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High resolution patterning of quadratic non-linear optical properties in doped photopolymer thin films

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We demonstrate the patterning of the quadratic non-linear optical (QNLO) properties in a photopolymerizable resin doped with push-pull chromophores. Advantage is taken of the crosslinking process to perform the patterning directly. QNLO gratings with a period of 8.5 μm have been achieved over areas of a few cm^2 . This spacing is comparable to the typical visible and near infrared coherence lengths in this material and is therefore suitable for the elaboration of quasi-phase matched waveguides. An accurate characterization of the QNLO gratings has been performed using a high spatial resolution second harmonic generation microscope with a femtosecond laser source.

1. Introduction

Quasi-phase-matching (QPM) is one of the most widely used methods to achieve efficient frequency conversion in quadratic non-linear optical (QNLO) materials. It was first described in the early 1960s [1], but in practice, applications have really started in the 1990s with the development of photolithographic techniques used to make the patterned electrodes needed for electrical poling [2] with spatially modulated fields. The goal of such a procedure is to create an appropriate periodicity for the spatial distribution of ferroelectric domains in inorganic crystals or of oriented chromophore areas in organic materials [3–5]. It is thus possible to build waveguides where the harmonic fields interfere constructively to generate a strong output signal. Organics are especially interesting materials for QNLO applications as their low cost, ease of functionalization and processing compete well with those of inorganic mate-

rials. Development of QNLO organics is also motivated by the possibility of setting up new processes. For example, a QPM pattern can be achieved in QNLO organics by the selective bleaching of chromophores using spatially modulated UV illumination [6].

QNLO properties of polymers are obtained by grafting on the polymer chain push-pull molecules possessing high quadratic hyperpolarizabilities. With such polar molecules, the non-centrosymmetrical order required for macroscopic QNLO properties is usually achieved by applying a static electric field. A convenient way to insure a permanent acentric organization of the chromophores is to freeze their orientation via hardening of the initially soft material through photopolymerization [7]. The spatial distribution of the quadratic susceptibility $\chi^{(2)}$ of the polymer is then defined by the illumination pattern (for example an alternation of bright and dark stripes) used during the photopolymerization. Therefore, the method simplifies greatly the patterning of $\chi^{(2)}$ since it avoids the numerous steps of classical lithography processes generally used for this purpose.

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In this paper, we present such a direct and simple method to achieve the patterning of second harmonic generation (SHG) properties in functionalized photopolymers. We demonstrate the validity of the approach developed by fabricating thin organic material films with patterned QNLO properties.

2. Experimental

The different compounds introduced in the formulation are schematically presented in Fig. 1. The organic network precursor has been chosen for its high stiffness after creation of the crosslinked 3D network structure. This property is essential to insure the efficient freeze of the chromophore orientation. The tris (2-hydroxy ethyl) isocyanurate triacrylate (SR368, Sartomer), a triacrylic monomer, fulfils this condition, exhibiting a very high glass transition temperature ($T_g = 272$ °C) when complete polymerization is achieved. The push-pull chromophores are sensitive to UV light. Therefore, a photoinitiator absorbing in the visible part of the spectrum has been employed to initiate the radical polymerization using an actinic wavelength outside of the absorption band of the QNLO molecules. The photoinitiator bis(η^5 -cyclopentadienyl) bis-[2,6-difluoro-3-(1H-pyrrol-1-yl)phenyl]-titanium (Irgacure784, Ciba), sensitive up to 550 nm, and the push-pull chromophore diacrylate 4'-methoxy 4-nitrostilbene (DiAcMONS) have been associated as they exhibit the desired properties. The chromophore has been specifically designed for this application taking into account the following requirements:

First, being a push-pull diazobenzene derivative molecule, it possesses a quadratic hyperpolarizability.

Second, the electron acceptor and donor groups have been chosen to achieve an absorption cut-off at 470 nm. This condition is not only required to limit the absorption of the second harmonic beam in frequency conver-

sion experiments, but also to allow the photoinitiation of the polymerization. Indeed, no polymerization has been observed when using the Disperse Red 1 QNLO chromophore which presents an absorption band fully overlapping those of the photoinitiator. Using the couple DiAcMONS/ Irgacure784, one gets an 80 nm wide spectral range for the photopolymerization, allowing the operation with the 514 nm line of an Ar⁺ laser, for example. This requirement on the chromophore absorption bands hinders the molecular QNLO properties which are rather low. By Electric Field Induced Second Harmonic (EFISH) generation we have measured a value of $\mu\beta_0 = 240 \times 10^{-48}$ esu, where μ stands for the permanent dipole moment and β_0 for the molecular static quadratic hyperpolarizability.

Finally, the acrylate groups are designed to physically attach the chromophore to the 3D network and therefore to improve the freeze of non-centrosymmetric arrangement. It was also assumed that they may improve the solubility of the chromophore in the triacrylate monomer. However, some segregation has been observed for concentrations of DiAcMONS above 2–3% wt.

The initial formulation is a mixture of monomers (94% wt.), chromophores (2% wt.) and photoinitiators (4% wt.) dissolved in chloroform. After steering at room temperature for a few hours, the solution is deposited by spin coating on a borosilicate glass substrate. The rotation speed and amount of chloroform are adjusted to obtain 10 μ m thick films.

Corona poling is a convenient method to apply an electric field on thin films. Two tungsten wires, 30 μ m in diameter, separated by a distance of 1 cm and situated 1 cm above the sample, are set to a potential of +4.5 kV to generate the corona discharge. During photopatterning, the entire set-up is placed in an oxygen free atmosphere to avoid the inhibition of the radical polymerization process.

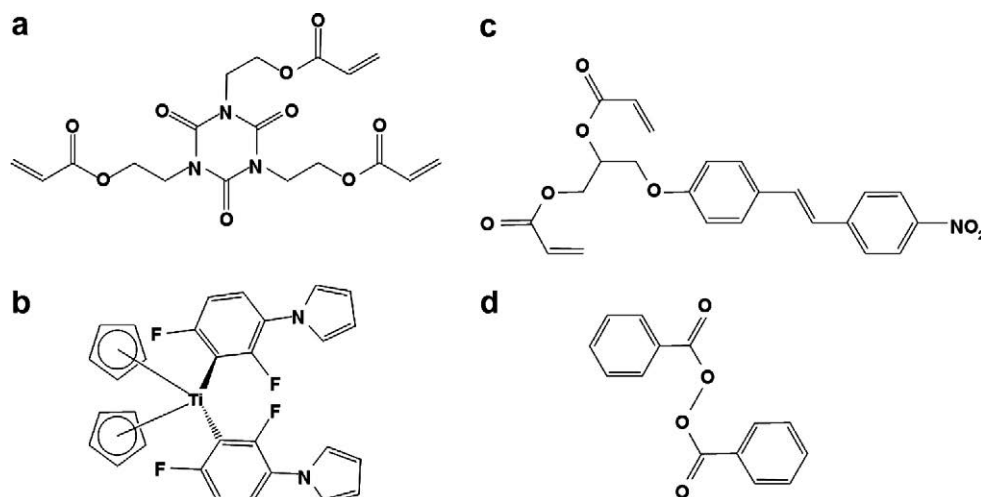


Fig. 1. Chemical formulas of the various compounds introduced in the formulation: (a) monomer SR368, (b) photoinitiator Irgacure784, (c) chromophore DiAcMONS, (d) thermal initiator (benzoyl peroxide).

3. Results

Prior to the fabrication of a QPM pattern, one has to determine the coherence length l_{coh} of the functionalized material. It is given by the relation (1):

$$l_{\text{coh}} = \frac{\lambda_{\text{fund}}}{4(n_{\text{SHG}} - n_{\text{fund}})} \quad (1)$$

where λ_{fund} stands for the fundamental wavelength, n_{fund} and n_{SHG} for the refractive indices of the fundamental and the second harmonic frequency respectively. For a 10 μm thick film, it is possible to measure the refractive index through the wavelength dependence of the transmission spectra: This modulation originates from the interference between the beams transmitted and reflected on the rear and front faces of the sample. Such a modulation is illustrated on Fig. 2 and is fitted using relation (2):

$$\Delta\alpha(\lambda) = \Psi \cos\left(\frac{4\pi}{\lambda}n(\lambda) + \Phi\right) \quad (2)$$

where $\Delta\alpha(\lambda)$ is the modulation of the transmission due to the interferences obtained by subtracting from the modulated spectrum a normalized spectrum with no oscillations performed on a thicker sample, Ψ the amplitude factor, e the thickness (measured with a mechanical profilometer DEKTAK), λ the wavelength, Φ a phase factor and $n(\lambda)$ the wavelength dependent refractive index. The refractive index is supposed to follow a Sellmeier law given by the relation (3):

$$n(\lambda) = \sqrt{1 + \frac{A\lambda^2}{\lambda^2 - B}} \quad (3)$$

The adjustment of the spectrum yields the parameters $A = 1.162$ and $B = 147 \text{ nm}^2$, leading to $n_{1064} = 1.47$ and $n_{532} = 1.50$, corresponding to a coherence length of 9 μm . The precision on the value and the slight variation of the

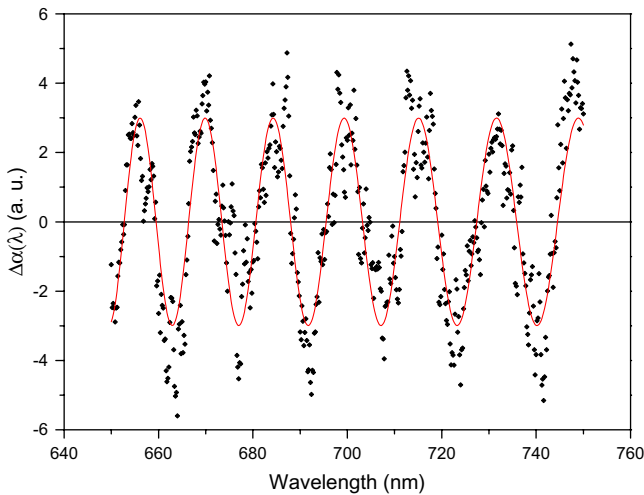


Fig. 2. Wavelength dependent modulation of the transmission spectra due to the interference of the reflections on the front and the back faces of the sample.

parameters with the polymerization conditions motivates the fabrication of a QPM pattern presenting a smaller period. Indeed, the key point here is to demonstrate that the spatial resolution of the $\chi^{(2)}$ distribution achievable in photopolymers is compatible with QPM.

To obtain a stable QPM structure, the freeze of the chromophore orientation by polymerization is achieved respecting an alternation of QNLO active and inactive domains in a two-step procedure. During the first step, the sample is illuminated through a binary grating (Ronchi ruling) with a 8.5 μm period for 30 min using a laser beam intensity of 4 mW/cm^2 at 514 nm. Without electric field, the orientation of the chromophores is randomly distributed and, therefore, the photopolymerization immobilizes the chromophore orientation in a centrosymmetric, QNLO inactive, configuration in the illuminated areas. As the stability of the orientation of the chromophores is one of the keys for success, the temperature is maintained at 80 $^\circ\text{C}$ to increase the degree of conversion in the crosslinked polymer. A further increase in temperature is harmful as it would lead to a uniform polymerization: Irgacure784 acts as a thermal initiator above 100 $^\circ\text{C}$. In the second step, the grating is removed and the corona discharge is switched on. The resulting poling of the sample induces the orientation of the free chromophores in the unpolymerized regions where they are still able to rotate. Then, the sample is fully illuminated under the same conditions as described above and the temperature is progressively increased. Both temperature and illumination contribute to achieve a high polymerization rate and therefore a strong immobilization of the chromophores in the highly crosslinked material. The heating is stabilized at 140 $^\circ\text{C}$ because the chromophores undergo degradation at higher temperatures. After 180 min, the sample is progressively cooled down to room temperature. As a result, samples with alternating domains, 8.5 μm wide, either with or without QNLO activity, are created over a $2 \times 2 \text{ cm}^2$ surface.

The measurement of the QNLO efficiency distribution over the sample is achieved by a direct scan using the SHG microscope setup shown in Fig. 3. This equipment allows the observation of the local QNLO properties with a 1 μm lateral resolution. The exciting beam for the SHG detection is provided by a Spectra Physics Tsunami laser delivering 100 fs pulses at 792 nm with an 80 MHz repetition rate and an average power of 50 mW. Two identical x20 microscope objectives (N.A. 0.35, 20 mm working distance) are used respectively to focus the light on the sample and to collect the transmitted SHG signal. To observe this signal, the sample is tilted at 15 $^\circ$ from the optical axis. The scan is performed while maintaining the focus point on the sample by using 3D motorized linear stages with a 55 nm resolution. The collected light is filtered to eliminate the high power fundamental beam and sent to a spectrometer where a CCD camera records the spectrum around 400 nm. The numerical integration over the spectrum of the SHG signal avoids possible fluorescence contributions. The SHG pattern observed under these conditions is pre-

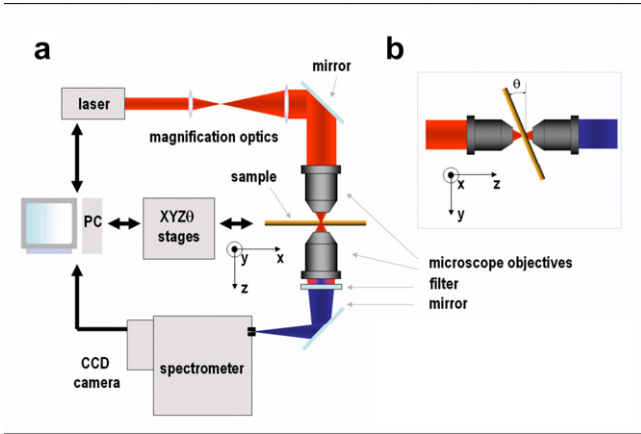


Fig. 3. (a) Experimental setup of SHG microscopy imaging; (b) side view: the sample is tilted ($\theta = 15^\circ$) to obtain the SHG signal. (For interpretation of the references in colour in this figure legend, the reader is referred to the web version of this article.)

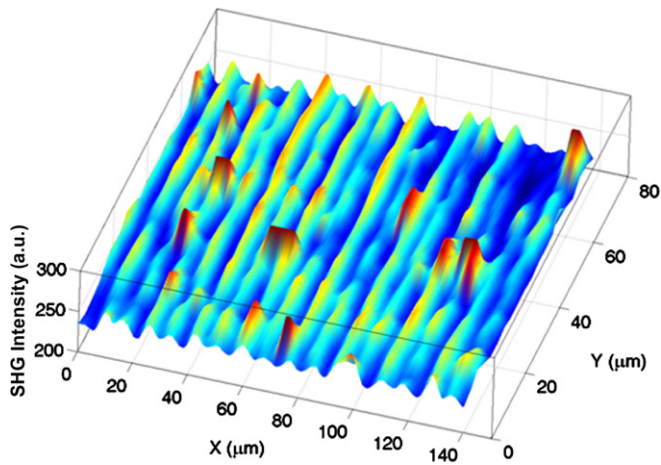


Fig. 4. SHG pattern reflecting the $8.5 \mu\text{m}$ grating created by selective orientation of the chromophores frozen by photopolymerization.

sented in Fig. 4. We indeed observe the $8.5 \mu\text{m}$ spacing corresponding to the period of the binary grating used in the patterning process. This value is compatible with the QPM conditions as the coherence length calculated from the refractive index measurements is close to $10 \mu\text{m}$ in the spectral domain from near-IR to visible.

In a previous work [8], it has been shown that a spatially modulated irradiation had produced a corrugation of the free surface due to the formation of an inhomogeneous polymer network, strain relaxation, and mass-transfer by flow of material toward the illuminated areas. This process is very similar to the one used here to structure the QNLO properties. During the first illumination, a densification of the photopolymerized areas is observed, leading to a decrease of the thickness. However, a slight thinning of the unphotopolymerized areas is also measured as some monomers flow from the dark regions to the bright regions. When the sample is fully illuminated, the photopolymerization of the remaining monomers leads again to a densification and, finally to domains with a lower thickness as less initial molecules are involved. Therefore, we have first verified that the SHG modulation was not related to a modulation of the interaction length through the thickness variations of the sample. Confirmation of the corrugation has been given by the atomic force microscopy (AFM) measurements, showing a modulation of the thickness of about 300 nm with an $8.5 \mu\text{m}$ periodicity. We have checked on a sample with a $25 \mu\text{m}$ pattern (see Fig. 5), that the NLO active domains indeed correspond to the lowest thickness areas. Here, the amplitude modulation ($4 \mu\text{m}$) was even more important as it represented nearly half of the sample thickness. The verification procedure has been performed by creating a specific defect on the sample surface (scratch) used as a position reference to compare optical, AFM and SHG microscopies. From these results it is

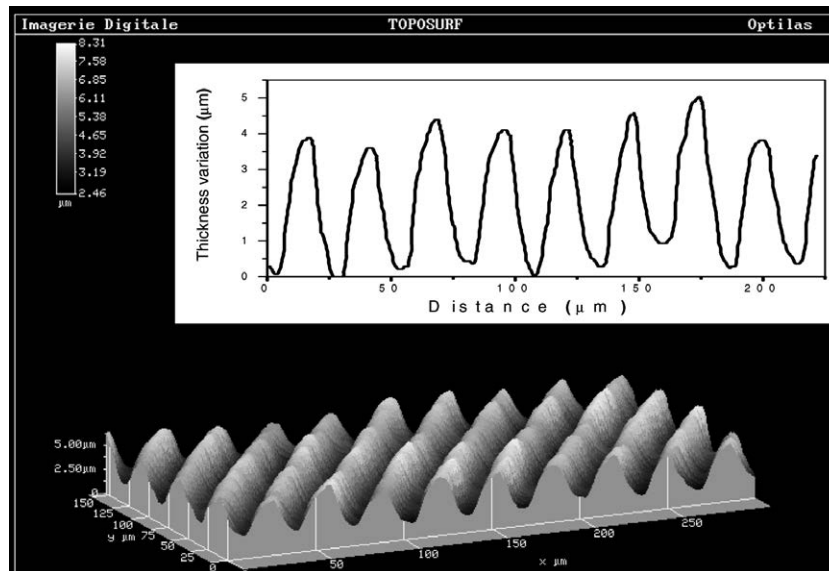


Fig. 5. Atomic force microscopy image of a microstructured sample corresponding to a $25 \mu\text{m}$ SHG pattern. Insert: Plot of the thickness variation along the grating.

clear that the thickness is higher in the regions polymerized during the first step [8] (no chromophore orientation) and that these regions are SHG inactive. The regions polymerized during the second step (oriented chromophores) are thinner and SHG active. Therefore, the SHG spatial distribution cannot be attributed to a modulation of the propagation length in the active medium, but is indeed to be ascribed to the chromophore orientation pattern.

The evaluation of the second-order non-linear coefficient d_{33} of the films has been achieved by performing Maker fringe experiments. For this, we have used a uniformly poled sample prepared according to the second step of the protocol described above. The measurement has been performed just after the sample preparation, using a Nd:YAG laser delivering 20 ns pulses at 1.064 μm with a 10 Hz repetition rate. The value $d_{33} = 0.2 \text{ pm V}^{-1}$ that we measured is mostly explained by the low efficiency of the chromophores which exhibit a relatively weak static quadratic optical non-linearity. Moreover, the second limiting factor in efficiency is the poor solubility of this molecule in the matrix (2% wt.). In addition, the orientational lifetime has been evaluated by monitoring the decrease of the SHG signal at room temperature over a time span of 4000 h. The adjustment of the data by a stretched exponential function [9] leads to a mean decay time of $\langle\tau\rangle = 4700 \text{ h}$ for a stretching exponent of 0.4. A similar sample prepared by a thermo-initiated polymerization using benzoyl peroxide (see Fig. 1(d)) was investigated and led to an improved stability of over 10,000 h. Therefore, a third limiting factor is the conversion degree of the monomer and the efficiency of the crosslinking reaction. Polymerization initiated under visible light is a soft process allowing structuration at a microscopic scale, but it does not yet lead itself to a degree of crosslinking approaching 95%.

4. Concluding remarks

We have demonstrated that a photopolymerization technique permits the direct patterning of the quadratic

non-linear optical properties of functionalized thin films at a micrometric scale. Large areas structures, over $2 \times 2 \text{ cm}$, with a resolution compatible with quasi-phase matching conditions have been achieved. The delicate problems due to the migration of materials during the various steps of the polymerization procedure have been analyzed and controlled in order to avoid opposite effects from relief and NLO gratings giving rise to an annihilation of the desired QPM pattern.

In the near future, we expect to improve the non-linear optical coefficient by doping the films with chromophores exhibiting both a better solubility and a higher quadratic hyperpolarizability. Moreover, high-performance matrices with a more efficient crosslinking process will be used in order to fabricate effective QPM waveguides.

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