

## Synthesis of novel $\pi$ -conjugated boron polymers containing transition metal in the main chain and their optical properties

Fukashi Matsumoto, Noriyoshi Matsumi, Yoshiki Chujo (✉)

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

e-mail: chujo@chujo.synchem.kyoto-u.ac.jp, Tel.: +81-75-753-5655, Fax: +81-75-753-5675

Received: 16 April 2001/Accepted: 27 April 2001

### Summary

Novel  $\pi$ -conjugated boron polymers containing transition metals in the main chain were prepared by hydroboration polymerization between tetrayne monomer including metal complex and tripylborane. From gel permeation chromatographic analysis (THF, PSt standards), the number-average molecular weights of the polymers obtained were found to be 9,000. The polymers were soluble in common organic solvents such as THF, chloroform and benzene. The absorption peaks due to  $\pi$ - $\pi^*$  transition were observed around 390nm in the UV-vis spectra of these polymers. The fluorescence emission spectra exhibited intense peaks at 490nm (in chloroform, room temperature, excitation wavelength at 390nm).

### 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  $\pi^*$ -orbitals of the alkynyl moiety.

On the other hand, the conjugated polymers containing boron atoms in their backbone are known for the extended  $\pi$ -conjugation through the vacant p-orbital of boron atom. For example, it was reported that the polymer prepared by hydroboration polymerization between 1,4-diethynylbenzene and mesitylborane showed excellent third-order non-linear optical property [2]. More recently, we succeeded in synthesis of  $\pi$ -conjugated boron polymer including a ruthenium complex and observed the bathochromic shift of absorption peak assignable to  $d\pi$ - $p\pi^*$  transition in the UV-vis absorption spectrum, as much as 141nm longer compared with the corresponding monomer [3]. In this system, a significant activation of MLCT (Metal to Ligand Charge Transfer) in the complex followed by an interaction between the highly electron-accepting boron atom and the ruthenium complex might possibly occur.

In this study, novel  $\pi$ -conjugated boron polymers containing platinum or palladium in their main chain were successfully synthesized by hydroboration polymerization to investigate the relationship between the energy levels of d-orbitals and the unusual activation of  $d\pi$ - $p\pi^*$  transition due to boron-metal interaction.

## Experimental

### Materials and instruments

Tetrahydrofuran (THF) was dried over sodium and distilled before use.  $^1\text{H}$ -,  $^{31}\text{P}$ - and  $^{11}\text{B}$ -NMR spectra were recorded in  $\text{CDCl}_3$  on a JEOL EX-270 instrument. Gel permeation chromatographic analysis was carried out on a TOSOH G3000HXL 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], 1-ethynyl-4-(triisopropylsilyl)ethynylbenzene [5] and metal complexes [6] were prepared according to the reported methods, respectively.

### Monomer synthesis

**Pt complex (1a).** A mixture of 0.94g (1.40mmol) of  $\text{trans-[PtCl}_2(\text{P}n\text{Bu}_3)_2]$ , 0.83g (2.93mmol) of 1-ethynyl-4-(triisopropylsilyl)ethynylbenzene, 10mg of CuI, and 60ml of diisopropylamine is refluxed for approximately 24h. After removing the solvent, the reaction mixture was extracted with  $\text{Et}_2\text{O}$ /water, and recrystallized from MeOH to yield 0.98g (60%) of yellow solid. NMR data (solution in  $\text{CDCl}_3$ ):  $\delta$  ( $^1\text{H}$ , ppm) = 7.17-7.40 (Ar-H, 8H), 2.10 (m, P- $\text{CH}_2$ , 12H), 1.12 (s,  $^i\text{Pr}$ -H, 42H);  $\delta$  ( $^{31}\text{P}$ , ppm) = -18.19.

**Pt-tetrayne monomer (2a).** To a THF solution of 1a 0.98g (0.84mmol), 0.46ml (0.46mmol) of  $\text{Bu}_4\text{NF}$  was added and the reaction mixture was stirred for 10min. After removing the solvent, the crude compound was purified by column chromatography using hexane/ $\text{CHCl}_3$  as an eluent and recrystallized from MeOH. The desired product was obtained in 40% yield. NMR data (solution in  $\text{CDCl}_3$ ):  $\delta$  ( $^1\text{H}$ , ppm) = 7.17-7.55 (Ar-H, 8H), 3.19 (s,  $\text{C}\equiv\text{C}$ -H, 2H), 2.10 (m, P- $\text{CH}_2$ , 12H);  $\delta$  ( $^{31}\text{P}$ , ppm) = -18.19. IR: ( $\text{cm}^{-1}$ ) = 2096 ( $\nu$   $\text{C}\equiv\text{C}$ ).

**Pd complex (1b).** To a mixture of 0.83g (1.42mmol) of  $\text{trans-[PdCl}_2(\text{P}n\text{Bu}_3)_2]$ , 0.80g (2.85mmol) of 1-ethynyl-4-(triisopropylsilyl)ethynylbenzene, and 20ml of dry  $\text{Et}_2\text{O}$ , 70ml of dry diethylamine was added at  $0^\circ\text{C}$  under inert atmosphere, and the mixture was stirred for 3h. After removing the solvent, the resultant ammonium salt was filtered and washed with THF. A white solid was recrystallized from hexane in a yield of 1.26g (83%). NMR data (solution in  $\text{CDCl}_3$ ):  $\delta$  ( $^1\text{H}$ , ppm) = 7.18, 7.30 (d, d, Ar-H, 8H), 1.97 (m, P- $\text{CH}_2$ , 12H), 1.12 (s,  $^i\text{Pr}$ -H, 42H);  $\delta$  ( $^{31}\text{P}$ , ppm) = 11.44.

**Pd-tetrayne monomer (2b).** The compound was prepared in a similar manner to that described above (2a) by reacting 1.24g (1.15mmol) of 1b and 0.58ml (0.58mmol) of  $\text{Bu}_4\text{NF}$ . The colorless crystals (0.57g, 65%) were obtained. NMR data (solution in  $\text{CDCl}_3$ ):  $\delta$  ( $^1\text{H}$ , ppm) = 7.20, 7.31 (d, d, Ar-H, 8H), 3.08 (s,  $\text{C}\equiv\text{C}$ -H, 2H), 1.97 (m, P- $\text{CH}_2$ , 12H);  $\delta$  ( $^{31}\text{P}$ , ppm) = 11.44. IR: ( $\text{cm}^{-1}$ ) = 2094 ( $\nu$   $\text{C}\equiv\text{C}$ ).

### Polymerization

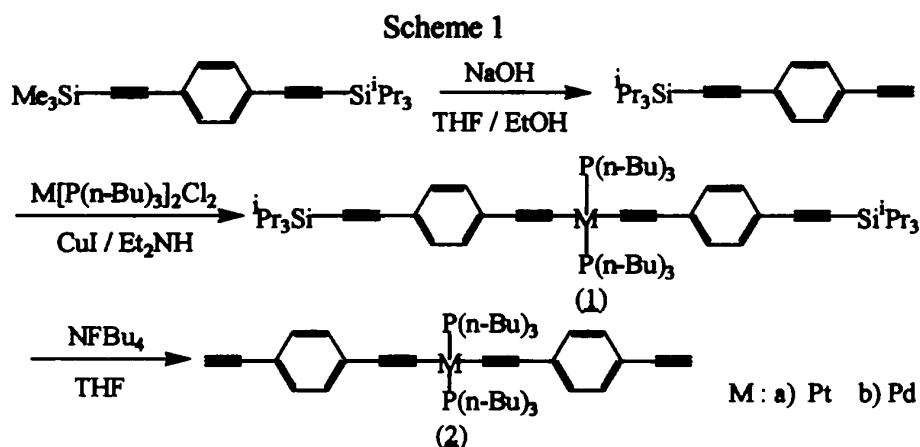
A THF (1ml) solution of a slightly excess amount of tripylborane 3 (0.28g, 1.29mmol) was added dropwise to a suspension of Pt-monomer 2a (0.50g, 1.18mmol) in THF (2ml) under nitrogen atmosphere at room temperature, and the resulting mixture was stirred for 12h. After evaporation of the solvent, the Pt-containing polymer 4a was reprecipitated into MeOH to afford the yellow powder (0.27g, 21%). NMR data (solution in  $\text{CDCl}_3$ ):  $\delta$  ( $^1\text{H}$ , ppm) = 6.90-7.54 (Ar-H, 8H), 2.62, 2.92 [ $\text{CH}$  ( $^i\text{Pr}$ ), 3H], 2.12 (P- $\text{CH}_2$ , 12H);  $\delta$  ( $^{31}\text{P}$ , ppm) = -18.19;  $\delta$  ( $^{11}\text{B}$ , ppm) = 8.52. IR: ( $\text{cm}^{-1}$ ) = 2096 ( $\nu$   $\text{C}\equiv\text{C}$ ), 1585 ( $\nu$   $\text{C}=\text{C}$ ).

Pd-containing polymer **4b** was also obtained in a similar manner as described above. The reaction of **2b** (0.39g, 0.52mmol) and **3** (0.12g, 0.54mmol) gave the red powder of **4b** (0.25g, 50%). NMR data (solution in CDCl<sub>3</sub>):  $\delta$  (<sup>1</sup>H, ppm) = 6.95-7.50 (Ar-H, 10H), 2.62, 2.92 [CH (<sup>i</sup>Pr), 3H], 2.07 (P-CH<sub>2</sub>, 12H);  $\delta$  (<sup>31</sup>P, ppm) = 11.44;  $\delta$  (<sup>11</sup>B, ppm) = 8.04. IR: (cm<sup>-1</sup>) = 2094 (ν C≡C), 1597 (ν C=C).

## Results and Discussion

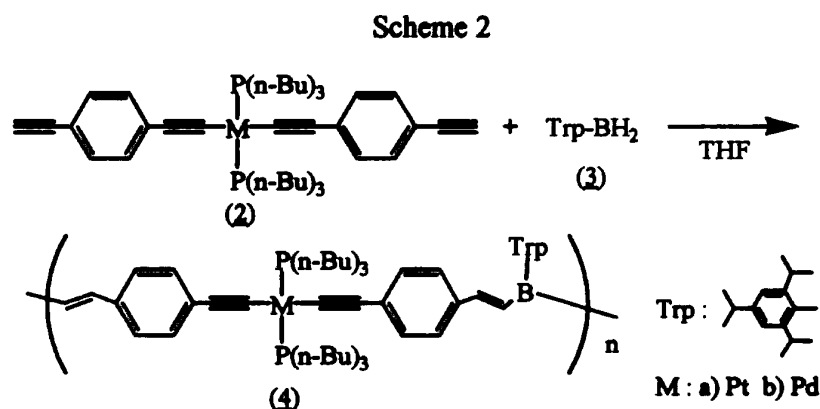
### Monomer synthesis

The monomers **2a** and **2b** were synthesized following 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. The desired product was obtained without Cu catalyst in this manner. 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.



### Polymer synthesis

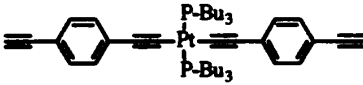
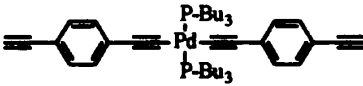
The polymerization procedure is illustrated in Scheme 2.



Hydroboration polymerization progressed successfully when the triarylborane was reacted with the end-alkynyl group of the monomer **2**. Inner alkynyl bonds directly associated to the transition metal might undertake the similar addition, however, a selective addition to the end

moiety has achieved owing to the structural hindrance of tributylphosphine and triply group. Furthermore, such an intermolecular cross-linking reaction could be controlled at low temperature or extremely slow addition of triplyborane. The obtained polymers were soluble in common organic solvents such as chloroform, benzene and THF. The polymerization results are summarized in Table 1.

**Table 1. Polymerization results**

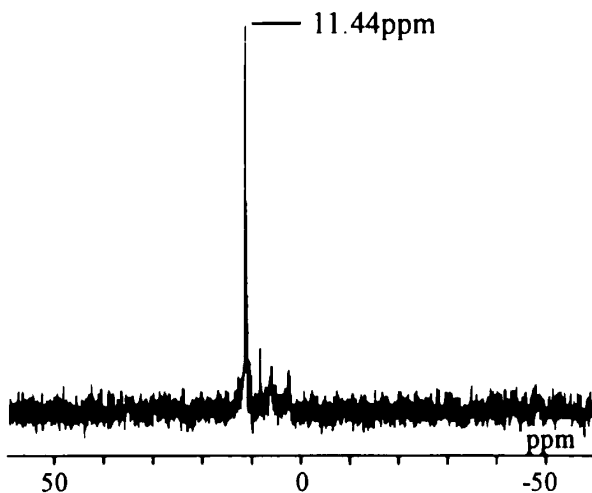
Monomer	$M_w^a$	$M_n^a$	$M_w/M_n^a$	Yield (%) <sup>b</sup>
 (2a)	16380	9100	1.8	21
 (2b)	18900	9000	2.1	50

<sup>a</sup> GPC (THF), PSt standards.

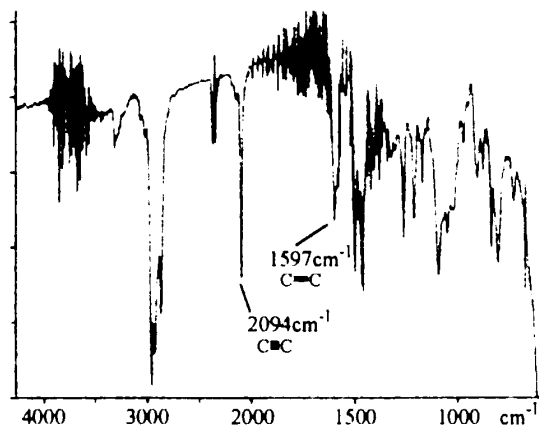
<sup>b</sup> Isolated yield after washing with methanol.

### Polymer structures

The structures of the obtained polymers were examined by <sup>1</sup>H-, <sup>31</sup>P-, <sup>11</sup>B-NMR, and IR spectra. In the <sup>31</sup>P-NMR spectrum of the polymer 4b (Fig. 1), a sharp peak was observed at -11.44ppm (same position as the monomer 2b). 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 alkynyl bonds (2094cm<sup>-1</sup>) and alkenyl bonds (1597cm<sup>-1</sup>). The structure was also supported by the <sup>1</sup>H-, and <sup>11</sup>B-NMR spectra.



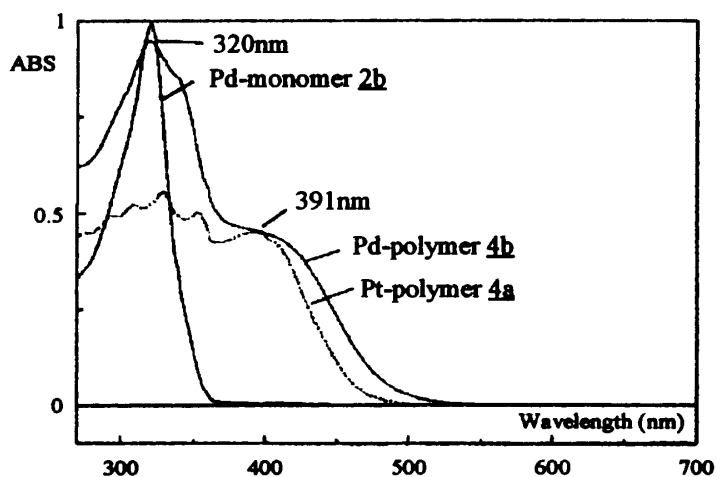
**Figure 1.** <sup>31</sup>P-NMR spectrum of polymer 4b.



**Figure 2.** IR spectrum of polymer 4b.

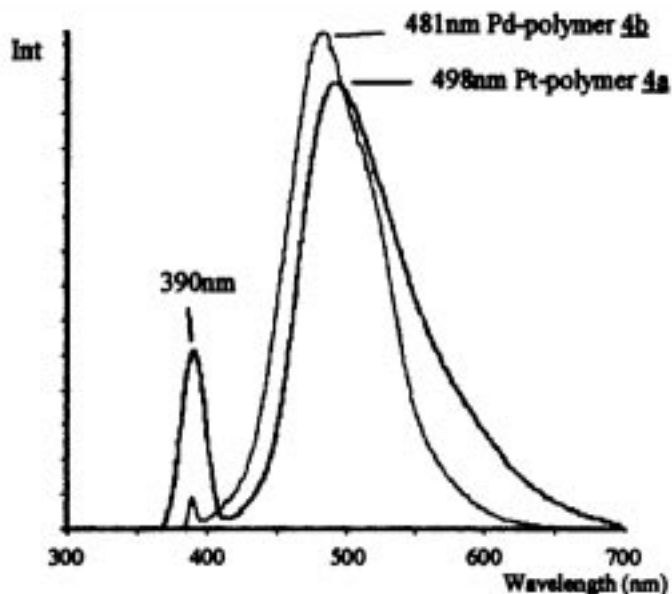
### Optical properties

The UV-vis absorption spectra of the obtained polymers measured in chloroform at room temperature are shown in Figure 3. The peak due to  $\pi$ - $\pi^*$  transition of the polymer backbone was observed at longer wavelength region compared with the absorption peak of the monomer 2b and the absorption edge of the polymer 4b was slightly wider than that of the Pt-containing polymer 4a. These results indicate a highly extended  $\pi$ -delocalization length via



**Figure 3.** UV-vis absorption spectra of **2b**, **4a** and **4b** in  $\text{CHCl}_3$  at room temperature.

transition metal and boron atom. The difference in absorption peaks between two polymers **4a** and **4b** is mainly associated with the nature of the transition metal used. The fluorescence emission spectra measurement was also adopted to these polymers. As shown in Figure 4, the obtained polymers exhibited an intense emission at 498 nm (**4a**) and 481 nm (**4b**) respectively when they were excited at 390 nm. A bright green emission of dilute chloroform solution was observed upon irradiation with ultraviolet light.



**Figure 4.** Fluorescence emission spectra of **4a** and **4b** in  $\text{CHCl}_3$  at room temperature (excited at 390 nm).

As a result, the significant activation of MLCT shown in the system of ruthenium [3] was not observed in the case of platinum or palladium. This result indicates that the interaction between transition metal and boron atom has great relation to energy levels of the transition metal although the structural difference of ligands that coordinate to the metal should be concerned, actually that must affect the energy levels of these transition metals. On the contrary, the absorption peaks assignable to  $\pi\text{-}\pi^*$  transition through polymer backbone of the

polymers obtained in this study were farther red-shifted compared with that of the ruthenium-containing polymer. Generally, the expansion of polymer  $\pi$ -conjugation depends on the degree of polymerization to some extent. However the polymers interested here are in almost same range of polymerization degree, so that an effective delocalization of  $\pi$ -electrons in the polymers **4a** and **4b** must occur more significantly than in the ruthenium containing polymer.

## Conclusions

Novel  $\pi$ -conjugated organoboron polymers containing transition metals in their backbone were prepared by hydroboration polymerization between tetrayne monomer containing transition metal complex 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 were found to show some interesting properties such as expansion of  $\pi$ -conjugation length via transition metal and boron atom, and bright fluorescence emission of green light. Further investigation must be performed to clarify the interesting interaction between transition metal and boron atom.

## References

1. For example, (a) Takahashi S, Kariya M, Yatake T, Sonogashira K, Hagihara N (1978) *Macromolecules* 11:1063 (b) Takahashi S, Murata E, Kariya M, Sonogashira K, Hagihara N (1979) *Macromolecules* 12:1016 (c) Lavastre O, Even M, Pacreau A, Varion JP, Dixneuf PH (1996) *Organometallics* 15:1530
2. Matsumi N, Naka K, Chujo Y (1998) *J Am Chem Soc* 120:5112
3. Matsumi N, Chujo Y, Lavastre O, Dixneuf PH (2001) *Organometallics* in press.
4. (a) Pelter A, Smith K, Buss D, Jin Z (1992) *Heteroatom Chem* 3:275 (b) Smith K, Pelter A, Jin Z (1993) *J Chem Soc, Perkin Trans* 1:395. For the synthesis of 2-tripylbromide, see Whitesides GM, Eisenhut M, Bunting W M (1974) *J Am Chem Soc* 96:5398
5. Olivier L, Dixneuf PH (1996) *Tetrahedron* 15:5495
6. Kauffman GW, Teter LA (1963) *Inorg Syn* 7:245