

## New Facile Process for Synthesis of Borosiloxane Resins

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Received: 20 August 2014 / Accepted: 23 September 2014 / Published online: 30 September 2014  
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**Abstract** The first example of a new, one pot synthesis of polyborosiloxane resins by dehydrocarbon condensation of trimethyl borate with diphenylsilane in the presence of tris(pentafluorophenyl)borane is reported. The new condensation process, which leads to the formation of Si–O–B linkages with a release of methane, was performed in hydrocarbon solvent under mild conditions. The obtained polyborosiloxane glassy product is halogen-free and has a low content of hydroxyl groups. High temperature decomposition of polyborosiloxane resin yields a silicon-boron-oxycarbide ceramic with a high yield above 54 %, when the process is carried out under a nitrogen atmosphere. The char yield is about 10 % lower for thermal decomposition in the presence of air than in nitrogen. The polyborosiloxane resins obtained by the new process could find applications as high temperature adhesives, precursors to ceramic materials and novel halogen-free flame retardants.

**Keywords** Polyborosiloxane · Trimethyl borate · Organohydridosilanes · Dehydrocarbon condensation · High temperature resin

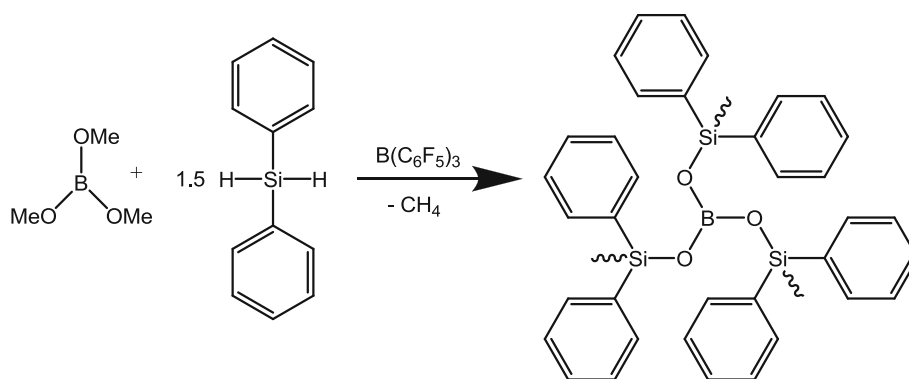
Organohalogen flame retardants are considered as toxic, persistent organic pollutants and according to the Stockholm Convention were banned globally in 2009 [1]. This

legislation increased interest in halogen-free flame retardants, especially for electrical and electronic applications [2]. Boron, oxygen and silicon containing polymers so called polyborosiloxanes (PBS) possess high thermal stability and high char yield [3]. They are miscible and form stable blends with polyethylene terephthalate [4], polycarbonate [5] and polypropylene [6]. Due to these properties, they are considered as a potential replacement of halogenated flame retardants by the plastics industry. PBS resins are also known as effective sintering additives for ceramic materials [7, 8], precursors to amorphous silicon-boron-oxycarbide (SiBCO) ceramics [9, 10] and high temperature adhesives [11]. These useful materials can be prepared by a direct high temperature condensation of boric acid with organochlorosilanes [3], organosilanols [12] or organoalkoxysilanes [13]. Alternative preparative methods involve cohydrolysis of trimethyl borate with organochlorosilanes [9] or organoalkoxysilanes [11]. The reactions of organochlorosilanes with boric acid or trimethyl borate produce harmful hydrogen chloride as a byproduct and yield resins with a relatively high content of residual halogen, which may not be suitable for electronic applications. Other co-hydrolysis based processes used large amounts of water and yield PBS resins with a high level of residual hydroxyl groups, which may limit the resins stability and solubility in organic polymers. We have previously described a successful preparation of a number of siloxane polymers via a new process, dehydrocarbon condensation of organoalkoxysilanes with organohydride-silanes in the presence of a catalytic amount of tris(pentafluorophenyl)borane (TPFPB) [14–16]. That reaction, the so called Piers–Rubinsztajn condensation, was applied subsequently to the preparation of various well defined polymers [17, 18], hyper-branched polysiloxane resins [19], functional siloxanes [20, 21] and silicone foams [22].

**Electronic supplementary material** The online version of this article (doi:10.1007/s10904-014-0094-0) contains supplementary material, which is available to authorized users.

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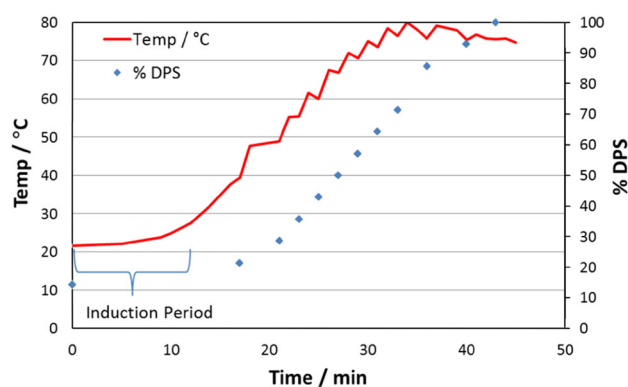
**Scheme 1** Preparation of polyborosiloxane resin by dehydrocarbon condensation process



In the present work, the synthesis and characterization of halogen-free PBS resins with a low content of hydroxyl groups by a new environmentally-friendly process, dehydrocarbon condensation, are reported.

In our search for an efficient process leading to halogen-free PBS resins with a low content of hydroxyl groups, we decided to investigate the dehydrocarbon condensation of alkyl borates with organohydridesilanes (Scheme 1).

In a typical experiment, diphenylsilane (DPS) was added to an anhydrous heptane solution of inexpensive and commercially available trimethyl borate in the presence of catalytic amount of tris(pentafluorophenyl)borane (TPFPB) at room temperature. Initially, after addition of about 15 mol % of DPS, only sluggish gas evolution was observed. The rapid formation of gas and moderate exotherm started after about 10 min of stirring at RT (Fig. 1). *Caution: In some cases an induction period is observed and the reaction does not start after addition of the first few drops of DPS. The reaction may start suddenly after a significant amount of DPS is added with a very high exotherm and abrupt gas evolution. It is important to be sure that the dehydrocarbon condensation reaction indeed has started, which is indicated by the moderate exotherm and gas evolution, before the addition of the next portion of DPS. It is advised to run initial experiments on a small scale and in an oversized flask, so a significant volume is available for expansion of the reaction mixture.* A similar induction period was observed previously with the dehydrocarbon condensation of alkoxy silanes with organohydridesilanes and can be explained by a slow conversion of an unproductive TFPFB-water complex to the free TFPFB, by a reaction of water with organohydridesilane (supporting information Scheme 1). Water free TFPFB serves as the effective catalyst of the dehydrocarbon condensation reaction [16]. Another portion of DPS was added drop-wise when the initial rate of gas evolution slowed. The addition of DPS led to an immediate increase of the reaction temperature and more vigorous gas evolution. The temperature of the reaction mixture and a velocity of gas evolution were



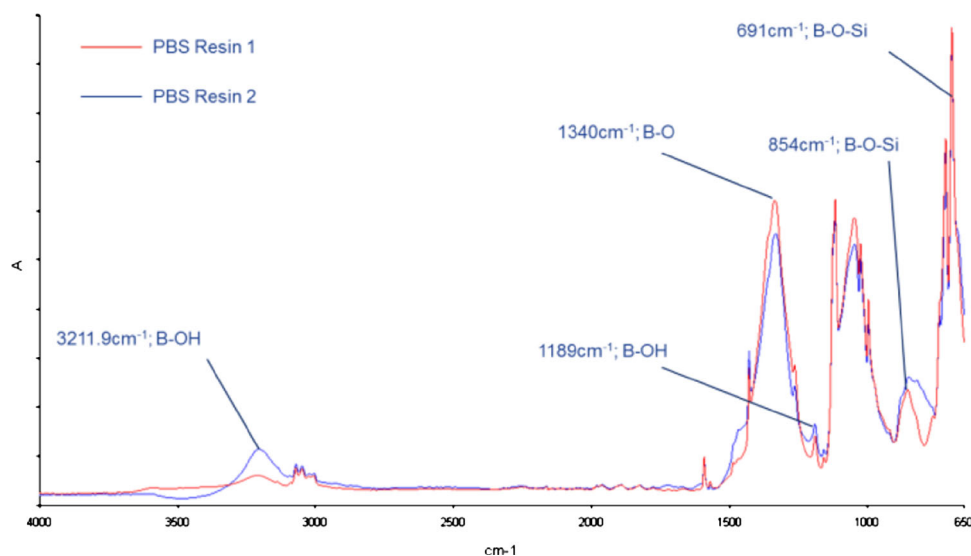
**Fig. 1** Progress of dehydrocarbon condensation monitored by the temperature of the reaction mixture versus time and mol % of added DPS

easily controlled by the rate of the DPS addition. Formation of a white precipitate was observed after addition of about 70 mol % of DPS. The addition of DPS was completed in 45 min and was followed by further mixing at 60 °C for 1 h. The isolated white solid product was washed three times with heptane.

The removal of residual solvent was accomplished by vacuum stripping and subsequent heating at 180 °C for 3 h. under dry nitrogen. The resulting colorless glassy material, PBS-1 resin, was obtained with 73 % yield based on DPS. In an additional experiment the isolated PBS resin was heated at 180 °C for 3 h. in ambient air, to also yield the glassy PBS-2 resin. Elemental analysis of the final PBS-1 resin showed boron content of 3.83 wt%, which is higher than the value previously reported by Yajima of 3.68 wt% for polyborodiphenylsiloxane obtained by a condensation of boric acid with diphenyldichlorosilane [3]. The higher boron content implies that a heptane-soluble, silicon-rich fraction was removed from the PBS resin during a washing step.

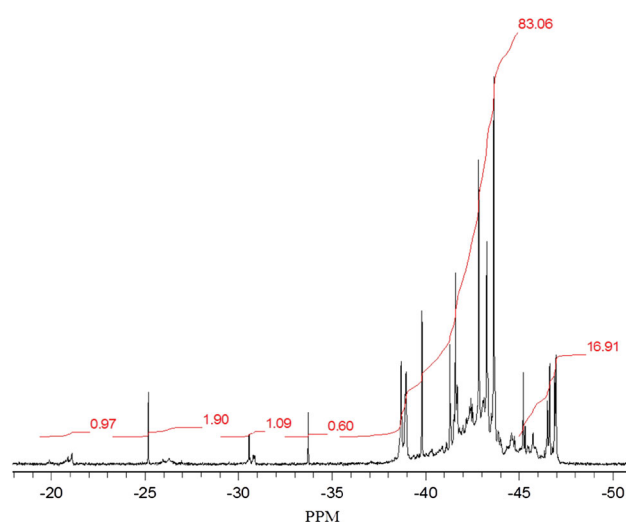
The final PBS resins did not show a melting point by differential scanning calorimetry (DSC), which confirms

**Fig. 2** ATR FTIR spectra of PBS resins obtained by dehydrocarbon condensation. Red line—PBS-1 resin; Blue line—PBS-2 resin (Color figure online)



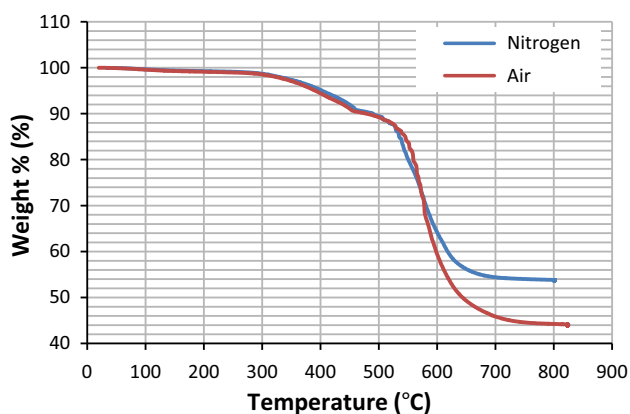
their glassy state. The softening point determined by thermal mechanical analysis (TMA) was between 50 and 60 °C. Attenuated Total Reflection-Infra Red (ATR-FTIR) spectra of the PBS-1 and PBS-2 resins are presented in Fig. 2. Spectra of both materials displayed similar features. The strong bands at 895 and 675  $\text{cm}^{-1}$  are associated with stretching and bending modes of Si–O–B bonds respectively. This clearly confirms that the dehydrocarbon condensation of trimethyl borate with DPS in the presence of TPFPB leads to the creation of Si–O–B linkages. Additionally, the presence of boron results in the broad, strong absorption at 1,300–1,500  $\text{cm}^{-1}$ , which is assigned to the stretching mode of B–O bonds [9, 23]. However, a strong absorption at 3,212  $\text{cm}^{-1}$ , characteristic for the dangling B–OH group, is present only in the PBS-2 resin which was heated in ambient air. This suggests that the PBS resin has limited hydrolytic stability and undergoes partial hydrolysis of B–O–Si linkages, which leads to the formation of the terminal B–OH groups when heated in the presence of moisture. The same isolated solid resin heated in dry nitrogen, PBS-1 resin, showed weak absorption in this region, which is consistent with a very low level of residual B–OH groups.

The PBS resins were soluble in many organic solvents such as chloroform, methylene chloride and toluene. They were characterized by solution  $^1\text{H}$  NMR,  $^{29}\text{Si}$  NMR and  $^{11}\text{B}$  NMR spectroscopy.  $^1\text{H}$  NMR spectrum of the final solid resin showed the complete conversion of Si–H groups and only a small content of residual methoxy groups (supporting information Fig. 1). This is consistent with the formation of methane as the by-product of the dehydrocarbon condensation. The complex resonance of phenyl groups indicates a branched structure of the resin. The branched, irregular structure is clearly confirmed by  $^{29}\text{Si}$



**Fig. 3**  $^{29}\text{Si}$  NMR spectrum of the PBS resin obtained by dehydrocarbon condensation

NMR spectrum (Fig. 3), which shows numerous peaks in the range from –38 to –47 ppm. Signals with a chemical shift below –45 ppm indicate the presence of SiPh<sub>2</sub>–O–SiPh<sub>2</sub> units [24]. Formation of Si–O–Si bonds could be explained by a functional group exchange between trimethyl borate and DPS, which may compete with the dehydrocarbon condensation process. The functional group exchange process was observed previously in the dehydrocarbon condensation of diphenylmethylsilane with trimethyloctyloxysilane [16]. The product of that side-reaction, diphenylmethoxysilane [H–Si(OMe)Ph<sub>2</sub>] may react with a second molecule of DPS to create the SiPh<sub>2</sub>–O–SiPh<sub>2</sub> bonds (supporting information, Scheme 2). Mechanistic aspects of these new reactions are under



**Fig. 4** TGA curves run under nitrogen and air of PBS-1 resin obtained by dehydrocarbon condensation

investigation and will be reported shortly.  $^{11}\text{B}$  NMR (supporting information, Fig. 2) of PBS resin showed a broad peak at 18 ppm, which confirms the presence of a borosiloxane network.

It is known that PBS resins have high thermal stability [3]. Thermal stability of the PBS resin obtained by the dehydrocarbon condensation process was evaluated by thermogravimetric analysis (TGA) under nitrogen and air atmospheres (Fig. 4). The thermal decomposition occurred in two steps for analyses run under both conditions. A similar initial weight loss, with a relatively low onset temperature of 336 °C, could be related to evaporation of the lower molecular weight oligomers. The major decomposition step had an onset temperature above 520 °C, which confirms the high thermal stability of polyborosiloxanes. The thermal decomposition process run under nitrogen had an end-set temperature of 624 °C and produced a black ceramic silicon-boron-oxycarbide residue with a high yield of 54.8 %. The decomposition process performed under air atmosphere showed a similar characteristic, however, the char yield was significantly lower and the final weight loss was reached at a higher temperature. The higher end point temperature observed under air atmosphere can be explained by a high temperature oxidation of the residual carbon and formation of silicon-boron-oxycarbide glass with lower carbon content. The detailed analysis of the formed silicon-boron-oxycarbide (SiBCO) glasses will be reported in a subsequent paper.

In summary, this study demonstrated the first example of a new one pot synthesis of borosiloxane resins by dehydrocarbon condensation of trimethyl borate with diphenylsilane in the presence of tris(pentafluorophenyl)borane. The condensation process was performed in a hydrocarbon solvent at room temperature and a by-product of this

reaction was methane. The obtained PBS resin is halogen-free and has a low content of hydroxyl groups. The glassy PBS resin is soluble in aromatic and chlorinated solvents and has a softening point above 50 °C. As expected, the PBS resin exhibits high thermal stability and has a high char yield when heated to 800 °C. The PBS resin obtained by this new, simple process could find applications in high temperature adhesives, precursors to ceramic materials and novel halogen-free flame retardants.

**Acknowledgments** The author would like to thank Tom Early and Tracy Zhang for assistance in acquisition of  $^{29}\text{Si}$  NMR and  $^{11}\text{B}$  NMR spectra and Robert Davis for help in interpretation of IR spectra. The financial support from General Electric Company is gratefully acknowledged.

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