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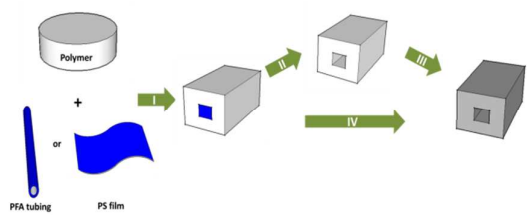
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Whole ceramic-like microreactors fabricated from inorganic polymers could outperform any organic polymer derived reactors under challenging conditions.

ARTICLE

Whole ceramic-like microreactors from inorganic polymers for high temperature or/and high pressure chemical syntheses

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Two types of whole ceramic-like microreactors were fabricated from inorganic polymers, polysilsesquioxane (POSS) and polyvinylsilazane (PVSZ), that were embedded with either perfluoroalkoxy (PFA) tube or polystyrene (PS) film templates, and subsequently removed the templates by physical removal (PFA tube) or thermal decomposition (PS). POSS derived ceramic-like microreactor with a 10 cm long serpentine channel was obtained by additional “selective blocking of microchannel” step and subsequent annealing at 300 °C for 1 hr, while PVSZ derived ceramic-like microreactor with a 14 cm long channel was yielded by co-firing process of the PVSZ/PS composite at 500 °C for 2 hrs that led to complete decomposition of the film template leaving a microchannel behind. The obtained whole ceramic-like microfluidic devices revealed excellent chemical and thermal stability in various solvents, and they were affordable to demonstrate unique chemical performance at high temperature or/and high pressure conditions such as Michaelis-Arbusov rearrangement at 150-170 °C, Wolff-Kishner reduction at 200 °C, synthesis of super-paramagnetic Fe₃O₄ nanoparticles at 320 °C and isomerisation of allyloxybenzene to 2-allylphenol (250 °C and 400 psi). These economic ceramic-like microreactors fabricated by facile non-lithographic method displayed excellent utility under challenging conditions that is superior to any plastic microreactors and comparable to glass and metal microreactors with high cost.

Introduction

Microfluidic devices, including lab on a chip systems, have attracted a great deal of interest in the various areas of chemistry, due to their unique characteristics such as miniaturized reaction volume, extremely large surface to volume ratio, efficient mass and heat transfer capability.¹⁻³ With the advent of this technology, it has also been considerably challenging to develop new structural materials and convenient fabrication processes for these microfluidic tools. Until date, metal,⁴ silicon,⁵ and ceramic⁶ are the most commonly employed materials for the fabrication of microfluidic devices. Despite their high mechanical stability and robust performance, fabrication of microfluidic devices using these materials requires sophisticated facilities with expensive equipments to fabricate channel through wet/dry etching or micromachining and to seal the devices via fusion, adhesive or anodic bonding.⁵ In the meantime, microfluidic devices made of polydimethylsiloxane (PDMS) have also been widely used due to their low cost and easy fabrication process based on soft lithographic technique.⁷ Recently, alternative materials such as polymethyl methacrylate (PMMA),⁸ polycarbonate,⁹ fluoropolymer,^{10, 11} thiol-ene resin,¹² polystyrene elastomer¹³ and polyimide¹⁴ have also been used to fabricate microfluidic devices. Despite their successful applications in certain area

such as biology, most of these microfluidic devices suffer from mechanical, chemical and thermal stability that restricts their applications for chemical syntheses.¹⁵ Recently, our group has demonstrated alternative technologies to partially overcome swelling problem in PDMS microfluidic devices by employing protective coating on the inner walls of the channels with inorganic polymers such as sol-gel hybrid,¹⁶ polyvinylsilazane^{17, 18} and polycarbosilane.¹⁹ However, at present, there is an increasing demand to develop durable and economic microfluidic devices, which can retain and exhibit high mechanical and chemical stability even under extremely harsh conditions. Unlike most of the organic polymers that undergo ready decomposition accompanied by high weight loss at elevated temperatures, silicon-containing inorganic polymers are thermally resistant and gradually transform into opaque Si-based ceramic phase, often with severe volume shrinkage. In particular, polyvinylsilazane and polysilsesquioxane have been used for precursors for SiCN and silica ceramics.²⁰ Furthermore, it would be anticipated that a transparent transient phase between polymer and ceramic phase with negligible or affordable shrinkage can be achieved at certain conditions, which would have significantly enhanced chemical and thermal stability like glass devices in conjunction with convenient and cost effective fabrication process like organic polymers. And

the inorganic polymer derived reactors may outperform any reactors fabricated from organic polymers.

Herein, we report a simple template based method for fabrication of novel, robust and cost effective ceramic-like microreactors embedded in preceramic polymers such as polysilsesquioxane (POSS) or polyvinylsilazane (PVSZ), that are capable of operating at high temperature or/and high pressure conditions for unaccommodating inorganic and organic chemical syntheses. The presented simple non-lithographic fabrication process does not require troublesome sealing step, which is a highly complex task to be performed on consolidated materials by conventional process. The two types of whole ceramic-like matrix microreactors were fabricated by taking advantage of intrinsic processability of viscous polymers without any use of sophisticated facility; the microreactors exhibited excellent chemical and thermal durability as comparable to a glass microreactor, and with much better performance as any plastic microreactors.

Experimental

Fabrication of polysilsesquioxane (POSS) microreactor by employing PFA tubing template

POSS precursor solution was prepared by mixing methacrylate functionalized polysilsesquioxane (MA0735, Hybrid Plastics) with 5 wt% methacrylate functionalized silica filler solution and 1 wt% 2,2-dimethoxy-2-phenyl-acetophenone (DMPA, Aldrich) photo initiator in methyl ethyl ketone solvent and stirring for 5 hrs at 80 °C, subsequently the solvent was removed by a rotary evaporator. The methacrylate functionalized silica filler was made by mixing silica filler (MEK-ST, Nissan Chemical Industries, Ltd.) solution with 5 wt% 3-(trimethoxysilyl)propyl methacrylate (MPTMS, Aldrich) and stirring for one day at room temperature. In order to fabricate the POSS microreactor with interconnected microchannel structures, a PDMS (Sylgard 184, Dow Corning) support boat (50 x 20 x 5 mm) was made by molding PDMS prepolymer against a stainless steel block. Then, the embedded template framework was assembled using commercially available perfluoroalkoxy (PFA) tubing (360 µm OD, Health & Science Co.) as a physically sacrificial template in the PDMS boat, in which POSS precursor solution was introduced and subsequently cured by UV (Heraeus Amba Ltd., 365 nm) irradiation for 5 min. Finally, the template tubings were carefully removed from the aforementioned solidified PFA tubing/POSS composite to create the interconnected microfluidic channels.

In order to make a serpentine microfluidic channel from the interconnected open channel structure, the POSS precursor solution was re-filled into the channel driven by capillary force. Subsequently, the channel was selectively blocked by 1 min of UV curing using a spot UV laser source (Hamamatsu Photonics K.K., 365 nm wave length, beam diameter 1 mm). Finally, the POSS microfluidic device with serpentine channel (10 cm length, 360 µm diameter) was thermally treated at 300 °C for 1 hr in an inert atmosphere after flushing out the uncured POSS solution from the channel. The inlet and outlet connection of the prepared POSS microreactor were made by inserting silica capillary into the channel and subsequently filling with polyvinylsilazane (HTT 1800, Clariant) adhesive with 1 % DMPA as a photoinitiator, followed by serial UV exposure for 5 min and thermal treatment at 200 °C for 1 hr.

Fabrication of polyvinylsilazane (PVSZ) microreactor by employing polystyrene (PS) film template

Alternative ceramic-like microreactor was fabricated from polyvinylsilazane (PVSZ, HTT 1800, Clariant) embedded with patterned polystyrene (PS) film as a thermally sacrificial

template. In order to achieve greater control over the accuracy and precision of the designed channels, PS film template was designed by CAD software (AutoCAD 2008), loaded in lab view program and subsequently cut by laser ablation process using femto-second laser pulses (150 fs, 1 kHz, 810 nm). The resultant PS template pattern (25 µm thickness x 500 µm width x 14 cm length, Goodfellow Cambridge Ltd.) was fixed onto a PDMS boat (0.5 x 3 x 4 cm) coated with a mold releasing agent (Clariant). A mixture of PVSZ and 0.5% dicumyl peroxide thermal initiator (Sigma Chemicals) was then poured into the PDMS boat installed with the PS template pattern. The boat was kept on a hot plate and slowly heated to 100 °C at a rate of 1 °C/min and held for 2 hrs to yield a cross linked solid. Subsequently, the free standing PVSZ/PS composite after demolding from PDMS boat was slowly heated again to 500 °C at a rate of 1 °C/min and held for 2 hrs. During the co-firing treatment, the PS film was completely decomposed, while the PVSZ was thoroughly cross-linked to produce solvent resistant ceramic-like material that was still transparent, but slightly yellowish in color. Inlet and outlet connections of the microreactor were made by a stainless steel capillary (od = 1/16 inch) using a ceramic SiC paste (Aremco Products) that was consolidated by annealing at 70 °C for 3 hrs.

High temperature or/and high pressure reactions of ceramic-like microreactors

The ceramic-like microreactor derived from POSS was used for high temperature reactions such as Michaelis-Arbuzov rearrangement at 150-170 °C, Wolff-Kishner reduction at 200 °C. Whereas the PVSZ derived ceramic-like microreactor was employed for high temperature or/and high pressure reactions such as synthesis of super-paramagnetic Fe₃O₄ nanoparticles at 320 °C and isomerisation of allyloxybenzene to 2-allylphenol in aqueous phase under conditions of 230-250 °C and 400-450 psi. Firstly, dibromopropane (Aldrich) and triethylphosphate (Aldrich) were mixed together in a molar ratio of 1:1 to be employed as reactant solution for Michaelis-Arbuzov rearrangement. The microchemical reaction was carried out by injecting the reactant solution through the inlet of POSS microreactor (10 cm length, 360 µm diameter) and by heating the microreactor at 150~170 °C by placing on a hot plate at various flow rates by using a syringe pump (Harvard). The product solution was collected from the outlet and the conversion was analyzed by GC-MS (Agilent 5975C, Agilent Tech). Secondly, 0.001 M benzophenone hydrazone (Aldrich) and 0.005 M potassium hydroxide (Aldrich) were added into 10 ml ethylene glycol (Aldrich) to be used as reactant solution for Wolff-Kishner reduction at 200 °C and the product was analyzed by GC-MS.

Monodisperse Fe₃O₄ (magnetite) nanocrystals were synthesized from iron-oleate complex as reported earlier.²¹ The iron-oleate complex was obtained by dissolving 4 mmol of iron chloride (FeCl₃·6H₂O) and 12 mmol of sodium oleate into 28 ml of the mixed solvent (8 ml ethanol + 6 ml distilled water + 14 ml hexane). Subsequently, the upper organic layer (hexane) containing the iron-oleate complex was separated after completion of reaction at 70 °C for 4 hrs, washed with distilled water and evaporated under reduced pressure to yield the iron-oleate complex in the form of a waxy solid. The 4 mmol of complex product dissolved in 20 g of 1-octadecene with oleic acid (2 mmol) and oleyl amine (2 mmol) was injected into the PVSZ microreactor (25 µm x 500 µm x 14 cm) at a flow rate of 0.5 to 2 µl/min, and heated at 320 °C by placing the wrapped microreactor with Al foil in a sand bath. The collected product

solution from the outlet was centrifuged to separate the Fe₃O₄ nanoparticles that were analyzed by TEM (JEM-2100, JEOL), XRD (D/MAX-2500/PC, RIGAKU), and vibrating sample magnetometer (3900 VSM, MicroMag™ Magnetometers) after washing with ethanol and drying. Finally, in order to illustrate the HTHP performance of the fabricated ceramic-like PVSZ microreactor, isomerization of allyloxybenzene to 2-allylphenol was conducted by injecting aqueous suspension of allyloxybenzene (0.1 M) into the microreactor by a HPLC pump (Iocratic Model 501, Analytical Scientific Instruments) at two sets of temperatures and pressures (230 °C - 400 psi, 250 °C - 450 psi) with a back pressure regulator. The product, 2-allylphenol was extracted in ethyl acetate and the yield was determined by GC/MS using anisole as an internal standard.

Characterization and device tolerance test

Thermal decomposition of PS film was investigated by carrying out thermo-gravimetric analysis (SDT-Q600, TA Instruments) at a ramping rate of 2 °C/min under constant N₂ purging. The ceramic-like microreactors fabricated from POSS and PVSZ were tested to evaluate their chemical, pressure and thermal stability. Firstly, the solvent compatibility of the ceramic-like material was tested with the annealed POSS blocks at 300 °C for 1 hr and PVSZ blocks (5 x 5 x 5 mm) at 500 °C for 2 hrs under N₂, respectively by soaking in the diverse solvents for 24 hrs. And, the swelling ratio, W/W_0 , where W and W_0 are the weight of sample in solvent for 24 hrs and that of the dried sample, respectively, was examined by following the reported method.¹³ The linear shrinkage of POSS or PVSZ was calculated by measuring the length of polymer bar before curing (L_0) in a PDMS boat and after curing and annealing at 300 °C or 500 °C (L), and the $(1-L/L_0)$ was denoted as the shrinkage ratio. The pressure tolerance of the fabricated PVSZ microreactor was investigated by connecting the inlet of the microreactor to a HPLC pump (SP-930D, Younglin, Korea) and the outlet with a back pressure regulator. Water contact angles were measured using a Ramé-Hart 200-F1 goniometer.

Results and discussion

One of the advantages of template or scaffold method to fabricate microfluidic devices is that no bonding step is required; as the monolithic microreactor is formed by physical or thermal removal of the template.²² The appropriate combination of templates and matrix materials is critical for fabricating the microchannel structures with no mechanical damage during removal of the templates. In this work, we selected the assembly structures of low surface energy perfluoroalkoxy (PFA) tubing that can be physically pulled out, and the patterned polystyrene (PS) thin film by laser ablation, which is thermally decomposable (refer ESI, Scheme S1).

Two types of inorganic polymers, POSS and PVSZ (refer ESI, Figure S1) were selected as structural materials for fabrication of high temperature or/and high pressure tolerable ceramic-like microreactors. Our first goal was to authenticate our assumption that the ceramic-like transparent transient phase existed between polymer and ceramic phase in POSS and PVSZ with affordable shrinkage at certain conditions, and which would possess excellent chemical and thermal stability like glass devices. Also, it was important to confirm if the selected inorganic polymers were comparable with cost-effective and convenient fabrication process. Thus, we firstly studied the ceramization process of two polymers to obtain information about the transparent transient phase followed by solvent resistant tests to demonstrate their robust stabilities. Unlike most of the solid POSS, which contain other functional

groups, the methacrylate functionalized POSS (in a liquid state) can be readily infiltrated into void gaps of the template assembly and consolidate via free radical polymerization of methacrylate groups by UV exposure to generate a monolithic solid.²³ Various thermal treatments of the UV cured POSS at temperatures between 200–400 °C for 1 hr in an inert atmosphere have been implemented to ensure the presence of fully cross-linked ceramic-like phase,²⁴ and it is pronounceable to find the existence of glassy transparent state of the polymer upon heating at 300 °C, which however became opaque with cracks at 400 °C, presumably due to appreciable thermal decomposition of organic parts (refer ESI, Figure S2). In case of organic polymers with identical functional groups such as poly(ethylene glycol) dimethacrylate (PEGDMA), severe decomposition was observed even only at 200 °C leading to formation of black residue. Hence, it is obvious that the thermal stability of inorganic polymers is superior to organic polymers due to the presence of inorganic parts, which increases the stability of organic parts. Shrinkage, which commonly occurs during the curing stage of polymers, may cause defects or cracks in the polymeric products. In the present study, 5 wt% addition of methacrylate functionalized silica filler into the POSS matrix led to affordable shrinkage (~1.1% linear shrinkage), with an improvement from 2.3% shrinkage of filler free POSS sample upon annealing at 300 °C. The solvent compatibility of the filler containing POSS annealed at 300 °C was tested by measuring swelling ratio after immersion into the respective solvents at room temperature and elevated temperatures (3 - 5 °C below boiling point of the tested solvents) for 24 hrs, respectively. Table 1 provides details on the chemical stability of inorganic POSS material against a series of organic solvents with different polarity such as ethanol, DMSO, DMF, IPA, acetonitrile, acetone, dichloromethane, chloroform, toluene, hexane, THF and CCl₄. This excellent solvent resistance property is comparable to glass and is much better than organic polymers such as PDMS or PDMS coated with inorganic polymers. In addition, the water contact angle of the annealed POSS block at 300 °C was 93° that was moderately hydrophobic (refer ESI, Figure S3).

Table 1. Comparative analysis of chemical stability of POSS annealed at 300 °C for 1 hr and PVSZ annealed at 500 °C for 2 hrs under nitrogen atmosphere on the basis of changes in sample weight before and after immersion in various solvents at different temperatures for 24 hrs.

Solvents	Swelling ratio of POSS		Swelling ratio of PVSZ	
	At room temp.	At elevated temp.	At room temp.	At elevated temp.
Acetone	1.00	-	1.00	-
DCM	1.00	-	1.00	-
MeOH	1.00	1.00 (60 °C)	1.00	1.00 (60 °C)
Hexane	1.00	1.00 (60 °C)	1.00	1.00 (60 °C)
THF	1.00	1.00 (60 °C)	1.00	1.00 (60 °C)
AN	1.00	1.00 (80 °C)	1.00	1.00 (80 °C)
Toluene	1.00	1.00 (105 °C)	1.00	1.00 (105 °C)
CB	1.00	1.00 (125 °C)	1.00	1.00 (125 °C)
Xylene	1.00	1.00 (130 °C)	1.00	1.00 (130 °C)
DMF	1.00	1.00 (150 °C)	1.00	1.00 (150 °C)
EG	1.00	1.00 (200 °C)	1.00	1.00 (200 °C)
OD	-	-	1.00	1.00 (320 °C)

MeOH (methanol), DCM (dichloromethane), AN (acetonitrile), CB (chlorobenzene), DMF (Dimethylformamide), EG(ethylene glycol), OD(octadecene)

Another inorganic polymer employed in this work was PVSZ. The solidification chemistry of PVSZ as a precursor of SiCN

ceramic has been extensively studied either in the presence or absence of curing initiators.²⁴ It is well documented that PVSZ could be consolidated by UV radiation or/and heating at 150–250 °C via inter- and intra-molecular hydrosilylation of vinyl groups attached to silicon. Thermal annealing at 500 °C for 2 hrs could generate a transparent transient phase between polymer and ceramic phase with affordable shrinkage (~4.1% linear shrinkage). But, higher temperature treatment (over 500 °C) rendered opacity to PVSZ with cracks due to ceramization accompanied with severe chemical decomposition (refer ESI, Figure S4).²⁵ The solvent compatibility of PVSZ annealed at 500 °C that also measured the swelling ratio using the aforementioned solvents revealed excellent chemical resistance of PVSZ (Table 1). In addition, the contact angle 100° of the annealed PVSZ at 500 °C indicated moderately hydrophobic surface (refer ESI, Figure S3). Based on the above discussion, it is obvious that when POSS and PVSZ polymers were annealed at 300 °C and 500 °C, respectively, the transition state of these two inorganic polymers retained the intrinsic transparency of polymer and revealed enhanced chemical robustness as good as ceramic phase.

Fabrication of ceramic-like microreactors

POSS derived ceramic-like microreactor was fabricated by following a three step process. In the first step, the PFA tubing template framework was assembled in a PDMS boat by crossing the aligned tubes with each other (refer ESI, Figure S5), and subsequently the mixed POSS polymer was infiltrated into the PDMS boat. In the second step, the PFA tubing template was manually removed from the PFA tubing/POSS composite to obtain the interconnected POSS microchannel structures after solidification by UV exposure. Subsequently, the liquid POSS mixture was re-filled into the entire microchannel, and then the selected parts of the channels were blocked by UV spot curing to form a serpentine type of 10 cm long channel after removing the uncured POSS. Finally, the POSS microreactor was annealed at 300 °C in an inert atmosphere to achieve a ceramic-like phase with enhanced chemical and thermal stability for high temperature organic reactions. The entire fabrication process is represented in Figure 1(a) and Figure S6 (refer ESI). The POSS derived ceramic-like reactor retained optical transparency with pale yellowish tint and the label 'POSTECH' can be easily visualized through the microreactor set (Figure 1(b)). The scanning electron microscopic (SEM) image (cross section view) of POSS derived ceramic-like microchannel reveals round shape with diameter of ~360 μm (refer ESI Figure S7 for SEM image and Figure S8 for connecting method).

Alternatively, PVSZ derived ceramic-like microreactor was fabricated using PS film template pattern made by laser cutting process. As shown in Figure 2(a), the PS film template was completely submerged into preceramic polymer, PVSZ, followed by co-firing at 500 °C for 2 hrs to completely burn off the PS film template, while the PVSZ matrix was converted into ceramic-like phase, leaving behind the microchannel structure. In order to confirm the thermal removal of the template, thermal stability of PS was investigated by TGA (refer ESI, Figure S9). The analysis revealed complete decomposition of template into gaseous products in the temperature range of 370–425 °C under the presence of inert atmosphere. The PVSZ derived ceramic-like reactor (shown in Figure 2(b)) displayed glass-like optical transparency and the microchannel was also clearly visible (25 μm x 500 μm x 14 cm, refer ESI, Figure S10). The pressure tolerance test exhibited

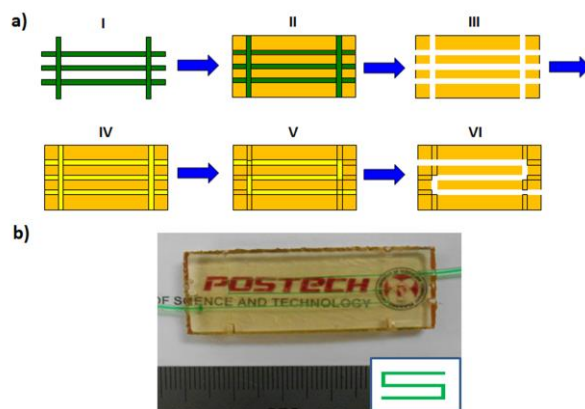


Figure 1. Fabrication of POSS derived ceramic-like microreactor using PFA tubing template method. a) Schematic illustration of fabrication process for serpentine microchannel: (I) Framework assembly of PFA tubing template, (II) Infiltration and UV curing of POSS, (III) Pullout of tube template, (IV) Re-infiltration of POSS into channel, (V) Selective curing of POSS to block the channel, (VI) Removal of uncured POSS. b) Optical image of a transparent and serpentine ceramic-like microreactor, inset shows the channel design of 10 cm length.

resistance of PVSZ reactor up to ~ 3100 psi (~213 bar) indicating the feasible utility of the microreactor in chemical applications requiring conditions of high temperature and high pressure (refer ESI, Figure S11).

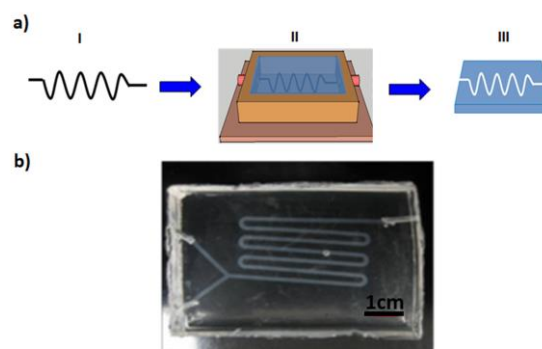


Figure 2. Fabrication of PVSZ derived ceramic-like microreactor from polystyrene (PS) film template. a) Schematic illustration of the fabrication process: (I) PS template processed by fs laser, (II) Introduction and curing of PVSZ, (III) Ceramic-like microreactor after co-firing at 500 °C for 2 hrs; b) Optical image of ceramic-like PVSZ microreactor.

In the present work, two types of whole ceramic-like microreactors with robust durability have been successfully fabricated by molding the silicon-based polymers, POSS or PVSZ into the sacrificial templates, with subsequent heat treatment step to obtain a transient phase between polymer and ceramic phase. This simple non-lithographic fabrication method avoids a troublesome sealing step in the ceramic chip, which makes it cumbersome to obtain the ultimate microfluidic devices by bonding two consolidated pieces with apparently no leakage. In addition, the channel with different size can be fabricated by employing template with required size.

Microchemical performance at high temperature or/and high pressure conditions

The miniaturized microreactor provides advantages of controlled fluid transport, rapid chemical reactions and cost efficiency when compared to conventional reactors. It is hypothesized that the developed ceramic-like microreactors with excellent thermal and chemical stability could be quite useful for organic or inorganic chemical synthesis under high temperature or/and high pressure conditions, when compared to PDMS and any plastic microreactors. In the following discussion, four types of model reactions were demonstrated to explore the utility of the two ceramic-like microreactors in a comparative manner to the results in bulk reactions. (Refer ESI, Figure S12 for experimental set-up)

The POSS derived ceramic-like microreactor (10 cm length, 360 μm diameter) was firstly tested for Michaelis-Arbuzov rearrangement reaction that is one of the versatile pathways for the formation of carbon-phosphorus bonds to produce various phosphonates, phosphinates and phosphine oxides. Generally this reaction requires high temperature and longer reaction time to complete the conversion.²⁶ The result presented in Figure 3(a) illustrates that the continuous flow reaction could be accelerated by elevating temperature in the range of 150–170 $^{\circ}\text{C}$ and by extending residence time in the range of 10–120 min. An increase in the conversion of dibromopropane from 21% (150 $^{\circ}\text{C}$) to 63% (170 $^{\circ}\text{C}$) at 25 min of retention time was observed, with further improvement to 72% at 170 $^{\circ}\text{C}$ for 42 min, and eventually 100% conversion was achieved at 170 $^{\circ}\text{C}$ for 120 min (refer GC-MS evidence provided in ESI, Figure S13). The observed enhancement in the rate of conversion was obviously superior to the bulk systems that required 20 hrs to obtain the comparable result.²⁶

In addition, Wolff-Kishner reduction reaction involving the formation of hydrocarbons from carbonyl compounds was chosen to test the performance of POSS derived ceramic-like microreactor under more challenging conditions. It is reported that this reaction involves heating crude hydrazone derivatives with alkali in a high-boiling ethylene glycol solvent; typically at temperatures of 195–200 $^{\circ}\text{C}$ for one day.²⁷ The POSS derived ceramic-like reactor was tested for its performance for continuous flow at 200 $^{\circ}\text{C}$. A strong increase in conversion from 28% for 3 min to 83% for 25 min of retention time was observed as can be seen in Figure 3(b) (refer GC-MS evidence provided in ESI, Figure S14). The conversion was comparable with bulk reaction for 24 hrs,²⁷ while the reaction time was significantly decreased. In addition, the chemical resistance of POSS derived ceramic-like reactor under the reaction condition of corrosive alkali solution was investigated by observing the changes in surface morphology when the tested sample (POSS block annealed at 300 $^{\circ}\text{C}$) was immersed in ethylene glycol with 1 wt% KOH at 200 $^{\circ}\text{C}$ for various time periods. The surface retained smooth texture after 1 hr exposure to alkali, and was still stable even after 24 hrs of exposure, except for the presence of little scratch, indicating the excellent thermal and chemically stable nature of the microreactor (refer ESI, Figure S15).

The alternative PVSZ derived ceramic-like microreactor (25 μm x 500 μm x 14 cm) was used for continuous flow synthesis of super-paramagnetic iron oxide (Fe_3O_4) nanocrystal that is usually carried out at high temperatures.²⁸ The Fe_3O_4 nanocrystals were synthesized by flowing a solution of iron (III) oleate in 1-octadecene at 320 $^{\circ}\text{C}$ as shown in Figure 4(a). A consistent increase in the size of nanoparticles was observed with increasing retention times: 5 \pm 1 nm at 12 min, 10 \pm 2 nm

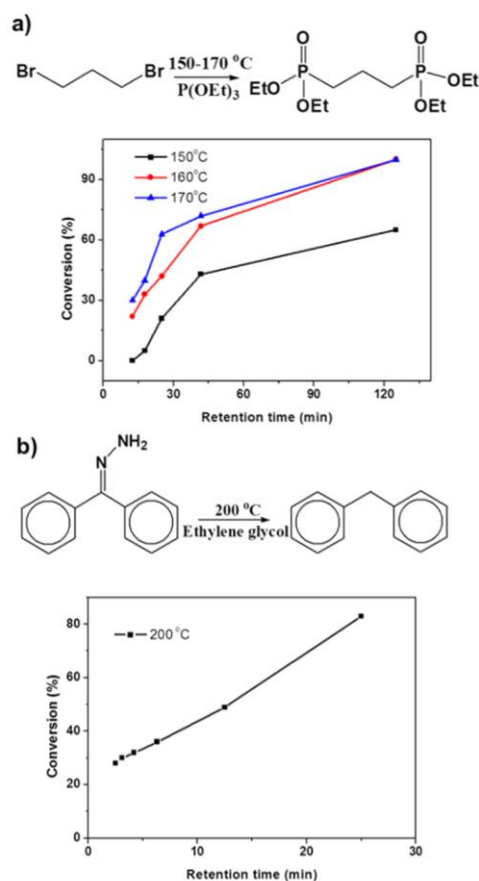


Figure 3. High temperature chemical syntheses by POSS derived microreactor. a) Michaelis-Arbuzov rearrangement reaction at 150–170 $^{\circ}\text{C}$, and b) Wolff-Kishner reduction reaction at 200 $^{\circ}\text{C}$.

at 24 min, and 20 \pm 2 nm at 48 min when mixed surfactants of oleic acid and oleyl amine were employed (refer ESI, Figure S16). Moreover, the shape of nanoparticles could be conveniently controlled by proper selection of dispersion agents in the continuous flow microchemical synthesis: spherical shape when oleic acid was employed, and rod shaped in the presence of mixture of oleic acid and oleyl amine (refer Figure 3(b) and (c)). The super-paramagnetic behaviour of highly crystalline Fe_3O_4 nanoparticles was confirmed by vibrating sample magnetometer (VSM) (refer ESI, Figure S17) and X-ray diffraction (XRD) measurements (refer ESI, Figure S18), respectively, the results of which were well-consistent with those of the earlier reported batch process product.²¹

Eventually, the PVSZ derived ceramic-like microreactor was tested for its performance under high temperature and high pressure (HTHP) conditions by performing the isomerization of allyloxyphenol to 2-allylphenol as a typical Claisen rearrangement reaction that is useful for syntheses of natural products or pharmaceutical intermediates.^{29, 30} The pressure during the reaction was generated by heating the aqueous mixture over 200 $^{\circ}\text{C}$, which is the desirable reaction condition. The reaction was performed by flowing aqueous solution of allyloxybenzene (0.1M) using a HPLC pump and a back pressure regulator at the outlet, and two HTHP conditions were achieved by heating at 230 $^{\circ}\text{C}$, and 250 $^{\circ}\text{C}$ and developing 400 psi, and 450 psi pressure, respectively. It can be seen in figure 4(d) that better conversion is achieved at higher temperature

even during a very short reaction time (3~14 sec), 70% of 2-allylphenol was formed at 250 °C (450 psi) for 14 sec of residence time. Whereas in the bulk, the reaction was usually performed at lower temperature for one day in the presence of catalyst.³⁰ In the contrary, in PVSZ derived microreactor fabricated by bonding two pieces at 150 °C for 3 hrs the performance was limited only at low temperature (< 60 °C) and ambient pressure as reported earlier.³¹ Based on the obtained results, it is stated that both the ceramic-like microreactors made from templates with bonding free method truly demonstrated the realistic use for continuous flow chemical reactions at high temperatures or/and high pressure conditions with reliable durability when compared to the microreactors fabricated by two piece bonding method, which also exhibited weak interface and poor pressure resistance.

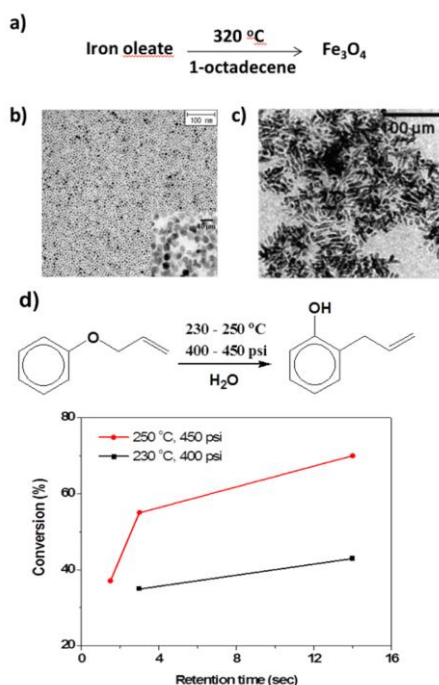


Figure 4. High temperature or/and high pressure chemical syntheses by PVSZ derived ceramic-like microreactor. a) Synthesis of super-paramagnetic Fe₃O₄ nanoparticles at 320 °C, b) Formation of spherical 10 nm sized nanocrystals from a mixture of surfactants, oleic acid and oleyl amine (1:1) after 24 min, inset shows 20 nm cluster after 48 min, c) Rod shaped Fe₃O₄ nanocrystals after 24 min by employing oleic acid as surfactant, and d) Isomerization of allyloxybenzene to 2-allylphenol at 230-250 °C and 400-450 psi.

Conclusions

In conclusion, we have developed whole ceramic-like microreactors from two inorganic polymers, POSS and PVSZ by template method without experiencing a troublesome bonding step. The POSS derived ceramic-like microreactor was fabricated by employing low surface energy PFA template and a final heating step at 300 °C to achieve a ceramic-like transparent phase, while the PVSZ derived ceramic-like microreactor was fabricated by employing PS film template and a co-firing step at 500 °C to achieve alternative ceramic-like transparent phase. These ceramic-like microreactors with excellent thermal and chemical stabilities were successfully utilized for Michaelis-Arbuzov rearrangement, Wolff-Kishner

reduction, synthesis of super-paramagnetic Fe₃O₄ nanoparticles, and isomerisation of allyloxybenzene to 2-allylphenol under high temperature or/and high pressure conditions. The performance of the microreactors was found to be far superior to the reported plastic microreactors and comparable to glass microreactors. For the first time, to the best of our knowledge, facile polymer derived microreactor devices have been successfully fabricated and utilized for organic and inorganic chemical syntheses under harsh conditions.

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Notes and references

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