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Photo-patterning of the quadratic optical properties of doped photopolymers

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Abstract

We present an original approach to structure the quadratic non-linear optical properties of doped polymers based on photopolymerizable resins. The orientation of the push–pull molecules incorporated in the material is locked by the polymerization process induced by an exposure to a visible light. The freeze of the orientation was investigated through second harmonic generation and infrared spectroscopy measurements. A mean relaxation time of over 4200 h was obtained with co-polymerizable chromophores. With the purely optical method we developed, one can durably photo-pattern the quadratic optical properties of photopolymers for applications in integrated optics.

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1. Introduction

Polymers doped with push–pull chromophores are of special interest to elaborate organic non-linear optical (NLO) devices [1,2]. In order to make such optical devices, the doped polymers are usually patterned using classical microlithography techniques [3,4]. An alternative approach to build up optical devices is the direct spatial control of the orientation of the NLO chromophores embedded in matrices. Indeed, since the linear and quadratic optical properties of the medium depend on the orientation of the NLO molecules [5], waveguides [6,7] or periodical structures for quasi-phase matching [8–10] can also be elaborated by patterning the areas where the chromophores are poled. Many techniques, such as contact poling with patterned electrodes [6–8], corona discharge through a grounded metallic mask [9], photothermal poling [10] or photoassisted poling [11,12], have been proposed to control the spatial distribution of the oriented areas.

In this Letter, we develop a low cost and easy approach to pattern the orientation of chromophores, based on photopolymerizable resins. Previous studies on such materials [13–22] have shown

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their ability to freeze the orientation of NLO molecules but, to our knowledge, no experiment has been reported concerning the photopatterning of the quadratic NLO properties. In this work, we demonstrate that photopolymerizable resins allow the creation of long lifetime molecular patterns at a microscopic scale. The procedure freezes oriented areas by appropriate illumination patterns and consequently allows to create complex structures by self-implementation. After a brief description of the compounds used, a first part will be devoted to the improvement of the length of time over which the push–pull chromophores remain oriented. A second part will address the possibility to create oriented NLO structures by photopatterning the materials.

2. Materials

The photopolymerizable formulation used in this study combines a tri-functional monomer: tris(2-hydroxy ethyl) isocyanurate triacrylate (SR368, Cray Valley) and 2 wt% of bis(η^5-cyclopentodienyl) bis-[2,6-difluoro-3(1H-pyrrol-1-yl)phenyl]-titanium (Irgacure 784, Ciba), a photoiniator sensitive in the blue/green part of the spectrum (see Fig. 1). The polymerization of this formulation leads to a polymer network with a high glass transition temperature ($T_g = 272$ °C for a complete polymerization) and to homogenous polymer films of good optical quality.

Two push–pull chromophores, denominated, respectively, EHOMONS and AcEONS, were synthesized to dope the resin. In order not to interact with the photopolymerization process, they are transparent at the actinic wavelength used (514 nm), as shown in Fig. 1. The molecule EHOMONS is employed in a guest–host configuration. The ethyl-hexoxy pendant on the left-hand side of the molecule improves its solubility, allowing more than 20 wt% doping of the photopolymerizable mixture. EHOMONS was prepared by using an etherification reaction (Williamson reaction) between the tosylester of 2-ethyl-1hexanol and 2-methoxy-4-[(1E)-2-(4-nitrophenyl)ethenyl]phenol (67% yield). The later compound was synthesized by using a modified procedure condensing vanillin with 4-nitrophenylacetic acid in DMF and subsequent decarboxylation catalyzed by piperidine

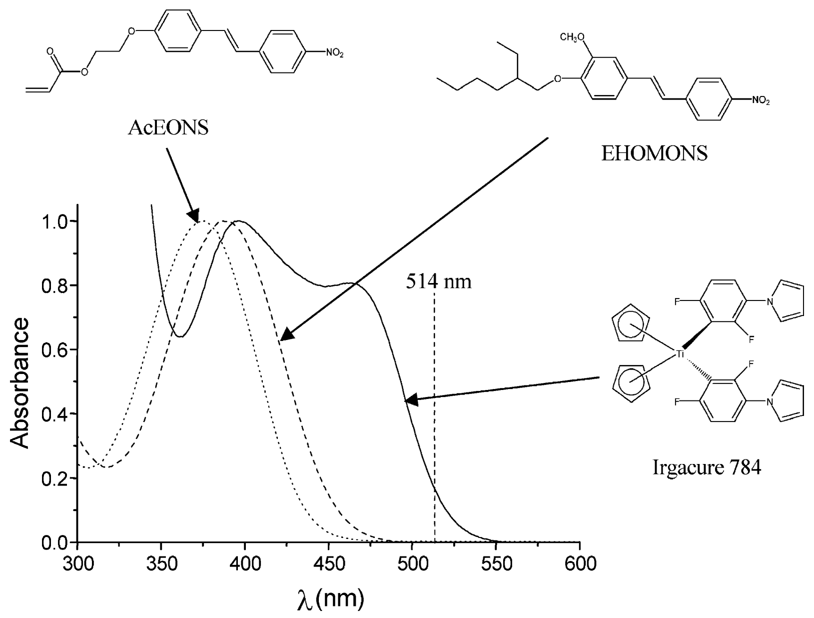


Fig. 1. Chemical structure of the photoinitiator Irgacure 784 and of the chromophores EHOMONS and AcEONS as well as their normalized absorption spectra.

(84% yield). In the AcEONS molecule, an acrylate function replaces the ethyl-hexoxy pendant to enable covalent bonding to the polymer backbone during polymerization. However, the solubility of this chromophore in the resin is limited to 1 wt%. AcMONS was prepared in one step by using an etherification reaction (Mitsunobu reaction) between the commercially available 4′-hydroxy 4-nitrostilbene and 2-hydroxyethyl acrylate (75% yield). The quadratic optical non-linearities $\mu\beta$ (where μ is the dipole moment and β the vector part of the quadratic hyperpolarizability tensor) of both molecules AcEONS and EHOMONS were characterized with the conventional EFISH technique [23]. We found the static values $\mu\beta_0 = 216$ and $\mu\beta_0 = 165 \times 10^{-48}$ e.s.u. for EHOMONS and AcEONS, respectively.

3. Photoinduced freeze of the chromophores

This part describes the ability of the photopolymerizable resin to freeze the chromophores in a given orientation. For these experiments, the doped photopolymerizable formulation was introduced between two indium tin oxide (ITO) coated glass slides. Calibrated glass beads were used as spacers to obtain 100 μm thick films. The cells were placed on top of a sample heater to control their temperature, then poled by gradually applying a static electric field and polymerized under an homogeneous exposure to the 514 nm expanded beam of an Ar^+ laser. After irradiation, the samples were slowly cooled down to 25 °C before the poling field was switched off. The relaxation dynamics of the chromophores were characterized by recording the temporal evolution of the second harmonic signal generated by the samples. For these measurements, the samples were placed in a thermally regulated oven to keep the temperature at 25 °C and pumped with the 1064 nm, p-polarized beam of a Q-switched Nd:YAG laser. In order to compare the stabilities of the orientation in different samples, all decay curves were fitted to a Kohlrauch–Williams–Watts (KWW) law:

$$\sqrt{I_{\mathrm{SHG}}(t)} = \sqrt{I_{\mathrm{SHG}}(0)}\exp[-(t/\tau)^{\beta}], \qquad (1)$$

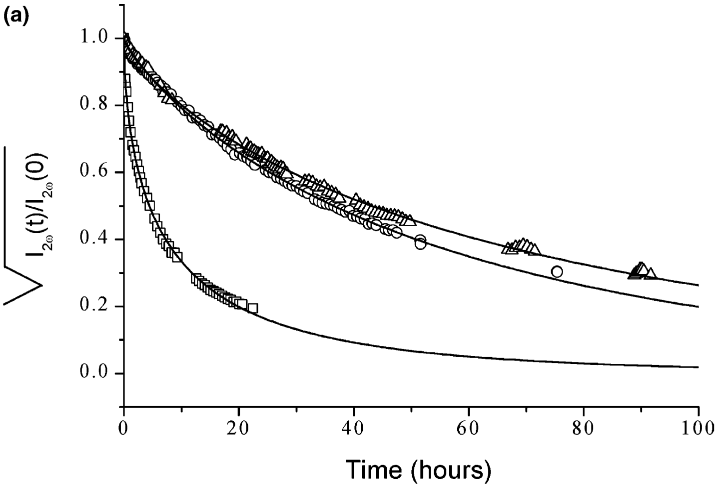
where τ and β are the KWW parameters. A mean relaxation time of the chromophores was defined by:

$$\tau_{\mathrm{relax}} = \int_0^{\infty} \exp[-(t/\tau)^{\beta}]\,\mathrm{d}t = \frac{\tau\Gamma(1/\beta)}{\beta}, \qquad (2)$$

where Γ is the gamma function.

The first studies were carried out using SR368 + Irgacure (2 wt%) doped at 5 wt% with the EHOMONS chromophore. The relaxation curve of the NLO molecules in a sample irradiated at 40 °C, upon a 200 s exposure to 50 mW/cm^2, is presented in Fig. 2a. The relaxation time of the chromophores which was subsecond before illumination, reached 14 h after polymerization. Using infra-red spectroscopy measurements and comparing the 1620–1640 cm^{-1} peak areas (C=C stretch) before and after polymerization, we determined that the monomer conversion degree was only of 55%. Since higher conversion degrees should involve a better stability of the chromophore orientation, we investigated the role of both actinic intensity and temperature on the photopolymerization process [22]. No influence of the conversion degree on the actinic intensity was found. In contrast, when the samples were heated, polymerization progressed longer before the reactive species were trapped in the growing polymeric network [24]. Therefore, the conversion degree, which was 55% at 40 °C, reached 83% when the process was carried out at 120 °C. Heating the samples enabled to obtain harder matrices but refinements (pre-polymerization, simultaneous poling and photopolymerization) should be used to prevent electrical breakdowns during poling. Furthermore, due to the dissociation of the photoinitiator Irgacure 784, a thermally initiated polymerization was observed above 100 °C, a process which could possibly induce a loss of the photopatterning properties of the materials. Therefore, we limited the temperature at 80 °C during the photopolymerization. Under these conditions, the stability of the chromophore orientation was improved to 80 h.

To further improve the stability of the NLO properties, we have explored an other route based on the use of the co-polymerizable chromophore AcEONS. As expected, an appreciable improve-



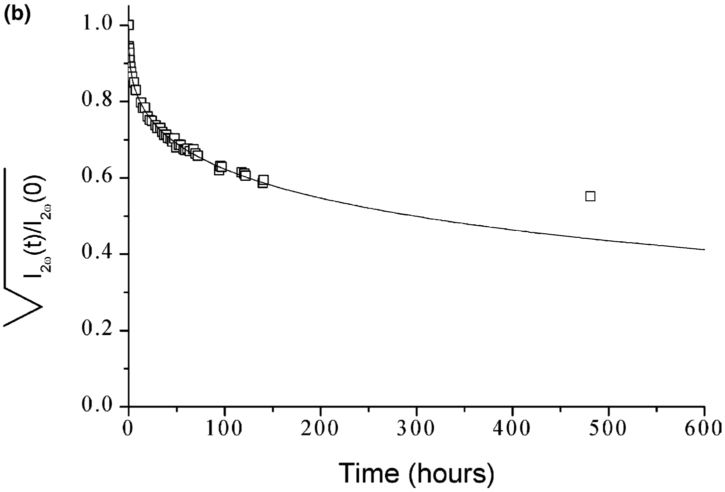


Fig. 2. (a) Normalized relaxation behavior for a SR368 + Irgacure 784 2 wt% + EHOMONS 5 wt% mixture photopolymerized at 40 °C (squares), 60 °C (circles) and 80 °C (triangles) upon a 50 mW/cm^2, 200 s exposure. The solid lines correspond to the theoretical KWW fits, leading to $\tau_{\mathrm{relax}} = 14$, 60 and 80 h, respectively. (b) Normalized relaxation behavior for a SR368 + Irgacure 784 2 wt% + AcEONS 1 wt% mixture, photopolymerized at 40 °C. The KWW fit (solid line) leads to $\tau_{\mathrm{relax}} = 4200$ h.

ment of the stability of the orientation was obtained with this chromophore, compared to the previous guest–host system (see Fig. 2b). Indeed, a value of $\tau_{\mathrm{relax}} = 4200$ h was deduced from the fit of the experimental data recorded during the first 150 h. Moreover, we noticed that experimental results deviated from the KWW law at long time scales and the value of 4200 h was obviously underevaluated. The d_{33} quadratic susceptibility of the AcEONS doped samples was evaluated using Maker fringe experiments. Due to the poor solubility and the weak $\mu\beta_0$ non-linearity of this chromophore, we obtained a low value for d_{33} of the order of 0.1 pm/V. The improvement of the chromophore solubility is then necessary. This will be achieved by multiplying the acrylate groups on the chromophore. This modification should also improve the connection between the chromophore and the network and lead to longer relaxation time.

4. Patterning of the non-linear optical properties

The patterning of the quadratic NLO properties was demonstrated by writing periodic sequences of alternatively oriented and isotropic areas. This arrangement is analogous to those used in quasi-phase matched structures. The NLO properties of the samples, 100 μm thick films of the resin SR368 + Irgacure 784 (2 wt%) + AcEONS (1 wt%), were structured through a two-step technique. First (Fig. 3I,), the cells were irradiated with a periodic pattern of illumination. This inhomogeneous irradiation, obtained by imaging an amplitude grating onto the samples, froze the chromophores in an isotropic distribution in the irradiated areas. In the second step (Fig. 3II), a static electric field was applied on the whole sample. While the chromophores remained randomly oriented in the previously polymerized areas, they aligned along the poling field in the non-polymerized zones. A periodic structure of oriented and non-oriented areas was thus created. By removing the mask, the polymerization of the whole sample was finally completed in order to stabilize the structure. The first irradiation step, without applied electric field, enabled to diminish the electrical conduction of the samples and allowed to apply a higher electric field in the second step of the procedure compared to a reverse order protocol. The polymerization was performed at 80 °C using the 514 nm light of an Ar^+ laser with an intensity of 10 $mW\,cm^{-2}$. The amplitude of the electric field promoting the orientation of the chromophores was 20 $V\,\mu m^{-1}$. The alternation of illuminated/non-illuminated areas was achieved by imaging a Edmund Cr on glass Ronchi ruling (10 lines/mm) on the sample with unity magnification through a f-2f-f optical system.

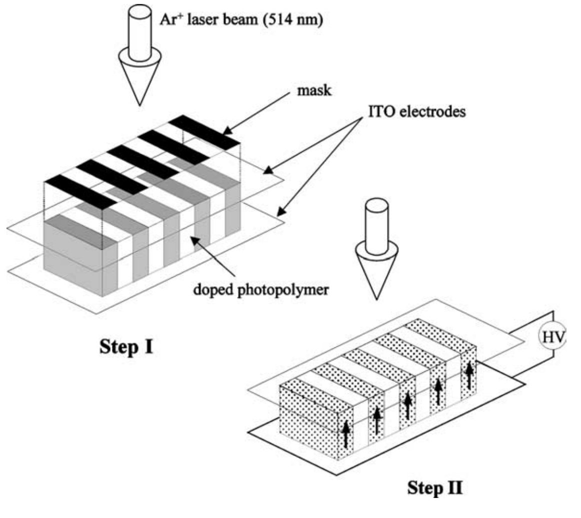


Fig. 3. Schematic procedure used for the patterning of quadratic optical properties. In step I, the actinic light polymerizes selected zones through the mask. In step II, the applied electric field orientates the chromophores in the previous non-illuminated areas. Then the light polymerizes and freezes the orientation of the chromophores in these areas.

The spatial distribution of the second harmonic emission was tested by scrolling the sample in front of the laser beam, s-polarized and at an incidence of 45° with respect to the sample. The source was a Nd:Yag laser, delivering 10 ns pulses at 10 Hz repetition rate and at a wavelength of 1064 nm. The patterning of the quadratic NLO properties of the sample is illustrated in Fig. 4, where the variation of the second harmonic light intensity is plotted versus the displacement of the sample. The periodic structure of the emitted light observed in Fig. 4 is the image of the square periodic modulation of the chromophore orientation, probed with a 70 μm FWHM gaussian beam. It is thus possible to create periodic domains of linear/non-linear properties with a sufficient accuracy for future quasi-phase matched structures. Furthermore, it should be noted that, theoretically, there is no hindrance to polymerize periodic areas with an alternate orientation

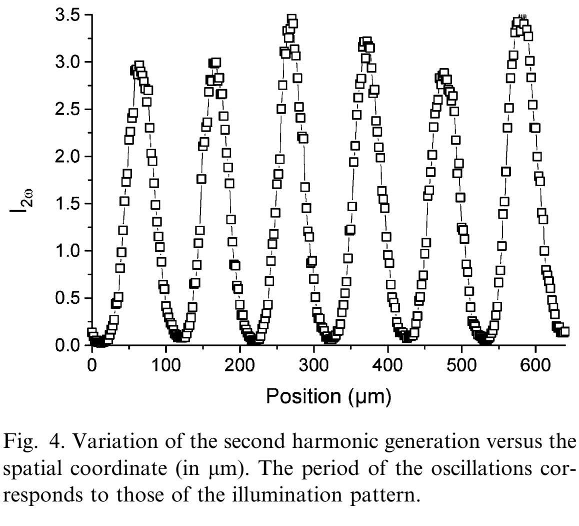


Fig. 4. Variation of the second harmonic generation versus the spatial coordinate (in μm). The period of the oscillations corresponds to those of the illumination pattern.

of the chromophores, with the goal of creating bipolar quasi-phase matched structures.

5. Conclusion

An acrylate-based photopolymerizable formulation doped with NLO chromophores has been developed in order to elaborate photoprocessable materials for quadratic optics. We have demonstrated that the hardening of the matrix associated to the photopolymerization process can be used to freeze the doping chromophores in a given orientation. Although the temporal stability of their orientation still remains below industrial expectations, the tailoring of the photopolymerization parameters and the use of a co-polymerizable chromophore lead to samples with long time duration of the photostructuration of their optical quadratic properties. Combined with optical permanent waveguide creation [25], these properties make such photopolymers choice materials for integrated optical devices.

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