Preparation, Cure Kinetics, and Thermal Properties of Novel Acetylene Terminated Silazanes

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ABSTRACT: A new kind of acetylene terminated silazanes, *N*-(3-acetylenephenyl)-diorganosilazanes (abbreviated as APSZs) with three kind of substituents, were synthesized by the aminolysis of dichlorosilane with 3-aminophenylacetylene (3-APA). Structure of APSZs was confirmed by Fourier transform infrared spectroscopy (FT-IR) and nuclear magnetic resonance (NMR). Thermal behavior of the cured silazanes was determined by thermogravimetry analysis (TGA), revealing that cured silazanes exhibited high temperature resistance. The ceramic yields of APSZ-Me$_2$, APSZ-MeVi, and APSZ-Ph$_2$ at 1000°C under nitrogen were 77.6, 81.9, and 68.7%, respectively. The peak separation of derivative thermogravimetric data was employed to evaluate the three major regions of the thermolysis, and the kinetic parameters of thermolysis were calculated by the method of Kissinger from dynamic thermogravimetric measurement in nitrogen atmosphere at several different heating rates. Influence of substituents on the thermal behavior of cured silazanes in each separated region was discussed. The results showed that the vinyl derivative exhibit higher thermal stability than methyl and phenyl derivatives due to the high decomposition activation energy and small pendant group. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1384–1391, 2012

Key words: silazane; cure kinetics; thermal properties

INTRODUCTION

Silazanes are a family of hybrid organic–inorganic materials prepared by the ammonolysis or aminolysis of chlorosilanes.[1] Various silazanes have been synthesized and investigated as precursors of silicon carbonitride ceramic,[2–4] surface modifiers[5] and additives of silicone rubbers.[6,7] Xie and Wang [6] proposed the concept of suppressing the reversion of polysiloxane by using a particular polysilazane as cure agent to improve the thermal stability of room temperature-vulcanized (RTV) silicone rubbers. Silazane effectively impede the rearranging degradation of polysiloxane chain by removal of trace water or Si—OH group using the reactivity of Si—N bond, and thus improve the thermal stability of silicone rubbers.

On the other hand, acetylene-contained organosilicon polymers have continued to be an active research area, because of incorporation of the acetylenyl group improved the thermal stability of the respective polymers. There are many articles available on the preparation of high performance thermosetting resins,[8–10] Si-based ceramic precursor[11–13] and elastomeric polymers containing vulcanizable acetylene moiety as part of the chains or as a pendant functional groups.[14,15] Keller and coworkers synthesized high-temperature elastomers from silarylene-siloxane-diacetylene linear polymers.[16] The linear polymers can be thermally cured through the diacetylene units to elastomeric materials. By varying the distance between two diacetylene units, the crosslinking density can be controlled.

In view of these facts, it is attractive to synthesis compounds containing both Si—N bond and acetylenyl group. Xu and coworkers synthesized 1,3-bis(phenylethynyl)disilazane by the condensation of 1,3-dichlorodisilazane and (phenylethynyl)lithium as a cure agent for silicon rubber.[17] But, to the best of our knowledge, the information of the acetylene terminated silazanes was very limited. In this article, we reported the synthesis of acetylene terminated silazanes with various substituents on silicon atom. The thermal studies were carried out using differential scanning calorimeter (DSC) and thermogravimetric analyzer (TGA) to reveal the influence of the substituents on their thermal behaviors. Cure and thermal decomposition kinetics were determined by the Kissinger method.

EXPERIMENTAL

Materials

All synthetic manipulations were carried out using standard inert atmosphere techniques described by Shriver and Drezdzon.[18] All liquid chlorosilanes were received from Kaihua Organosilicon Chem., and purified by distillation. Toluene and triethylamine were dried by refluxing over sodium benzophenone and distilled under nitrogen atmosphere. The 3-aminophenylacetylene (3-APA, A. R., Jiaozhou Chemicals, Shandong, China) was used as received.
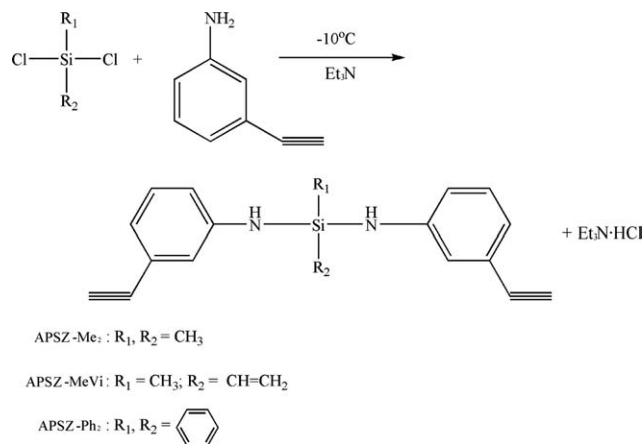
Measurement

Fourier transform infrared (FT-IR) spectrum was recorded on a Bruker 27 IR spectrometer with KBr plate for liquid sample and KBr disk for solid sample. ^1H and ^{29}Si nuclear magnetic resonance (NMR) data were collected using a Bruker DM 300 spectrometer, which was operated at 300.13 MHz for hydrogen-1 and 59.63 MHz for silicon-29 (^1H-decouping), respectively. The ^1H chemical shifts were referred to solvent peak (CDCl$_3$, 7.26 ppm), while the ^{29}Si chemical shifts were all referred to tetramethylsilane (0 ppm). DSC experiment was performed on a Mettler Toledo DSC822^e instrument under nitrogen gas at heating rates of 5, 10, 20, and $30°C$ min^{-1}. The TGA was carried out on a Netzsch STA 409 PC instrument in nitrogen atmosphere with ramping rates of 5, 10, 20, and 30°C min^{-1} from room temperature (RT) to 1000°C. X-ray diffraction (XRD) was carried out by using a PANalytical X'Pert PRO diffractometer with Cu Kα radiation.

Synthesis of N-(3-acetylenephenyl) diorganosilazanes

The syntheses of N-(3-acetylenephenyl)diorganosilazanes were according to the traditional aminolysis procedure (Scheme 1). As an example, N-(3-acetylenephenyl)dimethylsilazane (abbreviated as APSZ-Me$_2$) was synthesized as follows:

A three neck flask equipped with a condenser and a magnetic stirring bar was charged with dry toluene (50 mL) and dichlorodimethylsilane (0.1 mol, 12.1 mL). After cooled down to $-10°C$, 3-APA (0.2 mol, 11.3 mL) dissolved in toluene (30 mL) was added dropwise to the above mixture. The aminolysis reaction occurred and a white precipitation was observed immediately. The mixture was stirred for 1 h at $-10°C$, and then warmed to room temperature for further 4 h. The slurry was filtered under nitrogen atmosphere, and a colorless solution was obtained. After removing the solvent under vacuum, 24.6 g white solid was obtained (85% yield). FT-IR: (KBr, cm^{-1}): 3374 ($v_{=N-H}$, s); 3289 ($v_{C\equiv C-H}$, s); 3025

Scheme 1 Synthesis of APSZs.

(v_{Ph-H}, w); 2983 (v_{C-H}, w); 2103 ($v_{C\equiv C}$, s); 1597, 1576, 1480, 1461 ($v_{C=C}$, s); 1253 (δ_{Si-CH3}, s); 1158 (δ_{N-H}, s); 955 (δ_{Si-N}, s); 787 (δ_{Si-C}, s); ^1H NMR (ppm): 0.42 (s, Si—Me), 3.01 (s, C≡C—H), 3.74 (s, N—H), 6.82, 6.96 7.15 (w, phenylene ring protons). ^{29}Si—NMR (ppm): -11.97 (Me$_2$Si—N).

N-(3-acetylenephenyl)methylvinylsilazane (abbreviated as APSZ-MeVi) and N-(3-acetylenephenyl)diphenylsilazane (abbreviated as APSZ-Ph$_2$) were prepared similarly to APSZ-Me$_2$, using MeViSiCl$_2$ and Ph$_2$SiCl$_2$ (Ph: phenyl), respectively.

APSZ-MeVi was obtained as yellow viscous liquid (yield: 65%). FT-IR: (KBr, cm^{-1}): 3380 (v_{N-H}, s); 3289 ($v_{C\equiv C-H}$, s); 3025 (v_{Ph-H}, w); 2983 (v_{C-H}, w); 2103 ($v_{C\equiv C}$, s); 1599, 1578, 1490, 1470 ($v_{C=C}$, s); 1405 ($\delta_{Si-C=C}$, w); 1253 (δ_{Si-CH3}, s); 1159 (δ_{N-H}, s); 960 (δ_{Si-N-C} s); 787 (δ_{Si-C}, s); ^1H NMR (ppm): 0.48 (s, Si—Me), 3.02 (s, C≡C—H), 3.73 (s, N—H), 6.01, 6.20 (w, CH = CH$_2$) 6.79, 6.91, 7.05, 7.19 (w, phenylene ring protons). ^{29}Si—NMR (ppm): -21.78 (MeViSi—N).

APSZ-Ph$_2$ was obtained as a white solid (yield: 59%). FT-IR (KBr, cm^{-1}): 3366 ($v_{=N-H}$, w); 3289 ($v_{C\equiv C-H}$, w); 3025 (v_{ph-H}, w); 2983 (v_{C-H}, w); 2103 ($v_{C\equiv C}$, w); 1601, 1576, 1491, 1461 ($v_{C=C}$, s);1253 (δ_{Si-CH3}, s); 1160 (δ_{N-H}, s); 957 (δ_{Si-N-C} s); 787 (δ_{Si-C}, s); ^1H-NMR (ppm): 3.01 (s, C≡C—H), 4.22 (s, N—H), 6.87, 6.99, 7.40, 7.68 (w, phenylene ring protons). ^{29}Si-NMR (ppm): -29.38 (Ph$_2$Si—N).

Cure and pyrolysis of N-(3-acetylenephenyl) diorganosilazanes

To evaluate thermal behaviors of the silazanes, cured silazanes were prepared according to the following procedure. The sample was introduced into the aluminum oxide furnace, and N$_2$ of 200 cm^3 min^{-1} was purged for 15 min to remove oxygen. Then the gas flow was set at 50 cm^3 min^{-1} during the curing. The temperature program of cure was ambient temperature to 170°C at 10°C min^{-1}, hold at
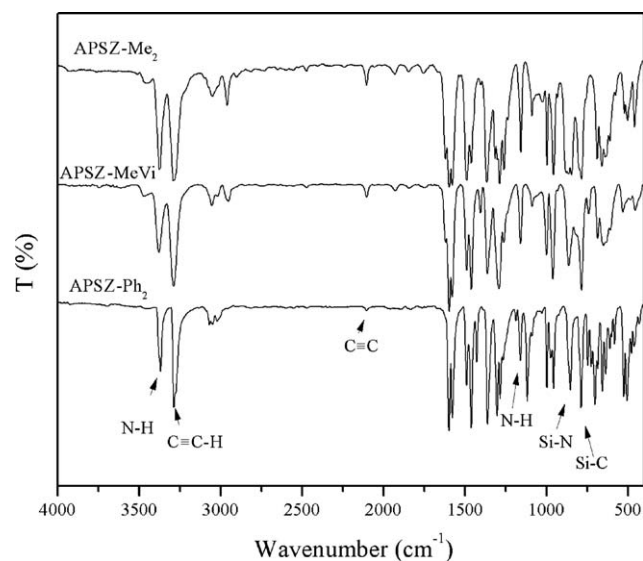
Figure 1 FT-IR spectra of APSZs.

170°C for 2 h, 170–200°C at 10°C min^{-1}, hold at 200°C for 2 h, 200–250°C at 10°C min^{-1}, and hold at 250°C for 4 h. The temperature program of pyrolysis was ambient to 1200, 1400, and 1600°C at 40°C h^{-1}, and hold at top temperature for 2 h, respectively.

RESULTS AND DISCUSSION

Synthesis and characterization of N-(3-acetylenephenyl)diorganosilazanes

A series of acetylene terminated silazanes, with different substituents on silicon atom, were prepared by aminolysis of dichlorosilane and 3-aminophenylacetylene as shown in Scheme 1. All N-(3-acetylenephenyl)diorganosilazanes, abbreviated as APSZs, are tractable and can be dissolved in organic solvents, such as toluene, hexane, and tetrahydrofuran (THF).

Structures of the silazanes were characterized by FT-IR and NMR. The FT-IR spectra (Fig. 1) show the characteristic absorption of Si—N group at 955 cm^{-1}, and secondary amine at 3374 cm^{-1}.[17] Peaks at 3289 and 2103 cm^{-1} are assigned to C:C—H and C:C group.[19] The ^{1}H NMR spectra of samples were shown in Figure 2. The peak at 3.01 ppm is assigned to acetylene and the wide peak at around 3.73 to 4.22 ppm is assigned to amino proton.[20] The ^{29}Si-NMR spectrum of sample (Fig. 3) consists of one resonance peak, indicate there are only one kind of Si in as-synthesized product.

It is well known that polysilazane can be formed from the aminolysis or ammonolysis reaction of halogenosilanes. But the structure characterization of APSZs indicated the as-synthesis product was monomer, suggesting that the reaction of N—H of APSZs and Si—Cl was restrained by the steric effect of phenyl pendant group.

Thermal cure studies of APSZs

The DSC diagrams of the three silazanes were given in Figure 4. The principally thermal characteristics of the silazanes, such as the melting point (T_m), cure onset temperature (T_o), cure peak temperature (T_p), and enthalpy of reaction (ΔH) were summarized in Table I. The three silazanes with different pendant group have different melting points. The asymmetrical substituted silazane APSZ-MeVi is liquid at room temperature, while APSZ-Me$_2$ and APSZ-Ph$_2$ with symmetrical substituents are solid. The molecular weight of pendant group also impacts the melting point. Methyl substituted silazane APSZ-Me$_2$ has 40°C lower melting point than that of phenyl substituted.

The thermal diagrams of three silazanes show only distinct exothermic peak from the polymerization of acetylenyl group in the temperature ranges of
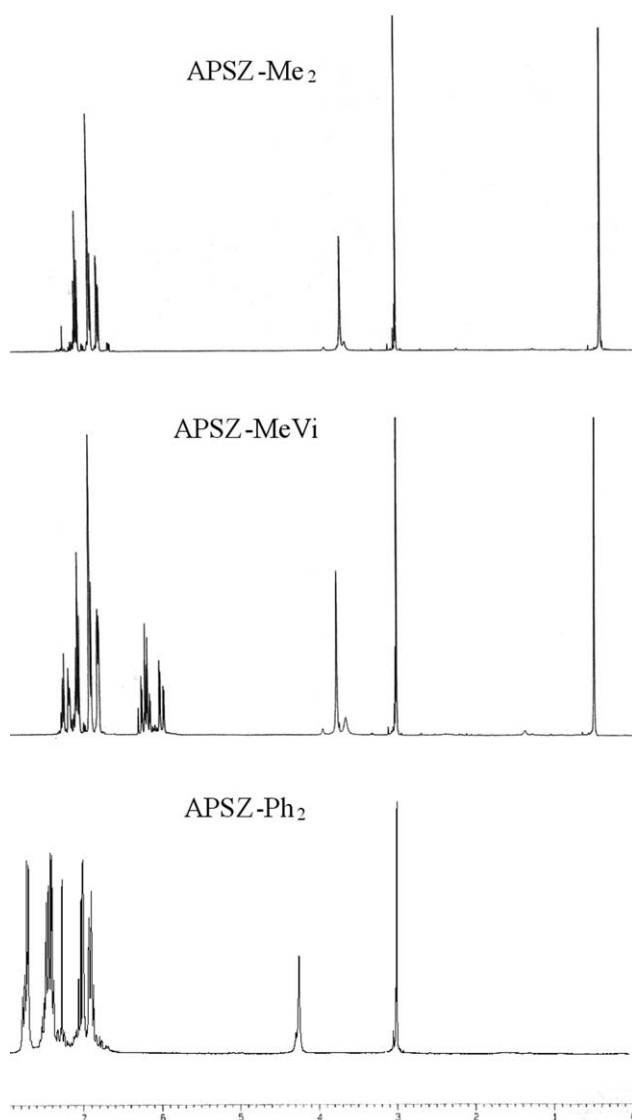

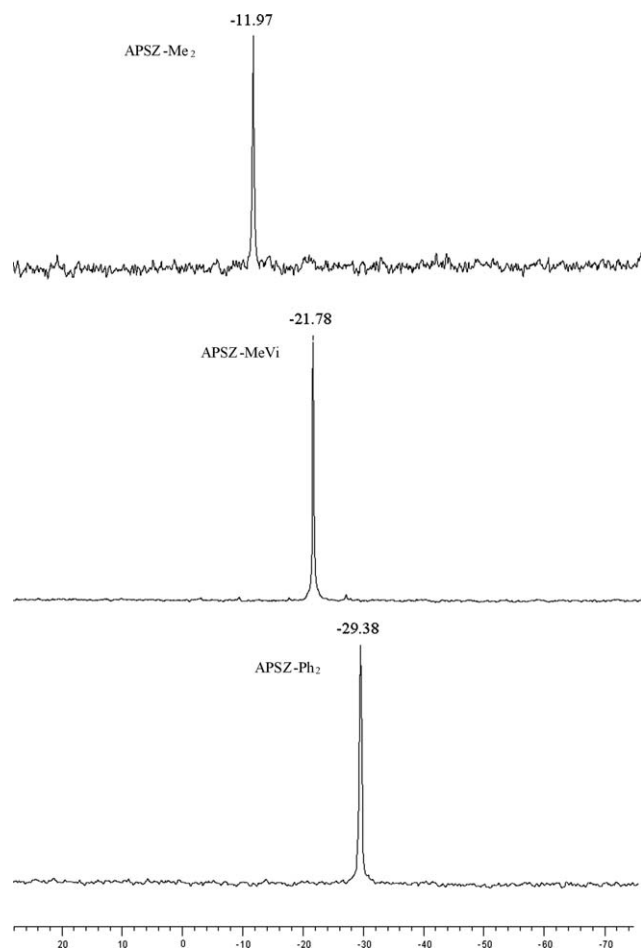**Figure 2** ^{1}H NMR spectra of APSZs.

Figure 3 ^{29}Si NMR spectra of APSZs.

TABLE I
Thermal Characteristics of DSC Curves

Compounds	T_m (°C)	T_o (°C)	T_p (°C)	ΔH (J g^{-1})
APSN-Me$_2$	90.7	217.2	243.8	329.3
APSN-MeVi	–	218.1	245.3	575.5
APSN-Ph$_2$	130.6	217.9	241.2	265.9

Heating rate 10°C min^{-1}, N2 50 mL min^{-1}.

linking density should suppress the decomposition pathways and result in high ceramic yields.

The cure reaction of APSZ-MeVi was also monitored by FT-IR. The spectra were recorded in the solid state as KBr pellets. As shown in Figure 5, the intensities of the bands at 3289 cm^{-1} (C≡C—H) and 1405 cm^{-1}(Si—Vi) simultaneously decreased with temperature increased,[21] suggesting partly vinyl group polymerization with acetylenyl group. After postcured at 250°C, the absorption of acetylenyl group at 3289 cm^{-1} almost disappeared, indicating the cure of acetylenyl group completed, but there were still weak absorptions of vinyl group at 1405 cm^{-1} which disappeared until heated to 400°C. The results of FT-IR analysis also confirm that partly vinyl group polymerization with acetylenyl group.

200–280°C. It is noteworthy that the vinyl substituted APSZ-MeVi have the same T_p of exothermic peak with phenyl and methyl derivatives, and the ΔH of APSZ-MeVi is 240 kJ mol^{-1} higher than methyl derivative, which indicating the partly vinyl group polymerization and increase the enthalpy. The high cross-
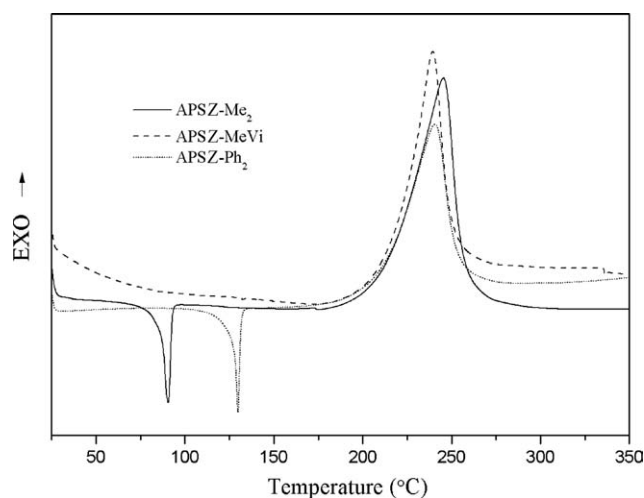
Cure kinetics of APSZs

DSC analysis has been widely utilized to elucidate the cure kinetics of thermosetting resins.[20] Here multiple-heating rate nonisothermal methods have been employed to determine the cure kinetics of the above silazanes.[22] This kind of method is isoconversion method, which assumes that the conversion value is constant at the peak exothermic temperature and does not depend on the heating rate. This makes it equally effective for both nth order and the
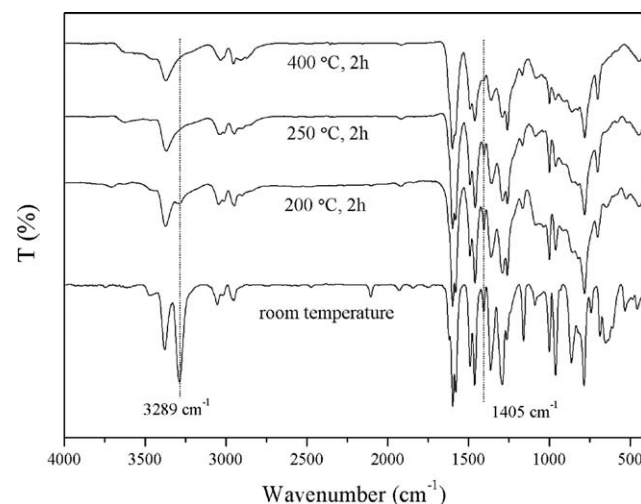

Figure 4 DSC diagrams of APSZs.

Figure 5 FT-IR spectra of APSZ-MeVi at different cure stages.

TABLE II
Characteristics of Nonisothermal DSC Scans for the APSZs

Monomer	5°C min⁻¹			10°C min⁻¹			20°C min⁻¹			30°C min⁻¹		
	T_o	T_p	T_e	T_o	T_p	T_e	T_o	T_p	T_e	T_o	T_p	T_e
APSN-Me₂	206.5	235.4	247.2	212.7	245.9	256.3	222.7	259.1	273.1	230.2	269.2	283.2
APSN-MeVi	203.8	227.4	238.8	212.6	239.8	250.4	222.8	253.5	265.6	236.8	265.2	280.4
APSN-Ph₂	203.9	230.4	242.8	211.8	241.0	253.3	222.3	253.9	268.1	230.5	263.7	279.7

N2, 50 mL min⁻¹.

autocatalytic reactions. Here the cure kinetics analysis is performed using a general nth order reaction model without consideration of the cure reaction mechanism. The general rate equation was given as follows:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

$$k = A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where α is the degree of the cure reaction, t is the reaction time, k is the rate constant defined by Arrhenius relationship, n is the order of the cure reaction, A is frequency factor, E is activation energy, R is the universal gas constant, and T is temperature in Kelvin. Kissinger method, which has been shown to be effective, was used to calculate the cure kinetics parameters.[22]

Kissinger equation

$$\frac{-E}{R} = \frac{d\mathrm{Ln}(\varphi/T_p^2)}{d(1/T_p)} \tag{3}$$

where T_p is the temperature corresponding to the maximum in the DSC exotherm at heating rate φ.

A was found from the relation

$$A = \frac{\phi E\exp(E/(RT_p))}{RT_p^2} \tag{4}$$

and n was determined by crane equation

$$\frac{d\mathrm{Ln}\phi}{d(1/T_p)} = -\left[\frac{E}{nR} + 2T_p\right] \tag{5}$$

TABLE III
Cure Kinetic Parameters for APSZs

Monomer	Activation energy, E_d (kJ mol⁻¹)	Pre-exp. factor A (1/s)	Reaction order
APSZ-Me₂	112.9	1.16 × 10¹¹	1.08
APSZ-MeVi	111.6	1.17 × 10¹¹	1.09
APSZ-Ph₂	112.3	1.20 × 10¹¹	1.08

A plot of Lnφ versus $1/T_p$ will give a straight line with slope $(-E/nR)$, when $E/nR \gg 2T_p$

The cure reactions of the three silazanes were investigated by the nonisothermal DSC technique at different heating rates of 5, 10, 20, and 30°C min⁻¹ under nitrogen atmosphere. The characteristic temperatures of the cure reactions at different heating rates are listed in Table II.

Table III shows that the cure reactions of the three silazanes are all the first-order kinetic reaction. And they have the almost same activation energy and pre-exponential factor of 112 kJ mol⁻¹, and 1.17 × 10¹¹. These results reveal that the cure reactions of the three silazanes have the same mechanism, and in close agreement with the same shape and T_p of their DSC diagrams.

Proper cure schedule can guarantee good thermal properties to cured resin. In this part the results from nonisothermal DSC scans at different heating rates have been processed to get reasonable cure schedule. To get the processing parameters for silazanes, the T_o, T_p, and T_e in Table II were linear-fit with heating rate φ and the intercepts of the lines were regarded as gel temperature, cure temperature, and postcure temperature, respectively. According to the results in Table IV, the order of cure reactivity of three silazanes was APSZ-MeVi, APSZ-Ph₂, and APSZ-Me₂, with limited difference, and the cure program of silazanes was determined.

TABLE IV
Determination of Cure Processing Parameters for APSZs by Means of Linear-Fitting Method

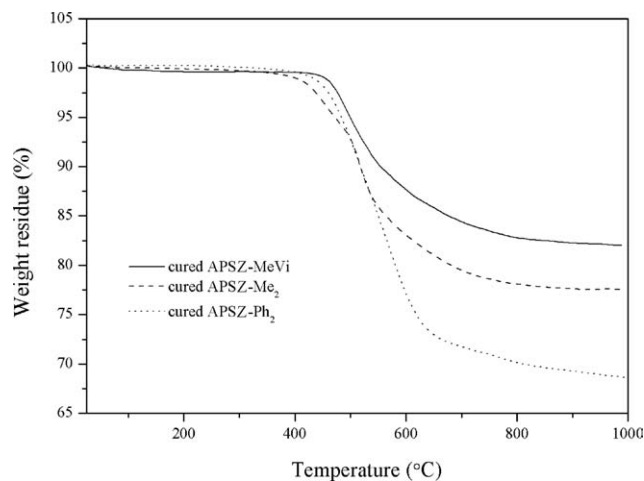| Cure parameter		Linear expression for Fig.	Correlation coefficient (R^2)	Cured parameters determined (°C)
APSZ-Me₂	T_o	$Y = 0.94x + 475.84$	0.9860	202.7
	T_p	$Y = 1.32x + 504.04$	0.9714	230.9
	T_e	$Y = 1.45x + 514.51$	0.9764	241.4
APSZ-MeVi	T_o	$Y = 1.27x + 471.51$	0.9899	198.4
	T_p	$Y = 1.46x + 495.82$	0.9680	222.7
	T_e	$Y = 1.63x + 505.51$	0.9892	232.4
APSZ-Ph₂	T_o	$Y = 1.05x + 473.29$	0.9773	200.4
	T_p	$Y = 1.32x + 498.73$	0.9757	225.6
	T_e	$Y = 1.46x + 510.48$	0.9816	237.3

Figure 6 TGA profiles for cured APSZs.

TABLE V
Typical Parameters of TGA Curves for Cured APSZs

Sample	T_{10} (°C)	T_{max} (°C)	M_{1000} (%)
APSZ-Me$_2$	472.4	494.3	77.6
APSZ-MeVi	499.6	515.4	81.9
APSZ-Ph$_2$	483.9	572.4	68.7

Thermal behavior of the cured APSZs

The thermal behavior of the cured silazanes was examined by thermogravimetric analysis, as shown in Figure 6. Typical parameters for TGA curves, including the temperature at the maximum decomposition rate (T_{max}), temperature where the residual weight is 90% (T_{10}) and residual weight at 1000°C (M_{R1000}), were given in Table V. As shown in Figure 6, all the three cured silazanes exhibit high temperature resistance, whose ceramic yields at 1000°C were 77.6, 81.9, and 68.7% for APSZ-Me$_2$, APSZ-MeVi, and APSZ-Ph$_2$, respectively. The shape of TGA curves indicate that decomposition rate of APSZ-
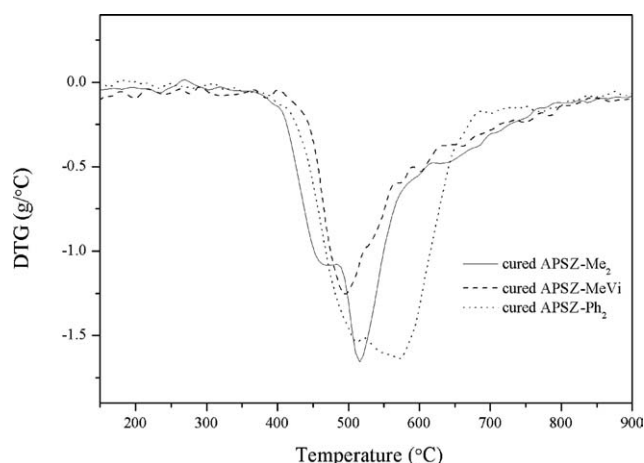
MeVi is much lower than those of APSZ-Me$_2$ and APSZ-Ph$_2$. T_{10} of APSZ-MeVi is 499.6°C, which is the highest among the three silazanes. The ceramic yield of APSZ-MeVi is 4.3% higher than that of APSZ-Me$_2$, indicating the enhancement in the thermal stability. This should be attributed to the
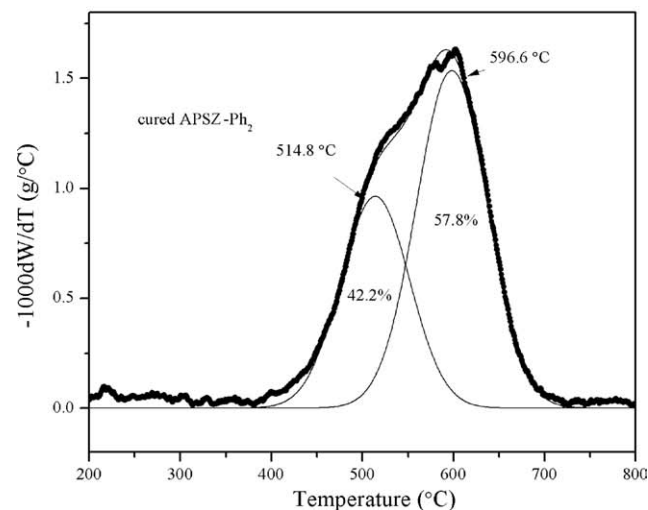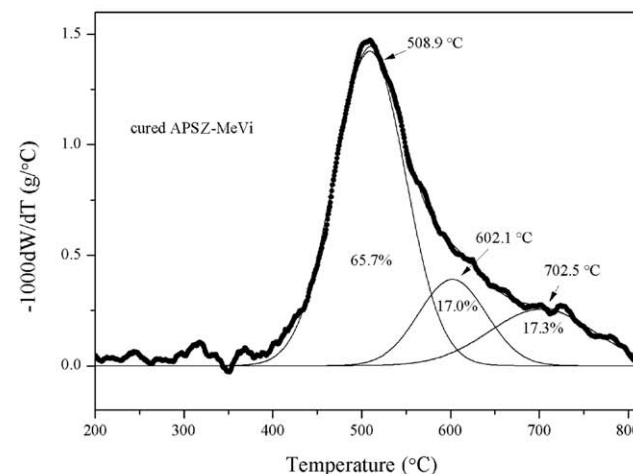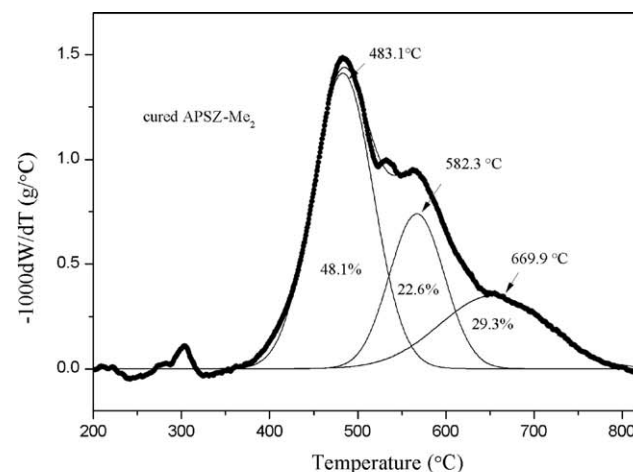

Figure 7 DTG profiles for cured APSZs.

Figure 8 Peak separation of the APSZs mass loss data obtained at 10°C min^{-1} Gaussian curves fit to the mass loss peaks.

TABLE VI
Temperature and Percent Areas Under Curve of Each Separated Peaks

Sample	Heating rate (°C min^{-1})	Peak 1		Peak 2		Peak 3	
		Peak center (°C)	Percent area under curve (%)	Peak center (°C)	Percent area under curve (%)	Peak center (°C)	Percent area under curve (%)
APSZ-Me$_2$	5	452.9	42.2	552.6	28.7	625.9	29.1
	10	483.1	48.1	567.1	22.6	653.3	29.3
	20	504.3	54.4	581.9	26.1	687.4	19.5
	30	511.5	50.8	582.3	31.9	669.9	17.3
	average	–	48.9	–	27.4	–	23.7
	weight loss (wt%)	–	11.2	–	6.1	–	5.3
APSZ-MeVi	5	494.2	69.3	588.9	13.9	677.9	16.8
	10	508.9	65.7	602.1	17.0	702.5	17.3
	20	525.1	68.3	609.6	17.6	697.2	14.1
	30	539.1	62.3	630.2	22.8	725.1	14.9
	average	–	66.4	–	17.8	–	15.8
	weight loss (wt%)	–	12.0	–	3.2	–	2.9
APSZ- Ph$_2$	5	491.8	41.2	573.1	58.8	–	–
	10	514.8	42.2	596.6	57.8	–	–
	20	525.5	47.1	608.9	52.9	–	–
	30	534.9	41.4	619.9	58.6	–	–
	average	–	42.9	–	57.1	–	–
	weight loss (wt%)	–	13.4	–	17.9	–	–

increase of crosslinking density by the polymerization of vinyl group and acetylenyl group. T_{10} of APSZ-Ph$_2$ is 12°C higher than that of APSZ-Me$_2$, indicating the phenyl group effectively suppressed the decomposition at the preliminary stage. However it should be noticed that the large phenyl group eliminated at high temperature and induced the largest weight loss in three silazanes. Compared with other acetylene-contained organosilicon polymers, the residual weight of APSZs is lower, because the Si—N bond is not as stable as Si—C bond in the pyrolysis process. The above analyses reveal that the introduction of vinyl group indeed imparts APSZ-MeVi with better thermal stability.

Decomposition kinetics of APSZs

To study the thermal behavior of silazanes with different pendent groups, weight loss data from the pyrolysis of silazanes in a nitrogen atmosphere were obtained at four heating rates. The pyrolysis behaviors of the three cured silazanes are similar, which has also been reported in many literatures.[21] With increasing heating rate the weight loss curves shift to higher temperature without changing shape. This shift is due to the temperature dependency of the reaction rate and was used by many traditional TGA data analysis methods to calculate kinetic rate expression constants. From the DTG curves as shown in Figure 7, it was found that there are multi peaks in the DTG curves of each sample, indicating the decomposition mechanism was not sustaining.

The thermolysis process of phenol-formaldehyde resin consists of analogous three regions. Trick developed a model to calculate thermal decomposition kinetics of phenolic/carbon composite.[23] He used software PEAKFIT to separate the thermogravimetric weight loss data to three major regions, and calculate the kinetic parameters of each separated region. Wang used the multiple rate isothermal method to calculate the kinetic parameters.[24] The same method was employed to separate DTG curves of APSZs, and calculate the kinetic parameters of each peak based on their peak temperatures. The area under every separated curve represents mass lost of each region.[23,24] The resulting peak separation for the typical decomposition is shown in Figure 8. An average percent mass loss for each region and the fraction of total mass loss associated with each region are listed in Table VI. The kinetics parameters of thermal degradation at each region, calculated by the Kissinger methods were summarized in Table VII. Based on this method, it is convenient to evaluate the influence of different substituents on

TABLE VII
Apparent Kinetic Parameter of Each Pyrolysis Region of APSZs

Sample	Region	E (kJ mol^{-1})	A (1/s)
APSN-Me$_2$	Region 1	119.63	4.61×10^7
	Region 2	238.80	2.85×10^{14}
	Region 3	157.80	1.75×10^8
APSN-MeVi	Region 1	197.57	1.13×10^{13}
	Region 2	271.62	1.26×10^{16}
	Region 3	288.16	2.58×10^{15}
APSN-Ph$_2$	Region 1	208.85	7.37×10^{13}
	Region 2	255.98	2.39×10^{15}
	–	–	–
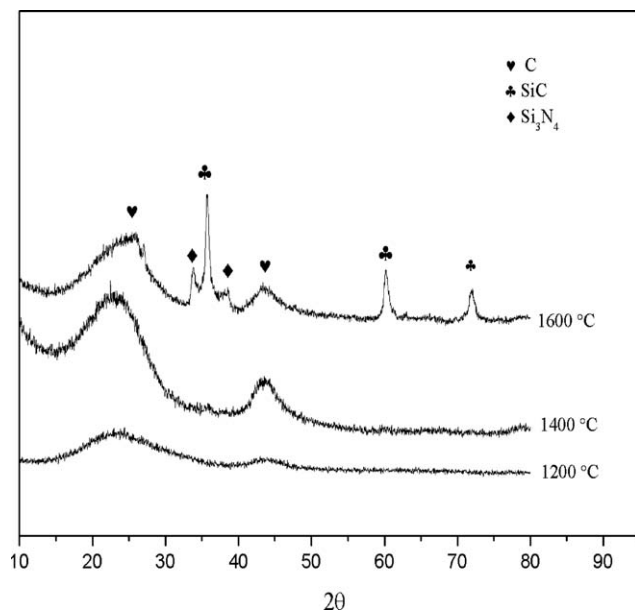
Figure 9 X-ray diffraction patterns of pyrolysis product of APSZ-MeVi heat-treated at 1200–1600°C (Ar).

the thermal behavior of cured silazanes at every separated region. In the first region, vinyl derivative has highest activation energy followed by phenyl and methyl derivatives. These results suggest the retroversion reaction was suppressed by the cross-linking structure and large pendant group.[21] In the second range, while breakage and decomposition of the side groups,[3] the three silazanes have the same order of activation energy as in the first region. There are only two peaks in the DTG curve of APSZ-Ph$_2$. So the thermal decomposition kinetics of APSZ-Ph$_2$ in the third range can not be calculated.

As shown in Table VI, all of the three silazanes show similar weight loss in the first region. But APSZ-Ph$_2$ with phenyl substituted has the largest weight loss in the second region, which account for 58.6% of total weight loss. Compared with APSZ-Me$_2$, APSZ-MeVi with vinyl substituted retain more weight residue and higher peaks temperature at the second and third regions, indicating the decomposition of APSZ-MeVi was retarded by the higher crosslinking density.

The pyrolysis products were further characterized by XRD. As shown in Figure 9, the pyrolysis product of APSZ-MeVi at 1200°C was amorphous. At 1400°C, the peak ranging from 20 to 30° increases which indicated that the *C* is more order in comparison with that at 1200°C. Further heated to 1600°C in argon, the characteristic peaks of β-SiC and Si$_3$N$_4$ appear.

CONCLUSIONS

A new kind of acetylene terminated silazanes, *N*-(3-acetylenephenyl)-diorganosilazanes with different sub-

stituents were synthesized by aminolysis of dichlorosilane with 3-aminophenylacetylene and the structure was confirmed by FT-IR and NMR. Investigation on cure and thermolysis of these silazanes with different substituents indicated that the silazanes possessed excellent thermal properties. Vinyl group introduced to the silazanes could increase crosslinking density, which are helpful for increasing ceramic yield. The kinetics characteristics of the cured silazanes are not constant and vary as function of the extent of pyrolysis, which is made up of three consecutive and overlapped regions. The overlapping regions of the pyrolysis process were separated by the software PEAKFIT. Influence of different substituted groups on the thermal behavior in each separated region was discussed. The results shown vinyl-substituted silazane has better thermal stability due to the high thermolysis activation energy and small pendant group.

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