Macromolecules **2001,** *34,* 7331−7335

Synthesis of Poly(cyclodiborazane)s by Hydroboration Polymerization of Dicyanooligothiophenes and Their Light-Emitting Properties

Mamoru Miyata, Noriyoshi Matsumi, and Yoshiki Chujo*

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

Received March 9, 2001; Revised Manuscript Received July 13, 2001

ABSTRACT: Hydroboration polymerization of dicyanooligothiophenes bearing various numbers of thiophene repeating units gave the corresponding π-conjugated poly(cyclodiborazane)s having oligothiophene units, and their light-emitting properties were studied. The polymerization was carried out by adding a THF solution of mesitylborane (or tripylborane) to a suspension of dicyanooligothiophene monomer in THF at room temperature under nitrogen. The reaction mixture was stirred overnight, and the polymer was isolated by reprecipitation as a powder. These polymers were soluble in common organic solvents such as THF and chloroform, and stable under air and water. In UV−vis absorption spectra and fluorescence emission spectra of the polymer solutions, their absorption and emission maxima were bathochromic shifted as the number of thiophene repeating units increased. The light-emitting properties of the poly(cyclodiborazane)s were successfully controlled in this way.

Introduction

π-Conjugated polymers have attracted much attention for the past few decades owing to their important and useful properties such as conductivity, electroluminescence, optical nonlinearity, and so on. Though many types of electron-rich p-type π-conjugated polymers were reported, the number of reports on electron-deficient n-type π-conjugated polymers was relatively limited.[1] Recently, we have reported the synthesis of n-type π-conjugated organoboron polymers by hydroboration polymerization of aromatic diynes.[2] These polymers show interesting properties such as intense blue emission and excellent third-order nonlinear optical properties.

On the other hand, poly(cyclodiborazane)s[3] are prepared by hydroboration polymerization of dicyano compounds, and they show good stability toward air and moisture. Although fully aromatic poly(cyclodiborazane)s should be also regarded as π-conjugated organoboron polymers, no significant extension of π-conjugation length was observed in the previously reported systems. However, incorporation of donor and acceptor units in their backbone brought about a dramatic change in the electronic structure, and dramatically bathochromic shift in UV−vis absorption spectra and blue-green emissions were observed.[4]

Recently, many methods were reported about tuning of light-emitting properties of π-conjugated polymers.[5] In these reports, the tuning was achieved by changing the π-conjugation length of the polymers. Here, we report the preparation of poly(cyclodiborazane)s which show various light-emitting colors by using dicyanooligothiophenes with different numbers of thiophene repeating units.

Results and Discussion

Monomer Synthesis. Oligothiophene monomers were prepared as follows. Treatment of thiophene with *n*-BuLi followed by $CuCl_2$ gave 2,2′-bithiophene (**1a**).[6] 2,2′:5′,2″-Terthiophene (**1b**) was prepared by the coupling reaction of 2,5-dibromothiophene with 2 equiv of thienylmagnesium bromide in the presence of $NiCl_2(dppp)_2$.[5a]

As dicyanooligothiophenes with longer oligothiophene units showed lower solubilities, *n*-octyl side chain was introduced to improve their solubilities. First, 2,5-dibromo-3-octylthiophene was prepared by the reaction between *n*-octylmagnesium bromide and 3-bromothiophene[7] and subsequent bromination with 2 equiv of *N*-bromosuccinimide (NBS). 3′-Octyl-2,2′:5′,2″-terthiophene (**1c**) was obtained by the reaction of 2,5-dibromo-3-octylthiophene with 2 equiv of thienylmagnesium bromide. Repeat of the bromination and the coupling reaction with thienylmagnesium bromide gave 3″-octyl-2,2′:5′,2″:5″,2‴:5‴,2⁗ -pentathiophene (**1d**).

Bromination of **1a**−**d** with 2 equiv of NBS gave the corresponding dibromooligothiophene, and dicyanooligothiophene monomers (**2a**−**d**) were obtained by cyanidation of corresponding dibromooligothiophene with CuCN.[8]

Mesitylborane (**3x**) (mesityl = 2,4,6-trimethylphenyl) and tripylborane (**3y**) (tripyl = 2,4,6-triisopropylphenyl) were prepared according to the reported methods.[9−11]

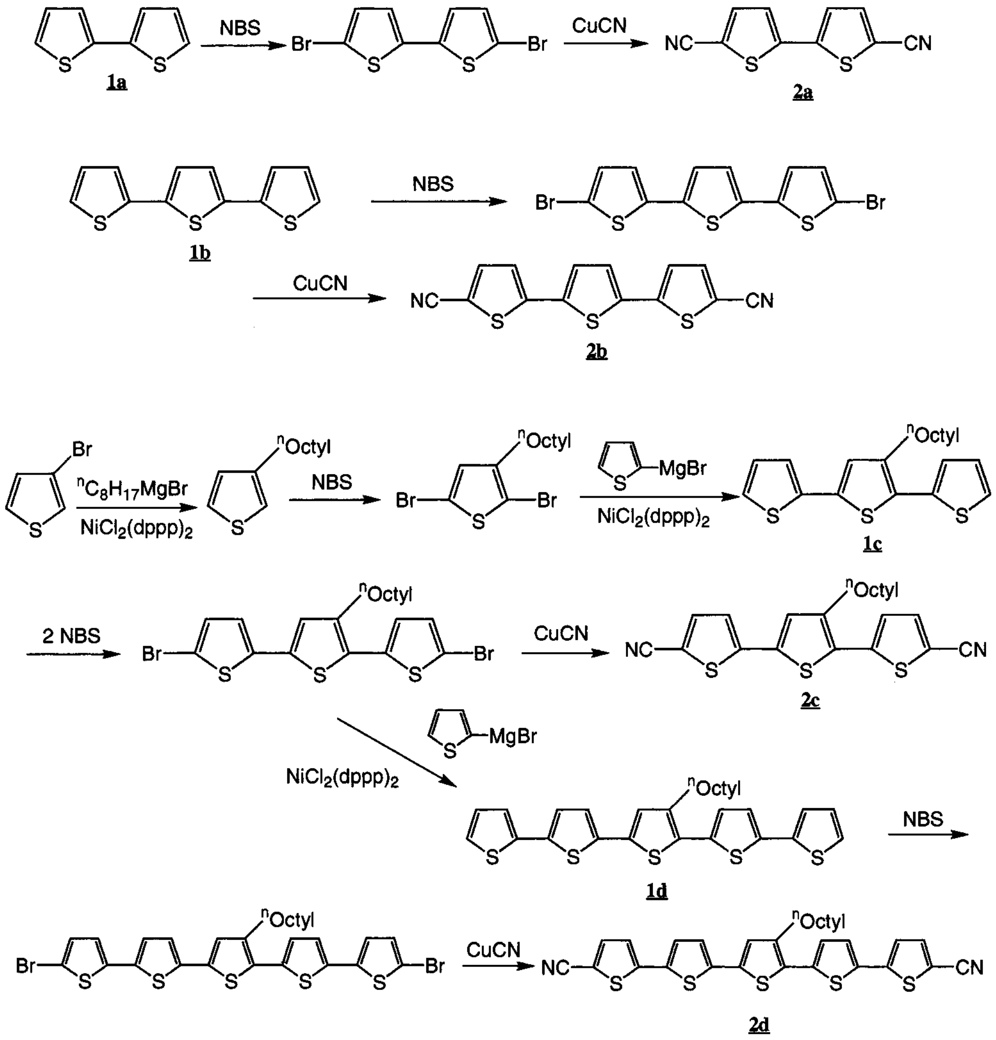
Synthesis of Poly(cyclodiborazane)s by Hydroboration Polymerization of Dicyanooligothiophenes. First, hydroboration polymerization of 5,5′-dicyano-2,2′-bithiophene (**2a**) was examined (Scheme 2). Polymerization was carried out by adding a THF solution of mesitylborane (**3x**) or tripylborane (**3y**) to a suspension of **2a** at room temperature under nitrogen and the reaction mixture was stirred overnight. The polymer was isolated by reprecipitation into hexane (**4ax**) or methanol (**4ay**) and obtained as a yellow powder. These polymers showed good solubilities. **4ax** and **4ay** were soluble in THF and chloroform. In addition, **4ay** was soluble in hexane and diethyl ether.

The molecular weights of the polymers **4ax** and **4ay** were found to be 3300 and 3200 respectively (Table 1) by GPC measurements (THF, PSt standards). The structures of the polymers were supported by ^{1}H NMR, ^{11}B NMR, and IR spectra.

Next, hydroboration polymerization using 5,5″-dicyano-2,2′:5′,2″-terthiophene (**2b**) was examined. By using

10.1021/ma010424t CCC: \$20.00

Scheme 1. Preparation of Dicyano Monomers (2a–d)



2b, the conjugation length of the obtained polymer should be extended more effectively. Therefore, the band gap would become smaller and the control of the luminescence property might be possible. Polymerization was carried out in a similar manner as described for **2a**. After reprecipitation into methanol, M_n of the obtained polymers were found to be 1800 (**4bx**) and 2500 (**4by**), respectively (Table 1). The low molecular weight of the polymers might be due to impurity and poor solubility of the monomer. The structures of the polymers were also supported by ^{1}H NMR, ^{11}B NMR, and IR spectra.

To obtain the poly(cyclodiborazane)s, which show various emission properties, we prepared the polymers containing longer oligothiophene units. As the monomers have poor solubilities, *n*-octyl group was introduced as a side chain to improve their solubilities. Here, 3′-octyl- 2,2′:5′,2″-terthiophene (**4c**) and 3″-octyl-2,2′:5′,2″:5″,2‴:5‴,2⁗-pentathiophene (**4d**) were prepared and their polymerization behaviors were studied. Polymerization and purification were carried out in similar ways.

Characterization of Poly(cyclodiborazane)s. As mentioned above, the structures of the poly(cyclodiborazane)s obtained were supported by ^{1}H NMR, ^{11}B NMR, and IR spectra. The ^{1}H NMR spectrum of **4ax** is shown in Figure 1a. The characteristic peak of imine proton (CH=N) was observed around 8.1 ppm and the peaks for aromatic protons (benzene and thiophene) around 7 ppm. The peaks for aliphatic protons (methyl groups in mesitylborane unit) were observed between 2 and 3 ppm. A small peak at 5.2 ppm might be due to amine species formed by degradation during the polymerization or the measurement of NMR spectrum. In the ^{11}B NMR spectrum (Figure 1b), a major peak was observed around 3 ppm. This peak is assigned to the cyclodiborazane structure. In addition, a minor peak was observed around 30 ppm, corresponding to uncyclolized iminoborane. In the IR spectrum (Figure 1c), the peaks due to B–H stretching and C=N stretching were observed at 2404 and 1633 cm^{-1}, respectively.

The structures of the other polymers were also supported by ^{1}H NMR, ^{11}B NMR, and IR spectra.

UV—Vis Absorption Spectra of Poly(cyclodiborazane)s. UV–vis absorption spectra of the polymers were measured in chloroform at room temperature. All spectral data are listed in Table 2. Figure 2 shows UV–vis absorption spectra of **4ax**–**4dx**. The polymers showed their absorption maxima at 387 (**4ax**), 415 (**4bx**), 415 (**4cx**), and 426 nm (**4dx**), respectively. Compared to the spectrum of oligothiophene system, these peaks should be due to effective extension of π-conjugation by introduction of donor part and acceptor part in their main chains. As previously reported, the polymer obtained from 2,5-dicyanobenzene and mesitylborane (**3x**) showed an absorption maximum at 364 nm.[4] These results

Scheme 2. Hydroboration Polymerization of Dicyanooligothiophenes (2a–d)

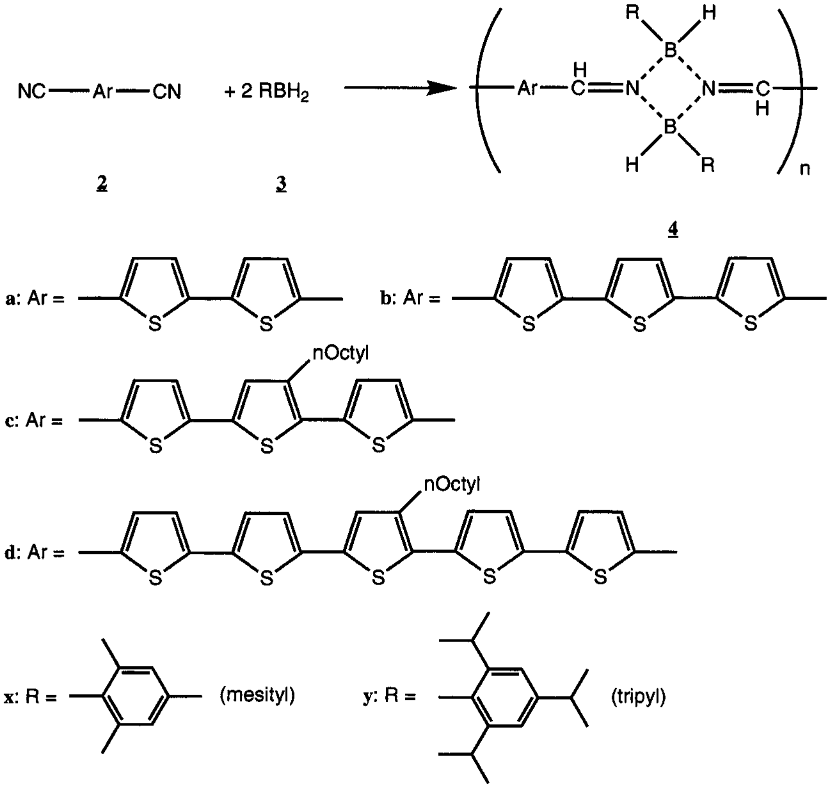


Table 1. Hydroboration Polymerization of Dicyanooligothiophenes[a]

polymer (**4**)	**3**/**2**	M_n[b]	M_w[b]	M_w/M_n[b]	yield (%)[c]
4ax	2.21	3300	9300	2.8	64
4ay	2.20	3200	8700	2.8	60
4bx	2.25	1800	3800	2.1	74
4by	2.21	2500	6100	2.4	51
4cx	2.20	4200	6300	1.4	60
4cy	2.17	2500	4700	1.9	64
4dx	2.09	3300	8500	2.6	75
4dy	2.09	2100	3100	1.5	33

[a] Polymerizations were carried out in THF at room temperature. [b] GPC (THF) polystyrene standards. [c] Isolated yield after reprecipitation into hexane or methanol.

showed that the longer thiophene repeating units of the polymers were, the more bathochromic shifted their absorption maxima were. In other words, as the number of thiophene repeating units increases, π-conjugation length extends effectively and the red shift of absorption maxima in UV–vis absorption spectra is observed.

Fluorescence Emission Spectra of Poly(cyclodiborazane)s. Fluorescence emission spectra of poly(cyclodiborazane)s were measured in chloroform solution at room temperature. All spectral data are shown in Table 2, and the spectra of **4ax**–**4dx** are shown in Figure 3. In fluorescence emission spectra, the bathochromic shift was also observed as the number of thiophene repeating units in the main chain increased. Emission colors ranged from blue to yellow-orange. This result would be also explained by an effective extension of π-conjugation length. The fluorescence quantum yields of the polymers are also listed in Table 2. These values are estimated by using 9-anthracenecarboxylic acid as a reference, excited at 380 nm.[5a]

These emission spectra showed fine structure especially in the spectra of the polymer bearing short oligothiophene moiety, though structureless bands were shown in UV–vis absorption spectra. This phenomenon has been observed for other oligothiophenes and is ascribed to a more rigid structure of the polymers in their first relaxed excited state than in ground state. The rotational energy barrier is smaller in the ground state, and this leads to the molecular disorder. This is why UV–vis absorption spectra are broad and structureless.[5b]

We have also studied fluorescence emission spectra of the polymer films. Figure 4a shows the spectrum of the polymer film of **4ax**. The film was prepared by casting from chloroform solution and dried in vacuo. The intensity was weaker than that of the spectrum of the solution, the emission maximum was quite bathochromically shifted, and a yellow emission was observed (536 nm, excited at 390 nm). This result might be explained by the existence of some interactions between polymer chains and higher planarity of polymer backbone due to packing of polymers. In the case of the polymer prepared from pentathiophene (**4dx**), the bathochromic shift was also observed (632 nm, excited at 425 nm) (Figure 4b).

Stabilities and Thermogravimetric Analyses of Poly(cyclodiborazane)s. The stability of poly(cyclodiborazane)s toward air was monitored by checking the change of the GPC curve after air bubbling into THF solutions of the polymers (**4b**) at room temperature. Since no decrease of the molecular weight was observed after 24 h, the polymers were believed to be stable toward air. The stability toward water was checked by comparing the GPC curves before and after stirring THF solution containing water for 24 h. Also in this experiment, the GPC curve did not change, and the stability toward water was confirmed.

Thermogravimetric analyses (TGA) of the polymers were carried out, and a TGA plot of **4dx** is shown in Figure 5. As shown in the figure, the polymer was found

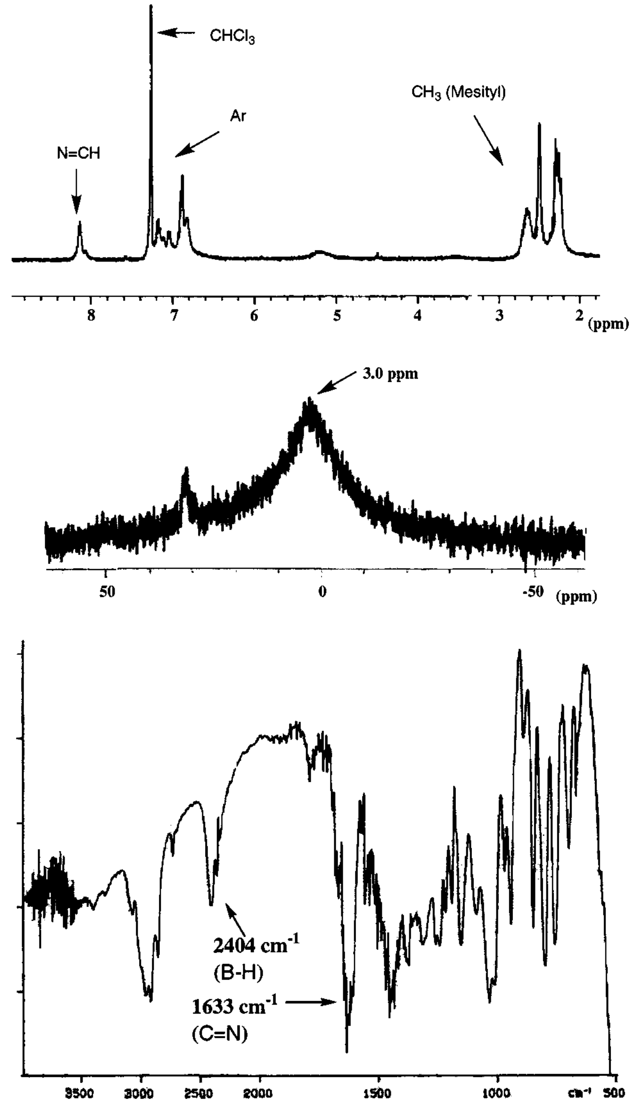


Figure 1. (a) ^{1}H NMR Spectrum of **4ax** (in $CDCl_3$). (b) ^{11}B NMR spectrum of **4ax** (in $CDCl_3$). (c) IR spectrum of **4ax**.

Table 2. UV–Vis Absorption and Fluoroescence Emission Spectral Data of Poly(cyclodiborazane)s[a]

polymer	UV λ_{max} (nm)	PL λ_{em} (nm)	(excitation wavelength) (nm)	fluorescence quantum yield[b]
4ax	387	451, 478	(390)	0.131
4ay	391	453 (sh), 492, 518 (sh)	(400)	0.151
4bx	415	487, 525 (sh)	(400)	0.136
4by	418	494, 525 (sh)	(400)	0.165
4cx	415	499, 530 (sh)	(415)	0.126
4cy	415	496, 526 (sh)	(415)	0.151
4dx	426	536	(425)	0.109
4dy	421	532	(420)	0.168

[a] In $CHCl_3$, at room temperature. [b] 9-Anthracenecarboxylic acid as a standard, excited at 380 nm.

to be stable up to 200 °C and 10% weight loss was observed at 229 °C. Other polymers showed similar thermal decomposition patterns but T_{10} (10% weight loss temperature) were somewhat higher. This is probably due to the absence of side alkyl group. The weight residue was in the range of 15–30%.

Conclusion

In this paper, hydroboration polymerization of dicyanooligothiophenes was carried out. In this system, by changing the number of thiophene repeating units, poly(cyclodiborazane)s having various emitting properties were obtained. This can be explained by effective extension of π-conjugation length in the polymers as the number of thiophene repeating units increases. If

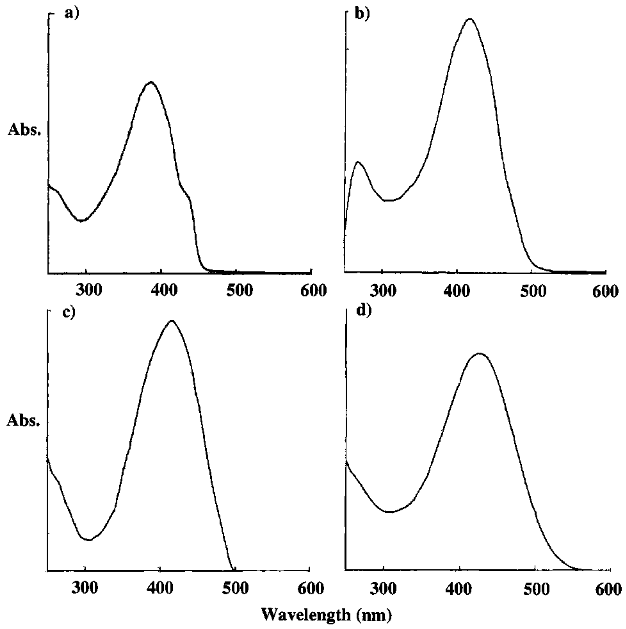


Figure 2. UV–vis absorption spectra of poly(cyclodiborazane)s in $CHCl_3$: (a) **4ax**, (b) **4bx**, (c) **4cx**, and (d) **4dx**.

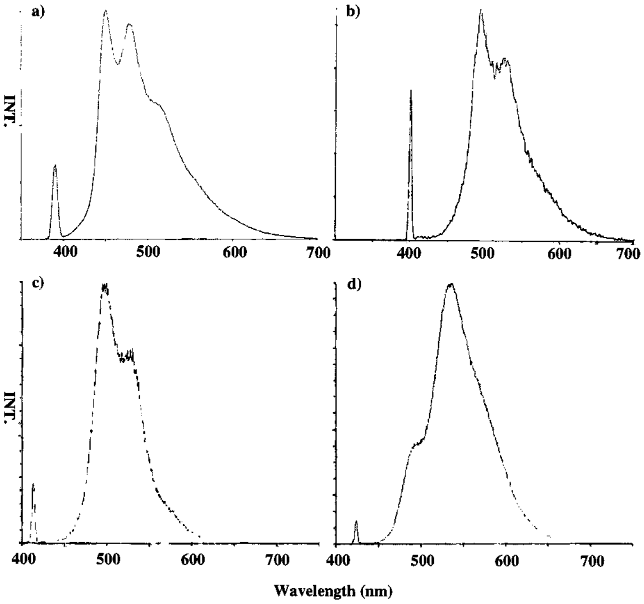


Figure 3. Fluorescence emission spectra of poly(cyclodiborazane)s in $CHCl_3$: (a) **4ax**, (b) **4bx**, (c) **4cx**, and (d) **4dx.**

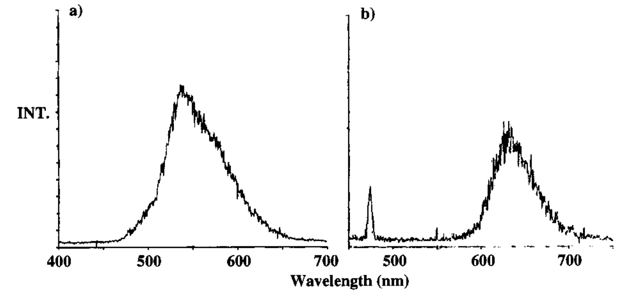


Figure 4. Fluorescence emission spectra of polymer films: (a)-**4ax**, (b) **4dx**.

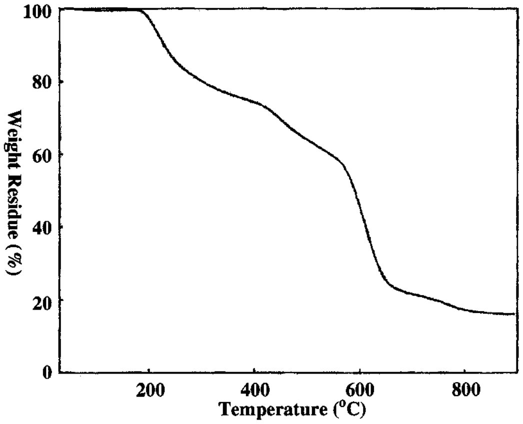


Figure 5. TGA trace of poly(cyclodiborazane) **4dx**.

polymers with longer thiophene units are synthesized, orange and red emitting polymers will be obtained; that is, the poly(cyclodiborazane)s may emit all the range of visible lights.

Experimental Section

Materials and Instruments. Tetrahydrofuran was dried over sodium and distilled before use. Hexane was dried over sodium and distilled. Methanol was dried and distilled from magnesium methoxide. Mesitylborane was prepared by the modified procedure[9] of the reported method.[10] Tripylborane was prepared according to the reported procedure.[11] Dicyano-oligothiophene monomers were synthesized by cyanidation[8] from the corresponding dibromooligothiophenes.

^{1}H NMR and ^{11}B NMR spectra were recorded in $CDCl_3$ on a JEOL EX-270 instrument. Gel permeation chromatographic analysis was carried out on a Tosoh G3000H_{XI} by using THF as an eluent after calibration with standard polystyrene samples. IR spectra were obtained on a Perkin-Elmer 1600 spectrometer. UV−vis absorption spectra were recorded on a JASCO V-530 spectrophotometer. Fluorescence emission spectra were recorded on a Perkin-Elmer LS50B luminescence spectrometer. Thermogravimetric analysis (TGA) was made on a Seiko TG/DTA 6200 (10 °C/min).

Hydroboration Polymerization between 5,5′-Dicyano-2,2′-bithiophene (2a) and Mesitylborane (3x) (Preparation of 4ax). To a THF (0.5 mL) suspension of 2,5′-dicyano-2,2′-bithiophene (**2a**) (74.0 mg, 0.342 mmol) was added mesitylborane (**3x**) (99.6 mg, 0.754 mmol) in THF (0.5 mL) dropwise at room temperature under nitrogen. The reaction mixture became homogeneous gradually and was stirred overnight at room temperature. The polymer was purified by reprecipitation into hexane, and dried in vacuo. The obtained polymer was subjected to ^{1}H NMR, ^{11}B NMR, IR, and GPC measurements. Yield was 64%. ^{1}H NMR (δ, ppm): 2.05−2.65 (CH_3, 18H), 6.70−6.94 (Ar, mesityl, 4H), 6.95−7.30 (Ar, 4H), 8.13 (N=CH, 2H). ^{11}B NMR (δ, ppm): 3.0, 31.3. IR (cm^{-1}) 2404 (B−H), 1633 (C=N).

Hydroboration Polymerization between 5,5′-Dicyano-2,2′-bithiophene (2a) and Tripylborane (3y) (Preparation of 4ay). To a THF (1.0 mL) suspension of 5,5′-dicyano-2,2′-bithiophene (**2a**) (85.4 mg, 0.395 mmol) was added tripylborane (**3y**) (188 mg, 0.870 mmol) in THF (1.0 mL) dropwise at room temperature under nitrogen. The reaction mixture became homogeneous gradually and was stirred overnight at room temperature. The polymer was purified by reprecipitation into methanol and was dried in vacuo. The obtained polymer was subjected to ^{1}H NMR, ^{11}B NMR, IR, and GPC measurements. Yield was 60%. ^{1}H NMR (δ, ppm): 0.85−1.45 (CH_3, tripyl, 36H), 2.80−3.00 (CH, tripyl, 6H), 6.76−7.30 (Ar, 8H), 8.11 (N=CH, 2H). ^{11}B NMR (δ, ppm) −0.8. IR (cm^{-1}): 2409 (B−H), 1632 (C=N).

References and Notes

(1) For example: (a) Yamamoto, T.; Maruyama, T.; Zhou, Z.; Ito, T.; Fukuda, T.; Yoneda, Y.; Begum, F.; Ikeda, T.; Sasaki, S.; Takezoe, H.; Fukuda, A.; Kubota, K. *J. Am. Chem. Soc.* **1994**, *116*, 4832. (b) Yamamoto, T.; Sugiyama, K.; Kushida, T.; Inoue, T.; Kanbara, T. *J. Am. Chem. Soc.* **1996**, *118*, 3930. (c) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686.
(2) Matsumi, N.; Naka, K.; Chujo, Y. *J. Am. Chem. Soc.* **1998**, *120*, 5112.
(3) (a) Chujo, Y.; Tomita, I.; Murata, N.; Mauermann, H.; Saegusa, T. *Macromolecules* **1992**, *25*, 27. (b) Chujo, Y.; Tomita, I.; Saegusa, T. *Polym. Bull.* **1993**, *31*, 553. (c) Chujo, Y.; Tomita, I.; Saegusa, T. *Macromolecules* **1994**, *27*, 6714. (d) Matsumi, N.; Naka, K.; Chujo, Y. *Polym. J.* **1998**, *30*, 833. (e) Matsumi, N.; Naka, K.; Chujo, Y. *Macromolecules* **1998**, *31*, 8047.
(4) (a) Matsumi, N.; Umeyama, T.; Chujo, Y. *Macromolecules* **2000**, *33*, 3956. (b) Matsumi, N.; Chujo, Y. *Macromolecules* **2000**, *33*, 8146.
(5) (a) Musick, K.-Y.; Hu, Q.-S.; Pu, L. *Macromolecules* **1998**, *31*, 2933. (b) Kang, B.-S.; Seo, M.-L.; Jun, Y.-S.; Lee, C.-K.; Shin, S.-C. *Chem. Commun.* **1996**, 1167. (c) Berggren, M.; Inganas, O.; Gustafsson, G.; Rasmusson, J.; Andersson, M. R.; Hjertberg, T.; Wennerstrom, O. *Nature* **1994**, *372*, 444. (d) Noda, T.; Imae, I.; Noma, N.; Shirota, Y. *Adv. Mater.* **1997**, *9*, 239. (e) Noda, T.; Ogawa, H.; Noma, H.; Shirota, Y. *J. Mater. Chem.* **1999**, *9*, 2177. (f) Noda, T.; Shirota, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9714. (g) Shirota, Y. *J. Mater. Chem.* **2000**, *10*, 1.
(6) Zagorska, M.; Krische, B. *Polymer* **1990**, *31*, 1379.
(7) Pham, C. V.; Mark, H. B., Jr.; Zimmer, H. *Synth. Commun.* **1986**, *16*, 689.
(8) Sandler, S. R.; Karo, W. *Organic Functional Group Preparations*; Academic Press: New York and London, 1968; p 462.
(9) Matsumi, N.; Chujo, Y. *Polym. Bull.* **1997**, *38*, 531.
(10) Smith, K.; Pelter, A.; Jin, Z. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 851.
(11) (a) Pelter, A.; Smith, K.; Buss, D.; Jin, Z. *Heteroatom Chem.* **1992**, *3*, 275. (b) Smith, K.; Pelter, A.; Jin, Z. *J. Chem. Soc., Perkin Trans. 1* **1993**, 395. For the synthesis of 2-tripylbromide, see: Whitesidees, G. M.; Eisenhut, M.; Bunting, W. *J. Am. Chem. Soc.* **1974**, *96*, 5398.

MA010424T