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$\sigma$-$p$ Conjugated copolymers via dehydrocoupling polymerization of phenylsilane and mesitylborane

Conjugated organoboron/organosilicon copolymers based on a novel mode of conjugation ($\sigma$-$p$ conjugation) were prepared by the dehydrocoupling copolymerization of hydroborane and hydrosilane in the presence of a rhodium catalyst. Conjugative interaction between oligosilanylene and borane was supported both by experiments and DFT calculations. The obtained copolymers showed "turn-on" type sensing behavior toward fluoride anions.

σ–p Conjugated copolymers via dehydrocoupling polymerization of phenylsilane and mesitylborane†

Puhup Puneet,a,b Raman Vedarajan,a and Noriyoshi Matsumia*

There are a number of π-conjugated organoboron polymers in which π-conjugation is extended via the vacant p-orbital of the boron atom. However, boron incorporation into σ-conjugated systems has not been reported so far. A novel σ–p conjugated copolymer of phenylsilane and mesitylborane was synthesized by dehydrocoupling polymerization using a rhodium catalyst. Change in electronic states due to the incorporation of the boron moiety was determined both by DFT calculations and experiments. The obtained colorless polymers were characterized by 1H-NMR and 11B-NMR spectra. Incorporation of boron was confirmed by 11B-NMR, while the Si/B ratio was calculated by 1H-NMR integration ratios. GPC analysis showed the Mn of the polymer as 1200–2900 g mol⁻¹. The copolymers showed high sensitivity towards fluoride ions both optically and electrochemically exhibiting a “turn on” type of sensing mechanism.

1. Introduction

Conjugated polymers have been widely investigated as a key material for plastic electronics1 and are potentially useful for versatile applications such as organic semiconductors,2 light emitting materials,3,4 sensing materials5,6 and so forth. In particular, conjugated polymers bearing exotic elements in their main chain were also extensively studied because of their unique electronic state under specific orbital interactions.7–18 A series of π-conjugated organoboron systems19 with extended p–π conjugation through the boron was developed by several research groups independently.20,21 The boron incorporation into π-conjugated systems led to unique characteristics such as n-type electrochemical activity, intense fluorescence emission, 3rd order non-linear optical properties, anion sensing properties and so on.22

On the other hand, the boron incorporation into σ-conjugated systems has not been known to the best of our knowledge. As a unique example of orbital interaction of the σ-conjugation system,23 σ–π interaction is widely known.24–26 Usually, σ–π interaction is more significantly observed in the

<table>
<thead>
<tr>
<th>Chemical structure</th>
<th>Conjugation type</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Si}_n \text{H}_2 \text{Si}_n \text{H}_2 \text{Si}_n \text{H}_2 )</td>
<td>( \sigma^{23} )</td>
</tr>
<tr>
<td>( \text{C}_n )</td>
<td>( \pi^{10} )</td>
</tr>
<tr>
<td>( \text{R} \text{B} \text{C}_n )</td>
<td>( p\pi^{21} )</td>
</tr>
<tr>
<td>( \text{Si}_n \text{H}_2 \text{Si}_n \text{B} \text{Si}_n \text{H}_2 )</td>
<td>( \sigma\pi^{27} )</td>
</tr>
<tr>
<td>( \text{Si}_n \text{H}_2 \text{Si}_n \text{B} \text{Si}_n \text{H}_2 )</td>
<td>( \sigma\pi ) (This work)</td>
</tr>
</tbody>
</table>

†Electronic supplementary information (ESI) available: The predicted 1H-NMR spectrum using DFT calculation of a polymer mimic model. See DOI: 10.1039/c6py00205f

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photoexcited state than in the ground state. This is due to the intramolecular charge transfer from the oligosilylene moiety to the aromatic moiety. σ-Electrons flow to the vacant π-orbital of the aromatic moiety after the excitation of valence electrons at the π-level to the π* level (Table 1). In this context, when the boron atom bearing the vacant p-orbital is incorporated into σ-conjugated systems, there will be a possibility of observing significant σ-p orbital interaction in the ground state. There have been only a few examples of perhydrogeno derivatives and low molecular weight silylboranes.28,29

Based on the above mentioned idea, in the present work, we have undertaken the synthesis of poly(phenylsilane/mesitylborane) by dehydrocoupling polymerization of phenylsilane and mesitylborane in the presence of a transition metal catalyst. Although Wurtz coupling polymerization31 of chlorosilane containing polymers is the most common synthetic route for polysilanes, this method will not be useful for relatively unstable boron containing polymers.

In the present work, dehydrocoupling polymerization using a Rh catalyst successfully afforded the desired poly(phenylsilane/mesitylborane) whose molecular weights were several thousands. Various feed ratios of the starting materials in dehydrocoupling polymerization of mesitylborane and phenylsilane were examined in the presence of the rhodium catalyst (Scheme 1). The details of amounts of starting materials, yields and B/Si unit ratios are summarized in Table 2. The reaction was carried out under a nitrogen atmosphere at room temperature with constant vigorous stirring. The obtained copolymer 1 was reprecipitated in n-hexane then 1 was dried under vacuum for 3 hours. A relatively high molecular weight was observed when mesitylborane and phenylsilane were taken in a molar ratio of 1:10, respectively.

![Scheme 1 Synthesis of copolymer 1.](image)

### 2. Experimental

#### Materials and methods

Phenylsilane (TCI), tris(dimethylphenylphosphino)(2,5-norbornadiene)rhodium(i) hexafluorophosphate (Aldrich), toluene (WAKO), and tetrabutylammonium fluoride (TCI) were purchased. Phenylsilane and toluene were dried over activated molecular sieves and used. Mesitylborane was freshly synthesized according to the literature and used. A 400 MHz Nuclear Magnetic Resonance (NMR) spectrometer (Ultra-shield™ Plus Bruker, Z101355) was used to characterize the polymers. A fluorescence spectrophotometer (JASCO, FP-8200) and a UV-Vis spectrometer (JASCO V-630) were used for optical measurements in the solution state. Cyclic voltammetry was carried out on an EC stat-100. For gel permeation chromatography (GPC) a Shimadzu-LC-20AD was used. IR spectra were recorded on a JASCO FT/IR-4100.

#### Synthetic procedure

The typical polymerization procedure is as follows. Freshly prepared mesitylborane (500 mg, 3.78 mmol) was dissolved in toluene (15 mL) with the metal catalyst tris(dimethylphenylphosphino)(2,5-norbornadiene)rhodium(i) hexafluorophosphate (15 mg, 0.019 mmol) in a 100 mL round bottom flask under a nitrogen atmosphere. To this, phenylsilane (818 mg, 7.56 mmol) was added dropwise by using a syringe and the reaction mixture was stirred at room temperature for 12 hours. The reaction mixture was reprecipitated in n-hexane and the supernatant solution was removed by using a syringe. The resulting polymer was dried under vacuum for 3 hours to obtain the product.

#### Characterisation

The structures of the polymers were supported by 1H, 11B NMR and IR spectra (Fig. 1). The presence of one peak of boron (Si–B–Si, 19 ppm) was observed in 11B-NMR which indicated the presence of one type of boron in the system. From the IR spectra, the broad peak assignable to Si–B stretching was observed at 630 cm⁻¹. The gel permeation chromatography (GPC) showed the number average molecular weight to be in the range of 1200–2900 g mol⁻¹ (THF as eluent/PSt standards) having a polydispersity index (PDI) of 1.1–1.4. NMR spectra, 1H-NMR: (δ, ppm, 400 MHz): 2.12 (s, 3H, CH₃), 2.22 (s, 3H, CH₃), 2.37 (s, 3H, CH₃), 3.18, 4.13, 4.37, 4.61

### Table 2 Synthetic results in various reaction conditions

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Mesitylborane (mg, mmol)</th>
<th>Phenylsilane (mg, mmol)</th>
<th>Rhodium cat. (mg)</th>
<th>Yield (mg)</th>
<th>B/Si (%)</th>
<th>Mol. Wt (g mol⁻¹)</th>
<th>No. of repeated units (Ca.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500, 3.780</td>
<td>818, 7.56</td>
<td>15</td>
<td>315.0</td>
<td>35.7</td>
<td>1200</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>50, 0.378</td>
<td>409, 3.78</td>
<td>10</td>
<td>79.0</td>
<td>20.0</td>
<td>2300</td>
<td>19</td>
</tr>
<tr>
<td>3</td>
<td>370, 2.803</td>
<td>3030, 28.0</td>
<td>15</td>
<td>420.0</td>
<td>24.9</td>
<td>2900</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>200, 1.515</td>
<td>1967, 18.1</td>
<td>15</td>
<td>680.0</td>
<td>14.2</td>
<td>2100</td>
<td>17</td>
</tr>
</tbody>
</table>

*The B/Si ratio means the percentage ratio of boron and silicon units in the polymer sequence structure and it was calculated by the integral ratio of peaks in the 1H-NMR (methyl peaks of the mesityl group as well as aromatic protons of both the mesityl group and phenyl group were compared).*
The resultant polymers were highly fluorescent when irradiated with UV light in various solvents. Moreover, solvatochromism of the absorption was also observed in solvents of various polarities. The moderately intense fluorescence emission and the presence of the Lewis acidic boron unit indicated the sensing potential for various Lewis bases and anions. The density functional optimizations of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of several models of Si/B systems having two, three and nine Si/B units were carried out using Gaussian 09W DFT (basis set 6-311G, B3LYP) algorithms. These calculations suggested the effective overlap of bonding orbitals in the case of the long chain model which can mimic the copolymer (Table 3, entry 3). For this system, the HOMO was extended through the boron atom supporting $\sigma$-$p$ conjugation. The band gap of the copolymer largely decreased with increasing Si–B based chain length. This can be explained by considering the charge transfer between $\sigma$-electrons and the $p$-orbital of boron. The presence of charge each on boron and silicon atom as a result of charge transfer was implied by the DFT calculation (Table 3). To confirm the intramolecular charge transfer, electronic charge distributions on boron and silicon atoms were compared for various models used for DFT calculations. The boron was found to have a negative charge in the longer polymer chain length. This was complementary to the HOMO, where orbitals were effectively overlapping in the longer chain of the model (Table 4).

The polymer was also studied by UV-Vis spectroscopy and the wavelength of maximum absorbance was around 320 nm. Also, the band gap energy was calculated using the method proposed by Morita et al.\textsuperscript{32} (Fig. 2) and it was found to be 3.8 eV which was very close to the calculated value (3.6 eV) for the polymer mimic calculated by DFT. We measured the UV-Vis spectra of 1 in the non-coordinating solvent CH$_2$Cl$_2$ and found no significant change in the spectra. We conclude here that the different coordination powers of THF and CH$_2$Cl$_2$ did not significantly affect absorption behavior.

Various arylborane based fluoride anion sensors have already been studied and many of them have been reported to show good sensitivity due to extended $\pi$-conjugation through boron. In those sensors, the $\pi$-conjugation is interrupted by forming a borate complex between the organo-boron moiety and fluoride anion, leading to quenching of...
Table 3  3D optimised structures, HOMO and band gap energies of models (DFT calculation, basis set: 6-311G, B3LYP)

<table>
<thead>
<tr>
<th>Chemical structure</th>
<th>Optimized chemical structure</th>
<th>HOMO</th>
<th>$E_{\text{gap}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical structure" /></td>
<td><img src="image2" alt="Optimized chemical structure" /></td>
<td><img src="image3" alt="HOMO" /></td>
<td>16.9</td>
</tr>
<tr>
<td><img src="image4" alt="Chemical structure" /></td>
<td><img src="image5" alt="Optimized chemical structure" /></td>
<td><img src="image6" alt="HOMO" /></td>
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<td><img src="image7" alt="Chemical structure" /></td>
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<td><img src="image9" alt="HOMO" /></td>
<td>3.60</td>
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</table>

Table 4  Charge distribution on boron and silicon atoms in different models of 1 optimised by Gaussian 09 (6-311G, B3LYP, DFT)

<table>
<thead>
<tr>
<th>No. of units</th>
<th>Charge distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$\text{Charge-distribution (B, Si)} = -0.038, 0.520$</td>
</tr>
<tr>
<td>3</td>
<td>$\text{Charge-distribution (B, Si)} = -0.086, 0.432$</td>
</tr>
<tr>
<td>11</td>
<td>$\text{Charge-distribution (B, Si)} = -0.050, 0.626$</td>
</tr>
</tbody>
</table>

Mulliken charge distribution: $-1$ to $+1$.

Fig. 2  UV-vis absorption spectra of 1 in THF (A) and band gap energy calculation of 1 (B).
fluorescence. On the other hand, in this work we have synthesized σ-p conjugated polymers showing turn on type sensitivity towards the micro molar concentrations of the fluoride ion. The fluoride anion sensing was examined by fluorescence emission spectroscopy using tetrabutylammonium fluoride (TBAF) as the fluoride anion source. The “turn on” type of mechanism has been considered to be desirable, as it reduces the human error. The sensing behavior was found to be a turn on type in which the emission intensity increased linearly with increasing concentration of fluoride ion (Fig. 3(a), sample number 2 in Table 2). In the poly(silane/borane), tricoordinate boron had more or less quenched the emission of the oligosilanylene group. However, when the tricoordinate boron was converted to borate, the inherent fluorescence property of oligosilanylene was recovered to show “turn-on” type emission. Cyclic voltammetry was carried out to observe the sensitivity of $1\text{-}^\text{TBAF}$. In the cyclic voltammograms, the only new peak appeared at 0.3 V and the magnitude of current kept on increasing linearly. The appearance of a reduction peak at 0.3 V in the cathodic half can possibly correspond to the irreversible decomposition of $\text{B}^-\text{F}^-\text{Si}$. With an increase in the concentration of fluoride ions (Fig. 3(b), sample number 2 in Table 2) the magnitude of current linearly increased.

4. Conclusions

Experimental data and DFT calculation suggested the formation of σ-p conjugated poly(silane/borane). The design of Si/B based σ-p conjugated systems will provide a novel strategy for the design of conjugated polymers. Due to their unique electronic state, versatile optical and electronic applications are expected. Further modifications and applications of these copolymers are underway.

Fig. 3  Fluoride ion sensing of $1$ (a) in THF after the addition of various conc. of TBAF by fluorescence emission spectra. (Excitation wavelength = 290 nm) (b) cyclic voltammograms of $1$ (1 mM) with various conc. of TBAF in TBAP (0.1 M) at a scan rate of 0.1 V s$^{-1}$ vs. Ag/Ag$^+$; WE : Pt; CE : Pt.

Notes and references