

Synthesis of novel poly(cyclodiborazane)s containing transition metal complexes in the main chain and their properties

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Summary

Novel poly(cyclodiborazane)s containing transition metal in the main chain were synthesized by hydroboration polymerization between dicyano monomers including metal complexes and tripylborane. From gel permeation chromatographic analysis (THF, PSt standards), the number-average molecular weights of the obtained polymers were found to be 6,000. The polymers were soluble in common organic solvents and showed good stability toward air and moisture. The optical properties of these polymers were examined by UV-vis absorption and fluorescence emission measurements.

Introduction

In recent years, there have been plenty of studies about “rigid-rod-polymers” containing transition metals [1] because of their interesting properties such as non-linear optical, liquid crystalline and semiconducting behaviors. Normally, an incorporation of the transition metal in the conjugated backbone with alkynyl linkages does not exhibit a significant activation of $d\pi-\pi^*$ transition in comparison with monomeric complex because of an energy mismatch between d-orbitals of the transition metal and π^* -orbitals of the alkynyl moiety.

On the other hand, we have synthesized many organoboron polymers by means of hydroboration polymerization. Recently, we succeeded in synthesis of highly stable poly(cyclodiborazane)s by the hydroboration polymerization between mesitylborane and the dicyano compounds [2]. These polymers showed great stability toward air and moisture compared with other organoboron polymers previously reported. Surprisingly, a highly fluorescent polymer was obtained when the electron-donating dicyano compound was incorporated into the polymer backbone. In this polymer, effective intramolecular charge transfer should have occurred between the electron-donating moiety and the electron-accepting cyclodiborazane unit [3].

In this study, some transition metal complexes were utilized as an electron source toward the cyclodiborazane unit to examine the interaction between transition metal

and boron atom. Thus, novel poly(cyclodiborazane)s containing transition metals in the main chain were prepared by means of hydroboration polymerization as an example of functionalized poly(cyclodiborazane)s.

Experimental

Materials and instruments

Tetrahydrofuran (THF) was dried over sodium and distilled before use. ^1H -, ^{31}P - and ^{11}B -NMR spectra were recorded in CDCl_3 on a JEOL EX-270 instrument. Gel permeation chromatographic analysis was carried out on a TOSOH G3000HXI by using THF as an eluent after calibration with polystyrene standards. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV-vis spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. Tripylborane [4], 4-ethynylbenzonitrile [5] and metal complexes [6] were prepared according to the reported methods, respectively. Other reagents were obtained commercially.

Monomer synthesis

Pt-dicyano monomer (1a). A mixture of 0.94g (1.40mmol) of *trans*- $[\text{PtCl}_2(\text{PnBu}_3)_2]$, 0.35g (2.80mmol) of 4-ethynylbenzonitrile, 10mg of CuI, and 50ml of diisopropylamine was refluxed for approximately 24h. After removing the solvent, the reaction mixture was extracted with Et_2O /water, and purified by column chromatography using hexane/ CHCl_3 as an eluent to yield 0.86g (72%) of yellow solid. NMR data (solution in CDCl_3): δ (^1H , ppm) = 7.46, 7.29 (d, d, Ar-H, 8H), 2.10 (m, P- CH_2 , 12H); δ (^{31}P , ppm) = -19.2. IR: (cm^{-1}) = 2220 (v C \equiv N), 2099 (v C \equiv C).

Pd-dicyano monomer (1b). To a mixture of 0.65g (1.12mmol) of *trans*- $[\text{PdCl}_2(\text{PnBu}_3)_2]$, 0.28g (2.23mmol) of 4-ethynylbenzonitrile, 10mg of CuI, and 10ml of diethyl ether, 50ml of diethylamine was added at room temperature under inert atmosphere, and the mixture was stirred for 12h. After removing the solvent, the reaction mixture was extracted with Et_2O /water, and purified by column chromatography using hexane/ CHCl_3 as an eluent. A white solid was recrystallized from hexane in a yield of 0.62g (73%). NMR data (solution in CDCl_3): δ (^1H , ppm) = 7.47, 7.29 (d, d, Ar-H, 8H), 1.97 (m, P- CH_2 , 12H); δ (^{31}P , ppm) = 11.8. IR: (cm^{-1}) = 2224 (v C \equiv N), 2096 (v C \equiv C).

Polymerization

A THF (1ml) solution of a slightly excess amount of tripylborane **2** (0.19g, 0.89mmol) was added dropwise to a suspension of Pt-monomer **1a** (0.27g, 0.30mmol) in THF (2ml) under nitrogen atmosphere at room temperature, and the resulting mixture was stirred for 24h. After evaporation of the solvent, the Pt-containing polymer **3a** was reprecipitated into MeOH to afford the yellow powder (0.25g, 66%). NMR data (solution in CDCl_3): δ (^1H , ppm) = 7.92-8.10 (CH=N, 2H), 7.20-7.51 (Ar-H, 8H), 6.91-7.11 (Trp-H, 2H), 2.83 [$\text{CH}(\text{Pr})_3$], 0.85-1.91 (P- CH_2 , 12H); δ (^{31}P , ppm) = -20.4. IR: (cm^{-1}) = 2370 (v B-H), 1640 (v C=N).

Pd-containing polymer **3b** was also obtained in a similar manner as described above.

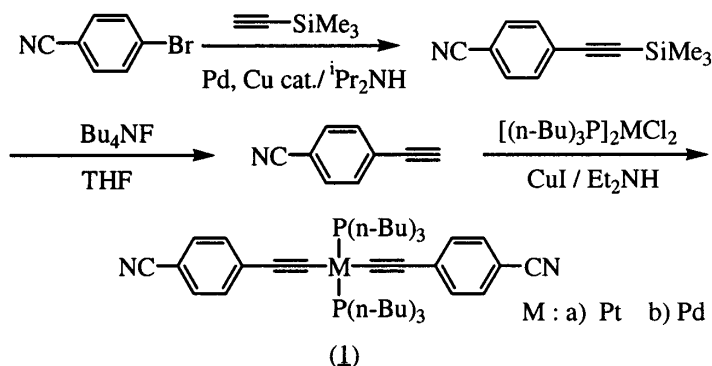
The reaction of **1b** (0.29g, 0.38mmol) and **2** (0.16g, 1.18mmol) gave the yellow powder of **3b** (0.25g, 65%). NMR data (solution in CDCl₃): δ (¹H, ppm) = 7.97-8.20 (CH=N, 2H), 7.20-7.55 (Ar-H, 8H), 6.95-7.10 (Trp-H, 2H), 2.83 [CH(ⁱPr),3H], 2.01-2.11 (P-CH₂, 12H); δ (³¹P, ppm) = 11.4. IR: (cm⁻¹) = 2411 (v B-H), 1644 (v C=N).

Results and Discussion

Monomer synthesis

The monomers **1a** and **1b** were synthesized using the literature procedure [1a] as described in Scheme 1. However, our attempts to utilize the procedure for the preparation of palladium-containing compound **1b** were unsuccessful, so that substantial modifications of the original method should be applied. Thus, diethylamine was added at 0-20 °C to an ether solution of the reactants. Generally, the platinum-phosphine complex has higher stability compared with those of palladium and nickel. Therefore lower reaction temperature should be applied to the synthesis of compound **1b** in order to prevent side-reactions and decomposition of the products.

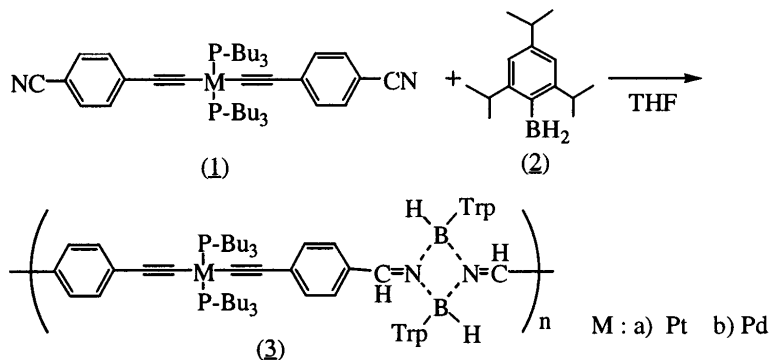
Scheme 1



Polymer synthesis

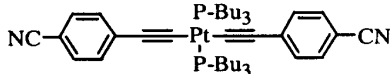
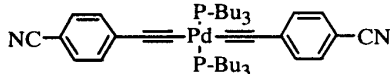
The polymerization procedure is illustrated in Scheme 2.

Scheme 2



Selective formation of the cyclodiborazane structure was achieved at relatively low temperature or extremely slow addition rate of tripropylborane. These polymers were obtained as yellowish powder and soluble in common organic solvents such as chloroform, benzene and THF. The polymerization results are summarized in Table 1.

Table 1. Polymerization results^{a)}

Monomer	M_w ^{b)}	M_n ^{b)}	M_w/M_n ^{b)}	Yield (%) ^{c)}
	9,700	6,300	1.5	66%
	10,400	6,000	1.7	65%

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

Polymer structures

The structures of the obtained polymers were examined by ¹H-, ³¹P-, ¹¹B-NMR, and IR spectra.

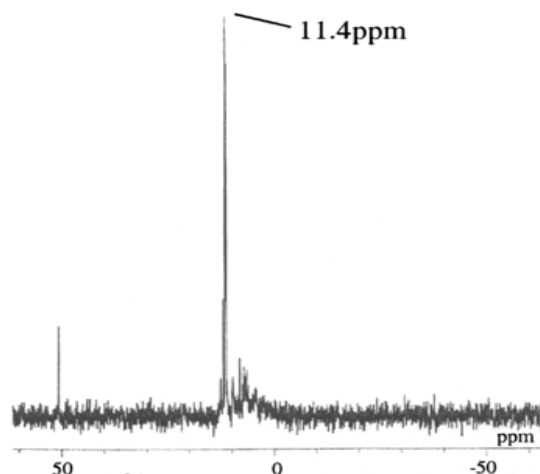


Figure 1. ³¹P-NMR spectrum of polymer 3b.

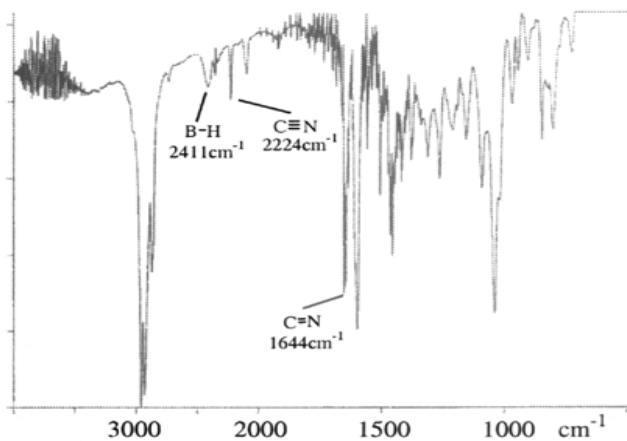


Figure 2. IR spectrum of polymer 3b.

In the ³¹P-NMR spectrum of the polymer 3b (Fig. 1), a sharp peak was observed at 11.4ppm (same position as the monomer 1b). This result indicates that the structure of metal complex was not affected during polymerization. In Figure 2, the successful hydroboration was confirmed by the presence of C=N bonds (1644cm⁻¹) and boron-hydrogen bonds (2411cm⁻¹). The unreacted or terminal cyano bonds (2224cm⁻¹) were also observed. The structure was also supported by the ¹H-, and ¹¹B-NMR spectra.

Optical properties

The UV-vis absorption spectra of the obtained polymers measured in chloroform at room temperature are shown in Figure 3 and 4. The peaks due to π - π^* transition of the polymer backbone were observed at slightly longer wavelength region compared with the absorption peaks of the monomers in both cases. Significant extension of π -conjugated length via transition metal and boron atom should be expected. However, the absorption edge of the polymer 3b was greatly broader than that of the polymer 3a. In the case of the rigid-rod polymers, which have transition metals but no boron atom, the shapes of absorption peaks are quite similar despite of the difference in metals. Thus, this result indicates that the interaction between boron atom and transition metal should be concerned, and that the interaction depends on the metals.

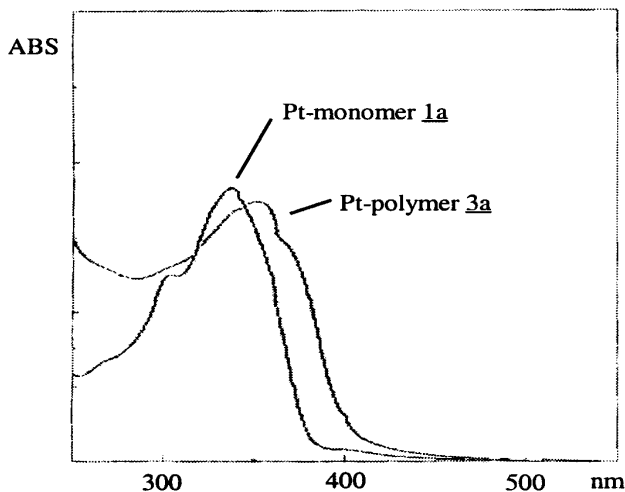


Figure 3. UV-vis absorption spectra of 1a and 3a in CHCl_3 at room temperature.

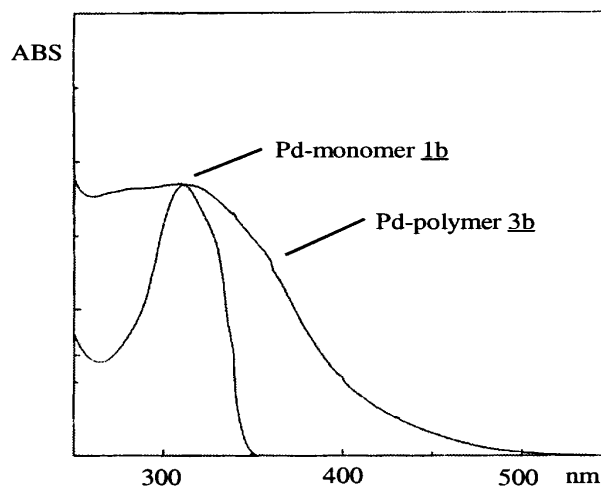


Figure 4. UV-vis absorption spectra of 1b and 3b in CHCl_3 at room temperature.

The fluorescence emission spectra measurement was also adapted to these polymers. The Pt-containing polymer 3a showed a weak emission peak around 460nm. As shown in Figure 5, the Pd-containing polymer 3b also exhibited an emission at 460nm (i) but relatively strong compared with 3a. Moreover, the polymer 3b showed the emission at 530nm (ii) when it was excited at 450nm. From this result, it is concluded that the polymer 3b changes the emission depending on the excited wavelength.

Stability of polymers

The stability of the polymers toward air and moisture was estimated by using GPC analysis. The obtained polymers were dissolved in THF and stirred for 1day with air-bubbling. During the experiment, the molecular weights of the polymers were monitored by GPC. As shown in Figure 6, the GPC curves of the polymer 3a were scarcely changed. Similar experiment was performed toward the mixture of the polymers and water. As a result, the obtained polymers showed good stability toward air and moisture. The stability of the polymers originates in the unique structures of cyclodiborazanes. The four-membered ring structure and sterically hindered triptyl group should prevent the oxidation of boron atoms.

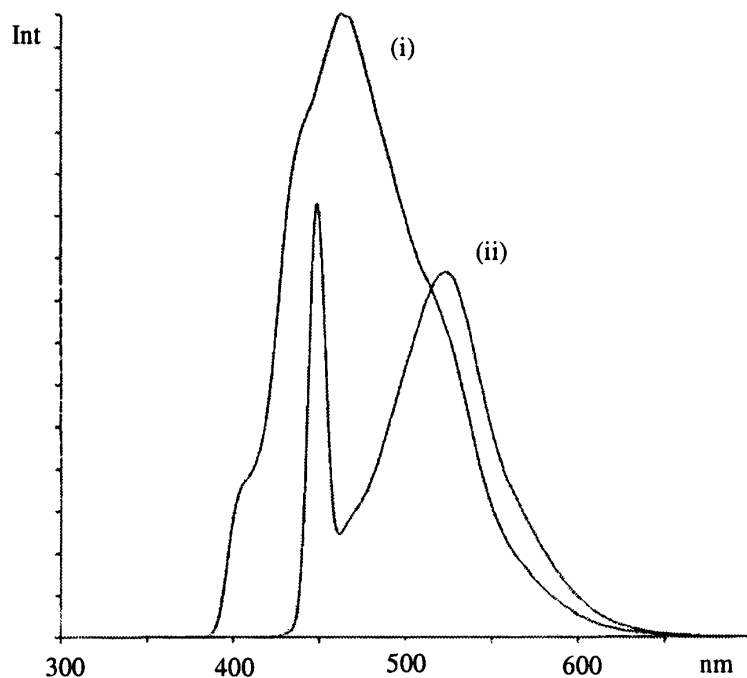


Figure 5. Fluorescence emission spectra of **3b** in CHCl_3 at room temperature excited at (i) 400 and (ii) 450nm.

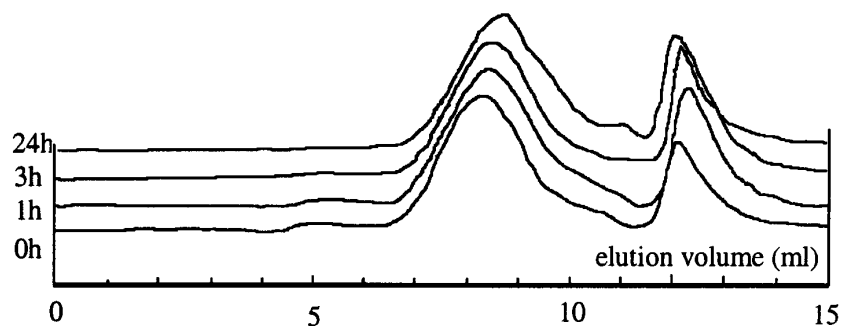


Figure 6. GPC curves of **3a** during the air-bubbling experiment.

Conclusions

Novel poly(cyclodiborazane)s containing transition metals in their backbone were prepared by hydroboration polymerization between dicyano monomers containing transition metal complexes and tripylborane. The obtained polymers are expected as a new kind of organometallic polymer materials including boron atom in the main chain. Furthermore, these polymers exhibited extension of π -conjugation length via transition metal and boron atom, and great stability toward air and moisture. Further investigation should be performed toward the interesting interaction between transition metal and boron atom.

References

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