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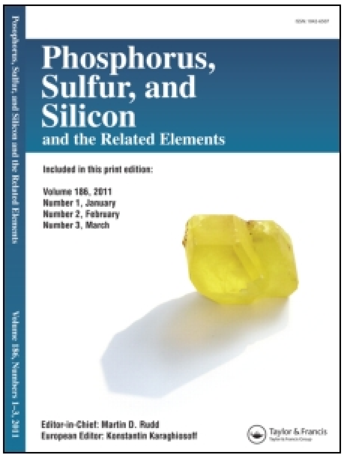

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Thermally Stable Borazine-Based Polymer

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Hydrosilylation polymerization of 2,4,6-triethynyl-1,3,5-trimethyl-borazine with *m*-bis(dimethylsilyl)benzene quantitatively gave a novel borazine-based polymer containing carbosilane units. The polymer was soluble in benzene and THF and was characterized by spectral analyses. Thermogravimetric analysis of the polymer was also carried out.

Keywords: silicon; hydrosilylation; borazine; polymer; thermal stability

Borazine ($B_3N_3H_6$) is known as a useful ceramics precursor for boron nitride and the related materials.[1] However, there are very few reports on other applications of borazine and its derivatives.[2] This is partly because such ceramics precursors are very unstable toward hydrolysis under air. Meanwhile, some silicon-based polymers are attractive because of their high thermal stability.[3] We have recently

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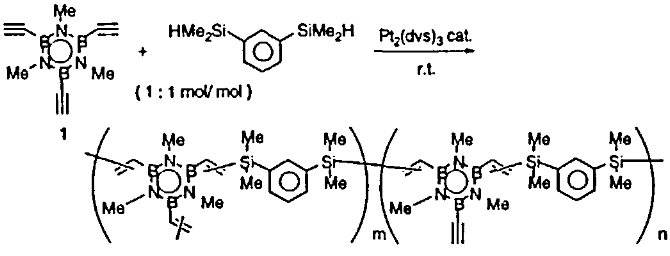
synthesized a novel and stable borazine-carbosilane polymer by hydrosilylation polymerization.

SYNTHESIS OF A BORAZINE MONOMER

The borazine monomer, 2,4,6-triethynyl-1,3,5-trimethylborazine (**1**) was synthesized by the reaction of 2,4,6-trichloro-1,3,5-trimethylborazine with ethynylmagnesium chloride in THF in 48 % yield. A symmetrically substitutetd structure was chosen for this monomer because redistribution reaction of substituents on boron atoms of borazine was previously reported.[4] Compound **1** was stable under air. The substituents on all nitrogen and boron atoms of **2** presumably protect the borazine skeleton from hydrolysis.

POLYMER SYNTHESIS AND THERMAL ANALYSIS OF THE RESULTING POLYMER

In the presence of a catalytic amount of $Pt_2(dvs)_3$ (dvs = 1,3-divynyl-1,1,3,3-tetramethyl-1,3-disiloxane) , hydrosilylation polymerization of triethynylborazine **1** with *m*-bis(dimethylsilyl)benzene (1 : 1 mol / mol)



(1)

2

proceeded to quantitatively give the polymer **2** containing borazine-carbosilane unit. Polymer **2** was soluble in benzene and THF. In ^{1}H-NMR spectrum of **2** in C_6D_6 (Figure 1(a)), the peaks for vinyl protons were observed in the region of δ 5.85 - 6.95 but no peak for Si-CH2-CH2-Si moieties was found at δ 0.9 - 2.0. This result indicated that single hydrosilylation of the ethynyl group of the monomer **1** selectively took place to form vinylsilane units in **2**. Double hydrosilylation of the ethynyl groups of **2** did not proceed at all. The structure of the polymer was further confirmed by ^{13}C, ^{11}B, ^{29}Si-NMR and IR analyses.

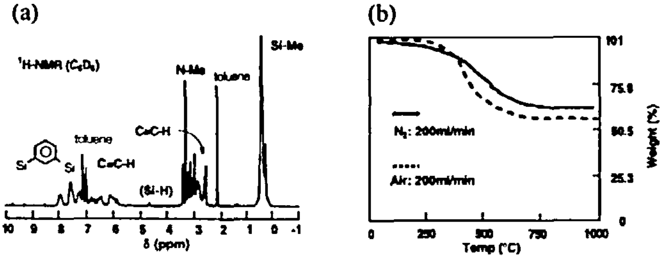


FIGURE 1 (a) ^{1}H-NMR spectrum of the polymer **2** in C_6D_6.

(b) Thermogravimetric analysis of the polymer **2** under nitrogen (unbroken line) and air (broken line).

Gel permeation chromatography of **2** was also carried out using polystyrene standards. Prior to analysis, a polymer solution in THF was filtered through a microfilter (pore size 0.45 μm) and the polymer was only partly filtered off because of its large network structure. The molecular weight of the filtrate was Mn (Mw/Mn) = 2,400 (1.8).

The polymer **2** was stable on heating under both N_2 and air. As shown in Figure 1(b), the results of the thermogravimetrical analysis (10°C/min raising rate and 200ml / min.gas flow rate) is as follows: 5% weight loss temperature (Td_5) are 281.9 °C (under nitrogen) and 324.4 °C (under air) and char at 985°C are 64.9% (under nitrogen) and 57.8% (under air).

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