

# Fabrication and Application in Microfluidics of Novel Transparent Preceramic Polymer Derived Glass Microchannels and Substrates

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## ABSTRACT

In this report, we have described the fabrication of preceramic polymer derived microchannels and substrates using softlithographic process, such as micro molding and imprinting lithography. Microchannels were fabricated by photocuring followed by thermal crosslinking process using commercially available poly(vinyl)silazane and allylhydridopolycarbosilane as polymer precursors. The resultant preceramic polymer channels were found to poses unique glass like characteristics, such as high transparency, high thermal stability, chemical inertness along with cost effectiveness and ease of fabrication. Microfluidic performance of inorganic polymer derived micro-reactors was demonstrated by the organic chemical synthesis in ethanol and THF solvent, as well as by the photochemical reaction using trimethylolpropanetriacrylate. The novel materials are promising as an alternative choice for the cost consuming glass microfluidics and also for the development of integrated microfluidic systems.

**Keywords:** poly(vinyl)silazane, polycarbosilane, preceramic microchannel, photo-polymerization, protein patterning.

## INTRODUCTION

Ever since their first introduction almost a decade ago microfluidic devices have undergone rapid development as they provide miniaturized systems with the flexibility in fabrication, improved speed of analysis, high sample throughput, cost effectiveness, and portability [1]. Micro-reactors are potentially powerful tools in the field of chemistry and biotechnology [2]. The excellent performance of micro reaction systems is achieved by rapid heat and mass transfer, and by larger surface / interface area. These devices have found wide applications as sensors, analytical platforms for biological analysis, reactors for chemical synthesis, and so on. Efforts towards the application of microfluidics in complex micro total analysis systems ( $\mu$ -TAS) are increasing at a substantial rate, by combining a variety of functions within a micro chip [3]. Usually, glass-wet etching [4], silicon etching [5] or molding of polymers using the LIGA technique [6] were employed for fabrication of microfluidic devices. Generally, glass-based microfluidics was widely used due to its chemical inertness and thermal stability. Even though plastics including PDMS have showed their convenience in

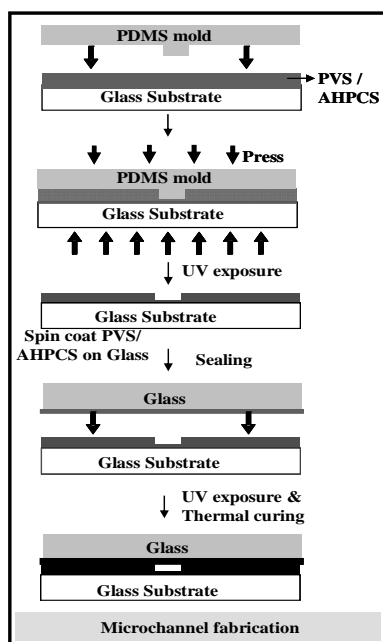
fabricating microfluidic devices, they showed swelling effect upon interaction with organic solvents. Therefore, our goal was to select a material with the reliable properties of the glass material and the economic processing of the plastics. In this point of view, it is an interesting fact that most preceramic polymers convert into the unique inorganic-organic hybrid phase and also it can be fabricated using near-net shape processing techniques. In this report we have described the fabrication of preceramic polymer-derived transparent, solvent resistant, thermally stable and bio-compatible microchannels and substrates. Both thermal and photo cured polymer channels were found to poses unique glass-like characteristics, such as transparency and chemical inertness. Finally, we demonstrate the organic chemical synthesis and photochemical reactions using the fabricated micro-reactors. These devices show a typical feature of microchannel systems for better synthetic yields and shorter reaction times, which was not possible in the batch wise reaction system with larger reaction apparatus. The novel materials are promising to replace the cost-consuming glass microfluidics for the development of integrated microfluidic systems.

## EXPERIMENTAL

Microchannel fabrication was done by using two soft lithographic techniques, namely micro molding and UV-imprinting. 20 wt% allylhydridopolycarbosilane (AHPCS, Starfiresystems, USA) in THF or poly(vinyl)silazane (PVS, VL 20, KION Corp., USA) were used as precursor after mixing with 0.5 wt% dicumyl peroxide (Aldrich, USA), as thermal initiator and 2 wt% of Irgacure 369 (Ciba Specialty, Japan), as photo initiator prior to application. The PDMS molds and stamps were fabricated by casting PDMS (Sylgard182, Dow Corning, Midland, USA) against a complimentary relief structure that was prepared by a photolithographic method. The liquid precursor was poured drop wise on to a pre-cleaned glass substrate with 80–90  $\mu\text{m}$  thickness under nitrogen atmosphere and allowed to stand for a few minutes. Subsequently, a mold release agent coated PDMS mold with microchannel pattern was placed gently above the liquid precursor to avoid trapping of air bubbles. UV radiation at 20  $\text{mW cm}^{-2}$  (ELC-4100 UV light system) was exposed for 20 min to solidify the patterned polymer. PDMS mold was peeled off and for complete curing, the open channel was further heat treated at 140°C

for 3 h for AHPCS / 150°C for 5 h for PVS polymer (with ramping rate of 5 °C.min<sup>-1</sup>) under nitrogen atmosphere. To bond the open channel, liquid precursor (dissolved in THF with 0.5 of thermal initiator, 2 wt% of photo initiator) with 3-4 μm thickness was spin coated on to a clean glass substrate and subsequently prebaked at 60°C for 2 h to remove the solvent. After complete removal of solvent, the patterned microchannel was placed on top of the polymeric precursor coated glass slide was UV cured under minimal pressure and post-heated similar to the previous step. As, glass-AHPCS/PVS-glass based micro-reactor with 100~500 μm wide, 50~100 μm depth and 1~2 cm long were fabricated with Y-type and double T-type microchannel and ready for micro-reaction.

Scheme 1, describes the complete fabrication procedure for both PVS and AHPCS polymeric microchannels. The solvent resistance and bio-compatibility of the cured polymers were tested according to a procedure reported elsewhere [7]. Solvent compatibility of the cured polymers against commonly used solvents such as ethanol, methanol, acetone, THF, n-hexane, isopropyl alcohol and water were investigated at different temperatures. For protein patterning, the PDMS mold with protein as ink was stamped over a cured preceramic polymer substrate, subsequently the stamp was gently peeled off and the substrate was further washed with deionized water to remove unbound protein. Later on the micro patterned structures were analyzed under a fluorescence microscope.



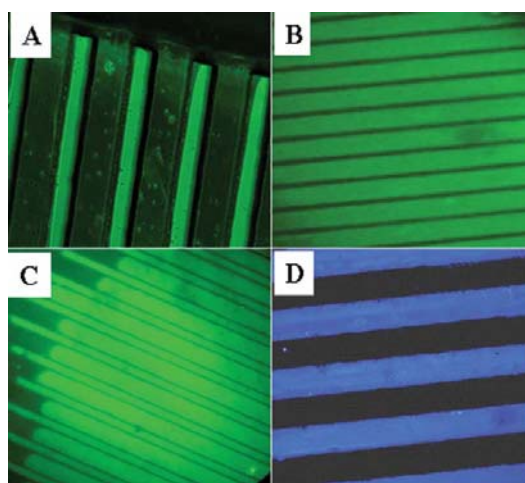
**Scheme 1.** Schematic representation for microchannel fabrication.

Photo-polymerization of trimethylolpropanetriacrylate (TPT) was carried out with an AHPCS-derived micro-reactor with a microchannel of 200 μm width, 50 μm depth, and 2 cm long. The TPT monomer was mixed with 0.3 wt%

of Irgacure 369 (Ciba Specialty, Japan), as photo initiator after diluting with 90 wt% ethanol prior to application. This monomer was pressure-driven into the microchannel at a flow rate 1-10 μl.min<sup>-1</sup>. And, we executed calibration curve of vinyl group with TPT concentration using UV-Visible spectroscopy.

## RESULT AND DISCUSSION

To have a complete understanding on the solidification chemistry of PVS and AHPCS and to obtain organic solvent resistant microfluidic channels, the solidification chemistry of PVS has been extensively studied either in presence or absence of a thermal initiator [11, 12]. In the present study curing chemistry for both polymers may be envisioned to proceed through inter and intra molecular hydrosilylation of vinyl groups attached to silicon by thermal treatment and photo radiation, in the case of PVS in addition amine group also take part in the curing process [11].

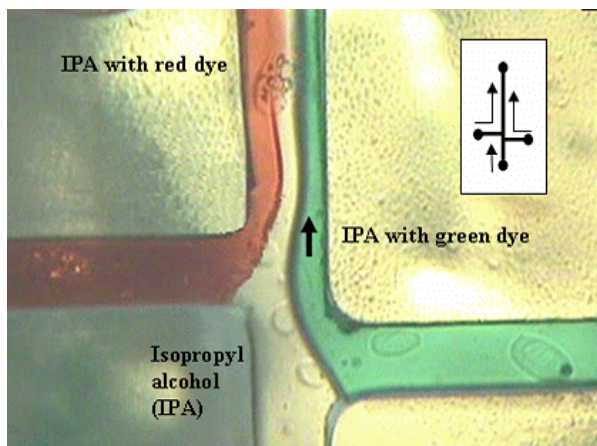


**Figure 1.** Fluorescence images of (A) GFP filled microchannels, (B) FITC-BSA line patterns (20 μm lines separated by 5 μm spacing) on cured polymer, (C) ANS line patterns on cured polymer (15 and 32 μm lines separated by 5 μm spacing) and (D) line patterns (100 μm lines separated by 100 μm spacing) of adduct (ANS and BSA).

Chemical resistance of the cured PVS and AHPCS samples was examined using commonly used solvents. Thermally-treated PVS and AHPCS showed excellent solvent compatibility in all the solvents tested with no deformation. It should be pointed out that plastic material like PDMS showed swelling effect upon interaction with organic solvents such as THF, acetone, and n-hexane. From a technical standpoint, plastic materials are not suited as building materials for micro-reactors involved in organic reactions. ATR-IR spectroscopy is a valuable tool for structural characterization of surface groups present in the cured inorganic polymer. From the ATR-IR spectrum of

PVS/AHPCS, it is evident that the absorption bands at  $2829\text{ cm}^{-1}$  and  $1593\text{ cm}^{-1}$  attributed to  $\text{C-H}_{\text{vinyl}}$  and  $\text{C=C}$  respectively, disappear almost after cross-linking at  $150\text{ }^{\circ}\text{C}$ , 5 h for PVS and at  $140\text{ }^{\circ}\text{C}$ , 3 h in case of AHPCS. In contrast, the intensity of Si-H absorbance band at  $2129\text{ cm}^{-1}$ , and  $1265\text{ cm}^{-1}$ , C-H absorbance band at  $1350\text{ cm}^{-1}$  were continuously becoming weak. Due to excess Si-H groups present in the polymer, the intensity change of the Si-H absorbance band at  $2129\text{ cm}^{-1}$  is not quantitative.

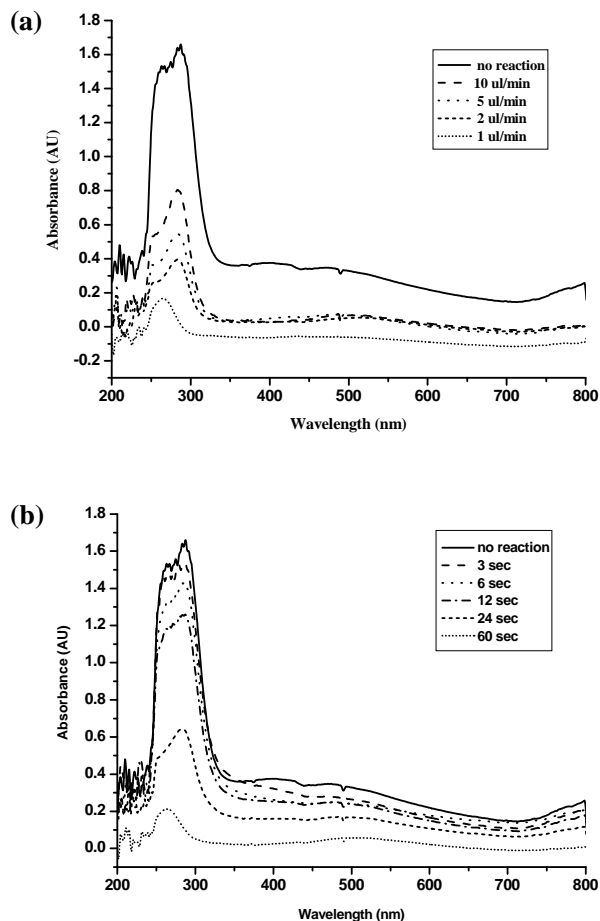
The wettability of the cured PVS polymer was analyzed by contact angle measurement, and the contact angle with water was noted to be around  $101^{\circ}$ , suggesting the highly hydrophobic nature of the surface. This unique nature of the transparent cured material in conjunction with solvent compatibility of the cured polymer was further exploited for direct patterning of protein and a fluorescent probe, as the nature of material employed plays a prime role to fabricate channels or pattern or print proteins. There are several methods to pattern proteins onto the solid surfaces, which can be divided into two categories; indirect and direct method [10]. We performed protein patterning by direct method. In here proteins are locally delivered in solution form as spots using inkjet printing by relatively simpler method of micro contact printing ( $\mu\text{-CP}$ ) as shown in Figure 1. As proteins are labile to denaturizing by heating or under the influence of solvents or through hydrophobic interactions, protein stability is an important issue to be governed during  $\mu\text{-CP}$  [7]. However, AHPCS polymer did not show any biocompatibility as shown by PVS polymer.



**Figure 2.** Laminar flow observed in the microchannel.

The flow dynamics of the AHPCS - glass microchannel was examined by pumping isopropyl alcohol and two different dyes (red and green) in the same solvent at a flow rate of  $10\text{ }\mu\text{l}\cdot\text{min}^{-1}$ . The flow pattern examined showed laminar flow in the microchannel with a width and depth of  $200\text{ }\mu\text{m}$  and  $50\text{ }\mu\text{m}$  respectively, as shown in Figure 2. Therefore, it is natural to expect transparent AHPCS glass derived microchannels and structures to poses tremendous potential in micro total analysis systems and as

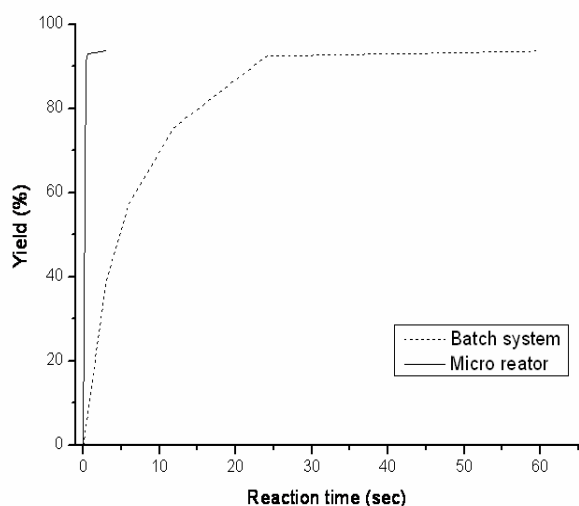
photochemical reactors, where materials with high optical transparency, thermal stability and chemical inertness are in demand.



**Figure 3.** UV absorbance for photo-polymerization of TPT in (a) micro-reactor and (b) batch system.

In order to demonstrate the intrinsic advantages with reaction miniaturization using inorganic polymer based micro-reactor over the conventional batch process, Photo-polymerization of trimethylolpropanetriacrylate (TPT) was carried out with an AHPCS-derived micro-reactor. In here intensity of vinyl group was calculated from the absorbance peak (at about  $280\text{ nm}$ ) and calibrated with a standard compound prepared on large scale. The influence of flow rate from  $1\text{-}10\text{ }\mu\text{l}\cdot\text{min}^{-1}$  on the % conversion of the photo-polymerization reaction in the micro-reactor was investigated. Figure 3a show the UV/Visible spectroscopy of the product after each reaction at different flow rate. Intensity of UV absorbance at  $280\text{ nm}$  for the vinyl group was continuously decreasing with decrease in flow rate; this confirms the direct dependence of flow rate upon photo-polymerization of TPT. We also performed a parallel reaction in a batch system and obtained UV/Visible

spectroscopy result (Figure 3b). Product conversions were based on the amount of vinyl group remaining in the sample. Microchannel reactors have interested as a novel reaction apparatus in synthetic chemistry. Micro-reactors have specific reactive systems that are different from those of a batch system. The reaction completion was faster in the micro-reactor than when performed in a bulk reaction. In general, bulk reactions were performed at much higher concentrations than micro reactions. In order to make better comparison between reaction time, we compared the conversion yield of TPT in the batch process, with the same concentration as used in the micro reaction studies. Figure 4 shows how the yield % increases with time; the graph shows that after 3 sec only about 35% conversion to vinyl group was observed in the bulk reaction. Where as, in the micro-reactor 95% conversion was obtained for the same reaction time. This result clearly shows that the rate of reactions is significantly enhanced when the reactions were conducted in a micro-reactor. The % Conversion was determined from the calibration curve for photo-polymerization of TPT.



**Figure 4.** Conversion yield in micro reactor and batch system at same reaction time.

## CONCLUSION

Based on this study, we strongly believe that glass derived transparent inorganic polymer microchannels and structures hold tremendous potential in the field of micro total analysis systems as well as in micro reaction technology, where materials with high optical transparency, thermal stability and chemical inertness are in demand. In particular, the inorganic polymer based microchannel demonstrated an efficient photo-polymerization reaction by regulating the flow rate of reactant in a microchannel, when compared to conventional batch process. Our results provide a basis for further research on inorganic polymer derived microchannels. We speculate that PVS/AHPCS

based micro structures will outperform conventional microfluidic devices made up of glass and polymer materials with regard to optical transparency, thermal stability and chemical inertness.

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