ELSEVIER

Functional polymers by two-photon 3D lithography

Robert Infuehr [a,b,*], Niklas Pucher [a,b], Christian Heller [a,b], Helga Lichtenegger [a],
Robert Liska [b], Volker Schmidt [c], Ladislav Kuna [c], Anja Haase [c], Jürgen Stampfl [a]

[a] *Institute of Materials Science and Technology, Vienna University of Technology, Favoritenstrasse 9-11, 1040 Vienna, Austria*
[b] *Institute of Applied Synthetic Chemistry, Vienna University of Technology, Karlsplatz 13, 1040 Vienna, Austria*
[c] *Institute of Nanostructured Materials and Photonics, Joanneum Research, Franz-Pichler-Straße 30, 8160 Weiz, Austria*

Abstract

In the presented work, two-photon 3D lithography and selective single-photon photopolymerization in a prefabricated polydimethylsiloxane matrix is presented as an approach with potential applicability of waveguide writing in 3D by two-photon polymerization.

Photopolymers based on acrylate chemistry were used in order to evaluate the optical capabilities of the available two-photon system. Several photoinitiators, tailored for two-photon absorption, were tested in a mixture of trimethylolpropane triacrylate and ethoxylated trimethylolpropane triacrylate. Best results were obtained with a recently synthesized diynone-based photoinitiator. Feature resolutions in the range of 300 nm were achieved. Due to the cross-conjugated nature of that donor-π-acceptor-π-donor system a high two-photon absorption activity was achieved. Therefore, a resin mixture containing only 0.025 wt% of photoinitiator was practical for structuring by two-photon polymerization. The required initiator content was therefore a factor of 100 lower than in traditional one-photon lithography.

The aim of the second part of this work was to fabricate optical waveguides by selectively irradiating a polymer network, which was swollen by a monomer. The monomer was polymerized by conventional single-photon polymerization and the uncured monomer was removed by evaporation at elevated temperatures. This treatment leads to a local change in refractive index. Refractive index changes in the range of $\Delta n = 0.01$ ($\Delta n/n = 0.7\%$) were achieved, which is sufficient for structuring waveguides for optoelectronic applications.

1. Introduction

Two-photon polymerization (2PP) is a new and modern field in solid freeform fabrication [1]. 2PP allows the fabrication of sub-micron structures from a photopolymerizable resin. By the use of low-energy near-infrared (NIR) lasers it is possible to produce 3D structures with a spatial fabrication resolution down to 120 nm [2]. This technique can be used e.g. in polymer-based photonic and microelectromechanical systems (MEMS), for 3D optical data storage or to inscribe waveguides into materials that are otherwise not accessible. Since the 2PP only takes place inside the focus of the laser beam, complex 3D structures (e.g. waveguides) can be inscribed into a matrix material.

In this paper we first report the use of new photoinitiators for 3D structuring by 2PP, in the second part we present an approach to write waveguides by selective one-photon polymerization in a preformed polydimethylsiloxane (PDMS) matrix. This approach is also potentially suitable for 2PP.

Successful structuring by 2PP is strongly dependent on the use of suitable initiators with high two-photon cross-section. In response to the low effectiveness of commercially available photoinitiators for 2PP efforts have been made to prepare novel photoinitiators possessing higher two-photon absorption (TPA) activity [3]. Recently new photoinitiators were synthesized, that were ideally suited for photopolymerization at processing wavelength of the TPA system in use ($\lambda = 750$–850 nm). A potential application of this technique would be the inscription of waveguides in 3D and to carry out such difficult tasks as connecting two optical

* Corresponding author at: Institute of Materials Science and Technology, Vienna University of Technology, Favoritenstrasse 9-11, 1040 Vienna, Austria. Tel.: +43 1 58801 30857; fax: +43 1 58801 30895.

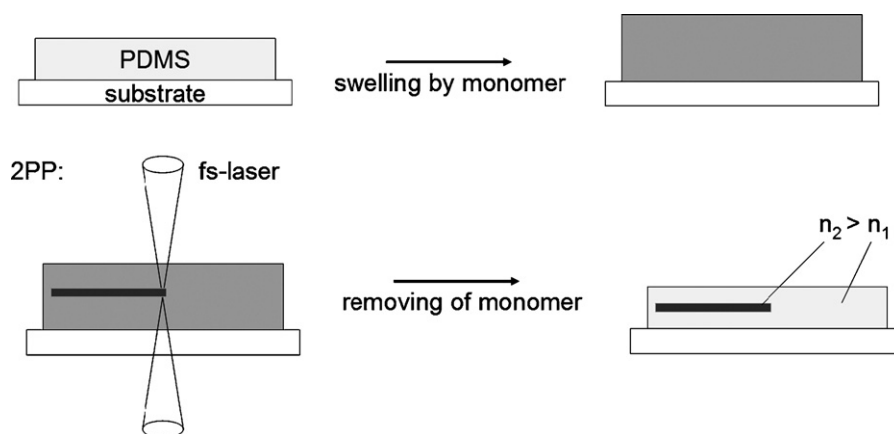*E-mail address:* robert.infuehr+e308@tuwien.ac.at (R. Infuehr).

Fig. 1. Principle of waveguide structuring by 2PP in a PDMS matrix.

components already embedded in a 3D block of transparent material.

For practical waveguide applications the 2PP has to induce a refractive index change in the range of $\Delta n/n \sim 0.1$–1% [1].

Inscription of waveguides in 3D therefore requires materials and methods suitable for a selective refractive index change in a preformed material block. Various approaches are reported in the literature, e.g. by selective curing of a component in a resin mixture [4] or by direct writing into various glasses [5].

The approach chosen in this paper to achieve a suitable refractive index change for waveguiding is based on selective photopolymerization of monomers within a preformed flexible PDMS matrix (Fig. 1). PDMS was selected because it is a cost effective, up to 540 K temperature-resistant material that has a low attenuation in optical applications (lower than 0.1 dB/cm at 850 nm). Waveguides made from polysiloxanes are usually fabricated from thermosetting siloxanes by lithographic methods combined with reactive ion etching or by using molds [6,7].

In this paper PDMS specimens are swollen by photoreactive monomer formulations, containing acrylates or vinyl compounds with higher refractive index than the PDMS. After swelling the PDMS matrix, the monomer is photopolymerized and the remaining monomer is removed by evaporation at increased temperature.

Prerequisites for this approach are on the one hand monomers which sufficiently swell the PDMS matrix without being too volatile during handling. On the other hand they should be removed easily after exposure to light. A useful monomer for structuring optical waveguides has to form a polymer that has a higher refractive index than the PDMS matrix itself so that total reflection inside the waveguide occurs. Using photoinitiators for TPA this approach is expected to be suitable for waveguide writing in 3D by TPP.

2. Experimental

2.1. Materials and characterization

Chemicals were purchased from Sigma–Aldrich unless otherwise noted and were used without further purification.

Silicone compounds and platin catalyst were purchased from ABCR. Genomer 1330 (trimethylolpropane triacrylate) and Sartomer 415 (ethoxylated trimethylolpropane triacrylate) were received as a gift from Rahn and Sartomer. The UV–vis absorption was measured with a Hitachi U-2001 spectrometer with spectrophotometric-grade acetonitrile as solvent. Fourier-transformed infrared measurements were performed on a Bruker "Tensor27" with a "DuraSampl IR II" ATR attachment. Shore A hardness was measured on a Hildebrand durometer. Refractive indices of PDMS specimens were measured by an Abbe refractometer at 590 nm and 298 K. As a light source for photopolymerization a mercury UV lamp was used.

2.2. Preparing of PDMS specimen

As PDMS matrix a platin catalyzed thermally curing system of VDT-731 (7–8 mol% vinylmethylsiloxane) and HMS-082 (7–8 mol% methylhydrosiloxane) was used. Two different types of test specimens were prepared by mixing VDT-731 with the Pt catalyst (SIP6831.0) according to 20 ppm (w/w) platin. Three and 1 equiv. of the catalyst containing VDT-731 mixture were blended with 1 equiv. of HMS-082. The pot time of this composition was more than 30 min, which was sufficient for handling. PDMS discs with a diameter of 8.0 mm and a thickness of 2.0 mm were cured for 20 h in a mold at 348 K.

The PDMS discs were swollen for 20 h at room temperature in the particular monomer mixture containing 1.0 wt% of bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (Ciba) as photoinitiator. Via the increase of weight, the content of monomer in the matrix was calculated. The silicone compounds have to be cured before swelling, otherwise the vinyl and acrylic moieties of the monomers would interfere with the platin catalyzed curing.

Swollen specimens were cured under argon by an UV lamp for 10 min and were heated to 348 K for 20 h to remove unreacted monomer. The monomers could also be removed more gently under reduced pressure. Some volatile compounds were dissolved from the PDMS matrix during swelling. The specific amount was dependent on the monomer mixture and was determined from the weight loss of the pristine PDMS after

swelling and removing of the monomer at 348 K. This systematic error in the range of 0.5–2.0 wt% was corrected.

Monomers were examined regarding their swelling properties in the PDMS matrix and their behavior during photopolymerization. 2-Phenoxyethyl acrylate (PEA), acrylic acid isobornyl ester (AIB), divinylbenzene (DVB) and 2-hydroxyethyl acrylate (HEA) were tested for their suitability.

2.3. Two-photon polymerization (2PP)

Samples for 2PP were exposed to the laser and the focus was scanned across the material volume, which left an embedded structure in the material. After laser writing, the unexposed material was removed by development of the structure in methanol (rinsing). The detailed procedure is described elsewhere [8].

3. Results and discussion

3.1. Cross-conjugated photoinitiators for 2PP

Based on the outstanding performance of 1,5-diphenylpenta-1,4-diyne-3-one (DPD) [9] as a single-photon photoinitiator (PI) for radical polymerization [10], new derivatives with auxochromic groups (–OMe, –SMe, –NMe$_2$, and –NPh$_2$) (see Fig. 2) were synthesized to shift the ultraviolet–visible (UV–vis) absorption into the visible range of the spectrum.

In 2PP commercially available PIs show low activity, and planar chromophores with extended π-system and donor (D) and acceptor (A) groups, e.g. based on a D-π-A-π-D system were ideal candidates having a large (TPA) cross-section [11]. By para-substitution of the benzo-aromatic moiety with different auxochromes like methoxy-group (O-DPD), thiomethyl-group (S-DPD) or dimethylamino-group (N-DPD) a red-shift in the absorption spectrum was achieved.

The influence of the donor substituents on the electronic transitions within the molecule was measured using UV–vis spectroscopy, as shown in Fig. 3.

The hetero-substituted PIs O-DPD, S-DPD and N-DPD showed a gradual shift to higher wavelength absorption and an increased extinction coefficient. Absorption of the PIs could be found up to 400 and 500 nm, respectively, indicating a strong donor capability. Therefore the new derivatives, especially
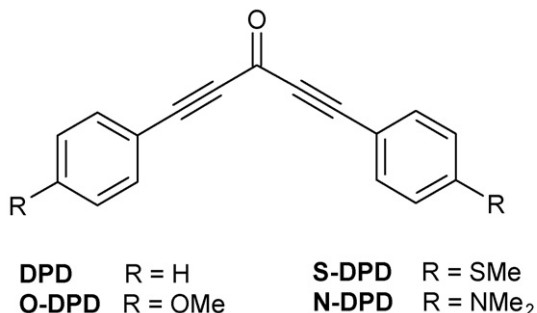

Fig. 3. UV–vis spectra in acetonitrile: (a) DPD (5×10^{-5} M); (b) O-DPD (5×10^{-5} M); (c) S-DPD (2.5×10^{-5} M); (d) N-DPD (2.5×10^{-5} M).

N-DPD, are highly suitable for 2PP at the utilized wavelength (800 nm).

Due to the D-π-A-π-D system of the new compounds two-photon induced 3D photopolymerization experiments were performed. Ultrafast Ti–S laser system proved the suitability of this photoinitiators in a 1:1 mixture of trimethylolpropane triacrylate and ethoxylated trimethylolpropane triacrylate. Compared to often applied single-photon initiators, N-DPD gave outstanding performance. Only 0.025 wt% of photoinitiator were necessary to successfully fabricate parts with a wall thickness down to 300 nm (Fig. 4) [8].

3.2. PDMS as matrix for 3D structuring of waveguides

For the fabrication of the PDMS specimens two different platin catalyzed addition curing compositions were used: PDMS with 1 equiv. VDT-731/equiv. HMS-082 and PDMS with 3 equiv. VDT-731/equiv. HMS-082.

The PDMS with 3 equiv. of VDT-731 formed a network that was crosslinked to a lesser extent than that with 1 equiv. VDT-731. Therefore the PDMS was softer and was swollen more
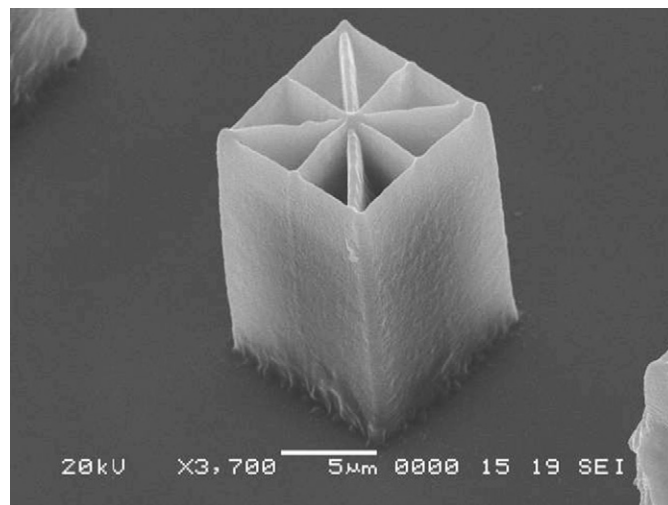

Fig. 2. 1,5-Diphenylpenta-1,4-diyn-3-one (DPD) and derivatives.

| DPD | R = H | S-DPD | R = SMe |
| O-DPD | R = OMe | N-DPD | R = NMe$_2$ |

Fig. 4. N-DPD showed best results in acrylate resin with 0.025 wt% photoinitiator (structure written with 800 nm at 12.5 μW, feed rate 1 mm/min).

Table 1
Content of monomers in PDMS with 1 and 3 equiv. VDT-731 after swelling by monomers, determined by precision weighing of the samples before swelling and after the given resting times

Monomer	1 equiv. VDT-731		3 equiv. VDT-731	
	Swelling after 20 h (wt%)	2 h in air (wt%)	Swelling after 20 h (wt%)	2 h in air (wt%)
AIB	34.8	33.9	48.5	47.8
DVB	27.0	19.6	40.7	33.1
HEA	0.7	0.1	1.2	0.7
PEA	2.4	1.7	5.0	2.7

Table 2
Shore A hardness and polymer content of PDMS after swelling in AIB with growing HEA content after photocuring

HEA (wt%)	1 equiv. VDT-731		3 equiv. VDT-731	
	Shore A hardness	Polymer content (wt%)	Shore A hardness	Polymer content (wt%)
10	85	27.9	80	36.8
20	83	23.4	75	30.3
30	81	19.2	71	25.9
50	77	14.5	65	18.6

easily. All investigated monomers were chosen with regard to their high boiling points in order to minimize evaporation during a processing time of 2 h at room temperature. The degree of swelling was found to be largely dependent on the type of monomer. In general HEA and PEA only penetrated the PDMS matrix very little due to their more polar properties, while AIB and DVB did swell the PDMS sufficiently. AIB showed very low evaporation after 2 h while almost a third of DVB was lost (see Table 1).

Swollen PDMS discs were cured under argon by an UV lamp for 10 min. After UV exposure the specimen with DVB and PEA became hazy while discs with AIB and HEA remained clear. An explanation for this effect was that the aromatic structures of DVB and PEA lead to crystallization after polymerization.

Photocured PDMS discs with a high content of polymer inside the matrix showed a decrease in flexibility and an increase in Shore A hardness. Furthermore, optical clarity was found to be compromised at greater polymer contents. For reducing the polymer content in the PDMS matrix it was necessary to control the degree of swelling. Therefore, monomers with high (AIB) and low (HEA) swelling abilities were used in combination.
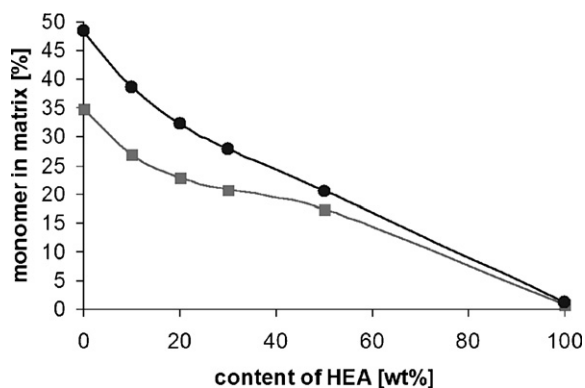
Fig. 5 shows the influence of the content of HEA in the monomer formulation on the swelling of PDMS discs. With growing content of HEA the swelling was reduced further.

Table 2 shows the correlation of the Shore A hardness with the content of polymer in PDMS matrix. The use of HEA gave good control of the amount of polymer in the PDMS matrix after curing and therefore also of the mechanical properties. In the case of PDMS prepared with 1 equiv. VDT-731, the Shore A hardness was 77 at a HEA content of 50 wt% while the PDMS prepared with 3 equiv. of VDT-731 had a Shore A hardness of 65. The pristine PDMS had a Shore A hardness of 67 (1 equiv. VDT-731) and 39 (3 equiv. VDT-731), respectively.

In addition to the weighing procedures used above to quantify the amount of additional matter in the swollen PDMS samples, IR spectroscopy was applied to unambiguously identify the polyacrylate component within the PDMS matrix. IR spectra of pristine PDMS samples (Fig. 6a) were measured as reference.

Fig. 5. Monomer content of PDMS ([●] 3 equiv. VDT-731 and with [■] 1 equiv. VDT-731) after swelling in AIB with increasing HEA content.
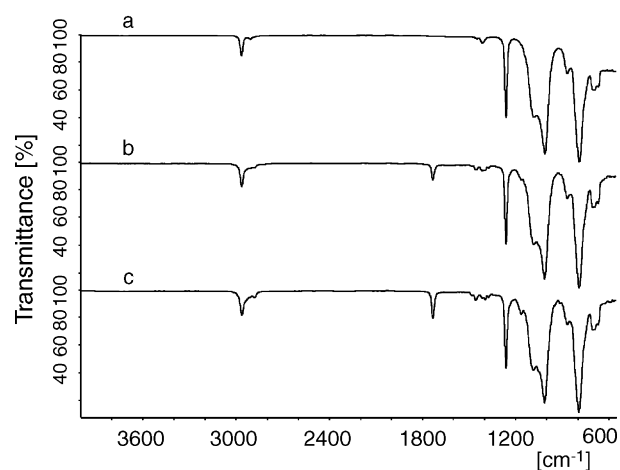

Fig. 6. ATR-IR spectra of PDMS specimens: (a) PDMS (1 equiv. VDT-731); (b) swollen in AIB with 30 wt% HEA after UV curing; (c) swollen in AIB after UV curing.
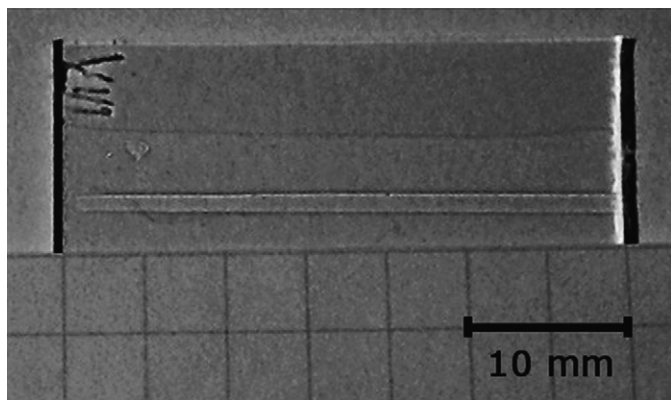
Fig. 7. PDMS soaked by monomer formulation and cured selectively by a photomask (horizontal streak of 1 mm width) by UV light.

The polyacrylate exhibited a band at 1735 cm^{-1} due to the stretching vibration of the C=O bond that showed clearly in the spectra taken from PDMS containing the photopolymer. Fig. 6b shows the spectra of PDMS (1 equiv. VDT-731) that was swollen by AIB with 30 wt% of HEA, correlating to 19.2 wt% of polyacrylate inside the matrix. The spectra of PDMS (1 equiv. VDT-731) that was swollen by AIB without HEA, correlating to 34.2 wt% of polyacrylate in the PDMS matrix, showed an increased absorption at the C=O band (Fig. 6c).

In order to visualize the change in refractive index by polymerizing of monomer moieties in the PDMS matrix, preformed films were cured selectively under UV-light using a photomask. A microscope slide with a 60 μm PDMS (3 equiv. VDT-731) layer was soaked in a monomer formulation containing 80 wt% of AIB and 20 wt% of HEA for 10 min and curing was allowed to take place only in a horizontal streak of 1 mm width (Fig. 7). A change in optical properties is already visible with the naked eye.

A refractive index increase in the range of $\Delta n = 0.01$ ($\Delta n/n = 0.7\%$) was achieved.

4. Conclusion

Two-photon polymerization is a new and modern field in 3D structuring. With especially tailored cross-conjugated photoinitiators we showed feature resolutions in the range of 300 nm with only 0.025 wt% of initiator in the photosensitive resin.

PDMS was tested as a matrix for optical waveguides that will be structured by 2PP. A flexible PDMS matrix was swollen by a monomer, which could be photopolymerized selectively by UV light to increase the refractive index in the exposed area. Afterwards the uncured remaining monomer was removed at increased temperature or reduced pressure. The degree of swelling of the PDMS matrix by the monomer formulation was tailored by increasing the amount of HEA, which reduced swelling. The achievable change of refractive index using this method is in the range of $\Delta n = 0.01$ ($\Delta n/n = 0.7\%$).

Acknowledgement

References

[1] H.-B. Sun, S. Kawata, Adv. Polym. Sci. 170 (2004) 169.
[2] H.-B. Sun, S. Kawata, J. Lightwave Technol. 21 (2003) 624.
[3] K.J. Schafer, J.M. Hales, M. Balu, K.D. Belfield, E.W. Van Stryland, D.J. Hagan, J. Photochem. Photobiol. A: Chem. 162 (2004) 497.
[4] M.P. Joshi, H.E. Pudavar, J. Swiatkiewicz, P.N. Prasad, Appl. Phys. Lett. 74 (1999) 170.
[5] K. Miura, J. Qiu, H. Inouye, I. Mitsuyu, K. Hirao, Appl. Phys. Lett. 71 (1997) 3329.
[6] A. Neyer, S. Kopetz, E. Rabe, W.J. Kang, S. Tombrink, in: Proceedings of 55th Conference on Electronic Components & Technology, 2005, p. 246.
[7] T. Watanabe, N. Ooba, S. Hayashida, T. Kurihara, S. Imamura, J. Lightwave Technol. 16 (1998) 1049.
[8] C. Heller, N. Pucher, B. Seidl, L. Kuna, V. Satzinger, V. Schmidt, H.C. Lichtenegger, J. Stampfl, R. Liska, J. Polym. Sci., Part A: Polym. Chem. 45 (2007) 3280.
[9] B. Seidl, R. Liska, J. Polym. Sci., Part A: Polym. Chem. 43 (2005) 101.
[10] B. Seidl, R. Liska, Macromol. Chem. Phys. 208 (2007) 44.
[11] B.H. Cumpston, S.P. Ananthavel, S. Barlow, D.L. Dyer, J.E. Ehrlich, L.L. Erskine, A.A. Heikal, S.M. Kuebler, I.Y.S. Lee, D. McCord-Maughon, J. Qin, H. Rockel, M. Rumi, X.-L. Wu, S.R. Marder, J.W. Perry, Nature (London) 398 (1999) 51.