

# Novel Heat Resistant Methyl-Tri(phenylethynyl)silane Resin: Synthesis, Characterization and Thermal Properties

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**ABSTRACT:** Methyl-tri(phenylethynyl)silane (MTPES) was successfully synthesized by the reaction of lithium phenylacetylide with methyltrichlorosilane. The structure was characterized by HRMS, FTIR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ ,  $^{29}\text{Si-NMR}$ , and elementary analysis. Thermal cure process was monitored by DSC, DMA, and FTIR. MTPES was heated to free flowing liquid around 130°C and thermally polymerized at 327–377°C to form thermoset. Thermal and oxidative properties were evaluated by TGA analysis. Thermoset exhibits extremely high heat-resistance and TGA curve in nitrogen shows the temperature of 5% weight loss ( $T_{d5}$ ) of 695°C and total weight loss at

800°C of 7.1%. TGA shows a high  $T_{d5}$  of 565°C even in air, although the total weight loss at 800°C was 56.1% of the initial weight, much higher than that in nitrogen. The high heat resistance of MTPES was ascribed to crosslinking reaction concerning ethynyl groups. Aging studies performed at elevated temperatures in air on a thermoset showed that MTPES is oxidatively stable to 300°C. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2488–2492, 2006

**Key words:** high temperature materials; thermal properties; crosslinking; aging; thermogravimetric analysis (TGA)

## INTRODUCTION

Fiber-reinforced composites are strong, lightweight materials that have many uses as structural materials in aircraft, missile, and space vehicles.<sup>1</sup> Polyfunctional arylacetylenes are highly crosslinked aromatic polymers, which contain only carbon and hydrogen atoms. Their principle advantages are the low moisture absorption and the high char yield during pyrolysis, which is desirable from the processing point as it can reduce the number of densification cycles needed in C/C composite processing. Keller and coworkers<sup>2–4</sup> and Walton and Gratz<sup>5</sup> have synthesized several new acetylenic resins with the primary goal of developing carbon-based materials that can afford high char yield.

The key to the development of high temperature polymers is the incorporation of thermally stable structure units such as aromatic, heteroaromatic rings within the backbone or incorporation of inorganic elements, such as silicon, boron, and phosphorous into polymeric material. Functional organosilicon polymers represent a diverse class of materials that have found wide spread use in a variety of applications, including medical implant devices, precursors of silicon carbide, and heat resistant materials.<sup>6,7</sup>

We have been interested in introducing phenylethynyl functional group into a molecular structure containing silicon, which gives scope for improving thermal stability of the resultant networks because of the higher aromatic content of the crosslinking. Phenylethynyl groups have received a great deal of attention as a means of thermally chain extending and crosslinking polymers. They have been used within the polymer backbone to achieve intermolecular cycloaddition to rigidize the polymer. On thermal curing, they provide a three-dimensional network exhibiting an excellent combination of properties, including high glass transition temperature, good thermal stability, moisture and solvent resistance, and mechanical properties.

In this study, we attempt to illustrate synthesis, characterization, and thermal properties of MTPES, which was designed as high heat-resistant material on the basis of the results of our previous studies on methyl-di(phenylethynyl)silane.<sup>8</sup>

## EXPERIMENTAL

### Materials

Tetrahydrofuran (THF) was distilled under a nitrogen atmosphere from sodium/benzophenone immediately before use. Methyltrichlorosilane, phenylacetylene and *n*-butyllithium (1.6M solution in hexane) were obtained from Aldrich Chemical Company and

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were used as received. All other chemicals were of reagent grade.

### Techniques

FTIR spectroscopic characterization was carried out with Nicolet Magna-IR550 by potassium bromide (KBr) pellets.  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and  $^{29}\text{Si-NMR}$  spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz for  $^1\text{H-NMR}$ , 125.77 MHz for  $^{13}\text{C-NMR}$ , and 99.36 MHz for  $^{29}\text{Si-NMR}$ ). The chemical shifts were recorded relative to tetramethylsilane ( $\delta$ , 0.0 ppm) for  $^1\text{H}$ ,  $^{29}\text{Si-NMR}$ , and  $\text{CDCl}_3$  ( $\delta$ , 77.7 ppm) for  $^{13}\text{C-NMR}$ . Elemental analysis was performed on an Elementar Vavio EL III elemental analyzer. Mass spectroscopic and purity were recorded by GC-MAS (Micromass GCTM plus HP-Agilent 6890). Melting point was recorded on Bchi B-540 at heating rate of  $2^\circ\text{C}/\text{min}$ . Thermogravimetric analysis (TGA) was performed on Perkin-Elmer Pyris Diamond from room temperature to  $800^\circ\text{C}$  at heating rate of  $10^\circ\text{C}/\text{min}$  in air and nitrogen.  $T_{d5}$  was defined as the temperature resulting in 5% weight loss based on the initial weight. The differential scanning calorimetry (DSC) study was performed on NETZSCH DSC 200PC at heating rate of  $10^\circ\text{C}/\text{min}$ . Dynamic mechanical analysis (DMA) was performed using Rheogel-E400 in nitrogen atmosphere at a frequency of 1 Hz and at heating rate of  $5^\circ\text{C}/\text{min}$ . Single-ply prepreg was used for cure characterization by DMA analysis.

### Synthesis of MTPES

An argon-flushed 250-mL three-necked reaction vessel equipped with a reflux condenser, an addition funnel, and a stirring motor was charged with phenyl acetylene (22.0 g, 216 mmol) and dry THF (100 mL). The solution was cooled down with a dry ice/methanol bath and equivalent of 1.6M butyllithium hexane solution were added dropwise. The solution was then stirred for 3 h. Subsequently methyltrichlorosilane (10.8 g, 72 mmol) dissolved in 30 mL of THF was added and the reaction solution was then refluxed for 3 h. This solution was cooled to room temperature, then poured into cold aqueous ammonium chloride and extracted with ether. The organic layer was separated, washed with water, dried over sodium sulfate, and the solvent removed by rotary evaporation to a yellowish solid. The solid was recrystallized from ethanol yielding a white powder (20.4 g, 82% yield). Purity (%): 98.9. Melting Point:  $126\text{--}127^\circ\text{C}$  (reported<sup>9</sup>:  $125\text{--}126^\circ\text{C}$ ).

IR (KBr,  $\text{cm}^{-1}$ ): 3045 (w), 2970 (w), 2163 (s), 1594 (w), 1571 (w), 1485 (s), 1256 (s), 840 (s).  $^1\text{H-NMR}$  ( $\delta$ , TMS, ppm): 0.71s (s, 3 H,  $\text{CH}_2\text{-H}$ ), 7.30–7.53 (m, 15H, Ph–H).  $^{13}\text{C-NMR}$  ( $\delta$ ,  $\text{CDCl}_3$ , ppm): 2.22 (s, Si– $\text{CH}_3$ ), 88.62 (s, Si– $\text{C}\equiv\text{C}$ ), 107.12 (s, Ph– $\text{C}\equiv\text{C}$ ), 122.94 (s, Ph), 128.91 (s, Ph), 129.88 (s, Ph), 132.95 (s, Ph).  $^{29}\text{Si-NMR}$  ( $\delta$ , TMS,

ppm):  $-64.32$ . Anal. calcd for  $\text{C}_{25}\text{H}_{18}\text{Si}$  (%): C 86.70, H 5.20; found (%): C 86.29, H 5.16. HRMS (EI)  $m/z$ : 346 (19.52), 333 (4.99), 332 (20.06), 331 (100), 129 (18.08); calcd for  $\text{C}_{25}\text{H}_{18}\text{Si}$  346.1178; found 346.1175.

### Preparation of thermoset

To remove any volatile material, the sample was heated at  $150^\circ\text{C}$ . The sample was placed in a furnace and cured under an atmosphere of dry argon at  $300^\circ\text{C}/2\text{ h}$ ,  $350^\circ\text{C}/2\text{ h}$ , and  $400^\circ\text{C}/2\text{ h}$ .

## RESULTS AND DISCUSSION

### Synthesis

The methods for the synthesis of multiple phenylethynylsilanes reported so far include three types of reactions: the reaction of lithium phenylacetylide, Grignard reaction, the reaction of sodium phenylacetylide.<sup>10</sup> It is convenient for us to adopt organic lithium method to synthesize MTPES. The preparation of MTPES is shown in Scheme 1. The lithium phenylacetylide was prepared from the reaction phenyl acetylene and butyllithium. This compound was further reacted with one-third of a molar equivalent of methyltrichlorosilane to obtain MTPES.

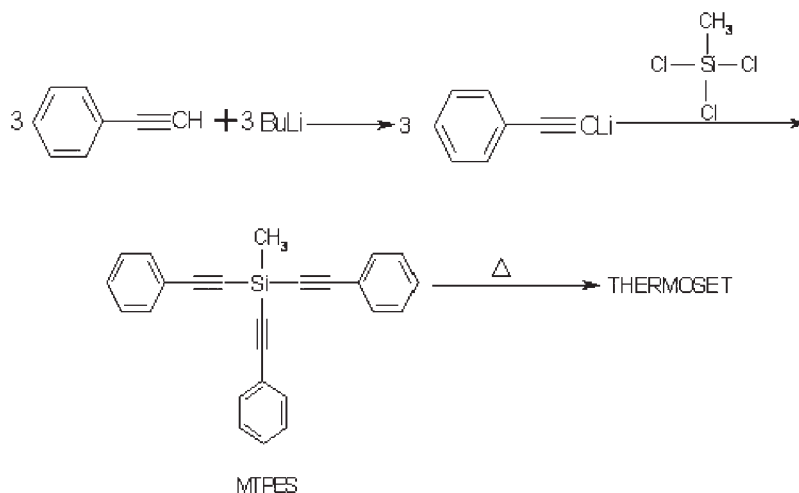
MTPES is a solid low molecular weight compound with melting point  $126\text{--}127^\circ\text{C}$  and is readily soluble in common organic solvents, such as THF, acetone, and ether. The solid is fusible and moldable. The thermoset was prepared from MTPES by bulk thermal polymerization without using of catalysts or initiators under argon atmosphere.

The acetylenic units provide sites for crosslinking purposes and remain dormant under ambient conditions. MTPES has to be heated to elevated temperature before conversion to thermoset. During reaction by thermal means, a conjugated crosslink is formed by an addition polymerization reaction without the formation or evolution of volatile by-products.

### Characterization

A typical FTIR spectrum is shown in Figure 4. MTPES showed a strong absorption around  $2163\text{ cm}^{-1}$  indicating the presence of acetylenic functionality. The absence of primary acetylenes is ascertained by the lack of an absorption in the  $3295\text{ cm}^{-1}$  ( $\text{C}\equiv\text{C-H}$ ). Other functionalities are identified by absorption at  $3045\text{ cm}^{-1}$  (Ph–H),  $2970\text{ cm}^{-1}$  ( $\text{CH}_2\text{-H}$ ),  $1594\text{--}1485\text{ cm}^{-1}$  (aromatic,  $\text{C}=\text{C}$ ),  $1256$  and  $840\text{ cm}^{-1}$  (Si– $\text{CH}_3$ ). All these bands are corresponding to the structure of MTPES given by Scheme 1.

$^1\text{H-NMR}$  analysis showed that the silicon methyl protons resonate at 0.71 ppm and aromatic hydrogen resonates at 7.30–7.53 ppm. In a precise study of NMR



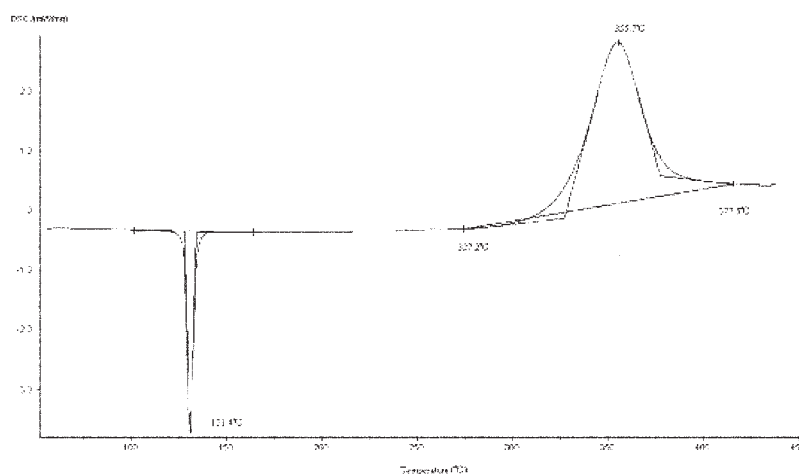
**Scheme 1** Synthesis of MTPES and thermoset.

peak integration, the ratio of methyl protons and aromatic hydrogen is calculated to 3:15. The result is in agreement with the structure of MTPES. In the  $^{13}\text{C}$ -NMR, the methyl substituent attached to the silicon has resonance with chemical shift of 2.22 ppm ( $\text{Si}-\text{CH}_3$ ). The second acetylenic carbons appear as a pair of resonances at 88.62 ppm and 107.12 ppm when bonded to the silicon and phenyl unit. The aromatic carbons are symmetrical and have resonances between 122.94–132.95 ppm. In the  $^{29}\text{Si}$ -NMR, the signal assigned to the tertiary silicon was observed at  $-64.32$  ppm.

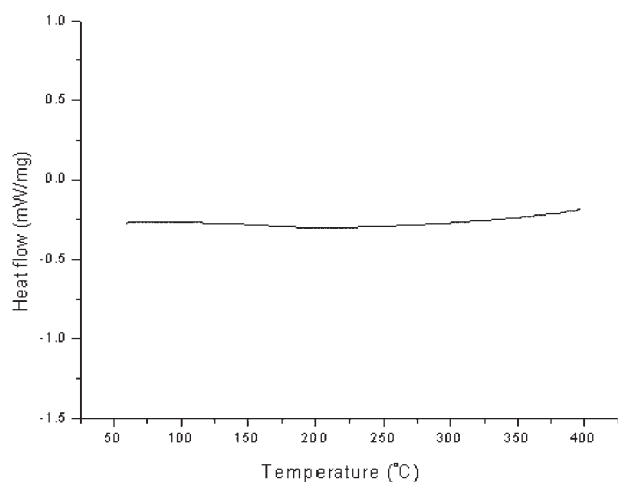
### Thermal cure characterization

For a resin, to be a suitable precursor for a useful high temperature polymeric material, it must possess an adequately large processing window; that is, a temperature range above the melting point of the resin

and below the onset of appreciable cure in which the resin can be held in a liquid flowable state. Ideally, the processing window should be as large as possible; practically, a processing window of at least  $5\text{--}10^\circ\text{C}$  is necessary to ensure adequate flow behavior within processing temperature fluctuations. The DSC curve for MTPES was shown in Figure 1. MTPES had a melting peak at  $131^\circ\text{C}$ , the discrepancy between DSC and melting point apparatus method arising from the different heating rate. MTPES exhibited an exothermic polymerization transition, which begins at  $327^\circ\text{C}$  and reaches a maximum at  $356^\circ\text{C}$ , which was typical for second aromatic acetylenic groups.<sup>3</sup> From the discussions above it is clear that material had a wide processing window of  $196^\circ\text{C}$ . Thus, this material should be easily processable and is an excellent candidate for further study as a high temperature polymer. The heat of polymerization,  $\Delta H_p$ , calculated from the area under the cure exotherm of MTPES is  $545.2$  J/g or  $272.6$  J/g



**Figure 1** DSC curve of MTPES at heating rate of  $10^\circ\text{C}/\text{min}$ .



**Figure 2** DSC curve of thermoset at heating rate of 10°C/min.

of the acetylenic group. The cure mechanism is not very obvious. A radical mechanism leading to polyene network was proposed earlier. Since these were secondary aromatic ethynyl groups having bulky substituents, trimerization of the ethynyl group to benzenoid rings was expected to be at a minimum.<sup>11–13</sup>

Upon cooling and reheating thermoset from room temperature to 400°C, the DSC curve (Fig. 2) showed the complete absence of the exothermic events assigned to the crosslinking reaction between second acetylenic groups of MTPES, which indicated the complete polymerization, and did not display glass transition temperature.

Since the uncured MTPES could not be served as specimen for DMA, it was indirectly evaluated using a single ply glass prepreg. The cure data derived from this can also be served for optimization of the cure during fabrication of composite. The nonisothermal DMA depicted in Figure 3 showed that MTPES begins to melt at 131°C and storage modulus ( $E$ ) is minimum. A single stage curing starts at 250°C.

FTIR spectra of MTPES and thermoset indicated some inclusive information concerning reaction. FTIR analysis (Fig. 4) showed the complete absence of the acetylenic stretching band that was present at 2074  $\text{cm}^{-1}$  in MTPES before curing. A strong and sharp band was present at 1256  $\text{cm}^{-1}$  (Si—C) along with a band at 2970  $\text{cm}^{-1}$  (aliphatic C—H stretching mode) indicating that the Si—CH<sub>3</sub> bonds remained intact. The other notable changes that occurred on curing are the increase in the relative intensities of the absorption at 3045  $\text{cm}^{-1}$  (=C—H) and at 1600  $\text{cm}^{-1}$  (C=C stretch). This is due to an increase in concentration of these groups formed by way of addition polymerization of ethynyl groups during curing. A broad absorption bands at 3500  $\text{cm}^{-1}$  was attributed to the presence of H<sub>2</sub>O, which was introduced by KBr pellets, rather than by sample itself.

## Thermal and oxidative property

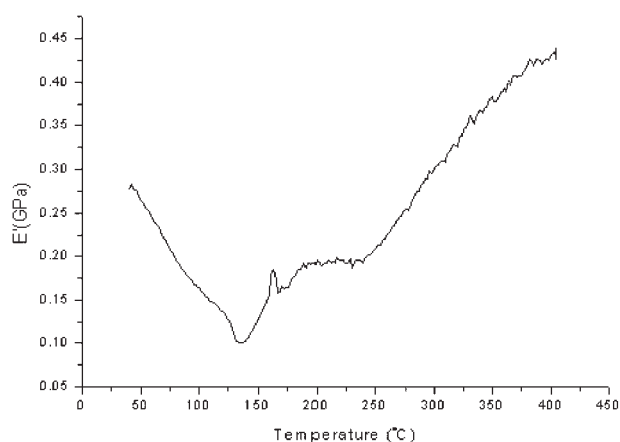
The thermal and oxidative stability of thermoset was determined by TGA study under a flow of N<sub>2</sub> and air. As shown in Figure 5, thermoset shows no weight until 520°C; Td<sub>5</sub> and char yield are 695°C and 92.9% in nitrogen, respectively. In air, however, thermoset shows a significant decrease both in Td<sub>5</sub> (565°C) and in char yield (43.9%), which elucidates that the existence of oxygen accelerates thermal decomposition of thermoset. For comparison, most organic-based polymers are usually observed to undergo catastrophic weight losses in the 500–600°C temperature range upon exposure to air. The outstanding thermal and oxidative property is attributed to the synergistic effects obtained via the incorporation of silicon unit into the molecular structure.

## Thermal aging studies

To determine the thermo-oxidative stability of thermoset, aging studies were performed in a flow of air at 200, 300, 400, 500°C for 3 h at each temperature. Aging at 200 and 300°C the sample gains weight (0.3%), which was attributed to surface oxidation. The sample showed no macroscopic change in appearance. Further heating at 400°C resulted in a weight loss of 20.2% and there was no obvious change in appearance except a little white powder on surface. After aging at 500°C, the sample was observed to undergo catastrophic weight losses (36.7%), and total weight loss was 56.9%. The final residue was white powder. The aging results indicate that thermoset is oxidatively stable to 300°C but degrade upon aging at 400°C.

## Summary

Thermally stable MTPES resin was successfully synthesized by the reaction of lithium phenylacetylide



**Figure 3** Nonisothermal DMA of MTPES at 1 Hz in nitrogen at heating rate of 5°C/min.

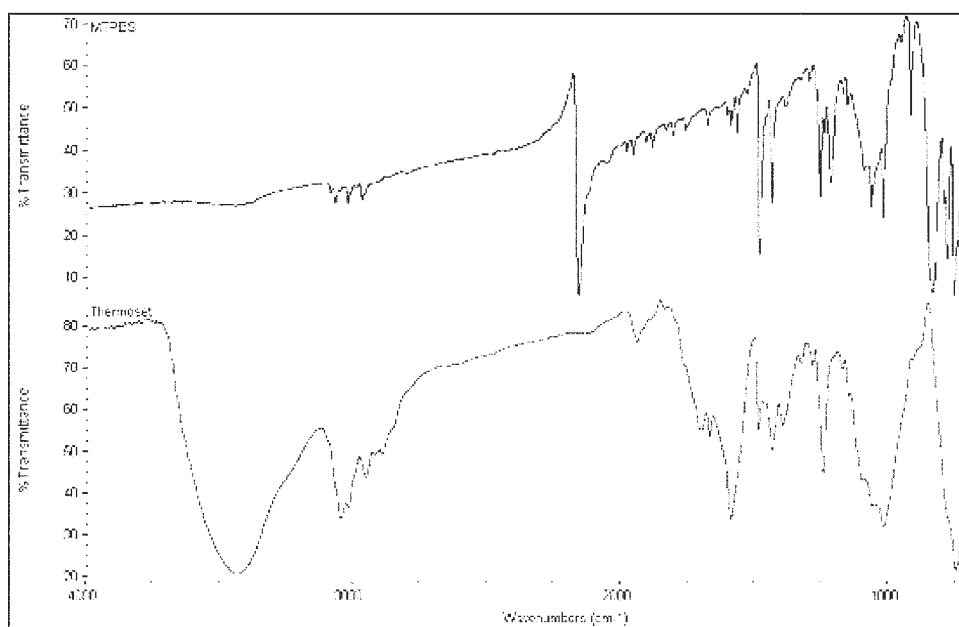


Figure 4 FTIR spectrum of MTPES and thermoset.

with methyltrichlorosilane and characterized by HRMS, FTIR,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ -NMR, and elementary analysis. MTPES is soluble in common organic solvent and exhibits a large processing window, therefore can be easily fabricated to shaped components in the presence of thermal. MTPES undergoes a single-step cure at around 327–377°C. Thermoset exhibits extremely high heat-resistance and TGA curves show  $T_{d5}$  is 695°C and total weight loss at 800°C is 7.1% in nitrogen. In air, however, thermoset shows a significant decrease both in  $T_{d5}$  (565°C) and in char yield (43.9%), which elucidates that the existence of oxygen accelerates thermal decomposition of thermoset. The high

heat resistance of MTPES is ascribed to crosslinking reaction concerning ethynyl groups. The aging results indicate that thermoset is oxidatively stable to 300°C but degrade upon aging at 400°C. The present studies suggest that introduction of ethynylphenyl groups is quite effective to increase thermal stability of silicon-based compound. Thus MTPES shows outstanding potential as matrix material for high temperature composite applications.

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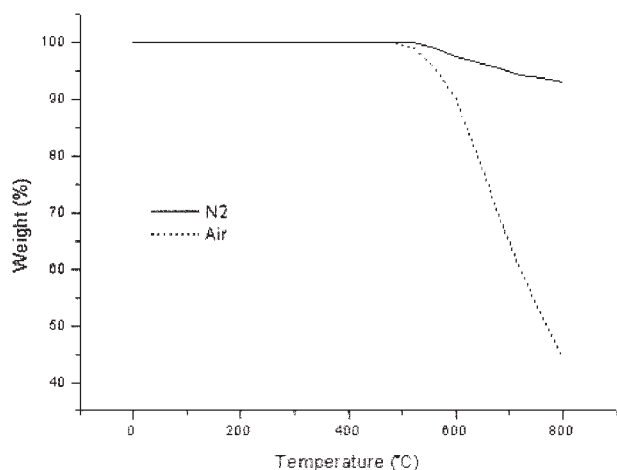


Figure 5 Thermal stability of thermoset and heated to 800°C in a flow of nitrogen and air.