

Synthesis and UV-curing behaviors of novel rapid UV-curable polyorganosilazanes

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Received 13 August 2005; received in revised form 5 January 2006; accepted 9 January 2006

Abstract

A novel ultraviolet-curable polyorganosilazane ceramic precursor was synthesized via ammonolysis from modified chorosilane, which had been synthesized by alcoholysis of trichloro(methyl)silane and 2-hydroxyethyl acrylate. The polyorganosilazane was well characterized by using Fourier transformed infrared spectroscopy (FTIR), ^1H nuclear magnetic resonance (^1H NMR), and multi-angle laser light scattering (LLS). Its UV curing behaviors investigated via FTIR and differential scanning calorimeter (DSC) clearly indicated that this polyorganosilazane precursor could be cured rapidly at either air atmosphere or nitrogen atmosphere. The curing reactions take place rapidly within about 15 and 40 s at nitrogen and air atmosphere under UV irradiation, respectively. After exposed under UV light for 40 s at air atmosphere, the conversion percentage of the unsaturated bond of the cured polyorganosilazane sample is near to 90%. The results suggest that incorporating acrylic pendant groups with high UV sensitivity into polyorganosilazane molecular structure is an effective way to increase its curing speed.

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Keywords: Ultraviolet; Rapid curing; Polyorganosilazane

1. Introduction

Polyorganosilazanes ceramic precursors, mainly synthesized via ammonolysis from chlorosilanes, can conveniently be crosslinking into unmeltable, preceramic network. At temperature of about 1000 °C, this network can be pyrolysed and further transformed to amorphous silicon carbonitrides, and at temperature above 1440 °C, the amorphous networks finally crystallize to silicon nitride and silicon carbide [1–3]. Such polyorganosilazanes derived ceramics can remain mechanically stable in both high temperature and high oxidation corrosive environments. So polyorganosilazanes precursors have attracted considerable interest in recent years, owing to their promising potential for formation of ceramic materials [4,5]. For example, they are considered as ultra-high temperature and oxidation resistance materials for the microelectromechanical systems (MEMS), which could be applied in aerospace, microcombustors, heat exchanges and high-energy microoptics systems fields [6,7].

However, one of the crucial technologies is how to fabricate these ceramic apparatuses of MEMS system by less processing steps or free-mould process, especially compared with traditional thermal crosslinking, pyrolysis and annealing process. The photo-polymerization including ultraviolet (UV) irradiation over polyorganosilazanes has been approved as an effective way to fabricate ceramics of MEMS. The method possesses several advantages. At first, UV-curing of precursor requires low cost mold or free mold. Secondly, it enables one easily to obtain freestanding polymer structure for crosslinking and pyrolysis. At last, by controlling the spin speed of precursor, some complex thin membrane-like layers ‘green’ sample can be retained [8].

Liquid silazanes or polysilazanes precursors containing vinyl groups, such as 1,3,5-trivinyl-1,3,5-trimethylcyclo-trisilazane and hydridopolysilazane can be used in this field. However, even with large amounts of photoinitiator, the curing speed of these precursors is low as compared with other typical UV-curable (meth)acrylates [9], branched oligo[(methylsilylene)methylene] [10], methacrylates hyperbranched poly(amine-ester)s [11] or photocrosslinkable polysiloxanes bearing gem di-styrenyl groups [12]. So the exploration of a novel polyorganosilazane, which could be cured more rapidly under UV irradiation, is one of the important issues for

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improving the process of fabrication ceramic apparatuses of MEMS.

A thiol-ene polymerization of these polyorganosilazane precursors has been reported as an effective method to overcome the significant limitations of low curing depths and slow polymerization rates [13,14]. In our viewpoint, the other effective solution is to incorporate high UV sensitivity groups such as (meth)acrylic pendant groups into polyorganosilazanes. In this paper, a novel ultraviolet-curable polyorganosilazane ceramic precursor was synthesized via ammonolysis from modified chorosilane, which could be synthesized by alcoholysis of trichloro(methyl)silane and 2-hydroxyethyl acrylate. This synthesized organometallic compound was well characterized by using Fourier transformed infrared spectroscopy (FTIR), ^1H nuclear magnetic resonance (^1H NMR), ^{29}Si nuclear magnetic resonance (^{29}Si NMR), and multi-angle laser light scattering (LLS). Its UV curing behavior determined via FTIR and differential scanning calorimeter (DSC) clearly shows that this polyorganosilazane precursor could be cured rapidly in either air atmosphere or nitrogen atmosphere. It demonstrates that incorporating acrylic pendant groups with high UV sensitivity into polyorganosilazane molecular structure is an effective way to increase its curing speed.

2. Experiments

2.1. Materials

Trichloro(methyl)silane (CH_3SiCl_3) (more than 99.0% purity) was purchased from Xin'an Chemical Ltd (Xin'an city, Zhejiang Province, China) and was distilled before the synthesis. 2-Hydroxyethyl acrylate ($\text{CH}_2=\text{CHCOOCH}_2\text{CH}_2\text{OH}$) was supported from Luoyang Hengguang Chemical Plant (Luoyang city, Henan Province, China). Pyridine was purchased from Xi'an agent plant (Xi'an city, Shannxi Province, China). Ammonia (received state, more than 99.9

purity) and nitrogen were purified by pass through successive columns of potassium hydroxide. Photoinitiator (commercial brand: IHT-PI 185) was commercially available from Insight High Technology Corporation Ltd (Beijing City, China). Tetrahydrofuran (THF) and pyridine were purchased from Tianjin kernel chemical reagents development center (Tianjin City, China) and dried with 4 Å grade molecular sieve before being used.

2.2. Synthesis of 2-(dichloro(methyl)silyloxy)ethyl acrylate

The polyorganosilazane and some starting materials are sensitive to moisture and air. Thus, the operations, e.g. synthesis, purification and depositary were carried out in an inert nitrogen atmosphere. In a typical experiment, 0.15 mol (22.4 g) of trichloro(methyl)silane (CH_3SiCl_3), 0.15 mol (11.8 g) of pyridine and 100 mL of tetrahydrofuran solvent were mixed in a 250 mL flask equipped with a nitrogen atmosphere inlet in ice-water bath. After the mixture was saturated with nitrogen atmosphere under vigorous magnetic stirring, 0.15 mol (17.4 g) of 2-hydroxyethyl acrylate was added to the mixture drop by drop within 30 min. The pyridinium hydrochloride precipitated soon as white deposition, and the schematic process of the reaction was presented in Fig. 1. After the reaction was performed in ice-water bath at about 0°C for 90 min, the deposition was filtered. The clear filtrate was the 2-(dichloro(methyl)silyloxy)ethyl acrylate (**1m**) solution in THF. **1m**: Annal. Found: IR (KBr): 1730 br ($\nu_{\text{as}} \text{C}=\text{O}$), 1410, 1637 ($\nu\text{-CH}=\text{CH}_2$), 1260 ($\nu\equiv\text{Si-CH}_3$). ^1H NMR(CDCl_3): ppm δ 0.17–0.19 ($\equiv\text{Si-CH}_3$), 3.91–4.05 ($\equiv\text{Si-O-CH}_2\text{-CH}_2\text{-O-}$), 4.28–4.32 ($\equiv\text{Si-O-CH}_2\text{-CH}_2\text{-O-}$), 6.12–6.21 ($-\text{CH}=\text{CH}_2$), 5.86–5.89 6.44–6.48 ($-\text{CH}=\text{CH}_2$); ^{29}Si NMR(CDCl_3): ppm δ : -2.5 ($\text{SiCl}_2\text{OCH}_2\text{CH}_2\text{COOCHCH}_2$), -11.2 ($\text{SiCl}(\text{OCH}_2\text{CH}_2\text{COOCHCH}_2)_2$), -14.5 ($\text{Si}(\text{OCH}_2\text{CH}_2\text{COOCHCH}_2)_3$). CH_3SiCl_3 monomer: ^{29}Si NMR(CDCl_3): ppm δ : 12.5 (CH_3SiCl_3).

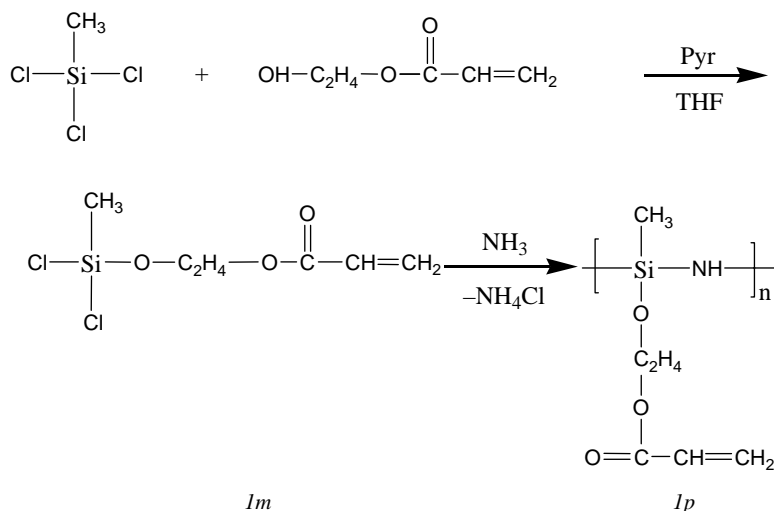


Fig. 1. Reaction scheme of synthesis of UV-curable polyorganosilazane.

2.3. Synthesis of UV-curable polyorganosilazane by ammonolysis

Sixty grams of dichloromethyl (2-hydroxyethyl acrylate) silane solution in tetrahydrofuran were added into a 250 mL flask equipped with a nitrogen atmosphere inlet, a mechanical stirrer and ice-water bath. Ammonia was slowly introduced under vigorous stirring, which caused immediate ammonium chloride precipitation at 0 °C. The reaction mixture were then warmed to 25 °C and conducted for 120 min.

When the reaction was end, the ammonium chloride precipitate was firstly removed by filtration. Subsequently, the ammonium chloride precipitate was thoroughly extracted three times with each 100 mL of tetrahydrofuran. After combining the filtrate and extract, the removing excess ammonia and solvent were evaporated under reduced pressure at 55 °C/10⁻⁴ bar in the vacuum revolving distillation apparatus. Thus, about 18.2 g of [-SiCH₃(OCH₂CH₂-OOCCHCH₂)-NH-]_n (**1p**) was obtained as a yellow viscous liquid. **1p**: ¹H NMR(CDCl₃): ppm δ 0.17–0.19 (≡Si-CH₃), 3.87–3.90 (≡Si-O-CH₂-CH₂-O-), 4.34–4.38 (≡Si-O-CH₂-CH₂-O-), 6.15–6.21 (-CH=CH₂), 5.80–5.82, 6.43–6.47 (-CH=CH₂); IR (KBr): 3340 (ν_{as} N-H), 1721 (ν_{as} C=O), 1410, 1637 (ν-CH=CH₂), 1260 (ν≡Si-CH₃); the viscosity (25 °C): 0.04 Pa s; weight-average molecular weight (*M_w*): 2050 g/mol, the average RMS radius (*R_z*): 9.8 nm (in THF).

2.4. UV irradiation process of polyorganosilazane

The ultraviolet light source used for irradiation is a lamp (HOK 4/12, 400 W, Philips, Netherlands), which emits light in the near UV (λ ≥ 300 nm; characterized wavelength, 340–360 nm). The UV irradiation apparatus in both air and nitrogen atmosphere is schematically shown in Fig. 2. The resin was prepared by adding 5 phr of photoinitiator (IHT-PI 185) into the original polyorganosilazane. A thinner uniform film of mixture was laid on the glass plate. Then the glass plate samples were put in the UV irradiation apparatus and were irradiated for different time. The distance between polyorganosilazane samples and UV lamp was about 10 cm.

2.5. FTIR spectra analyses

FTIR spectroscopy (WQF-31 model, Rui Li Co. Beijing, China) was employed to characterize synthesized polyorganosilazane using thin KBr as the sample holder. Transition mode

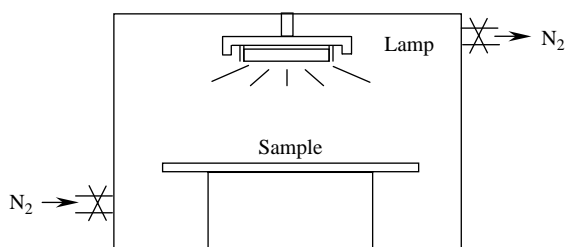


Fig. 2. UV irradiation apparatus at both air and nitrogen atmosphere.

was used and the wavenumber range was set from 4000 to 400 cm⁻¹ (resolution 1 cm⁻¹, measuring time 300 s).

2.6. NMR spectra analyses

¹H NMR and ²⁹Si NMR measurements of monomers and liquid polyorganosilazane were conducted on Avance 500 spectrometer (Bruker Biospin, Switzerland, frequency: ¹H 500 MHz) at room temperature using CDCl₃ as the solvent. Tetramethylsilane (TMS) in CDCl₃ was used as internal standard.

2.7. Laser light scattering analyses

The weight-average molecular weight (*M_w*) was determined by multi-angle laser light scattering (LLS) instrument equipped with a He-Ne laser (λ = 690 nm, DAWN[®] EOS[™], Wyatt Technology Co., St Barbara, CA, USA) at 25 °C. The HPLC grade tetrahydrofuran was used as solvent. The polymer solution of desired concentration was prepared, and optical clarification of the solution was achieved by filtration through a 0.45 μm pore size filter (PTFE, Paradise 13 mm Syringes Filters, Whatman, England) into the scattering cell of LLS. The value of refractive index increment (dn/dc) (in THF, 25 °C) was measured in the refractive index instrument (Optilab rEX, Wyatt Technology Co., St Barbara, USA). The dn/dc value of sample in THF solution was determined to be 0.055 mL/g. To calculate molecular weight of polymer, ASTRA software (Version 5.1.3.0) was utilized for data acquisition and analysis.

From the LLS data, we can obtain the weight-average molecular weight (*M_w*) and the average root-mean square radius of gyration of polymer in dilute solution from Zimm plot by the following equations.

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} \left[1 + \frac{16\pi^2 n^2}{3\lambda_0^4} \langle S^2 \rangle \sin^2(\theta/2) + \dots \right] + 2A_2 C \quad (1)$$

$$Kc = \frac{4\pi^2 n^2}{N_A \lambda_0^4} \left(\frac{dn}{dc} \right)^2 \quad (2)$$

where *R_θ*, *n*, *A₂*, *N_A*, λ₀, dn/dc are excess Rayleigh ratio, solvent refractive index, the second Virial coefficient, the Avogadro number, vacuum wavelength of incident light and refractive index increment, respectively.

2.8. Determination of conversion of unsaturated bond by FTIR

FTIR spectroscopy (WQF-31 model, Rui Li Co. Beijing, China) was employed to determine polyorganosilazane's relative conversion percentage (CP) of unsaturated bond during UV curing progress. The original polyorganosilazane and photoinitiator mixture (liquid) was spreading on the KBr plates and cured under UV irradiation directly. The relative conversion percentage of unsaturated bond in the UV-cured films was determined by using stretching vibration of the acrylate carbon-carbon double bond at 1637 cm⁻¹ [15].

The spectra were normalized with the carbonyl peak at 1721 cm^{-1} as an internal standard to account for variations in sample thickness and instrument recording [11]. The unsaturated bond content (A_0) of the uncured sample added with photoinitiator was defined as 100%. If the unsaturated bond content (A_t) of the sample irradiated with t time was defined as A_t , the CP of unsaturated bond could be calculated as follows.

$$\text{CP}(\%) = \left(\frac{A_0 - A_t}{A_0} \right) \times 100\% \quad (3)$$

2.9. DSC instrument analyses

The UV curing behaviors of polyorganosilazane were also investigated by differential scanning calorimeter (DSC) analysis to validate qualitatively the results from FTIR. DSC analysis was carried out with MDSC 2910 (TA instruments, New coast, USA). The temperature was calibrated with indium ($156.6\text{ }^\circ\text{C}$) and the heat flow rate was calibrated with the specific heat of fusion of indium (28.71 J/g) at a scanning rate of 10 K/min . The furnace was purged with dry nitrogen at a flow rate of 50 mL/min . The sample about 3.0 mg was sealed in aluminum pans and the temperature range was from 25 to $310\text{ }^\circ\text{C}$ at a scanning rate of 10 K/min .

2.10. Thermalgravimetric analyzer analyses

Thermalgravimetric analyzer (TGA) analysis of polyorganosilazane was performed on TQ-80 (TA Instruments, New coast, USA). About 10.0 mg of UV cured sample was put in alumina crucible and heated from 25 to $800\text{ }^\circ\text{C}$. The heating rate was set as 20 K/min (nitrogen atmosphere, flow rate of 150 mL/min).

3. Results and discussion

3.1. Spectra and LLS analyses of the UV-curable polyorganosilazane

The UV-curable polyorganosilazane (**1p**) was synthesized via ammonolysis from 2-(dichloro(methyl)silyloxy)ethyl acrylate (**1m**), which was prepared by alcoholysis of trichloro(methyl)silane and 2-hydroxyethyl acrylate. The FTIR and ^1H NMR spectra of the UV-curable polyorganosilazane (**1p**) were shown in Figs. 3(A) and 4, respectively.

As shown in Fig. 3(A), the variation peak of hydroxy groups (at 3400 cm^{-1}) was not existing in the spectrum. At the same time, the ^1H NMR spectrum also demonstrates the hydroxy group of 2-hydroxyethyl acrylate was not existing in the compound (Fig. 4). These indicated the hydroxy groups of 2-hydroxyethyl acrylate were consumed. The IR and ^1H NMR data listed in experimental section, such as double bond group (at 1637 cm^{-1}), methyl silicon group (at 1260 cm^{-1}), were in accordance with the objective molecular structure of synthesized compound. The weight-average molecular weight (M_w) of the yellow viscous liquid was determined with multi-angle laser light scattering instrument at $25\text{ }^\circ\text{C}$. Zimm plot of

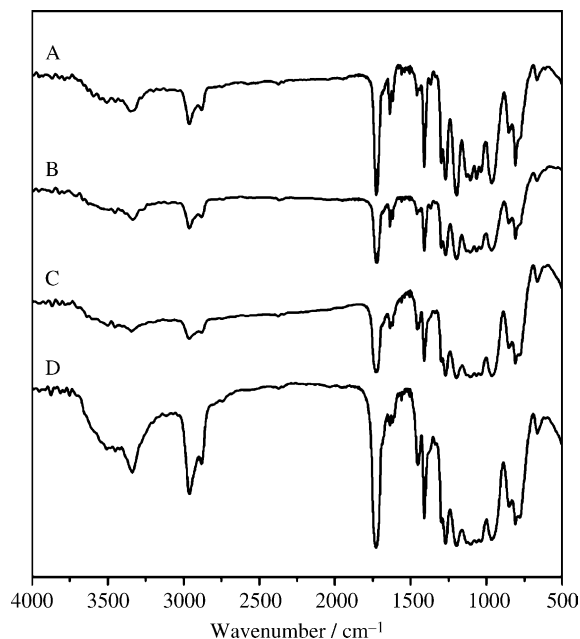


Fig. 3. FTIR spectra of UV-curable polyorganosilazane cured with different times.

UV-curable polyorganosilazane determined by LLS instrument was presented in Fig. 5. Based on the Zimm plot and the dn/dc value of sample in THF solution (0.055 mL/g), weight-average molecular weight of was determined to be 2050 g/mol . So the polyorganosilazane should be considered as an oligomer. In addition, since the molar ratio of trichloromethylsilane and 2-hydroxyethyl acrylate was 1, the dichloromethyl(2-hydroxyethyl acrylate)silane was the main product. This can be approved by the ^{29}Si NMR spectra of **1m** in THF and starting monomer of trichloro(methyl)silane presented in Fig. 6. The spectra (chemical shifts of silicon were listed in experiments) clearly demonstrate that only a few by-products exist in

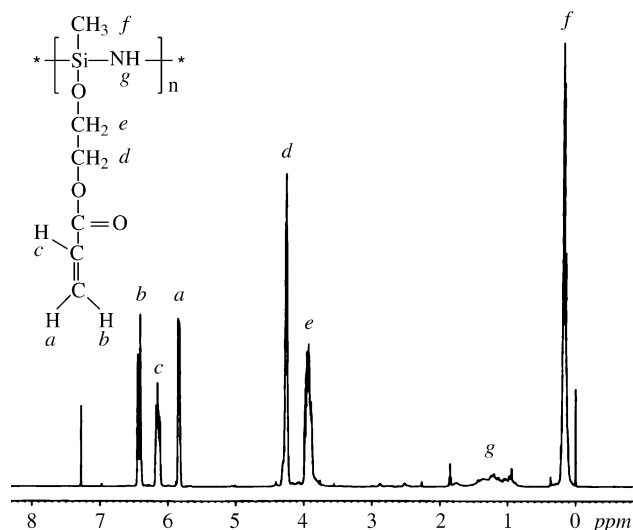


Fig. 4. ^1H NMR spectrum of UV-curable polyorganosilazane.

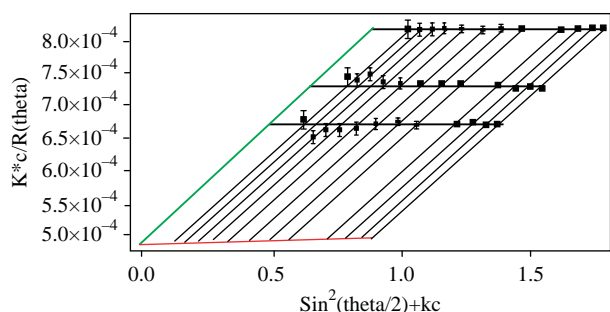


Fig. 5. Zimm plot of UV-curable polyorganosilazane determined by LLS instrument.

the monomer solution after alcoholysis of trichloro(methyl)silane and 2-hydroxyethyl acrylate.

3.2. UV curing behaviors of UV-curable polyorganosilazane

UV curing behaviors of polyorganosilazanes can be monitored by infrared spectroscopy techniques. That is, during the curing progress, by detecting the change of peak area of reactive groups, such as vinyl initiated by UV irradiation, one can understand relative conversion percentage (CP) of double bond and the cross-linking extent for the reaction [11,15].

However, the shortcoming of this method is that its accuracy is slightly affected by the sample themselves and the addition of additives. For the polyorganosilazane synthesized in this study, the stretching vibration of double band at about 1637 cm^{-1} can be altered by the band of phenyl group in photoinitiator as presented in Fig. 7. Fortunately, the amount of the photoinitiator in the reaction mixture is much smaller and the mixture added with this compound can be used as the reference just as described in Section 2. In this paper, the FTIR spectroscopy was employed to determine polyorganosilazane's relative CP of unsaturated bond during UV curing progress. Differential scanning calorimeter analysis was also conducted to validate qualitatively the results determined from FTIR. The spectra of polyorganosilazane cured with different time were presented in Fig. 3, and the DSC exothermal curves of original UV-curable polyorganosilazane and those samples cured with different times at air atmosphere were shown in Fig. 8. The CP of unsaturated band for polyorganosilazane mixture samples versus irradiation time at air and nitrogen atmosphere was presented in Fig. 9.

As can be seen from Fig. 9, the CP of unsaturated bond for polyorganosilazane is increasing with the increasing of irradiation time. It indicates that the synthesized polyorganosilazane is very sensitive to UV light just as expected as design. When the sample was exposed under UV light at air

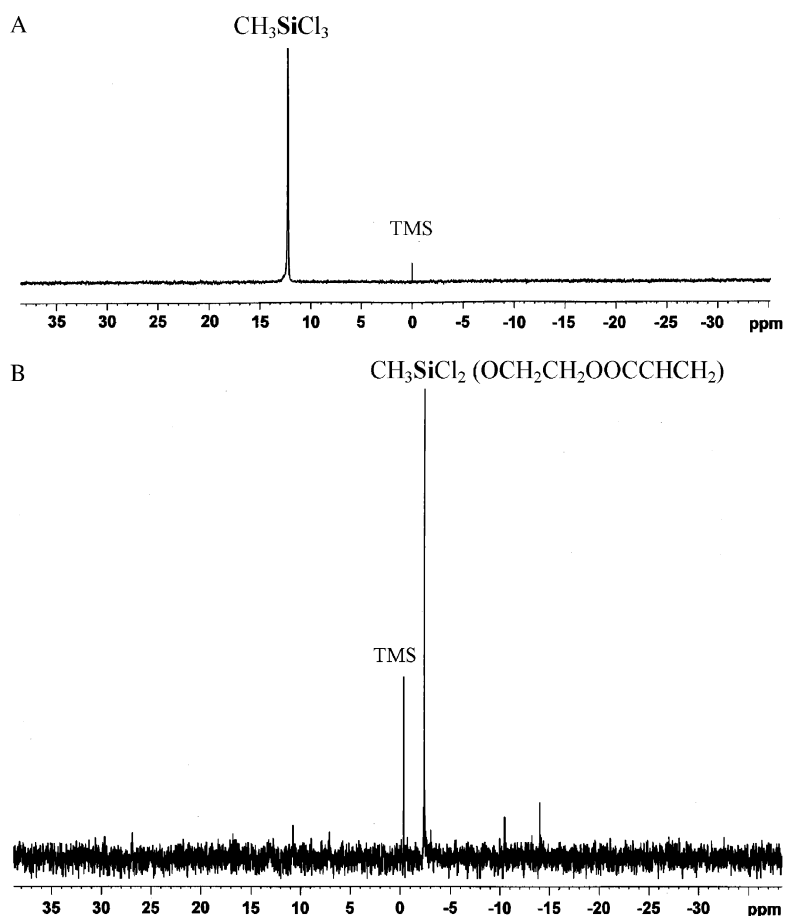


Fig. 6. ^{29}Si NMR spectra of monomers, (A) spectrum of trichloro(methyl)silane, (B) spectrum of **1m** in THF.

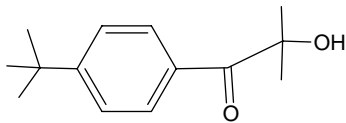


Fig. 7. Molecular formula of photoinitiator commercially named IHT-PI 185.

atmosphere for 40 s or at nitrogen atmosphere for 15 s, the CP of unsaturated bond for polyorganosilazane is near to 90%. The result can be approved by DSC exothermal curves of original UV-curable polyorganosilazane and its samples cured with different time at air atmosphere as shown in Fig. 8. For the polyorganosilazane samples cured under UV irradiation for different time, such as 10, 20 and 30 s, the area of exothermal peaks area decreases with the increase in irradiation time. But when the irradiation time is more than 40 s, the exothermal peak of unsaturated bond for the sample nearly disappears. The phenomena are due to the decreasing in content of residual unsaturated bond of polyorganosilazane, which has been consumed during the UV curing progress.

To our knowledge, the polyorganosilazanes containing silicon vinyl group ($\equiv\text{Si}-\text{Vi}$), i.e. polymethylvinylsilazane, could be cured at least for 20 min in the same UV irradiation environment [16,17]. So the results of UV curing for this polyorganosilazane demonstrate that it indeed can be cured much more rapidly compared with congeneric monomers. The main reason can be attributed to the high reactive properties of unsaturated bond covalence with carbonyl. On the other hand, only for 15 s, the sample reaches the high

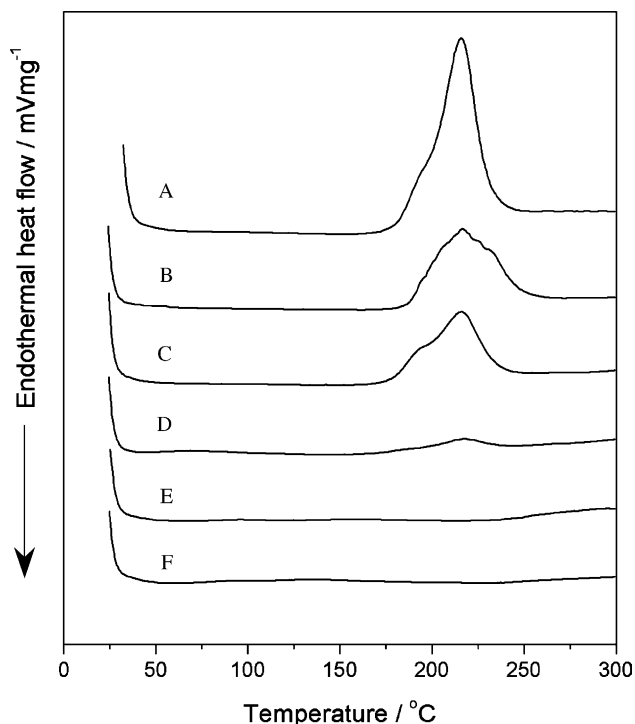


Fig. 8. DSC exothermal curves of polyorganosilazane cured with different times.

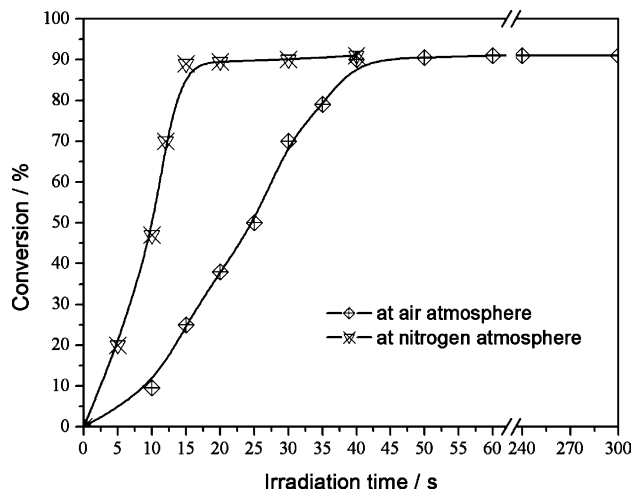


Fig. 9. Conversion percent of unsaturated bond for UV cured polyorganosilazane.

conversion percentage of about 90% at nitrogen atmosphere. It suggests that the polyorganosilazane can be cured even more rapidly in appropriate environment. The mechanisms of the reactions affected by different atmosphere may be attributed to the difference between the photo-initiated free radical polymerizations. As for UV-induced free radical polymerization, free radical can be coupled by oxygen in air and loses its reactivity. Thus, the polymerization can be halted consequently [18]. However, the oxygen can be eliminated through the nitrogen purging, as a result, the polyorganosilazane cures more rapidly at the nitrogen atmosphere.

3.3. Thermal stability of the UV-cured polyorganosilazane

Thermogravimetric analyzer (TGA) was employed to investigate the thermal stability of UV-cured polyorganosilazane. The weight and weight loss rate curves during heating were presented in Fig. 10. It can be seen that

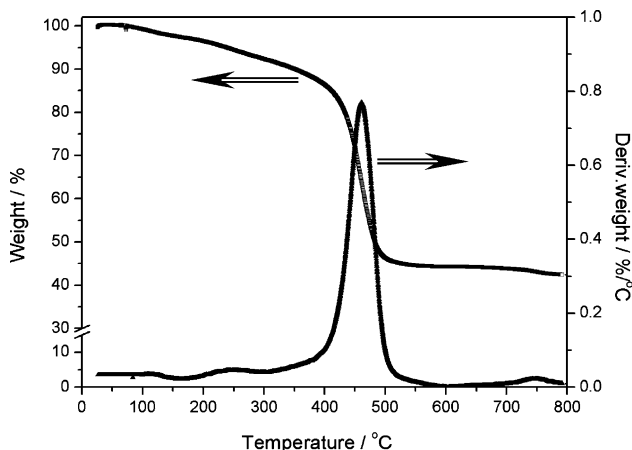


Fig. 10. Thermogravimetric analyzer curves for UV cured polyorganosilazane.

decomposition temperature (5 wt% loss) and temperature of maximum weight loss rate for cured polymers is about 244 and 450 °C, respectively. The residual weight of sample near to 800 °C is about 45%. Compared with other polysilazanes, such as hydridopolysilazane, polymethyl(hydro)silazane, polymethyl(hydro)/polydimethylsilazane and polymethyl/polymethylvinylsilazane, both the decomposition temperature and residual weight (ceramic yield) of the UV-cured polyorganosilazane is low [19]. The main reason is that much organic groups, i.e. acrylic pendant groups were introduced into the polysilazane. So at the higher temperature, the volatilization was more obviously than the precursors system with high silicon content. This problem might be resolved by introducing the high UV sensitivity groups with low carbon content into the polyorganosilazane. In fact, this is our next project on preparation of the rapid UV-curable polyorganosilazanes.

4. Conclusions

The main conclusions from this paper can be described as follows:

1. Incorporating acrylic pendant groups with high UV sensitivity into polyorganosilazane molecular structure is an effective way to increase its curing speed. Thus, a rapid UV-curable polyorganosilazane was synthesized via ammonolysis from modified chorosilane.
2. The polyorganosilazane can be rapidly cured within 15 and 40 s at nitrogen and air atmosphere under the UV irradiation, respectively. After exposed under UV light for 40 s or for more time at air atmosphere, the conversion percentage of the unsaturated bond of the cured polyorganosilazane is near to 90%.
3. The decomposition temperature and temperature of maximum weight loss rate for the UV cured polyorganosilazane is about 244 and 450 °C, and the residue weight near to 800 °C is about 45%.

Acknowledgements

The financial supports from China Postdoctoral Science Foundation (Grant No. 2005037243), NPU Youthful Teachers Scientific and Technological Innovation Foundation, and NPU Scientific and Technological Innovation Foundation are gratefully acknowledged.

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