

# Photo-induced Waveguide Formation in Polysiloxanes

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## ABSTRACT

The aim of this work was the development of materials for writing optical waveguides into flexible polydimethylsiloxane (PDMS) layers by means of laser structuring techniques. An important application would be the connection of optical components on flexible circuit boards in the communication technology. Well known techniques from the literature are based on the concept of photolocking. To avoid the additional step of swelling the low refractive PDMS matrix with the photocurable monomer, we present two concepts wherein curing of the PDMS matrix is possible in the presence of a variety of monomers. Classical radical polymerization was employed with a set of high refractive monomers that meet the requirements of optical interconnects. Optical waveguides were successfully written into the silicone matrix by 2-photon polymerization.

## INTRODUCTION

Two-photon polymerization (2PP) is a new and modern technology in solid freeform fabrication.<sup>[1]</sup> It allows the fabrication of sub-micron structures from a photopolymerizable resin. By applying low energy near-infrared (NIR) lasers 3D structures with a theoretical spatial fabrication resolution down to 120 nm and surface roughness well below 50 nm can be manufactured.<sup>[2]</sup> Polymer-based photonic and microelectromechanical systems (MEMS), 3D optical data storage or inscription of waveguides into materials that are otherwise not accessible are examples for areas of application. The fact that 2PP only takes place inside the focus of the laser beam allows for mastering such difficult tasks as connecting two optical components with a waveguide that are already embedded in a solid 3D-block of transparent material. 2PP has to induce a refractive index change in the order of  $\Delta n/n \sim 0.1$  for these applications.<sup>[1]</sup>

Inscription of waveguides in 3D therefore requires materials and methods suitable for a selective refractive index change in a preformed material block. Various ways for structuring of waveguides by 2PP have been reported, e.g. by selective curing of a component in a resin mixture<sup>[3,4]</sup> or by direct writing into various glasses.<sup>[5]</sup> Transparent polydimethylsiloxane (PDMS) is a cost effective, up to 270°C temperature-resistant material that has a low attenuation in optical applications (lower than 0.1 dB/cm at 850 nm). By using a mold made of SU-8 PDMS waveguides can be formed in several steps comprising casting of waveguides, embedding in a cladding and laminating.<sup>[6]</sup> Waveguides made from polysiloxanes are usually produced from thermosetting siloxanes by lithographic methods combined with reactive ion etching.<sup>[7]</sup>

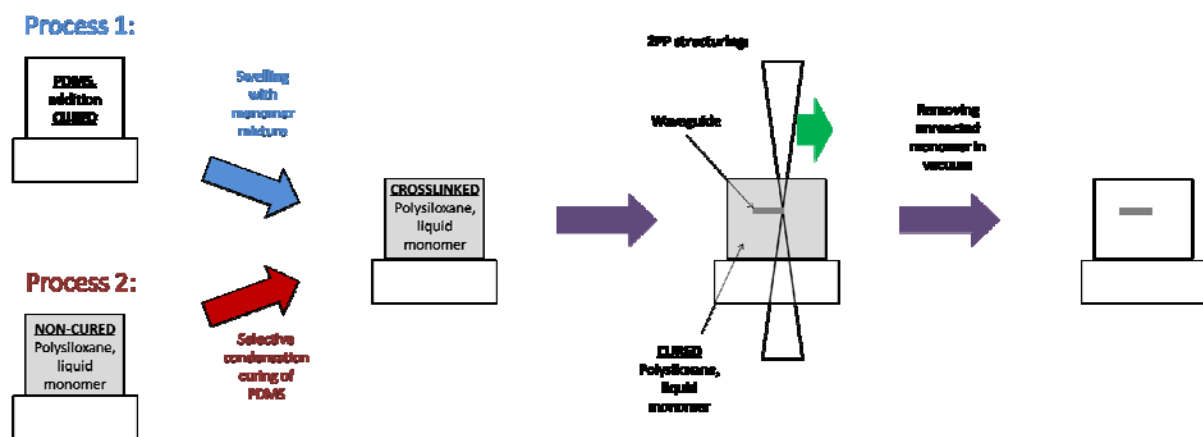
Our concepts to attain a suitable refractive index change for waveguiding are based on selective 2PP of monomers within a preformed flexible matrix. Prerequisites for this approach are on the one hand monomers which are sufficiently compatible with the PDMS matrix without being too volatile during handling. On the other hand they should be removed easily in the non-illuminated regions after exposure to light. A useful monomer for structuring optical waveguides has to form a polymer that has a higher refractive index than the polysiloxane matrix itself so that total reflection inside the waveguide occurs. Ultimately the photopolymer has to be sufficiently compatible with the silicone rubber, as hazy hybrid materials scatter the signaling photons.

The first successful approach in our group was to swell addition cured PDMS (Elastosil RT601) with a mixture of acrylate compounds with higher refractive index and a photoinitiator (Scheme1, Process 1).<sup>[8]</sup> Some first very promising 2PP experiments for the structuring of waveguides were performed in swollen PDMS specimens.

Due to the fact that the swelling process is rather time consuming and accompanied by a significant increase in volume, our next ambition was to be able to cure the PDMS matrix selectively in the presence of photoreactive monomers. The attempt of curing the above mentioned silicone rubber in the presence of acrylic monomers failed, because the acrylate monomers were hydrosilylated preferentially instead of the vinyl groups of the PDMS in Elastosil RT601. In case of methacrylic monomers, whose double bonds are less reactive, the procedure was successful, but, with regard to reactivity towards photopolymerisation this was no real breakthrough.<sup>[8]</sup>

Our concept of using acetoxy condensation curing systems provided a solution for this problem: The acetoxy curing agent exclusively reacts with the hydroxyl groups of the PDMS chains and leaves acrylates unaffected. Thus we were able to improve our first approach by reducing the process time and the change in volume.

High refractive index acrylates usually feature either sulfur or phenyl groups. As we wanted to increase the refractive index change we implemented in our third approach an acrylic monomer, which offers both functionalities. For compatibility reasons, however, we had to use dimethyl-diphenylsiloxane copolymers for manufacturing the acetoxy cured matrix.



**Scheme 1:** Manufacturing processes of polysiloxane-polyacrylate hybrid materials

## RESULTS AND DISCUSSION

### Selection of Monomers

For our application, only monomers with a higher refractive index than the corresponding polysiloxane matrix came into consideration. Candidates had to exhibit proper compatibility with the host material. With respect to the boiling point it was important that substances were volatile enough to be removed in vacuum, but on the other hand they should not evaporate significantly during the structuring process. Based on these requirements the following compounds were selected:

Acrylic acid isobornyl ester (**AIB**, Sigma-Aldrich):

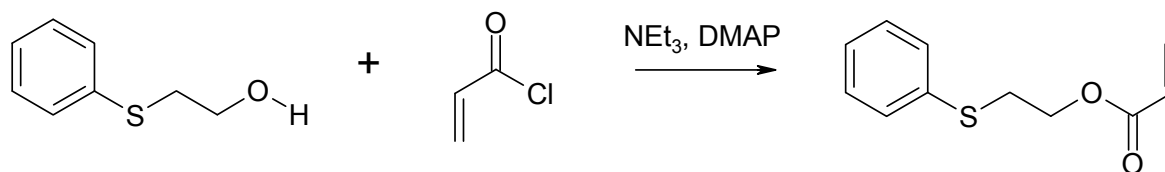
After screening a large variety of suitable acrylic monomers, **AIB** turned out to be the best option for applying it together with conventional PDMS silicone rubbers as excellent compatibility is given due to the hydrophobic residue.

1,4-Butanediol diacrylate (**BDA**, Sigma-Aldrich):

Despite of the worse compatibility of **BDA** with PDMS and lower refractive index compared to **AIB**, this monomer has been selected recently as a crosslinking agent in a mixture with **AIB**, as it helps to adjust the extent of swelling due to its poor compatibility.<sup>[8]</sup>

### 2-Phenylthioethyl acrylate (**PTEA**):

The highest refractive index of an acrylic monomer that combined the above mentioned criteria was featured by **PTEA**. This monomer can be prepared in a one-step synthesis similar to a procedure described by Olson (Scheme 2).<sup>[9]</sup>



**Scheme 2:** Synthesis of PTEA

Therefore, 2-phenylthioethanol was converted with an excess of acryloyl chloride in the presence of 4-(dimethylamino)pyridine (1eq.) and triethyl amine (1eq.) in toluene. The crude product was purified by column chromatography to give **PTEA** with a yield of 27%. Partial polymerization of the product during the evaporation of the solvent could be avoided by adding 1000 ppm of 4-methoxyphenol prior to evaporation of the eluent.

### Preparation of Polysiloxane-Polyacrylate Hybrid Materials:

In our investigations, the compatibility of the photoreactive monomers with the PDMS matrix and the increase of refractive index were a big issue as well as the ambition to avoid the swelling step. For these multiple reasons the PDMS matrix had to be well chosen.

**Table 1:** Components and mode of preparation of polysiloxane-polyacrylate hybrid systems

System number	Polysiloxane matrix	Crosslinking mechanism	Monomer system	Mode of preparation
1	Elastosil RT 601	Hydrosilylation	<b>AIB/BDA</b> Ratio depending on desired polymer content Photoinitiator: 1% Darocur 1173	Swelling of cured PDMS matrix
2	Polydimethyl siloxane, silanol terminated	Acetoxy condensation cure	<b>AIB/BDA 80:20</b> , Photoinitiator: 1% Darocur 1173	Mixing before vulcanization
3	Dimethyl-diphenylsiloxane copolymer, silanol terminated	Acetoxy condensation cure	<b>PTEA/BDA</b> 10:1 Photoinitiator: 0.5% Irgacure 819	Mixing before vulcanization

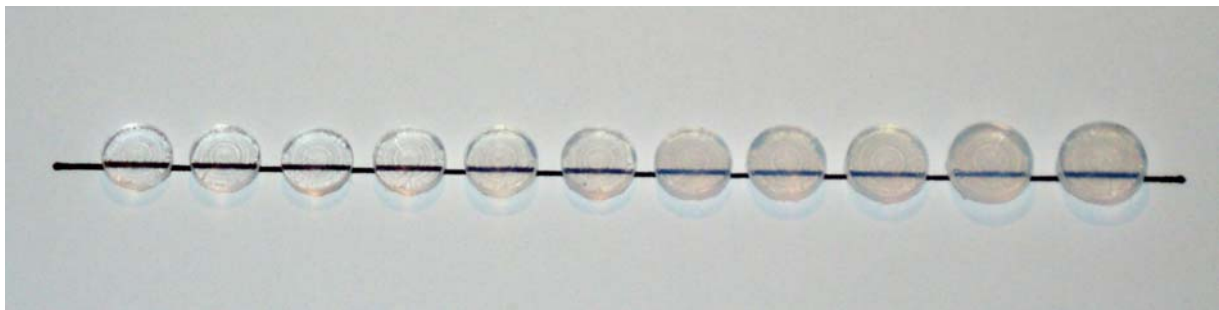
Table 1 gives an overview of the systems that we designed. In case of system 1, components A and B of Elastosil RT 601 were mixed together in a ratio 9:1, cast into molds, degassed at 5 mbar and cured at 75°C. The demolded material had to be swollen in the monomer mixture for at least 20 hours. Depending on the experiment, the swollen matrix was exposed to UV-light or used for structuring waveguides on the 2PP device. The unreacted monomer in the non-illuminated regions could be gently removed in a vacuum oven at 40°C within 20h.

In case of the acetoxy condensation cure systems 2 and 3 the appropriate silanol terminated PDMSs were mixed with the corresponding monomer mixture, the filler material Aerosil, the condensation catalyst dibutyltin dilaurate and the condensation crosslinking agent methyltriacetoxysilane/ethyltriacetoxysilane 80:20. After degassing and curing at room temperature for a period depending on the geometry of the mold, the sample was ready for exposure to UV-light (mercury arc lamp, 15 min, distance from of samples from lamp: 10 cm, samples kept in a nitrogen chamber) or 2PP structuring. The monomer mixture **AIB/BDA** was removed at 40°C in a vacuum oven over night. **PTEA/BDA** was completely evaporated in 5h at 40°C and 0.01 mbar.

### Testing of the Polysiloxane-Polyacrylate Hybrid Materials

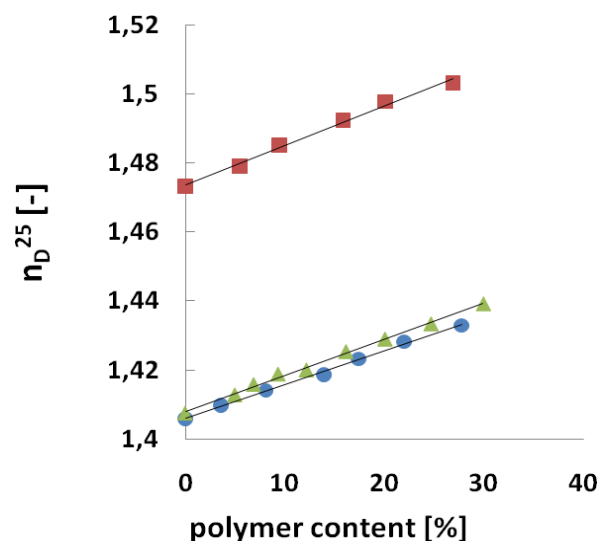
After confirmation of the executability of the three concepts, especially curability of the matrix and compatibility with the polyacrylates, the goal was to compare their performance with respect to refractive index increase and optical attenuation.

An important correlation is the dependence of the refractive index on the polymer content as depicted in Figure 2. For each data point discs that were composed of cured PDMS matrix and monomer mixture were produced either by swelling or by mixing and subsequent selective vulcanizing of the matrix (Figure 1).



**Figure 1:** Elastosil RT 601 with increasing polymer content from the left to the right

A series of pure silicone discs underwent the procedure in order to account for the loss of mass during the manufacturing process and the refractive index at polymer content zero. Accordingly half of the discs of each series were exposed to UV light as mentioned above while the other half was kept in a UV-light free environment. Finally all discs were liberated from the non-polymerized monomers. After each step, the samples were weighed enabling the calculation of polymer contents.



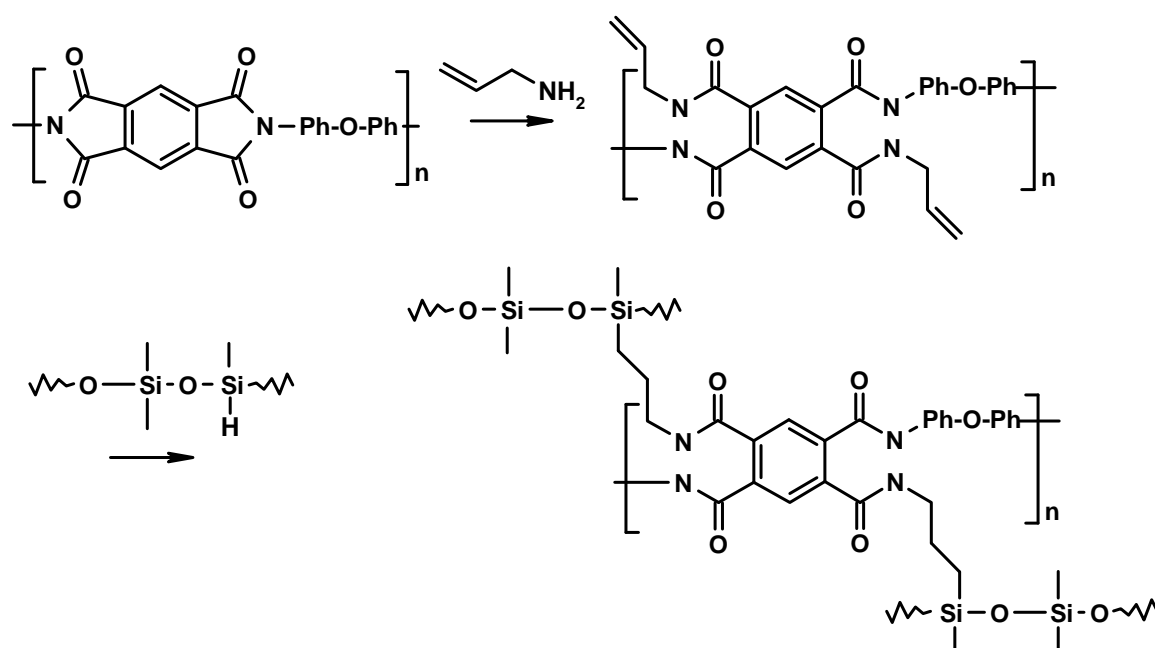
**Figure 2:** Polyacrylate content of polysiloxane-polyacrylate hybrid materials versus refractive index at 25°C (▲ System 1 ● System 2 ■ System 3)

Figure 2 shows that the trendline of system 3 exhibits the steepest slope with a refractive index change of 0.0011 per percent of polymer content. Also in case of the relative increase in refractive index ( $\Delta n/n=1.9\%$ ) calculated for a hybrid material with 25.0%, system 3 curtly prevails. For the acetoxo condensation curing systems 2 and 3 the linear relationship is more accurate than for system 1. This can be explained by the fact that for varying polymer contents different ratios **AIB/BDA** were required to adjust the extent of swelling, whereby **BDA** exhibited poor and **AIB** strong swelling ability, and a concentration gradient is possible. Within systems 2 and 3 it is possible to vary the polymer content with one single ratio of **AIB/BDA** or **PTEA/BDA**. System 3 allowed for measuring the refractive index until a polymer content of 25% due to haziness above this value, whereas for the concepts involving **AIB** this threshold was higher because of its better compatibility with **PDMS** compared to **PTEA**.

The optical attuation was determined for a waveguide of 30 mm, which had been fabricated via  $\mu$ -stereolithography in system 1. Light of 594 nm was coupled into the waveguide with a monomode fiber and at the exit face the light power was measured. This was conducted for several lengths of the waveguide by cutting it back. A best fit line gave a value of 2.3 dB/cm.

### Adhesion of Silicone Matrix

As a consequence of the promising results of the previous chapter it is desirable to write waveguides connecting optical components on a conductor board. One problem that we encountered yet was the poor adhesion of the PDMS film on the polyimide foil of the conductor board. This could be avoided by proper surface modification with coreactive allylamine as shown in Scheme 3.<sup>[10,11]</sup> For the acetoxo curing system, the same procedure using 3-(triethoxysilyl)-1-propane amine is possible.

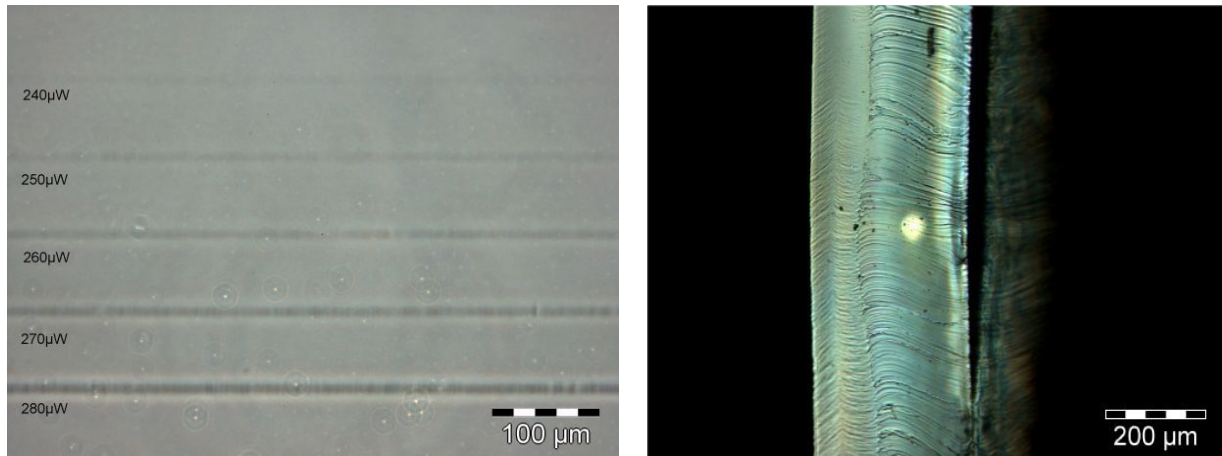


**Scheme 3:** Surface modification of polyimide with allylamine and subsequent hydrosilylation with Si-H groups of Elastosil RT 601 in system 1.

In the first step the cavity of the demonstrator was completely wetted with allylamine and for volatility reasons covered with a glass plate for a maximum period of 5 minutes, in order to open the imide rings. Subsequently, the dispensable allylamine was evaporated at 50°C over night. This step is important, because if there is still allylamine present the curing process fails. Next, the matrix film was applied and cured, whereby it was linked to the substrate via hydrosilylation.

## Waveguides

Finally we wanted to give a proof of concept, that it is possible to write waveguides by 2PP in system 1. Therefore, a PDMS film (480  $\mu\text{m}$  thick) was swollen for 20 h at room temperature with a monomer mixture of **AIB** and **BDA** (2:8) and 0.5 wt% of N-DPD<sup>[12]</sup> as photoinitiator. Subsequently waveguide structures were written in a depth of 375  $\mu\text{m}$  with a setup for 2PP shown elsewhere.<sup>[13]</sup> Removal of the unreacted monomer in the non-illuminated areas resulted in waveguides, which are shown in Figure 3 (left). A continuative structuring experiment at 250  $\mu\text{W}$  and 10mm/min feed rate yielded a bundle of 11 waveguide structures (Figure 3, right)



**Figure 3:** Waveguides written by 2PP at 280, 270, 260, 250 and 240  $\mu\text{W}$  (left image, from the bottom up) and a bundle of waveguide structures fabricated at 250  $\mu\text{W}$  (right image)

## Conclusion

In this paper we presented important progress towards an optical conductor board demonstrator. At this point three concepts were investigated: The concept of swelling Elastosil RT 601 (Karstedt catalyzed hydrosilylation crosslinking) with **AIB** and **BDA** has performed well in preliminary structuring tests and in combination with our innovation regarding the adhesion of PDMS to polyimide foil it should be possible to create a demonstrator by using this technology. Applying the same monomer mixture to an acetoxy condensation curing matrix is more practical than swelling the hardened silicone rubber. Structuring tests will be the next step in this concept. In the third concept with **PTEA**, a significantly higher refractive index was reached than with **AIB** or **BDA**.

## Acknowledgements

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