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Synthesis of Organoboron π-Conjugated Polymers by Hydroboration Polymerization between Heteroaromatic Diynes and Mesitylborane and Their Light Emitting Properties

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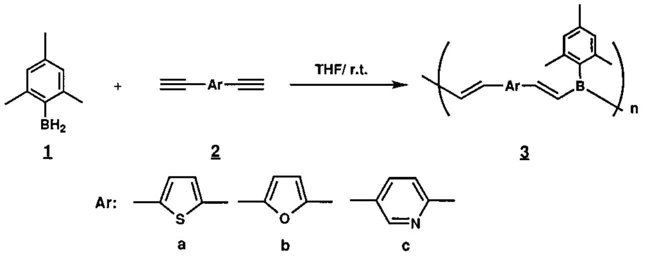
There has been a great deal interest in the synthesis of novel π-conjugated systems for a number of years. In particular, introducing an inorganic element in conjugated backbone[1] is an attractive approach to produce polymers showing unique characteristics such as conductivity, nonlinear optical properties, and light-emitting properties.

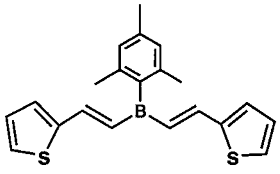
Previously, we have reported various methodologies for the preparation of organoboron main chain polymers by means of boration polymerizations.[2] Recently, the polymers prepared by hydroboration polymerization of aromatic diynes with mesitylborane were found to be highly stable toward air and moisture and they are expected to be a novel type of boron-containing material.[3] In their UV−vis spectra, absorption maxima were observed in a visible region, which indicated fairly extended π-conjugation length via a vacant p-orbital of the boron atom. All the polymers obtained were highly fluorescent, and an intense blue light emission was observed upon irradiation with UV light. Furthermore, the organoboron conjugated polymer can be expected to be considered a novel type of n-type conjugated polymer in which positive charge is built into every unit.

In the present paper, hydroboration polymerization of heteroaromatic diynes (2,5-diethynylthiophene, 2,5-diethynylfuran, and 2,5-diethynylpyridine) with mesitylborane was examined to give the corresponding donor−acceptor conjugated polymers (Scheme 1). Generally, incorporation of a donor−acceptor pair into a conjugated system is an interesting subject[4] in view of achieving a narrow band gap or improved third-order nonlinear-optical properties, due to the charge transferred structure in their backbone. The hydroboration polymerization between heteroaromatic diynes and mesityborane proceeded smoothly at room temperature without complex formation, probably because of the relatively low Lewis acidity of boron atom in mesitylborane due to the π-electron donation to the vacant p-orbital of the boron atom.

Scheme 1

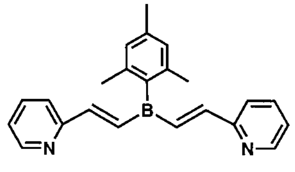


First of all, the polymerization between 2,5-diethynylthiophene (**2a**) and mesitylborane (**1**)[5] was carried out as follows. To a freshly distilled THF solution of **2a** was added a slightly excess amount of **1** in THF dropwise at room temperature under nitrogen atmosphere. After 5 h of stirring, the reaction mixture was directly subjected to gel permeation chromatographic analysis (GPC; THF, PSt standards), and the polymer was found to be formed. Then the solvent was removed, and the obtained reddish brown gum was purified by reprecipitation into methanol to give a brown powder in 58% yield. The GPC measurement showed that the number average molecular weight of the obtained polymer (**3a**) was 3000. The hydroboration polymerization with **2b** and **2c** also successfully proceeded to give the corresponding donor−acceptor conjugated polymers in moderate yields (Table 1). Each polymer showed good solubility in common organic solvents such as THF, chloroform and benzene. Since the polymer **3c** produced from **2c** was even soluble in methanol, **3c** was purified by reprecipitating into *n*-hexane. Haloboration−phenylboration polymerization between **2a**−**2c** and diphenylbromoborane was also examined. However, no polymerization or relatively low molecular weight oligomer formation was observed possibly due to coordination of heteroatoms to the boron atom.[6]



3a'

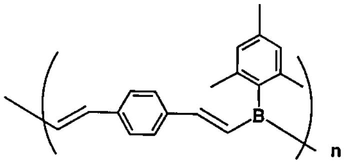
λmax 351 nm (shoulder)
reddish-brown



3c'

λmax 342 nm, 450 nm (shoulder)
purple

The structures of the polymers were supported by ^{1}H and ^{11}B NMR and IR spectra. For example, in the ^{1}H NMR spectrum of **3a**, the acetylene proton almost disappeared while peaks due to mesityl group were observed (2.21−2.35 and 6.86 ppm). The ^{11}B NMR spectrum shows the main peak corresponding to the dialkenylborane unit at 31.3 ppm. This chemical shift was almost the same as that of the polymer prepared from 1,4-diethynylbenzene (**4**) (31.4 ppm). The other small peak might be due to intra- or intermolecular coordination of sulfur to the boron atom. In the IR spectrum, a specific absorption due to the double bond was observed at 1608 cm^{-1}.



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The UV−vis spectra (in chloroform, at room temperature) of **3a**−**3c** demonstrate significant π-conjugation along the backbone, via the vacant p-orbital of the boron

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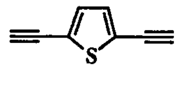
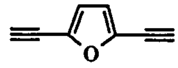
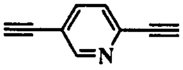
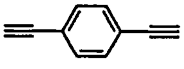
Table 1. Hydroboration Polymerization between Various Heteroaromatic Monomers and Mesitylborane[a]

Run	2	1/2	Mn b)	Mw b)	Mw/Mn b)	Yield (%) c)	λ_{max} (abs.) d)	λ_{max} (emission) e)
1	 (2a)	1.27	3000	4800	1.6	58	350	488
2	 (2b)	1.03	3000	5900	2.0	57	356	495
3	 (2c)	1.21	2900	4500	1.6	36	450	416, 495, 593
ref 4)		1.17	6500	16000	2.5	71	399	441

a) Reactions were carried out in THF at room temperature. b) GPC (THF), polystyrene standards. c) Isolated yields after reprecipitation into MeOH (runs 1-2) or n-hexane (run 3). d) In chloroform at room temperature. e) In chloroform at room temperature. Excitation wavelength was 350 nm.

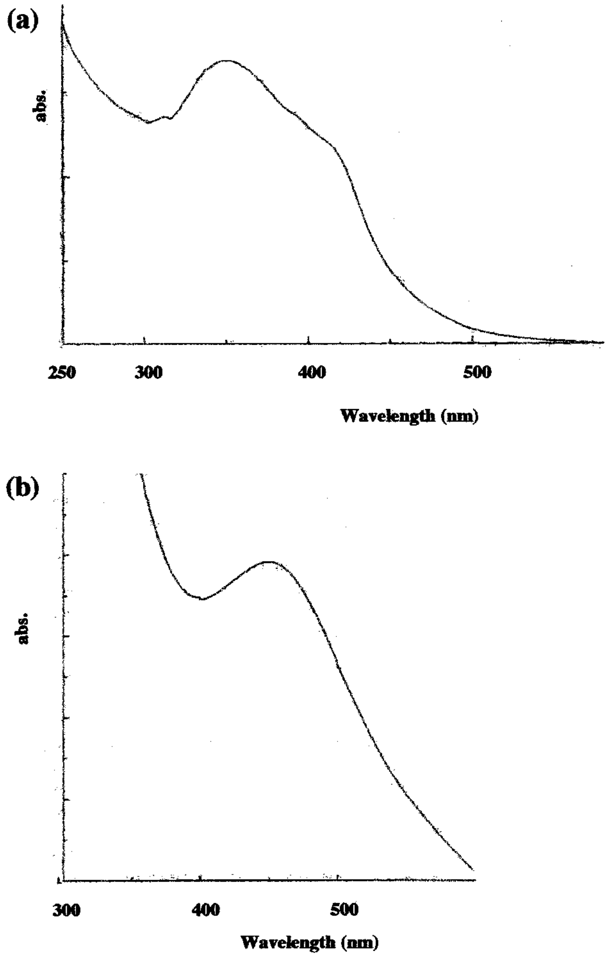


Figure 1. UV–vis absorption spectra of **3a** (a) and **3c** (b) in chloroform.

atom. For instance, in the case of **3a** (Figure 1a), the absorption maximum was observed at 350 nm. This value is not red-shifted in comparison with that of **4** (399 nm). Taking into account some charge-transfer interaction in model compound **3a′**, as was observed in the UV–vis spectrum [λ_{max} 351 nm (shoulder)], this blue shift might be due to the lower molecular weight of **3a** compared with **4**. However, in any case the ground-state charge-transfer interaction is weak in this system as indicated by the almost same ^{11}B NMR chemical shifts of polymers **3a** and **4**. On the other hand, it is interesting to note that a stronger ground-state interaction was observed in the case of **3c** (Figure 1b; 450 nm). Since the pyridine unit is much less electron donating compared with thiophene or the furan unit,[7] this result indicates that the combination of the imino group and the organoboron unit might be specially responsible for the red-shift. The UV–vis absorption spectrum of model compound **3c′** prepared from 2-ethynylpyridine showed its λ_{max} at 342 nm together with a broad shoulder peak at 450 nm.

The fluorescence emission spectra were also recorded for each polymer in chloroform at room temperature (excitation wavelength 350 nm). For example, the emission spectrum of **3a** (Figure 2a) exhibits the emission maximum at 488 nm, in the visible green region. Much larger Stokes shift in comparison with the case of **4** (38 nm) indicates that energy transfer might have taken place in excited states. In the emission spectrum of **3c** (Figure 2b), three emission maxima were observed at 416 (blue), 495 (green), and 593 (orange-red) nm. The emission spectra cover all the range of the visible region, which resulted in the observation of a white emission. The location of the emission maxima of **3a**–**3c** were independent of the excitation wavelength.

To investigate the air stability of the polymer, an air-bubbling experiment was performed. A stream of air was bubbled into a THF solution of **3a** and the change in the molecular weight was monitored by the GPC measurement. The result showed that **3a** was relatively stable toward air; however, the molecular weight was gradually decreased during the air bubbling for 24 h.

The TGA measurements of **3a**–**3c** were carried out under air and under nitrogen. 10% weight loss was observed at 190 (**3a**), 209 (**3b**) and 240 °C (**3c**), respectively, (under nitrogen). These are much higher than the case of **4**, which was stable only up to 110–120 °C (10% weight loss was observed at 128 °C). This difference might be due to the intra- or interchain coordination of donor moiety to the boron atom in solid state. The weight loss curves obtained under air were not so much different compared with those under nitrogen. This indicates that the thermal degradation of **3a**–**3c**

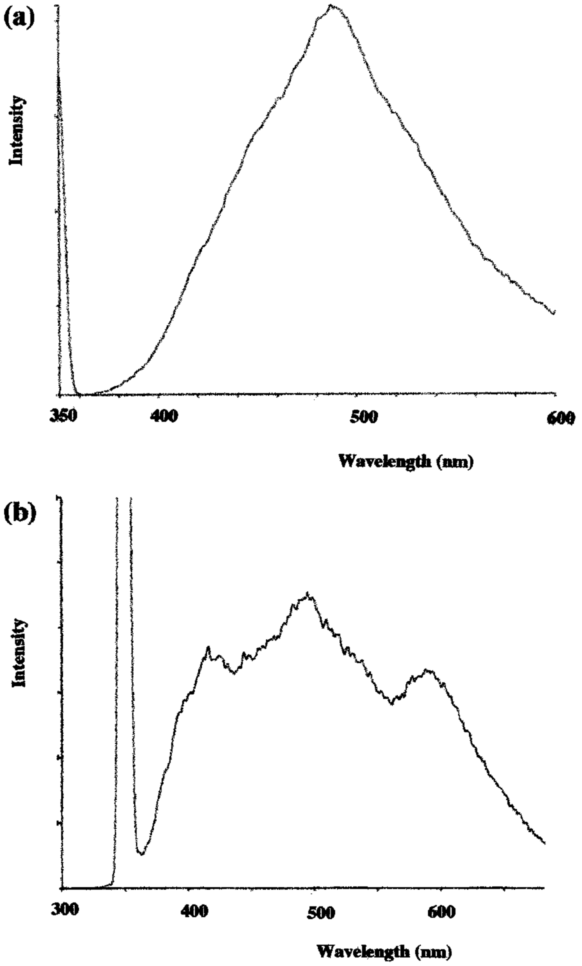


Figure 2. Fluorescence emission spectra of **3a** (a) and **3c** (b) in chloroform (excited at 350 nm).

was not dominated by the insertion of oxygen into C−B bond.

In conclusion, hydroboration polymerization between heteroaromatic diynes and mesitylborane gave successfully the corresponding donor−acceptor including conjugated polymers without complexation during polymerization. Although the UV−vis absorption maxima of **3a** and **3b** were not red-shifted in comparison with **4**, a significant ground-state charge-transfer interaction was observed in **3c**. Upon irradiation of UV light, visible green (**3a** and **3b**) or white (**3c**) emission was observed. The relative large Stokes shifts and broad emission peaks might be due to the energy transfer from donor to acceptor in the excited states.

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References and Notes

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(6) During the reaction between **3c** and Ph_2BBr, no obvious complex formation was observed; however, only a low molecular weight oligomer whose M_n was 1000 was obtained. The reaction using $PhBCl_2$ resulted in no polymerization.

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