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Synthesis of π-conjugated organoboron polymers by haloboration-phenylboration polymerization of aromatic diynes

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Summary

π-Conjugated organoboron polymers were prepared by haloboration-phenylboration polymerization beween diyne monomers and bromodiphenylborane. The polymerization was carried out by adding a slightly excess amount of bromodiphenylborane to a tetrachloroethane solution of diynes at room temperature under nitrogen and stirring the reaction mixture for 4 hours at 100°C. The obtained polymers were soluble in common organic solvents such as THF and chloroform. Their molecular weights were estimated to be several thousands by gel permeation chromatographic analysis. In UV-vis absorption spectra, bathochromic shift of λ_{max} and absorption edge in comparison with the corresponding monomers were observed, which indicates the π-conjugation via vacant p-orbital of boron atom.

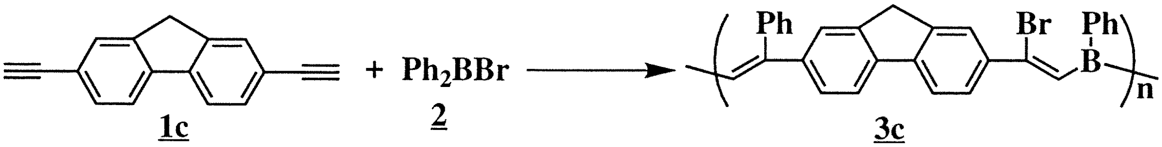
Introduction

We have recently developed a novel methodology for the preparation of n-type conjugated polymer [1] by hydroboration polymerization [2] as an extension of methods we have previously developed for synthesis of reactive organoboron polymers [3]. The obtained polymer exibited unique properties such as intense blue emission, excellent 3rd-order non-linear optical property and so on, as the consequence of the extension of π-conjugation via vacant p-orbital of the boron atom. In this paper, synthesis of organoboron polymers by means of haloboration-phenylboration polymerization [4] was examined to give the corresponding polymers in moderate yields. The polymers obtained showed characteristics as π-conjugated polymers in their optical behavior.

Results and discussion

Haloboration-phenylboration polymerization between 2,7-diethynylfluorene and Ph2BBr

The polymerization was carried out by adding slightly excess amount of bromodiphenylborane to a tetrachloroethane solution of 2,7-diethynylfluorene at room temperature under nitrogen, and then stirring the reaction mixture for 4 hours at 100°C. The resulting polymer was isolated by reprecipitation into dry n-hexane and the polymer was subjected to ^{1}H-, ^{11}B-NMR, IR and GPC measurements. The obtained polymer was soluble in common organic solvents such as THF and chloroform. In ^{11}B-NMR spectrum (Figure 1), the characteristic peak owing to dialkenylphenylborane unit was observed at 45.7 ppm. In addition, a small peak was observed at 29.5 ppm, which is assignable to crosslinked structure (trivinylborane unit). In IR spectrum, the characteristic absorption due to C=C was observed at 1602 cm^{-1}.



Scheme 1

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The polymerization under various conditions was examined. The results are listed in Table 1. At higher reaction temperature (run 1) or after long reaction time (run 7), a peak was observed around exclusion limit in the GPC measurement. The molecular weights in runs 1 and 7 in Table 1 were calculated excluding this peak. This peak is probably due to highly crosslinked materials formed by further phenylboration. In high concentration (run 4), gelation was observed in only 25 minutes, possibly due to the same reason.

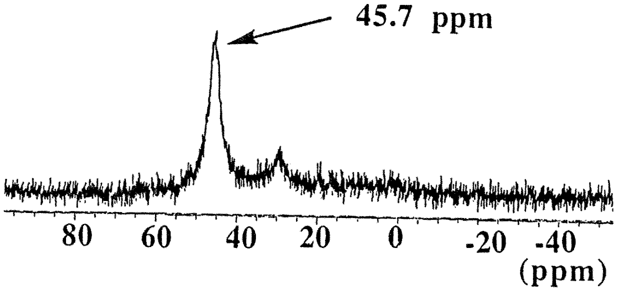


Figure 1. ^{11}B-NMR spectrum of 3c

Table 1. Dependence of Molecular Weight of 3c on Reaction Conditions$^{a)}$

Run	1c(mmol)	2(mmol)	2/1	solvent(ml)	Temp.(°C)	Time(h)	*Mn*	*Mw/Mn*	Yield(%)
1	0.501	0.565	1.13	0.5	130	4	2600	4.29	44
2	0.500	0.566	1.13	0.5	100	4	6300	6.85	48
3	0.500	0.571	1.14	0.5	80	4	2700	2.34	41
4	0.502	0.572	1.14	0.25	100	b)			
5	0.500	0.586	1.17	1.0	100	4	7500	3.66	53
6	0.500	0.572	1.14	0.5	100	2	2500	2.87	49
7	0.500	0.569	1.14	0.5	100	6	1700	3.80	54

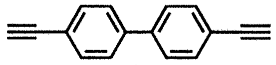
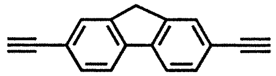
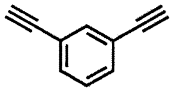
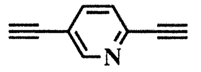
a) Reactions were carried out in tetrachloroethane.
b) Gelation was observed in 25 minutes.
c) GPC (THF) polystyrene standard.
d) Isolated yield after reprecipitation into n-hexane.

These results indicate that bromodiphenylborane works as a trifunctional monomer under severe conditions such as high temperature, high concentration and long reaction time. In lower concentration (run 5), however, the peak around exclusion limit disappeared and the molecular weight of the main peak was higher. This result shows that further phenylboration and crosslink was supressed under the mild reaction condition, which is desirable to obtain linear and soluble polymer.

Haloboration-phenylboration polymerization between Ph2BBr and various diynes

Haloboration-phenylboration polymerization between bromodiphenylborane and various diynes was examined. The results are summarized in Table 2. In runs 1 and 2, the polymerization was carried out at low concentration of the monomers, because of poor solubility of diyne monomers. This might have led to lower molecular weights of the obtained polymers compared with that of run 3 or 4. The polymerization in run 5 also resulted in relatively low moleculr weight of the obtained polymer. In the ^{11}B-NMR spectrum of the polymer, the chemical shift of the main peak was located in higher magnetic field, which indicates relatively electron-rich environment of boron atom. This can be due to some interaction between boron and nitrogen atoms, and this might have lowered the boration reactivity and the molecular weight of the resulting polymer.

Table 2. Haloboration-Phenylboration Polymerization of Various Aromatic Diynes with $Ph_2BBr^{a)}$

Run	Diynes		Feed Ratio Boron/Diyne	$Mn^{b)}$	$Mw^{b)}$	$Mw/Mn^{b)}$	Yield(%)$^{c)}$
1		(1a)	1.14	3100	13200	4.3	51
2		(1b)	1.16	2600	11200	4.3	50
3		(1c)	1.17	7500	27000	3.7	70
4		(1d)	1.16	3600	9400	2.6	48
5		(1e)	1.19	1000	2300	2.3	90

a) Reactions were carried out in tetrachloroethane at 100°C.
b) GPC(THF) polystyrene standard.
c) Isolated yield after reprecipitation into n-hexane.

Stability of the organoboron polymer

In order to study the stability of the organoboron polymer 3b toward air, an air bubbling experiment was performed in THF solution of the polymer. The air stability was monitored by tracing the change of the GPC curves during the air bubbling into the polymer solution. As shown in Figure 2, no obvious change of GPC curves was observed even after 1day. This result indicates the high air stability of the polymer. The stability might be due in part to the effective π-conjugation around boron atom. From thermo-gravimetric analysis of 3c (Figure 3), the weight loss of the polymer started at below 100°C and 10 wt% of residue remained after heating at 900°C under air.

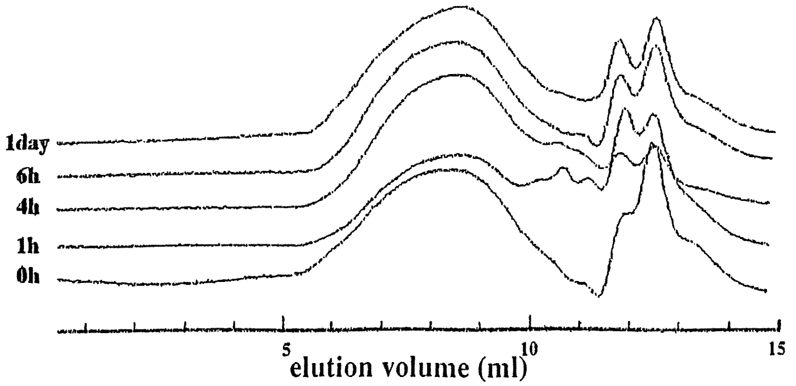


Figure 2. GPC traces of 3b before and after air-bubbling in THF solution

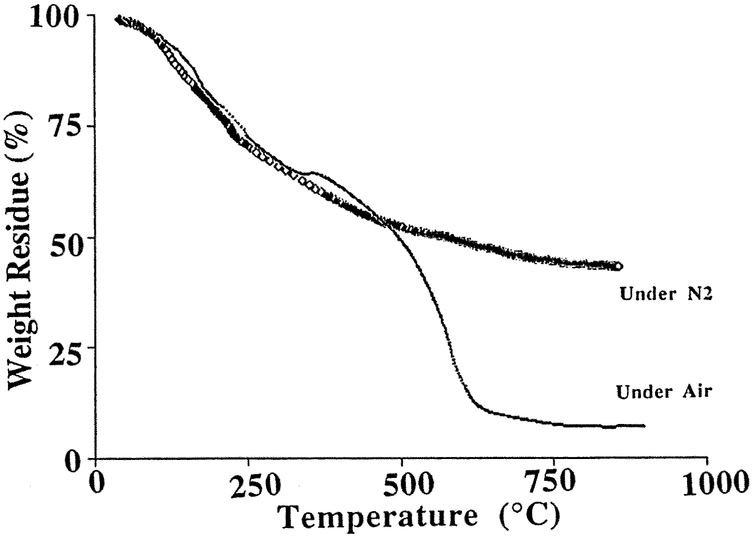


Figure 3. TGA (10°C/min) traces of organoboron polymer 3c under air and nitrogen

UV-vis absorption spectra and fluorescence emission spectra of organoboron polymers

The measurements of UV-vis absorption spectra and fluorescence emission spectra were examined, each in dilute chloroform solution. Table 3 summarizes the results of the measurements of UV-vis spectra. The red-shifted absorption edge of **3c** compared with that of **1c** (monomer) as represented in Figure 4 would be explained by considering the π-conjugation via vacant p-orbital of the boron atom. However, π-conjugation was not so efficient as the case of polymers previously prepared by hydroboration polymerization [2], in which absorption maxima were observed in visible region. Presumably, this is due to the presence of less planar trivinylborane structure (crosslinked structure) in which conjugative overlap between π-orbitals of the vinyl groups and the p-orbital of boron was reported to be very small [5].

Table 3. λ_{max} of the Polymers Prepared by Haloboration-Phenylboration Polymerization

Polymers	3a	3b	3c	3d	3e
λ_{max}(nm)	274	293	323	a)	a)

a) Absorption maxima were not observed clearly.

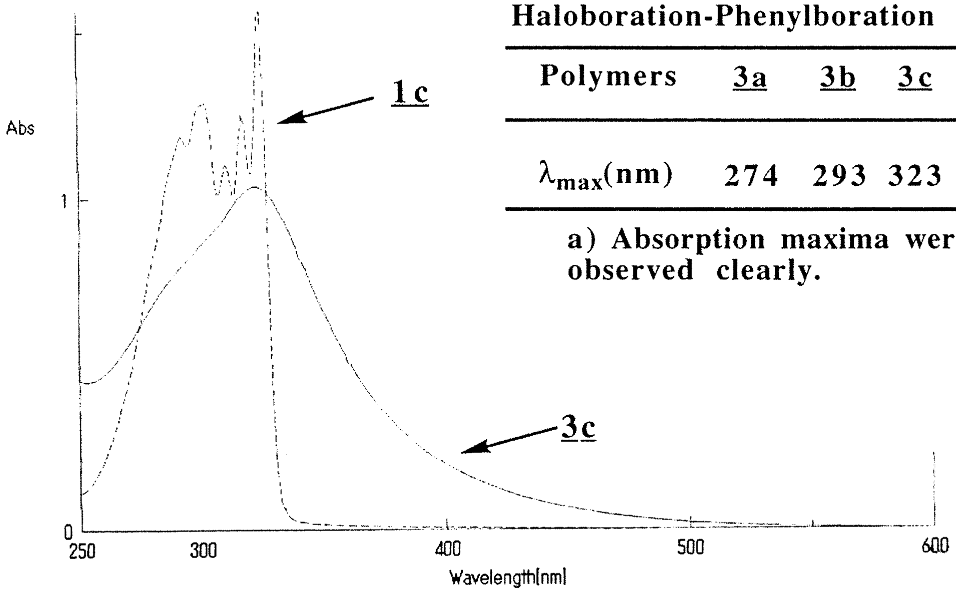


Figure 4. UV-vis spectra of 1c (monomer) and 3c (polymer)

The measurement of fluorescence emission spectra (excited at 300 nm) was also carried out for some polymers. As shown in Figure 5, the spectrum of **3c** showed its emission maximum at 477 nm, which was Stokes shifted by 154 nm. **3b** also showed blue emission (emission maximum was observed at 471 nm), although the intensity was weak.

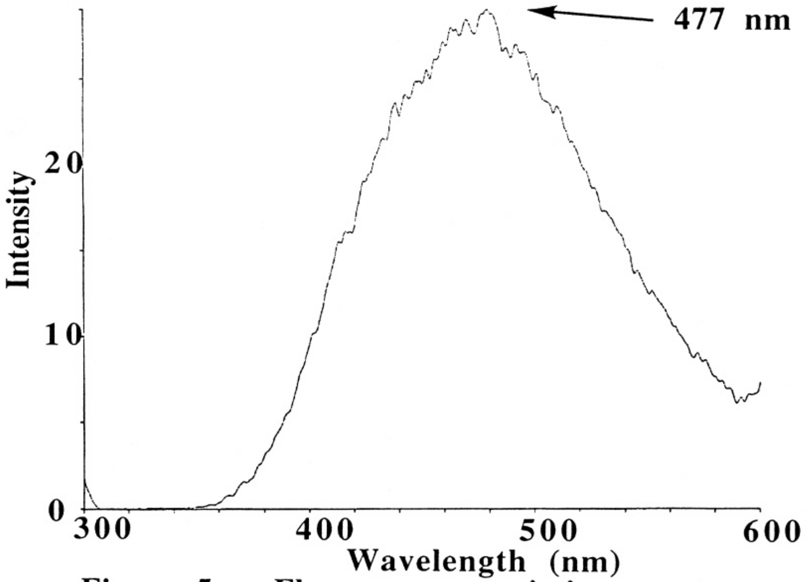


Figure 5. Fluorescence emission spectrum of 3c (excited at 300 nm)

Conclusion

Novel π-conjugated organoboron polymers were prepared by haloboration-phenylboration polymerization between aromatic diynes and bromodiphenyborane. The polymers obtained here were soluble in common organic solvents and found to be resonably stable toward air. These polymers are expected as n-type conjugated polymers because of the high electron affinity of the organoboron unit. Further investigation for physical properties such as conductivity, nonlinear optical property, electrochemical property is currently under study.

Experimental section

Materials and instruments

Tetrachloroethane was dried over CaH_2 and purified by distillation. n-Hexane was dried over Na and distilled. Bromodiphenylborane was prepared according to the reported method [5]. 1,4-Diethynylbenzene was purchased from Tokyo Kasei and purified by sublimation. 1,3-Diethynylbenzene was purchased from Lancaster and distilled under vacuum. Other diyne monomers were prepared according to the reported method [6].

^{1}H-NMR 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 G3000H_{XI} by using THF as an eluent after calibration with standard polystyrene samples. IR spectra were obtained on a Perkin Elmer 1600 spectrometer. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (10°C/min). UV-vis spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence emission spectra were recorded on a Perkin Elmer LS50B luminescence spectrometer.

*Haloboration-phenylboration polymerization between 2,7-diethynylfluorene (**1c**) and bromodiphenylborane (**2**)*

To a tetrachloroethane (1 ml) solution of **1c** (107.1 mg, 0.4998 mmol), **2** (143.4 mg, 0.5855 mmol) was added at room temperature under nitrogen and the reaction mixture was gradually warmed up to 100°C. After stirring for 4 hours, the polymer was isolated by reprecipitation into n-hexane and dried in vacuo. The product was obtained as a brown powder. The obtained polymer was subjected to ^{1}H-, ^{11}B-NMR, IR and GPC measurements. Yield 70%: ^{1}H-NMR (δ, ppm) 3.83 (Ph-CH2-Ph, 2H), 6.80-8.00 (Ar, vinyl, 18H). ^{11}B-NMR (δ, ppm) 45.7. IR (cm^{-1}) 1602($\nu_{C=C}$).

*Polymerization between various diyne compounds and **2***

The corresponding organoboron polymers were also obtained from **1a-b** and **1d-e** in a similar manner as described for **1c**. 63.3 mg (0.502 mmol) of **1a** in 2 ml of $CHCl_2CHCl_2$ and 140.2 mg (0.573 mmol) of **2**; Yield 51%: ^{1}H-NMR (δ, ppm) 6.80-8.20 (Ar, vinyl, 16H). ^{11}B-NMR (δ, ppm) 29.2. IR (cm^{-1}) 1600. 101.3 mg (0.501 mmol) of **1b** in 2 ml of $CHCl_2CHCl_2$ and 142.3 mg (0.581 mmol) of **2**; Yield 50%: ^{1}H-NMR (δ, ppm) 6.80-8.20 (Ar, vinyl, 20H). ^{11}B-NMR (δ, ppm) 46.4. IR(cm^{-1}) 1602. 61.0 mg (0.484 mmol) of **1d** in 0.5 ml of $CHCl_2CHCl_2$ and 147.0 mg (0.600 mmol) of **2**; Yield 34%: ^{1}H-NMR (δ, ppm) 7.20-8.15 (Ar, vinyl, 16H). ^{11}B-NMR (δ, ppm) 30.1, 46.4. IR (cm^{-1}) 1601. 63.5 mg (0.500 mmol) of **1e** in 0.5 ml of $CHCl_2CHCl_2$ and 145.9 mg (0.596 mmol) of **2**; Yield 90%: ^{1}H-NMR (δ, ppm) 6.20-7.80 (Ar, vinyl, 15H). ^{11}B-NMR (δ, ppm) 10.1. IR (cm^{-1}) 1614.

*Stability of the organoboron polymer **3b** toward air*

The stability of **3b** toward air was examined by monitoring the change of the molecular weight by GPC measurement. A stream of air was bubbled into a THF solution of **3b** and the resulting polymer was characterized by GPC after the designed time.

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