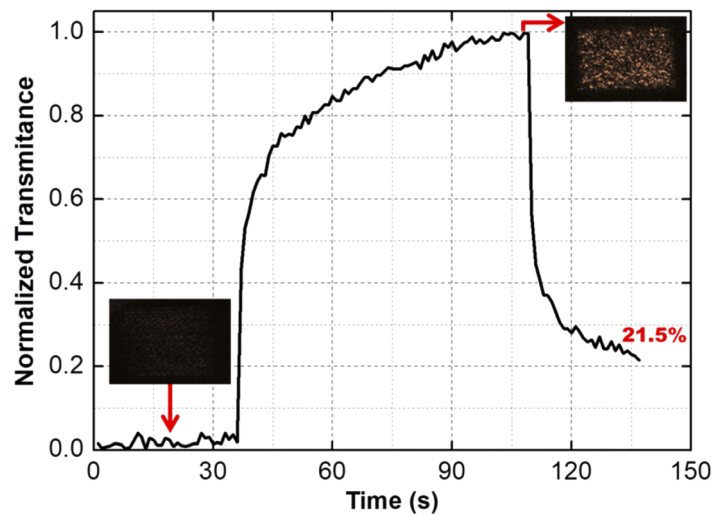


Fig. 5. Optically induced birefringence experiment for microstructures doped with 1.00 wt% of DR13.

In Fig. 5, when only the reading beam is turned on, no transmission is detected (from 0 s until ~ 35 s). In this configuration, since the polarizers are crossed, no light from the He-Ne laser is observed on the CCD camera (Fig. 5 - bottom inset on the left side), indicating the random orientation of the azochromophores. Turning on the writing beam (~ 35 s), the He-Ne transmittance increases fast due to photoinduced birefringence in the sample, until it reaches a maximum value (~ 110 s). It happens due to the molecular orientation that occurs during the incidence of the writing beam on the sample. To illustrate the He-Ne transmitted light during this process, in Fig. 5, it is displayed an image of the sample at 110 s (see top inset on the right side). Thus, the reading beam light passes through the polarizer. When the writing beam is turned off, the transmittance decreases until a certain value. The ratio between this value and the maximum signal is defined as the residual signal (21.5%).

Finally, it is interesting to highlight that the samples can pass through several cycles of writing and erasing, without any significant damage in its optical properties.

4. Conclusions

In this work, we demonstrate the fabrication of three-dimensional polymeric structures via TPP using azobenzene-based dyes as photoinitiator and optically active compound.

The SBB dye has the higher two-photon absorption cross-sections (σ_{TPA}) value, and consequently, a lowest energy is needed to begin the photopolymerization reaction. Although the σ_{TPA} for DR1, DR13, and DO3 are similar, the polymerization threshold values for DR13 is the lowest among them, indicating the chemical structure influence in the photoinitiating process. Such observation is probably related to the presence of a Cl in DR13, situated in the *ortho* position of the ring, which decreases the photostability of the molecule, favoring the radical formation. Only a small proportion of the dyes are used to promote the photopolymerization. The remaining dyes kept its properties; thus, it was also possible to evaluate the optically induced birefringence of the fabricated microstructures. The results obtained in this work showed an efficient method to produce optically active structures, using the own dye as photoinitiator, but maintaining unchanged the mechanical and optical properties of the devices.

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Disclosures

The authors declare no conflicts of interest.

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