

# Synthesis and kinetics of non-isothermal degradation of acetylene terminated silazane

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Received 4 May 2010

## Abstract

Novel acetylene terminated silazane compounds, with three types of substituent, were synthesized by the aminolysis of dichlorosilane with 3-aminophenylacetylene (3-APA). Thermal property of the compounds is studied by thermogravimetry analysis (TGA). It shows that the acetylene terminated silazane has high temperature resistance. The char yield at 1000 °C is 77.6, 81.9 and 68.7 wt% for methyl, vinyl, and phenyl substituted silazane, respectively. The pyrolysis kinetics of the silazane is investigated by non-isothermal thermogravimetric measurement. The pyrolysis undergoes three stages, which is resolved by PEAKFIT. The kinetic parameters are calculated by the Kissinger method. The role of functionalities on the thermal resistance is discussed. The vinyl-silazane exhibits higher thermal stability because of higher cross-linking density.

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**Keywords:** Silazane; Thermal properties; Pyrolysis kinetics

Various silazane compounds have been synthesized as a precursor for silicon carbonitride ceramics [1], surface modifiers [2] and additives for silicone rubbers [3,4]. Xie and Wang [3] developed a method to suppress the reversion of polysiloxanes with a polysilazane crosslinker by which the heat resistance of room temperature-vulcanized (RTV) silicone rubbers is improved. Silazane derivatives effectively impede the rearranging degradation of polysiloxane main chain by the removal of trace water or Si–OH groups with the reactive Si–N bond, and thus can improve the thermal stability of silicone rubbers.

Acetylene-contained silicon polymer have also been attractive for enhancing the thermal stability of polymer [5]. Keller and co-workers synthesized high-temperature elastomers from silarylene–siloxane–diacetylene linear polymers [5]. There is great interest to develop Si–N and acetylenyl containing polymers. Xu and co-workers synthesized 1,3-bis(phenylethynyl)disilazane as a crosslinker for silicon rubber [6]. However, to the best of our knowledge, the information of thermal decomposition kinetic of these compounds is very limited.

In this article, we report the synthesis of a novel acetylene terminated silazane compound with various substituent on silicon. The effect of the functionalities on thermal properties are studied by thermogravimetric analyzer (TGA),

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and PEAKFIT. The kinetics parameters are studied using and Kissinger method. The role of substituent on the thermal properties is discussed.

## 1. Experimental

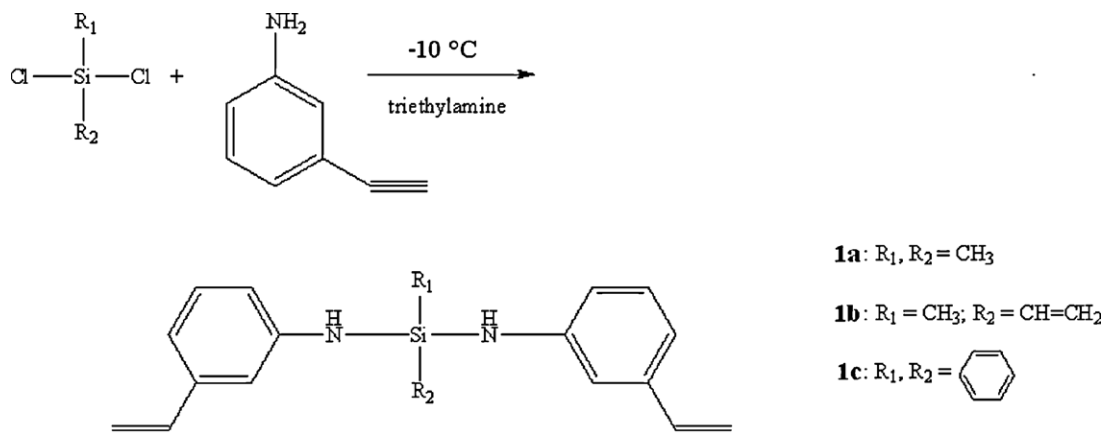
All experiments were carried out under a nitrogen atmosphere. Solvents were distilled from sodium/benzophenone prior to use. Other chemicals were purchased from Aldrich or Acros Co. and used as received.  $^1\text{H}$  NMR and  $^{29}\text{Si}$  NMR spectra were obtained on a Bruker DM 300 MHz spectrometer using  $\text{CDCl}_3$  as solvent. FT-IR spectra were recorded on a Bruker 27 spectrometer. TGA was carried out on a Netzsch STA 409PC instrument with ramping rates of 5, 10, 20, and  $30\text{ }^\circ\text{C}/\text{min}$  from room temperature (RT) to  $1000\text{ }^\circ\text{C}$  in nitrogen atmosphere.

Synthesis of di-(3-acetylenephénylamino)dimethylsilane (**1a**): The compound was prepared by traditional aminolysis procedure (Scheme 1). A three neck flask equipped with a condenser and a magic stirrer bar was charged with dry toluene (50 mL) and dichlorodimethylsilane (0.1 mol, 12.1 mL). After cooled down to  $-10\text{ }^\circ\text{C}$ , 3-aminophenylacetylene (0.2 mol, 11.3 mL) dissolved in toluene (30 mL) was added dropwise to the above mixture. The aminolysis reaction produced a white precipitation as observed immediately. The mixture was stirred for 1 h at  $-10\text{ }^\circ\text{C}$ , and then warmed to room temperature for 4 h. The slurry was filtered under nitrogen atmosphere, and a colorless solution was obtained. After removing the solvent under vacuum, 2.46 g white solid was obtained (85% yield). FT-IR: (KBr,  $\text{cm}^{-1}$ ): 3374 ( $\nu_{\text{N-H}}$ , s), 3289 ( $\nu_{\text{C}\equiv\text{C-H}}$ , w), 3025 ( $\nu_{\text{Ph-H}}$ , w), 2983 ( $\nu_{\text{C-H}}$ , w), 2103 ( $\nu_{\text{C}\equiv\text{C}}$ , w), 1619 ( $\nu_{\text{C}=\text{C}}$ , w), 1253 ( $\nu_{\text{Si-CH}_3}$ , s), 955 ( $\gamma_{\text{Si-N}}$ , s), 787 ( $\gamma_{\text{Si-C}}$ , s);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.42 (s, 6 H), 3.01 (s, 2 H), 3.74 (s, 2 H), 6.82, 6.96, 7.15 (m, 8 H).  $^{29}\text{Si}$  NMR (ppm):  $-10$  ( $\text{Me}_2\text{Si-N}$ ).

Di-(3-acetylenephénylamino)methylvinylsilane (**1b**) and di-(3-acetylenephénylamino)diphenylsilane (**1c**) were prepared similar to **1a**, but using  $\text{MeViSiCl}_2$  and  $\text{Ph}_2\text{SiCl}_2$  (Ph: phenyl), respectively. Compound **1b** was obtained as yellow viscous liquid (yield: 65%). FT-IR: (KBr,  $\text{cm}^{-1}$ ): 3380 ( $\nu_{\text{N-H}}$ , s), 3289 ( $\nu_{\text{C}\equiv\text{C-H}}$ , w), 3025 ( $\nu_{\text{Ph-H}}$ , w), 2983 ( $\nu_{\text{C-H}}$ , w), 2103 ( $\nu_{\text{C}\equiv\text{C}}$ , w), 1405 ( $\delta_{\text{Si-C}=\text{C}}$ , w), 1253 ( $\nu_{\text{Si-CH}_3}$ , s), 960 ( $\gamma_{\text{Si-N-C}}$ , s), 787 ( $\gamma_{\text{Si-C}}$ , s);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.48 (s, 3 H), 3.02 (s, 2 H), 3.73 (s, 2 H), 6.01, 6.20 (m, 3 H), 6.79, 6.91, 7.05, 7.19 (m, 8 H).  $^{29}\text{Si}$  NMR (ppm):  $-22$  ( $\text{MeViSi-N}$ ). Compound **1c** was obtained as a white solid (yield: 59%). FT-IR (KBr,  $\text{cm}^{-1}$ ): 3366 ( $\nu_{\text{N-H}}$ , w), 3289 ( $\nu_{\text{C}\equiv\text{C-H}}$ , w), 3025 ( $\nu_{\text{Ph-H}}$ , w), 2983 ( $\nu_{\text{C-H}}$ , w), 2103 ( $\nu_{\text{C}\equiv\text{C}}$ , w), 1253 ( $\nu_{\text{Si-CH}_3}$ , s), 957 ( $\gamma_{\text{Si-N-C}}$ , s), 787 ( $\gamma_{\text{Si-C}}$ , s);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.01 (s, 2 H), 4.15 (s, 2 H), 6.87, 6.99, 7.40, 7.68 (m, 18 H).  $^{29}\text{Si}$  NMR (ppm):  $-29$  ( $\text{Ph}_2\text{Si-N}$ ).

## 2. Results and discussion

A series of novel acetylene terminated silazanes (**1a**, **1b**, **1c**), having different substituents on silicon were prepared by the aminolysis of dichlorosilane and 3-aminophenylacetylene according to Scheme 1. All di-(3-acetylenephénylamino)silanes, abbreviated as APSN, are tractable and can be dissolved in common solvents, such as toluene, hexane and tetrahydrofuran (THF). The cured monomers (**2a**, **2b**, **2c**) were prepared by the following procedure: ( $200\text{ }^\circ\text{C}$ , 2 h), ( $230\text{ }^\circ\text{C}$ , 2 h), ( $250\text{ }^\circ\text{C}$ , 4 h) in  $\text{N}_2$  atmosphere.



Scheme 1. Synthesis protocol for di-(3-acetylenephénylamino)silane compounds.

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