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Main-Chain-Type Organoboron Quinolate Polymers: Synthesis and Photoluminescence Properties

Yuuya Nagata and Yoshiki Chujo*

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

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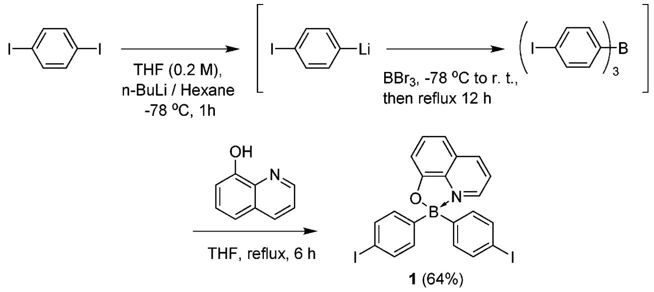
Introduction. We have synthesized a wide variety of organoboron polymers including boron atoms in the main chain by means of hydroboration polymerization. These polymers exhibited various interesting properties due to the high electron affinity of boron atoms, strong fluorescence emission, n-type electronic conductivity, third-order nonlinear optical properties, etc.[1−4] Because of these unique properties, they are expected as a novel type of optical and electrical materials.[5−7]

On the other hand, organoboron quinolates have considerable attention today because of their luminescence or potential applications in organic light-emitting devices (OLEDs). Tris(8-hydroxyquinoline)aluminum (Alq$_3$) and their derivatives were first reported by Tang and VanSlyke[8] and have been investigated extensively for their uses in OLEDs. Recently, Wang et al. revealed that boron compounds containing 8-hydroxyquinoline as a ligand showed efficient luminescence and good stability.[9−14] Alq$_3$ derivatives containing polymers have also been investigated. In contrast, there have been few examples of the investigation on polymers that contain boron quinolate derivatives. For example, Jäkle et al. reported the preparation of side-chain type organoboron quinolate polymers by utilizing poly(4-dibromoborylstyrene) as a reactive polymer,[15] and Weck et al. reported the synthesis of poly(styrene)-supported organoboron quinolate via 8-hydroxyquinoline-functionalized polymers.[16]

We report here on the synthesis and properties of the first example of conjugated polymers containing organoboron quinolate in their main chain. The present synthetic method is very attractive for preparing the organoboron quinolate polymers because the polymerization procedure is very simple and widely applicable to various organic monomers. Furthermore, characteristic luminescent property was observed in these polymers.

Results and Discussion. a. Synthesis. The key monomer B(4-iodophenyl)$_2$q (**1**) was prepared according to Scheme 1. The crystal structures of B(4-iodophenyl)$_2$q (**1**) have been determined by single-crystal X-ray diffraction analyses. The boron center in monomer **1** displays a typical tetrahedral geometry, as shown in Figure 1. The hydroxyquinoline groups in all four molecules are chelated to the boron in the same manner to form a five-membered chelate ring. In addition, the existence of iodo atoms on phenyl groups has been confirmed.

Scheme 1. Synthesis of B(4-iodophenyl)$_2$q (1)



We applied the Sonogashira−Hagihara coupling reaction to prepare the polymers. Coupling reactions utilizing Pd and Cu catalysts between B(4-iodophenyl)$_2$q (**1**) and diyne monomers **2** gave the corresponding polymers as described in Scheme 2. The resulting polymers were dissolved in chloroform and transferred into a separatory funnel and then washed three times with water to remove salts and catalysts. The desired polymers were purified by reprecipitation from diethyl ether. The obtained product was soluble in various organic solvents such as tetrahydrofuran or chloroform and easily gave a thin film. The polymerization results are summarized in Table 1. Comparing the molecular weights of polymers **3a** and **3b**, the degree of polymerization of polymer **3b** was larger than that of polymer **3a**. It may be due to the difference of solubility which depends on the length of the side chain. The structures of all products were supported by ^{1}H NMR, ^{11}B NMR, and elemental analysis. The end groups of the polymers should be iodophenyl or acetylene groups. Small peaks of acetylene groups were observed in both ^{1}H NMR spectra. While the peaks of iodophenyl groups were submerged by other aromatic peaks, the results of elemental analyses were reasonable with containing iodophenyl groups.

b. Optical Properties. The optical properties of the obtained polymers were investigated by UV−vis absorption and fluorescence emission spectroscopy. The results are summarized in Table 2. The absorption spectra of the monomer **1** and the polymer **3b**, as a typical representative example, are shown in Figure 2. The monomer **1** showed the weak absorption peak at 396 nm ($\epsilon = 3200$) arising from the quinolinol ligand and the strong absorption peak at 264 nm ($\epsilon = 38\,300$) derived from the $\pi-\pi^*$ transition. In contrast to the monomer **1**, the absorption spectrum of polymer **3b** exhibits a dramatically bathochromic shift owing to the π-conjugated segments in the main chain.

The fluorescence emission spectra of monomer **1** and polymer **3b** are shown in Figures 3 and 4, respectively. Noteworthily, the shapes of the emission spectra are quite similar to each other. Therefore, the fluorescence spectra of these polymers are thought to be characteristic of the organoboron quinolate moiety. In other words, the presence of organoboron quinolate in the polymer backbone is crucial in these fluorescence properties. The

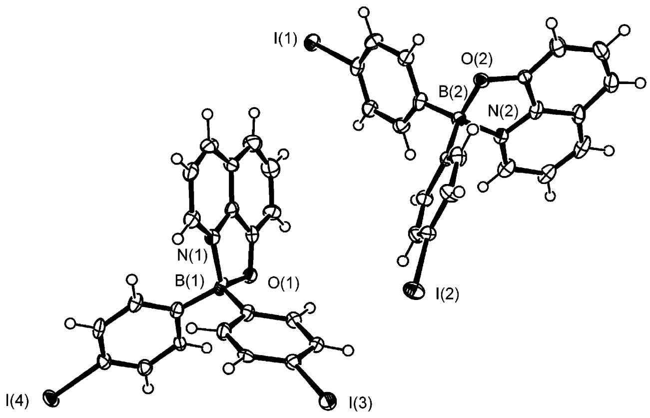


Figure 1. Structure of B(4-iodophenyl)$_2$q (**1**) with thermal ellipsoids drawn to the 50% probability level.

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* Corresponding author. E-mail: chujo@chujo.synchem.kyoto-u.ac.jp.

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Scheme 2. Polymerization of B(4-iodophenyl)$_2$q (1) with Diyne Monomers

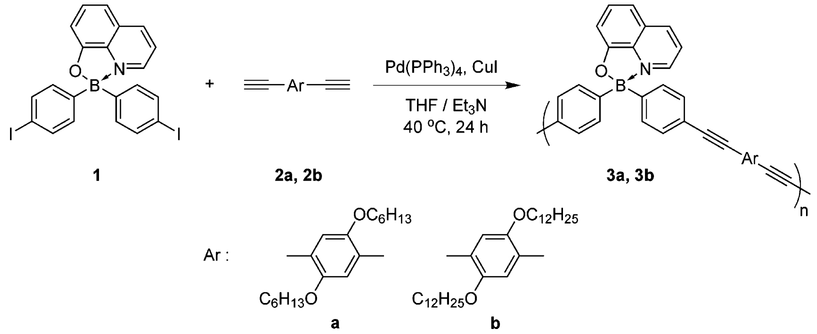

Table 1. Polymerization Results

polymer	yield (%)[a]	M_w[b]	M_n[b]	M_w/M_n[b]	DP[c]
3a	46	5300	3200	1.7	5.1
3b	50	20700	8800	2.4	11

[a] Isolated yields after reprecipitation into diethyl ether. [b] GPC (THF), polystyrene standards. [c] Degree of polymerization.

Table 2. Optical Properties of Monomer 1 and Polymers 3a and 3b

compound	condition	UV−vis (λ_{max}, nm)	excitation (λ_{max}, nm)	emission (λ_{max}, nm)	quantum yield[b] (%)
monomer **1**	solution[a]	264, 396	395	489	23
polymer **3a**	solution[a]	263, 312, 375	376	486	26
	film		389	505	
polymer **3b**	solution[a]	262, 313, 375	380	489	27
	film		395	512	

[a] Conditions: $CHCl_3$, room temperature. [b] Relative to 9,10-diphenylanthracene in cyclohexane at room temperature.

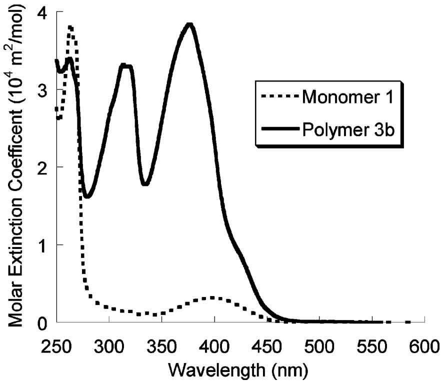

Figure 2. UV−vis absorption spectra of monomer **1** and polymer **3b** (per repeat unit) in chloroform at room temperature.

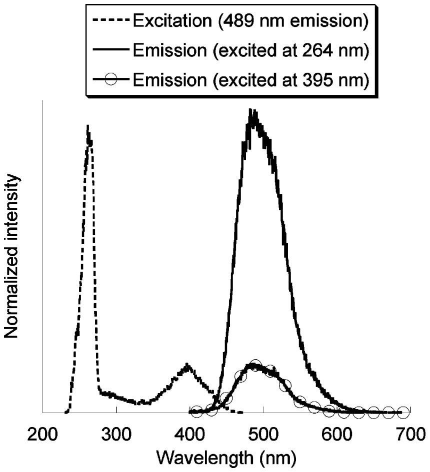

Figure 3. Fluorescence spectra of monomer **1** in chloroform at room temperature.

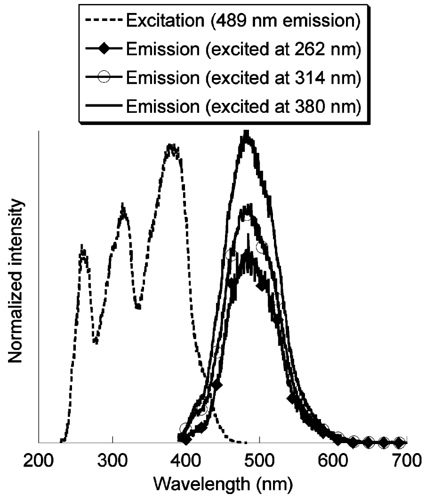

Figure 4. Fluorescence spectra of polymer **3b** in chloroform at room temperature.

fluorescence excitation spectrum of the polymer **3b** was broadened and red-shifted with respect to the monomer **1**. Wang and co-workers reported that an interligand charge transfer from the benzothienyl ligand to the quinolinol ligand.[12] According to the paper, a charge transfer from electron-delocalized segment in the main chain to quinolinol ligand was insisted in this system. Fluorescence quantum yields of monomer **1** and polymers **3a** and **3b** were determined relative to 9,10-diphenylanthracene in cyclohexane ($\Phi = 0.90$).[17] The luminescence of monomer **1** containing iodo atoms might be quenched by the heavy atom effect. Fluorescence quantum yields of polymers **3a** and **3b** tell us that an incorporation of organoboron quinolate into polymer backbone does not quench fluorescence emission. In addition, the quantum yields were reasonable values compared to the reported organoboron quinolates.[12] Strong green-blue emissions with good fluorescence quantum yields and excitable by a wide range of wavelength light were obtained from these polymers. The yielded polymers still retained the fluorescence ability in the film state while the peaks of fluorescence were inconsiderably red-shifted. This should be because of intermolecular stacking of aromatic rings.

Conclusion. A new class of organoboron polymers containing organoboron quinolate structures in the main chain was prepared by the Sonogashira−Hagihara coupling. These polymers exhibited intense green-blue photoluminescence. Moreover, efficient energy transfer from π-conjugated main chain to quinoline rings has been indicated. The present synthetic method is very useful for preparing the organoboron quinolate polymers because the polymerization procedure is very simple and widely applicable to introduce various functional moiety. Further investigations on the electronic conditions of boron atoms and the polymer structures will be performed.

Experimental Section. Materials and Instrument. THF was distilled from sodium benzophenone ketyl. Et_3N was distilled from KOH. ^1H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR spectra were recorded on a JEOL JNM-EX400 instrument. ^1H and ^{13}C NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane. Chemical shifts for ^{11}B NMR were measured in ppm relative to external $BF_3{\cdot}Et_2O$ (sealed capillary) in $CDCl_3$. Gel permeation chromatographic analysis was carried out on a TOSOH G3000HXI by using THF as an eluent after calibration with polystyrene standards. UV−vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. 1,4-Diethynyl-2,5-dialkoxybenzene (**2a** and **2b**) was prepared according to the literature.[18,19] Other reagents were commercially available. All reactions were performed under an argon atmosphere using standard Schlenk techniques.

B(4-iodophenyl)$_2$q (1). To the solution of 1,4-diiodobenzene (6.60 g, 20 mmol) in 100 mL of THF was added 12.5 mL (1.6 M, 20 mmol) of *n*-BuLi slowly at −78 °C, and the mixture was stirred at −78 °C for 1 h. BBr_3 (0.67 mL, 6.7 mmol) was added to the reaction mixture at −78 °C and then allowed to room temperature and refluxed for 12 h. 8-Hydroxyquinoline (0.98 g, 6.7 mmol) dissolved in 30 mL of THF in a separate flask was added to the reaction mixture and then refluxed for 6 h. The solvents were removed under vacuum. The residue was dissolved in 100 mL of CH_2Cl_2, and the insoluble salt was removed from the solution by filtration. The solvent was removed under vacuum. The remaining yellow oil was purified by dissolving in a small amount of CH_2Cl_2 and reprecipitating with 100 mL of ice cooled methanol, giving a yellow solid. The crude product was put in a small vial and then dissolved in CH_2Cl_2, on which hexane was slowly laid. The phase separated solution was allowed to stand for 24 h for diffusion, which gave yellow crystals of **1** in 64% yield. ^1H NMR (DMSO-d_6, δ, ppm): 9.14 (1H, d, $J = 5.12$ Hz), 8.81 (1H, d, $J = 8.29$ Hz), 7.92 (1H, dd, $J = 8.29, 5.12$ Hz), 7.72 (1H, dd, $J = 8.29, 7.56$ Hz), 7.59 (4H, d, $J = 7.80$ Hz), 7.45 (1H, d, $J = 8.29$ Hz), 7.20 (1H, d, $J = 7.56$ Hz), 7.16 (4H, d, $J = 7.80$ Hz). ^{13}C NMR (DMSO-d_6, δ, ppm): 157.43, 146.04, 141.43, 140.22, 136.28, 133.69, 132.35, 130.29, 128.04, 124.27, 120.56, 113.33, 109.03. ^{11}B NMR ($CDCl_3$, δ, ppm): 11.04. Anal. Calcd for $C_{21}H_{14}BI_2NO$ (mol wt 560.96): C, 44.96; H, 2.52; B, 1.93; I, 45.25; N, 2.50; O, 2.85. Found: C, 44.95; H, 2.69; I, 45.39; N, 2.53.

Polymer 3a. A mixture of B(4-iodophenyl)$_2$q (**1**) (0.20 g, 0.36 mmol), 1,4-diethynyl-2,5-dihexyloxybenzene (**2a**) (0.18 g, 0.36 mmol), 41 mg of $Pd(PPh_3)_4$, 7 mg of CuI, 14 mL of THF, and 7 mL of Et_3N was placed in a 50 mL Pyrex flask equipped with a magnetic stirring bar and a reflux condenser under an argon atmosphere. The reaction was carried out at 40 °C for 24 h with stirring. After the reaction mixture was cooled, the precipitated ammonium salts were filtered off and washed with THF. The filtrate was concentrated, and the residue was dissolved in 50 mL of $CHCl_3$ and poured into a separatory funnel and then washed three times with 50 mL of water to remove salts and catalysts. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was dissolved in 2 mL of $CHCl_3$ and poured into Et_2O (50 mL) to precipitate the polymer. The resulting polymer **3a** was filtered, washed with Et_2O, and dried in vacuo to give 0.26 g (0.33 mmol, 93%) as a yellow powder. ^1H NMR ($CDCl_3$, δ, ppm): 8.56 (1H, d, $J = 4.63$ Hz), 8.44 (1H, d, $J = 8.28$ Hz), 7.70−7.56 (2H, m), 7.45−7.39 (8H, m), 7.23−7.11 (5H, m), 6.97 (2H, s), 3.98 (4H, t, $J = 6.33$ Hz), 1.85−1.74 (4H, m), 1.51−1.49 (4H, m), 1.31 (8H, br s), 0.91−0.80 (6H, m). ^{11}B NMR ($CDCl_3$, δ, ppm): 7.23. Anal. Calcd for $C_{43}H_{42}BNO_3$ (mol wt 631.61): C, 81.77; H, 6.70; N, 2.50. Found: C, 78.98; H, 6.59; N, 1.87.

Polymer 3b. The reaction was carried out by following the procedure described above. The polymerization between 0.28 g (0.50 mmol) of **1** and 0.16 g (0.50 mmol) of **2b** gave the corresponding polymer **3b** 0.22 g (0.36 g, 70%) as a yellow powder. ^1H NMR ($CDCl_3$, δ, ppm): 8.56 (1H, d, $J = 5.12$ Hz), 8.45 (1H, d, $J = 8.28$ Hz), 7.72−7.62 (2H, m), 7.49−7.36 (2H, m), 7.23−7.07 (2H, m), 6.96 (2H, s), 3.98 (4H, t, $J = 6.21$ Hz), 1.84−1.75 (4H, m), 1.53−1.44 (4H, m), 1.39−1.16 (32H, m), 0.91−0.81 (6H, m). ^{11}B NMR ($CDCl_3$, δ, ppm): 7.13. Anal. Calcd for $C_{55}H_{66}BNO_3$ (mol wt 799.93): C, 82.58; H, 8.32; N, 1.75. Found: C, 79.28; H, 8.29; N, 1.54.

Supporting Information Available: ^1H NMR and fluorescence spectra of polymers **3a** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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