

Acrylation of polyvinylsilazane with allyl bromide for an UV photosensitive inorganic polymer

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Abstract

A novel inorganic polymer resin with high photosensitivity was prepared by grafting acrylate functional groups onto the backbone of polyvinylsilazane through a reaction with methyl-2-(bromo-methyl)acrylate via the highly efficient electrophilic substitution of allyl bromide. The as-modified polymer was characterized by ¹H NMR and 2D-¹H-¹H NMR (COSY) methods to determine the reaction mechanism. Differential photocalorimetry, FT-IR spectroscopy and TGA were used to examine its properties. The modified polyvinylsilazane is a promising inorganic polymer photoresist with a high UV sensitivity and a 55% ceramic yield, which is useful for fabricating non-oxide ceramic microstructures using mold free photocuring shaping processes.

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1. Introduction

Pre-ceramic polymers as non-oxide ceramic precursors have a considerable potential in structural ceramic applications, including SiC fibers and its related composites, which are subjected to harsh environments owing to their tolerance to high temperature, corrosion resistance, and good tribological properties [1–3]. Since the Whitesides group reported various soft lithography techniques, there has been increasing interest in fabrication of ceramic microstructures using inorganic polymers [4]. Our group reported the fabrication of versatile SiC-based ceramic microstructures, such as 2-dimensional surface patterning and highly ordered porous structures, using polyvinylsilazanes (PVSZ) and polycarbosilanes (PCS) [5,6]. The fabrication process mainly involved a thermal curing step in the presence of certain thermal initiator after the appropriate

step for incorporating the ceramic precursors into molds or stamps with special relief structures by transfer the liquid polymer into the crosslinked solid state. However, considerable effort was needed to fabricate the molds or stamps. In particular, adhesion at the interface between the mold and resin was enhanced by curing for several hours at elevated temperatures leading to serious defects on the homogeneity and quality of large area patterning [1,7]. On the other hand, the photolithography technique is a well-accepted technology that provides quasi-instantaneous transformation through UV-radiation curing in selectively illuminated areas. In addition, the use of a low cost mask or free mold is a distinct advantage [8]. The photoresists used for conventional photolithography are formulated by acrylate-containing organic resins [9–11]. To the best of our knowledge, there are only a few reports on the synthesis of photocurable inorganic polymers for microstructural fabrication using adapted lithography processes except for the vinyl group-induced cases with slow curing kinetics [1]. Recently, we reported the fabrication of 3-dimensional SiC-based ceramic structures using a stereolithography process with the acrylated polyvinylsilazane

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(PVSZ), as an inorganic polymer photoresist [6]. The acrylate group containing isocyanate was effectively linked and added to the silazane bond by forming an amide bond. However, a new chemical process to functionalize PVSZ is still needed [8].

This paper reports an alternative route for grafting UV sensitive acrylate groups onto the backbone of a PVSZ precursor through an allyl bromine substitution reaction to produce an inorganic resin with promising UV sensitive properties. And it is believed that the developed inorganic polymer photoresist is useful for fabricating the non-oxide ceramic microstructures using mold free photocuring shaping processes.

2. Results and discussion

2.1. Mechanism for acrylating process

The starting material, PVSZ, was composed of silazane repeating units with vinyl groups, where silicon and nitrogen atoms are bonded in an alternating sequence. The nitrogen atom of PVSZ contains a lone pair of electrons, which can be the active site for a substitution reaction.

Fig. 1 shows the ^1H NMR spectrum of PVSZ and *m*-PVSZ (modified PVSZ). The spectrum of PVSZ shows the following peaks: peak a' at 0.12 ppm ($-\text{CH}_3$), n' 0.65 ppm (NH), e' at 5.63 ppm and f' 6.03 ppm (2H, s, $=\text{CH}_2$), while the peaks at 4.34–4.61 ppm are assigned to Si–H groups of PVSZ. The spectrum of *m*-PVSZ shows the following peaks: peak a at 0.12 ppm ($-\text{CH}_3$), n 0.65 ppm (NH), c at 3.07 ppm (2 H, s, CH_2), e at 5.63 ppm and f 6.03 ppm (2H, s, $=\text{CH}_2$), while the peak b at 2.13 ppm and the peak g at 7.01 ppm are originated from the solvent toluene. The ^1H NMR spectrum of MBMA [12] showed peaks at 3.83 ppm (3H, s, OCH_3), 4.23 ppm (2H, s, CH_2), 6.00 ppm and 6.37 ppm (2H, s, $=\text{CH}_2$). After the modification reaction, the peak at 4.23 ppm (2H, s, CH_2), which originated from MBMA, disappeared while one new peak at 3.07 ppm appeared in the *m*-PVSZ spectrum, which was assigned to (2H, s, NCH_2). The new peak suggests the formation of $\text{N}-\text{CH}_2$. More-

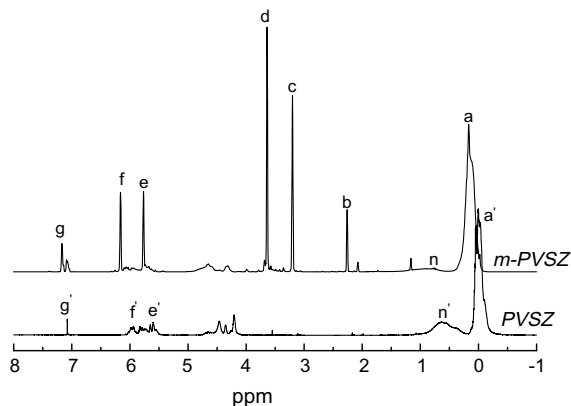


Fig. 1. ^1H NMR spectrum of PVSZ and *m*-PVSZ.

over, as the methyl group bonded to Si was not involved with chemical change during the modification reactions, it is suitable as a reference peak. The relative integrated area ratio of NH/CH_3 was 0.31 for PVSZ (peak n'/peak a'), whereas 0.15 for *m*-PVSZ (peak n/peak a). The reduction of integrated area ratio was attributed to the consumption of $-\text{NH}-$ groups through the introduction of an acrylate group into the silazane units. Therefore, the allyl bromine group of MBMA reacts preferentially with the nucleophilic NH groups of PVSZ.

The ^{13}C NMR spectrum also provides an additional evidence for the modification of PVSZ, as shown in Fig. 2. The new peak p at 56.0 ppm was assigned to " $\text{N}-\text{CH}_2$ ", which supports the grafting reaction of the acrylic group onto the PVSZ backbone. In addition, the following four peaks originated from MBMA: 52.2 ppm (s, OCH_3), 129.1 ppm ($=\text{CH}_2$), 137.3 ppm (s, $=\text{C}$), 165.2 ppm (s, $\text{C}=\text{O}$).

The 2D- $^1\text{H}-^1\text{H}$ NMR (COSY) spectrum of *m*-PVSZ was examined in order to further confirm the reaction chemistry in the *m*-PVSZ, as shown in Fig. 3. In addition, peak

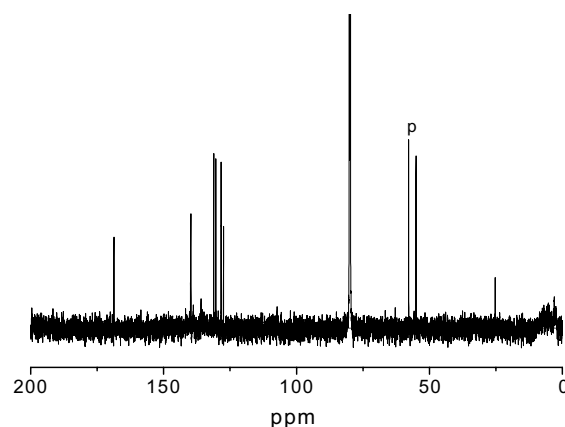


Fig. 2. ^{13}C NMR spectrum of *m*-PVSZ.

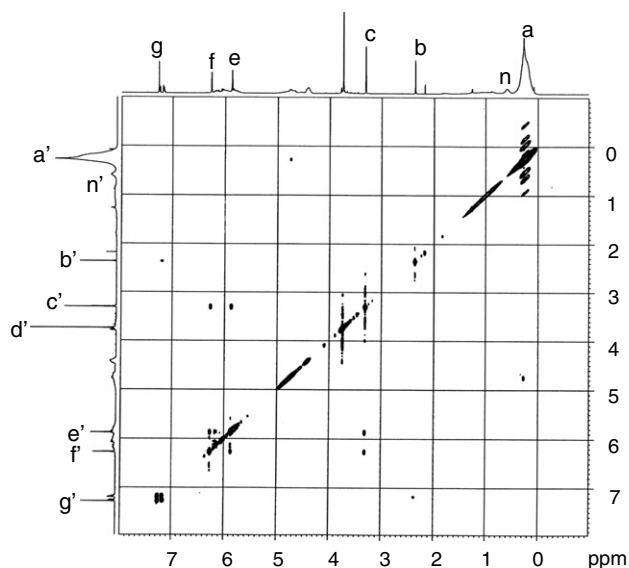


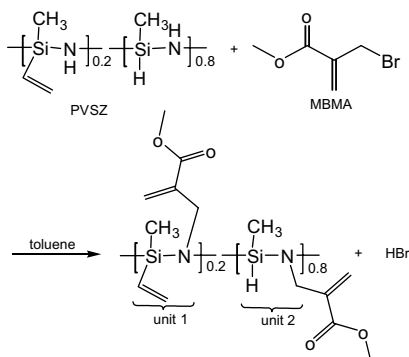
Fig. 3. 2D- $^1\text{H}-^1\text{H}$ NMR (COSY) spectrum of *m*-PVSZ.

c at 3.07 ppm, which was assigned to the $-\text{CH}_2$ group, was correlated with peaks e and f at 5.63 ppm and 6.03 ppm (2H , s, $=\text{CH}_2$), respectively. The new peak observed at c clearly shows the presence of $(\text{N}-\text{CH}_2-\text{C}=\text{CH}_2)$ groups grafted on the backbone of polyvinylsilazane. The mechanism of the proposed reaction routes is as follows (Scheme 1): an acrylation reaction occurs between the NH group of PVSZ and the allyl bromine group of MBMA.

2.2. Photosensitivity

The photosensitivity of the acrylated PVSZ was examined by obtaining the exothermic spectrum induced by UV curing using differential photocalorimetry (DPC), as shown in Fig. 4. There was a sharp exothermic peak of *m*-PVSZ, which indicates that the crosslinking reaction was almost complete within 1 min. However, there was low and broad exothermic peak on the DPC spectrum of the unmodified PVSZ. These results suggest that the relatively stronger photosensitivity of *m*-PVSZ is due to the acrylation modification of PVSZ.

Fig. 5 shows FT-IR transmittance spectrum highlighting the fast curing kinetics of the modified polymer. When the



Scheme 1. Reaction route for the synthesis of photosensitive PVSZ.

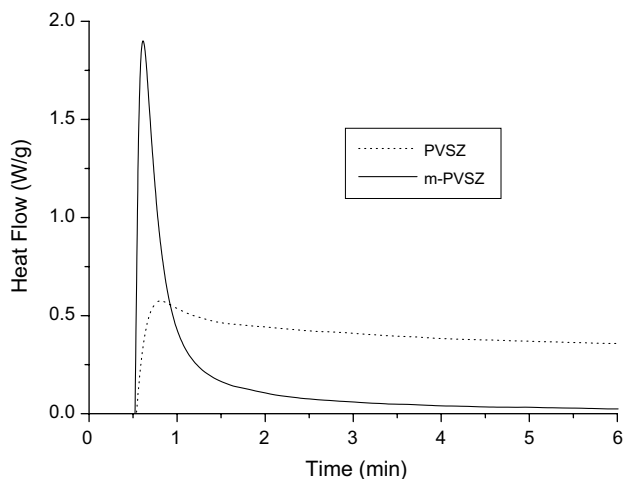


Fig. 4. Comparative DPC spectrum of PVSZ and *m*-PVSZ.

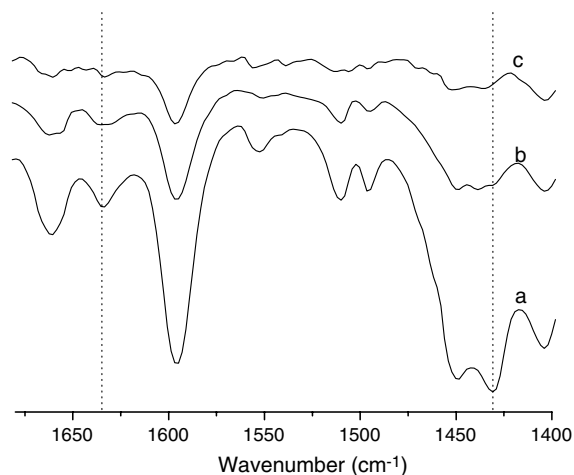


Fig. 5. FT-IR spectrum of *m*-PVSZ at different UV irradiation times: (a) 0; (b) 20 and (c) 60 s.

samples were exposed to $10 \text{ mW}/\text{cm}^2$ UV irradiation for a period of 20 s and 60 s, the peaks corresponding to the $\text{C}=\text{C}$ bond of acrylate groups in *m*-PVSZ at 1640 cm^{-1} and 1428 cm^{-1} had decreased dramatically [9,10]. The curing behavior is in contrast to the kinetics reported by Liew et al., where ≈ 20 min of UV-radiation was needed for the PVSZ to be cured under the same conditions [1]. This shows that *m*-PVSZ behaves as a negative type of inorganic photoresist resin with a relatively high concentration of UV sensitive acrylate groups.

2.3. Ceramic yield

PVSZ is widely used as a precursor for high temperature stable SiCN ceramics [1,5–7]. Therefore, it is important to know the ceramic yield of PVSZ and *m*-PVSZ, as shown in Fig. 6. In the case of PVSZ, there was continuous weight loss to $780 \text{ }^\circ\text{C}$, with no further weight loss up to $1000 \text{ }^\circ\text{C}$. This means there is a continuous transformation process from the preceramic polymer to the SiCN ceramic phase. The final ceramic yield at $1000 \text{ }^\circ\text{C}$ was 63.1%. In the case of *m*-PVSZ, the thermal behavior to form the ceramic

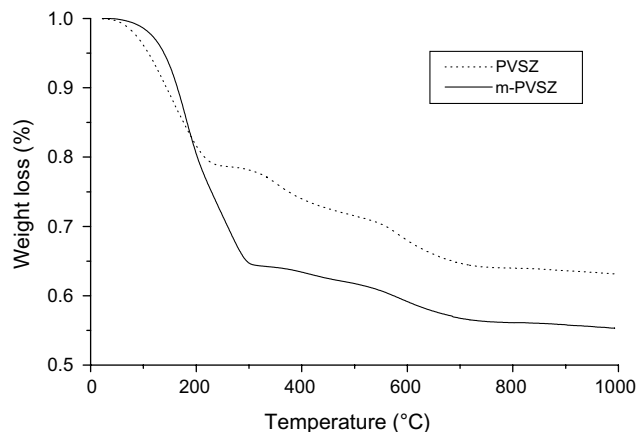


Fig. 6. Thermal behavior of PVSZ and *m*-PVSZ.

phase was similar to PVSZ. The ceramic yield was 55.3%, which was lower due to the introduction of thermally decomposable acrylate groups during the pyrolysis process.

These results suggest that the synthesized inorganic polymer resin can be used as a novel photoresist for the fabrication of tribological SiCN ceramic microstructures, including ceramic MEMS components, using mold free photocuring shaping processes.

3. Conclusions

A new synthetic route for the acrylated polyvinylsilazane, as an inorganic polymer photoresist, was developed using a highly efficient electrophilic substitution reaction between the secondary amine and the allyl bromide. The reaction occurred through the formation of a N–CH₂ bond, as observed by the 3.0 ppm ¹H NMR peak, and 56.0 ppm ¹³C NMR peak. The curing behavior of *m*-PVSZ was enhanced dramatically taking less than 1 min after exposure to UV radiation compared with the 20 min needed for PVSZ, which is consistent with the accelerated decrease in the C=C bond intensity in the IR-spectrum. *m*-PVSZ had a 55 wt% ceramic yield. *m*-PVSZ is currently being investigated for its potential in fabricating ceramic microstructures using a mold free UV curing process.

4. Experimental

4.1. Synthesis of photosensitive PVSZ

Methyl-2-(bromo-methyl)acrylate (MBMA, 97%, Aldrich), Toluene (99.8%, Aldrich), and PVSZ (the commercially available Ceraset™, from Kion Corp., NY, USA) were used as received. In a typical procedure, 1.0 g MBMA was added dropwise to a solution containing 3.0 g of PVSZ in 20 ml toluene. The mixture was heated in an oil bath at 60°C for 48 h with constant stirring. The white HBr precipitate produced by the reaction was removed using a high-speed centrifugal treatment followed by a filtration process. The solvent and the unreacted precursor were then removed using a vacuum pump. Finally, a clear viscous product (*m*-PVSZ) was obtained. All the processes were carried out using standard Schlenk techniques in an inert gas atmosphere to avoid exposure to moisture.

4.2. Characterization

The molecular structure and photosensitivity of *m*-PVSZ was characterized using various analytical techniques. The ¹H, 2D-¹H-¹H – Nuclear Magnetic Resonance spectra were recorded on a 600 MHz instrument (Bruker DMX600) using CDCl₃ as the solvent. The UV photosensitivity of the *m*-PVSZ was examined by Differential PhotoCalorimetry (DPC, TA instruments, 250 nm) and Fourier Transform Infrared (FT-IR, Mattson Genesis II spectrometer). The samples for UV and FT-IR were prepared by dissolving 60 wt% of *m*-PVSZ in toluene, and adding 5 wt% of an Irgacure369 photoinitiator. The samples were used after drying in a vacuum. The ceramic yield was determined using Thermogravimetric analyzer (TGA, TA instrument 2950) up to 1000 °C in a high purity nitrogen atmosphere with a flow rate of 70 ml/min and a heating rate of 10 °C/min.

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