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Novel π-conjugated organoboron polymers: Poly(ethynylene-phenylene-ethynylene-borane)s

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Summary

Novel poly(ethynylene-phenylene-ethynylene-borane)s were prepared by polycondensation between bifunctional lithium acetylide and aryldimethoxyborane. The polymers obtained are expected as a novel type of organoboron π-conjugated polymers via vacant p-orbital of boron atom. The polymerization between dilithium 2,5-didodecyloxybenzene-1,4-diethynilide and tripyldimethoxyborane [tripyl=2,4,6-triisopropylphenyl] gave the corresponding polymer in 67% yield. From gel permeation chromatographic analysis (THF, PSt standards), the number-average molecular weight of the polymer was found to be 2700. In the UV-vis spectrum of the polymer (in chloroform at room temperature), an absorption maximum was observed at 397 nm. The fluorescence emission spectrum (in chloroform, room temperature, excitation wavelength at 400 nm) showed its λ_{max} at 456 nm in the visible blue region. The polymers obtained were very soluble in common organic solvents such as THF, chloroform and benzene.

Introduction

There has been considerable interest in the synthesis of novel π-conjugated systems since they have unique optical, electrochemical and non-linear optical properties. Especially, π-electron deficient n-type π-conjugated polymers (1-3) are desired owing to their potential utility for appropriate electron transport materials in light emitting diodes and organic negative electrodes in energy storage systems.

Recently, we reported the synthesis of a series of π-conjugated organoboron polymers via the empty p-orbital of boron atom by hydroboration polymerization of aromatic diynes or aromatic dicyano compounds with monoarylborane (4, 5). These polymers exhibited conspicuous characteristics such as intense fluorescense emission, excellent 3rd order non-linear optical behavior and n-type electrochemical activity. We also reported the synthesis of π-conjugated poly(p-phenylene-borane)s (PPBS) by means of polycondensation between aryldimethoxyborane and bifunctional Grignard reagents (6). This provided a methodology for the synthesis of π-conjugated organoboron polymers as an alternative to hydroboration polymerization.

In this paper, the polycondensation between bifunctional lithium acetylide and aryldimethoxyborane was examined to give novel poly(ethynylene-phenylene-ethynylene-borane)s. These polymers are expected as novel n-type conjugated polymers with higher thermal stability due to the absence of retro-hydroboration (β-elimination) process during their thermal degradation, similarly to PPBs.

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Experimental

Materials and Instruments

Tetrahydrofuran (THF) was dried over sodium and distilled before use. 1,4-Bis[(trimethylsilyl)ethynyl]-2,5-bis(dodecyloxy)benzene (**1**), tripyldimethoxyborane (**2a**) and mesityldimethoxyborane [mesityl=2,4,6-trimethylphenyl] (**2b**) were prepared according to the reported methods (7-9). ^{1}H- 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.

Polymerization

To a freshly distilled THF solution of **1** (128 mg, 0.20 mmol), two equivalent amounts of 1.6M n-butyllithium / n-hexane (0.25 ml, 0.40 mmol) was added and the reaction mixture was stirreed for 1 hour at room temperature. Then an equimolar amount of **2a** (55mg, 0.20 mmol) was added and the resulting mixture was stirred for 12 hours. The solvent was removed, and the resulting red-brown gum was dissolved in chloroform and then the insoluble-part was filtrated. The solvent of filtrate was removed, and the obtained red-brown powder was washed with methanol repeatedly to afford the poly(ethynylene-phenylene-ethynylene-borane) (**3a**) in 67% yield (95 mg). ^{1}H-NMR (δ, ppm) 0.85 (CH$_3$, 6H), 1.23 [CH$_2$, CH$_3$ (^{i}Pr), 54H], 1.74 (O-CH$_2$-C*H*$_2$, 4H), 2.59, 2.84 [CH (^{i}Pr), 3H], 3.91 (O-CH$_2$, 4H), 6.87-6.93 (Ar-H, 4H). ^{11}B-NMR (δ, ppm) 31.9. IR (cm^{-1}) 2150 ($\nu_{C\equiv C}$).

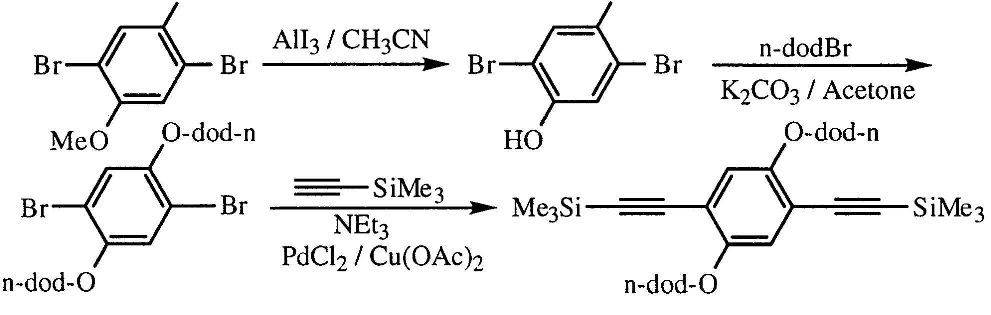
3b was also synthesized in a similar manner as described for **3a**. **3b**; 128 mg (0.20 mmol) of **1**, 0.25 ml (0.40 mmol) of 1.6M n-butyllithium / n-hexane and 38 mg (0.20 mmol) of **2b**; 96 mg of **3b** (77%). ^{1}H-NMR (δ, ppm) 0.88 (CH$_3$, 6H), 1.26-1.45 (CH$_2$, Ar-CH$_3$, 45H), 1.80 (O-CH$_2$-C*H*$_2$, 4H), 3.97 (O-CH$_2$, 4H), 6.95 (Ar-H, 4H). IR (cm^{-1}) 2150 ($\nu_{C\equiv C}$).

Results and Discussion

Polymer Synthesis

1,4-Bis[(trimethylsilyl)ethynyl]-2,5-bis(dodecyloxy)benzene (**1**) was prepared according to the reported method (7), as depicted in Scheme 1. Long alkyl chains were introduced to the aromatic ring through ether linkage to increase the solubility of the polymer formed. This might lead to higher molecular weights and longer conjugated backbones in the products. Scheme 2 provides an overview for the polymerization. Since the dodecyloxy group acts as an electron donor, the resulting polymers can be regarded as donor-acceptor conjugated organoboron polymers. Generally, incorporation of a donor-acceptor pair into conjugated system is an interesting subject in view of achieving the narrow band gap or improved 3rd order non-linear optical properties due to the charge transferred structure in their backbone. The results of polymerization are summarized in Table 1. The obtained polymer was soluble in common organic solvents such as THF, chloroform and benzene.

Scheme 1



Scheme 2

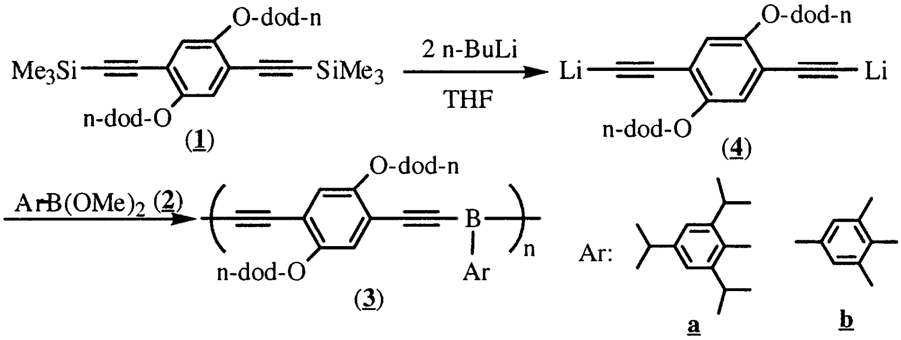
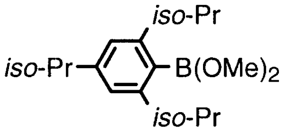
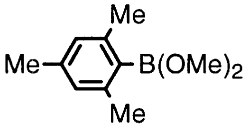


Table 1. Results of polymerization

Borane	M_w a)	M_n a)	M_w/M_n a)	yield(%) b)
 (2a)	3400	2700	1.3	67
 (2b)	2000	1800	1.1	80

a) GPC (THF), polystyrene standards. b) Isolated yield after washing with methanol.

Polymer Structures

The structures of the polymers were supported by ^{1}H-, ^{11}B-NMR and IR spectra. The ^{1}H-NMR spectrum of **3a** showed the peaks corresponding to tripyl group at 1.23, 2.59 and 2.84 ppm in addition to the peaks assignable to dodecyloxy group in the aliphatic region. As shown in Figure 1, in the ^{11}B-NMR spectrum of **3a**, there was only one peak at 32 ppm due to the aryldiethynylborane unit. This result indicates that the polymer has only one kind of unit structure. From the IR spectrum of **3a** (Figure 2), a sharp absorption peak assignable to C≡C stretching was observed at 2150 cm^{-1}.

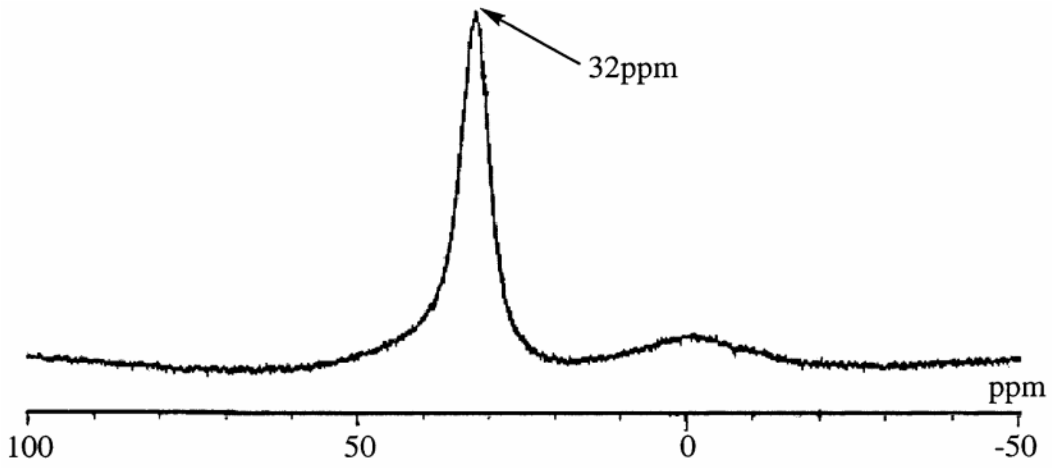


Figure 1. ^{11}B-NMR spectrum of **3a**.

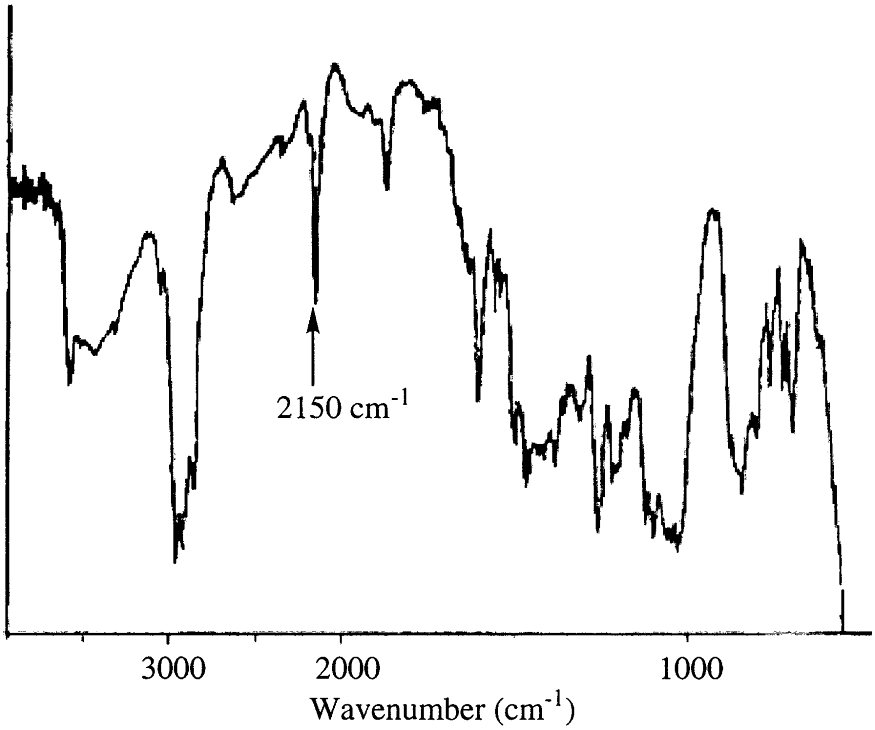


Figure 2. IR spectrum of **3a**.

Optical Properties

The UV-vis absorption spectrum of **3a** was recorded in chloroform at room temperature and is represented in Figure 3. The peak due to π-π^* transition of the polymer backbone was observed at 397 nm, while **1** exhibited the peak at 345nm. This result indicates highly extended π-delocalization length via vacant p-orbital of boron atom, in spite of the presence of bulky tripyl group substituent on the boron atom.

The polymer obtained showed a visible blue emission when the dilute chloroform solution of **3** was irradiated with ultraviolet light. For example, the fluorecence emission spectrum of **3a** (Figure 4; in chloroform at room temperature; excitation wavelength at 400 nm) exhibited an intense peak at 456 nm in the visible blue region.

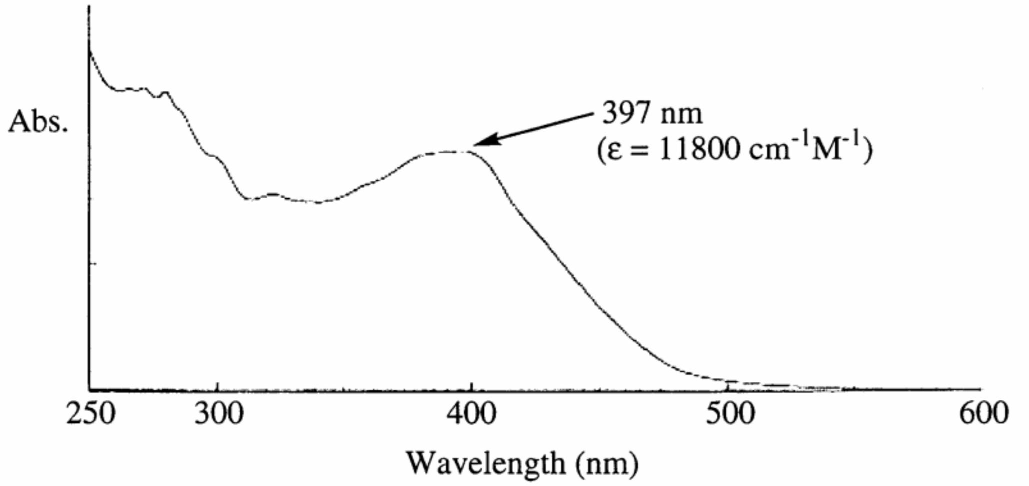


Figure 3. UV-vis absorption spectrum of **3a** in CHCl$_3$ at room temperature.

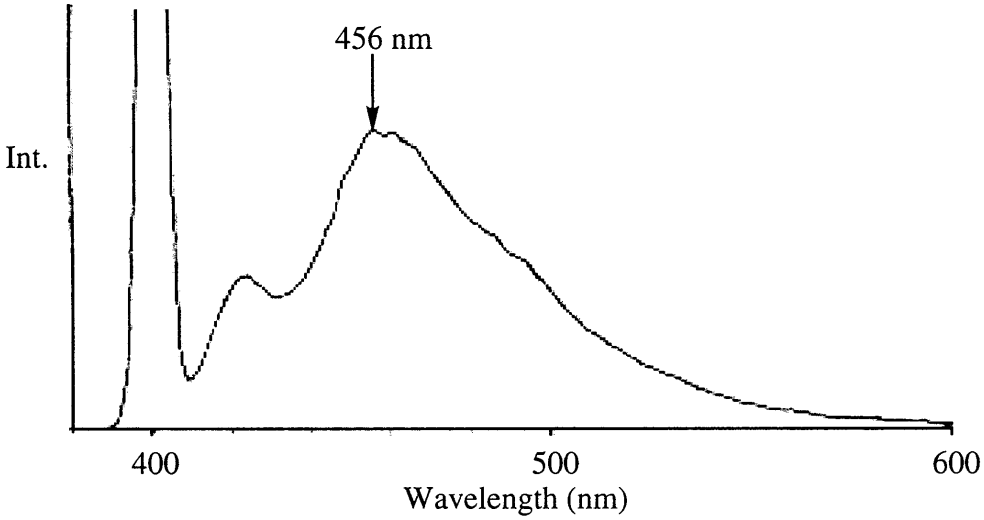


Figure 4. Fluorescence emission spectrum of <u>3a</u> (excited at 400 nm) in $CHCl_3$ at room temperature.

Stability of Polymers toward Air and Moisture

The stability of <u>3a</u> toward air and moisture was investigated by the following experiments. A stream of air was bubbled into a THF solution of <u>3a</u> for 24 hours and the change of the molecular weight was monitored by GPC measurement. The stability of <u>3a</u> toward moisture was similarly observed during the treatment with water. As shown in Figure 5, no significant decrease in the molecular weight was observed in both cases. These results indicate fairly high stability of <u>3a</u> toward air and moisture.

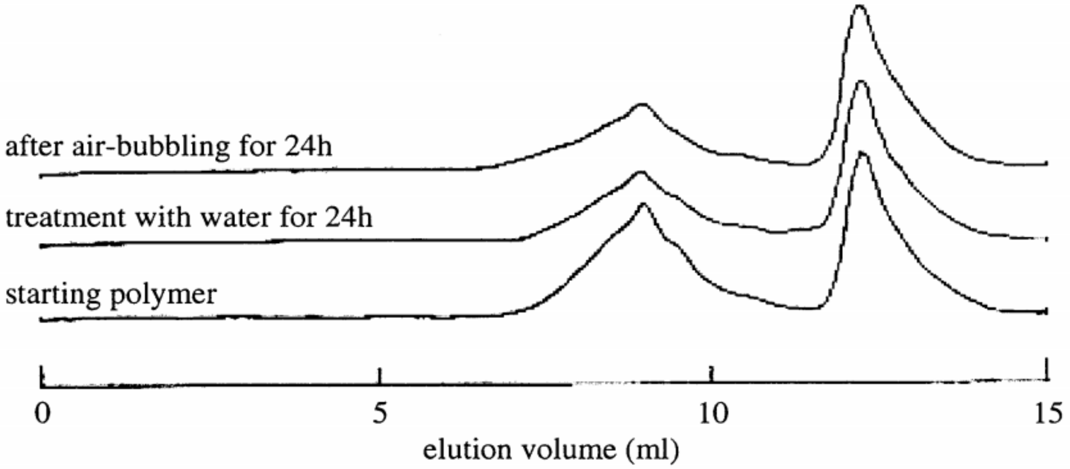


Figure 5. Stability of <u>3a</u> toward air and moisture.

Conclusions

Novel poly(ethynylene-phenylene-ethynylene-borane)s were prepared by polycondensation between dilithium 2,5-didodecyloxybenzene-1,4-diethynilide and aryldimethoxyboranes. The polymers obtained are expected to act as n-type conjugated polymers with fairly high stability toward air and moisture. These characteristics of the polymers might allow the application to various electronic devices. In addition, these polymers might exhibit prominent 3rd order non-linear optical behavior owing to their rigid rod conjugated backbones.

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