Hydroboration Polymerization of Dicyanoanthracene Using Mesitylborane

Noriyoshi Matsumi, Kensuke Naka, and Yoshiki Chujo*

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

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ABSTRACT: Hydroboration polymerization between mesitylborane and 1,9-dicyanoanthracene (DCA) gave the corresponding polycyclodiborazane having anthracene as the repeating unit. The polymer obtained can be expected to be a novel type of an electron-transporting material or polymer catalyst in photochemistry. Polymerization was carried out under nitrogen by adding a tetrahydrofuran (THF) solution of mesitylborane (2 equiv) to a suspension of DCA in THF at room temperature. After the reaction mixture was stirred for 12 h, an insoluble precipitate was filtrated off. The soluble part was purified by reprecipitation into MeOH to give a yellow powder. Gel permeation chromatography (chloroform, PSt) analysis showed that the M_n of the polymer was 4400 (yield 91%). The polymer obtained was highly soluble in common organic solvents such as THF, chloroform, and benzene, despite the presence of an anthracene ring containing repeat unit. The proposed polymer structure was supported by ^{1}H NMR, ^{11}B-NMR, and IR spectra. An intense green fluorescence emission spectrum was observed at 494 nm. The relatively high stability of the polymer was shown by its resistance to reaction with air or water and from thermogravimetric analysis behavior.

Introduction

Recently, we developed a novel method for polymerizing dicyano compounds by boration polymerization[1] (Scheme 1). For example, a reaction between a *tert*-butylborane−trimethylamine complex and aromatic dicyano compounds proceeds to give air and moisture-stable poly(cyclodiborazane)s whose molecular weights were in the several thousands. These highly inorganic polymers are generally interesting as polymeric precursors to ceramics.[2] Furthermore, the relatively high stability of the polymers allows further functionalization to give a new class of poly(cyclodiborazane)-based functional materials. This polymerization system should enable the polymerization of various compounds bearing cyano groups. In this polymerization system, cyano groups can be used for polymerization; however, the electron-withdrawing properties will be retained to some extent even after reaction because the boron unit is an electron acceptor. For example, hydroboration copolymerization of TCNQ (tetracyanoquinodimethane) with adiponitrile gave polymeric electron acceptors with good solubility in common organic solvents.[3] The obtained polymer was found to form a charge-transfer complex with *p*-phenylenediamine. Very recently, it was found that hydroboration polymerization of dicyano compounds with mesitylborane proceeded under mild reaction conditions to give relatively high molecular weight materials irrespective of the kinds of monomers employed[4] (Scheme 1d).

In this paper, hydroboration polymerization of 1,9-dicyanoanthracene (DCA) with mesitylborane is described (Scheme 2). Since DCA is highly fluorescent and widely used as a photocatalyst,[5] a polymer homologue of DCA might be expected to act as a novel type of electron-transport material or a polymer photocatalyst.

Results and Discussion

Polymerization. Hydroboration polymerization of DCA with mesitylborane was examined as follows. To a suspension of DCA in THF, a THF solution with a slight excess of mesitylborane was added dropwise under nitrogen at room temperature. After the addition of mesitylborane, the reaction mixture became relatively homogeneous and was stirred for another 12 h. Filtration of an insoluble precipitate followed by the evaporation of the solvent gave a yellow gum. This polymeric product was purified by the reprecipitation into MeOH to give a yellow powder in an excellent yield (91%). Surprisingly, the obtained polymer was very soluble in common organic solvents such as THF, chloroform, and benzene despite the presence of the anthracene unit. Gel permeation chromatographic (GPC) analysis ($CHCl_3$, PSt standards) showed that the number-average molecular weight of the polymer was 4400.

The results of boration polymerization of DCA using various boron reagents are summarized in Table 1. In the reaction with thexylborane (run 2), only traces of oligomers were produced. This result is elucidated as follows. In the present polymerization system, cyclodiborazane is formed by dimerization of the monomeric iminoborane which is generated by monohydroboration of a cyano group.[1] Accordingly, the selectivity between monohydroboration and dihydroboration should be quite important. Thus, sterically less hindered thexylborane gave the lower molecular weight products with a less regulated structure. The hydroboration polymerization of aromatic dicyano compounds with a *tert*-butylborane−trimethylamine complex is a well-established system.[1a] However, in the reaction between DCA and the *tert*-butylborane−triethylamine complex (run 3), no polymerization was observed due to the poor solubility of DCA. Allylboration polymerization of DCA with triallylborane (run 4) also gave the relatively low molecular weight oligomer owing to a too high viscosity of the bulk reaction mixture.

Polymer Structure. The structure of the polymer was determined by ^{1}H-NMR, ^{11}B-NMR, and IR spectra.

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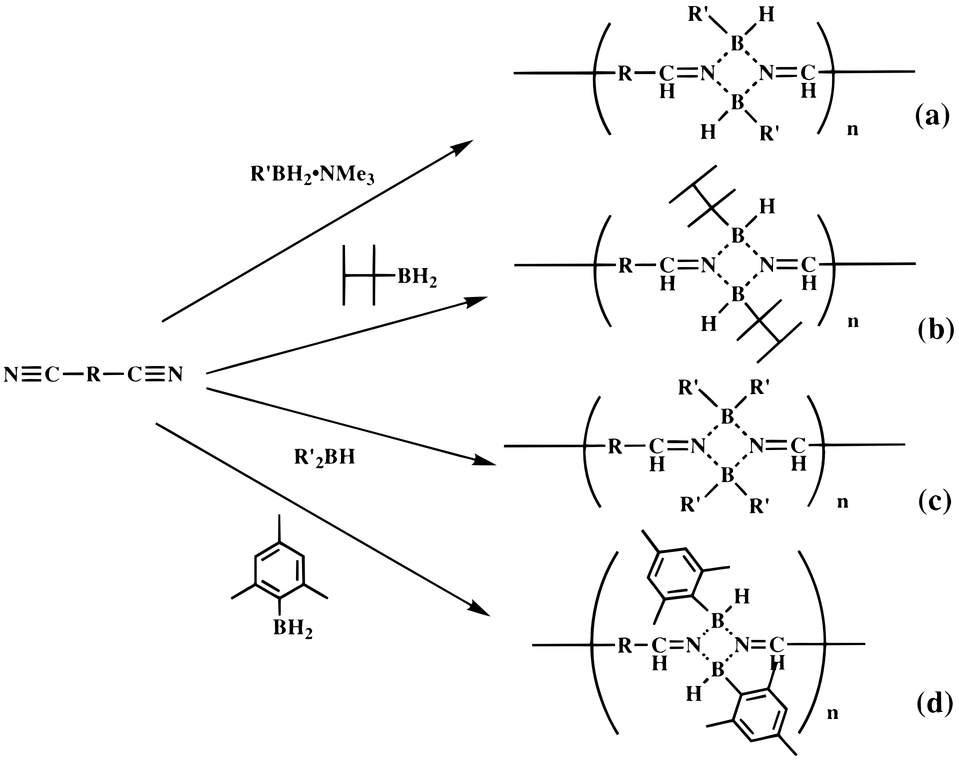
Scheme 1



Scheme 2

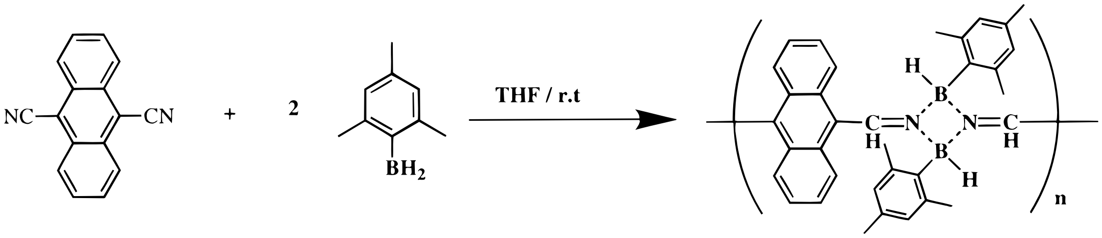
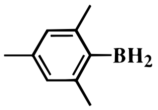
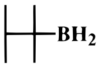
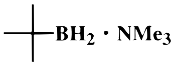
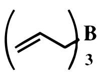


Table 1. Boration Polymerization of Dicyanoanthracene Using Various Borane Reagents[a]

run	borane reagent	B/DCA	M_n[b]	M_w[b]	M_w/M_n[b]	yield (%)[c]
1		2.07	4400	8800	2.0	91
2		2.54	700	1100	1.4	trace
3		2.44	no polymerization			
4		2.39	1500	2200	1.4	20

[a] The reactions were carried out under nitrogen at room temperature in THF (runs 1 and 2), at 100 °C in diglyme (run 3), and at room temperature in bulk (run 4). [b] GPC ($CHCl_3$, PSt standards). [c] Isolated yields after reprecipitation into MeOH.

In the ^{1}H-NMR spectrum, the imino proton (CH=N) was observed at 9.06 ppm and aromatic protons on anthracene and the mesityl group appeared at 6.8−8.0 ppm. The methyl group was observed at 1.3−2.9 ppm; the breadth of this peak might be due to both shielding and deshielding effects of the anthracene ring according to the four possible configurations of the four-membered structure (i.e., *cis*−*syn*, *trans*−*syn*, *cis*−*anti*, and *trans*−*anti* isomeric structures). In the ^{11}B-NMR spectrum (Figure 1a), the main peak corresponding to cyclodiborazane was observed at −2.98 ppm. This indicates that the air-stable four-coordinated structure was formed selectively. The small peak at 31.0 ppm is attributable to monomeric iminoborane at the end group, or a dihydroborated structure. In the IR spectrum (Figure 1b), specific peaks at 1655 cm^{-1} (C=N) and 2431 cm^{-1} (B−H) were observed.

Optical Properties of the Polymer. Figure 2 represents the UV−vis spectrum of the polymer (a) and DCA (b); both were recorded in chloroform solution at room temperature. In the UV−vis spectrum of DCA, three strong bands were observed at 377, 402, and 426 nm. Interestingly, in the spectrum of the polymer only one broad band was observed (406 nm). This might be because of the stronger solvation due to the improved solubility of the polymer or some conjugative interaction within the unit structure. The fluorescence emission spectra (Figure 3) were also recorded for the polymer (a) and DCA (b) in chloroform at room temperature (excitation wavelength at 300 nm). In the DCA spectrum, two sharp emission peaks were observed at 437 and 461 nm, in the blue region. In the case of the polymer, relatively broad emission was observed in the green region (494 nm). This relatively large Stokes shift

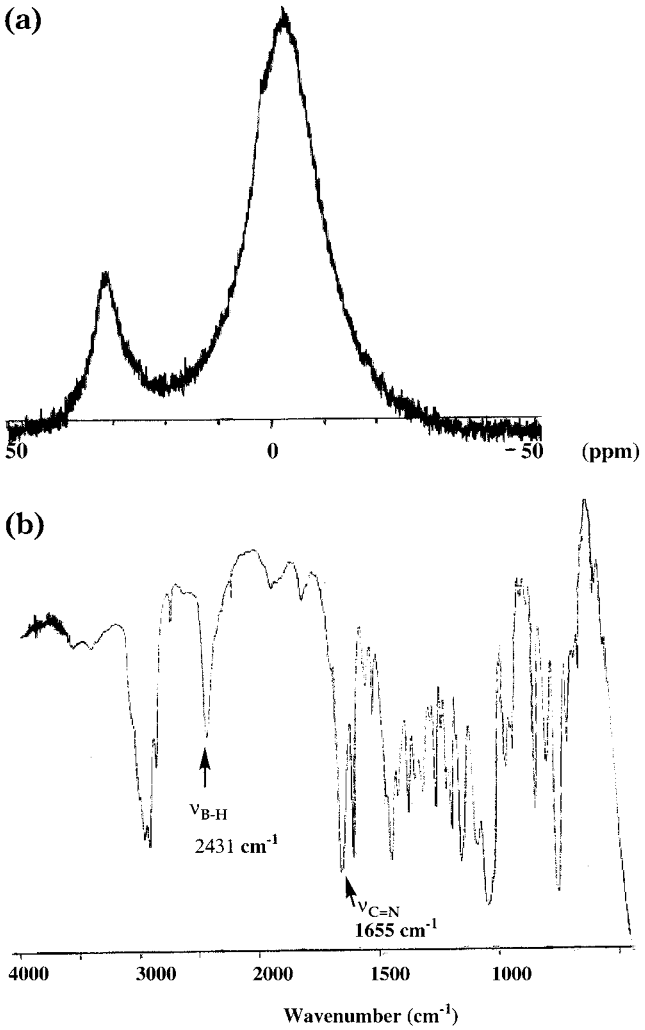


Figure 1. (a) ^{11}B-NMR spectrum of the DCA polymer. (b) IR spectrum of the DCA polymer.

and broad emission imply that some energy transfer might take place in the unit.

Stability of the Polymer. Air-bubbling experiments were performed for the DCA polymer to assess the air stability of the polymer in a THF solution. A stream of air was bubbled into a THF solution for 24 h, and the change of the molecular weight was checked by the GPC measurement. Stability toward moisture was also investigated by adding water to a THF solution of the polymer and stirring the mixture for 24 h. From the results shown in Figure 4, only a slight decrease or no decrease in the molecular weight was observed after the air-bubbling or the treatment with water for 24 h. This indicates relatively high polymer stability and also strongly suggests that the air-stable four-coordinated structure was formed selectively.

To study the thermal stability, thermogravimetric analyses (TGA, 10 °C/min) were recorded for the DCA polymer both in air and nitrogen. The results are depicted in Figure 5. In the measurement under nitrogen, the temperature at which a 10% weight loss was observed was 300 °C (278 °C under air). This relatively high thermal stability suggests potential utility in electronic devices.

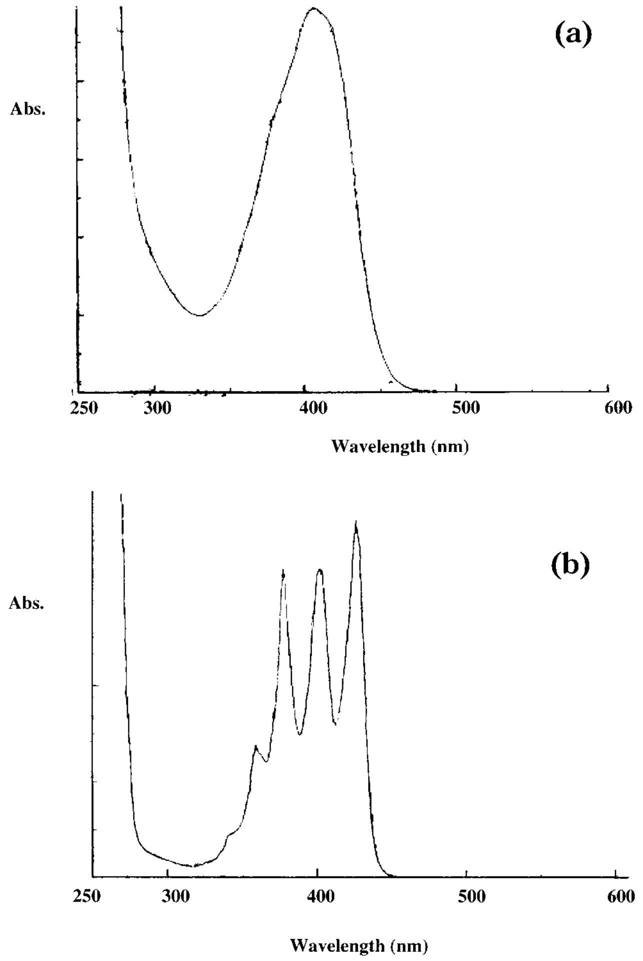


Figure 2. UV−vis spectra of the DCA polymer (a) and DCA (b) in chloroform at room temperature.

Experiental Section

Materials and Instruments. Tetrahydrofuran was dried over sodium and distilled before use. Mesitylborane was prepared by a modified procedure[6] of the reported method.[7] 1,9-Dicyanoanthracene was purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification.

^{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 K803 by using chloroform as an eluent after calibration with standard polystyrene samples. An IR spectrum was 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. Thermogravimetric analysis (TGA) was made on a Shimadzu DT-30 instrument (10 °C/min).

Hydroboration Polymerization between DCA and Mesitylborane. As a typical example of polymerization, a THF solution containing a slight excess of mesitylborane (125.3 mg, 0.949 mmol) was added dropwise to a suspension of DCA (104.9 mg, 0.459 mmol) in THF under a nitrogen atomosphere at room temperature. After the reaction mixture was stirred for 12 h, the insoluble part was filtered off and evaporation of the resulting solution gave a yellow gum quantitatively. After reprecipitation in MeOH, the polymer was obtained as a yellow powder (205.5 mg, yield 91%). ^{1}H-NMR (δ, ppm): 1.3−2.9 (CH_3, 18H), 6.8−8.0 (Ar−H, 12H), 9.06 (CH=N, 2H). ^{11}B-NMR (δ, ppm): −2.98. IR (cm^{-1}): 1655 ($\nu_{C=N}$), 2431 (ν_{B-H}).

Air Stability of the Organoboron Polymer. The stability of the organoboron polymer toward air oxidation was examined by monitoring the change in the molecular weight by GPC during the oxidation in a stream of air bubbled into a THF solution of the organoboron polymer. After 24 h, the resulting polymer was characterized by GPC.

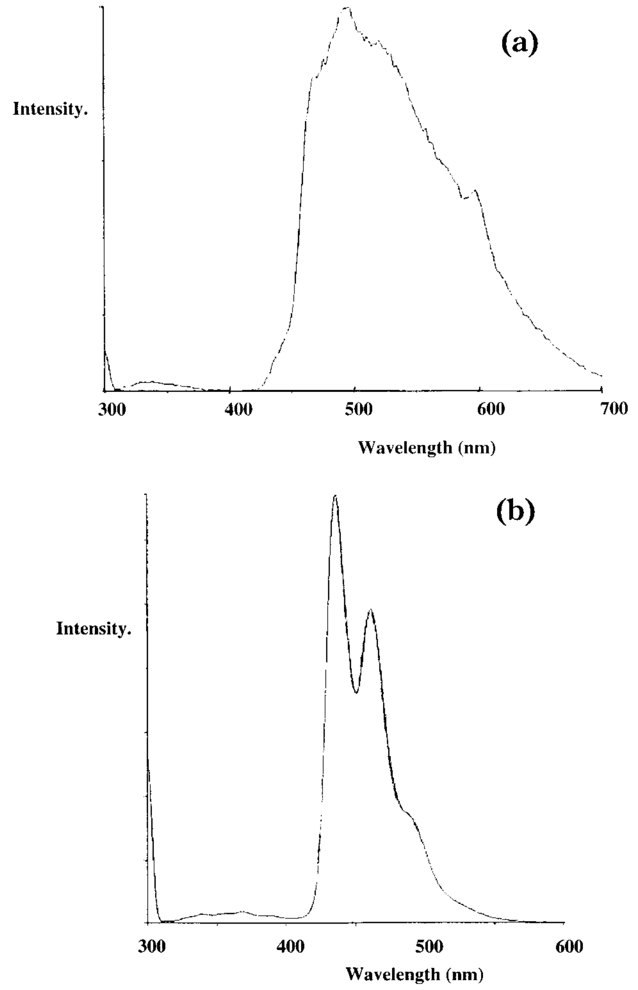


Figure 3. Fluorescence emission spectra of the DCA polymer (a) and DCA (b) in chloroform at room temperature (excitation wavelength at 300 nm).

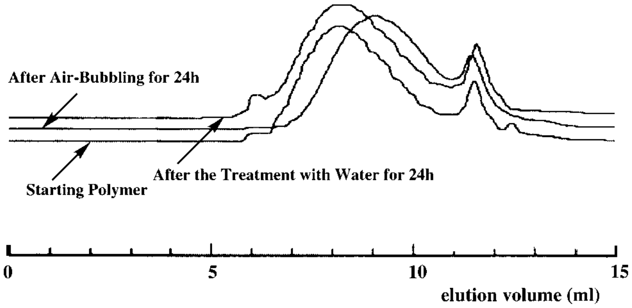


Figure 4. Stability of the DCA polymer toward air and moisture.

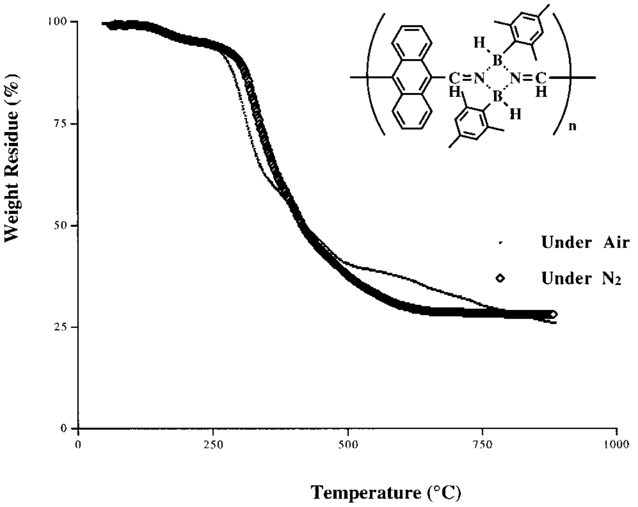


Figure 5. TGA traces (10 °C/min) of the DCA polymer under air and under nitrogen.

Stability of the Organoboron Polymer in the Presence of Moisture. To a THF solution of the polymer, water was added under nitrogen and the mixture was magnetically stirred for 24 h. From the GPC measurement, no decrease of the molecular weight was observed.

References and Notes

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