Synthesis of New Fluorescent Organoboron Polymers Based on Pyrazaboles

Fukashi Matsumoto and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan

Received April 11, 2002; Revised Manuscript Received May 6, 2003

ABSTRACT: Novel organoboron polymers containing pyrazaboles in the main chain were prepared by Heck−Sonogashira coupling. The coupling reaction between diyne monomers and pyrazabole derivatives gave the corresponding polymers in good yields. The number-average molecular weights of the obtained polymers were relatively high compared with the organoboron polymers prepared by hydroboration polymerization. The obtained polymers were further investigated by UV−vis absorption and fluorescence spectroscopy.

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] Because of their unique properties, they are expected as a novel type of optical and electrical materials. In this polymerization method, we have mainly applied the sterically hindered boranes such as mesitylborane (mesityl: 2,4,6-trimethylphenyl) and tripylborane (tripyl: 2,4,6-triisopropylphenyl) as borane monomers. Although the obtained polymers are highly stable, these borane monomers themselves are not so stable against air and moisture. Thus, the purifications of these boranes are practically impossible, and the trace contaminations of these reagents influence the polymerization to yield relatively low molecular weight polymers. From these reasons, we should find a novel synthetic method for the organoboron polymers as an alternative method for hydroboration polymerization.

On the other hand, pyrazaboles are known as a novel class of boron heterocycles. Since its first synthesis[2] in 1967, a number of pyrazaboles have been prepared and characterized; their structures and properties are not fully understood. Pyrazaboles are highly stable so that the derivatives containing various functional groups are easily prepared by usual organic reactions. Some conformational structures as described in Figure 1 are suggested according to the functional groups on the boron atoms. Several applications of pyrazaboles have been performed recently such as possible building blocks for discotic liquid crystals[3] or good bridges for *ansa*-ferrocenes to form the active container molecule for supramolecular applications.[4] In this study, novel organoboron polymers were synthesized by incorporating pyrazaboles into the polymer backbone as an alternative synthetic method for hydroboration polymerization. The present synthetic method is very attractive for preparing the organoboron polymers because the polymerization procedure is very simple and widely applicable to various organic monomers. Furthermore, characteristic fluorescence emission was observed in these polymers.

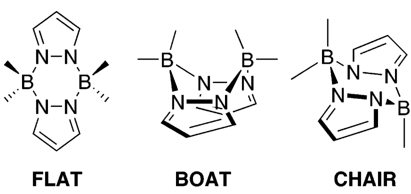
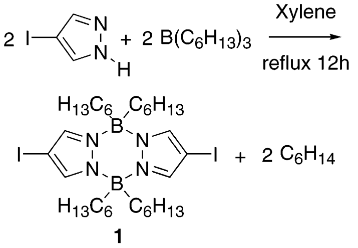


Figure 1. Conformations of pyrazabole.

Scheme 1. Synthesis of Pyrazabole



Results and Discussion

Synthesis. The pyrazabole **1** was prepared according to Scheme 1. Generally, the purity of monomers applied in a polymerization is crucial to obtain high molecular weight polymers. In this point, the pyrazabole **1** could be purified by recrystallization due to the stability of the heterocycle, which is the remarkable difference to tripylborane previously employed in hydroboration polymerization. Although the optimized structure estimated by semiempirical molecular orbital calculations suggested that a flat conformation was the most stable for the obtained pyrazabole in a solution state, the differences in the energy levels among the conformations were not notable so that the prompt conversion of the conformations should occur among them.

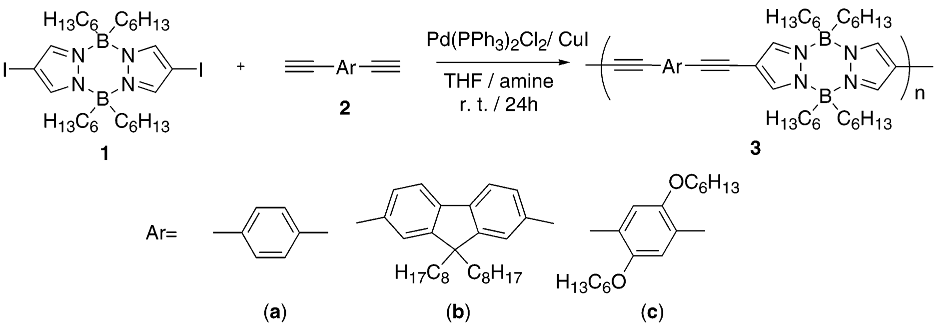
The polymerization procedure is described in Scheme 2. Coupling reactions utilizing Pd and Cu catalysts between the pyrazabole **1** and diyne monomers **2** gave the corresponding polymers (**3a**−**c**). The resulting polymers were purified by reprecipitation from methanol. The obtained polymers showed good solubility and easily gave a thin film. The number-average molecular weights

---

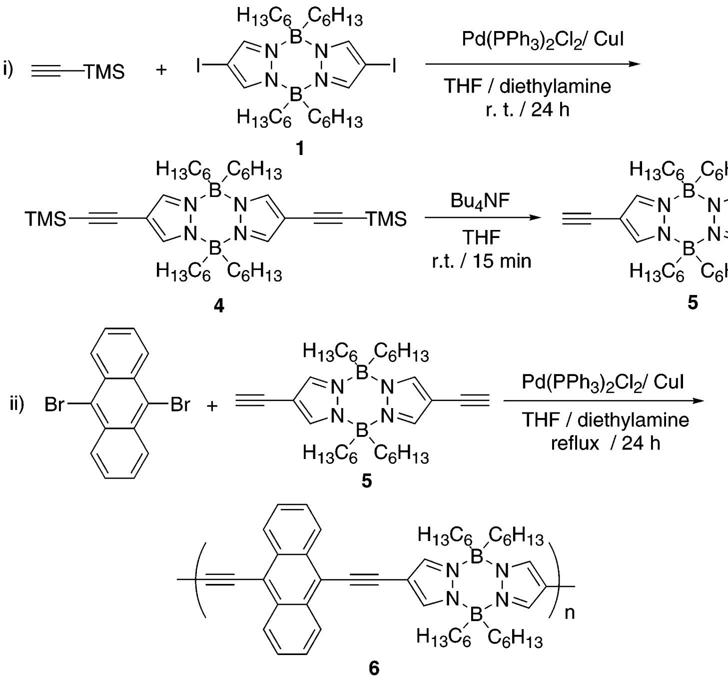
* Corresponding author. E-mail: chujo@chujo.synchem.kyoto-u.ac.jp.

10.1021/ma020577w CCC: $25.00

Scheme 2. Polymerization (i)



Scheme 3. Polymerization (ii)



of the obtained polymers were relatively high compared with those of the organoboron polymers prepared by hydroboration polymerization. Therefore, the purity and stability of the borane monomers were thought to have a significant role in the progress of polymerization.

Two pyrazabole analogues were applied in this polymer synthesis. The 2,6-dibromopyrazabole yielded low molecular weight oligomers even at the high reaction temperature because of its inferior reactivity to the 2,6-diiodopyrazabole. On the contrary, the highly reactive 2,6-diiodopyrazabole sometimes gave an insoluble polymer gel at a high concentration. Although this synthetic method can be applied to various diyne monomers, further simple applications to dihalo monomers would be offered by the procedure described in Scheme 3.

At first, 2,6-diiodopyrazabole (**1**) was reacted with trimethylsilylacetylene to yield the intermediate compound **4** and changed to the diyne derivative **5** by a desilylation reaction. Then the polymerization between 9,10-dibromoanthracene and 2,6-diethynylpyrazabole (**5**) was successfully performed in the similar way as Scheme 2. After removing the ammonium salt, the resulting polymer was also purified by reprecipitation to yield the polymer **6**. The polymerization results are summarized in Table 1. The structures of all products were supported by ^{1}H, ^{13}C, and ^{11}B NMR and IR spectra.

Optical Properties. The optical properties of the obtained polymers were investigated by UV−vis absorption and fluorescence emission spectroscopy. The UV−vis absorption spectra of the polymers are shown in Figure 2. The sharp absorption peaks of the polymer **3a**−**c** due to $\pi-\pi^*$ transitions were observed around 300−400 nm. In the polymer **6**, the typical absorption bands for the anthracene moiety were observed above 400 nm. Basically, the shapes of the absorption peaks of all polymers were analogous to corresponding monomers such as 1,4-diethylnylbenzene and so on. As described in the literature,[5] the boron bridge of pyrazabole is a poor electron relay so that electronic interactions between π-orbitals of pyrazole moiety are small. Therefore, the poor expansion of π-conjugation through the backbone should be expected in these polymers. The absorption peaks of the obtained polymers are relatively sharp and observed at short wavelength region due to the localized π-electrons. Nevertheless this transparency of visible light should have advantage for practical

Table 1. Polymerization Results[a]

polymer	M_w [b]	M_n [b]	M_w/M_n [b]	yield (%)[c]
3a	42 000	34 000	1.2	70
3b	19 700	9 000	2.2	80
3c	61 000	33 000	1.8	74
6	18 000	9 000	2.0	85

[a] The reactions were carried out in THF and Et_2NH. [b] GPC (THF) PSt standards. [c] Isolated yields after reprecipitation into MeOH.

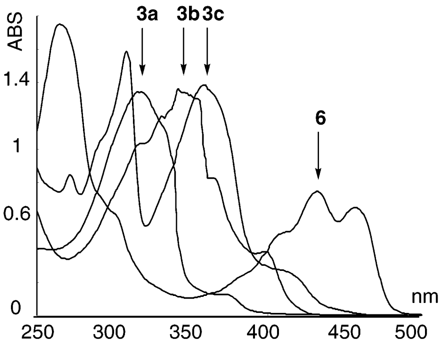


Figure 2. UV–vis absorption spectra of polymers **3a–c** and **6** in chloroform at room temperature.

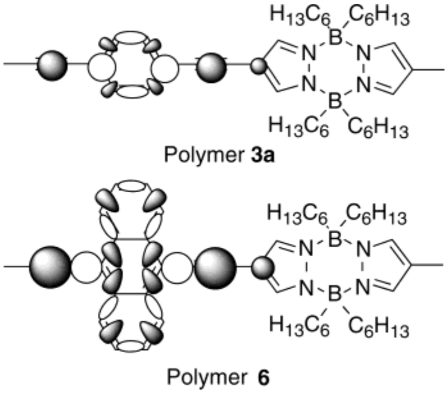


Figure 3. Differential electron density between the ground and the lowest excited states for the models of polymer **3a** and **6** calculated by the MOPAC2000 with the AM1 Hamiltonians: black, electron density decreases; white, electron density increases.

application as an optical material against the colored organic polymers.

To estimate the electron migration during the excitation by UV radiation, semiempirical molecular orbital calculations were performed on some oligomer models of the obtained polymers. We have calculated the differential electron density between the ground and the lowest excited states, which is described in Figure 3. The black region indicates the region in which electron density decreases upon transition to the excited state, and the white region indicates the region in which electron density increases upon the transition. Apparently, the density changes occurred only at the spacer moiety such as benzene and anthracene, and the estimated absorption wavelengths are agreeable with the experimental results of UV–vis absorption spectroscopy. This result suggests that the HOMO–LUMO transitions in these models are local excitation and that no intramolecular electron charge transfer occurred during the excitation procedure.

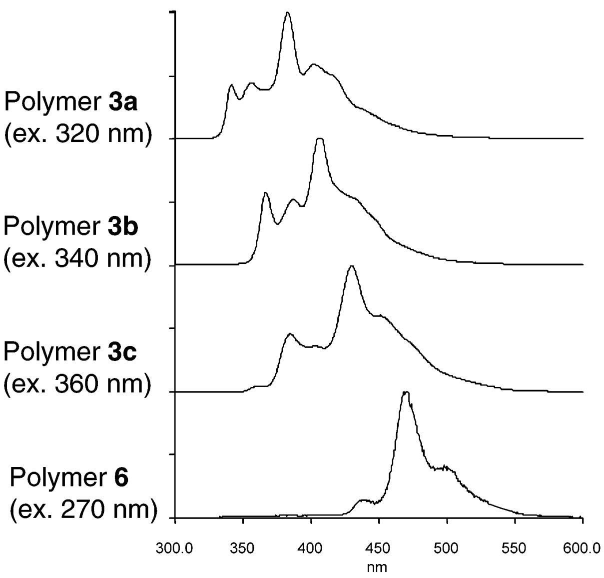


Figure 4. Fluorescence spectra of polymers **3a–c** and **6** in chloroform at room temperature.

Table 2. Optical Properties[a] of Polymers 3a–3c and 6

polymer	λ_{max} (nm)[b]	ϵ[c]	Ex (nm)[d]	FL (nm)[e]	Φ_F[f]
3a	320	50 000	320	383	0.43
3b	350	52 000	350	406	0.56
3c	360	32 000	360	430	0.67
	308	36 000	310		0.55
6	430	22 000	430	470	0.53
	265	52 000	270		0.27

[a] Measured in chloroform at room temperature. [b] Absorption maximum wavelengths. [c] Molar absorption coefficients at λ_{max}. [d] Excited wavelengths. [e] Fluorescence maximum wavelengths. [f] Fluorescence quantum yields using 9-anthracenecarboxylic acid as a standard.

The fluorescence emission spectra of the obtained polymers are shown in Figure 4. Noteworthily, the shapes of the emission spectra are very similar to each other. From the results of the UV–vis absorption and the calculation described above, the π–π* transitions should occur topically at the spacer moiety such as benzene, fluorene, and anthracene, so that the characteristic emissions to these structures would be expected in the fluorescence measurements. However, the observed shapes of the emissions were similar to each other and approximately the same as the spectrum of the pyrazabole **1** rather than those of the corresponding monomers **2**. Therefore, the fluorescence spectra of these polymers are thought to be characteristic of pyrazabole. In other words, the presence of pyrazabole in the polymer backbone is crucial in these fluorescence properties. Speculatively, the energy migration should occur from the spacer moiety to the pyrazabole at the excited states, or a charge-transfer state in which electron density has been transferred from boron atoms to the hetrocyclic rings should be considered. The conformations of pyrazabole might have influence on the emission properties, and the further investigation would be performed in these mechanisms. The optical properties of these polymers are summarized in Table 2. Purple-to-green emissions with good fluorescence quantum yields were obtained from these polymers.

Conclusion

Novel organoboron polymers were prepared by utilizing pyrazaboles as an alternative method for hydroboration polymerization. These polymers showed good stability and were obtained in relatively high molecular weights compared with the polymers prepared by hydroboration polymerization. The obtained polymers exhibited strong fluorescence emission in a short wavelength region. Therefore, they are expected as a novel type of the organoboron polymers with unique fluorescence properties. Pyrazaboles seem to have a significant role in the fluorescence emission. Further investigations on the electronic conditions of boron atoms and the polymer structures would be performed.

Experimental Section

Materials and Instrument. Tetrahydrofuran (THF) and diethylamine were distilled before use. ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded in $CDCl_3$ on a JEOL EX-270 instrument. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. 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 JASCO V-530 spectrophotometer. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. Trihexylborane,[6] 2,7-diethynyl-9,9-dioctylfluorene (**2b**),[7] and 1,4-diethynyl-2,5-dihexyloxybenzene (**2c**)[8] were prepared according to the literature. Other reagents were commercially available and purified before use. All reactions were performed under a nitrogen atmosphere. Geometry optimization was performed using the MOPAC2000 program[9] with the AM1 Hamiltonians. Calculations for the excited states were carried out using the Fujitsu MOS-F program packages[10] with the CNDO/S Hamiltonians.

4,4,8,8-Tetrahexyl-2,6-diiodopyrazabole (1). To a mixture of 4-iodopyrazole (1.18 g, 6.0 mmol) and 30 mL of degassed xylene, 12 mL (0.5 M) of THF solution of trihexylborane was added and refluxed at 120 °C for 12 h. After removing the solvents, the resulting product was washed with methanol to yield white solid (1.58 g, 2.11 mmol, 70%). Anal. Calcd for $C_{30}H_{56}B_2N_4I_2$ (mol wt 748.23): C, 48.16; H, 7.54; N, 7.49. Found: C, 48.00; H, 7.31; N, 7.56. NMR data (solution in $CDCl_3$): δ (^{1}H, ppm) = 7.59 (s, 4H, Pz = pyrazole), 1.14−0.60 (52H, hexyl); δ (^{13}C, ppm) = 138.42, 56.75 (Pz), 32.80, 31.79, 24.98, 22.70, 14.13 (hexyl); δ (^{11}B, ppm) = 3.58.

4,4,8,8-Tetrahexyl-2,6-bis(trimethylsilylethynyl)pyrazabole (4). 2.0 g (2.67 mmol) of diiodopyrazabole **1** was dissolved into the mixture of 30 mL of dried THF, 90 mg of $Pd(PPh_3)_2Cl_2$, and 24 mg of CuI. Then 0.83 mL (5.88 mmol) of trimethylsilylacetylene and 15 mL of diethylamine were added, and the mixture was stirred for 24 h at room temperature. After evaporating the solvents, the crude product was extracted with diethyl ether and water and dried over Na_2SO_4. Finally, purification by column chromatography using hexane as an eluent and washing with methanol gave the desired product in 90% yield (1.67 g, 2.41 mmol). Anal. Calcd for $C_{40}H_{74}B_2N_4Si_2$ (mol wt 688.84): C, 69.74; H, 10.83; N, 8.13. Found: C, 68.90; H, 10.78; N, 8.18. NMR data (solution in $CDCl_3$): δ (^{1}H, ppm) = 7.67 (s, 4H, Pz), 1.13−0.60 (52H, hexyl), 0.26 (18H, $-(CH_3)_3Si$); δ (^{13}C, ppm) = 136.46, 103.97 (Pz), 96.59, 94.72 ($-C\equiv C-$), 32.85, 31.84, 25.02, 22.73, 14.14 (hexyl), −0.12 ($-(CH_3)_3Si$); δ (^{11}B, ppm) = 3.46.

2,6-Diethynyl-4,4,8,8-tetrahexylpyrazabole (5). To a THF (35 mL) solution of **4** (1.26 g, 1.83 mmol), 1.0 mL of tetrabutylammonium fluoride (1.0 M) was added and stirred for 15 min at room temperature. A crude product was obtained by evaporating the solvent. After recrystallization from methanol, a white product was prepared in a yield of 87% (0.87 g, 1.59 mmol). Anal. Calcd for $C_{34}H_{58}B_2N_4$ (mol wt 544.45): C, 75.00; H, 10.74; N, 10.29. Found: C, 74.73; H, 10.87; N, 10.24. NMR data (solution in $CDCl_3$): δ (^{1}H, ppm) = 7.70 (s, 4H, Pz), 3.10 (s, 2H, $-C\equiv CH$), 1.14−0.60 (52H, hexyl); δ (^{13}C, ppm) = 136.19, 102.35 (Pz), 79.01, 73.32 ($-C\equiv CH$), 32.35, 31.36, 24.53, 22.23, 13.64 (hexyl); δ (^{11}B, ppm) = 3.38. IR (cm^{-1}) = 3306 (ν $\equiv C-H$), 2126 (ν $C\equiv C$).

Polymer 3a. To a mixture of 1,4-diethynylbenzene (0.068 g, 0.54 mmol), diiodopyrazabole **1** (0.40 g, 0.54 mmol), 25 mg of $Pd(PPh_3)_2Cl_2$, 5 mg of CuI, and 10 mL of THF, 5 mL of diethylamine was added at room temperature. After stirring for 24 h, the solvents were removed in vacuo. The residue was poured into diethyl ether, and the ammonium salt was removed from the solution by filtration. The desired product (0.23 g, 70%) was reprecipitated from methanol and dried. NMR data (solution in $CDCl_3$): δ (^{1}H, ppm) = 7.77 (4H, Pz), 7.50 (4H, Ar), 1.17−0.69 (52H, hexyl); δ (^{11}B, ppm) = −0.92.

Polymer 3b. The reaction was carried out by following the procedure described above. The polymerization between 0.13 g (0.30 mmol) of **2b** and 0.23 g (0.30 mmol) of **1** gave the corresponding polymer **3b** (0.22 g, 80%). NMR data (solution in $CDCl_3$): δ (^{1}H, ppm) = 7.80 (4H, Pz), 7.70−7.19 (6H, Ar), 1.96−0.68 (88H, hexyl, octyl); δ (^{11}B, ppm) = 2.24.

Polymer 3c. The reaction of 0.16 g (0.50 mmol) of **2c** and 0.37 g (0.50 mmol) of **1** gave the polymer **3c** in 74% yield (0.30 g). NMR data (solution in $CDCl_3$): δ (^{1}H, ppm) = 7.75 (4H, Pz), 7.03 (2H, Ar), 4.05 (4H, $-OCH_2$), 1.87−0.65 (74H, hex); δ (^{11}B, ppm) = 0.66.

Polymer 6. The polymerization procedure was almost same as above except for the reaction temperature. The reaction of 0.10 g (0.30 mmol) of dibromoanthracene and 0.16 g (0.30 mmol) of **5** was performed at 60 °C and yielded the polymer **6** (0.18 g, 85%). NMR data (solution in $CDCl_3$): δ (^{1}H, ppm) = 8.71 and 7.69 (8H, Ar), 8.00 (4H, Pz), 1.25−0.72 (52H, hexyl); δ (^{11}B, ppm) = −1.74.

References and Notes

(1) (a) Matsumi, N.; Umeyama, T.; Chujo, Y. *Macromolecules* **2000**, *11*, 3956. (b) Matsumi, N.; Naka, N.; Chujo, Y. *Polym. J.* **1998**, *10*, 833.
(2) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3165.
(3) Barberá, J.; Giménez, R.; Serrano, J. L. *Adv. Mater.* **1994**, *6*, 470.
(4) (a) Jäkle, F.; Priermeier, T.; Wagner, M. *Organometallics* **1996**, *15*, 2033. (b) Herdtweck, E.; Jäkle, F.; Opromolla, G.; Spiegler, M.; Wagner, M.; Zanello, P. *Organometallics* **1996**, *15*, 5524.
(5) Novak, I.; Kovač, B. *J. Electron Spectrosc. Relat. Phenom.* **2001**, *113*, 175.
(6) Brown, H. C.; Kanth, J. V. B.; Zaidlewicz, M. *Tetrahedron* **1999**, *55*, 5991.
(7) Lee, S. H.; Nakamura, T.; Tsutsui, T. *Org. Lett.* **2001**, *3*, 2005.
(8) Egbe, D. A. M.; Klemm, E. *Macromol. Chem. Phys.* **1998**, *199*, 2683.
(9) MOPAC2000 ver. 1.0, Fujitsu Ltd, Tokyo, Japan, 1999.
(10) Matsuura, A. MOS-F 4.2C, Fujitsu Ltd, Tokyo, Japan, 2000.

MA020577W