A Polystyrene Photoresin for Direct Lithography of Microfluidic Chips

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Polystyrene (PS) is the material of choice for many medical, biological, and biomedical applications given its advantageous properties such as high biocompatibility, optical transparency, and the possibility to shape PS using high-throughput manufacturing methods at low production costs. Due to its properties, PS is an interesting material for the fabrication of microfluidic systems. In microfluidics, rapid prototyping is of high importance for testing new chip layouts and designs during the product development with the aim of significantly accelerating the manufacturing. To allow transitioning and thus significantly faster translation from research to scalable manufacturing, it would be ideal if the same material could be used throughout the whole design pipeline. However, rapid prototyping and high-resolution shaping of PS, especially on the micron scale, is still limited. In this work, a novel photocurable polystyrene photoresin, is presented which can be shaped using direct optical lithography. Using this PS photoresin, microfluidic chips with feature sizes down to 50 µm and a high optical transparency can be fabricated. The cured PS photoresin shows comparable surface and material properties to commercial PS. This method will enable researchers in the medical, biological and biomedical fields to produce suitable PS structures with commercial equipment.

1. Introduction

Microfluidic chips are of great importance given their wide range of applications in optofluidics,\textsuperscript{[1,2]} cell culture,\textsuperscript{[3–5]} and tissue engineering.\textsuperscript{[6–8]} Rapid prototyping and direct printing of microfluidic chips have gained great interest in recent years allowing quick realization of a great variety of chip designs in an early stage of the product development cycle.\textsuperscript{[9,10]} Optical lithography-based printing technologies, especially stereolithography (SL), allow the fabrication of microfluidic chips with tens of micron resolution within a few minutes.\textsuperscript{[11,12]} However, optical lithography has so far been mostly limited to acrylic- and epoxy-based resins limiting the usage of these methods. Further, these resins usually have high crosslinking degrees making industrial upscaling problematic. Moreover, the composition of acrylic-based resins is often not known.\textsuperscript{[13]}

Even though polystyrene (PS) is one of the most important materials in cell culture biology, life science, and biochemistry, it has so far not been accessible to direct optical lithography processes. In general, PS is a highly relevant material for microfluidic applications due to its high biocompatibility, optical transparency, high-throughput manufacturing potential, and low production costs.\textsuperscript{[3]} Being a thermoplastic material, PS is usually structured using molding processes like injection molding or hot embossing. While these methods are ideal for mass-market manufacturing, they lack flexibility when it comes to laboratory-scale prototyping as they require a high number of replicas to be economically viable due to the time-consuming and expensive fabrication of a mold. Several methods have been presented to shape PS on the laboratory scale including room temperature solvent- or precursor-based replication methods, which, however, still require a mold.\textsuperscript{[14,15]} PS can also be structured using mold-free methods like direct microstructuring, laser-based structuring or micromilling.\textsuperscript{[16]} The surface and edge roughness of the produced structures through these processes (Rₚ between 30 to 70 nm),\textsuperscript{[17]} strongly depends on the milling tool used or the parameter of voxel-based structuring.\textsuperscript{[18–19]} “Shrinky dink” microfluidics has been introduced using an expanded PS sheet, which is structured using milling and subsequently shrunk to the micrometer-scale using a heat treatment. However,
the control of the final channel dimensions is challenging due to the anisotropic shrinkage.\cite{20} Recently, microfluidic PS chips have been 3D printed for the first time using fused deposition modeling (FDM).\cite{21} However, FDM printing is limited in terms of resolution and creates channels with rough wall surfaces.\cite{22} This additive manufacturing method is suitable for the production of microfluidic structures with minimum features of \(\approx 325 \, \mu\text{m}\) and surface roughness of \(11 \, \mu\text{m}\).\cite{23}

We have recently introduced “Liquid Polystyrene” a PS prepolymer consisting of PS dissolved in the monomer styrene blended with an appropriate photoinitiator. Liquid PS can be cured with UV-light and microstructured by curing the material using a soft replication mold made from, e.g., polydimethylsiloxane (PDMS).\cite{24} Liquid PS would be an ideal candidate for direct optical lithography. Unfortunately, curing Liquid PS is time-consuming requiring up to 45 min for a layer thickness of 5 mm. Furthermore, Liquid PS contains a broad molecular weight distribution of the polymeric component within the monomer, which causes a decrease in the resist resolution as a consequence of the increment in resist sensitivity.\cite{25} Similar to “Liquid Polysterene,” we have recently developed polymethylmethacrylate (PMMA) prepolymer that allows to shape microfluidic chips made out of PMMA using tens of micron resolution.\cite{26}

In this work, we demonstrate a novel photocurable PS photoresin that allows for direct optical lithography of PS. The PS photoresin is fabricated by dissolving PS powder with a defined molecular weight of \(M_W \approx 35,000 \, \text{g mol}^{-1}\) in 1,3-divinylbenzene at a temperature of 50 °C. Divinylbenzene is a common cross-linker used for co-polymerizing styrene and is known for significantly enhancing polymerization speed in radical polymerization processes.\cite{27,28} Due to the strong cross-link, the chemical stability of the resulting PS network is enhanced compared to a thermostable PS polymerized from pure styrene.\cite{29} A strong cross-link also results in a significantly increased contrast between illuminated and non-illuminated areas allowing for the removal of the non-cured PS photoresin using an appropriate solvent. By adding high amounts of PS powder, the viscosity of the PS photoresin can be significantly increased (see Figure S1, Supporting Information), consequently reducing the curing time (see Figure S2, Supporting Information). This effect is caused as a consequence of the auto-acceleration of the rate of the radical polymerization of the PS photoresin (Trommsdorff–Norish effect).\cite{30,31}

Several crosslinkers were investigated in order to develop a suitable PS photoresin with a short curing time. A ratio of 50:50 wt.% PS to 1,3-divinylbenzene was found to have the best compromise between viscosity and curing time for the direct lithography process (see Figure S3, Supporting Information). In addition, a higher solid loading increased the risk of entrapped bubbles within the resin. For effective structuring, the mixture was blended with the highly reactive photoinitiator bis (4-methoxybenzoyl)diethylgermanium (Ivocerin) and, to prevent polymerization in non-illuminated areas, the inhibitor hydroquinone. After the addition of these components, the PS photoresin mixture could be polymerized. The PS photoresin is preferably structured using a collimated light source, e.g., using a commercially available SL system.

The optical lithography process for the generation of microfluidic channels using the PS photoresin is shown in Figure 1A.

**Figure 1.** Optical structuring of polystyrene using PS photoresin. A) Process scheme 1) A commercial microscope glass slide is functionalized and used as a base substrate. 2) A layer of the PS photoresin is dropped and then photocured on the base substrate. 3) PS photoresin is structured using a collimated light source from a commercial SL system, 4) Non-cured areas are developed using a mixture of cyclohexane and 2-propanol. B) Bonding protocol based on radical polymerization to close the microfluidic chip with a commercial PS film. C) The PS photoresin consists of PS powder, 1,3-divinylbenzene, initiator, and inhibitor after preparation. D) Microfluidic channel spiral after development with a channel width of 1 mm (scale bar: 5 mm). E) Successfully bonded microfluidic chip filled with dyed water demonstrating that no leakage occurred (scale bar: 5 mm).
A layer of the PS photoresin was photocured onto a previously functionalized microscope glass slide. The system was closed with a fluorinated glass slide, thus preventing the evaporation of the PS photoresin. The thickness of the structure can be adjusted using spacer elements. A benchtop stereolithography system (Asiga Pico 2) with a wavelength of 385 nm and a pixel resolution of 50 µm was employed to project the desired image onto the substrate and polymerizing the photocurable PS photoresin. Subsequently, the fluorinated glass slide was removed and the structures were developed in a mixture of cyclohexane and 2-propanol (3:2, v/v) for 3 min in an ultrasonic bath. Afterwards, the structures were cleaned with 2-propanol and dried using compressed air. The created open channel structures must be closed in order to create a functional microfluidic chip. Since state-of-the-art bonding protocols for PS (e.g., thermal or solvent-based bonding) are based on the thermoplastic properties of PS, these protocols could not be applied for bonding the highly cross-linked PS photoresin used in this work.\(^\text{12,33}\) We, therefore, developed a novel bonding protocol based on radical polymerization of the photocurable PS photoresin. The process is shown in Figure 1B. In this process, the PS photoresin was spin-coated as an 11 µm thick layer onto a commercially available PS substrate that was subsequently pressed onto the open channel structure (see Figure S4, Supporting Information). The stack was then exposed to light for 5 min at a wavelength of 415 nm creating a strong bond between the structure and the PS film. Figure 1D shows a fully developed microfluidic spiral channel using the described direct lithography method. Figure 1E shows the same functional microfluidic spiral channel sealed using the described novel bonding protocol. Figure 2 shows exemplary microfluidic structures like a multiple-entrance mixer, a Tesla microfluidic mixer, and a microfluidic spiral with a channel width down to 300 µm fabricated by the described method.

To achieve higher resolution, a custom build maskless lithography system based on a digital mirror device (DMD) was used.\(^\text{14}\) Using a pixel resolution of 1.25 µm, we were able to fabricate microstructures of PS with a lateral resolution of 50 µm and a layer height of 50 µm at a wavelength of 415 nm, Figure 3A shows a pair of microposts with a diameter of 100 µm and a height of 50 µm. Figure 3B shows an array of triangular micropillars with a base length of 50 µm and height of 50 µm. Using the maskless lithography system a ring with an inside diameter of 250 µm and a wall thickness of 300 µm was structured (Figure 3C).

Figure 2. Direct structuring of the PS photoresin using a commercial SL system. A) Three-entrance-microchannel mixer with a channel width of 500 µm sealed and filled with dyed water (scale bar: 2 mm). B) Tesla microfluidic-mixer with a 300 µm channel width sealed and filled with dyed water (scale bar: 1.5 mm). C) Circular spiral with a channel width of 300 µm (scale bar: 3 mm).

The height of the structures produced with the PS photoresin is defined using spacers with a determined thickness. Moreover, the resolution of the PS photoresin strongly depends on the layer thickness as this directly affects the exposure dose of the light source. The required exposure dose for achieving a microstructure with a resolution of 100 µm was found to be 369.6 mJ cm\(^{-2}\), 379.1 mJ cm\(^{-2}\), and 412.9 mJ cm\(^{-2}\) for structures fabricated with 20 µm, 50 µm, and 100 µm thick spacers, respectively.

To characterize the minimal possible resolution of the PS photoresin in dependence of the layer thickness, a test mask with different structure resolutions was designed. It was found that the minimal achievable resolution using spacers with a thickness of 20, 50, and 100 µm layer thickness was 18.75, 25, and 37.5 µm, respectively. On the other hand, without the use of spacers, the minimal structure resolution was found to be 18.75 µm (see Figure S5, Supporting Information).

To demonstrate that the structures fabricated with the photocurable PS photoresin can be employed in the same manner as for regular PS devices, material properties like optical transparency, autofluorescence, and water contact angle of the structures were investigated (see Figure 4). As shown in Figure 4A the PS photoresin structures show a high optical transmission, comparable to commercial PS. The cured PS photoresin showed a decrease in transmission between 400 and 450 nm due to some residual photoinitiator. After the development of the PS photoresin, there is a slight decay of transmission in this range. Furthermore, the autofluorescence shown by the cured PS photoresin is comparable to the same low autofluorescence of commercial PS. Due to some residual photoinitiator in the...
cured PS photoresin, a difference of autofluorescence for the DAPI filter was observed (see Figure 4B). The leaching of the residual initiator or inhibitor out of the PS photoresin could hinder its use in biological applications like tissue engineering or cell culture. Although Ivocerin does not present a menace to biological organisms per se,[35] it may interfere with the assay to be performed. On the other hand, hydroquinone is in fact a toxicologically relevant reagent,[36] therefore a leaching protocol was investigated in order to evaluate the leakage of these components.

Rectangular samples of cured PS photoresin (220 mg) were placed in a sealed container with 2 mL ethanol absolute (99.8%) for 12 h and then placed again for another 12 h in a different container with another 2 mL of ethanol absolute. The samples were characterized using high-resolution mass spectroscopy, after the first ethanol wash no peaks corresponding to hydroquinone could be identified, however, some peaks corresponding to germanium isotopes (corresponding to Ivocerin) could be identified (see Figure 4C). Further, the mass spectrum after a second 12 h ethanol wash of the polymerized PS photoresin did not present any peaks corresponding to Ivocerin or hydroquinone (see Figure 4D).

The static contact angle of water on the cured PS photoresin was found to be 97.6 ± 1.4° which is comparable to commercial PS which was measured at 95.2 ± 1.3°. Both values are in good accordance with the value of 91° reported for PS in literature.[37,38]

The surface energy of the cured PS photoresin was characterized by the Owens-Wendt-Rabel & Kaelble model (OWRK)[39] using water, ethylene glycol and diiodomethane as test liquids. The surface energy was found to be 3760 mN m⁻¹ for cured PS photoresin and 39.55 mN m⁻¹ for commercial PS. This data is also in accordance with reported literature of 35 mN m⁻¹ for PS.[37]

The surface roughness of the top surface of cured PS photoresin was characterized using white light interferometry with a R_a ≈ 19 nm outside the channel and a R_a ≈ 20 nm inside the channel that is well within the smoothness values reported for microfluidic devices.[40] The surface roughness increased as a consequence of the developing protocol and was found to be R_a ≈ 21 nm.

Tensile tests were performed with a starting speed of 4 mm min⁻¹. The Young’s modulus of the PS photoresin was compared to the Young’s modulus of the commercial PS. The Young’s modulus of the PS photoresin was found to be 761 MPa, which was lower in comparison to the Young’s modulus of the commercial available PS which was measured at 23.3 MPa. The PS photoresin is a more brittle material than the commercial PS, this might be a consequence of the high amount of initiator involved.

Solvent resistance was characterized using fully cured PS photoresin and commercial PS samples. The weight of the samples was assessed after these were fully immersed in different solvents after 1 and 24 h. Table 1 shows the mass swelling results for both PS photoresin and commercial PS.
To demonstrate that this process is capable of rapid prototyping PS, the process times are outlined in Table 2, showing that a microfluidic channel can be structured, developed, and bonded in less than 20 min.

In this work, we have developed a new direct lithography-based process for fabricating fully functional microfluidic chips in PS. For this, a novel photocurable PS photoresin was developed which can be structured using a commercial stereolithography system. Microstructures with 20 μm resolution could be produced using a custom-made DMD-based microlithography system. This process opens the door to rapid manufacturing and (micro-) structuring of PS-based microfluidics on direct optical lithography and thus allows creating high-resolution microstructures in one of the most important technical polymers in cell biological and biomedical engineering via state-of-the-art prototyping equipment.

Future work will concentrate on the development of post-processing protocols for removing residual initiator and demethylation PS, the process times are outlined in Table 2, showing that a microfluidic channel can be structured, developed, and bonded in less than 20 min.

Table 2. Time required for the fabrication of a microfluidic chip using PS photoresin.

| Processing step | Time [min] |
|-----------------|------------|
| Exposure<sup>a</sup> | 2.27 |
| Micro lithography | 1.83 |
| Development | 3 |
| Ultrasonic bath (25 °C) | |
| Bonding | 5 |
| Immersion in 2-propanol | 0.5 |
| Drying (compressed air) | 0.17 |
| Spin coating | 0.5 |
| Pressing | 5 |
| Light exposure | |

<sup>a</sup>Exposure time depends on the intensity, the wavelength of the used light source, and the absorption of the used photoinitiator.

2. Experimental Section

Materials: PS powder with molecular weight of \( M_W = 35.000 \text{ g mol}^{-1} \), divinylbenzene (mixture of the meta- and para-isomers), styrene, hydroquinone, methanol, 3- (dimethylchlorosilyl) propyl methacrylate (MACS), 1H,1H,2H,2H-perfluorooctylmethyliclorsilane, and cyclohexane were purchased from Sigma–Aldrich (Germany). Bis(4- methoxybenzoyl)–diethylgermanium (Iovercin) was purchased from Synthon chemicals (Germany). 2-Propanol (99.55%), acetone, tetrahydrofuran, dichloromethane, and diethylformamide were purchased from Carl Roth (Germany). 1,3-Divinylbenzene was purchased from BLD Pharmatech GmbH (Germany), and hydrochloric acid was purchased from VWR (Germany). Ethanol absolute and toluene were purchased from Merck (Germany).

Direct Lithography: The PS photoresin was structured using a benchtop stereolithography system of type Asiga Pico 2 (purchased from 3DXs, Germany). Here, the PS photoresin is exposed to a light with a wavelength of 385 nm for 136 s (intensity: 8.8 mW cm\(^{-2}\)). Microlithography of the PS photoresin is done using a custom build system based on a DMD (digital mirror device) that was previously reported.[34] Exposure dose in dependence of the layer thickness was added to the main part of the manuscript during the revision process.

Bonding: The channels were sealed using a bonding protocol based on radical polymerization. For this, 1 mL of the PS photoresin was spin-coated (6000 rpm, 10 s) onto a commercial sheet of PS of 25 × 25 mm (purchased from Evergreen scale models, USA) with a thickness of 0.13 mm. The commercial PS sheet was clamped onto the structured PS (purchased from Evergreen scale models, USA) with a thickness of 0.7 mm. The PS photoresin was structured using a DMD-based microlithography system. The channels were then cleaned with 2-propanol and deionized water, and then functionalized in a mixture of 100 × 10\(^{-3}\) MACS (polymerization substrate) and 1H,1H,2H,2H-perfluorooctylmethyliclorsilane (cover slide) in toluene for 30 min and once again cleaned with 2-propanol and deionized water.[40]

Surface Functionalization: Glass slides were cleaned using a mixture (1:1 v/v) of methanol and concentrated hydrochloric acid (37%) for 30 min, then they were cleaned with 2-propanol and deionized water, and then functionalized in a mixture of 100 × 10\(^{-3}\) MACS (polymerization substrate) and 1H,1H,2H,2H-perfluorooctylmethyliclorsilane (cover slide) in toluene for 30 min and once again cleaned with 2-propanol and deionized water.[40]

Material Characterization: UV–vis transmission spectra were measured using a UV–vis spectrophotometer (Evolution 201, Thermo Scientific, Germany). The autofluorescence characterization was performed using an inverted microscope (DMi8, Leica, Germany) with a 2.5× objective (NA = 0.07, Leica, Germany) arranged with the following filter sets: Cy5 (Em: 590–650 nm/ Ex: 662–738 nm), Cy3 (Em: 570–640 nm/ Ex: 532–558 nm), FITC (Em: 512–542 nm/ Ex: 460–500 nm) and DAPI (Em: 435–485 nm/ Ex: 327–383 nm). The spectra were recorded using a 130 μm cured layer of the PS photoresin (50:50 wt.% commercial PS, 50:50 wt.% commercial PS).
powder and 1,3-divinylbenzene). Contact angle and surface energy measurements were done using the contact angle measuring device OCA 15Pro (Data physics, Germany) using 5 µl of the test liquids at room temperature. Surface energy was calculated using the OWRK method\cite{37} using water, ethylene glycol, and diiodomethane as test liquids. The viscosity was measured using a rheometer (Anton Paar MCR 72/92, Austria). Surface roughness data were measured using a light interferometer (NewView 9000 Zygo, USA). Mass spectra were recorded using a mass spectrometer (Exactra, Thermo Scientific, Germany) with the ionization in the positive APCI mode. Tensile tests were performed using a universal testing machine (Inspekt 1500 kN, Hegewald & Peschke, Germany).

Statistical Analysis: The data were presented as mean ± SE. The mass spectra of the polymerized PS photosens were plotted relative to the intensity of the first ethanol wash. The surface roughness data were processed using the open-source software Gwyddion.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

lithography, microfluidics, photocuring, polystyrene, rapid prototyping

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