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Kokou D. Dorkenoo [a], Stéphane Klein [a], Jean-Philippe Bombenger [a], Alberto Barsella [a], Loïc Mager [a] & Alain Fort [a]

[a] IPCMS-GONLO, CNRS UMR, Strasbourg Cedex, France

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Kokou D. Dorkenoo
Stéphane Klein
Jean-Philippe Bombenger
Alberto Barsella
Loïc Mager
Alain Fort
IPCMS-GONLO, CNRS UMR, Strasbourg Cedex, France

Photopolymeric matrices functionalized with optically active molecules are of special interest to elaborate low cost organic components for use in integrated optics. We have first studied the patterning of the optical properties using appropriate masks for the actinic light inducing the polymerization through a one-photon absorption process. The modulation of the refractive index can be used to make optical waveguides or quasi phase-matching structures. We have then studied, both experimentally and theoretically, the various growth forms of self-written waveguides created in the bulk of photopolymerizable resins under quasi-solitonic propagation conditions. By using another approach, we have taken advantage of the high spatial selectivity of the two-photon absorption procedure to design controlled optical polymerized pathways. As an example, we have realized fibers connections, Y-branch splittings, and finally, a passive Mach-Zehnder interferometer structure, opening the way to the fabrication of fully organic electro-optical modulators.

Keywords: optical integrated circuits; photopolymerization; push-pull molecules; solitonic propagation; two-photon absorption; waveguides

INTRODUCTION

The significant advances obtained these last years in polymeric electro-optic materials will make them valuable candidates for organic electro-optical modulators in the near future [1–3]. In this domain, photopolymers functionalized with optically active chromophores

Address correspondence to Alain Fort, 23 rue du Lœss, BP 43, 67034 Strasbourg Cedex 2, France. E-mail: alain.fort@ipcms.u-strasbg.fr

are increasingly attractive organic materials for manufacturing components for optical integrated circuits. Such optical devices must meet two requirements, first to fulfill the functions related to the desired applications, and second to confine the light into the polymerized guides. For the first goal, when embedded in the matrix, push-pull chromophores, having a permanent dipole moment and a quadratic hyperpolarizability (second-order non-linearity), are especially suited to functionalize polymers [4–6]. By controlling their orientation in the sample, it is possible to spatially modulate the non linear optical (NLO) properties of the material [7–9]. Different sophisticated techniques, largely based on microlithography [10], are usually employed to achieve the second goal. In this work, we demonstrate how doped photopolymers, together with appropriate and easy techniques, can offer an interesting alternative to conventional organic materials for fabricating optical integrated devices.

The paper is organized as follows. In the first part, we show how it is possible to create spatially structured NLO properties and optical waveguides by polymerization through one-photon absorption. In the second part, we use the powerful two-photon absorption (TPA) technique to fabricate the fundamental elements (connections, Y-splitters) needed to create an optical circuit. Finally, we present a Mach-Zehnder structure built using this approach and which opens the door to future electro-optic modulators based on functionalized photopolymers.

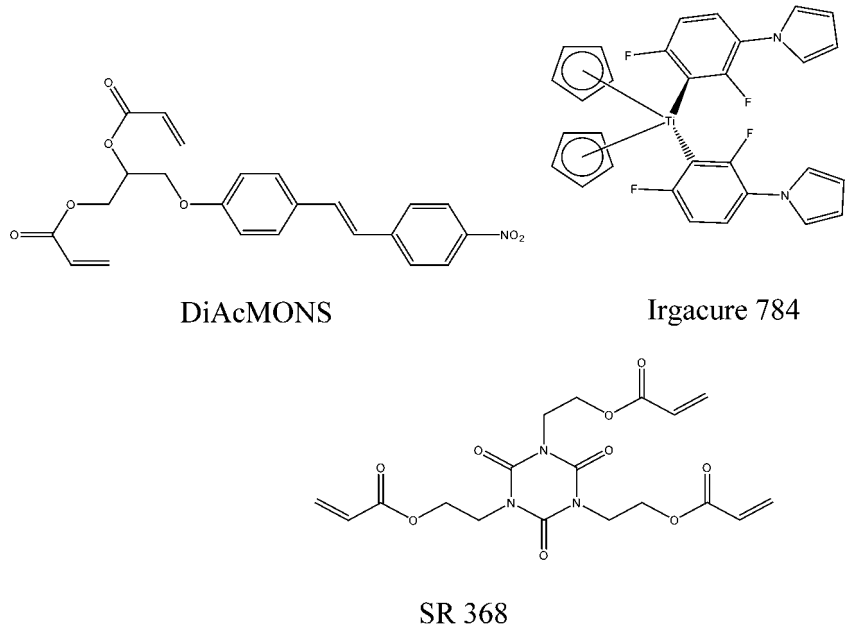
ONE-PHOTON ABSORPTION POLYMERIZATION

A. Periodic-Poled Materials

In order to make electro-optical devices, NLO polymers are usually patterned using classical microlithography techniques. Moreover, the linear and quadratic optical properties of the medium depend on the orientation of the NLO chromophores and different well-known techniques using electric or optical fields have been proposed to maintain the orientation of these chromophores in selected areas [11,12].

We have developed an alternative, low cost and easy approach to pattern the orientation of push-pull chromophores, using the process of polymerization to freeze the molecules imbedded in the resins. It was already known [13,14] that it was possible to freeze the orientation of molecules in such materials but, to our knowledge, we were the first to report the photopatterning of the quadratic NLO properties of doped photopolymers. The method we used has been described elsewhere [15]. The demonstration of the validity of our method has been obtained by using a photopolymerizable resin which combines

a tri-functional monomer : tris(2-hydroxy ethyl) isocyanurate triacrylate (SR368, Cray Valley), 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, and a co-polymerizable chromophore DiAcMONS (see Scheme 1). The relaxation time for the orientation of the chromophores was evaluated to a value of $\tau_{relax} = 4200$ hours, and was deduced from the fit of the experimental data recorded during the first 150 hours. Indeed, experimental results deviate from the stretched exponential law at long time scales and the value of 4200 hours was obviously under-evaluated. Further improvement of the stability demands a higher polymerization rate to increase the chromophore orientation freeze efficiency. This is achieved by a polymerization at higher temperature. We have been able to achieve photopatterning up to 140°C, limited by the thermal degradation of the chromophore. The crosslinking rate was then improved and the viscosity increased leading to a better stability of the orientation of the chromophores in the mixture. This stability has been checked by measuring the evolution of the second harmonic generation as a function of temperature. Figure 1 shows the variation



SCHEME 1 Schematic drawings of the molecular compounds used for the freeze of the quadratic optical properties of photopolymers.

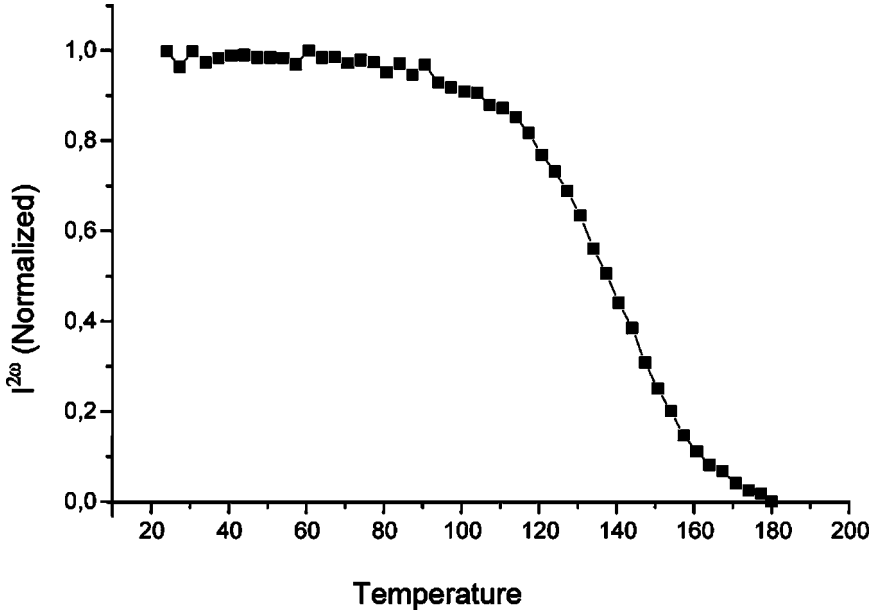


FIGURE 1 Evolution of the second harmonic generation of a photopolymer with frozen DiAcMONS push-pull molecules imbedded in the material, as a function of temperature (rate 10°C/mn).

of the optical quadratic properties of such a sample, with DiAcMONS as nonlinear optical chromophores. The decrease of the second harmonic generation begins for temperatures higher than 100°C, indicating a good stability of the orientation of the chromophores.

In these conditions, the hardening of the matrix associated to the photopolymerization process can be used to freeze chromophores embedded in a matrix in a given orientation, and to realize long time duration of the photo-structuration of the optical quadratic properties needed to fabricate, for example, quasi-phase matching structures.

B. Solitonic Waveguides

Under particular conditions, the permanent increase of the refractive index associated to the photopolymerization induced by a laser beam, can lead to the formation of a permanent waveguide as the reaction proceeds. This phenomena has been referred to as light induced self-written (LISW) waveguides [16,17] and results from the competition of the diffraction of the incident Gaussian beam and photopolymerization which tends to increase the refractive index where the

light intensity is highest. More recently, Sugihara *et al*. [18] have proposed a refined technique based on a judicious blend of two kinds of photosensitive materials to create the core and the cladding of the guide. With this technique they obtained 20 mm long LISW waveguides with propagation loss less than 1 dB/cm.

We have both experimentally and theoretically explored the different stages of guide propagation in bulk photopolymerizable media, the experimental details and the main theoretical results concerning the creation of LISW have been given previously [19,20]. The photopolymerizable resin was a mixture of three main compounds: a sensitizer dye (eosin Y: 2′, 4′, 5′, 7′–tetrabromofluorescein disodium salt, at 0.1 wt%), a cosensitizer (methyldiethanolamine at 5 wt%) and a multifunctional acrylate monomer (pentaerythritol triacrylate) which is the solvent of the two other products. When absorbing an incident photon the dye is converted to its triplet state: a redox reaction takes place between the dye and the amine that generates free radicals capable of initiating the polymerization of the monomer.

By injecting an Ar laser beam in the resin via a 3 μm core optical fiber, we create a polymerized area which propagates as a permanent optical waveguide. We characterize this guide by using the usual V-factor defined as: $V = \left(2\pi/\lambda a\sqrt{n_{core}^2 - n_{cladding}^2}\right)$, where a is the fiber diameter, λ the wavelength, n_{core} and $n_{cladding}$ the refractive index of respectively the polymerized area and the surrounding non-polymerized matter. In order to fabricate a single mode guide and ensure a quasi-solitonic mode propagation, this V-factor has to be less than 2.4. This can be achieved by a pre-polymerization of the sample in order to increase $n_{cladding}$ to a value around 1.508 [21] to fine-tune the gap between the refractive index of the core and the cladding in the 10^{-3}–10^{-4} range. In these conditions, we can control the formation of permanent polymerized waveguides over long distances (we have been able to fabricate waveguides of up to 10 cm length). Figure 2 shows an example of such a waveguide, with the characteristic breathings of the solitonic propagation (left), and as an application, the connection of two monomode fibers separated by a distance of 1 mm (right).

PHOTOPOLYMERIZATION INDUCED BY TWO-PHOTON ABSORPTION: APPLICATION TO OPTICAL INTEGRATED COMPONENTS

One limitation of light induced self-written waveguides is inherent to the straight-line propagation of the light, which doesn't allow the

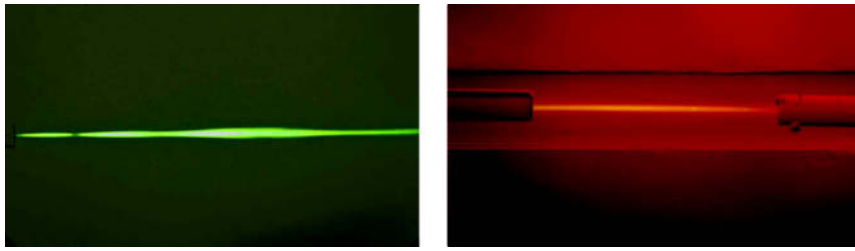
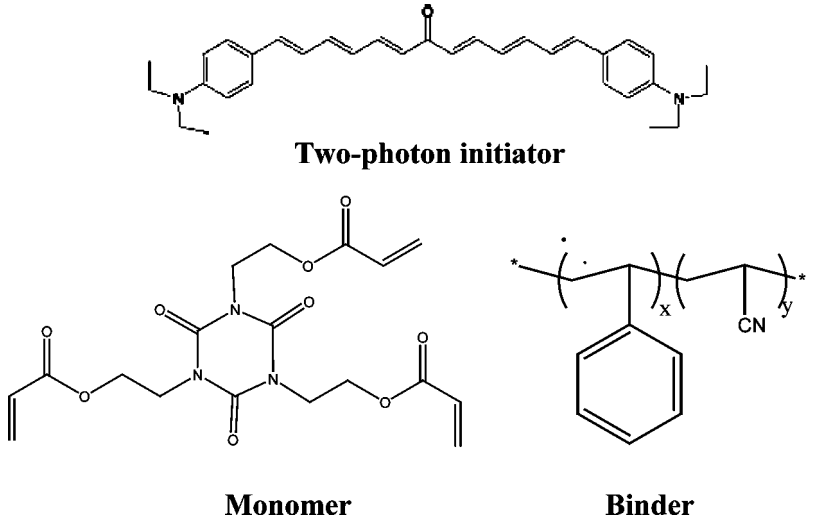


FIGURE 2 Solitonic polymerized wave guide (left) and example of fibers separated by 1 mm distance and connected by a polymerization process controlled by a quasi-solitonic propagation of the actinic light (right).

realization of complex structures. We have therefore developed a second approach based on polymerization induced by a two-photon absorption (TPA) process. Two-photon absorption process in photopolymerizable materials is becoming a very convenient tool to create 3D microstructures with well-defined sub-micron details [22,23]. This is due to the many advantages of this technique, especially the ease of fabrication compared to etching or UV lithography processes. The 3D control of the photopolymerization through TPA allows drawing guides with arbitrary designs. The first attempt to fabricate optical waveguides trough two-photon absorption process was made few years ago by the group of P. N. Prasad [24] who used a mixture of two resins to create separately the core and the cladding of some guiding structures.

Our approach is both more simple and more efficient. We use as a resin (see Scheme 2) 70% isocyanurate triacrylate as single monomer, a binder (poly(styrene-co-acrylonitrile, 29,.5%), and a two-photon initiator (E, E, E, E, E, E)-1,13-bis-[4-(dyethilamino)phenyl]-tri-deca-1,3,5,6,8,10,12-hexaen-7-one, 0.5%). The polymerization is obtained by focusing the output of a femtosecond laser beam emitting a wavelength at 900 nm in the bulk of the sample. By a computer-controlled displacement of the sample it is then possible to create arbitrarily shaped polymerized structures [25].

We first created straight waveguides connected to standard optical fibers in order to verify the light guidance properties. After inscription, we can visualize the field distribution inside the waveguide by injecting a visible laser beam (He-Ne) in the fiber and by detecting with a CCD the weak diffusion from the sample. From the material and voxels properties we showed that the polymeric guide is a multimode index-graded guide. We have estimated that the losses originate from the mismatch of the fiber core (diameter 3 μm) and the multimode



SCHEME 2 Schematic drawings of the molecular compounds used for the polymerization induced through two-photon absorption (see text).

nature of the waveguide. An efficiency of about 36% at the end of the waveguide with a non-optimized optical system has been obtained, in agreement with numerical simulations [19].

The second validation of the technique consisted in connecting two optical fibers placed in arbitrary positions in the bulk of a sample. Figure 3 shows such fibers separated by a distance of 1.3 mm and connected by a TPA photopolymerized guide. The few dark spots seen in the figure are due to the diffusion of a He-Ne laser beam by residual impurities in the material. Then, we made a Y-splitter connecting an input fiber to two output fibers. This structure was the first optical divider made by TPA and made possible the fabrication of a Mach-Zehnder interferometer. Figure 4 (top) shows the image of such a structure we created by TPA. In order to observe the modes supported by our guides,

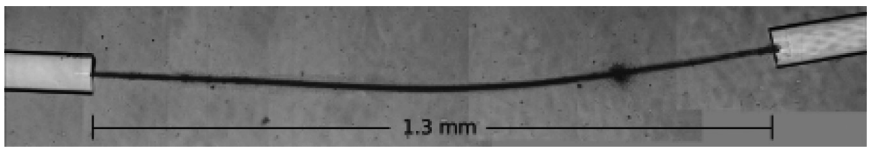


FIGURE 3 Example of connection of two monomode optical fibers placed in arbitrary positions in the volume of a photopolymerizable resin.

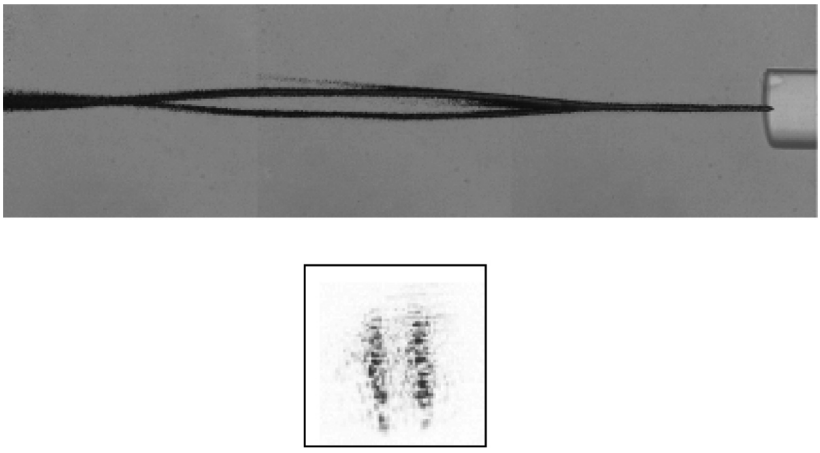


FIGURE 4 Image of a Mach-Zehnder structure created by two-photon absorption technique (top) and distribution of the light intensity of a He-Ne laser beam split into the two arms of the interferometer (bottom).

we have cut a sample along a vertical plane to expose the waveguide cross-section and polished the surface. Figure 4 (bottom) shows the distribution of the light intensity at the output surface indicating both the multimode nature of the propagation as well as the ability of the Y-split to separate the input beam in the two output guides.

CONCLUSION

We have shown trough some examples, how photopolymeric matrices functionalized with optically active molecules can be of special interest to elaborate low cost organic components for use in integrated optics. First, the freezing of quadratic push-pull chromophores by a conventional one-photon absorption polymerization has been used to elaborate materials with spatially distributed second harmonic generation. The technique is especially easy and well suited for the fabrication of quasi-phase matching structures using appropriate masks or illumination gratings. Then, we have studied how the control of a quasi-solitonic propagation of the actinic light inducing the polymerization can be employed to make straight and long waveguides, connecting aligned optical fibers. Finally, we have developed an other approach, based on two-photon absorption technique, for the polymerization of well-defined 3D microstructures in order to fabricate active optical circuits. First, optical fibers, located in arbitrary positions in

the volume of a sample, have been connected. Then, Y-splitters have been fabricated. Finally, we have realized a more complex design, a Mach-Zehnder structure.

Our results demonstrate the feasibility of elaboration of some basic optical components needed in optical circuits and using the TPA technique applied to photopolymers. Moreover, combined with the spatial control of the orientation of push-pull chromophores by the freezing process induced by photopolymerization, TPA approach emerges as a very promising technique for the fabrication of optical organic devices for integrated optics.

REFERENCES

[1] Shi, Y., Zhang, C., Zhang, H., Bechtel, J. H., Dalton, L. R., Robinson, B. H., & Steier, W. H. (2000). *Science*, *288*, 119.
[2] Donval, A., Toussaere, E., Hierle, R., & Zyss, J. (2000). *J. of Appl. Phys.*, *87*, 3258.
[3] Dalton, L. R. (2001). *Advances in Polymer Sciences*, Sringer Verlag: Heidelberg, Vol. 158, 1.
[4] Chemla, D. S. & Zyss, J. (Ed.), (1987). *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press: Orlando, Vol. 1–2.
[5] Marder, S. R., Cheng, L.-T., Tienmann, B. G., Friedli, A. C., Blanchard-Desce, M., Perry, J. W., Skindh Oslash, J., & Oslash Rgen, J. (1994). *Science*, *263*, 511.
[6] Burland, D. M., Miller, R. D., & Walsh, C. A. (1994). *Chem. Rev.*, *94*, 31.
[7] Singer, K. D., Kuzyk, M. G., & Sohn, J. E. (1987). *J. Opt. Soc. Am.*, *B14*, 968.
[8] Norwood, R. A. & Khanarian, G. (1990). *Electron. Lett.*, *26*, 2105.
[9] Martin, G., Toussaere, E., Soulier, L., & Zyss, J. (2002). *Synthetic Met.*, *127*, 49.
[10] Helbert, J. N. (2001). *Handbook of VLSI Microlithography – Principles, Tools, Technology and Applications*, William Andrew Publishing/Noyes.
[11] Azumai, Y., Kishimoto, M., & Sato, H. (1992). *Jpn. J. Appl. Phys.*, *31*, 1358.
[12] Sekkat, Z. & Dumont, M. (1992). *Appl. Phys. B*, *54*, 486.
[13] Robello, D. R., Willand, C. S., Scozzafava, M., Ullman, A., Williams, D. J. (1991). In: "*Materials for Non Linear Optics, Chemical Perspectives*", ACS Symposium Series 455, Marder, S. R., Sohn, J. E., & Stucky, G. D. (Eds.), American Chemical Society: Washington, DC.
[14] Serhatli, I. E., Yagci, Y., Hattemer, E., Zentel, R., Schmälzin, E., Hohenadl, S., Bräuchle, C., & Meerholz, K. (2001). *J. Polym. Sci. Part A: Polym. Chem.*, *39*, 1589.
[15] Gillot, F., Mager, L., Dorkenoo, K. D., Méry, S., Carré, C., & Fort, A. (2003). *Chem. Phys.*, *379*, 203.
[16] Monro, T. M., De Sterke, C. M., & Poladian, L. (1995). *Opt. Comm.*, *119*, 523.
[17] Kewitsch, S. & Yariv, A. (1996). *Opt. Lett.*, *21*, 24; *Appl. Phys. Lett.*, *68*, 455.
[18] Sugihara, O., Tsuchie, H., Endo, H., Okamoto, N., Yamashita, T., Kagami, M., & Kaino, T. (2004). *IEEE Phot. Tech. Lett.*, *16*, 804.
[19] Dorkenoo, K. D., Crégut, O., Mager, L., Gillot, F., Carré, C., & Fort, A. (2002). *Optics Lett.*, *27*, 1782.
[20] Dorkenoo, K., Gillot, F., Crégut, O., Sonnefraud, Y., Fort, A., & Leblond, H. (2004). *Phys. Rev. Lett.*, *93*, 143905.
[21] Dorkenoo, K. D., van Wonderen, A. J., Bulou, H., Romeo, M., Crégut, O., & Fort, A. (2003). *Appl. Phys. Lett.*, *83*, 2474.

[22] Cumpston, B. H., Ananthavel, S. P., Barlow, S., Dyer, D. L., Ehrlich, J. E., Erskine, L. L., Heikal, A. A., Kuebler, S. M., Lee, I.-Y., McCord-Maughon, D., Qin, J., Röckel, H., Rumi, M., Wu, X., Marder, S. R., & Perry, J. W. (1999). *Nature*, *398*, 51.
[23] Kawata, S., Sun, H. B., Tanaka, T., & Takada, K. (2001). *Nature*, *412*, 698.
[24] Joshi, M. P., Pudavar, H. E., Swiatkiewicz, J., Prasad, P. N., & Reianhardt, B. A. (1999). *Appl. Phys. Lett.*, *74*, 170.
[25] Klein, S., Barsella, A., Leblond, H., Bulou, H., Fort, A., Andraud, C., Lemercier, G., Mulatier, J.-C., & Dorkenoo, K. D. *Appl. Phys. Lett.*, to be published.