Reversible birefringence in microstructures fabricated by two-photon absorption polymerization

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This paper reports the fabrication of birefringent microstructures using two-photon absorption polymerization. The birefringence is caused by a light-driven molecular orientation of azoaromatic molecules (Disperse Red 13) upon excitation with an Ar^+ laser at 514.5 nm. For an azoaromatic dye content of 1% by weight, we obtain a birefringence of 5×10^{-5}. This birefringence can be completely erased by overwriting the test spot with circularly polarized laser light or by heating the sample. Our results open the door to the development of alternative applications in optical data storage, waveguiding, and optical circuitry. © *2007 American Institute of Physics.*
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INTRODUCTION

The interest in two-photon absorption induced processes has increased enormously during the past ten years. These processes involve the simultaneous absorption of two photons at wavelengths far from a material's linear absorption region. Whenever the material has an electronic energy level at twice the frequency of the input beam, two-photon absorption can occur. Because the two-photon absorption rate is proportional to the square of the excitation intensity, the absorption is confined to the focal volume. This nonlinear optical process has been used in applications requiring high spatial resolution such as two-photon microscopy,[1] two-photon photodynamic therapy,[2] and three-dimensional optical data storage.[3] Two-photon absorption is also a valuable tool in the fabrication of complex three-dimensional microstructures because of the three-dimensional confinement of the nonlinear absorption process to the focal volume. In the past few years, two-photon absorption polymerization has been used to fabricate three-dimensional micromechanical actuators, photonic crystals, and optical devices.[4]

Most of the microstructures fabricated using two-photon polymerization are passive—their optical properties cannot be altered by external means.[5] The lack of active elements motivated us to study microfabrication in photopolymerizable resins containing the azoaromatic chromophore DR13. The birefringence of these resins can be induced and erased optically, due to a reversible *trans-cis* photoisomerization of the azo group and a subsequent molecular orientation.[6,7] In this paper we demonstrate the fabrication of optically active microstructures containing DR13 using two-photon absorption polymerization. The resulting microstructures become birefringent upon excitation with an Ar^+ laser at 514.5 nm

and the optically induced birefringence can be erased with circularly polarized light or by heating the sample.

EXPERIMENT

The resin used in this work consists of a mixture of two triacrylate monomers and a monoacylphosphine oxide photoinitiator. We use tris(2-hydroxyethyl)isocyanurate triacrylate (monomer A) to increase the microstructure hardness and ethoxylated(6) trimethylolpropane triacrylate (monomer B) to reduce its shrinkage upon polymerization.[8] The photoinitiator used to polymerize the resin is ethyl-2,4,6-trimethylbenzoylphenylphosphinate.[8] To the photosensitive resin we add Disperse Red 13, an azoaromatic chromophore which is known to exhibit photoinduced birefringence. We prepare ethanol solutions containing the desired proportion of monomers A and B (0%/100%, 30%/70%, 50%/50%, 70%/30%, 100%/0% by weight). To this solution we add DR13 (1% by weight), and stir it for 1 h in order to properly mix the components. Ethanol is then eliminated by evaporation at room temperature for 24 h, yielding a deep red viscous liquid. We add the photoinitiator (1% by weight) to this liquid and mix it for 1 h prior to use.

To evaluate the optical properties of the photopolymerized resin, we measured the absorbance of 200-μm-thick films polymerized using an UV lamp. Figure 1 shows the absorption spectrum of such a polymerized film measured with a spectrophotometer equipped with an integrating sphere detector. The spectrum exhibits an absorption band at approximately 510 nm which corresponds to the $\pi \rightarrow \pi^*$ electronic transition of the azochromophore DR13. Excitation at 514.5 nm in this band is responsible for the photoisomerization and the subsequent molecular orientation process of DR13, yielding optical birefringence in the sample. The sample is completely transparent in the near infrared
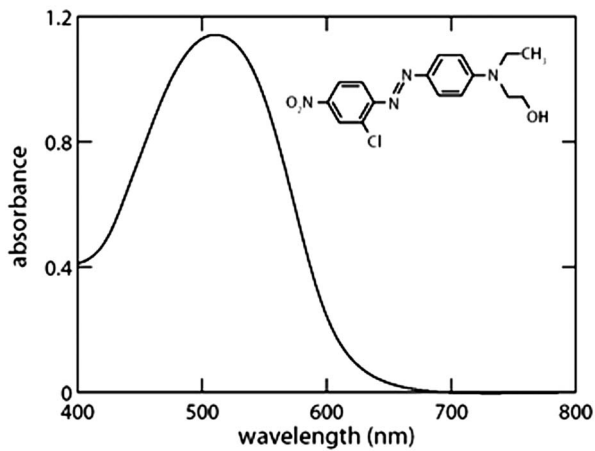
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FIG. 1. Absorbance spectrum of a cast film (70%/30% by weight of monomers A and B) containing 1% of DR13. The inset shows the molecular structure of DR13.

FIG. 2. (Color online) Experimental setup for birefringence measurements in film samples.

region, where two-photon polymerization is carried out. We obtained identical spectra for all resin compositions.

To fabricate active microstructures, we place a drop of the resin inside a spacer located on a microscope slide whose surface is treated with (3 acryloxypropyl)trimethoxysilane in order to increase adhesion of the final structure to the glass substrate.[8] After introducing the resin, a cover slip is placed on top of the spacer. The resin is polymerized using 130 fs pulses at 800 nm from a Ti:sapphire laser oscillator operating at 80 MHz. The average laser power is 20 mW before the 0.65 numerical aperture (NA) objective that focuses the laser beam into the sample. The sample is positioned in the axial z direction using a motorized stage, and the laser is scanned across the resin in the x-y direction with a pair of galvano mirrors. After fabricating the desired microstructure, the sample is immersed in ethanol to wash away any unsolidified resin and then dried.

RESULTS

To determine the composition that provides the largest and most stable birefringence, we studied the optically induced birefringence in films of various compositions. The birefringence in these films was induced by exposure to a continuous-wave, linearly polarized Ar$^+$ ion laser with an intensity of 6 kW/m^2 operating at 514.5 nm. To monitor the birefringence during the Ar$^+$ laser exposure, we measured the transmission of a low-power, linearly polarized 632.8 nm He–Ne laser beam through the sample and a set of crossed polarizer, as illustrated in Fig. 2.

Figure 3(a) shows the time evolution of the probe beam transmission for a 200-μm-thick film containing 70%/30% by weight of monomers A and B, respectively. Before exposure ($t < 60$ s), the probe beam transmission is zero, indicating that the chromophores are isotropically distributed. When the Ar$^+$ ion laser is switched on at $t = 60$ s, the transmission increases and saturates in about 1 min. At $t = 140$ s the Ar$^+$ ion laser is switched off and the transmission decreases to a nearly constant nonzero value of approximately 10% of the maximum value.
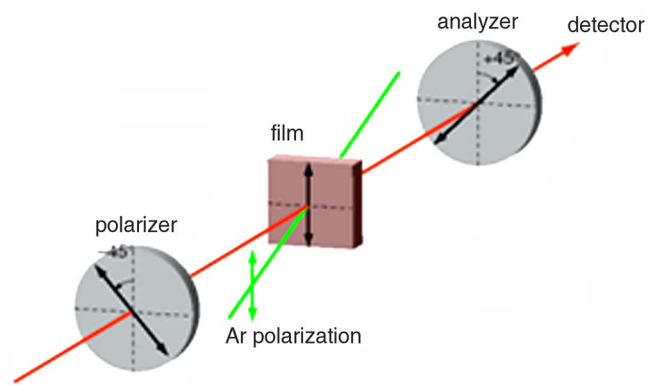
The optically induced birefringence Δn can be determined from the probe beam transmission T using

$$\Delta n = \lambda/\pi d \sin^{-1} \sqrt{T}, \tag{1}$$

where λ is the wavelength of the incident radiation and d is the film thickness.[9] The maximum birefringence value achieved for this sample composition is 10^{-4} and the residual birefringence is about 4×10^{-5}. The residual birefringence can be completely erased with circularly polarized light or by heating the sample.

Films prepared with different resin compositions exhibit results similar to Fig. 3(a). Figure 3(b) shows the residual ratio for films that contain different proportions of monomers A and B (the final transmission divided by the maximum
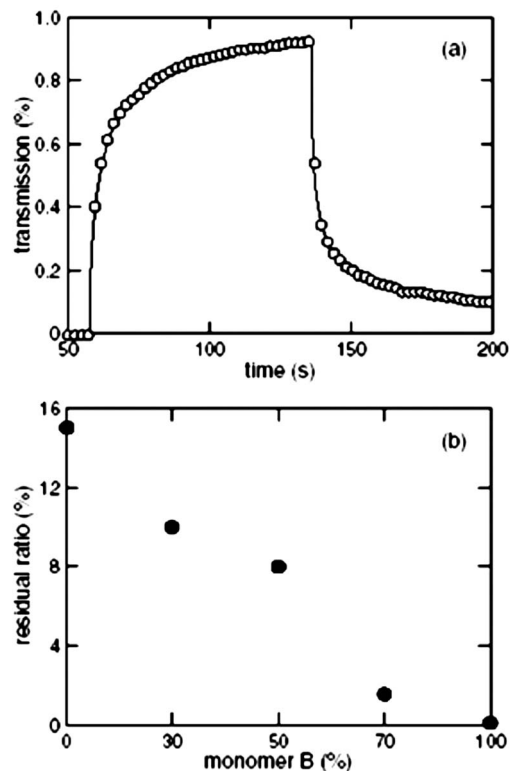

FIG. 3. (a) Time evolution of the transmission of an azopolymeric film illuminated by an Ar$^+$ laser between $t = 60$ s and $t = 140$ s. (b) Dependence of the residual birefringence ratio obtained on resin composition.
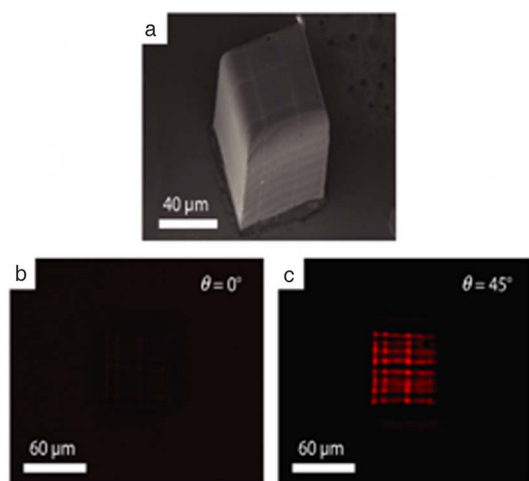
FIG. 4. (Color online) (a) Scanning electron micrograph of a solid square microstructure (70%/30% by weight of monomers A and B) containing DR13. The microstructure is about 70 μm tall, with transverse dimensions of approximately 60 μm. [(b) and (c)] Polarization microscope images of a microstructure like the one shown in (a) at two angles between the polarizer and sample axis.

transmission). As expected, the residual ratio decreases with increasing concentration of monomer B in the resin because monomer A increases the hardness of the polymer. For the fabrication of the microstructures, we selected a composition of 70% (by weight) monomer A, 26% monomer B, 3% photoinitiator, and 1% Disperse Red 13. This composition yields a relatively high residual ratio while still containing enough of monomer B to minimize microstructure shrinkage upon polymerization.

We induced optical birefringence in the fabricated microstructures by irradiating the samples for 1 min with a polarized Ar$^+$ ion laser at an intensity of 6 kW/m^2. After exposure to the Ar$^+$ ion laser light, the microstructure exhibits residual birefringence because the chromophore molecules become oriented in the direction perpendicular to the laser polarization. Figure 4 shows a scanning electron micrograph of a typical microstructure and the corresponding transmission microscope images obtained in the setup shown in Fig. 5. The microstructure is visible when the angle θ between the sample axis (defined by the Ar$^+$ ion laser exposure) and the
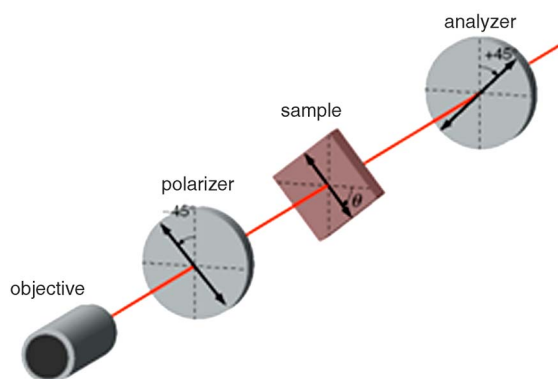

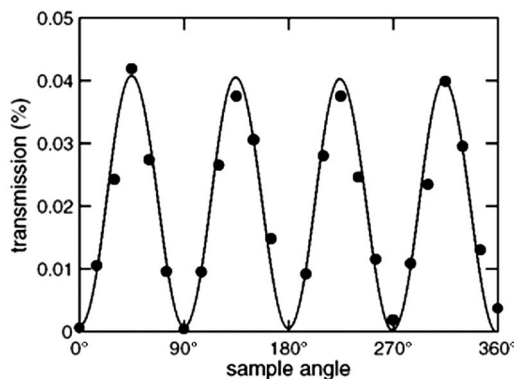FIG. 5. (Color online) Experimental setup for birefringence measurements in microstructures.

FIG. 6. Transmitted signal as a function of the sample angle θ for the microstructure shown in Fig. 4. The solid line represents a fit of Eq. (2) to the data.

polarizers is an odd multiple of 45° [Fig. 4(b)]; at even multiples of 45° the structure is not visible [Fig. 4(c)]. The stripes that are visible in the microstructure are surface imperfections that are produced during microfabrication.

Figure 6 shows the transmission of light as a function of the angle θ for the microstructure shown in Fig. 4. When the angle θ is zero, no light passes through the analyzer. The same occurs as the sample is rotated by integer multiples of 90°. Maximum transmission is obtained for angles that are odd multiples of 45°. The data in Fig. 6 show that the orientation of the chromophores in the microstructure leads to a sinusoidal behavior characteristic of birefringence. The solid line is obtained by fitting the following expression to the data:[9]

$$T = \sin^2\left(\frac{k\Delta nL}{2}\right)\sin^2(2\theta), \qquad (2)$$

where k is the wave vector ($k=2\pi/\lambda$), Δn is the birefringence, and L is the sample thickness. Using a microstructure thickness $L=70$ μm, obtained from the scanning electron microscope [Fig. 4(a)], we obtain a birefringence value $\Delta n = 5 \times 10^{-5}$. This value is in good agreement with the one obtained for the same resin composition in a film ($\Delta n = 4 \times 10^{-5}$), as expected because this property should depend only on the polymer rigidity.

The induced birefringence in the microstructure can be completely erased by exposing it to circularly polarized light, using the same irradiance employed for the writing process. Under these conditions the erasing process takes about 1 min. Erasure can also be achieved by heating the sample for approximately 30 min to a temperature close to the polymer glass transition temperature.

DISCUSSION

The change in molecular orientation is brought about by the absorption of the pump beam light. Upon absorbing linearly polarized light of appropriate wavelength, the azochromophore undergoes a *trans-cis* isomerization. Subsequently, the *cis* form thermally relaxes back to the more stable *trans* form, a process that is accompanied by a change in the chromophore orientation.[6,7] Once molecules have their dipole moments aligned perpendicular to the electric field, they no

longer absorb light and so they undergo no further conversions. At the end of several molecular isomerization cycles, the net result is a large fraction of molecules oriented perpendicularly to the laser polarization direction, yielding macroscopic birefringence.[10,11] When the light source is switched off, molecular relaxation takes place, but a considerable number of molecules maintain their orientation, yielding stable birefringence. The low residual ratio observed in Fig. 3(a) is typical of azoaromatic dyes in guest-host films, where the chromophores are not covalently attached to the polymer chain and consequently there is large free volume for rotational diffusion.[6,12] The final birefringence values remain stable for several weeks, despite exposure to ambient light, which suggests the microstructures may be sufficiently robust for optical applications. The writing and relaxation times for azoaromatic dyes in polymer films are usually on the order of several seconds, as expected for a molecular orientation mechanism. The maximum and residual values of induced birefringence are the most flexible parameters for engineering the optical properties of structures. Both values are determined by the polymer rigidity: a higher polymer rigidity yields a lower maximum induced birefringence.

Applications of these optically induced birefringent microstructures are limited by the small residual birefringence, which is a consequence of the large angular diffusion, typical of guest moieties in a polymer host. This limitation can be overcome if the azochromophore is attached as a side chain to the polymer backbone.[11,13] The induced birefringence can also be enhanced by using different azochromophores or higher dye concentrations. Such modifications also affect the orientation response time, which might lead to faster response times.

The microstructures we fabricated, such as the one shown in Fig. 4(a), exhibit excellent integrity and good definition, indicating that the presence of the DR13 chromophore does not affect the two-photon absorption polymerization. Given the relatively small two-photon absorption cross section of DR13 (100 GM at 800 nm),[14] we can conclude that this azocompound does not affect fabrication via two-photon absorption polymerization.

CONCLUSION

In conclusion, we demonstrated the fabrication of optically active microstructures doped with the azoaromatic compound DR13 via two-photon absorption polymerization. The optically induced birefringence achieved in our structures is caused by a light-driven orientation of the DR13 molecules. The optimum compositions for two-photon absorption polymerization and optically induced birefringence are 70% (by weight) of monomer A, 26% monomer B, 3% photoinitiator, and 1% Disperse Red 13. Using this combination, we achieved a birefringence of 5×10^{-5}. This birefringence can be completely erased with circularly polarized light or by heating the sample close to the polymer glass transition temperature.

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