

## Chiral $\pi$ -conjugated organoboron polymers\*

Fukashi Matsumoto and Yoshiki Chujo<sup>‡</sup>

*Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

**Abstract:** A novel  $\pi$ -conjugated organoboron polymer with a chiral side chain was prepared by way of hydroboration polymerization between an optically active diyne monomer and triisopropylphenylborane. The achiral analog of this organoboron polymer was also prepared as reference material. Optical properties and optical activity were investigated by UV–vis absorption, fluorescence emission, and circular dichroism (CD) spectroscopy. Concentration dependence and the influence of solvent effects upon chiroptical activity are described.

**Keywords:** conjugated polymers; organoboron polymers; chiral group; chiroptical property; hydroboration; polymerization.

### INTRODUCTION

Conjugated polymers containing boron atoms in their backbone are known to extend  $\pi$ -conjugation through the vacant p-orbital of the boron atom [1–4]. For example, it has been reported that the polymer prepared by hydroboration polymerization between 1,4-diethynylbenzene and mesitylborane shows excellent third-order nonlinear optical properties. Despite the good stability of these polymers toward air and moisture, some are relatively fragile from the viewpoint of long-term stability.  $\pi$ -Conjugated organoboron polymers can be regarded as n-type conductive materials because of the high electron affinity of the boron atom. Matsuyama et al. have measured the electrical conductivity of a  $\pi$ -conjugated organoboron polymer by doping with triethylamine or  $I_2^-$  [5]. However, the result was as low as  $\sim 10^{-7}$  S/cm.

On the other hand, a molecular dynamics calculation has been conducted for the model oligomer of a  $\pi$ -conjugated polymer. From the calculation, one can see substantial changes of conformation of the target polymer. In terms of electrical conductivity, such conformational changes are undesirable because they may perturb or even disrupt the  $\pi$ -conjugation capacity of the polymer chain. Therefore, the conformation of the polymers should be controlled to optimize their conductivity properties.

One strategy to generate structurally defined polymer material is through attachment of a chiral side chain to the  $\pi$ -conjugated backbone [6–9]. That can impart optical activity to the polymer chain, and generate a helical structure in favorable cases. In this paper, we describe recent progress in preparing a novel  $\pi$ -conjugated organoboron polymer with chiral side chains, and investigations into their optical and chiroptical properties in various solvents and mixed solvents.

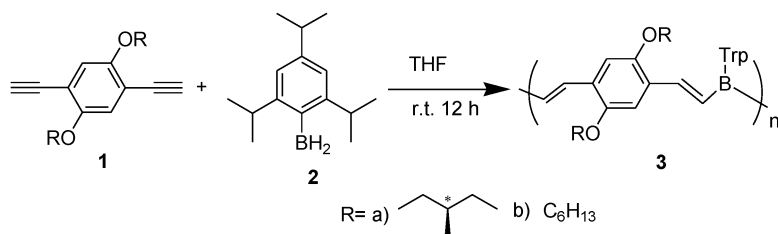
---

\*Paper based on a presentation at POLYCHAR 16: World Forum on Advanced Materials, 17–21 February 2008, Lucknow, India. Other presentations are published in this issue, pp. 389–570.

<sup>‡</sup>Corresponding author

## RESULTS AND DISCUSSION

The hydroboration polymerization between chiral monomer (**1a**) and tripylborane (**2**, tripyl: tri-isopropylphenyl) was carried out as follows (Scheme 1). Under nitrogen atmosphere, to a tetrahydrofuran (THF) solution of **1a** was added dropwise a slightly excess amount of **2** in THF at room temperature. After stirring the reaction mixture for 12 h, evaporation of the solvent gave a reddish solid. After the reprecipitation into methanol, the corresponding polymer CPPVB (**3a**) was obtained as a yellow powder in 76 % yield. From the gel permeation chromatographic (GPC) analysis (THF, PSt standards), the number-average molecular weight of **3a** was estimated to be 5600. The dihexyloxy monomer (**1b**) also gave the HPPVB (**3b**,  $M_n$  3900) in 71 % yield. The polymerization results are summarized in Table 1. The structures of the obtained polymers were well supported by  $^1\text{H}$ -,  $^{13}\text{C}$ -,  $^{11}\text{B}$ -NMR, and IR spectra. It is notable that these polymers seem to be highly stable against air and moisture compared with the organoboron polymers having no substitution on the phenylene moiety. It can be concluded that the electron-donating alkoxy group gave the stability to the boron atom via the charge transfer effect.



**Scheme 1** Polymerization.

**Table 1** Polymerization results.

Polymer	$M_n^a$	$M_w^a$	$M_w/M_n^a$	Yield (%) <sup>b</sup>
CPPVB ( <b>3a</b> )	5600	11 500	2.0	73
HPPVB ( <b>3b</b> )	3900	9000	2.3	71

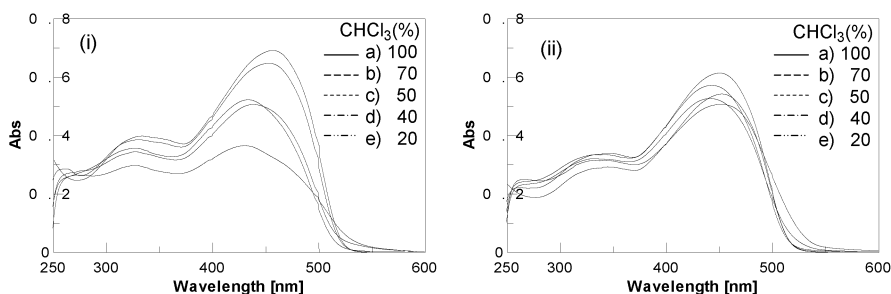
<sup>a</sup>Measured by GPC (THF). Polystyrene standards.

<sup>b</sup>Isolated yields after reprecipitation into MeOH.

## Optical properties

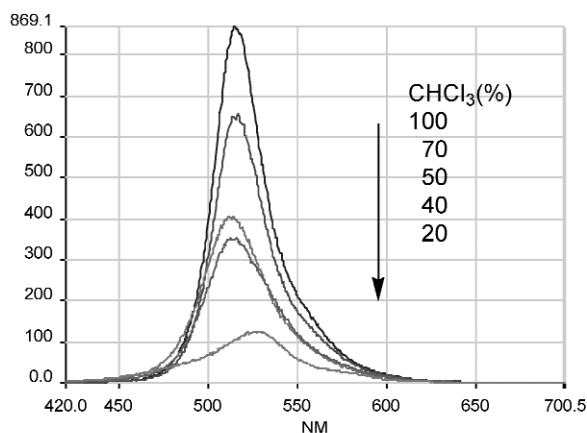
The UV–vis spectra (in chloroform, at room temperature) of **3a** and **3b** demonstrate the significant  $\pi$ -conjugation along the backbone via vacant p-orbital of boron atom. For instance, in the case of CPPVB (**3a**), the absorption maximum was observed at 453 nm. This value was red-shifted in comparison with that of **1a** (325 nm).

To get a picture of the difference between CPPVB (**3a**) and HPPVB (**3b**) in optical properties, we started the measurement of UV–vis spectra in  $\text{CHCl}_3/\text{MeOH}$  mixture. Interestingly, the absorption behavior of HPPVB (**3b**) in the mixed solvents, Fig. 1 (ii), was nearly independent in respect of the solvent used, and the behavior was completely different from that of CPPVB (**3a**). As shown in Fig. 1 (i), there is a continuous decrease of the molar absorbance with increasing methanol contents and a slight tailing of the absorption peak into the low-energy region, accompanied by the formation of aggregates. Moreover, CPPVB (**3a**) showed a distinct solvatochromism, which should be attributed to conformational changes. As a result, **3a** and **3b** had a significant difference in the formation of aggregates, due to the difference in chirality and/or solubility of the side chain.



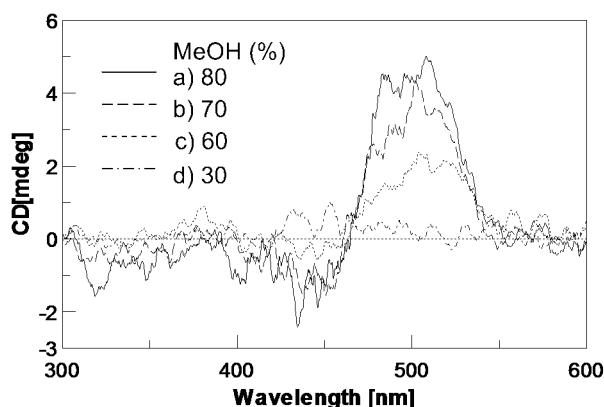
**Fig. 1** UV-vis absorption spectra of (i) CPPVB (**3a**) and (ii) HPPVB (**3b**) in chloroform/methanol solutions ( $4.0 \times 10^{-5}$  M);  $\text{CHCl}_3$  %: (a) 100, (b) 70, (c) 50, (d) 40, (e) 20.

On the contrary, fluorescence emission spectra of these polymers showed no significant difference. They had a distinct peak at 520 nm, and showed a constant decrease of the intensity as methanol contents increased. The emission spectra of CPPVB (**3a**) are described in Fig. 2.



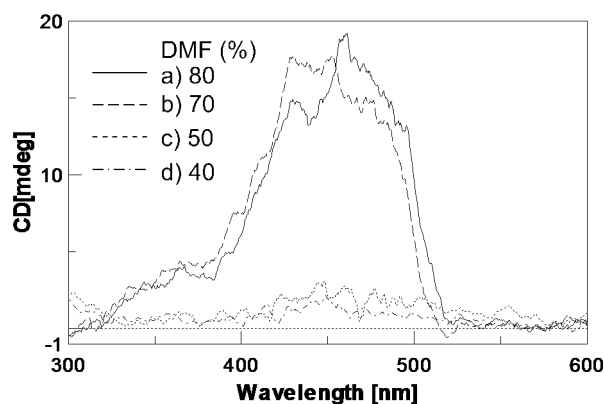
**Fig. 2** Fluorescence emission spectra of CPPVB (**3a**) in chloroform/methanol solutions ( $4.0 \times 10^{-5}$  M).

Circular dichroism (CD) spectra of CPPVB (**3a**) in  $\text{CHCl}_3/\text{MeOH}$  mixtures containing an increasing amount of methanol are illustrated in Fig. 3. From 0 up to 50 % of methanol in the mixture, any chiroptical activity could not be observed. From 50 up to 80 % of methanol, the intensity of the Cotton effect increased parallel to the continuous decrease of the absorbance. It is notable that the chiroptical activity was observed within 450–550 nm, which was red-shifted compared with the absorption spectra. Therefore, the continuous increase of the chiroptical activity of CPPVB (**3a**) should be assigned to the progressive aggregation of individual polymer chains.



**Fig. 3** CD spectra of CPPVB (**3a**) in chloroform/methanol solutions ( $4.0 \times 10^{-5}$  M);  $\text{CHCl}_3$  %: (a) 80, (b) 70, (c) 60, (d) 30.

Remarkably, a different chiroptical behavior was observed when toluene/dimethylformamide (DMF) mixture was applied as a solvent system. As shown in Fig. 4, a chiroptical activity was obtained about four times as large as that of chloroform/methanol mixture. Furthermore, the solvent mixture moved the CD spectra to 400–500 nm, within the delocalized  $\pi$ - $\pi^*$  transition of the polymer chain. However, when the toluene/methanol mixture was applied, the result was the same as that of chloroform/methanol. These results might offer the assumption that a coordination bond between boron and nitrogen would give the improvement of the chiroptical activity throughout the polymer chain accompanied by the formation of the aggregates.



**Fig. 4** CD spectra of CPPVB (**3a**) in toluene/DMF solutions ( $4.0 \times 10^{-5}$  M);  $\text{CHCl}_3$  %: (a) 80, (b) 70, (c) 50, (d) 40.

## CONCLUSION

Novel  $\pi$ -conjugated organoboron polymer with chiral side chain was prepared by way of hydroboration polymerization. The obtained polymer showed good stability against air and moisture. A chiroptical activity was induced to the polymer chain via the chiral side chain. Interestingly, the chiroptical activity was improved in the solvent of toluene/DMF mixture.

## EXPERIMENTAL SECTION

**Materials and instruments:** THF was distilled before use.  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{11}\text{B}$ -NMR spectra were recorded in  $\text{CDCl}_3$  on a JEOL EX-270 instrument. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. GPC analysis was carried out on a TOSOH G3000HXL by using THF as an eluent after calibration with polystyrene standards. UV-vis spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. CD spectra were measured on a Jasco spectropolarimeter J-715. 2,5-Bis(2-(*S*)-methylbutoxy)-1,4-diethynyl-benzene (**1a**) [11], 1,4-diethynyl-2,5-dihexyloxybenzene (**1b**) [12], and tripylborane (**2**) [13,14] were prepared according to the reported procedure. Other reagents were commercially available and purified before use. All reactions were performed under nitrogen atmosphere.

**CPPVB (3a):** A THF (1 mL) solution of a slight excess of tripylborane **2** (0.128 g, 0.593 mmol) was added dropwise to a solution of **1a** (0.169 g, 0.565 mmol) in THF (1 mL) under nitrogen atmosphere at room temperature, and the resulting mixture was stirred for 12 h. After evaporation of the solvent, the polymer **3a** was reprecipitated into MeOH to afford the reddish powder (0.214 g, 73 %). Anal. Calcd for  $\text{C}_{35}\text{H}_{51}\text{BO}_2$  (unit wt 514.47): C, 81.69; H, 9.99. Found: C, 79.28; H, 9.96. NMR data (solution in  $\text{CDCl}_3$ ):  $\delta$  ( $^1\text{H}$ , ppm) = 7.84 (2H,  $-\text{CH}=\text{CH}-$ ), 6.96 (4H, Ar), 3.78–3.64 (4H,  $-\text{OCH}_2-$ ), 2.89 and 2.47 [3H,  $^i\text{Pr}-\text{CH}(\text{Tripyl})$ ], 1.95–0.82 (36H,  $-\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5$ ,  $-\text{CCH}_3(\text{Tripyl})$ );  $\delta$  ( $^{13}\text{C}$ , ppm) = 151.82, 121.81, and 109.96 (Ar), 148.92, 147.14, and 119.36 [ $\text{Ar}(\text{Tripyl})$ ], 134.27 ( $-\text{CH}=\text{CH}-$ ), 73.36 ( $-\text{OCH}_2-$ ), 35.00–34.17 ( $-\text{CH}-$ ), 25.96 ( $-\text{CH}_2-$ ), 24.66 [ $-\text{CH}_3$  (Tripyl)], 16.66 and 11.32 ( $-\text{CH}_3$ );  $\delta$  ( $^{11}\text{B}$ , ppm) = 7.52. IR ( $\text{cm}^{-1}$ ) 1576 ( $-\text{CH}=\text{CH}-$ ).

**HPPVB (3b):** To a solution of **1b** (0.163 g, 0.500 mmol) in THF (1 mL), THF (1 mL) solution of a slight excess of tripylborane **2** (0.114 g, 0.525 mmol) was added dropwise under nitrogen atmosphere at room temperature, and the resulting mixture was stirred for 12 h. After evaporation of the solvent, the polymer **3b** was reprecipitated into MeOH to yield the yellow powder (0.192 g, 71 %). Anal. Calcd for  $\text{C}_{27}\text{H}_{33}\text{BO}_2$  (unit wt 542.64): C, 81.89; H, 10.22. Found: C, 81.22; H, 10.29. NMR data (solution in  $\text{CDCl}_3$ ):  $\delta$  ( $^1\text{H}$ , ppm) = 7.81 (2H,  $-\text{CH}=\text{CH}-$ ), 6.97 (4H, Ar), 4.00–3.75 (4H,  $-\text{OCH}_2-$ ), 2.89 and 2.49 [3H,  $^i\text{Pr}-\text{CH}(\text{Tripyl})$ ], 1.82–0.86 [31H,  $-\text{C}_5\text{H}_{11}$ ,  $-\text{CCH}_3(\text{Tripyl})$ ];  $\delta$  ( $^{13}\text{C}$ , ppm) = 151.72, 121.81, and 110.63 (Ar), 148.96, 147.23, and 119.30 [ $\text{Ar}(\text{Tripyl})$ ], 129.05 ( $-\text{CH}=\text{CH}-$ ), 69.02 ( $-\text{OCH}_2-$ ), 35.00, 34.31 ( $-\text{CH}-$ ), 29.24, 28.81, 25.59, 22.51 ( $-\text{CH}_2-$ ), 24.56 [ $-\text{CH}_3$  (Tripyl)], 14.01 ( $-\text{CH}_3$ );  $\delta$  ( $^{11}\text{B}$ , ppm) = 8.52. IR ( $\text{cm}^{-1}$ ) 1556 ( $-\text{CH}=\text{CH}-$ ).

## REFERENCES

1. N. Matsumi, K. Naka, Y. Chujo. *J. Am. Chem. Soc.* **120**, 5112 (1998).
2. N. Matsumi, K. Naka, Y. Chujo. *J. Am. Chem. Soc.* **120**, 10776 (1998).
3. N. Matsumi, T. Umeyama, Y. Chujo. *Macromolecules* **33**, 3956 (2000).
4. N. Matsumi, Y. Chujo. *Polym. J.* **40**, 77 (2008).
5. H. Kobayashi, N. Sato, Y. Ichikawa, M. Miyata, Y. Chujo, T. Matsuyama. *Synth. Met.* **135**, 393 (2003).
6. M. Andersson, P. O. Ekeblad, T. Hjertberg, O. Wennerström, O. Inganäs. *Polym. Commun.* **32**, 546 (1991).
7. M. M. Bouman, E. E. Havinga, R. A. Janssen, E. W. Meijer. *Mol. Cryst. Liq. Cryst.* **256**, 439 (1994).
8. B. M. W. Langeveld-Voss, E. Peeters, R. A. J. Janssen, E. W. Meijer. *Synth. Met.* **84**, 611 (1997).
9. G. Bidan, S. Guillerz, V. Sorokin. *Adv. Mater.* **8**, 157 (1996).
10. R. Fiesel, U. Scherf. *Macromol. Rapid Commun.* **19**, 427 (1998).
11. C.-Z. Zhou, T. Liu, J.-M. Xu, Z.-K. Chen. *Macromolecules* **36**, 1457 (2003).
12. A. Pelter, K. Smith, D. Buss, Z. Jin. *Heteroat. Chem.* **3**, 275 (1992).
13. K. Smith, A. Pelter, Z. Jin. *J. Chem. Soc., Perkin Trans. 1* **1**, 395 (1993).