Synthesis and Thermal Property of Boron–Silicon–Acetylene Hybrid Polymer

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ABSTRACT: Inorganic–organic boron–silicon–acetylene hybrid polymer (PABS) was prepared by the polycondensation reaction between phenylboric acid and diphenyldichlorosilane and then terminated by phenylacetylene. The structure was characterized by using FTIR, ^{13}C-NMR, ^{1}H-NMR, and GPC. PABS was a kind of resin exhibited high viscous at room temperature and good solubility in common organic solvents. The thermal and oxidative properties were evaluated by DSC and TGA. Exothermal peak at 370°C observed by DSC was attributed to reaction of the acetylene units. PABS showed excellent thermal and oxidative stability, and TGA exhibited the temperature of 5% weight loss (Td_5) was 625°C and char yield at 900°C was 90.0% in nitrogen. Surprisingly, both Td_5 and char yield at 900°C showed slightly increase in air, which was 638°C and 90.9%, respectively. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 47–52, 2011

Key words: inorganic–organic hybrid; acetylene; boron; thermo properties; high temperature materials

INTRODUCTION

There has been the ever-increasing demand for high temperature polymers with excellent thermal stability, especially in the aerospace, such as sealing assemblies for landing gears, flight control systems, fuel systems, and for insulations on cables.[1–3] However, current commercial organic-based systems are limited to be used below 371°C. The incorporation of inorganic elements into an organic polymeric system has the potential for extending these temperature limitations, in addition, to enhance properties such as hardness, chemical inertness, processability, and solubility.[4–6] Lin and coworkers[7–9] reported that the introduction of the inorganic nano materials into polymer matrix can lead to substantially enhanced thermal and mechanical properties of the polymer material, due to the mini size effect, surface and interface effects of the nano composites. Organosilicon polymers containing acetylene group, which are considered as inorganic–organic hybrid polymers have attracted great attention in such advanced applications, owing to their low cost, simple synthesis processes, and high thermal stability. Corriu et al.[10–13] reported that organosilicon polymers containing a π–electron system, in which a regular alternating arrangement of a silylene unit and a diacetylene group $[-(SiR_1R_2)_m-C\equiv C-C\equiv C-]_n$ ($R_1=R_2=$ alkyl, aryl, m = 1, 2) were synthesized by coupling reaction involving the use of the dilithiobutadiyne and various dihalosilanes. The pyrolysis of $[-Si(CH_3)_2-C\equiv C-C\equiv C-]_n$ under a stream of argon to 1400°C gave a β–SiC containing ceramic in high yield (84%). Itoh et al.[14–16] reported the thermal and oxidative properties of poly(phenylsilylene)ethynylene-1,3-phenyl-eneethynylene (MSP) resins, which were prepared by the dehydrogenative coupling polymerization reaction between phenylsilane and *m*-diethynylbenzene with the catalyst of magnesium oxide. Thermogravimetric analysis (TGA) of the polymers in an argon atmosphere revealed 3–12% weight loss at 1000°C.

Previous research in our group[17–24] focused on approaches to design and synthesize silylene–acetylene hybrid monomer as precursors to high temperature thermosets and ceramics, such as methyl-di(phenylethynyl)silane (MDPES), methyl-tri(phenylethynyl)silane (MTPES), and tetra(phenylethynyl)silane (TPES). Thermosets exhibited excellent thermal properties and TGA curves showed Td_5 in nitrogen were 615, 695, and 710°C for MDPES, MTPES, and TPES, respectively. In air, however, thermosets showed a significant decrease in Td_5, corresponding to 562, 565, and 595°C, respectively. To improve thermal oxidative of silylene–acetylene hybrid polymer, we have attempted to introduce carborane into backbone. Carborane containing
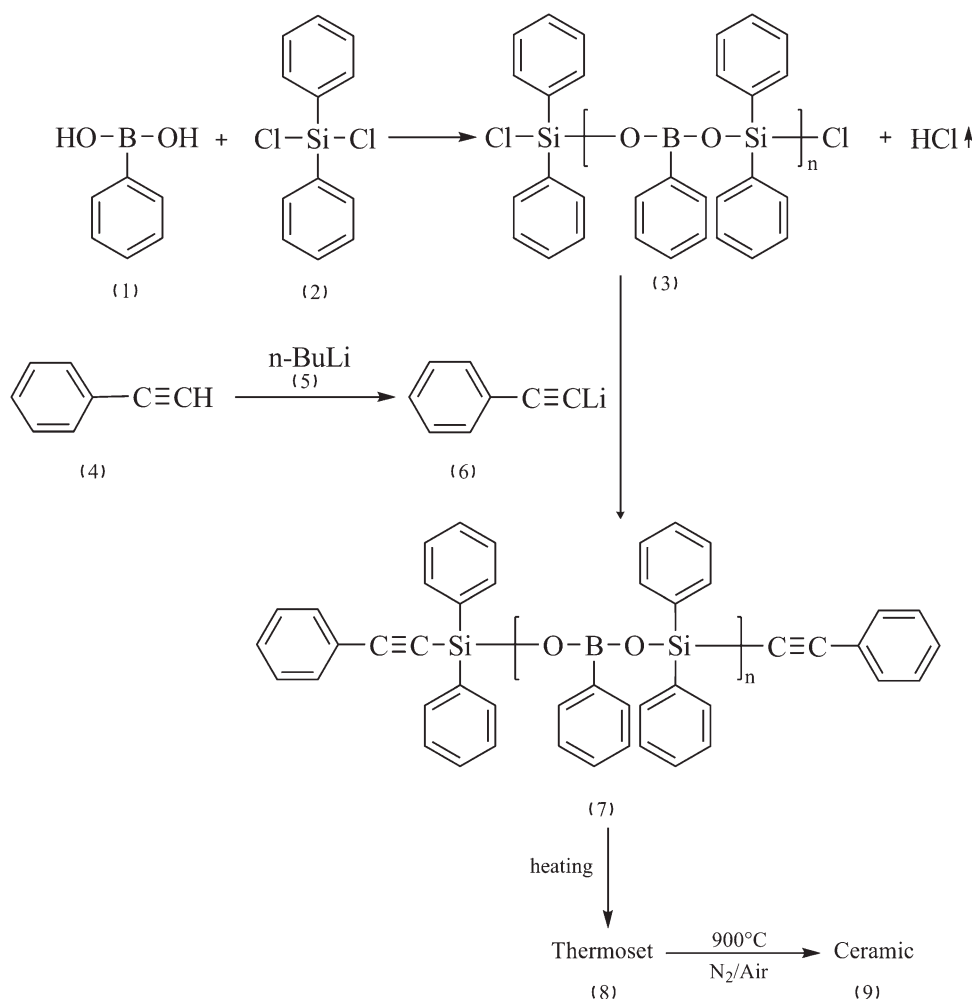
Scheme 1 Synthesis of PABS.

polymers have remarkable chemical and thermal properties and exhibit good protection against oxidative degradation. In our studies,[24] phenylacetylene terminating poly(carborane–silane) (PACS) was synthesized by the couple reaction of methyldichlorosilane with 1,7-dilithio-*m*-carborane and lithium phenylacetylide. The Td_5 of the PACS was 762°C and char yield at 800°C was 94.2% in nitrogen. In comparison, both Td_5 and char yield at 800°C in air showed slight increase, which was greater than 800°C and 95.6% respectively. However, the relative high cost and current limited source of carborane make significant difficulties for the utilization and development of polymers and ceramics based on carborane units. The goal of this research is to determine whether the thermal and oxidative properties can be retained or improved through the incorporation with boron, as a replacement for carborane, and silicon in the polymer backbone.

In this article, we offered a convenient method to prepare inorganic–organic boron–silicon–acetylene hybrid polymer (PABS, **7**) (Scheme 1). In addition, cure behavior, thermal, and oxidative properties were described, which would give important information for the design of boron, silicon, and acetylene hybrid heat resistant materials.

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 before use. Diphenyldichlorosilane, phenyl- boric acid and *n*-butyllithium (2.5 *M* solution in hexane) 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}H-NMR, ^{13}C-NMR spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz for ^{1}H-NMR, 125.77 MHz for ^{13}C-NMR). The chemical shifts were recorded relative to tetramethylsilane (d, 0.0 ppm) for ^{1}H-NMR and CDCl$_3$ (d, 77.7 ppm) for ^{13}C-NMR. TGA was performed on PerkinElmer Pyris Diamond from room temperature to 900°C at heating rate of 10°C/min in air and nitrogen atmosphere. Td$_5$ 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°C/min. The DSC instrument was calibrated by indium standard and the samples were placed in aluminum sample pans and experiments were performed under a flow of dry nitrogen gas. Gel permeation chromatography (GPC) analysis was performed on a Waters 1515 using THF as eluent with Optilab rex refractive index detector and Dawn Heleos light scattering detector.

Synthesis of PABS

A THF solution containing phenylboric acid **1** (30 mmol) and diphenyldichlorosilane **2** (45 mmol) was added to a flame-dried 250 mL three-necked round-bottomed flask by syringe and then was refluxed in N$_2$ gas atmosphere. The exhaust stream was checked with moist litmus paper and was found without HCl vapor after 5 h. Meanwhile, a flame-dried 100 mL three-necked round-bottomed flask containing THF (20 mL) and phenylacetylene **4** (30 mmol) was added by syringe, the solution was cooled to −78°C. *n*-butyl lithium **5** (12 mL of 2.5 *M* in hexane, 30 mmol) was added dropwise via syringe over a 30 min period. After addition, the cold bath was removed and the mixture was stirred at room temperature for 1 h, the resultant of phenylacetylide **6** was generated. Afterwards, the solution of the first flask was cooled to −78°C, and then the resultant of the phenylacetylide **6** was added in. After addition, the reaction mixture was stirred at room temperature for 5 h. The solution was then poured into cold aqueous ammonium chloride. The organic layer was separated, washed with water until neutral, and dried over sodium sulfate, and the solvent was removed by rotary evaporation, a yellowish–brown high viscous PABS **7** was obtained (12.73 g, 86.1% yield).

Thermal curing of PABS

To remove all volatile material, the sample of PABS **7** was heated at 100°C for 1 h. The sample was cured in an oven by heating under nitrogen as the following cure schedule: 200°C/2 h → 250°C/2 h → 300°C/2 h → 350°C/2 h → 400°C/2 h. After the curing cycle, PABS **7** was transformed to a void-free, hard solid. Then, the cured resins were cooled slowly to room temperature to prevent cracking and get required specimens for analysis.

RESULT AND DISCUSSION

Synthesis and physical properties

The preparation of inorganic–organic boron–silicon–acetylene hybrid polymer PABS **7** was illustrated in scheme **1**. The synthetic method used was a simple two-pot, three-step reaction. Firstly, polymer **3** with Si-Cl as terminating group was synthesized by the polycondensation between phenylboric acid **1** and dichlorodiphenylsilane **2.** Afterwards, PABS **7** was generated by the reaction of **3** with phenylacetylide **6**, generated *in situ* from phenylacetylene **4** with n-BuLi **5**, with the formation of LiCl and n-butane, which was the typical way to synthesize the polymer of oligosilylene with dichloro-oligosilanes and dimetalated π-conjugated compounds. Incorporation inorganic elements, such as boron and silicon, into the polymeric backbone improved the thermo-oxidative stability. The presence of phenylacetylene group within the mainchain not only provided the opportunity to convert the initially formed linear polymers into thermosets via thermolysis without the evolution of volatiles but also as a terminating reagent for the polymerization occurred and chain growth process. The acetylene moieties remained relatively long shelf stability under ambient conditions. Thermoset **8** was prepared from the PABS **7** by bulk thermal polymerization without the use of catalysts or initiators under a nitrogen atmosphere. Polymerization occurred through the ethynyl moiety, which resulted in an infusible, insoluble solid. Ceramic **9** was obtained by heating either the thermoset **8** or polymer **7** up to 1000°C in air or nitrogen (Scheme 1). PABS **7** was a yellowish–brown high viscous resin, and was stable in air. It was easily soluble in common organic solvents, such as THF, acetone, and ether so that it had advantage of being extremely easy to process into thermoset to fabricate composite components with or without solvent.

In general, as for the couple reaction, the molecular weight of the polymer produced was relatively low compared with normal condensation polymerization.[25] The molecular weight and distribution of PABS **7** was measured by GPC. The result showed molecular weight distribution with a polydispersity value (M_w/M_n) of 2.7 and weight-average molecular weight (M_w) of 5641 g/mol, average to about 17 repeat units.
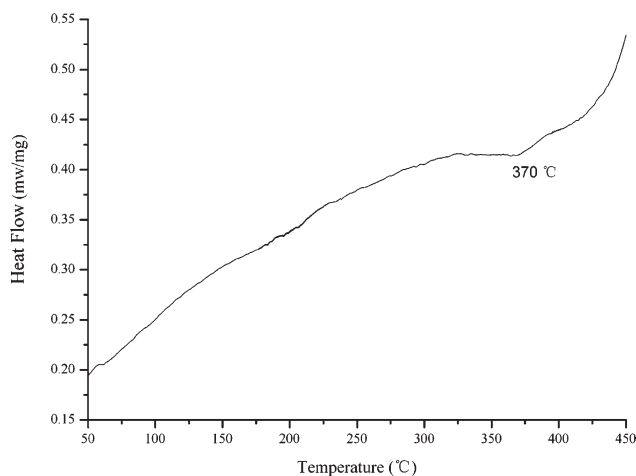
Figure 1 DSC curve of PABS.

Characterization

The structure of PABS **7** was confirmed by FTIR spectroscopy. Polymer propagation was achieved via the formation of the B—O—Si linkage, which was confirmed by strong absorptions at 1070 cm^{-1} and 1320 cm^{-1}, corresponding to Si—O and B—O groups, respectively. Additionally, the broad B—OH stretch with peak maximum at 3274 cm^{-1} was notably absent in PABS **7**. The absorption around 2160 cm^{-1} indicated the presence of the secondary acetylene group, and the lack of the absorption of primary acetylenes was confirmed by the absence region of 3300 cm^{-1}. Other functionalities were identified by absorptions at 3070 cm^{-1} (Ar—H), 1590 cm^{-1} (aromatic, C=C), 850 cm^{-1} (Si—C), 1120 cm^{-1} (Si—Ar) and 1430 cm^{-1} (B—Ar).

NMR spectra for PABS **7** were also investigated to confirm the structure. There were six different hydrogen atoms in the PABS **7**, as shown in the ^{1}H-NMR analysis. The chemical shifts of ortho position, meta position and para position hydrogen of benzene ring, which was substituted of silicon atom were 7.3 ppm, 7.7 ppm and 7.4 ppm. 7.9 ppm, 8.3 ppm and 8.1 ppm of the chemical shifts showed the ortho position, meta position, and para position hydrogen of benzene ring with substitution of boron atom. In the ^{13}C-NMR, the second carbons of the internal acetylenic group appeared as a pair of resonances at 87.9 ppm and 107.8 ppm when attached to silicon atom and aromatic ring. The chemical shifts of the carbon atom of benzene ring, which boned boron, silcon, acetylenic group are 133.9 ppm, 133.3 ppm, and 121.4 ppm. The chemical shifts of ortho position, meta position, and para position hydrogen of benzene ring, which was substituted of aromatic ring, silicon atom, and boron atom were 132.0 ppm, 127.0 ppm, 128.2 ppm, 132.3 ppm, 130.7 ppm, 131.3 ppm, 133.9 ppm, 129.6 ppm.

Thermal curing characterization

The DSC plot for PABS **7** was shown in Figure 1. A broad exotherm peaking at 370°C was corresponding to the reaction of the secondary acetylene units to form the crosslink. Cooling and rescanning to 400°C, no endothermic or exothermic transitions were observed, indicating that the PABS **7** had fully reacted and was homogeneously distributed throughout the thermoset **8**. Meanwhile no obvious glass transition temperature was detected.

It was not clear about curing mechanism from FTIR of PABS **7** and thermoset **8**, however, the important point was that the curing of PABS **7** was reproducible from the standpoint of providing material with an excellent thermal and oxidative properties. Comparison of Figure 2(a,b), the existence of absorptions at 3070 cm^{-1}, 1320 cm^{-1} 1256 cm^{-1} and 1120 cm^{-1} indicated the stability of Ar—H, Si—O, Si—C, and B—O groups remaining intact in thermoset **8**. The notable change was the absorption of C≡C at 2160 cm^{-1} totally disappeared accompanying by the increasing of intensity of absorption bands at 1600 cm^{-1} and 754 cm^{-1}. Although the overlaps of absorptions lead to complications in analysis, the appearance of absorptions between 700–800 cm^{-1} after curing at 400°C gave an indication of characteristic of cis-polyene structure. Meanwhile, the trans structure was absent associated with the range of 900–1000 cm^{-1}, which was attributed to stereo hindrance in the thermoset **8**.

Proposed cured structures

As it was difficult to derive evidences for cure mechanism directly by analyses of the insoluble cured resins, the cure mechanism of secondary acetylenic resin is not sufficiently clearly known by now. However, some insight was obtained into the overall cure
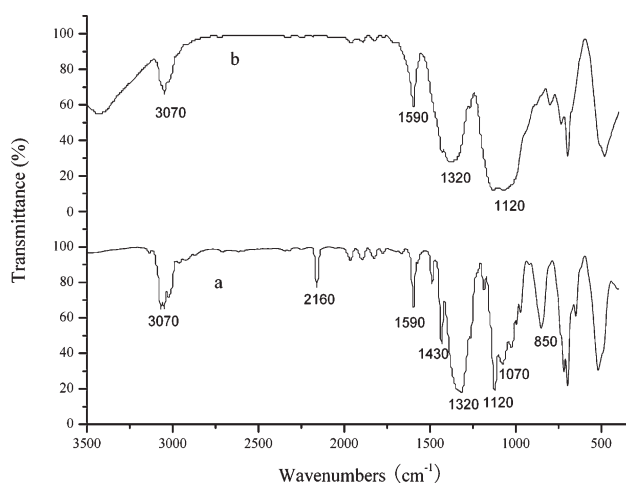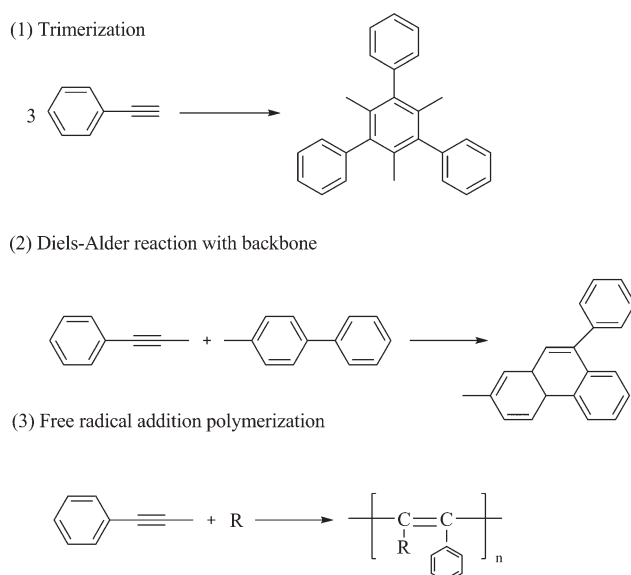

Figure 2 FTIR spectra of (a) PABS **7** and (b) Thermoset **8**.

(1) Trimerization

(2) Diels-Alder reaction with backbone

(3) Free radical addition polymerization

Scheme 2 Possible cure mechanisms of PABS.

Scheme 3 Thermosetting possible mechanism of PABS.

mechanism. Kovar[26] and Admur[27] have discussed the mechanism of the thermal polymerization of phenylacetylene with and without radical initiators. In the absence of initiators, in general, the observed polymerizations were predominantly initiated by the thermal homolysis of impurities, including peroxides or hydroperoxides formed due to oxygen, present in the monomer. Once initiated, a number of reaction routes were possible during thermal polymerization of acetylene compounds. For instance, as shown in Scheme 2, cyclotrimerization to form trisubstituted benzene, Diels-Alder coupling with aromatic backbone, free radical polymerization with the formation of linear and branched conjugated products were the main ways by which chain propagation could occur. Generally, as the molecular chain of a thermally cured resin changes from high entropy to a network structure with low entropy during thermal cure, an exothermic reaction occurs.

Thermal polymerization of PABS **7** was believed to proceed by an addition reaction between ethynyl groups to generate a polyene network as shown in Scheme 3. As there were mangy secondary ethynyl groups having bulky substituents, trimerization of the ethynyl group to benzenoid rings was expected to be at a minimum.[28–31] It was not clear from the infrared spectra whether the crosslinking mechanism generated exclusively a vinylic network or a combination of vinyl and some benzenoid products. Theoretical calculations of bond energies had suggested a predominately polyene network. In either case, however, the inorganic elements were homogeneously distributed throughout the thermoset and upon further heat treatment produced a homogenous ceramic.
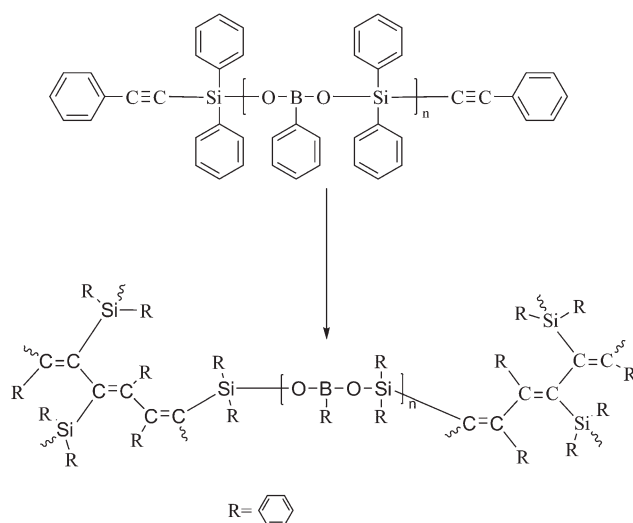
Thermal and oxidative properties

The thermal and oxidative stability of thermoset **8** was determined by TGA study under a flow of N_2 and air. The TGA curves of thermoset **8** (Fig. 3) provided valuable information regarding its thermal and oxidative property. As shown in Figure 3, thermoset **8** exhibited excellent heat resistant property in nitrogen. When heating rate was 10°C/min, there was no weight loss up to 576°C. Meanwhile Td_5 and char yield at 900°C were 625°C and 90.0%, respectively, which was attributed to the synergistic effects obtained via the incorporation of silicon unit and boron unit into the molecular structure and acetylene linkages within the polymeric main chain that provided the opportunity to convert linear polymer into thermoset. Surprisingly, thermoset **8** showed a slight
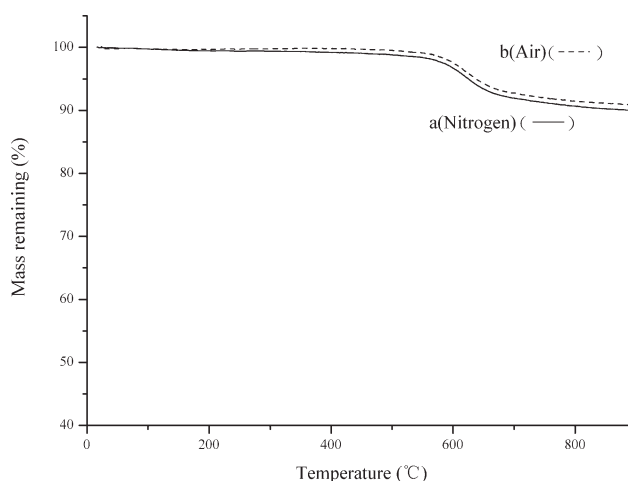
Figure 3 TGA curves of Thermoset **8** in nitrogen (a) and air (b) atmosphere (heating rate: 10°C/min).

increase both in Td_5 and in char yield in air, Td_5 was 638°C and char yield at 900°C was 90.9%. This slight weight increase was attributed to the oxidation of boron to B_2O_3 and of silicon to SiO_2 upon exposure to oxidizing atmosphere at elevated temperature and the resulting oxidized layer serves to protect the internal components from oxidation.[24,32] However, most organic-based systems are usually observed to undergo catastrophic weight losses in the 500–600°C temperature range upon exposure to air. From aforementioned results, the high thermal and oxidative stability of PABS **7** make it potentially useful as high performance matrix resin and precursor for ceramics.

CONCLUSIONS

Inorganic–organic linear boron, silicon, and acetylene hybrid polymer (PABS, **7**) was synthesized and evaluated as potential matrix materials for high temperature applications. PABS **7** showed broad prominent exotherms with peak at 370°C, which was attributed to curing/crosslinking of the secondary acetylene. Further analysis of the residue via second DSC runs showed featureless traces, indicating completion of the acetylene addition reaction. Heating PABS **7** at elevated temperatures produced thermoset. The incorporation of boron and silicon into polymeric backbone was found to improve thermal and oxidative properties. When heated to 900°C under air and nitrogen atmosphere, the thermoset showed weight retention of 90 and 90.9%, respectively. Thus, PABS showed outstanding potential as matrix materials for high temperature composite applications. The mechanical properties of PABS will be the subject of future work.

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