

REVIEW ARTICLE

π -Conjugated Organoboron Polymers *via* the Vacant *p*-Orbital of the Boron Atom

By Noriyoshi MATSUMI¹ and Yoshiki CHUJO^{2,*}

A decade has passed since organoboron π -conjugated systems highly extended through the empty *p*-orbital of the boron atom emerged as a new class of π -conjugated materials. Making use of convenient hydroboration polymerization, a variety of π -conjugated organoboron polymers exhibiting fluorescence emission, *n*-type electrochemical activity, electrical conductivity, third order non linear optical property, anion sensing ability is easily prepared. The organoboron π -conjugated polymers having highly bulky substituent on the boron atom shows high stability under air and moisture and therefore, potentially useful for versatile applications.

The design of electron deficient organoboron π -systems led to observation of unique photophysical behavior such as extraordinary high third order non linear optical susceptibility, facilitation of $p\pi-d\pi^*$ transition, intramolecular charge transfer, unusually activated σ - π conjugative interaction and so forth.

In addition to boration polymerization methods, polycondensation using di-Grignard reagent, Sonogashira type polycondensation, polycondensation *via* tin-boron exchange are useful for synthesis of π -conjugated organoboron polymers.

KEY WORDS: Organoboron Polymers / π -Conjugated Polymers / Hydroboration Polymerization / Inorganic Polymers / Light Emitting Materials / Ion Sensors /

After the discovery of electrically conductive polyacetylenes,¹ π -conjugated polymers² have played great roles in the development of functional materials exhibiting conductivity, electrochemical activity, light emitting property, third order non linear optical property and so forth. It did not take so long before versatile convenient synthetic methods for π -conjugated materials such as oxidative polymerization, organometallic polycondensation and electrochemical polymerization were widely developed. A variety of unique π -conjugated systems in which exotic elements are incorporated has been synthesized. For instance, polysiloles,³ polygermoles,⁴ polyphospholes,⁵ poly(vinylene-arsine)⁶ are reported. The present review focuses on π -conjugated organoboron polymers in which π -conjugation is extended through the vacant *p*-orbital of the boron atom.

The extension of π -conjugation through the boron atom was first theoretically studied in detail by Good *et al.*⁷ It was reported that ¹¹B-NMR chemical shifts and absorption data for low molecular weight vinylborane derivatives were in good accordance with the results of calculation based on Hückel MO theory. From these results, it was demonstrated that π -orbitals of vinyl group conjugatively overlap with the vacant *p*-orbital of the boron atom. Therefore, fully aromatic organoboron polymers were expected to act as π -conjugated polymers which possess unknown electronic states with positive holes built in (Figure 1). U. Salzner and J. B. Lagowski *et al.* predicted that polyboroles⁸ would show fairly small bandgaps owing to their quinoidal structures in their ground state. Poly(bora-acety-

lene)s⁹ were also theoretically predicted by T. Yamabe and K. Tanaka, to show metallic conductivity without doping. In spite of such intriguing property of organoboron π -conjugated system, highly extended π -conjugated organoboron polymers had not been prepared during more than 30 years after the discovery of hydroboration¹⁰ by Brown *et al.*

π -CONJUGATED ORGANOBORON POLYMERS VIA HYDROBORATION POLYMERIZATION OF AROMATIC DIYNES

Synthesis of π -conjugated organoboron polymers was first undertaken¹¹ by us *via* hydroboration polymerization¹² of mesitylborane¹³ with aromatic diynes as depicted in Scheme 1. When polymerization was examined using thexylborane, extension of π -conjugation was not observed because dihydroboration of sterically less hindered thexylborane prevented the π -conjugation (Figure 2). Using mesitylborane, reasonable air stability was rendered to the resulting polymers, which was convenient for further characterization. Corriu *et al.* also examined hydroboration polymerization between $BH_2Br-SMe_2$ and unsaturated thiophene derivative independently.¹⁴ However, extension of π -conjugation was not supported spectroscopically possibly because of instability of the resulting materials. Hydroboration polymerization between mesitylborane and 1,4-diethynylbenzene afforded the corresponding polymer **3a** whose M_n was 6500. In the UV-vis absorption spectrum (in $CHCl_3$, at room temperature) of **3a**, the absorption

¹Graduate School of Bioagricultural Sciences, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8601, Japan

²Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

*To whom correspondence should be addressed (E-mail: chujo@chujo.synchem.kyoto-u.ac.jp).

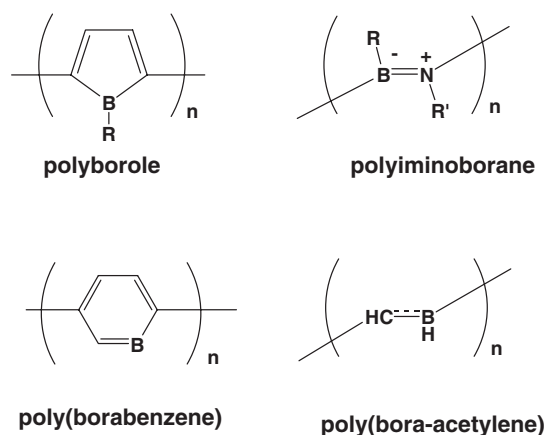


Figure 1. Potential π -conjugated organoboron polymers.

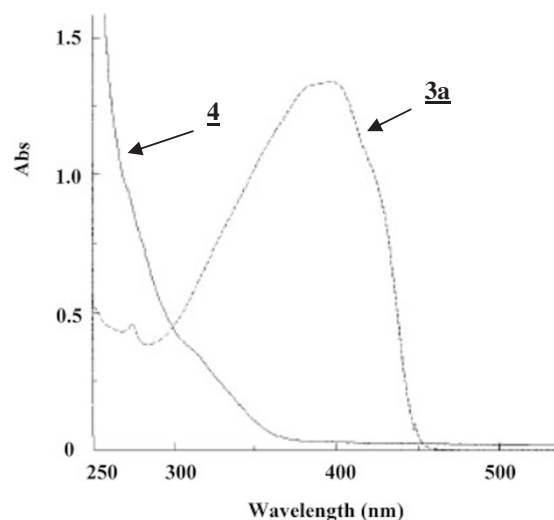
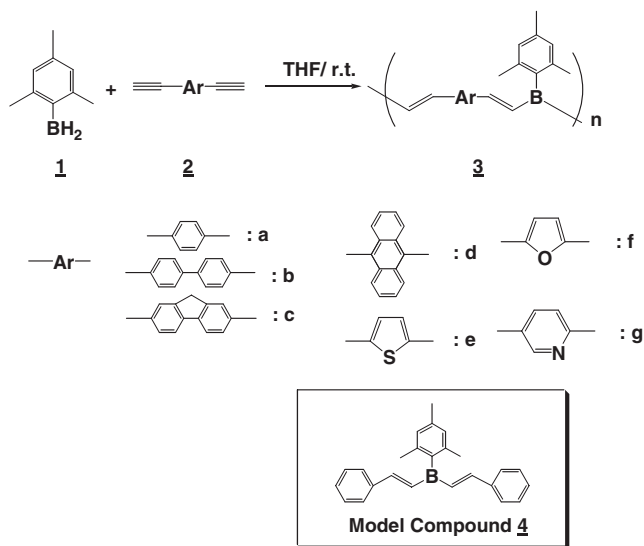


Figure 3. UV-vis absorption spectra for polymer **3a** and model compound **4** in chloroform at room temperature.



Scheme 1.

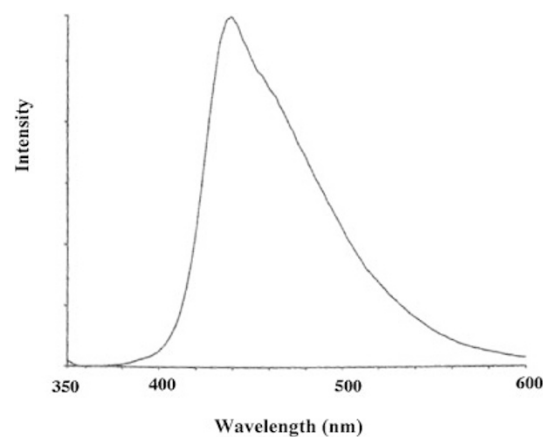


Figure 4. Fluorescence emission spectrum for polymer **3a** in chloroform at room temperature (excited at 350 nm).

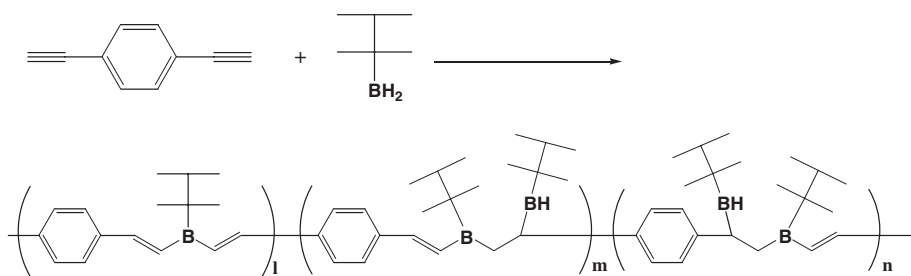


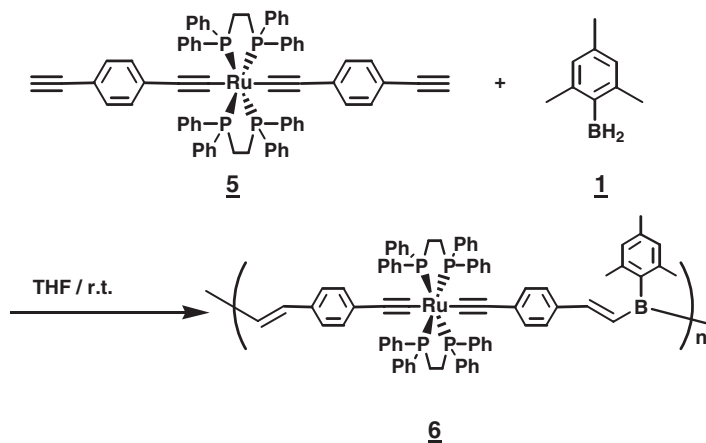
Figure 2. Interruption of π -conjugation by dihydroboration of sterically less hindered thexylborane.

maximum was observed at 399 nm which was highly red shifted in comparison with that of the model compound **4** (Figure 3). The polymer showed intense blue light emission when dilute CHCl_3 solution of **3a** was irradiated with UV light (Figure 4).

The electrochemical property of the polymers was also investigated by cyclic voltammetry. In a 0.1 M THF solution of

$n\text{Bu}_4\text{NClO}_4$, **3a** showed a reduction peak at -1.61 V vs Ag/Ag^+ and a reoxidation peak at -0.90 vs Ag/Ag^+ at the sweep rate of 100 mV/s. The observed electrochemical activity showed the polymer to be typical electron deficient n-type conjugated polymer.

Third order non-linear optical property of the polymers was evaluated by degenerate four wave mixing method. The



Scheme 2.

observed third order non linear susceptibility was unusually high (6.87×10^{-6} – 3.56×10^{-7} esu). The observed large $\chi^{(3)}$ values compared with those for low molecular weight borylated NLO chromophores¹⁵ reported by Marder *et al.* should be due in part to highly extended π -conjugation.

To improve the air stability of the polymers, hydroboration polymerization was also examined using triethylborane (2,4,6-triisopropylphenylborane) instead of mesitylborane. In this case, the resulting polymer did not show any change in molecular weight even after continuous air bubbling of polymer solutions for 24 h.

Electrical conductivity of the polymer prepared from triethylborane and 2,7-diethynylfluorene was studied in detail.¹⁶ When this polymer was exposed to triethylamine vapor (n-type doping), electrical conductivity was elevated to about 10^{-6} S/cm within 100 min. Stationary-state photocurrent measurements also suggested that this polymer is a n-type π -conjugated polymer. Transient photocurrent measurements showed that drift mobility of electron was about five times higher than that of hole in this system.

Heteroaromatic π -Conjugated Organoboron Polymers

Since organoboron π -conjugated system is electron deficient, design of donor-acceptor type polymer is an attractive approach for tuning of optical or electrochemical properties. When 2,5-diethynylthiophene (**2e**), 2,5-diethynylfuran (**2f**) and 2,5-diethynylpyridine (**2g**) were employed instead of **2a**, the corresponding donor-acceptor type π -conjugated polymers¹⁷ were readily obtained (Scheme 1). The number-average molecular weights of these polymers were around 3000. The polymers **3e** and **3f** did not show particularly red shifted absorption, indicating that ground state charge transfer did not take place. However, these polymers showed intense green light emission upon irradiation with UV light. The observed much larger Stokes shift in comparison with that of **3a** should be due to energy transfer in the excited state. The polymer **3g** showed significantly red shifted absorption maximum compared with **3a**. When irradiated with UV light, **3g** exhibited a white light emission.

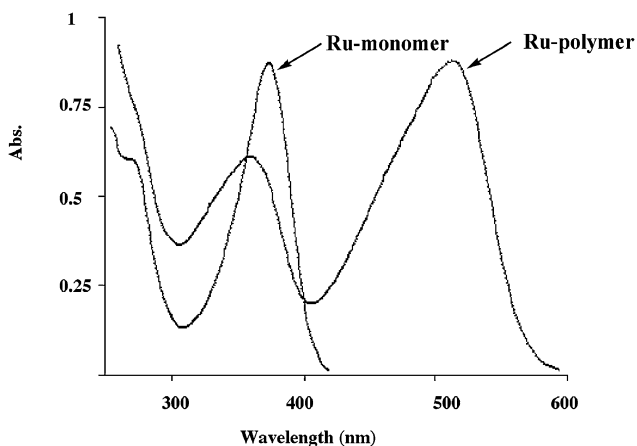
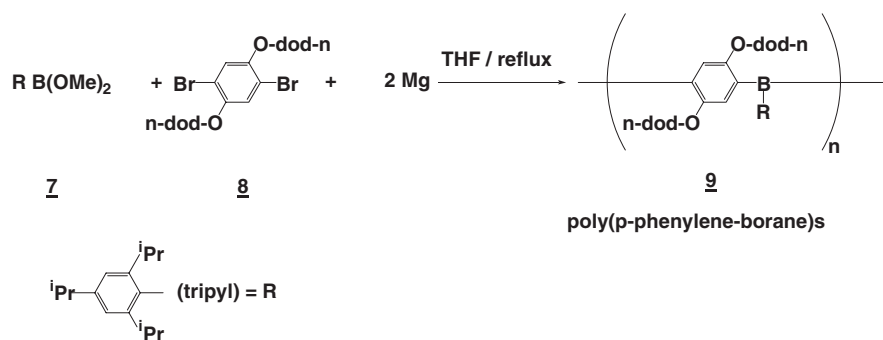


Figure 5. UV-vis absorption spectra for Ru-monomer **5** and Ru-polymer **6** in chloroform at room temperature.

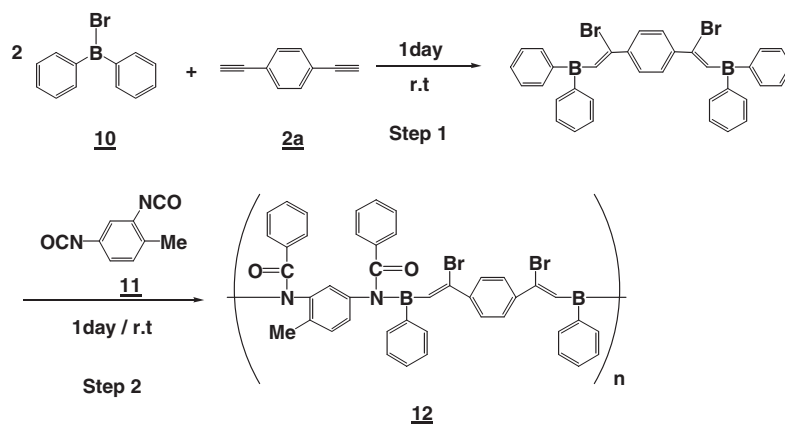
Facilitation of $d\pi$ - $p\pi^*$ Transition in π -Conjugated Organoboron Polymer Including Ruthenium Complex

A π -conjugated organoboron polymer containing ruthenium-phosphine complex¹⁸ (Scheme 2) showed particularly interesting optical behavior. A tetrayne type monomer containing ruthenium-phosphine complex **5** was reacted with a slight excess amount of mesitylborane. Although **5** was poorly soluble in tetrahydrofuran, the reaction mixture became homogeneous during hydroboration polymerization. An intensely reddish polymer **6** whose M_n was 13000 was obtained in 91% yield. In the UV-vis spectrum of **6**, two absorption maxima due to π - π^* transition and $d\pi$ - $p\pi^*$ transition were observed at 359 nm and 514 nm, respectively (Figure 5). It should be noted that the latter peak was unusually red-shifted by 141 nm in comparison with that of monomer **5**. A push-pull effect between electron-rich ruthenium complex and electron-deficient organoboron unit as well as extension of π -conjugation should be responsible for this observation.

The electrochemical behavior of **6** was also evaluated by cyclic voltammetry. **6** showed electrochemical responses due to



Scheme 3.



Scheme 4.

Ru^{III}/Ru^{II} couple at higher potential than that observed for **5**. This would be also due to lower π -electron density in **6** in comparison with **5**.

POLY(*p*-PHENYLENE-BORANE)S VIA GRIGNARD REAGENT

The π -conjugated organoboron polymers prepared by hydroboration polymerization were not thermally very stable because of retro-hydroboration reaction (β -elimination) at high temperature ($T > 100^\circ\text{C}$). Therefore, synthesis of π -conjugated organoboron polymers *via* other polymerization system is of strong interest. Using the reaction of alkoxyborane with Grignard reagent, polycondensation between aryldimethoxyborane and di-Grignard reagents was examined to afford novel poly(*p*-phenyleneborane)s (PPBs)¹⁹ (Scheme 3). The polymerization was successful only when bulky aryl group was attached on alkoxyborane, possibly because such bulky substituent retarded disproportionation of alkoxyborane monomers. The M_n of the polymers obtained were 2400 to 3000. In the UV-vis spectra of PPBs (λ_{max} 359 nm–367 nm), significantly extended π -conjugation was implied. When the polymer solution was irradiated with UV light, visible green fluorescence emission was observed. After air bubbling experiment or treatment with water for 24 h, no significant decrease in M_n was observed from the GPC measurements.

π -CONJUGATED ORGANOBORON POLYMERS VIA B-N BOND

As a potential organoboron polymer, preparation of poly(iminoborane)s composed of B-N bonds has been examined. Since B-N bond possesses a double bond like nature due to $p\pi$ - π interaction, the polymer extended through B-N bonds is expected as a novel class of π -conjugated polymers whose properties are unknown. So far, poly(iminoborane) has been reported only as insoluble solid²⁰ and therefore, soluble defined poly(iminoborane) has never been reported. We have examined the synthesis of π -conjugated polymer *via* B-N bond by alternating boration copolymerization between aromatic diynes and aromatic diisocyanates²¹ (Scheme 4). Generally, phenylboration reaction of isocyanates proceeds smoothly under mild reaction conditions. Phenylboration reaction of acetylenes requires severe reaction conditions. Therefore, it is considered that alternating copolymerization between diyne and diisocyanate is possible using diphenylbromoborane. After the reaction of 1,4-diethynylbenzene with two equivalents of diphenylbromoborane, the resulting haloboration adduct was subjected to phenylboration polymerization with 2,4-tolylene diisocyanate. The M_n of the obtained polymer **12** was estimated to be 4300 from the GPC measurement. In the ¹¹B-NMR spectrum of **12** (Figure 6b), the main peak due to β -haloalkenylamidoborane

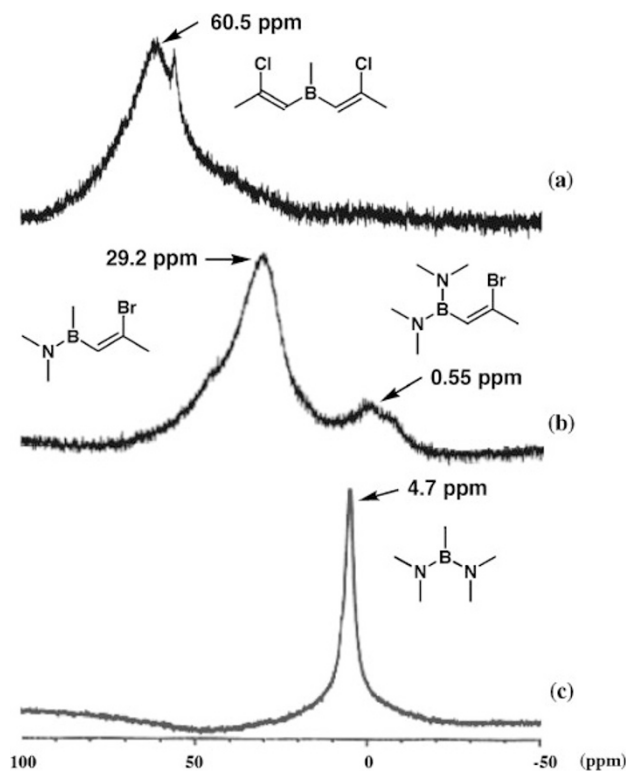
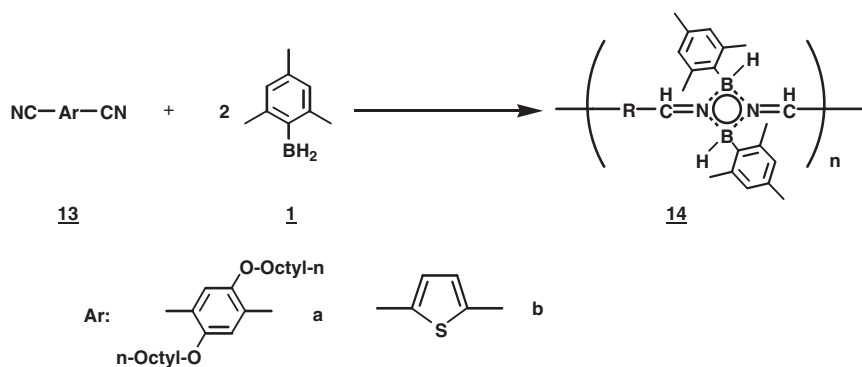


Figure 6. ^{11}B -NMR spectra for organoboron polymers prepared by boration polymerization. (a) A polymer having di(β -haloalkenyl)borane unit. (b) polymer **12**. (c) A polymer having diamidoborane unit.

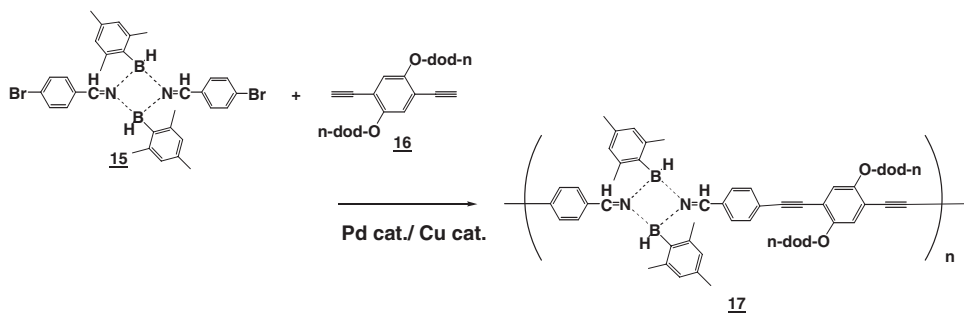
structure was observed in the mid point of those for di(β -haloalkenyl)borane and diamidoborane, suggesting that polymerization proceeds in highly alternating manner. At 0.55 ppm, a small peak assignable to diamido(β -haloalkenyl)borane structure was also observed. This indicates that further phenyl-boration reaction (crosslinking reaction) takes place during the polymerization. In the UV-vis spectrum, although absorption edge was red-shifted, absorption maximum was not clearly observed. This should be because of interruption of π -conjugation by the crosslinking.

π -CONJUGATED POLY(CYCLODIBORAZANE)S WITH INTRAMOLECULAR CHARGE TRANSFERRED (ICT) STRUCTURE

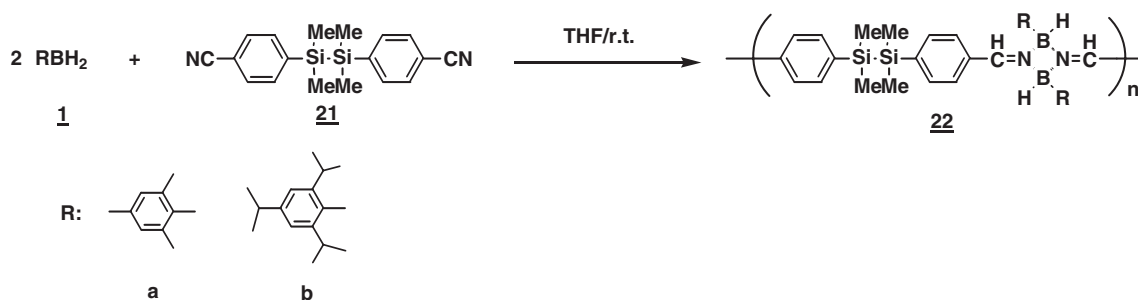
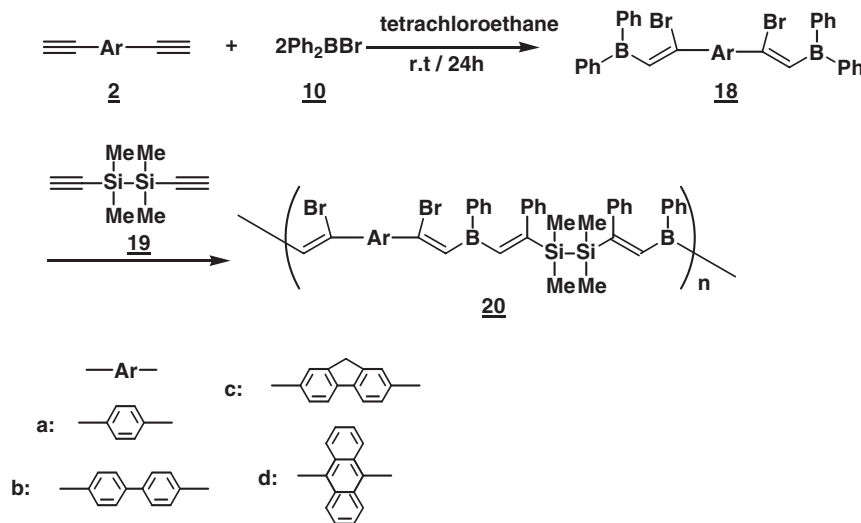
A series of fully air stable poly(cyclodiborazane)s was prepared by us *via* hydroboration polymerization or allylboration polymerization of dicyano compounds.²² Generally, fully aromatic poly(cyclodiborazane)s do not show extended π -conjugation. However, significant extension of π -conjugation was observed in donor-acceptor type poly(cyclodiborazane)s bearing thienylene unit or 2,5-dialkoxy-1,4-phenylene unit²³ (Scheme 5). In the UV-vis absorption spectra of these polymers **14**, both absorption edges and absorption maxima were dramatically red-shifted compared with those for model compounds or monomers **13**, demonstrating that π -conjugation is certainly extended beyond the repeating units. These polymers exhibited intense blue-green emission when irradiated with UV light or near-UV light. The fluorescence emission



Scheme 5.



Scheme 6.



wavelength showed dependency on the kind of solvent. This should be because intramolecular charge transferred (ICT) structure is retained even after polymerization.

Oligothiophenes containing cyclodiborazane units were also prepared by us.^{23b} In this system, emission wavelength and quantum yield were finely tunable by changing oligothiophene chain length.

A π -conjugated poly(cyclodiborazane) was successfully prepared by organometallic polycondensation²⁴ (Scheme 6). Sonogashira coupling reaction between cyclodiborazane-containing dibromide (**15**) and 2,5-didodecyloxy-1,4-diethynylbenzene (**16**) afforded π -conjugated poly(cyclodiborazane) (**17**) in 47% yield. The M_n of **17** corresponds to 8500 in the GPC measurement. The polymer **17** showed absorption maximum at 414 nm in chloroform. The fluorescence emission spectrum of **17** showed an intense blue-green emission peak at 466 nm when irradiated at 414 nm. The π -conjugated poly(cyclodiborazane) was electrochemically active toward n-doping. A reduction peak was observed at -1.76 eV (*vs* Ag/Ag⁺) with a reoxidation peak at -1.14 eV (In 0.1 M THF solution of $n\text{Bu}_4\text{N}^+\text{ClO}_4^-$; at the sweep rate of 100 mV/s). The reduction peak potentials were independent of the sweeping rate in the range of 10 mV/s to 100 mV/s, indicating that this system is electrochemically reversible.

σ - π CONJUGATED ORGANOBORON POLYMERS

Using a diene monomer bearing disilanylene unit, σ - π conjugated organoboron polymers were prepared utilizing alternating boration polymerization method²⁵ (Scheme 7). In tetrachloroethane, two equivalents of diphenylbromoborane were reacted with aromatic diene monomer (at room temperature) to form haloboration adduct. The obtained compounds were polymerized with equimolar amount of 1,2-diethynyl-1,1,2,2-tetramethyldisilane **19** at 80 °C for 2 h. When 2,7-diethynylfluorene was used as aromatic diene, the M_n of the obtained polymer **20** was 5700. In the UV-vis absorption spectrum of **20**, two absorption peaks due to π - π^* transition and σ - π interaction were observed at 284 nm and 315 nm, respectively. This polymer exhibited blue fluorescence emission (419 nm–449 nm) in a moderate intensity when irradiated with UV light.

σ - π Conjugated poly(cyclodiborazane)s were prepared by hydroboration polymerization of dicyano monomer including polymerization of disilanylene unit²⁶ (**21**) (Scheme 8). The M_n of the polymers prepared (**22**) was 9400 to 4800. In the UV-vis absorption spectra of these polymers, both absorption maxima and absorption edges were significantly red-shifted compared with

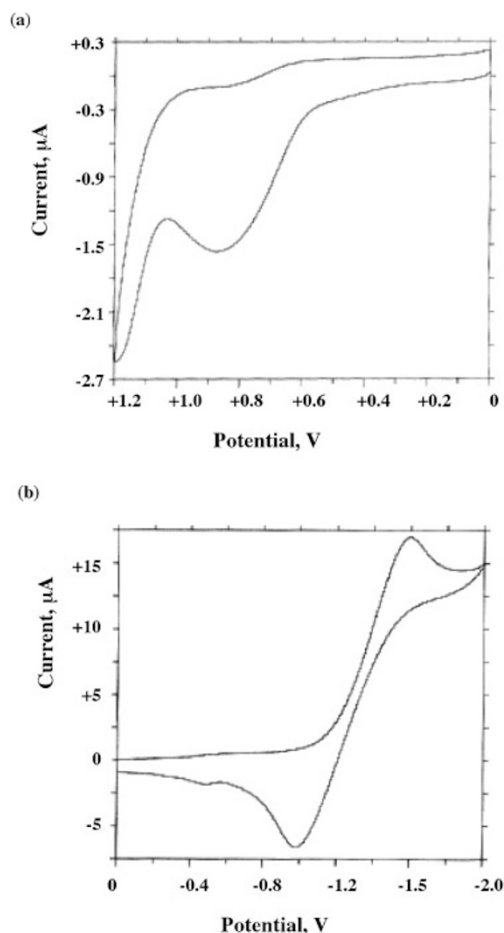


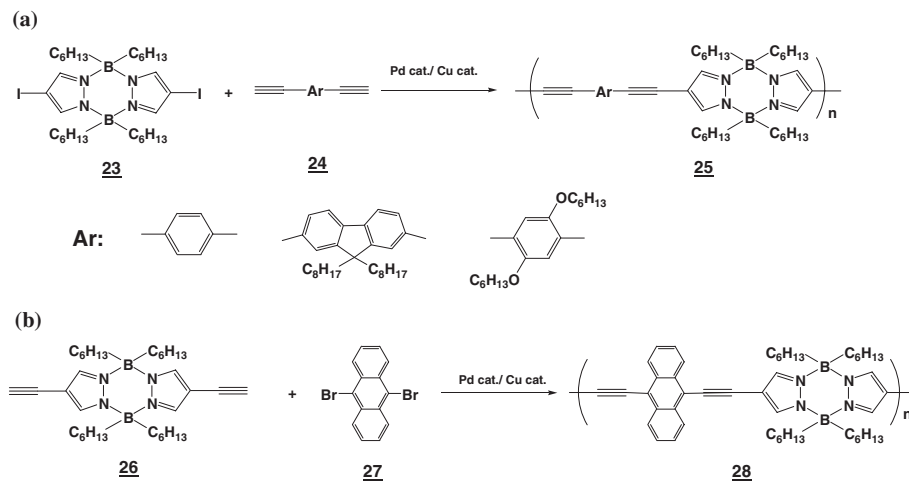
Figure 7. Cyclic voltammograms of polymer **22** in (a) 0.1 M CH_2Cl_2 solution of nBu_4NPF_6 or (b) 0.1 M THF solution of $\text{nBu}_4\text{NClO}_4$ vs Ag/Ag^+ at the sweep rate of (a) 50 mV/s or (b) 100 mV/s.

those of dicyano monomers. The fluorescence emission spectra of the polymer prepared using mesitylborane showed an intense emission peak in the visible blue region (430 nm).

The polymers were electrochemically active both for oxidation and reduction (Figure 7). From a measurement of cyclic voltammetry in the potential region of 0 V to 1.2 V (vs Ag/Ag^+ ; in 0.1 M THF solution of $\text{nBu}_4\text{NClO}_4$ or 0.1 M CH_2Cl_2 solution of nBu_4NPF_6), an anodic wave was observed at 0.87 V (Figure 7a). The observed oxidation potential was fairly lower than those for σ - π conjugated organosilicon polymers reported so far. Since σ - π conjugation between Si-Si chain orbitals and the π -unit orbitals increases the HOMO energy and results in a decrease in the first ionization potential, the observed low oxidation potential indicates unusually enhanced σ - π interaction between disilanylene unit and adjacent cyclodiborazane unit.

POLY(PYRAZABOLE)S

Pyrazabole is a highly stable boron containing heterocycle in which a variety of functional groups can be readily introduced. Poly(pyrazabole)s were prepared by organometallic polycondensation of 2,6-diiodopyrazabole with aromatic diyne monomers utilizing Sonogashira-coupling²⁷ (Scheme 9a). Polycondensation between 9,10-dibromoanthracene and 2,6-diethynylpyrazabole was also carried out (Scheme 9b). The M_n of the obtained poly(pyrazabole)s **25** and **28** was 34000 to 9000 from the GPC measurements. In the UV-vis absorption spectra of these poly(pyrazabole)s, absorption maxima were not particularly red-shifted compared with those for aromatic monomers, indicating that π -conjugation was poorly expanded through the repeating units. This is because electronic interaction between π -orbitals of pyrazole moiety are small as previously reported. However, optical transparency would be advantageous for various applications as optical materials. The poly(pyrazabole)s showed intense fluorescence emission when irradiated with UV light. Purple to green emissions were observed in good quantum yields. The observed fluorescence emission peak was composed of multi-emission peaks possibly because of various conformations (flat, boat and chair etc.) of the pyrazabole unit. The presence of pyrazabole in polymer



Scheme 9.

backbone was crucial in the observed fluorescence emission behavior.

Poly(pyrazabole)s bearing various electron-withdrawing groups in their main chain²⁸ were also prepared by similar methods. By incorporating electron-withdrawing group, fluorescence emission wavelength shifted to shorter wavelength region. The ¹¹B-NMR spectra of poly(pyrazabole)s showed fluorescence emission wavelength shifts to shorter wavelength region with decreasing the electron density on the boron atoms (as increasing the ¹¹B-NMR chemical shift). Therefore, tuning of emission wavelength was possible by introducing designated aromatic groups having various electron density.

Transition-metal-containing poly(pyrazabole)s were also prepared by copper catalyzed dehydro-halogenation.²⁹ MLCT (metal-to-ligand charge transfer) absorption was observed only in the case of Pt-containing polymers while such behavior was not observed for Pd or Ni containing polymers.

π-CONJUGATED ORGANOBORON QUINOLATE POLYMERS

Organoboron quinolates are valuable light emitting materials potentially useful in organic light emitting diodes (OLEDs). Wang *et al.* reported that organoboron quinolate shows a high luminescent efficiency and high thermal stability³⁰ (Figure 8a). Di- and triboron type boron quinolates³¹ were also designed, and improved thermal stability and unique photophysical properties originating from their anisotropic shape was reported. Polymer supported organoboron quinolates³² were also

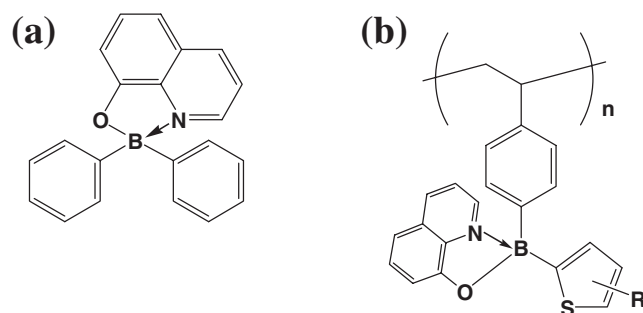
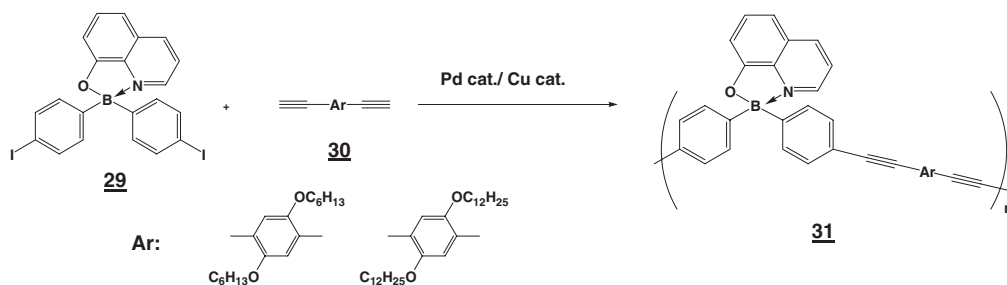


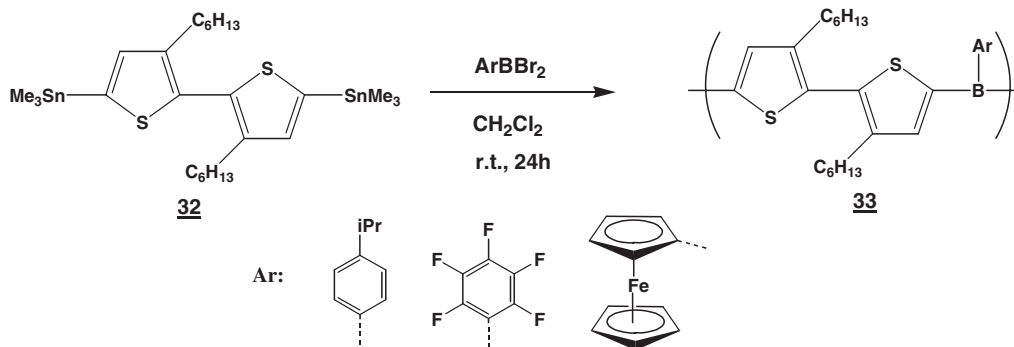
Figure 8. Structures of (a) light emitting boron quinolate (b) polystyrene supported boron quinolate.

reported by Jäkle *et al.* (Figure 8b). Side chain type organoboron quinolate polymers were prepared *via* polymer reaction of poly(4-dibromoborylstyrene).

The first example of boron quinolate polymer having π-conjugated backbone³³ was recently reported by our group (Scheme 10). Diiodo type boron quinolate monomer **29** was polymerized by organometallic polycondensation (Sonogashira coupling). From the GPC measurements, the M_n of the obtained polymers **31** were 8800 to 3200. In both UV-vis absorption spectra and fluorescence emission spectra, **31** showed much bathochromic shifted absorption and emission compared with **29** because of the presence of π-conjugated unit. Intense blue-green emission was observed in good quantum yields under a wide range of excitation wavelength.



Scheme 10.



Scheme 11.

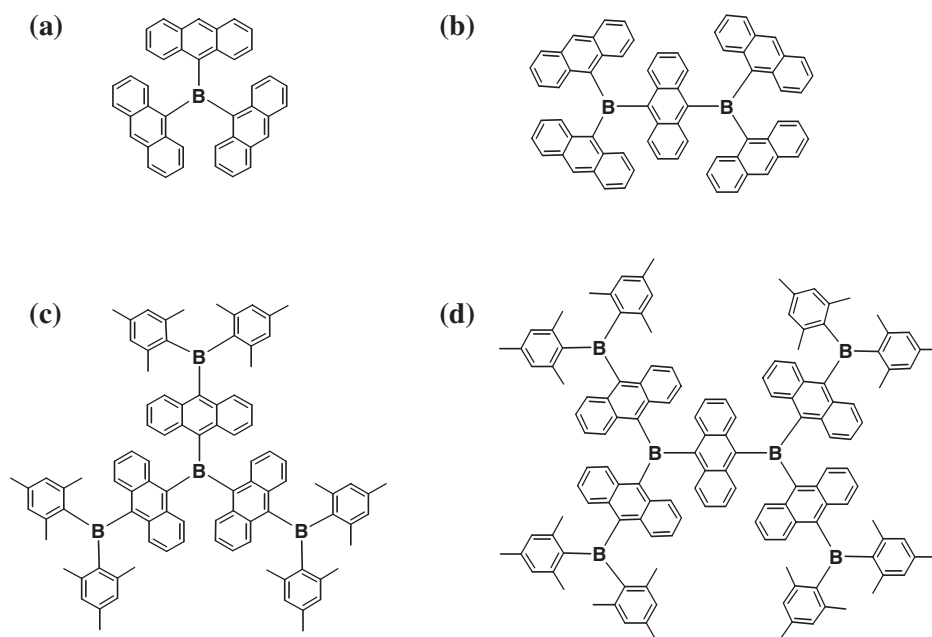


Figure 9. Structures of tri-9-anthrylborane derivatives with divergently extended π -conjugation.

BORON-MODIFIED POLYTHIOPHENES VIA TIN-BORON EXCHANGE

Jäkle *et al.* reported the facile synthesis of polystyrenes bearing organoboron unit in their side chain by Si-B exchange reaction.³⁴ They have extended this strategy to the preparation of polythiophenes including boron atom in their main chain by highly selective Sn-B exchange³⁵ (Scheme 11). The polycondensation between distannylated bithiophene and bifunctional arylboron halide was achieved under mild conditions. From the GPC measurements, the M_n of 9000 to 5000 were observed for polymers **33**. The solution absorption spectra, it showed π -conjugation to be extended within the polymer chain to a considerable degree. Their luminescence emission wavelength differed depending on substituents on the boron atom. The binding of **33** with pyridine was also examined to study the potential of **33** as a sensor. From the ^{11}B -NMR spectra, the binding was indicated from the upper field shift of the main peak from 50–60 to 0 ppm. In the UV-vis absorption spectra, visible absorption band decreased during a titration with pyridine. The fluorescence emission was also effectively quenched simultaneously.

DIVERGENTLY EXTENDED ORGANOBORON π -CONJUGATED SYSTEMS

Yamaguchi and Tamao *et al.* reported tri-9-anthrylborane derivatives³⁶ (Figure 9) in which π -conjugation is divergently extended *via* the boron atom. It was demonstrated that LUMO over three identical π -system extends through the boron atom. In the X-ray crystallography of tri-9-anthrylborane, the boron atom and three carbons adjacent to the boron atom were

completely in planar geometry. In the UV-vis absorption spectra of tri-9-anthrylborane derivatives, absorption maxima showed bathochromic shift with increasing number of anthracene units. This indicates π -conjugation extends in three directions.

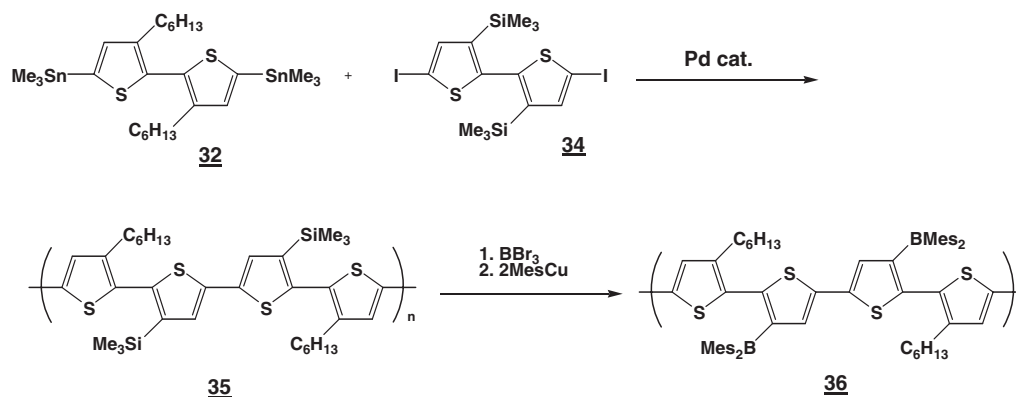
In the cyclic voltammograms of tri-9-anthrylborane derivatives, irreversible reduction peaks were observed. With increasing number of dianthrylboryl or dimesitylboryl groups, reduction potentials shifted to the positive direction.

Their reduction potentials were comparable to or lower than those for π -electron deficient π -conjugated polymers such as poly(2,2'-bithiazole-5,5'-diyl) and poly(quinoxaline-2,6-diyl).

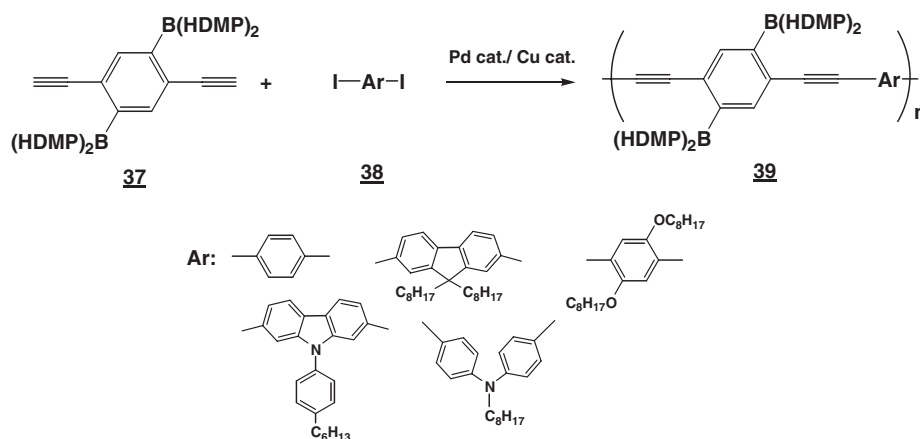
π -CONJUGATED POLYMERS BEARING ORGANOBORON UNIT IN THEIR SIDE CHAIN

So far, there has been limited number of examples of π -conjugated polymers bearing organoboron unit in their side chain. Electrochemical synthesis of π -conjugated polymers having boronate moieties has been examined by Fabre *et al.* and Freund *et al.*³⁷

Very recently, Jäkle *et al.* reported well-defined polythiophenes bearing dimesitylboryl group in their side chain³⁸ (Scheme 12). Polythiophenes having trimethylsilyl side chain **35** were prepared by organometallic polycondensation (Stille coupling). These polymers were treated with tribromoborane and then with mesitylcopper (MesCu)_n ($n = 4, 5$). From the X-ray analysis of the obtained borylated polythiophene **36**, it was seen that thiophene rings were in almost coplanar conformation with small dihedral angles of $15.16(9)^\circ$ in spite of large steric hindrance of dimesitylboryl group. The absorption maximum of **36** was largely bathochromic shifted by 60 nm in comparison



Scheme 12.



Scheme 13.

with that of silyl substituted precursor polymer. The borylated polythiophene **36** showed red emission at 617 nm, which was also largely shifted from the emission maximum of **35** at 554 nm. In cyclic voltammograms (in 0.1 M THF solution of $n\text{Bu}_4\text{N}^+\text{PF}_6^-$; at the sweep rate of 100 mV/s), **36** showed reduction potentials at $E_{1/2}(1) = -2.18$ V and $E_{1/2}(2) = -2.41$ V (vs Fc/Fc^+), which were similar to those for 5,5'-bis(dimesitylboryl)-2,2'-bithiophene derivatives reported by Shirota *et al.*³⁹

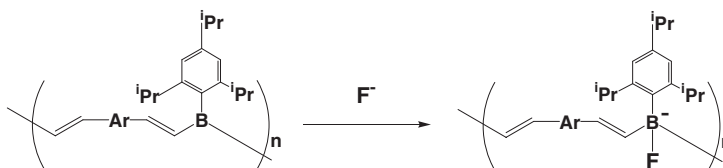
Boryl substituted poly(arylene-ethynylene)s (PAEs)⁴⁰ have been reported by Yamaguchi *et al.* PAEs are known as a highly fluorescent materials, however, they usually do not exhibit very efficient emissions because of the formation of aggregation.

As a new boryl group, bis(4-hexyl-2,6-dimethylphenyl)-boryl [(HDMP)₂B] was introduced instead of dimesitylboryl group, because it was necessary to introduce long alkyl chain to carry out the polymerization successfully. The polymerization was carried out by polycondensation (Sonogashira coupling) of 1,4-diethynyl-2,5-di(4-hexyl-2,6-dimethylphenyl)borylbenzene (**37**) with various diiodoarene (Scheme 13). From the GPC measurements, the M_n of the polymers **39** were 5.77×10^4 to 1.26×10^4 . In the UV-vis absorption spectra of **39**, absorption

maximum due to intramolecular charge transfer from π -conjugated unit to organoboron unit was observed at 432 nm. This was largely bathochromic shifted in comparison with that of model compound (400 nm; shoulder peak). **39** exhibits intense bluish-green emission. The quantum yield for **39** was much higher (0.85) than that of model compound (0.14). Interestingly, the polymer film showed identical fluorescence emission spectra with that for polymer solutions because of the absence of aggregate or excimer/excimer formation.

FLUORIDE ION SENSING USING ORGANOBORON π -CONJUGATED SYSTEMS

The efficient sensing of a fluoride ion is an important subject both industrially and biologically. So far, several synthetic chemosensors for fluoride ion have been prepared.⁴¹ Making use of strong Lewis acid-Lewis base interaction between the boron atom and the fluoride ion, some chemosensors whose colorimetric change was detectable visually have been prepared. Yamaguchi and Tamao *et al.* reported fluoride ion sensing using divergently extended organoboron π -conjugated system.⁴² In these systems, π -conjugation through the boron atom was interrupted by complexation of the boron atom



Scheme 14.

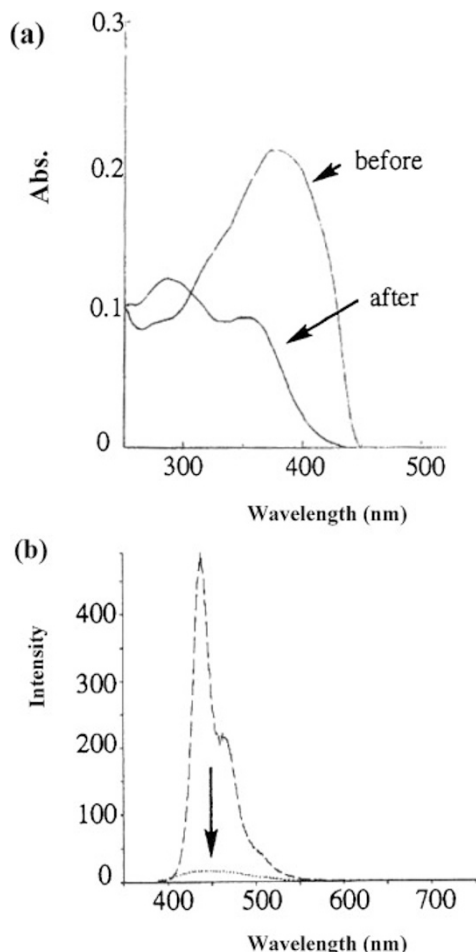


Figure 10. (a) UV-vis absorption spectra of a π -conjugated organoboron polymer in chloroform before and after addition of $n\text{Bu}_4\text{NF}$. (b) Fluorescence emission spectra of a π -conjugated organoboron polymer in chloroform before and after addition of $n\text{Bu}_4\text{NF}$.

with the fluoride ion. After the addition of $n\text{-Bu}_4\text{NF}$ (TBAF) to a THF solution of each borane, color of the solutions changed from yellow or orange to colorless. In the UV-vis absorption spectra for tri-9-anthrylborane derivatives, absorption maxima at 470–420 nm disappeared upon complexation with a fluoride ion, while new peaks appeared at 406–403 nm. In the case of extended organoboron π -conjugated system, multistage sensing with the second and third fluoride ions was also possible.

π -Conjugated organoboron polymers prepared by hydroboration polymerization was also examined as a fluoride ion sensor⁴³ by our group (Scheme 14). After addition of fluoride

ions in polymer solutions, drastic blue shift of the absorption maximum was observed (Figure 10a). Other anions (Cl^- , Br^- and I^-) did not bring about such drastic change even after a few days. In the fluorescence emission spectra of the polymers, blue light emission was also efficiently quenched after the addition of fluoride ions (Figure 10b).

An interesting low molecular weight organoboron compound which shows fluorescence emission upon addition of fluoride ion⁴⁴ (turn-on type fluoride ion sensor) was recently reported by Wang *et al.* U-shaped π -conjugated molecule in which triarylamine unit coordinates to organoboron unit was prepared. Although this molecule showed a weak emission in the absence of fluoride ion, the emission was enhanced when fluoride ions were added and the intramolecular coordination was interrupted.

CONCLUSIONS

Since widely extended organoboron π -conjugated system was first synthesized in 1998, research on these intriguing π -electron systems has rapidly spread world wide within a decade. From these researches, it was clearly demonstrated that π -conjugated organoboron polymers are reasonably stable new class of materials potentially useful for versatile applications. In view of application for light emitting devices, π -conjugated organoboron materials are not only interesting as emitter, but also as electron transporting materials having high electron affinity. Some organoboron polymers were found to show unusually high third order non-linear optical susceptibility. Many organoboron polymers show n-type electrochemical activity. Moreover, some organoboron polymers were found to be efficient anion sensors for fluoride anion. Each of these potential application is based on unique electronic state of π -electron deficient organoboron π -conjugated polymers.

The specific electronic state of π -conjugated organoboron polymer makes possible the observation of unusual photo-physical behavior such as facilitated $p\pi\text{-d}\pi^*$ transition, activated $\sigma\text{-}\pi$ interaction, intramolecular-charge transfer and so forth.

In addition to convenient hydroboration polymerization, recently developed synthetic methods *via* organometallic polycondensation using Sonogashira coupling or tin-boron exchange should promote the development of this research area.

Received: October 15, 2007

Accepted: October 20, 2007

Published: December 26, 2007

REFERENCES

1. a) T. Ito, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 11 (1974).
b) H. Shirakawa, E. J. Lois, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 578 (1977).
2. "Handbook of Conductive Polymers," vol. I and II, T. A. Skotheim, Ed., Marcel Dekker, New York, 1986.
3. a) J. Shinar, S. Ijadicmaghsoodi, Q. X. Ni, Y. Pang, and T. J. Barton, *Synth. Met.*, **28(1-2)**, C593 (1989).
b) S. Y. Hong and D. S. Marynick, *Macromolecules*, **28**, 4991 (1995).
c) K. Tamao, S. Ohno, and S. Yamaguchi, *Chem. Commun.*, 1873 (1996).
d) H. L. Sohn, R. R. Huddleston, D. R. Powell, R. West, K. Oka, and Y. H. Xu, *J. Am. Chem. Soc.*, **121**, 2935 (1999).
e) S. Yamaguchi, R. Z. Jin, Y. Itami, T. Goto, and K. Tamao, *J. Am. Chem. Soc.*, **121**, 10420 (1999).
f) B. H. Kim and H. G. Woo, *Organometallics*, **21**, 2796 (2002).
g) A. J. Boydston, Y. Yin, and B. L. Pagenkopf, *J. Am. Chem. Soc.*, **126**, 3724 (2004).
4. a) B. L. Lucht, M. A. Buretea, and T. D. Tilley, *Organometallics*, **19**, 3469 (2000).
b) H. Sohn, M. J. Sailor, D. Magde, and W. C. Troglor, *J. Am. Chem. Soc.*, **125**, 3821 (2003).
5. a) C. Hay, M. Hissler, C. Fischmeister, J. Rault-Berthelot, L. Toupet, L. Nyulaszi, and R. Reau, *Chem. Eur. J.*, **7**, 4222 (2001).
b) C. Hay, C. Fave, M. Hissler, J. Rault-Berthelot, and R. Reau, *Org. Lett.*, **5**, 3467 (2003).
c) M. Hissler, P. W. Pyer, and R. Reau, *Coord. Chem. Rev.*, **244(1-2)**, 1 (2003).
d) H. S. Na, Y. Morisaki, Y. Aiki, and Y. Chujo, *Polym. Bull.*, **58**, 645 (2007).
e) Y. Morisaki, H. S. Na, Y. Aiki, and Y. Chujo, *Polym. Bull.*, **58**, 777 (2007).
6. a) K. Naka, T. Umeyama, and Y. Chujo, *J. Am. Chem. Soc.*, **124**, 6600 (2002).
b) T. Umeyama, K. Naka, A. Nakahashi, and Y. Chujo, *Macromolecules*, **37**, 1271 (2004).
c) T. Umeyama, K. Naka, and Y. Chujo, *Macromolecules*, **37**, 5952 (2004).
7. a) C. D. Good and D. M. Ritter, *J. Am. Chem. Soc.*, **84**, 1162 (1962).
b) C. D. Good and D. M. Ritter, *J. Chem. Eng. Data*, **1**, 416 (1962).
8. U. Salzner, J. B. Lagowski, P. G. Pickup, and R. A. Poirier, *Synth. Met.*, **96**, 177 (1998).
9. K. Tanaka, K. Ueda, T. Koike, M. Ando, and T. Yamabe, *Phys. Rev. B.*, **32(6)**, 4279 (1985).
10. a) H. C. Brown, in "Hydroboration," W. A. Benjamin, Inc., New York, 1962.
b) A. Pelter, K. Smith, and H. C. Brown, in "Borane Reagents," Academic Press, London, 1988.
11. N. Matsumi, K. Naka, and Y. Chujo, *J. Am. Chem. Soc.*, **120**, 5112 (1998).
12. a) Y. Chujo, I. Tomita, Y. Hashiguchi, H. Tanigawa, E. Ihara, and T. Saegusa, *Macromolecules*, **24**, 345 (1991).
b) Y. Chujo, I. Tomita, N. Murata, H. Mauermann, and T. Saegusa, *Macromolecules*, **25**, 27 (1992).
c) Y. Chujo, N. Takizawa, and T. Sakurai, *J. Chem. Soc., Chem. Commun.*, 227 (1994).
13. K. Smith, A. Pelter, and Z. Jin, *Angew. Chem., Int. Ed. Engl.*, **33**, 851 (1994).
14. R. J.-P. Corriu, T. Deforth, W. E. Douglas, G. Guerrero, and W. S. Siebert, *Chem. Commun.*, 963 (1998).
15. Z. Yuan, N.-J. Taylor, R. Ramachandran, and T. B. Marder, *Appl. Organomet. Chem.*, **10**, 305 (1996).
16. a) N. Sato, H. Ogawa, F. Matsumoto, Y. Chujo, and T. Matsuyama, *Synth. Met.*, **154**, 113 (2005).
b) H. Kobayashi, N. Sato, Y. Ichikawa, M. Miyata, Y. Chujo, and T. Matsuyama, *Synth. Met.*, **135** (2003).
17. N. Matsumi, M. Miyata, and Y. Chujo, *Macromolecules*, **32**, 4467 (1999).
18. N. Matsumi, Y. Chujo, L. Oliver, and P. H. Dixneuf, *Organometallics*, **20**, 2425 (2001).
19. N. Matsumi, K. Naka, and Y. Chujo, *J. Am. Chem. Soc.*, **120**, 10776 (1998).
20. a) P. Paetzold, *Adv. Inorg. Chem.*, **31**, 123 (1987).
b) P. Paetzold, *Chem. Br.*, **114**, 298 (1981).
21. a) N. Matsumi, K. Kotera, and Y. Chujo, *Macromolecules*, **33**, 2801 (2000).
b) N. Matsumi, K. Kotera, K. Naka, and Y. Chujo, *Macromolecules*, **31**, 3155 (1998).
22. a) Y. Chujo, I. Tomita, N. Murata, H. Mauermann, and T. Saegusa, *Macromolecules*, **25**, 27 (1992).
b) Y. Chujo, I. Tomita, and T. Saegusa, *Polym. Bull.*, **31**, 553 (1993).
c) Y. Chujo, I. Tomita, and T. Saegusa, *Polym. Bull.*, **31**, 547 (1993).
d) Y. Chujo, I. Tomita, and T. Saegusa, *Macromolecules*, **27**, 6714 (1994).
e) N. Matsumi, K. Naka, and Y. Chujo, *Polym. J.*, **30**, 833 (1998).
23. a) N. Matsumi, T. Umeyama, and Y. Chujo, *Macromolecules*, **33**, 3956 (2000).
b) M. Miyata, N. Matsumi, and Y. Chujo, *Macromolecules*, **34**, 7331 (2001).
24. N. Matsumi and Y. Chujo, *Macromolecules*, **33**, 8146 (2000).
25. N. Matsumi and Y. Chujo, *Polym. J.*, **33**, 383 (2001).
26. N. Matsumi, T. Umeyama, and Y. Chujo, *Macromolecules*, **34**, 3510 (2001).
27. F. Matsumoto and Y. Chujo, *Macromolecules*, **36**, 5516 (2003).
28. F. Matsumoto, Y. Nagata, and Y. Chujo, *Polym. Bull.*, **53**, 155 (2005).
29. F. Matsumoto and Y. Chujo, *Pure Appl. Chem.*, **78**, 1407 (2006).
30. a) Q. Wu, M. Esteghamatian, N.-X. Hu, Z. Popovic, G. Enright, Y. Tao, M. D'Iorio, and S. Wang, *Chem. Mater.*, **12**, 79 (2000).
b) S.-F. Liu, C. Seward, H. Aziz, N.-X. Hu, Z. Popovic, and S. Wang, *Organometallics*, **19**, 5709 (2000).
c) Y. Cui, Q.-D. Liu, D.-R. Bai, W.-L. Jia, Y. Tao, and S. Wang, *Inorg. Chem.*, **44**, 601 (2005).
31. Y. Cui and S. Wang, *J. Org. Chem.*, **71**, 6485 (2006).
32. Y. Qin, C. Pagba, P. Piotrowiak, and F. Jäkle, *J. Am. Chem. Soc.*, **126**, 7015 (2004).
33. Y. Nagata and Y. Chujo, *Macromolecules*, **40**, 6 (2007).
34. Y. Qin, G. Cheng, A. Sundararaman, and F. Jäkle, *J. Am. Chem. Soc.*, **124**, 12672 (2002).
35. A. Sundararaman, M. Victor, R. Varughese, and F. Jäkle, *J. Am. Chem. Soc.*, **127**, 13748 (2005).
36. S. Yamaguchi, S. Akiyama, and K. Tamao, *J. Am. Chem. Soc.*, **122**, 6335 (2000).
37. a) M. Nicolas, B. Fabre, G. Marchand, and J. Simonet, *Eur. J. Org. Chem.*, 1703 (2000).
b) G. Douglade and B. Fabre, *Synth. Met.*, **129**, 309 (2002).
c) E. Shoji and M. S. Freund, *Langmuir*, **17**, 7183 (2001).
d) M. Nicolas, B. Fabre, and J. Simonet, *Chem. Commun.*, 1881 (1999).
e) M. Nicolas, B. Fabre, and J. Simonet, *J. Electroanal. Chem.*, **509**, 73 (2001).
f) E. Shoji and M. S. Freund, *J. Am. Chem. Soc.*, **123**, 3383 (2001).
g) E. Shoji and M. S. Freund, *J. Am. Chem. Soc.*, **124**, 12486 (2002).
38. H. Li, A. Sundararaman, K. Venkatasubbaiah, and F. Jäkle, *J. Am. Chem. Soc.*, **129**, 5792 (2007).
39. a) T. Noda and Y. Shirota, *J. Am. Chem. Soc.*, **120**, 9714 (1998).
b) T. Noda, H. Ogawa, and Y. Shirota, *Adv. Mater.*, **11**, 283 (1999).
40. C.-H. Zhao, A. Wakamiya, and S. Yamaguchi, *Macromolecules*, **40**, 3898 (2007).
41. a) C. Dusemund, K. R. A. S. Sandanayake, and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, 333 (1995).
b) C. R. Cooper, N. Spencer, and T. D. James, *Chem. Commun.*, 1365 (1998).
c) M. Nicolas, M. Fabre, and J. Simonet, *Chem. Commun.*, 1881

- (1999).
- d) S. Yamaguchi, S. Akiyama, and K. Tamao, *J. Am. Chem. Soc.*, **122**, 6793 (2000).
- e) P. Jr. Anzenbacher, K. Jursíková, and J. L. Sessler, *J. Am. Chem. Soc.*, **122**, 9350 (2000).
- f) C. B. Black, B. Andrioletti, A. C. Try, C. Ruiperez, and J. L. Sessler, *J. Am. Chem. Soc.*, **121**, 10438 (1999).
- g) P. A. Gale, L. J. Twyman, C. I. Handlin, and J. L. Sessler, *Chem. Commun.*, 1851 (1999).
- h) H. Miyaji, W. Sato, and J. L. Sessler, *Angew. Chem., Int. Ed. Engl.*, **39**, 1777 (2000).
- i) H. Miyaji and J. L. Sessler, *Angew. Chem., Int. Ed. Engl.*, **40**, 154 (2001).
42. S. Yamaguchi, S. Akiyama, and K. Tamao, *J. Am. Chem. Soc.*, **123**, 11372 (2001).
43. M. Miyata and Y. Chujo, *Polym. J.*, **34**, 967 (2002).
44. X. Y. Liu, D. R. Bai, and S. Wang, *Angew. Chem., Int. Ed. Engl.*, **45**, 5475 (2006).



Yoshiki CHUJO completed his Ph.D. at Kyoto University in 1980 and then joined Nagoya University as assistant professor in 1981. In 1983, he joined the group of Prof. J. E. McGrath at Virginia Tech in the U.S.A. as a postdoctoral research fellow. He returned to Kyoto University as a lecturer in 1986 and has been Professor of Polymer Chemistry there since 1994. His research interests focus on polymer synthesis, inorganic polymers, and polymeric hybrid materials.



Noriyoshi MATSUMI received a B.S. degree from Kyoto University in 1995 and obtained Dr. of engineering in polymer chemistry from Graduate School of Engineering, Kyoto University in 2000 under the guidance by Professor Yoshiki Chujo. During 1999–2000, he received a Japan Society for Promotion of Science (JSPS) fellowship for research on π -conjugated organoboron polymers. Then he became assistant professor at Tokyo University of Agriculture and Technology, working with Professor Hiroyuki Ohno. Therein, he studied selective cation transport in organoboron polymer electrolytes and organoboron ionic liquids. In 2006, he joined the group of Professor Keigo Aoi at Graduate School of Bioagricultural Sciences, Nagoya University as associate professor. He received the award for encouragement of research in polymer science from SPSJ in 2006. His current research interest is organoboron functional materials, polymer electrolytes, ionic liquids, bio-sensors based on π -conjugated materials and bio-based polymers.