

Novel Phenyl Acetylene Terminated Poly(carborane-silane): Synthesis, Characterization, and Thermal Property

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ABSTRACT: Phenyl acetylene terminated poly(carborane-silane) (PACS) was synthesized by the couple reaction of methylchlorosilane with 1,7-dilithio-*m*-carborane and lithium phenylacetylide. The structure was characterized using FTIR, ¹H-NMR, ¹³C-NMR, ²⁹Si-NMR, and gel permeation chromatography. PACS exhibits solubility in common organic solvents. Thermal and oxidative properties were evaluated by thermogravimetric analysis (TGA). Thermoset exhibits extremely thermal and oxidative property and TGA curves show that the temperature of 5%

weight loss (Td₅) is 762°C and char yield at 800°C is 94.2% in nitrogen. In air, surprisingly, both Td₅ and char yield at 800°C show slight increase, which is greater than 800°C and 95.6%, respectively. After pyrolysis, the char has no additional weight loss up to 800°C in air. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2498–2503, 2007

Key words: carborane; phenyl acetylene; thermal and oxidative stability; thermoset; ceramic

INTRODUCTION

Advanced polyimide matrices have been formulated for service at high temperature, and composites using these matrices are already in use in engine cowls, ducts, thrust reversers, and other parts.¹ However, a critical problem preventing more widespread use of these materials is the aging and degradation of the matrix. Continuous exposure to high temperatures is observed to cause mass loss, degradation of properties, shrinkage, and cracking. Lacking of capability to quantify matrix degradation and its effect on composite properties and behavior are limiting factors in the application of composite materials to these problems.

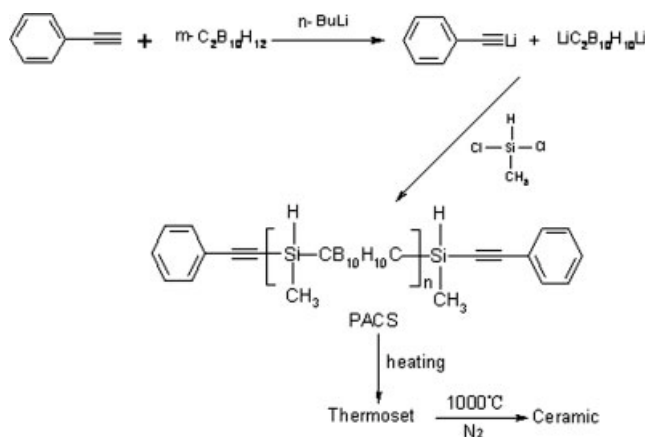
The term carborane is used to refer to the compounds composed of boron, hydrogen, and carbon in which both boron and carbon atoms are incorporated into three-dimensional polyhedron skeletons. Pertinent studies have concentrated on the utilization of carborane as building blocks for high temperature elastomers. The most promising of these were the carborane-siloxane polymers. Poly(carborane-siloxane) was discovered in the early 1960s and the presence of the carborane moiety in the backbone of polysiloxanes blocks ring forming depolymerization reaction by

which polysiloxanes normally degrade on extended heating. Hence, poly(carborane-siloxane) showed superior thermo-oxidative properties under extreme conditions. These polymers were prepared by the ferric chloride-catalyzed copolymerization of dichloro and dimethoxy-terminated monomers.^{2–6}

On the basis of poly(carborane-siloxane), recently, Henderson and Keller^{7,8} have reported the synthesis of poly(carborane-siloxane-diacetylene). Incorporation of acetylenic groups into the poly(carborane-siloxane) backbone provides many advantages. The acetylenic group remains dormant during processing under ambient conditions. During reaction by thermal or photochemical means, a crosslink is formed by an addition polymerization reaction without the formation of volatile by-products. Poly(carborane-siloxane-diacetylene) was synthesized through equal amounts of dilithiobutadiyne and 1,7-bis(chlorotetramethyldisiloxy)-*m*-carborane. Polymer possesses exceptional thermal and oxidative stability. Pyrolysis of polymer in a stream of argon to 900°C at 10°C/min affords a black monolith in 85% ceramic yield, which retains its shape except for some shrinkage. However, these research have been limited to use dichloro terminated carborane-siloxane monomer as raw material, such as 1,7-bis(chlorotetramethyldisiloxy)-*m*-carborane, which is not easy to be obtained.

Our current studies have focused on a new synthesis route to novel phenyl acetylene terminated poly(carborane-silane) (PACS, Scheme 1). There are three distinctions between PACS and poly(carborane-silox-

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Scheme 1 Synthesis of PACS, thermoset, and ceramic.

ane-diacetylene). First, PACS is one kind of nonsiloxane silicon polymers, which offers better thermal stability. Second, phenyl acetylene was introduced to backbone instead of butadiyne, and rigid and high temperature resistance was afforded by benzenoid ring. Therefore, PACS is an excellent candidate as high performance matrix resin for high performance composites; however, poly(carborane-siloxane-diacetylene) can be applied for high temperature elastomer. Finally, we adopt new preparation route to introduce carborane into backbone instead of dichloro terminated carborane-siloxane (Scheme 1). In this paper, we describe the synthesis and characterization of PACS. The thermal and oxidative properties of thermoset and ceramic will be discussed.

EXPERIMENTAL

Materials

The synthesis was conducted in a dry/inert atmosphere because the starting materials were sensitive to oxygen and moisture. Tetrahydrofuran (THF) was distilled under a nitrogen atmosphere from sodium/benzophenone immediately prior to use. Methylchlorosilane, phenylacetylene, *n*-butyllithium (2.5M solution in hexane), and *m*-carborane were obtained from Aldrich Chemical Company and 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 for solid samples and film deposited on NaCl plate for liquid sample. $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, 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 (δ , 0.0 ppm) for ^1H , $^{29}\text{Si-NMR}$ and CDCl_3 (δ , 77.7 ppm) for $^{13}\text{C-NMR}$. Thermogravimetric analysis (TGA) was performed on PerkinElmer Pyris Diamond from room temperature to 800°C at heating rate of 10°C/min in air and nitrogen. Td_5 was defined as the temperature resulting in 5% weight loss based on the initial weight. Gel permeation chromatography (GPC) analysis was performed on a Waters 1515 using THF as eluent with 2414 refractive index detector. Polystyrene standards were used for calibration.

Synthesis of PACS

A 50 mL three-necked round-bottomed flask was equipped with glass stopper, septum, and gas inlet tube. After the flask was flame dried, it was charged with *m*-carborane (0.21 g), phenyl acetylene (0.22 mL), and THF (2 mL). The solution was cooled down with a dry ice/acetone bath. Subsequently, butyllithium hexane solution (2.4 mL, 2.5M) was added dropwise. After completion of addition, the cold bath was removed and the mixture was then stirred at room temperature for 3 h. Afterwards, methylchlorosilane (0.36 mL) dissolved in 30 mL of THF was added dropwise over a period of 15 min and the reaction solution was then allowed to warm to room temperature and stirred for 4 h. This solution was 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 viscous liquid in 86% yield. IR (cm^{-1}): 3069 (w), 2965 (w), 2601 (s), 2165 (s), 1594 (w), 1571 (w), 1488 (s), 1442 (w), 1260 (s), 840 (s). $^1\text{H-NMR}$ (δ , TMS, ppm): 0.55 (m, $\text{CH}_2\text{-H}$), 1.0–3.5 (br, $\text{B}_{10}\text{H}_{10}$), 4.6–4.7 (m, Si-H), 7.2–7.6 (m, C_6H_6). $^{13}\text{C-NMR}$ (δ , CDCl_3 , ppm): -1.8 (s, Si-CH_3), 68.7 (s, $\text{C-B}_{10}\text{H}_{10}\text{-C}$), 87.9 (s, $\text{Si-C}\equiv\text{C}$), 107.8 (s, $\text{Ph-C}\equiv\text{C}$), 123.0 (s, Ph), 129.0 (s, Ph), 129.8 (s, Ph), 132.8 (s, Ph). $^{29}\text{Si-NMR}$ (δ , TMS, ppm): -60.9.

Preparation of thermoset

To remove any volatile material, the sample was heated at 100°C. The sample was placed in a furnace and cured under an atmosphere of nitrogen at 150°C/2 h, 200°C/2 h, 250°C/2 h, 300°C/2 h, 350°C/4 h, and 400°C/2 h.

Preparation of ceramic

The thermoset was further pyrolyzed to 1000°C under an atmosphere of air at the heating rate of 5°C/min.

RESULTS AND DISCUSSION

Synthesis and Physical Characteristics

The couple reaction of dichloro-oligosilanes with dimetalated π -conjugated compounds is a typical way to synthesize the polymer of oligosilylene units and π -units, in general, the molecular weights of the polymers produced are relatively low.⁹ The synthetic method used is a simple one pot, two-step reaction. The synthesis of PACS, by the reaction of methylchlorosilane with lithium phenylacetylide, and 1,7-dilithio-*m*-carborane that can be generated *in situ* from phenyl acetylene and *m*-carborane with *n*-BuLi, as is shown in Scheme 1. The *m*-carborane provides high temperature and oxidative stability. Upon exposure to air at elevated temperatures, boron is oxidized to compliant sealant glass (B_2O_3) that is reported to fill and seal microcracks that develop from thermal cycling at elevated temperatures.¹⁰ Methylchlorosilane shows thermal stability and offers Si—H reaction group, which is effective way for further crosslinking and modification, and phenyl acetylene provides the site for crosslinking and conversion to the thermoset. Moreover, these phenyl acetylene moieties are integrated in the macromolecular backbone, inhibition of the polymerization occurs, and chain growth process is stopped. Therefore, phenyl acetylene plays roles of both crosslinking and terminating agent.

PACS is viscous liquid at room temperature and is soluble in common organic solvent, such as THF, diethyl ether, and acetone. It has advantage of being extremely easy to process into thermoset to fabricate composite components. The acetylenic moieties remain dormant under ambient conditions and PACS must be heated to elevated temperature before conversion to thermoset is achieved. Ceramic is obtained by heating either the thermoset or PACS up to 1000°C in air (Scheme 1).

Characterization

FTIR analysis

The FTIR spectrum [Fig. 3(a)] of PACS showed a strong absorption around 2165 cm^{-1} , indicating the presence of Si—H group. However, since the internal acetylenic group absorption overlaps the absorption of Si—H group, it is quite difficult to be distinguished. The absence of primary acetylenes was confirmed by the lack of an absorption in the region of 3300 cm^{-1} . The presence of carborane was confirmed by an absorbance at 2601 cm^{-1} (B—H). Other functionalities were identified by absorption at 3069 cm^{-1} (Ar—H), 2965 cm^{-1} (H—CH₂), $1594\text{--}1442\text{ cm}^{-1}$ (benzenoid ring), and 1260 cm^{-1} (Si—C).

NMR-analysis

Structural confirmations were also obtained by NMR analyses. In the ^{13}C -NMR, the methyl substituents attached to silicon had resonances with chemical shifts of -1.8 ppm . The internal acetylenic carbons appeared as a pair of resonances at 87.9 and 107.8 ppm when attached to silicon atom and aromatic ring, respectively. The two carbons in the carborane cage were symmetric and resonated at 68.7 ppm. The aromatic carbons had resonances of 123.0, 129.0, 129.8, and 132.8 ppm. ^1H -NMR showed broad signals attributed to the protons of the carborane cage between 1.0 and 3.5 ppm. The silicon methyl protons resonated at 0.55 ppm, while the protons bonded to silicon resonated at 4.6–4.7 ppm. The aromatic protons resonated in the 7.2–7.6 ppm region. In the ^{13}Si -NMR, the signal assigned to the tertiary silicon was observed at -60.9 ppm .

GPC analysis

Molecular weight and distribution was measured by GPC. The result shows molecular weight distribution with a polydispersity value (M_w/M_n) of 1.67. Average of molecular weight (M_n) of 2853 g/mol was determined relative to linear polystyrene standards, average about 18 units.

Thermal curing characterization

The DSC plot for PACS is shown in Figure 1. The DSC exothermic peaks are at 127, 209, and 364°C, respectively. During reaction by thermal means, crosslinking was believed to proceed by hydrosilylation reaction between Si—H and $\text{C}\equiv\text{C}$ and an addition polymerization reaction between phenylethynyl units without the formation or evolution of volatile by-products, which results in insoluble, void free, hard solid (Scheme 2).¹¹ Strong exothermic

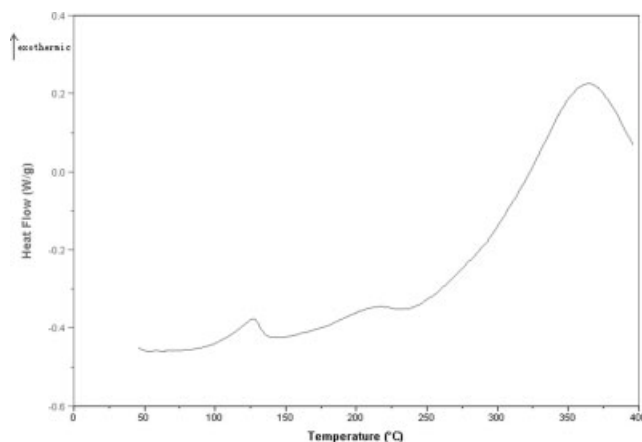
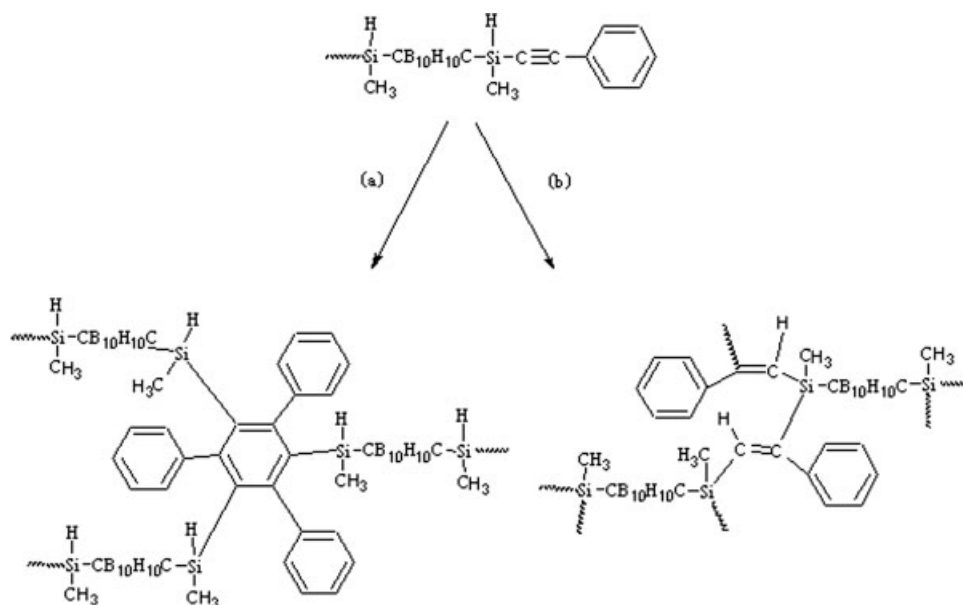


Figure 1 DSC curve of PACS at heating rate of 10°C/min.



Scheme 2 Thermosetting possible mechanism of PACS. (a) The Diels–Alder reaction between $\text{C}\equiv\text{C}$ and $\text{C}\equiv\text{C}$ and (b) the hydrosilylation between Si-H and $\text{C}\equiv\text{C}$.

peak at 364°C indicated crosslinking reaction of second aromatic acetylenic group.¹² The curing of phenylethynyl group was expected to be significantly different from that of the ethynyl ($\text{C}\equiv\text{C}$) primarily because of the large steric impact of the phenyl groups; therefore, trimerization of the phenylethynyl group to benzenoid ring was expected to be at a minimum. Upon cooling and reheating thermoset from room temperature to 400°C (Fig. 2) showed the complete absence of the exothermic events assigned to the crosslinking reaction between second acetylenic groups and between Si-H and $\text{C}\equiv\text{C}$ of PACS, which indicated the complete polymerization and did not display glass transition temperature.

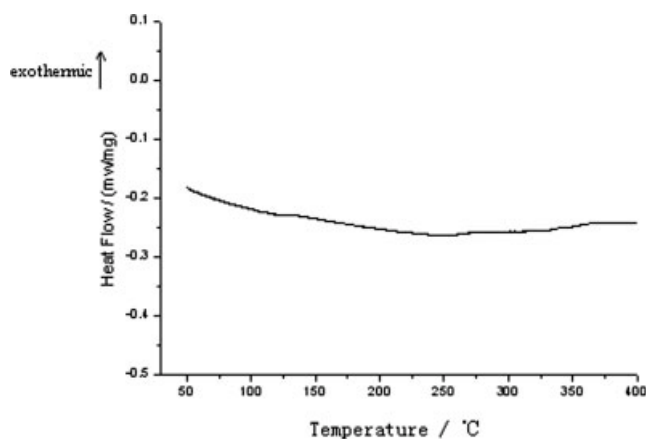


Figure 2 DSC curve of thermoset at heating rate of $10^\circ\text{C}/\text{min}$.

Structure change during curing and pyrolyzing

Figure 3 shows the IR absorption variation of PACS during thermal curing and pyrolyzing. The thermoset was completely insoluble in common organic solvents. FTIR analysis [Fig. 3(b)] showed complete absence of the acetylenic and Si-H group stretching band that was present at 2165 cm^{-1} in linear PACS. A sharp B-H stretching band was observed at 2601 cm^{-1} , indicating that under these conditions in an inert atmosphere the carborane remained intact. A strong and sharp band was present at 1260 cm^{-1} (Si-C) along with a band of medium intensity at 2965 cm^{-1} (H-CH_2), indicating that the Si-CH_3 bonds also remained stable. It is not clear about curing mechanism from FTIR; however, the important point is that the curing of PACS is reproducible from the standpoint of providing material with an excellent thermal and thermal-oxidative property.

FTIR [Fig. 3(c)] of the ceramic showed that the absorption peaks of benzene ring at $1594\text{--}1442\text{ cm}^{-1}$ and 3069 cm^{-1} disappear completely at 1000°C . Comparison of Figure 2(a,b) with 2(c), the disappearance of the absorption bands at 1200 and 1260 cm^{-1} , as well as the increase in intensity of the bands at 1100 cm^{-1} , are indications of the completion of decomposition of the organic constituents and the formation of SiO_2 . Very minor absorption corresponding to C-H groups was observed at $2900\text{--}2980\text{ cm}^{-1}$ and presence of -OH groups was evident from the peak at $3300\text{--}3600\text{ cm}^{-1}$ and 1640 cm^{-1} that was attributed to the presence of H_2O , which was introduced by KBr pellets rather

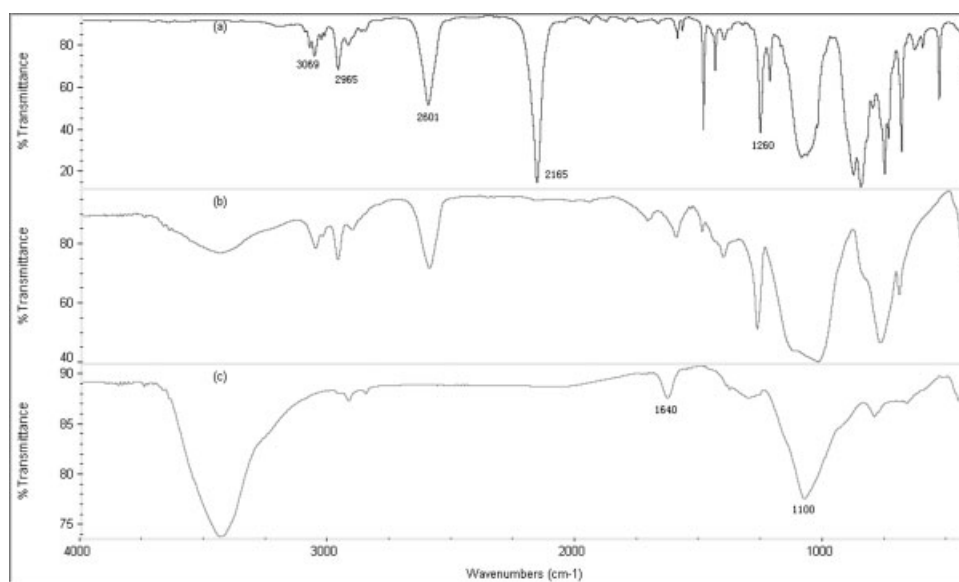


Figure 3 FTIR spectra of (a) PACS, (b) thermoset, and (c) ceramic.

than by sample itself. Loss of the B—H peak (2601 cm^{-1}) confirms that the carborane on the backbone has been totally damaged at 1000°C , which is in agreement with results reported by Patel and Swain. They¹³ reported that on heating at temperatures above 580°C , the carborane cage was destroyed, which was verified by TGA, FTIR, and DTA.

Thermal and oxidative property

The thermal and oxidative stability of PACS was determined by TGA study under a flow of N_2 and air. The TGA curves of thermoset (Fig. 4) provided valuable information regarding its thermal and oxidative property. As shown in Figure 4, thermoset exhibits excellent heat resistant property in nitrogen.

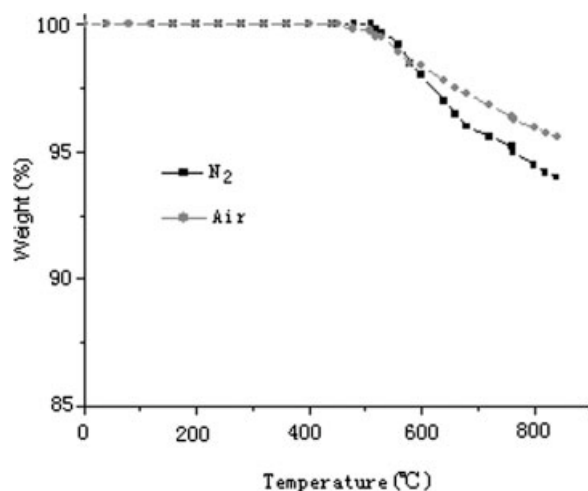


Figure 4 TGA curves of Thermoset in air and nitrogen atmosphere at heating rate of $10^{\circ}\text{C}/\text{min}$.

When heating rate is $10^{\circ}\text{C}/\text{min}$, there is no weight loss up to 510°C . Meanwhile Td_5 and char yield at 800°C are 762°C and 94.2% , respectively, which is attributed to high energy content of carborane, high stability associated with pseudoaromatic character, and acetylenic linkages within the polymeric main chain that provides the opportunity to convert linear polymer into thermoset. Surprisingly, in air thermoset shows a slight increase both in Td_5 and in char yield. Td_5 is greater than 800°C and char yield at 800°C is 95.6% . This slight weight increase is attributed to the oxidation of boron to B_2O_3 and of silicon to SiO_2 upon exposure to oxidizing atmosphere at elevated temperatures and the formation of a protective layer on the sample. However, most organic based systems are usually observed to undergo catastrophic weight losses in the $500\text{--}600^{\circ}\text{C}$ temperature range upon exposure to air. The outstanding thermal and oxidative properties is accredited to the synergistic effects obtained via the incorporation of both boron and silicon units into the polymer backbone. After pyrolysis, the thermo-oxidative stability of ceramic in air was determined by TGA (Fig. 5). We found that ceramic possesses excellent oxidative stability. When heated in air to 800°C , no additional weight loss was observed. For comparison, Kolel-Veetil et al.¹⁴ reported that for diacetylene-containing polycarbora-nylenesiloxanes, the temperature resulting in 10% weight loss (Td_{10}) in nitrogen is in the range of $623\text{--}555^{\circ}\text{C}$ and char yield at 1000°C is from 46 to 70% according to diacetylene content and copolymer sequence. From aforementioned, the high thermal and oxidative stability of PACS make it potentially useful as high performance matrix resin and precursor for ceramics.

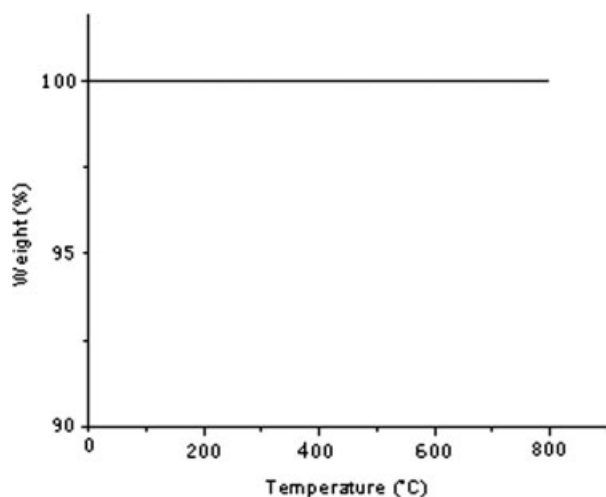


Figure 5 TGA curve of ceramic in air at heating rate of 10°C/min.

SUMMARY

Phenyl acetylene terminated poly(carborane-silane) was synthesized by a simple one-pot, two-step reaction and characterized by FTIR, ^{29}Si , ^{13}C , ^1H NMR spectroscopy, and GPC. Liquid PACS exhibits solubility in common organic solvents. Therefore, it offers good processability to fabricate composite. PACS exhibits excellent thermal and oxidative property. TGA analysis shows that in nitrogen, T_{d5} and char yield at 800°C are 762°C and 94.2%, respectively. In

air, surprisingly, both T_{d5} and char yield show slight increase. T_{d5} is greater than 800°C and char yield at 800°C is 95.6%. After pyrolysis, the ceramic has no additional weight loss up to 800°C in air. Therefore, PACS is a suitable candidate as a matrix resin for advanced composites and as a precursor for ceramics.

References

1. Volksen, W. In *Advances in Polymer Science: High Performance Polymers*; Hergenrother, P. M., Ed.; Springer-Verlag: Berlin, 1994; Vol. 117, p 111.
2. Heying, T. L.; Papetti, S.; Schaffling, O. G. Fr. Pat. 1,484,253 (1967).
3. Heying, T. L.; Papetti, S.; Schaffling, O. G. U.S. Pat. 3,388,090 (1968).
4. Heying, T. L.; Papetti, S.; Schaffling, O. G. U.S. Pat. 3,388,091 (1968).
5. Heying, T. L.; Papetti, S.; Schaffling, O. G. U.S. Pat. 3,388,092 (1968).
6. Peters, E. N. *J Macromol Sci Rev Macromol Chem* 1979, C17, 173.
7. Henderson, L. J.; Keller, T. M. *Macromolecules* 1994, 27, 1660.
8. Kolel-Veetil, M. K.; Keller, T. M. *J Mater Chem* 2003, 13, 1652.
9. Yamaguchi, S.; Tamao, K. In *Silicon-Containing Polymers*, Jones, R. G.; Ando, W.; Chojnowski, J., Ed.; Kluwer Academic Publishers: London, 2000; p 463.
10. Schwamm, D.; Kulig, J.; Litt, M. H. *Chem Mater* 1991, 3, 616.
11. Itoh, M.; Inoue, K.; Iwata, K.; Mitsuzuka, M.; Kakigano, T. *Macromolecules* 1997, 30, 694.
12. Jones, K. M.; Keller, T. M. *Polymer* 1995, 36, 187.
13. Patel, M.; Swain, A. C. *Polym Degrad Stab* 2004, 83, 539.
14. Kolel-Veetil, M. K.; Beckham, H. W.; Keller, T. M. *Chem Mater* 2004, 16, 3162.