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Josef Kumpfmüller\textsuperscript{a}, Klaus Stadlmann\textsuperscript{b}, Zhiquan Li\textsuperscript{a}, Valentin Satzinger\textsuperscript{c}, Juergen Stampfl\textsuperscript{b} & Robert Liska\textsuperscript{a}

\textsuperscript{a} Institute for Applied Synthetic Chemistry, Vienna University of Technology, Lehargasse 2-6, A-1060, Vienna, Austria.
\textsuperscript{b} Institute of Material Science and Technology, Vienna University of Technology, Vienna, Austria.
\textsuperscript{c} MATERIALS-Institute for Surface Technology and Photonics, Joanneum Research, Weiz, Austria.

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Two-photon-induced thiol-ene polymerization as a fabrication tool for flexible optical waveguides

Josef Kumpfmüller*a, Klaus Stadlmannb, Zhiquan Lia, Valentin Satzingerc, Juergen Stampflib and Robert Liska*a

aInstitute for Applied Synthetic Chemistry, Vienna University of Technology, Lehargasse 2-6, A-1060 Vienna, Austria; bInstitute of Material Science and Technology, Vienna University of Technology, Vienna, Austria; cMATERIALS-Institute for Surface Technology and Photonics, Joanneum Research, Weiz, Austria

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In this contribution, we present two flexible thiol-ene-based hybrid materials based on epoxy and acetoxy polysiloxane matrix materials. The latter cross-linking mechanisms allow for orthogonal curing of the matrix in the presence of thiol-ene monomers enabling fast one-step access to two-photon-polymerization (2PP) curable substrates for waveguide fabrication. Another time-saving feature of our concept is the straightforward UV-flood-curing after 2PP, which is also a progress compared to previous works with elaborate postprocessing. Optimization of the ratio of thiol/ene moieties with respect to reactivity and analyses of the thermal stability of the materials, which is required for the industrial process, were carried out. Besides investigations regarding the refractive index of the materials, the proof of principle for successful waveguiding will be given. Flexible optical waveguides were successfully fabricated inside a low refractive polysiloxane matrix material.

Keywords: two-photon-polymerization; waveguides; thiol-ene; polysiloxane

Introduction

Flexible integrated electronic circuits offer a wide range of advantages such as the applicability on uneven surfaces, cheap roll to roll production, and low weight.[1] Despite of these achievements, typical copper-circuit-related drawbacks like cross-talking and overheating remain. These difficulties are not present in optical signaling, so waveguides and integrated optics in flexible materials are hot research topics these days.

The communication industry has started to become interested in flexible optical printed circuit boards, where waveguides connect optical elements. Efficient coupling-in of photons is only possible, if the waveguide is aligned very precisely to the signal emitter. This requirement is hard to meet with conventional techniques such as reactive ion etching [2] or hot embossing giving the emerging two-photon-polymerization (2PP) an opportunity to prove itself. Compared with conventional lithography, the crucial advantage of this novel real 3D printing technique is that it enables polymerization of transparent photoreactive resins exclusively in the very tiny volume pixel (VOXEL) in the focus of a femtosecond pulsed laser.[3] Responsible for this unique feature is the principle of two-photon-absorption, for which the photon-density must be much higher than for one-photon-absorption limiting the subsequent initiation process to such a small space as the focal point of the laser. Two photons must be absorbed simultaneously causing a square dependence of the absorption on the intensity.

2PP has been mainly performed using radically polymerizing (meth)acrylates but also cationic systems such as SU-8 [4] and thiol-ene chemistry have played a role.[5–7] 2PP waveguide inscription commenced with nonflexible substrates such as special glasses.[8] Later on, sol/gel-based materials and organic polymers followed with the most prominent example being the organic modified ceramics. These are sol/gel-based materials with organic moieties, which yield a local refractive index change upon 2PP.[9] Polydimethylsiloxane (PDMS) has been introduced as a flexible and very transparent carrier material for embedding waveguides in recent days by locally 2PP-curing high refractive (meth)acrylic monomers.[10,11] Additionally, PDMS is thermally stable at temperatures around 250 °C, which it needs to withstand for a short time during the industrial processing of the printed circuit boards. There are still several shortcomings to tackle on the road to industrial application, be-it the decline of the refractive index due to thermal polymerization in the cladding material of the waveguides, the optical damping, elaborate pre- and postprocessing or insufficient fabrication speeds.

*Corresponding author. Email: robert.liska@tuwien.ac.at

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Very recently, we contributed concepts of 2PP waveguide fabrication, where cured silicone rubber had been swollen with photoreactive monomer formulation and after 2PP processing the unreacted monomer had been evaporated in order to fully develop the local refractive index change.

In this paper, we present two very time-saving approaches for the pre- and post-processing in the course of 2PP-fabrication of waveguides inside PDMS. In this very specialized field, we apply the thiol-ene reaction as a curing mechanism due to the following reasons: Thiol-ene networks lacking ester moieties exhibit excellent thermal and hydrolytic stability, the sulfur atoms cause a high refractive index and shrinkage is less of a problem compared with acrylic resins. With a focus on the compatibility of the thiol-ene photonetwork with the PDMS matrix, a siloxane-based thiol-ene monomer system was developed. Apart from the goal to produce waveguides, we were interested in the performance of our home-made two-photon-initiators in terms of initiating the thiol-ene reaction. Literature with a focus on the chemistry of two-photon-induced thiol-ene polymerization is rather sparse. Our novel waveguide fabrication procedure (Figure 1) is straightforward and fast.

The preprocessing step comprises only the mixing of a high refractive, photoreactive thiol-ene monomer formulation with low refractive PDMS RTV-1 curing systems. The RTV-1 mechanisms of choice are the acetoxy condensation and the epoxy-based ring-opening polymerization. Note that in both primary PDMS cross-linking reactions neither the thiol nor the ene components of the radically reacting thiol-ene formulation participate to a noteworthy extent. Hence, this orthogonal reactivity yields a low refractive silicone rubber with a high refractive, two-photon-sensitive resin inside, which is a practical improvement over works from the past, where this was achieved by a time consuming and unreliable swelling step.

After selective curing of the PDMS matrix material, the waveguide structures are inscribed by inducing a local refractive index change by means of 2PP-thiol-ene curing. Upon two-photon-illumination high refractive thiol-ene material becomes enriched in the waveguide region via diffusion. This effect makes the ‘development step’ from earlier concepts dispensable, where unreacted high refractive monomer had been removed (e.g. in vacuum) mainly to lower the refractive index of the cladding material. In our process, it is sufficient to UV-flood-cure the remaining unreacted monomer, creating an interpenetrating network of silicone rubber with lower content of high refractive thiol-ene photopolymer in the cladding region than in the core (Figure 1).

An array of analytical methods was very helpful for the improvement of both the epoxy and the acetoxy-based material concept: The reactivity and double-bond conversion (DBC) of our material was assessed by means of photo-DSC and ATR-IR and helped to find optimized ratios of thiol to ene moieties in each case. Furthermore, the thermal stability of the PDMS/thiol-ene hybrid materials had to be proven by DMTA as a requirement for the industrial process of printed circuit boards. Moreover, we had to investigate the behavior of the refractive index in our materials as this property is a crucial one to waveguiding. Finally, promising 2PP writing and waveguiding results will be presented.

Experimental

Chemicals

1,3-Bis(chloromethyl)-1,1,3,3-tetramethyldisiloxane (TMMD), tris(vinylidimethylsiloxy) methylsilane (TVMS), silanol-terminated polydimethylsiloxane with molecular weight 4200 (PDMS 4200), di-n-butyl diacetoxytin (DBTDA), epoxy cyclohexylethylmethyldisiloxane (8–10 mol%)-dimethyl siloxane copolymer (ECES) and triacetoxy vinyl silane (TAVS) were purchased from ABCR, thiourea from Fluka, ethylene diamine and trifluoro acetic acid (TFA) from Aldrich, Darocur 1173 from BASF and pyrogallol from Merck. All chemicals were used without further purification. Column chromatography was carried out on VWR silica gel 60 (0.040–0.063 mm).

Figure 1. Manufacturing process of 2PP-borne waveguides.
Notes: Grey snake lines: silanol or epoxy cyclohexyl functional PDMS, yellow dots: thiol monomers, blue dots: ene monomers, pink squares: PDMS cross-links, green interconnected dots: PDMS/thiol-ene hybrid cladding material.
**Synthesis of 1,3-bis(mercaptomethyl)-1,1,3,3-TMMD**

TMMD was synthesized by a procedure derived from that proposed by Mogi [14]. Therefore, 1,3-bis(chloromethyl)-1,1,3,3-TMMD (25.0 g, 108 mmol) and thiourea (49.3 g, 644 mmol) were dissolved in 225 mL of DMF under nitrogen atmosphere and stirring. The solution was heated to 120 °C and stirred at this temperature for 5 h. Subsequently, the reaction mixture was cooled to 60 °C by means of an ice bath and a mixture of ethylene diamine (39.0 g, 648 mmol), and 39 mL methanol was added dropwise over a period of 10 min. The reaction solution was stirred at 60 °C overnight. After adding 225 mL of water, the reaction mixture was extracted with three volumes of n-hexane and dried with sodium sulfate. From the combined organic phases, the solvent was distilled off followed by vacuum distillation at 3 mbar in a range of 75–95 °C. Column chromatography (RF: 0.38, PE) yielded 4.9 g (20%) of a colorless liquid. 

\[ \text{[x]}_{20}^{\text{D}} = 1.476, \ \text{H NMR (CDCl}_3; \ \delta, \text{ppm}): 1.68–1.64 \ (d, J = 7.1 \text{ Hz \ CH}_2), 1.21–1.15 \ (m, \text{SH}), 0.2 \ (s, 12 \text{H}, \text{CH}_3), \]

**Photo-DSC and ATR-IR**

For the photo-DSC measurements, a Netzsch DSC 204 F1 Phoenix device was used. A double light guide, which was attached to the DSC unit from top, enabled irradiation of the sample with filtered UV-light (280–500 nm) from an EXFO-Omnicure 2001 lamp where the light intensity on the tip of the light guide was 3000 mW cm\(^{-2}\) from an EXFO-Omnicure 2001 lamp where the light intensity on the tip of the light guide was 3000 mW cm\(^{-2}\) from an EXFO-Omnicure 2001 lamp where the light intensity on the tip of the light guide was 3000 mW cm\(^{-2}\) from an EXFO-Omnicure 2001 lamp where the light intensity on the tip of the light guide was 3000 mW cm\(^{-2}\). The measurements were conducted in an isocratic mode at 25 °C under nitrogen atmosphere. Thiol-ene resins with the ratios 1.4, 1.2, 1.0, 0.8 and 0.6 of thiol:ene moieties were prepared according to Table 1. The formulations were weighed into Al-pans with an accuracy of 10 ± 1 mg. Note that TMMD (g mol\(^{-1}\)) and TVMS (g mol\(^{-1}\)) are required.

Table 1. Basic thiol-ene formulations (\(T_{0.6-1.4}\)) for photo-DSC measurements. Ratios of chemicals are given in wt.%.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>(T_{0.6})</th>
<th>(T_{0.8})</th>
<th>(T_{1.0})</th>
<th>(T_{1.2})</th>
<th>(T_{1.4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMMD</td>
<td>60.00</td>
<td>56.30</td>
<td>51.80</td>
<td>46.20</td>
<td>39.10</td>
</tr>
<tr>
<td>TVMS</td>
<td>39.22</td>
<td>42.84</td>
<td>47.25</td>
<td>52.75</td>
<td>59.71</td>
</tr>
<tr>
<td>Darocur 1173</td>
<td>0.78</td>
<td>0.86</td>
<td>0.95</td>
<td>1.05</td>
<td>1.19</td>
</tr>
</tbody>
</table>

The DBC (%) for the pure thiol-ene resins \(T_{0.6-1.4}\) (only TMMD, TVMS, pyrogallol, and Darocur 1173) without matrix material was determined by means of a Perkin Elmer Spectrum 65 FT-IR spectrometer (with Golden Gate ATR unit) device. Herein, the peak areas of the C=C stretch vibration peak at 1595 cm\(^{-1}\) were compared in relation to the area of the Si-CH\(_3\) reference peak at 1253 cm\(^{-1}\). This information was combined with the actual heat of polymerization \(\Delta H_p\) (J g\(^{-1}\)) obtained from photo-DSC to calculate the theoretical heat of polymerization released by the vinyl moieties \(\Delta H_{0,p,V_n}\) [J mol\(^{-1}\)], Equation (1)). Furthermore, the molecular weight \(M_M\) (g mol\(^{-1}\)) and the functionality of the ene \(f\), which is 3 in case of TVMS, are required.

\[
\Delta H_{0,p,V_n} = \frac{\Delta H_p M_M}{DBCf} \times 100
\]

The rate of polymerization \((R_{p,max} \text{ mol L}^{-1} \text{ s}^{-1})\), Equation (2) was determined from the height of the photo-DSC peak maximum \(h\) (mW mg\(^{-1}\)), the density of the thiol-ene resin \(\rho\), which was considered to be approximately the value for PDMS (970 g L\(^{-1}\)) and the theoretical heat of polymerization of the vinyl moieties \(\Delta H_{0,p,V_n}\) (J mol\(^{-1}\)).

\[
R_{p,max} = \frac{h \rho}{\Delta H_{0,p,V_n}}
\]
For samples involving the epoxy and acetoxy matrix material, the theoretical heat of polymerization was applied to calculate the DBC for photo-DSC-experiments as the ATR-IR peaks were not intense enough due to the dilution by the matrix material.

**Mechanical properties**

DMTA tests were carried out applying a DMA 2980 device (TA Instruments) using a single cantilever clamp over a temperature range from $-140$ to $300^\circ C$ for those measurements. The temperature gradient was $3 K \text{ min}^{-1}$, the frequency $1 Hz$ and the amplitude $10 \mu m$.

Test bars were casted in $40 \times 5 \times 2 mm$ molds fabricated with an OBJET 3D printer with adhesive foil on the bottom for easier removal after moisture and/or UV-flood-curing. For the latter, an INTELLI-RAY 600 UV device at an intensity of $120 \text{ mW cm}^{-2}$ at a distance of $130 \text{ mm}$ from the lamp was used illuminating the samples for 2 min from two opposite sides under nitrogen atmosphere.

For both the epoxy and the acetoxy concept, test bars were prepared for the photo-polymer containing cladding materials and the pure matrix materials: In case of the epoxy matrix sample, no proper concentration for the cationic cross-linking catalyst TFA was found for homogenous curing. Hence, TFA was substituted by a photoacid generator: $0.5\%$ of (p-isopropylphenyl)(p-methyl phenyl)-iodonium tetrakis(pentafluorophenyl) borate dissolved in a drop of isopropanol (IPA) was mixed with $99.5\%$ ECES (formulation $E_{\text{mat}}$) and cationically photocured as mentioned above.

The moisture-curable acetoxy matrix sample (formulation $A_{\text{mat}}$) was formulated using $8\%$ of TAVIS, $0.5\%$ of DBTDA and $92.5\%$ of PDMS 4200. The corresponding test bar was cured for 5 days at room temperature.

The formulations for the epoxy and acetoxy cladding materials (containing thiol-ene photoinitiator) are given in Table 1 ($E_{1.0}$, epoxy cross-linking for one hour after casting) and Table 2 ($A_{1.4}$, moisture curing for 5 days after casting), respectively. After orthogonal curing of the epoxy and acetoxy polysiloxanes in the presence of thiol-ene monomers, the latter were photoocured as mentioned above.

**Refractive index**

Refractive indices were in all cases measured applying the photo-DSC cured samples on a Abbé Refractometer, manufactured by the Carl Zeiss Company, Germany, and equipped with a Schott Geraete CT 050 Thermostat, filled with distilled water (adjusted to $20^\circ C$). The operating wavelength was $589 nm$ (sodium D-line). Formulations are shown in the photo-DSC section above.

**Formulation for waveguide fabrication**

Waveguides were fabricated in epoxy- and acetoxy-based silicone materials. For the epoxy-based concept (see formulation $E_{\text{opt}}$ in Table 3) pyrogallol was dissolved in the thiol TMMD followed by adding the vinyl monomer TVMS (ratio thiol/ene moieties 1.0), the photoinitiator Darocur 1173, and the two-photon-initiator P3 K (see Figure 2) and the catalyst TFA in IPA under light protection.

For the sake of uniformity of curing, it was important to add the epoxy-based silicone ECES in the last step and vigorously stir the formulation. The mixture was rapidly degassed at $10 mbar$ vacuum and cast into molds made of adhesive tape on top of a glass slide yielding a film of approximately $200 \mu m$. Although gelling of the film was observed already after a few minutes, the material was stored in the dark at room temperature for one hour to complete cross-linking of the silicone matrix.

For the acetoxy-based material (see formulation details $A_{\text{opt}}$ in Table 3), the above-mentioned solution of the inhibitor pyrogallol in TMMD was added to the siloxane-based trivinyl siloxane TVMS (ratio thiol: ene moieties 1.0). Next, the novel two-photon-initiator 2,6-bis(4'-dimethylaminobenzylidene)4-methylcyclohexa-none (M2CHK, see Figure 2) and Darocur 1173 were mixed into the thiol-ene resin. Silanol-terminated PDMS 4200 was added to the thiol-ene resin followed by the condensation catalyst DBTDA and TAVIS as a condensation cross-linker. From the mixture, $200 \mu m$ films were casted as mentioned above and cured at air moisture for an hour in the dark.

![Figure 2. Home-made two-photon photoinitiators for thiol-ene-based waveguide structuring.](image-url)
2PP setup and processing
An amplified ultrafast Ti/sapphire laser system from Spectra Physics (Mai Tai®-Spitfire® combination) was applied for the 2PP experiments providing pulses in the range of 800 nm wavelength and a pulse duration of a 130–150 fs. The repetition rate was 1 kHz and the maximum pulse energy 1 mJ sufficing even for laser ablation metals. By means of a single shot autocorrelator (Femtos), the pulse width of the laser was monitored. The sample was moved on a 3-axial stage (Aerotech), which exhibited an accuracy with respect to positioning of 100 nm and a travel range of several centimeters. By an extra cavity electro-optical modulator, which featured a remote control of the high voltage applied to the Pockets cell, the laser power was computer-controlled. A combination of a 20× microscope objective (Zeiss) with a numerical aperture of 0.5 was combined with a cylindrical telescope served as focusing optics. A threefold reduction of the spherical beam cross-section was accomplished with the telescope, which comprised a pair of cylindrical lenses exhibiting focal lengths of f1 = 75 mm and f2 = 25 mm. The elliptic beam cross-section formed by this apparatus allowed for astigmatic beam focusing and shaping of the focal volume. The home-made LabView Program allowed for controlling the lithographic setup. Waveguide structures were written in depth of approximately 125 μm. The 2PP processed samples were cured by means of a UV 236 A UV-lamp under nitrogen atmosphere (Waldmann Medizintechnik; 5 min at 360 mJ cm⁻² min⁻¹; lamp to sample distance 10 cm).

Results and discussion
Selection of matrix material and monomers
The two-photon-lithography without doubt provides very unique advantages for a challenging task as structuring a precisely aligned waveguide between tiny optical elements. In this contribution an emerging technique encounters a niche application, which makes special endeavor in material development necessary. In past works, we successfully used PDMS as a matrix material for waveguides due to its outstanding flexibility and the ability to withstand temperatures around 240 °C for 20 min during the manufacturing process of printed circuit boards. Also the low optical damping and its rather low refractive index around 1.4 are well appreciated.

Based on PDMS, the monomer selection was made with the claim to create thiol-ene networks interpenetrating the PDMS matrix upon 2PP. Experience had shown that compatibility with the hydrophobic PDMS matrix material is rather tricky to achieve: Many resins were compatible with the cross-linked PDMS rubber but finally showed incompatibility after formation of the thiol-ene network upon illumination.

A good solution for this problem might be found by using a siloxane-based system consisting of the oligosiloxane-based thiol TMMD and the trifunctional ene TVMS (Figure 3(b)) mimicking the PDMS matrix material. Thus, phase separation should be avoided. Photopolymers from TMMD and TVMS, just like the matrix material, do not feature any functional groups like esters that would endanger the required temperature stability of the waveguide material. Therefore, TMMD had to be synthesized first by a procedure similar to the one presented by Mogi et al. [14] (Figure 3(a)): in the course of this S-alkylation, 3-bis(chloromethyl)-1,1,3,3-TMMD forms an intermediary isothiouronium salt by reaction with thiourea. The reaction mixture is then treated with ethylene diamine in order to liberate the desired dithiol.

In previous studies, the liquid polymerizable monomer had been introduced into silicone rubbers via a

![Figure 3. (a) Synthesis of dithiol TMMD and (b) cross-linking reaction with the ene TVMS.](image-url)
time consuming swelling process. Now, an elegant way to a specimen, where the liquid monomer is on hand for 2PP curing inside an already cured PDMS rubber, could be paved by selecting PDMS cross-linking chemistries with vastly orthogonal reactivity to the monomer system. RTV-2 addition cure systems involving Si-H addition, which are often favorable for photonic applications, failed in this aspect probably due to catalyst poisoning by the mercapto groups. Cationic ring opening curing of the epoxy cyclohexyl functional PDMS (ECES) as well as RTV-1 acetoxy condensation of silanol-terminated PDMS turned out as good methods for this purpose. Besides reacting selectively, additional compatibility could be introduced in both cases:

For the epoxy concept, primary amino-terminated PDMS had been added to ECES with the intention to trigger amino-epoxy cross-linking, whereas it was expected that one primary amino group is able to react with two epoxy groups. It turned out that the amino functionalities are dispensable as cationic ring-opening polymerization took place. The polyether domains generated during the ring opening polymerization (Figure 4(a)) allowed for a good polarity matching of the matrix material and the thio-ether containing photopolymer. Catalysts as citric or butyric acid also successfully catalyzed the cross-linking and should be preferred over amines due to yellowing. But due to incompatibility and unpleasant odor of the latter, TFA was finally the catalyst of choice. It was well compatible with the formulation and would evaporate gradually.

In the alternative condensation type concept, Si-OH-terminated PDMS should be cross-linked with the acetoxy-based TAVS (Figure 4(b)) in the presence of our thiol-ene formulation (TVMS + TMMD). The additional ene groups of TAVS enabled a covalent linkage between the PDMS matrix and the polymerizable photopolymer enhancing compatibility of both materials.

In former contributions, high refractive monomers in the cladding material were removed by means of heat or vacuum. In contrast, we found that in our concept the good diffusibility of the rather small monomers TMMD and TVMS yielded a significant enrichment of high refractive material in the two-photon-illuminated regions. Thus, the refractive index increase was already generated during the structuring step and the manufacturing process could once again be shortened, by simple UV flood-curing after 2PP structuring utilizing Darocur 1173 as initiator.

**Photo-DSC and ATR investigations**

A major issue of the two-photon-lithography is the level of throughput. For waveguide inscription on a mass production scale, highly two-photon reactive materials are required. Influencing factors range from the concentration and kind of photoinitiator to the type of monomers. Additionally, thiol-ene photoreactivity is also influenced by the ratio of thiol:ene moieties present.

Photo-DSC is a fast and reliable method to quantify the reactivity of a formulation under one-photon
conditions. To get a hint toward the optimum ratio of thiol and ene moieties, this technique was used despite of the limited comparability to the 2PP situation. The photo-DSC curve provides direct access to the polymerization speed measured by the time from the onset to the photo-DSC peak maximum ($T_{\text{max}}$, s), the height of the latter (h, mW mg$^{-1}$) and the actual heat of polymerization ($\Delta H_p$, J g$^{-1}$). From the latter, two values one can calculate the DBC and $R_p$ if the theoretical heat of polymerization with respect to the ene ($\Delta H_{0,\text{P,V}_n}$, kJ mol$^{-1}$) is known. According to the DBC values yielded by ATR spectra prior to and after curing of the pure thiol-ene system (ratios of thiol:ene moieties 0.6, 0.8, 1.0, 1.2, 1.4, see Supplemental material F1) in the photo-DSC device (Table 4), $\Delta H_{0,\text{P,V}_n}$ has been calculated to be 70.1 kJ mol$^{-1}$ per vinyl moiety. Hence, DBC and $R_p$ determination was also possible in the presence of diluting matrix from photo-DSC data.

For the basic investigation of the pure thiol-ene system, a series of mixtures of the dithiol TMMD and the vinyl monomer TVMS with thiol/ene functional groups ratios from 0.6 to 1.4 (see Table 4) were carried out. Increasing thiol content gave increasing DBCs reaching a maximum of 100% at equimolarity of thiol and ene functionalities. In formulations, $T_{0.6}$ and $T_{0.8}$ with ene excess all available thiol groups were reacted. The DBC values 64% is actually higher than the stoichiometry 0.6 would allow, which is attributed to inaccuracy of the DBC determination. The reaction speed, represented by the rate of polymerization $R_p$ and by $T_{\text{max}}$, is slightly higher for the mixtures with an excess of ene. The reason for the latter could be that the speed of the thiol-ene reaction in question is limited by the reaction step, where the thiol radical adds to the ene and thus dependent on the ene concentration. The viscosity of this monomer formulation is very low and also the gel point is reached quite late due to the step growth mechanism, so diffusion is not thought to be the limiting factor for a single waveguide writing step.

When the thiol-ene formulations were cured in the epoxy matrix, which mimics the conditions for 2PP, the highest DBC was surprisingly observed at ratio 1.0 (see Table 5). The tendency regarding $T_{\text{max}}$ and $R_p$, however, is similar to the pure thiol-ene resins. Lower reactivity at higher thiol concentrations might be addressed to reduced mobility due to disulfide bridge formation. Due to a comparatively low DBC, $R_p$ in case of the sample with stoichiometry 0.6 does not follow the trend of increasing $R_p$ with increasing ratio of ene. These deviations of the trends between pure thiol-ene system and the thiol-ene system in the epoxy matrix were surprising as the epoxy matrix material had been thought to only dilute the monomer.

The acetoxy matrix material (Table 6) provides a significant amount of additional ene moieties for the combination with the thiol-ene formulation. Thus, the matrix is thought to participate in the thiol-ene curing. As expected formulations $A_{0.6-1.4}$ showed that the thiol-ene system in the acetoxy matrix behaved similarly as in the pure system (Table 3). Figure 5 in the Supplemental material shows clearly that the polymerization kinetics are almost identical for the acetoxy series ($A_{0.6-1.2}$) compared to the pure monomer system ($T_{0.6-1.4}$). Only in formulation $A_{1.4}$ the DBC develops slower. This is thought to be due the fact that the gel point is reached later than in formulations $A_{0.6-1.4}$ with lower thiol content.

Moreover, it can be seen that compared with the epoxy matrix the values for DBC and $R_p$ are comparatively low in case of the acetoxy concept. This is probably due to higher dilution of monomer with matrix material in the acetoxy material: in the epoxy concept, the matrix material could be cured in the presence of a higher concentration of monomer than it was the case for the acetoxy matrix material (see Table in experimental part). The latter would not cure any more at monomer contents of around 35%. Furthermore, the vinyl-based crosslinker TAVS hinders diffusion and therefore also leads to lower DBC.

Table 5. Photo-DSC data of thiol-ene photopolymerization inside an epoxy cross-linked matrix.

<table>
<thead>
<tr>
<th>Thiol:ene ratio</th>
<th>DBC (%)</th>
<th>$R_p$ (mol s$^{-1}$ L$^{-1}$)</th>
<th>$T_{\text{max}}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{0.6}$</td>
<td>37</td>
<td>0.058</td>
<td>6.8</td>
</tr>
<tr>
<td>$E_{0.8}$</td>
<td>61</td>
<td>0.065</td>
<td>8.4</td>
</tr>
<tr>
<td>$E_{1.0}$</td>
<td>83</td>
<td>0.060</td>
<td>9.5</td>
</tr>
<tr>
<td>$E_{1.2}$</td>
<td>69</td>
<td>0.038</td>
<td>11.7</td>
</tr>
<tr>
<td>$E_{1.4}$</td>
<td>72</td>
<td>0.033</td>
<td>12.2</td>
</tr>
</tbody>
</table>

Table 6. Photo-DSC data of thiol-ene photopolymerization inside an acetoxy cross-linked-matrix containing vinyl functionalities.

<table>
<thead>
<tr>
<th>Thiol:ene ratio</th>
<th>DBC (%)</th>
<th>$R_p$ (mol s$^{-1}$ L$^{-1}$)</th>
<th>$T_{\text{max}}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{0.6}$</td>
<td>33</td>
<td>0.024</td>
<td>11.5</td>
</tr>
<tr>
<td>$A_{0.8}$</td>
<td>46</td>
<td>0.023</td>
<td>14.2</td>
</tr>
<tr>
<td>$A_{1.0}$</td>
<td>60</td>
<td>0.020</td>
<td>16.9</td>
</tr>
<tr>
<td>$A_{1.2}$</td>
<td>70</td>
<td>0.018</td>
<td>17.1</td>
</tr>
<tr>
<td>$A_{1.4}$</td>
<td>79</td>
<td>0.012</td>
<td>25.7</td>
</tr>
</tbody>
</table>
Based on these results and other practical considerations the optimum formulation should be defined: Generally, higher thiol contents could have advantages though: The tendency of systems with thiol excess to form less dense networks than with equimolar ratios made us expect facilitated diffusion of thiol-ene monomers into the waveguide core region and enhanced enrichment of high refractive material. Another advantage of thiol excess worth mentioning is the higher amount of high refractive sulfur atoms incorporated into a mercapto-terminated photopolymer. Considering the DBC behavior and the latter aspects a thiol to ene ratio of 1.4 has been selected for the following investigations in case of the acetoxy concept. Regarding the epoxy concept, the maximum in terms of DBC and an acceptable $R_p$ were the reasons, why a thiol to ene ratio of 1.0 was chosen.

**DMTA tests**

During the processing of the optical printed circuit boards, the waveguide material has to withstand temperatures around 240 °C for 20 min. In contrast to the cladding materials, the waveguide core materials exhibit an unknown distribution and content of thiol-ene polymer, so their mechanical behavior would be very difficult to investigate. To check this industrial criterion for our concepts, the storage moduli of the pure matrix materials $E_{\text{mat}}$ and $A_{\text{mat}}$ (for formulations see section mechanical properties in experimental part) and the optimized epoxy and acetoxy waveguide materials $E_{1.0}$ and $A_{1.4}$ (for formulations see Tables 2 and 3 in the experimental part) were measured by DMTA over a temperature ramp from 100 to 300 °C (see Figure 5).

The epoxy matrix material $E_{\text{mat}}$ exhibited generally a low storage modulus over this temperature range and no failure. It underwent a slight increase until approximately 190 °C, which could be explained by additional thermal polymerization during the temperature ramp. Until 300 °C a slight decrease to 15 MPa was detected as it is expected for cross-linked materials. The epoxy cladding material $E_{1.0}$ exhibits a similar DMTA curve with a displacement of approximately 10 MPa.

The pure cross-linked acetoxy material $A_{\text{mat}}$ underwent a slight increase in the temperature range in question from 9 to 20 MPa, which might again be assigned to additional cross-linking reactions. On the other hand, the corresponding cladding material $A_{1.4}$ exhibited a much steeper rise of the storage modulus from approximately 14 MPa at 100 °C to 100 MPa at 280 °C indicating pronounced thermal cross-linking of excessive thiol groups in the test bar. At the latter maximum, the material underwent failure, which can be observed by a sudden drop of storage modulus. Failure at this temperature is not problematic for the industrial process.

**Optical properties**

In our concept, the refractive index change as the essence of waveguide structuring is generated by high refractive monomer which becomes enriched upon 2PP in the waveguide regions.

![Figure 5. DMTA curves of waveguide matrix and cladding materials.](image-url)
The refractive indices of the pure uncured thiol-ene mixture $T_{1.0}$ and $T_{1.4}$ fit well the calculated values obtained from weighing the refractive indices of TMMD and TVMS (Table 7). After curing, however, they reach the same refractive index. This can be explained by two effects contributing to the high refractive indices in $T_{1.0}$ and $T_{1.4}$: Compared to formulation $T_{1.0}$, formulation $T_{1.4}$ exhibits a higher concentration of sulphur atoms. On the other hand the cured formulation $T_{1.0}$ features a cross-link density higher than in case of $T_{1.4}$. These latter two effects are thought to compensate for each other in the cured formulations of question causing equal values for $\alpha / C_{138}^{20}$.

The refractive index of the cladding materials (formulations $E_{1.0}$ and $A_{1.4}$, Table 7) was also accessible by simple Abbé-refractometer measurements. The quantitative refractive index distribution within the waveguide core, however, was beyond our experimental possibilities. As high refractive thiol-ene photopolymer is enriched in the core region, the refractive index there must lie between that of the pure thiol-ene networks (1.484) and that of the claddings ($E_{1.0}$ cured and $A_{1.4}$ cured).

It can be seen that in the epoxy concept a refractive change of 0.020 is caused by the thiol-ene network when comparing $E_{1.0}$ and $E_{\text{mat}}$ (for formulation $E_{\text{mat}}$ see section mechanical properties of experimental part). The acetoxy-based materials $A_{\text{mat}}$ and $A_{1.4}$ behave similarly with a refractive index change of 0.023. For waveguiding applications, a relative change in refractive index $\Delta n/n$ of at least 0.1% is required.[15] This criterion would be more than fulfilled for the acetoxy as well as the epoxy material, if the core material was pure thiol-ene photopolymer.

2PP and waveguiding

After assessing the reactivity of our specially tailored photoreactive, optical materials the task was to find out about the laser intensities and feed rates, at which effective waveguide structuring can be performed. It turned out in the epoxy as well as in the acetoxy concept that the higher the monomer content in the material, the higher the 2PP-induced refractive index change would be. This can be explained by more effective monomer diffusion and enrichment in the two-photon illuminated regions giving reinforced waveguide channels. The monomer content, however, was limited by the curability of the matrix material in the presence of the orthogonally reacting monomer. In case of the epoxy concept (formulation $E_{\text{opt}}$), the most successful waveguide structuring took place in a window around 200 $\mu$W laser power and 4 mm min$^{-1}$ feed rate (Figure 6(a)). It turned out that moving the focal point of the laser over the structuring region five times resulted in significantly enhanced phase contrasts. This happened because monomer diffusing into the waveguide after each run could be cured there in the next writing step.

In a first waveguiding experiment, a waveguide bundle was cut through to a piece of 6 mm and white light was successfully coupled into it. This served as a proof of principle for successful waveguiding (Figure 6(b)).

The same was carried out for the acetoxy-based system (formulation $A_{\text{opt}}$, Table 3) applying an elevated

| Table 7. Relevant refractive indices of monomers, matrix materials and 2PP formulations. Exact formulations are given in the photo-DSC experimental section. |
|---|---|
| Sample | $\alpha / C_{138}^{20}$ |
| TMMD | 1.476 |
| TVMS | 1.417 |
| $T_{1.0}$ uncured | 1.446 |
| $T_{1.0}$ cured | 1.484 |
| $T_{1.4}$ uncured | 1.452 |
| $T_{1.4}$ cured | 1.484 |
| $E_{\text{mat}}$ | 1.423 |
| $E_{1.0}$ cured | 1.443 |
| $A_{\text{mat}}$ | 1.410 |
| $A_{1.4}$ cured | 1.423 |

Figure 6. (a) Phase contrast image of waveguide structures fabricated at writing speed of 4 mm/min and 170–200 $\mu$W laser power with material $E_{\text{opt}}$. (b) Cross-section of a 6+1 waveguide bundle.
thiol/ene ratio of 1.5 due to the good results from photo-DSC for thiol excess. Note that due to better phase contrast the monomer content was elevated in comparison to the samples from the photo-DSC section. The phase contrast appears higher judging from the image and the coupling-in experiment, although the monomer content in the sample is significantly lower than in the above-mentioned epoxy system $E_{opt}$. This might be due to the different photoinitiators P3 K and M2CHK having different activity as recently demonstrated.[16,17] P3 K was the initiator of choice for the epoxy concept as it was not prone to salt formation with TFA as e.g. similar equivalents as B3 K. [17]. M2CHK was found to serve as a straightforwardly synthesized two-photon-initiator allowing for 2PP at a concentration as low as 0.04 wt.% in the acetoxy concept. Another possible explanation for the above mentioned higher phase contrast is that by means of the vinyl functionality in the acetoxy cured silicone rubber, the system reaches the gel point faster. Furthermore, in case of the more successful acetoxy concept, the thiol is present in excess assuring a saturation of virtually any double bond in the illuminated region. The structuring window with fivefold structuring has its optimum at around 150 µW and 10 mm min$^{-1}$ (Figure 7(a)). Coupling-in experiments look promising (Figure 7(b)). Changing the shape of the VOXEL allows for further optimization of the waveguiding performance.

In future developments, it would be desirable to improve the sharpness of the waveguide boundaries, which would improve on the waveguiding efficiency. Radical scavengers might be a possibility to achieve this. The resolution would also be better, if the resin was reactive enough to allow for sufficient refractive index change after a single writing step.

**Conclusion**

Summing up, we contributed a novel, straightforward approach for waveguide fabrication using the thiol-ene polymerization to locally create a refractive index change in two different silicone materials using home-made state-of-the-art two-photon-initiators. Incompatibility problems were tackled by molecular mimicry and covalent bonding between high refractive photopolymer and silicone matrix to give transparent hybrid materials. Photo-DSC and FT-IR studies paved the way to optimized formulations that allowed for successful proof of principle for waveguiding. Thermal stability at 240 °C, which is required for the industrial manufacturing process of printed circuit, was proven by DMTA investigations.

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**Supplemental data**

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**References**


