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Synthesis and Properties of Alternating Acceptor−Donor π-Conjugated Copolymers of Cyclodiborazane with Dithiafulvene

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ABSTRACT: Alternating acceptor−donor π-conjugated copolymers of cyclodiborazane with dithiafulvene were prepared by hydroboration polymerization of 2,6-bis(*p*-cyanophenyl)-1,4-dithiafulvene (**1**) with tripylborane (**2a**) or mesitylborane (**2b**). The structures of the polymers **3** were supported by ^{1}H NMR, ^{11}B NMR, and IR spectra. The obtained polymers were soluble in common organic solvents such as tetrahydrofuran, chloroform, and benzene. The peak due to the $\pi-\pi^*$ transition of **3a** was observed at 415 nm, which was bathochromic shifted in comparison with that of the monomer **1** and the corresponding homopolymers. The emission peaks of **3a** was observed at 531 nm (excitation wavelength at 415 nm). The cyclic voltammogram showed that **3a** was electroactive either in the cathodic or in the anodic region. A soluble charge-transfer (CT) complex of **3a** with 7,7,8,8-tetracyanoquinodimethane (TCNQ) was formed when TCNQ was added to a DMSO solution of **3a**. Before doping, **3a** exhibited an electrical conductivity of 2×10^{-5} S cm^{-1} as measured on a cast film from DMSO. The cast film of the CT complex of **3a** with TCNQ had a conductivity of 1×10^{-4} S cm^{-1}.

Introduction

The synthesis of π-conjugated polymers having alternate donor−acceptor repeating units has been an area of intense interest due to their low optical band gaps and unique optoelectronic properties. Several papers have recently been published on the preparation and properties of π-conjugated polymers with charge-transfer (CT) structure.[1] Derivatives of dithiafulvene, including tetrathiafulvalenes (TTF), act as strong electron donors and form stable CT complexes and radical ion salts with a wide range of organic and inorganic acceptor species.[2] There have been several attempts to incorporate dithiafulvene derivatives into the backbones of π-conjugated polymers.[3] However, the examples of alternating acceptor−donor copolymers containing dithiafulvene units as a strong electron donating unit have been limited.[4]

Recently, we developed a novel method for polymerizing dicyano compounds by hydroboration polymerization.[5] The resulting poly(cyclodiborazane) is a new class of highly inorganic polymeric materials that exhibits reasonable stability toward air and moisture. Fully aromatic poly(cyclodiborazane)s should be regarded as π-electron deficient π-conjugated polymers via the vacant p-orbital of the boron atom.[6] This polymerization system should enable the polymerization of various compounds bearing cyano groups. In this paper, we report the synthesis and properties of alternating acceptor−donor copolymers of cyclodiborazane with dithiafulvene by hydroboration polymerization of 2,6-bis(*p*-cyanophenyl)-1,4-dithiafulvene with mesitylborane or tripylborane.

Results and Discussion

Polymerization. Alternating acceptor−donor π-conjugated copolymers of cyclodiborazane with dithiafulvene were prepared by hydroboration polymerization of 2,6-bis(*p*-cyanophenyl)-1,4-dithiafulvene (**1**) with tripylborane (**2a**) or mesitylborane (**2b**) according to Scheme 1. To a tetrahydrofuran (THF) solution of **1** was added a slight excess of **2** in THF dropwise at room temperature. After the reprecipitation into MeOH, the corresponding polymers were obtained as orange powders. The results of hydroboration polymerization of **1** with mesitylborane or tripylborane are summarized in Table 1. The obtained polymers were soluble in common organic solvents such as THF, chloroform, and benzene. The number-average molecular weights of **3a** and **3b** were 3700 and 2800, respectively. The relatively low molecular weights of **3a** and **3b** are probably due to the low solubility of **1**. In the case of hydroboration polymerization of dicyano compounds with **2a**, the molecular weights of the polymers were relatively lower than the case where **2b** was employed.[5d] This result is possibly due to lower reactivity or less solubility of **2a**. The relatively low yield of **3a** is due to removal of the low molecular weight oligomer by reprecipitation.

Polymer Structure. The structure of polymer **3a** prepared with tripylborane was confirmed by ^{1}H NMR, ^{11}B NMR, and IR spectra. In the ^{1}H NMR spectrum of **3a**, the imino proton (CH═N) was observed at 7.95 ppm. A broad peak for the benzylidene proton appeared at 6.5−6.7 ppm, along with the dithiol proton appeared at 6.89 ppm. The aromatic protons on the tripyl group and the phenylene protons were observed at 7.1−7.7 ppm. The integral ratio between these protons and others was in good agreement with the calculated value for the expected structure. The ^{11}B NMR spectrum of **3a** shows its main peak around 4.8 ppm corresponding to the four-coordinated structure (Figure 1). A small peak at 32 ppm is attributable to monomeric iminoborane at the end group, or a dihydroborated structure. In the IR spectrum (Figure 2), the peaks due to B−H stretching (2420 cm^{-1}) and C═N stretching (1640 cm^{-1}) were observed. The IR also showed a strong peak at 1580 cm^{-1} due to a C═C vibration of the dithiafulvene unit.

Optical Properties of the Polymers. The UV−vis spectra of **3a** and **1** were recorded in chloroform solution at room temperature (Figure 3). The peak due to the

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Scheme 1

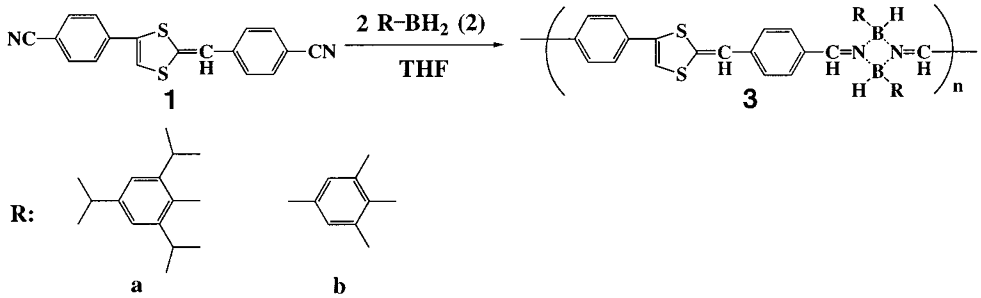


Table 1. Hydroboration Polymerization between 1 and 2[a]

run	2	1/2	M_n[b]	M_w[b]	M_w/M_n[b]	yield (%)[c]
1	**2a**	2.15	3700	5700	1.5	21
2	**2b**	2.07	2800	6800	2.4	75

[a] The reactions were carried out in THF at room temperature. [b] GPC ($CHCl_3$). PSt standards. [c] Isolated yields after reprecipitation into MeOH.

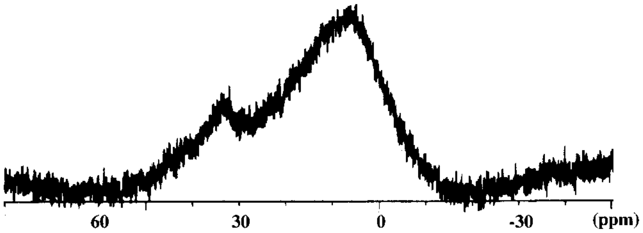


Figure 1. ^{11}B NMR spectrum of **3a** in $CDCl_3$.

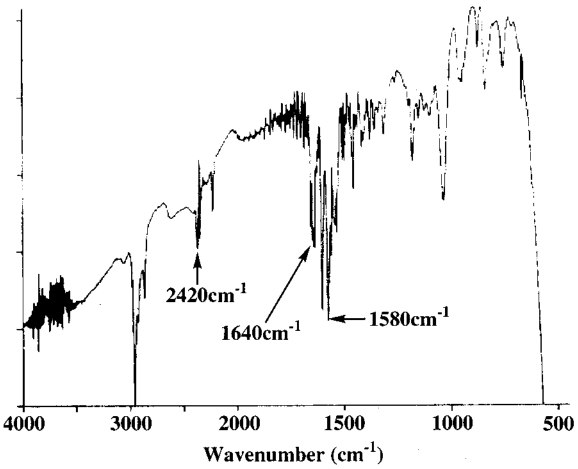


Figure 2. IR spectrum of **3a**.

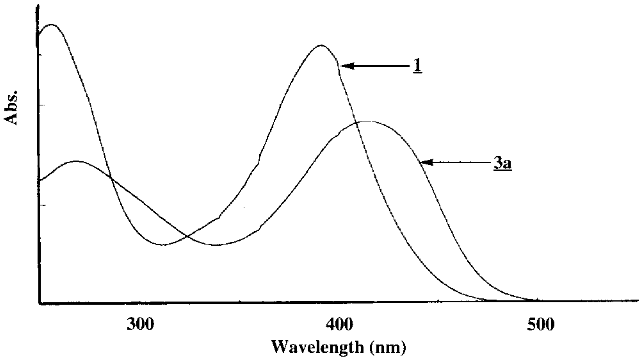


Figure 3. UV–vis absorption spectra of **3a** and **1** in chloroform at room temperature.

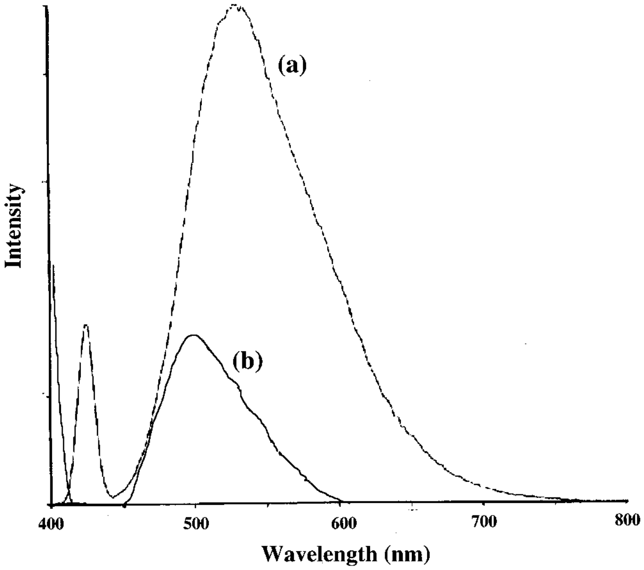
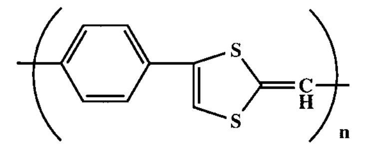


Figure 4. Fluorescence emission spectra of **3a** (excitation wavelength at 415 nm) (a) and **1** (excitation wavelength at 390 nm) (b) in chloroform at room temperature.

π–π* transition of the polymer was observed at 415 nm ($\epsilon = 3.5 \times 10^4$ M^{-1} cm^{-1}). The value was bathochromic shifted in comparison with that of the monomer, 392 nm ($\epsilon = 2.6 \times 10^4$ M^{-1} cm^{-1}). Polymer **3a** exhibited an absorption band at longer wavelengths than those of corresponding homopolymers. The absorption maximum of poly(dithiafulvene) (**4**) appeared at 398 nm.[3e] The UV–vis spectrum of poly(cyclodiborazane) (**5**) derived from terephthalonitrile exhibited no absorption maximum in visible regions. Previously, we have reported that a donor–acceptor poly(cyclodiborazane) (**6**) prepared from 1,4-dioctoxy-2,5-dicyanobenzene exhibited the absorption maximum at 381 nm and showed largely bathochromic shift in comparison with its model compound.[6c] These results indicate that incorporation of a strong electron donating dithiafulvene unit into a π-conjugated poly(cyclodiborazane) in its backbone leads to extend the degree of conjugation between the consecutive repeat units. The peak due to the π–π* transition of **3b** was also observed at 416 nm.

The fluorescence emission spectra were recorded for **3a** and **1** in chloroform solution at room temperature (Figure 4). The emission peak of **3a** was observed at 531 nm (excitation wavelength at 415 nm). The corresponding homopolymers, i.e., poly(dithiafulvene) (**4**) and poly(cyclodiborazane) (**5**), showed no emission spectra. A much larger Stokes shift of the polymer **3a** in comparison with the case of the polymer (**6**) prepared from 1,4-dioctoxy-2,5-dicyanobenzene (465 nm) was observed.[6c] This relatively large Stokes shift implies that effective energy transfer might take place from the dithiafulvene unit to the cyclodiborazane unit in the polymer.



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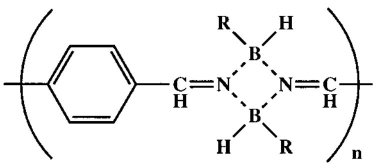

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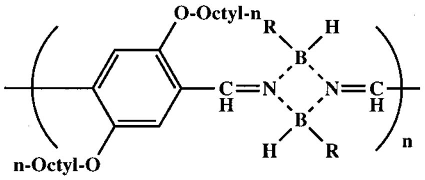

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Electrochemical Analysis. As shown in Figure 5, polymer **3a** is electroactive either in the cathodic or in the anodic region. The polymer was electrochemically active toward n-doping owing to a high electron affinity of the organoboron unit. On sweeping the polymer cathodically, a cathodic peak appears at −1.56 V vs Ag/Ag$^+$. A corresponding reoxidation (n-dedoping) peak occurs at −0.94 V vs Ag/Ag$^+$. For the p-doping process, an anodic current peak occurs at 0.45 V vs Ag/Ag$^+$. 2-Benzylidene-4-phenyl-1,3-dithiole (**7**) showed a single oxidation peak at 0.40 V vs Ag/Ag$^+$. The value of the oxidation peak in the p-doping process was positively shifted by 0.05 V than that of **7**, indicating that the electron accepting ability of cyclodiborazane unit. A reduction (p-dedoping) peak can be observed at 0.39 V vs Ag/Ag$^+$. In cyclic voltammograms of simple one-electron reversible redox reactions, the potential difference (E_p) between the oxidation peak (E_{pa}) and reduction peak (E_{pc}) was 60 mV. The p-doping process of the polymer gives potential difference of 60 mV, which indicates the one-electron reversible redox reaction. In the previous report,[3e] a reduction (p-dedoping) peak was not observed after an anodic current peak occurs. This is due to an inter- and/or an intramolecular dimerization of the dithiafulvene unit.[3e,7] In the present polymer, this process might be inhibited by the bulky cyclodiborazane unit. The dicyano monomer showed a single oxidation peak at 0.88 V vs Ag/Ag$^+$. The fairly higher oxidation potential of the monomer compared with that of **7** was due to the electron accepting nature of the cyano group.

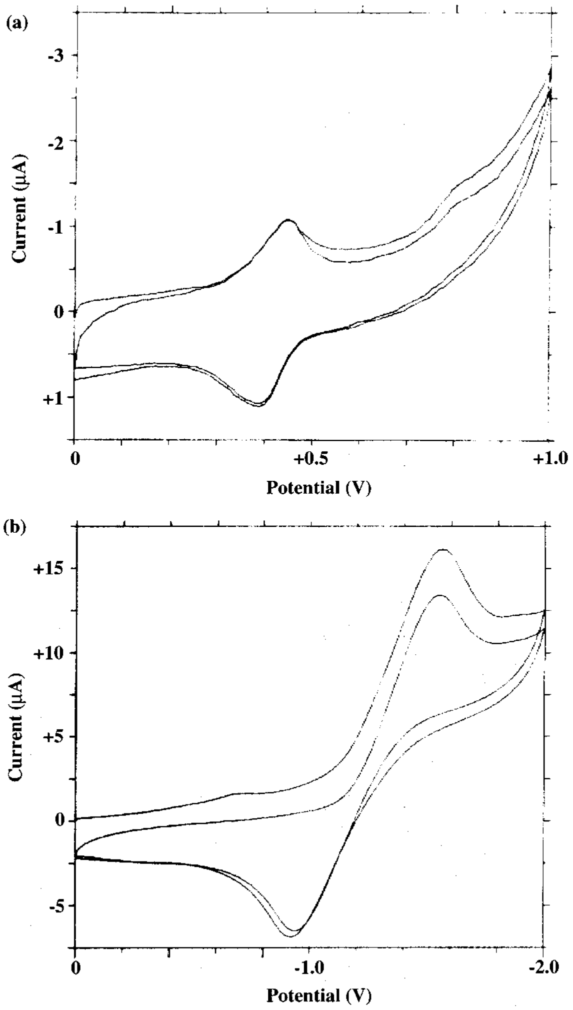
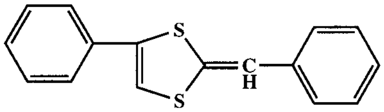


Figure 5. Cyclic voltammograms of **3a**, measured in 0.1 M THF solution of 0.1 M n-Bu_4NClO_4 at 300 mV s^{-1}. Potential sweep range (vs Ag/Ag$^+$): (a) 0−1.0 V; (b) −2.0 to 0 V.



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Conductivity. Before doping, polymer **3a** exhibited an electrical conductivity of 2 × 10^{-5} S cm^{-1} as measured on a cast film from DMSO at room temperature by conventional two-probe technique. The undoped poly(dithiafulvene) (**4**) showed an electrical conductivity of 3 × 10^{-7} S cm^{-1}.[3c] The undoped **3a** showed relatively high conductivity probably due to its donor−acceptor pair of the dithiafulvene and the cyclodiborazane units.

Previously, we have shown that the π-conjugated poly(dithiafulvene) (**4**) formed a stable CT complex with 7,7,8,8-tetracyanoquinodimethane (TCNQ).[3d,f] The resulting CT complex had a conductivity of 1 × 10^{-4} S cm^{-1}, 3 orders of magnitude greater than that for the uncomplexed **4**. In DMSO, the polymer **3a** was reacted with TCNQ to produce a dark green homogeneous solution. An excess amount of TCNQ against the repeating unit of **3a** was added to a solution of **3a** in DMSO, and the mixture was stirred for 15 min at room temperature. The polymer solution gradually turned dark green, which indicates the CT complex formation. Because of very low solubility of TCNQ itself in DMSO at room temperature, the unreacted TCNQ remained as a precipitate. After the precipitated TCNQ was filtered off, a cast film was prepared from the filtrate. The cast film of the CT complex of **3a** had a conductivity of 2 × 10^{-4} S cm^{-1}, 1 order of magnitude greater than that for the uncomplexed polymer.

Experimental Section

Materials and Instruments. THF was dried over sodium and distilled before use. 2,6-Bis(p-cyanophenyl)-1,4-dithiafulvene (**1**),[8] tripylborane (**2a**),[9] and mesitylborane (**2b**)[10] were prepared according to the reported methods. ^{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 Shodex K-803 by using CHCl$_3$ 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. Cyclic voltammetry was carried out on a BAS−CV50W Electrochemical analyzer. Electrical conductivity was measured at room temperature by two-probe technique using a Keithley 2400 sourse meter. The polymer film was prepared by dropping a DMSO solution onto a glass plate equipped with a platinum electrode.

Hydroboration Polymerization between 1 and 2. A typical hydroboration polymerization was carried out as follows. To a suspension of **1** (63.0 mg, 0.198 mmol) in THF was added **2a** (88.7 mg, 0.410 mmol) slowly, and the reaction mixture was stirred for 12 h at room temperature. The resulting polymer was purified by reprecipitation into methanol to afford **3a** as an orange solid in 21% yield (31.8 mg). ^{1}H NMR (δ, ppm): 1.28 [CH$_3$ (^{i}Pr), 36H], 2.90 [CH (^{i}Pr), 6H], 6.47−6.71 [C═CH (benzylidene), 1H], 6.89 [C═CH (dithiol), 1H], 7.05−7.66 (Ar−H, 12H), 7.95 (CH═N, 2H). ^{11}B NMR (δ, ppm): 4.78. IR (KBr, cm^{-1}): 2420 ($\nu_{\mathrm{B-H}}$), 1640 ($\nu_{\mathrm{C=N}}$), 1580 ($\nu_{\mathrm{C=C}}$).

3b: 45.0 mg of **1** (0.141 mmol) and 41.0 mg of **2b** (31.1 mmol); 61.6 mg of **3b** (75%). ^{1}H NMR (δ, ppm): 2.27−2.61 [CH$_3$ (mesityl), 18H], 6.5−6.8 [C═CH (benzylidene), 1H], 6.88 [C═CH (dithiol), 1H], 7.15−7.65 (Ar−H, 12H), 7.9−8.2 (CH═N, 2H). IR (KBr, cm^{-1}): 2370 ($\nu_{\mathrm{B-H}}$), 1640 ($\nu_{\mathrm{C=N}}$), 1570 ($\nu_{\mathrm{C=C}}$).

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