

# NOVEL INORGANIC POLYMER DERIVED MICROREACTORS FOR THE APPLICATION OF ORGANIC MICROCHEMICAL SYNTHESIS

Tae-Ho Yoon<sup>1</sup>, Lan-Young Hong<sup>1</sup>, Sang-Hee Park<sup>1</sup>, Kyung-Ik Min<sup>1</sup>,  
Sung-Joon Park<sup>1</sup> and Dong-Pyo Kim<sup>1,2</sup>

<sup>1</sup> Dept of Finechem Eng, Chungnam Nat'l Univ., Daejeon, 305-764, SOUTH KOREA

<sup>2</sup> Center for Ultramicrochemical Process Systems (CUPS), KAIST, 305-701, SOUTH KOREA

## ABSTRACT

Microreactors fabricated with optically transparent inorganic polymers from two types of ceramic precursors using a UV-micro-imprinting process demonstrated reliable solvent resistance, biocompatible and capability for performing photo catalytic and organic synthetic reactions, which were compared with batch systems and glass based microreactors. It is for the first time that the polymer-based microreactors fabricated *via* a cheap and simple technique demonstrated the reliable microchemical performance in organic solvents with no swelling problem even for a long period of exposure, which is very promising for developing an integrated microfluidics by taking advantage of available microstructuring techniques of the polymers.

**KEYWORDS:** Inorganic polymer, Softlithography, Microreactor, Microchemistry

## INTRODUCTION

A wide variety of materials have been used to fabricate microfluidic devices[1]. But these materials have some disadvantages in the view of expensive fabrication or the durability[2]. Therefore, there has been an increasing need to develop novel material based microchannels with reliable durability by facile fabrication process. We report the development of microreactors using two types of commercially available inorganic polymers, based on a UV micro-imprinting lithography. Moreover the developed inorganic polymer derived microreactors were evaluated by performing three model organic chemical reactions; synthesis of 3,5-Dimethylpyrazole, exothermic Diels-Alder cyclo-addition and Knoevenagel reaction, which are carried out in commonly used organic solvents including THF and DMF[3]. It is believed that, to our knowledge, this is the first attempt to demonstrate these organic reactions within polymer derived microreactors.

## MATERIAL AND METHODS

The microreactor was fabricated by UV-imprinting techniques with PDMS (polydimethylsiloxane, Sylgard 184, Dow Corning, USA) replica molds which were prepared using the conventional soft lithography method with silicon wafer with SU-8 photoresist (Microchem, USA). To fabricate the microreactor, allylhydrido-polycarbosilane (AHPCS, SMP-10®, Starfire systems, USA) and polyvinylsilazane (PVSZ, KION VL-20®, Clariant, USA) with low viscosity were used directly or

with dilution using tetrahydrofuran (THF, Sigma-Aldrich, USA), depending on the coating thickness. In addition, 2 wt% of dicumylperoxide (Sigma-Aldrich, USA) and Irgacure 500 (Ciba Specialty, Japan) as a thermal and a photo initiator, respectively, were mixed into the inorganic polymers. The Microchannels were created by placing the stamp with relief structures (typically 50  $\mu\text{m}$  high and 380~500  $\mu\text{m}$  wide) on the viscous inorganic polymer layer which was formed by dropping the liquid inorganic polymer on a pre-cleaned glass slide under nitrogen atmosphere. Subjected to a UV exposure (ELC-4100 UV light system) for 20 min the liquid inorganic polymer was cured and solidified. After peeling off the PDMS stamp, the patterned microchannel was thermally post-cured for 3 h at either 160 $^{\circ}\text{C}$  for AHPCS, or 150 $^{\circ}\text{C}$  for PVSZ at a heating and cooling rate of 2.5  $^{\circ}\text{C}/\text{min}$  under the nitrogen atmosphere. To close the microchannel using the same material, a thin polymer film (3~4  $\mu\text{m}$ ) was spin-coated on a top glass slide which was then gently placed on the patterned structure.

## RESULTS AND DISCUSSION

The inorganic polymer derived microreactors showed high optical transparency where the channel layout can be clearly seen (Fig. 1(a)). A cross section of the sealed microchannel and 3D-image of the microchannel are listed in Fig. 1(b) and 1(c). PVSZ cured at 150 $^{\circ}\text{C}$  for 3 h exhibited reliable solvent resistance against almost all the solvents used except a less resistance to THF causing slight changes in sample dimensions by swelling, subject to 24 hours soaking[4]. In case of AHPCS samples cured at 160 $^{\circ}\text{C}$  for 3h displayed excellent stability in all solvents showing insignificant defects. These microreactors demonstrated capability for performing three model organic synthetic reactions, which were compared with batch systems and glass based microreactors. The synthesis of 3,5-dimethylpirazole in THF solvent was run by an AHPCS derived microreactor with Y shaped channel (50  $\mu\text{m}$  deep, 500  $\mu\text{m}$  wide and 2 cm long). Both microre

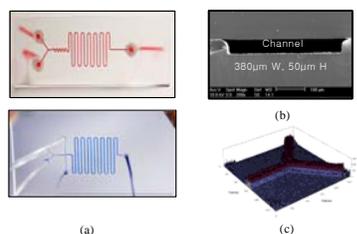


Figure 1. (a) Image of microreactors devices with fabricated with AHPCS (upper) and PVSZ (lower), (b) SEM image of the cross-section and (c) topographical image of the Y-junction using profiler.

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Table 1. Summarized performance of Knoevenagel condensation reaction as a function of flow rate, solvent and reaction temperature.

Flow rate		5 $\mu\text{L}/\text{min}$			10 $\mu\text{L}/\text{min}$			20 $\mu\text{L}/\text{min}$			40 $\mu\text{L}/\text{min}$		
Retention time		30 sec.			15 sec.			8 sec.			4 sec.		
Solvents	Temp	R.T.	40	60	R.T.	40	60	R.T.	40	60	R.T.	40	60
	Mat.												
Ethanol	PVSZ	95.5	98.1	99.5	93.1	96.4	98.2	87.3	95.1	95.0	85.7	94.1	93.8
Methanol		96.8	95.6	-	95.3	94.5	-	91.4	91.4	-	90.1	90.1	-
DMF		70.5	77.5	78.5	63.7	70.8	72.5	56.0	63.5	65.4	51.4	55.8	60.2
ACN		65.0	66.8	70.4	61.7	62.3	65.3	54.2	58.7	61.2	48.5	53.3	56.5
THF	AHPCS	89.1			86.3			85.3			80.1		

actors showd that the product yield remarkably increased with the extended residence time with no leaking and swelling problems with 63.6% of conversion yield at 65.7 sec of residence time. The exothermic Diels-Alder cycloaddition in THF solvent was also performed using AHPCS microreactor with same Y shaped channel with 100% of conversion yield at 100sec of residence time. Finally, the sophisticated inorganic polymer microreactors with 16 cm long channel were tested with Knoevenagel condensation reaction under various solvents and temperatures[5]. The summary in Table 1 exhibited that the reliable chemical reactions were successfully demonstrated at temperature range room temperature to 60°C as well as in typical organic mediums such as dimethylformamide (DMF), tetrahydrofuran (THF) and acetonitrile (ACN) by showing reasonable synthetic yields, depending on the solvent polarity.

## CONCLUSIONS

The softlithography technique, which has advantages in terms of low-cost and mass production, has been employed for the fabrication of inorganic polymer-based microreactors in a cheap and simple manner. Such produced microreactors technique demonstrated reliable microchemical characteristics with high optical transparency, strong organic solvent resistance and stabilities for running organic synthesis reactions. It was demonstrated that the microchemistry performance of the inorganic polymer based microreactors was well in accordance with that of glass made microreactors, and both were significantly advantageous over batch reaction systems. The Knoevenagel condensation as well as synthesis of 3,5-dimethylpirazole and xothermic Diels-Alder cycloaddition have been successfully carried out under different reaction conditions. These novel inorganic polymer derived microreactors proved to be promising for organic microchemistry applications

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