Synthesis of Poly(cyclodiborazane)s Bearing a Disilanylene Unit and Their Optical and Electrochemical Properties

Noriyoshi Matsumi, Tomokazu Umeyama, and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

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Generally, the alternating copolymers composed of a disilanylene unit and a π-electron system are of interest because of the σ−π conjugation[1] along the polymer chain, which is important with respect to their semiconducting[2] or light-emitting properties.[3] Considering that these unique characteristics of organosilicon materials originate from the ground state σ−π conjugation or formation of intramolecular charge transferred excited states between Si−Si (donor) and the aromatic group (acceptor), the construction of a novel σ−π conjugated system in combination with an electron-accepting π-electron system or pseudo-π-electron system leads to an interesting experiment to develop unknown electronic states with enhanced σ−π interactions.

As a π-electron-deficient pseudo-π-conjugated system, we have recently succeeded in the synthesis of a new class of organoboron π-conjugated polymers via the vacant p orbital of the boron atom by hydroboration polymerization of aromatic diynes or aromatic dicyano compounds with monoarylborane.[4] The polymers obtained showed their absorption maxima in the visible region and exhibited intense fluorescence emissions, excellent third-order nonlinear optical properties, and n-type electrochemical behavior and so on. From the results of a theoretical calculation (based on self-consistent-field crystal orbital method) for π-conjugated organoboron polymers prepared from aromatic diyne monomers, the relatively π-electron deficient nature of the organoboron π-conjugated systems as a consequence of π-electron donation to the vacant p orbital of the boron atom was suggested.[5]

Here, the synthesis of σ−π conjugated poly(cyclodiborazane)s by hydroboration polymerization of disilanylene-containing dicyano monomer using mesitylborane or tripylborane is described together with their optical and electrochemical properties. The polymers obtained exhibited characteristics as a novel type of σ−π conjugated polymers in their optical behaviors.

1,2-Bis(*p*-cyanophenyl)-1,1,2,2-tetramethyldisilane (**2**) was prepared by a palladium-catalyzed reaction between 1,2-bis(*p*-bromophenyl)-1,1,2,2-tetramethyldisilane and sodium cyanide. The hydroboration polymerization between mesitylborane (**1a**) and **2** (Scheme 1) was examined as follows, under nitrogen atmosphere at room temperature. To a THF solution of **2**, a slightly excess amount of **1** in THF was added dropwise. After the resulting mixture was stirred for 12 h, the solvent was removed to give a colorless gum, which was purified by reprecipitation into MeOH to afford **3a** as a white powder in 83% yield. Polymer **3a** was very soluble in common organic solvents such as THF, chloroform and benzene. The gel permeation chromatographic analysis (GPC; PSt standards) performed in THF showed a monomodal distribution with a number-average molecular weight of 4300. Instead of **1a**, tripylborane (**1b**) also gave the corresponding polymer in a good efficiency (Table 1).

Table 1. Hydroboration Polymerization between 1 and 2[a]

run	**1**	**1/2**	M_n[b]	M_w[b]	M_w/M_n[b]	yield (%)[c]
1	**1a**	2.15	4800	7600	1.6	83
2	**1b**	2.80	9400	13900	1.5	57

[a] The reactions were carried out in THF at room temperature. [b] GPC (THF). PSt standards. [c] Isolated yields after reprecipitation into MeOH.

Table 2. Optical Data of 2 and 3

run	**2** or **3**	abs (λ_{max})[a]	ϵ[a]	PL (λ_{max})[a]
1	**2**	263	19 600	384
2	**3a**	297	22 600	434
3	**3b**	301	30 100	380, 403

[a] The measurements were carried out in $CHCl_3$ at room temperature.

The polymers obtained (**3a**,**b**) were characterized by ^1H, ^{11}B, and ^{29}Si NMR and IR spectra. In the ^1H NMR spectrum of **3a**, a peak assignable to the imino proton was observed at 7.99−8.13 ppm, indicating cyclodiborazane formation. The ^{11}B NMR spectrum of **3a** ($CDCl_3$) showed its main peak at 4.35 ppm, which is a typical chemical shift for the cyclodiborazane structure. A smaller peak at 32 ppm is attributable to monomeric iminoborane and the borazine ring. In the ^{29}Si NMR spectrum of **3a** ($CDCl_3$), the main peak due to the disilanylene structure was observed at −21.1 ppm, indicating that the polymerization condition did not have an effect on the disilanylene unit. The IR spectrum of **3a** exhibited strong absorption peaks at 1650 and 2400 cm^{-1} due to stretching of C=N and B−H, respectively.

The optical data of the monomer (**2**) and the polymers obtained (**3a**,**b**) are listed in Table 2. In their UV−vis absorption spectra recorded in $CDCl_3$, absorption maxima and edges of **3a**,**b** were fairly red-shifted compared with those for **2**, suggesting that σ−π conjugation is prevailing in their main chain. The polymers **3a**,**b** were highly fluorescent. For instance, the fluorescence emission spectra of **3a** showed an intense emission peak in the visible blue region (at 430 nm), owing to intramolecular charge transferred structure in the excited states.

Cyclic voltammograms of **3a** are represented in Figure 1. The measurements were carried out in a 0.1 M CH_2Cl_2 solution of tetrabutylammonium hexafluorophosphate or a 0.1 M THF solution of tetrabutylammonium perchlorate using platinum electrode vs Ag/Ag^+. Polymer **3a** was found to be electrochemically active both for oxidation and for reduction. When the measurement was carried out within the potential region from 0 to +1.2 V (Figure 1a), an anodic wave was observed at +0.87 V while a cathodic wave was not clearly observed. This irreversibility of the peak indicates that degradation of **3a** was taking place during the scanning by electrochemical oxidation. Since the poly(cyclodiborazane)s we have reported to date do not show an anodic wave in this potential range, the observed oxidative peak can be attributable to oxidative degradation of the disilanylene unit. This potential of the peak was relatively smaller than those reported for σ−π conjugated

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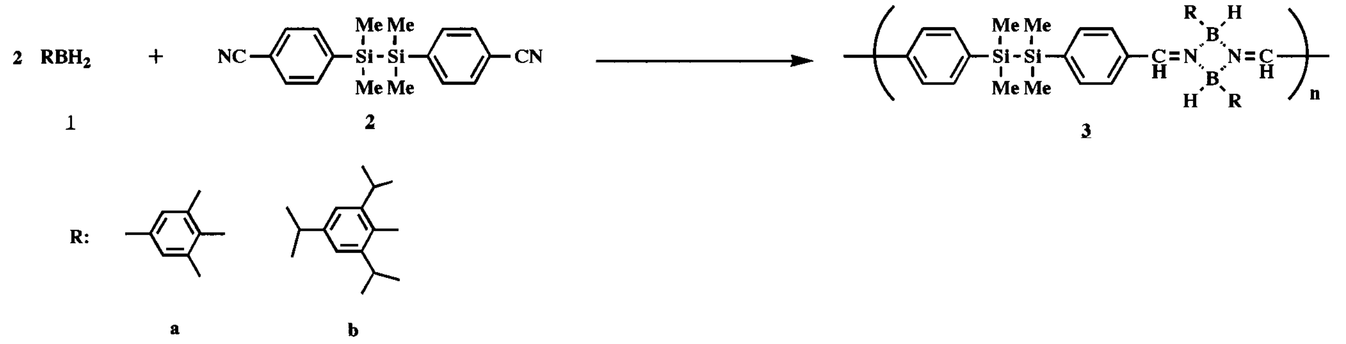
Scheme 1



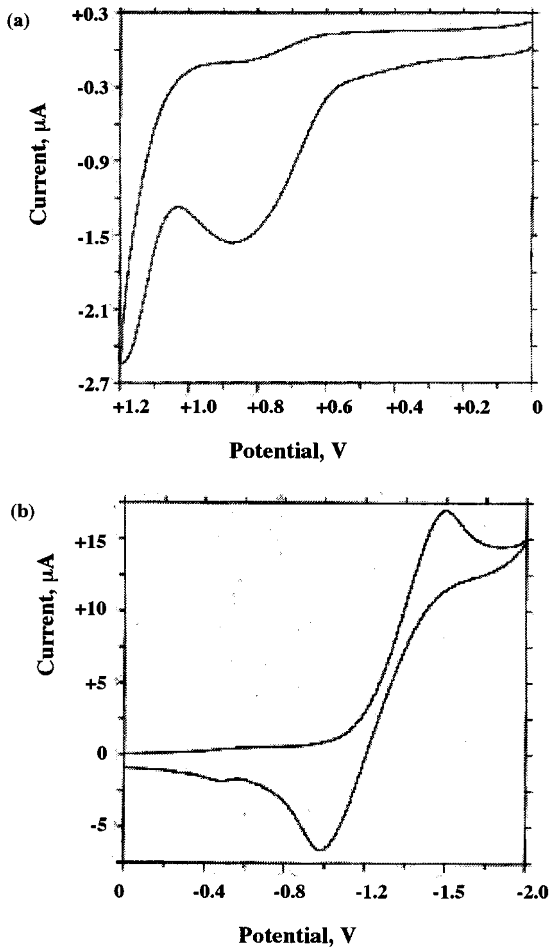


Figure 1. Cyclic voltammograms at **3a** in a 0.1 M CH_2Cl_2 solution of $^nBu_4NPF_6$ (a) or a 0.1 M THF solution of $^nBu_4NClO_4$ (b) vs Ag/Ag^+ at a sweep rate of 50 (a) or 100 mV s^{-1} (b).

organosilicon copolymers prepared by Fang et al.,[6] indicating the enhanced $\sigma-\sigma$ interaction between disilanylene unit and adjacent cyclodiborazane unit. Generally, the $\sigma-\pi$ conjugation between the Si−Si chain orbitals and the π-unit orbitals increases the HOMO energy and results in a decrease in the first ionization potential.[6] The effect of sweep rate on the oxidative potential of **3a** was also investigated. As the sweep rate was increased, the oxidative peak was observed in a higher potential region with increasing current intensity. The observed dependence of diffusion process of the redox species on the oxidation potential also suggests the irreversible nature of the redox cycle.

On the other hand, a reversible cycle was observed when scanning was performed within the potential range from −2.0 to 0 V (Figure 1b). In the 0.1 M THF solution of $^nBu_4NClO_4$, the peak due to the first reduction potential was observed at −1.60 V with a reoxidation peak at −0.98 V. A similar electrochemical behavior was also observed for **3b**. From these observations, **3a**,**b** can be expected as a novel type of electrochemically n-dopable $\sigma-\pi$ conjugated polymers, although they are unstable toward electrochemical oxidation.

Supporting Information Available: Text giving experimental details of the work, a scheme showing the preparation of the monomer, a table giving the dependence of the oxidation potential on the sweep rate, and figures showing NMR, IR, and UV−vis specrta for **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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