Thermal Curing Reaction and Heat-Resistance of Methyl-di(*m*-ethynylphenyl-amino)silane

Ning Song, Fang Xu, Lizhong Ni, Jianding Chen

Key Laboratory of Special Functional Polymeric Materials and Related Technology of the Ministry of the Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

Received 12 August 2011; accepted 13 February 2012
DOI 10.1002/app.37005
Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Methyl-di(*m*-ethynylphenyl-amino)silane (MEAS) is a new kind of silazane with ethynylphenyl groups in the end of the molecule. The studies about the curing reaction kinetics and curing reaction mechanism are important for its application and performance. In this article, differential scanning calorimeter was used to study the curing reaction kinetics of MEAS. The results showed that both of the apparent activation energy (E_a) and the reaction order (n) that were evaluated with the method of Kissinger (113.4 kJ/mol, 0.93) agreed well with those using the method of Ozawa (116.1 kJ/mol, 0.95). According to structural changes during curing characterized using Fourier-transform infrared spectra, it was inferred that MEAS resin underwent the main four kinds of cross-linking reaction under the condition of heating. Thermogravimetric analysis was used to characterize the heat-resistance of MEAS thermoset. The results showed that the temperature of 5% weight loss based on the initial weight (T_{d5}) of the thermoset was 632.4°C and the residue yield at 900°C was 86.4% in nitrogen. The thermoset sintered at 1450°C in argon transformed into a ceramic with yield of 71%, which was studied by scanning electron microscopy and X-ray diffraction. The sintered products were smooth and hard solid and its chemical composition was made up of β-SiC, α-Si_3N_4 ceramic and free carbon. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: high temperature materials; thermal properties; curing of polymers; pyrolysis

INTRODUCTION

Silicon-containing polymers, such as polysiloxane, polysilazane, polycarbonsilane, and polysilane, have recently attracted increasing attention due to their remarkably high-temperature resistance. These kinds of polymers were urgently required in many fields, such as ceramics precursors, insulators for microelectronic components, sealants for fuel tanks in high speed aircraft, coatings on cookware, and components in space vehicles.

Some studies of silicon-containing acetylenic polymers[1-3] have been reported because of their excellent properties such as: (1) ease of processing: the acetylenic unit could be able to cross-link at elevated temperatures and pressures, (2) no volatility with cure, (3) high decomposition temperature, and (4) high residue after pyrolysis. Thermosets formed in this type are void-free and exhibit excellent thermal and physical properties. Itoh et al.[3,4] synthesized poly(phenylsilyeneethynylene-1,3-phenyleneethynylene) (MSP). The results showed that the polymer had an extremely high thermal stability after curing. Research in our laboratory has been focused on the design and synthesis of phenylethynylsilanes made from phenylacetylene. Methyl-di(phenylethynyl)silane (MDPES)[5,6] and methyl-tri(phenylethynyl)silane[7,8] were obtained using organic magnesium reagents and *n*-butyllithium respectively, all of which exhibited the surprisingly high thermal and thermal-oxidative properties and played an virtually important role on the further research of the related fields.

Polysilazanes-derived silicon nitride (Si_3N_4), silicon carbide (SiC), and its composites have been studied for several years;[9-13] however, few works concerning silazanes-containing acetylene were reported. Hu et al.[10] reported the synthesis and properties of poly(silylacetylene silazane)s for the application of light-emitting materials and Hu et al.[9] reported the synthesis of 1,3-*bis*(phenylethynyl)disilazanes with the absence of the studies of the corresponding properties. Methyl-di(*m*-ethynylphenyl-amino)silane (MEAS) (Scheme 1) is easy to obtain by the ammonolysis of methyldichlorosilane and *m*-amino-phenylacetylene (APA) at 5–10°C. Because of the high activity of terminal acetylene groups in the molecule, MEAS cross-linking reactions can occur at a lower temperature than resins containing *bis*-substituted ethynyl groups, which was benefit to its forming process and application. Up to now,

Correspondence to: L. Ni (lzhni@ecust.edu.cn).

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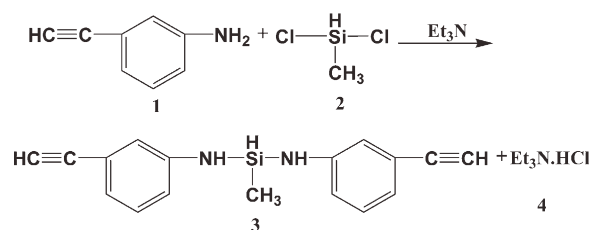


Scheme 1 Synthesis of MEAS resin.

there was no report about the synthesis and curing reactions of MEAS resin expect for our report in a Chinese patent.[14] In this article, the curing reaction kinetics and the curing mechanism of MEAS has been reported. The contents of the elementaries, the high-temperature resistance, and sintered products were studied using X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and X-ray diffraction (XRD), respectively.

EXPERIMENTAL

Preparation of MEAS

MEAS was prepared according to a previously applied method from a Chinese patent[14] (Scheme 1). Tetrahydrofuran (THF: 15 mL), APA (**1**) (0.04 mol, 4.69 g), and triethylamine (Et_3N: 4.05 g) were added to a 50-mL three-necked flask equipped with a dropping funnel, a magnetic stirring bar, and flushed with N_2. After the solution was cooled to -10 ± 2°C, the mixture of THF (5 mL) and methyldichlorosilane (**2**) (0.02 mol, 2.30 g) was added dropwise over 30 min to the stirred solution. After completion of the addition, the reaction mixture was warmed to room temperature and stirred for 3–3.5 hr, and then the reaction mixture turned to a white suspension because triethylammonium chloride (**4**) was formed. The resulting solution was filtered to remove triethylammonium chloride. The volatile product was removed from the filtrate under reduced pressure, MEAS (**3**) was obtained as a yellow liquid (4.4 g, crude yield: 95.5%) and its purity was measured to be 78.9% by the gas chromatography-mass spectrum (GC-MS) analysis.

Measurements

Differential scanning calorimeter (DSC) experiments were performed on a NETZSCH DSC 200F3 instrument under nitrogen at heating rates of 5, 10, 15, 20°C/min. Fourier-transform infrared (FTIR) spectra of samples were obtained with a Nicolet 5700 IR spectrometer in the wave number range of 4000–500 cm^{-1} and pressed by potassium bromide (KBr) pellets. XPS was performed on ESCALAB 250 (THERMO VG SCIENTIFIC LTD.) using monochromic Al X-ray source. TGA was carried out on a NETZSCH STA409PC instrument at a heating rate of 10°C/min under flowing nitrogen. The XRD measurements were carried out on a Digaku (Japan) D/max 2552 VB/PC diffractometer with Cu-Kα radiation ($\lambda = 0.1542$ nm). Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-6360LV microscope.

Thermal curing of MEAS

To remove all volatile materials, the sample of MEAS was heated at 50°C under vacuum for 20 min. The sample was cured in an oven by heating as follows: 190°C/2 hr → 210°C/4 hr → 230°C/4 hr → 250°C/4 hr → 270°C/4 hr → 300°C/3 hr → 330°C/3 hr. Then, the sample turned into a black, compact, and glassy solid.

Pyrolysis of cured MEAS

The thermoset of MEAS was sintered in a stream of argon according to the following schedule: 800°C/0.5 hr → 1000°C/0.5 hr → 1450°C/6 hr.

RESULTS AND DISCUSSION

Curing reaction kinetics of MEAS resin

Table I showed the dynamic DSC results of MEAS at different heating rates. From the data shown in Table I, the onset, peak, and offset temperatures of the curing reaction moved to higher temperatures and the enthalpy (ΔH) decreased, with increasing of the heating rates.

According to the methods of Kissinger, Ozawa, and the Crane equation, the apparent activation energy (E_a) and the reaction order (n) were evaluated.[5] The results showed that E_a were 113.4 and 116.1 kJ/mol, evaluated using the method of Kissinger and Ozawa, respectively. The reaction order (n) was calculated with the value of 0.93 and 0.95, which indicated that the curing reaction of MEAS resin approached a first-order reaction. The results showed that E_a (113.4 kJ/mol) of MEAS resin was close to that of *m*-diacetylene-benzene (117.6 kJ/mol) and lower than that of modified MDPES (158.1 kJ/mol).[5] The low E_a was sometimes favorable to the processability of the resin.

TABLE I
Dynamic DSC Testing Results of MEAS Resin

β [a] ($K \cdot min^{-1}$)	T_i [b] (°C)	T_p [c] (°C)	T_f [d] (°C)	ΔH [e] (J/g)
5	211.8	245.1	267.5	1122.0
10	222.8	250.1	273.5	1076.0
15	229.3	263.2	288.7	931.6
20	234.1	268.5	284.9	736.4

[a] Heating rate.
[b] Onset temperature.
[c] Peak temperature.
[d] Offset temperature.
[e] Enthalpy.

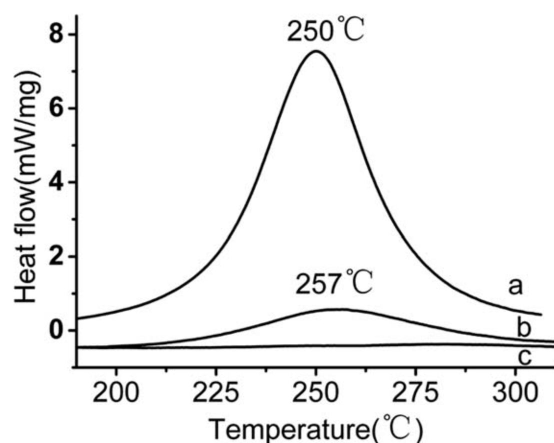


Figure 1 DSC curves of MEAS before curing and after curing at different temperatures (a, before curing; b, after curing at 190°C for 2 hr; c, after curing at 190°C for 2 hr and 210°C for 2 hr).

Dynamic thermal analysis of MEAS

DSC curves of MEAS before curing and after curing at different temperatures measured under nitrogen were shown in Figure 1. In the curve a, there was an evident exothermal peak with the onset, peak, and offset temperatures of 222.8, 250.1, and 273.5°C, respectively, which was attributed to the cross-linking reaction of ethynyl groups and the addition cross-linking reaction involving the Si—H and C≡C bond or C=C bond generated by the additional polymerization of acetylene groups. The enthalpy (ΔH_1) of the curing reaction of MEAS was 1076 J/g. After curing at 190°C for 2 hr, MEAS changed from liquid to brown solid which was difficult to dissolve or melt. Its DSC curve was shown as curve b, on which, there was an exothermal peak with the onset, peak, and offset temperatures of 200, 257, and 315°C, respectively. Compared with curve a, the enthalpy (ΔH_2) of the curing reaction was 283 J/g, which accounted for 26.3% of ΔH_1. Based on the data, the crosslinking reaction of MEAS at 190°C occurred in a great degree. After curing for 2 hr at 190 and 210°C, MEAS tuned to black and compact solid which was not dissolved or melted completely. Its DSC curve was shown as the curve c. The curve c tends to be a line, from which no exothermic peak was observed. The fact suggested that the curing reaction was complete. These results showed that MEAS resin processed at lower curing temperatures than resins containing *bis*-substituted ethynylene groups, which was beneficial to its application.

Structural changes of MEAS resin during curing

FTIR spectra of MEAS cured at different temperatures were shown in Figure 2. The peaks at 3291 cm^{-1} of uncured resin was assigned to the ≡C—H group, and the peak at 2159 cm^{-1} assigned to the

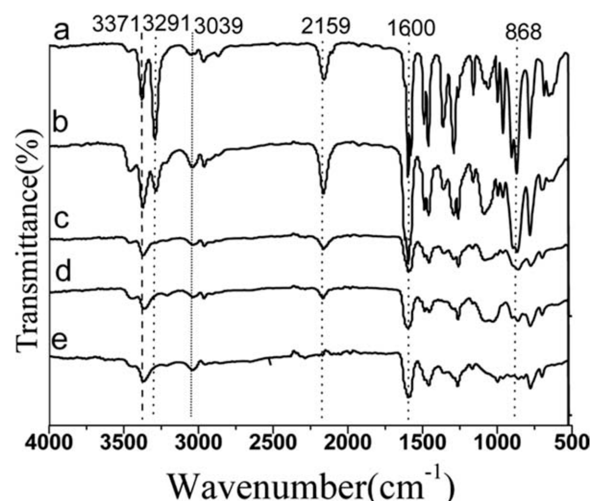
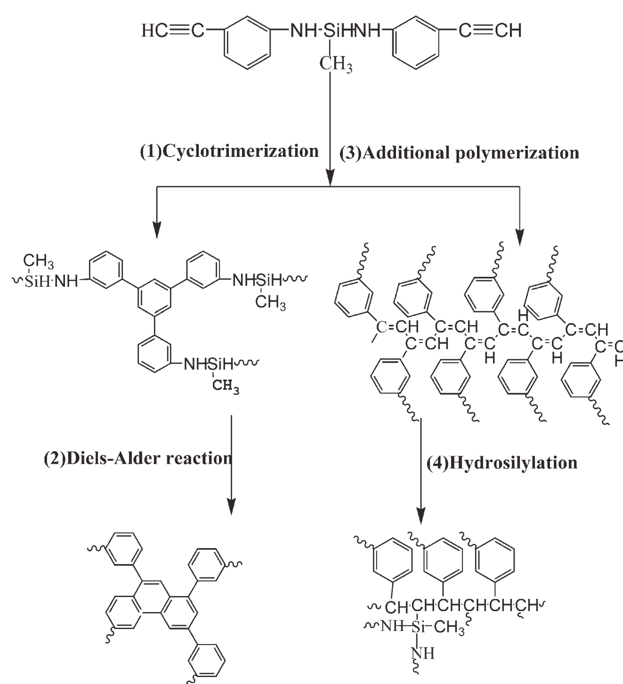


Figure 2 FTIR spectra of MEAS resin cured at different temperatures (a, uncured; b, 190°C/2 hr; c, 190°C/2 hr +210°C/2 hr; d, 190°C/2 hr +210°C/2 hr +250°C/2 hr; e, 190°C/2 hr +210°C/2 hr +250°C/2 hr +300°C/2 hr).

overlap of the Si—H group and C≡C group. The peak at 3371 cm^{-1} was attributed to N—H bond of MEAS. When the resin was heated at 190°C for 2 hr, the peaks at 3291 cm^{-1} decreased, while the peaks at 3039 and 1600 cm^{-1} assigned to C—H and C=C in benzene ring, respectively, increased and broadened. When the resin continued curing at the 210°C, the peak at 3291 cm^{-1} assigned to ≡C—H group disappeared. Because the intensity of the absorption peak of Si—H group was much higher than that of C≡C group, the peak at 2159 cm^{-1} assigned to the overlap of the Si—H group and C≡C group had no



Scheme 2 Thermal curing reactions of MEAS resin.

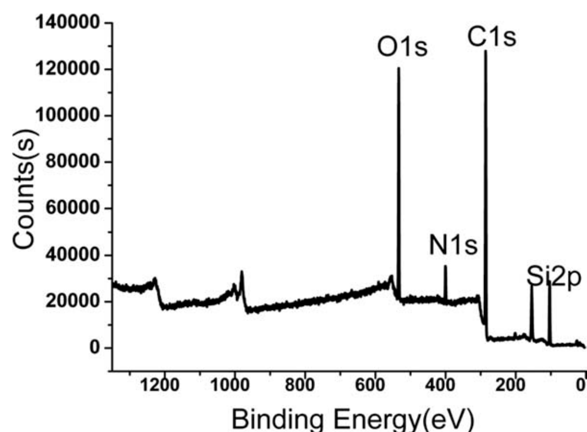


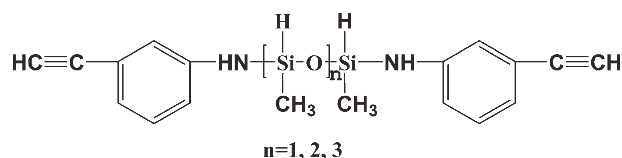
Figure 3 XPS spectrum of MEAS thermoset.

significant change. These facts indicated that the ≡C—H group underwent cyclotrimerization reaction to form polycyclic aromatic hydrocarbon structures or additional polymerization to form the conjugated polyene structures. When the resin was cured at 250 and 300°C, the peaks at 2159 cm^{-1} and 950–860 cm^{-1} decreased and eventually vanished. The changes were attributed to hydrosilylation that occurred between Si—H group and conjugated polyene.

The thermal-cure mechanism of MEAS resin

The cure reaction mechanism of terminal acetylene has been investigated by several research groups. The mechanism of cure is believed to be aromatization of the acetylenic end group, but it is difficult to verify due to the intractability of the cross-linked resin. Under conditions of direct heating in the absence of catalyzer, the crosslinking reaction of the terminal acetylene is complicated, which leads to different structures due to various reactions.[15-18]

According to the structural changes during the curing of MEAS resin in Figure 2 and researches of Ding[17] and Tseng[18] about the reaction mechanisms of different structure compounds terminated with acetylene, the cross-linking reactions of MEAS resin under conditions of direct thermal were proposed. MEAS took place four kinds of reactions, as shown in Scheme 2. (**1**) A part of acetylenic groups underwent cyclotrimerization. (**2**) A part of acetylenic groups underwent Diels-Alder reaction[18] with polymer backbone to form polycyclic aromatic hydrocarbon structures, which took benefit of extremely high



Scheme 3 Polymers containing Si—O bond.

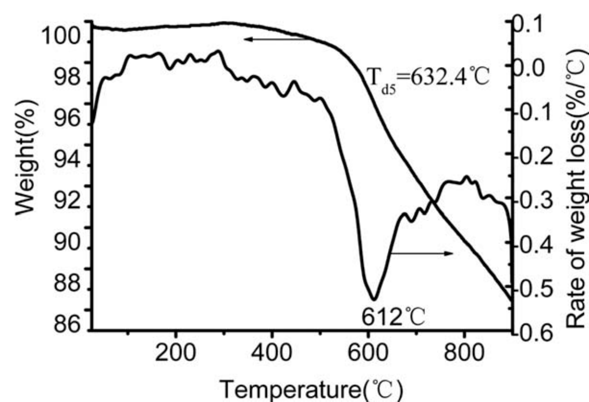


Figure 4 TGA and DTG curves of MEAS thermoset.

thermal stability for the thermosets. (**3**) The remainder acetylenic groups appeared to occur additional polymerization to form the conjugated polyene structures. (**4**) When heated at higher temperatures, the conjugated polyene structure generated in reaction (**3**) occurred hydrosilylation with Si—H unit, which increased the cross-linking density of the thermosets network.

The elementary analysis of MEAS thermoset

The contents of the elementaries in the thermoset were measured using XPS. The results showed that the contents of the elementaries were as follows: silicon (17.65%), carbon (60.51%), oxygen (17.57%), nitrogen (3.64%), chlorine (0.62%), as shown in Figure 3. The results showed that the thermoset contained oxygen with 17.6%. There were two reasons for the introduction of oxygen elementary. First, methyldichlorosilane occurred hydrolysis with traced water in the reaction system to create polymers containing Si—O bond (Scheme 3). Second, MEAS resin occurred oxidation during being cured in an oven. The results showed that the thermoset

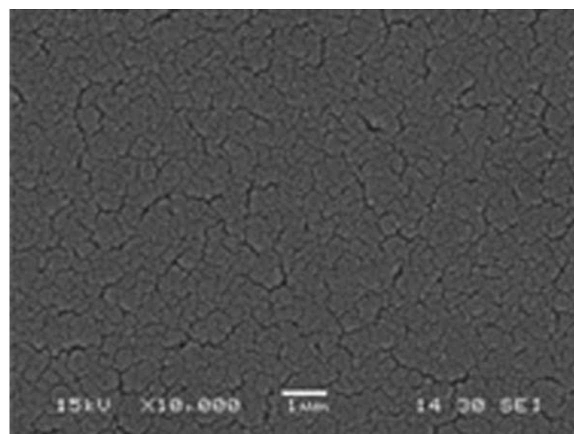


Figure 5 SEM photomicrograph of MEAS sintered product.

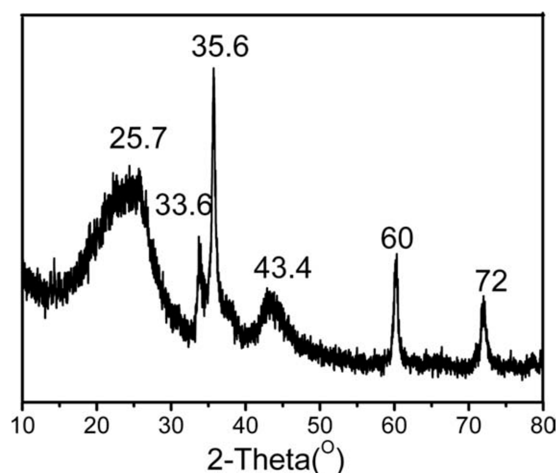


Figure 6 XRD of MEAS sintered product.

contained chlorine with 0.6%. The reason was that MEAS resin was mixed with an extremely small amount of triethylammonium chloride. More detailed study is now in progress in our laboratory.

Heat-resistance of MEAS thermoset

To detect the heat-resistance of MEAS thermoset, TGA was carried out with the heating rate of 10°C/min in nitrogen. TGA and DTG thermograms shown in Figure 4 indicated the weight loss was a three-stage process. In the first stage, the weight loss was 1.1% ranging from 300 to 500°C, which was attributed to the release of low molecular weight oligomers. The second stage resulted in the weight loss of 5.6% ranging from 500 to 675°C in which the degradation rate reached the maximum at 612°C. The degradation rate decreased rapidly as the temperature continued to rise. The third stage resulted in the weight loss of 6.9% ranging from 675 to 900°C. The most weight loss of MEAS thermoset occurred in the second and third process, with the temperature higher than 500°C. The TGA measurements showed that MEAS thermoset possessed outstanding heat-resistance and a slight weight loss occurred when heated to 500°C. T_{d5} of the thermoset was 632.4°C and the weight residue at 900°C was 86.4%.

Formation of ceramic

Polymers containing elements, such as silicon, nitrogen, and carbon, could be used as a precursor to Si/C/N ceramic. After MEAS thermoset was sintered at 1450°C for 6 hr under argon, a sintered product was obtained with the yield of 71%. As shown in Figure 5, the resulting ceramic was smooth and pore free, and the surface was full of small cracks which was caused by the decomposition of organic composition in surface layer.

XRD was performed on the sintered product to understand the composition of the inorganic phases formed. As shown in Figure 6, two broad diffraction peaks at $2\theta = 25.7°$ and 43.4° attributed to free carbon, Peaks at $2\theta = 35.6°$, 60.0°, and 72.0° attributed to β-SiC at {111}, {220}, and {311}. Peaks at $2\theta = 26.0°$, 33.6° were attributed to α-Si_3N_4, among which the peak at 26.0 overlapped with the peak at 25.7° of free carbon.

CONCLUSIONS

High reactive activity of acetylene brought MEAS with lower curing temperatures. The curing reaction was completed in a great degree after curing for 2 hr at 190 and 210°C. On the condition of heating, MEAS resin underwent the main four kinds of cross-linking routes: the cyclotrimerization, the Diels-Alder reaction, the additional polymerization between two C≡C bonds contributing to form the conjugated polyene structures and the hydrosilylation between the Si—H and the conjugated polyene. TGA analysis indicated that MEAS thermoset had extremely high heat-resistance. After sintering at 1450°C in argon, MEAS composite was composed of Si_3N_4, SiC, and carbon, which indicated MEAS had the potential to be used as a ceramic precursor.

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