

# Chemical development of preceramic polyvinylsilazane photoresist for ceramic patterning

Yi-He Li · Xiao-Dong Li · Dong-Pyo Kim

Received: 31 May 2007 / Accepted: 12 September 2007 / Published online: 27 September 2007  
© Springer Science + Business Media, LLC 2007

**Abstract** In order to develop a preceramic photoresist for the fabrication of non-oxide SiCN ceramic microstructures by a mold-free photocuring shaping process, UV sensitive acrylate functional groups were successfully grafted onto the backbone of polyvinylsilazane by its reaction with ethyl-4-bromocrotonate via a high efficiency allyl bromide electrophilic substitution process. The as-modified polymer was characterized by  $^1\text{H}$  Nuclear Magnetic Resonance ( $^1\text{H-NMR}$ ) and 2D- $^1\text{H-}^1\text{H-NMR}$  (COSY) spectroscopy, and its UV sensitivity was investigated by Differential PhotoCalorimetry (DPC) and Fourier Transform InfraRed (FT-IR) spectroscopy. The reaction mechanism was discussed in detail and the results showed that the as-modified polyvinylsilazane (m-PVSZ) is a promising preceramic photoresist.

**Keywords** Preceramic polymer · Polyvinylsilazane · Modification · UV sensitivity

## 1 Introduction

Polyvinylsilazane (PVSZ) is a novel ceramic precursor which is intended to be used for the fabrication of SiCN non-oxide ceramic microstructures, such as microreactors

or microscale gas turbines which are subjected to harsh environments, because of its tolerance to high temperature, resistance to corrosion, and good tribological properties [1]. The fabrication of ceramic microstructures by using a preceramic precursor is usually carried out by a series of complex and costly shaping processes, which usually needs a thermal curing step employing a special mold at higher temperature with the addition of a thermal initiator to convert the liquid polymer into the crosslinked solid state. Many studies have been devoted to the fabrication of suitable molds and to their removal after curing, which strongly affects the resolution of the as-fabricated fine microstructures [2, 3]. UV-radiation curing is a well-accepted technology which has the distinct advantage of bringing about the quasi-instantaneous transformation of a liquid resin into a solid polymer selectively in the illuminated areas. UV curing has many advantages over thermal curing, since it makes use of a low cost or free mold and enables one to easily obtain freestanding preceramic structures by UV induced crosslinking and thereafter pyrolysis [4–6]. On the other hand, acrylate-containing resins are by far the most widely used in UV-curing applications, due to their high photo-induced reactivity [7–9]. However, to the best of our knowledge, there have been no many reports on UV curable preceramic polymers, except for certain cases involving vinyl group induced photocuring, a process which exhibits relatively slow kinetics with UV exposure. Therefore, the introduction of a highly photosensitive acrylate group to enhance the photosensitivity to the level of a photoresist for use in photolithography methods is of great interest [10].

In this study, we successfully grafted UV sensitive acrylate groups onto the backbone of a PVSZ precursor via the allyl bromine substitution chemical reaction for the first time, thereby demonstrating a promising preceramic photoresist.

---

Yi-He Li is working at Prof. Kim's lab under a co-advisor program.

Y.-H. Li · X.-D. Li  
CFC key lab of National University of Defense Technology,  
Changsha 410073, Hunan, People's Republic of China

Y.-H. Li · D.-P. Kim (✉)  
Department of Fine Chemical Engineering and Chemistry,  
Chungnam National University,  
Daejeon 305-764, South Korea  
e-mail: dpkim@cnu.ac.kr

## 2 Experimental procedures

Ethyl-4-bromocrotonate (EBC, 95%, Aldrich), toluene (99.8%, Aldrich), and PVSZ (the commercially available Ceraset™, from Kion Corp., NY, USA) were used as received.

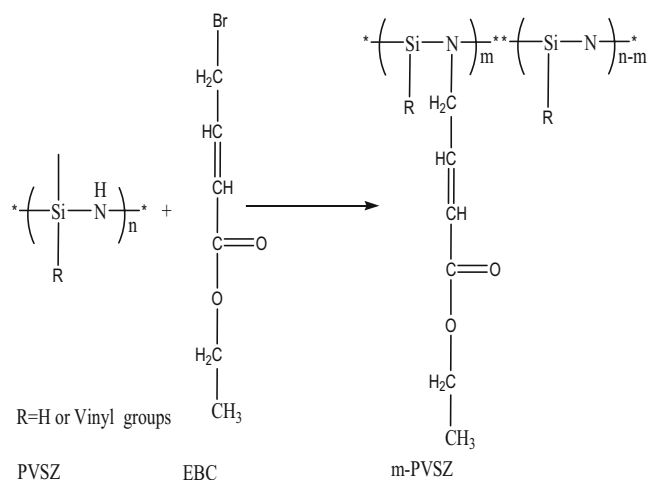
In a typical reaction, 3 g of EBC was added dropwise to 4 g of a solution of PVSZ in 20 ml of toluene. The mixture was heated in an oil bath at 90°C for 72 h. Finally, the white HBr precipitate was removed by high speed centrifugal treatment and a filtration process; the solvent and unreacted precursor was subsequently removed by vacuum pump. All of the processes were carried out in an inert gas atmosphere to avoid exposure to moisture, utilizing standard Schlenk techniques.

The molecular structures of the modified PVSZ (m-PVSZ) were characterized by <sup>1</sup>H Nuclear Magnetic Resonance (<sup>1</sup>H-NMR) and 2D-<sup>1</sup>H-<sup>1</sup>H-NMR(COSY) spectroscopy. The UV photosensitivity of m-PVSZ was investigated by Differential PhotoCalorimetry (DPC) and Fourier Transform InfraRed (FT-IR) spectroscopy. The samples for UV irradiation and FT-IR were prepared by adding 5 wt.% of Irgacure369 photoinitiator to 60 wt.% of m-PVSZ dissolved in toluene, followed by the removal of the solvent. The ceramic yield was checked by Thermogravimetry (TG) in a high purity nitrogen atmosphere. The ceramic patterns were fabricated by a photolithography process with UV irradiation at about 10 mW/cm<sup>2</sup> (BLB-4W, 352 nm, Sankyo Denki, Japan) for 1 min, subsequently developed by ethanol and pyrolyzed at 800°C under a high purity nitrogen atmosphere. The surface patterns were observed by a optical microscope (SV32, Somethech, Korea) under a magnification of 40 times.

## 3 Results and discussion

As is shown in Scheme 1 (where R represents hydrogen or vinyl groups), the backbone of molecular structure of PVSZ is composed of silicon and nitrogen atoms which are bonded in an alternating sequence, and there are paired electrons on every amine nitrogen atom, which are active and easily able to carry out substitution reactions. In the case of EBC, there is an allyl bromine group which is reactive toward any of the nucleophilic NH groups of PVSZ.

To confirm the supposed reaction mechanism shown in Scheme 1, we obtained the <sup>1</sup>H-NMR spectra of PVSZ, EBC and m-PVSZ, as shown in Fig. 1. The intensity of the peak at 0.65 ppm of m-PVSZ, which is assigned to the NH group, is dramatically decreased compared with the NMR spectrum of PVSZ, which means that the NH groups were consumed during the chemical modification reactions. At the same time, one new peak appears at 2.23 ppm of m-PVSZ, which is assigned to be the (–CH<sub>2</sub>–N) that was

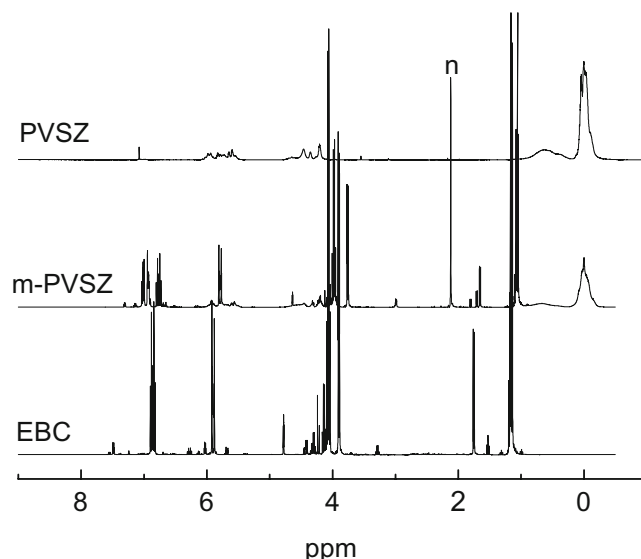


**Scheme 1** Reaction route used to modify PVSZ

introduced through the chemical reaction between PVSZ and EBC. These changes give strong supports to the grafting reaction of acrylate groups onto the PVSZ repeating units.

As shown in Fig. 2, in order to confirm the new peak *n* in the NMR spectrum of m-PVSZ in Fig. 1, we obtained the 2D-<sup>1</sup>H-<sup>1</sup>H-NMR(COSY) spectrum of m-PVSZ. The results show that peak *n* at 2.23 ppm (–CH<sub>2</sub>–N) is correlated to peak *g* at 7.01 (C=CH<sub>2</sub>), which provides evidence that there are (N–CH<sub>2</sub>–C=CH<sub>2</sub>) groups with a new chemical bond (N–CH<sub>2</sub>) on the m-PVSZ molecules.

To investigate the photosensitivity of m-PVSZ, we obtained its differential photocalorimetry (DPC) spectrum, which is shown in Fig. 3. There is a sharp exothermic peak for m-PVSZ, whose duration is short and which indicates that the crosslinking reaction induced by the irradiation



**Fig. 1** <sup>1</sup>H-NMR spectra of PVSZ, EBC and m-PVSZ

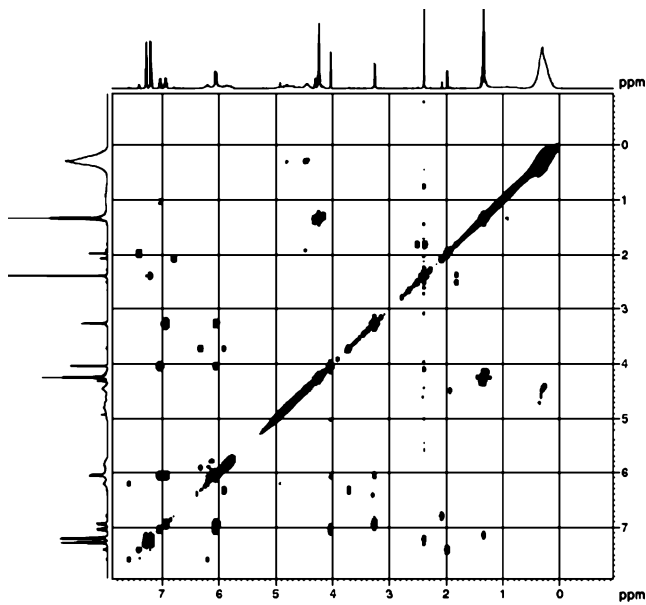


Fig. 2 2D-<sup>1</sup>H-<sup>1</sup>H-NMR (COSY) spectrum of m-PVSZ

with UV is almost 90% finished within 1 min. However, in the case of the unmodified PVSZ, there is no obvious exothermic peak in the curve. The relatively stronger photosensitivity of m-PVSZ is attributed to the acrylation of PVSZ.

As shown in Fig. 4, the FT-IR transmittance spectra of m-PVSZ, which was cured by UV irradiation at about 10 mW/cm<sup>2</sup> for different times, show strong UV sensitivity. The peaks at and 1404 cm<sup>-1</sup> are due to the acrylate groups of m-PVSZ (vibration related to double bond of acrylate [7, 8] ), and the strength of this peak decreased rapidly within 1 min, which shows much stronger UV sensitivity as compared to that observed in the study by

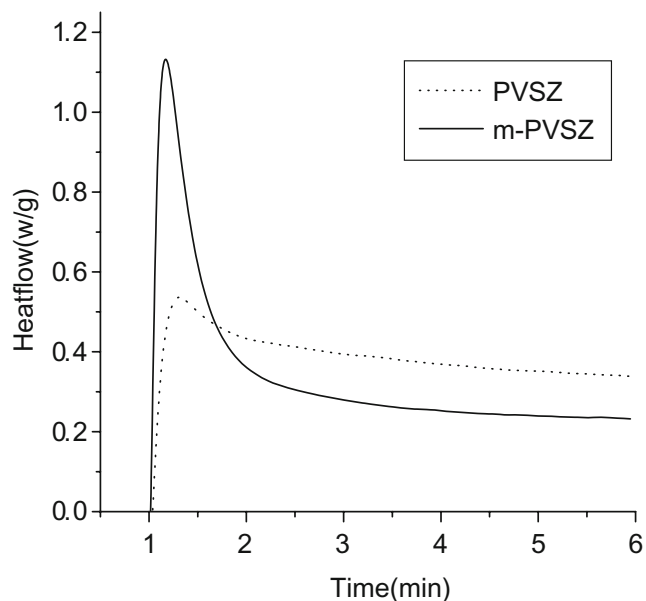


Fig. 3 DSC spectra of PVSZ and m-PVSZ

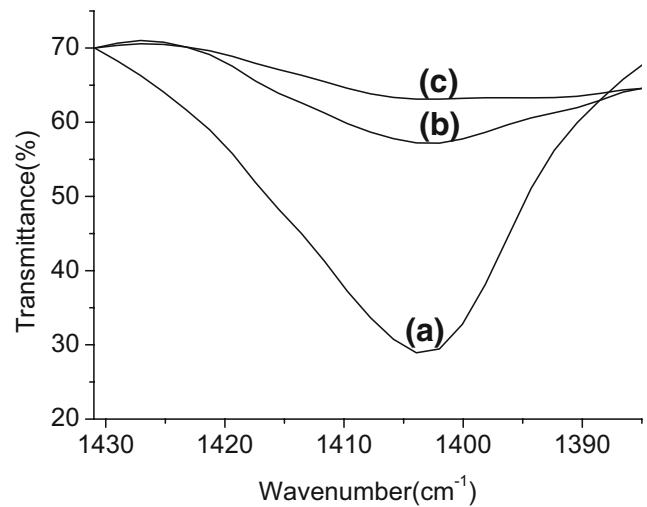


Fig. 4 FT-IR spectral changes in C=C double bond at 1404 cm<sup>-1</sup> in transmittance spectra of m-PVSZ after UV exposure for different irradiation times of 0 (a), 60 (b), and 120 (c) seconds

Liew [1], where it took about 20 min for PVSZ to be cured under the same curing conditions. This reveals that m-PVSZ behaves as a negative type of inorganic photoresist resin due to its highly UV sensitive acrylate groups.

Figure 5 shows the TGA curves of EBC, PVSZ and m-PVSZ. EBC is almost completely degraded at about 150°C. In the case of PVSZ, there is continuous weight loss from 22°C to 780°C, following which there is no obvious weight loss as the temperature is further increased up to 1000°C, which means there is a continuous transformation process from the preceramic polymer PVSZ, to SiCN ceramic and that this transformation process was finished at 780°C, with the final ceramic yield being about 63.13% at 1000°C. In the case of m-PVSZ, the ceramic transformation process is quite similar to that of PVSZ and the ceramic yield is about 46.38%. The lower ceramic yield for m-PVSZ is caused by the addition of acrylate groups, which are partly transformed into ceramic and partly lost during the pyrolysis process. As 75 wt.% of PVSZ and 25 wt.% of

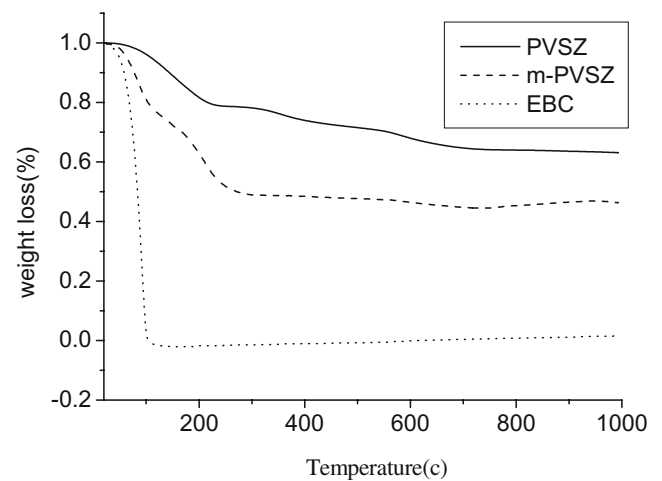
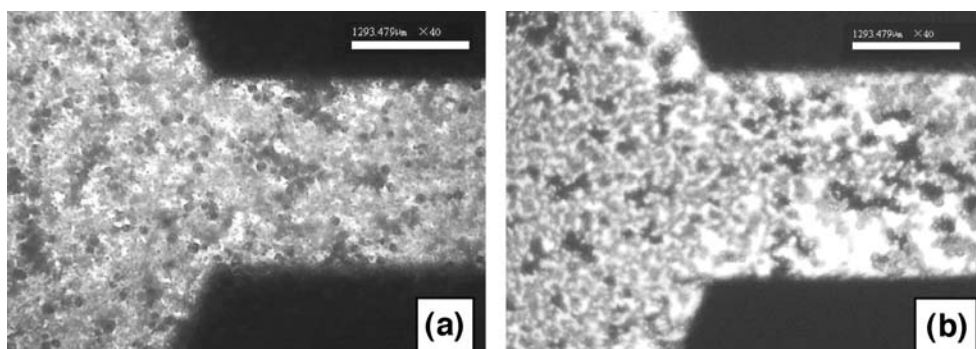


Fig. 5 TGA curves of EBC, PVSZ and m-PVSZ

**Fig. 6** Optical microscope pictures of UV irradiated m-PVSZ coatings through a mask, (a) developed by ethanol; (b) pyrolyzed at 800°C



EBC were added in the synthesis experiment, and the final ceramic yield for m-PVSZ is about 73.47% of that of PVSZ, it can be inferred that the addition of EBC has no effect on the final ceramic transformation.

Furthermore, the ceramic patterns were fabricated from m-PVSZ by a UV irradiated photolithography process, as is shown in Fig. 6. The pattern remains a well fidelity after developed by solvent ethanol (a), however, the surface of the pattern change into a bit rough and porous (b), which was aroused from the shrinkage and weight loss during pyrolysis at high temperature.

#### 4 Conclusions

In this study, we developed a new method of modifying the molecular structure of polyvinylsilazane by the acrylation substitution reaction using allyl bromine, through which a highly UV sensitive preceramic photoresist was synthesized, and the modification reaction was demonstrated to be a high efficiency electrophilic substitution process. Further research into the fabrication of non-oxide SiCN ceramic

microstructures by m-PVSZ through a mold free UV curing process is still in progress.

**Acknowledgements** This work was financially supported by the Center for Ultramicrochemical Process Systems in KAIST. The authors would want like to thank the Korea Basic Science Institute (KBSI) for their NMR supports.

#### References

1. L.A. Liew, Y. Liu, R. Luo, T. Cross, L. An, V.M. Bright, M.L. Dunn, R. Raj, *Sens. Actuators A*, **95**, 120 (2002)
2. R.A. Dorey, R.W. Whatmore, *J. Electroceram.* **12**, 19 (2004)
3. L.A. Liew, W. Zhang, L. An, S. Shah, *Am. Ceram. Soc. Bull.* **80**, 25 (2001)
4. Y.N. Xia, G.M. Whitesides, *Annu. Rev. Mater. Sci.* **28**, 153 (1998)
5. R. Mehnert, S. Naumov, W. Knolle, *Macromol. Chem. Phys.* **17**, 201 (2000)
6. M.R. Mucalo, N.B. Milestone, *J. Mater. Sci.* **29**, 4487 (1994)
7. K. Studer, C. Decker, E. Beckb, R. Schwalm, *Prog. Org. Coat.* **48**, 92 (2003)
8. C. Decker, *Polym. Int.* **45**, 133 (1998)
9. J. Kang, X.D. Fan, G.B. Xiao, X. Xie, *Polymer.* **47**, 1519 (2006)
10. T.A. Pham, D.P. Kim, T.W. Lim, S.H. Park, K.S. Lee, *Adv. Funct. Mater.* **16**, 1235 (2006)