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Synthesis of poly(cyclodiborazane)s by hydroboration polymerization of dicyano compounds with tripylborane

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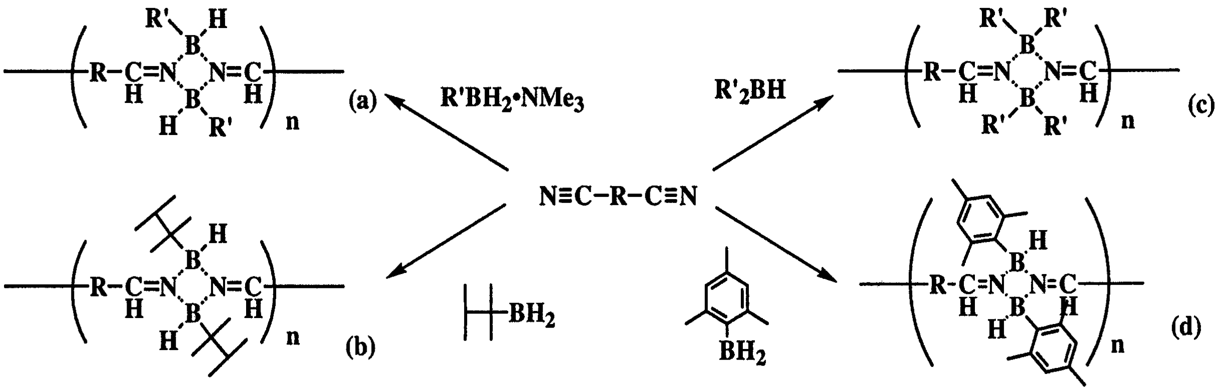
Summary

Hydroboration polymerizaton of dicyano compounds was examined by using tripylborane, which is known as a fairly stable hydroborating agent, to give the corresponding poly(cyclodiborazane)s in good yields. The number average molecular weights of the obtained polymers were in the range of several thousands. These polymers exhibited high stability toward air and moisture.

Introduction

Poly(cyclodiborazane)(1) is a new class of highly inorganic polymeric materials(2) that exhibit reasonable stability toward air and moisture (Scheme 1). Hydroboration polymerization of aromatic dicyano compounds with *tert*-butylborane-trimethylamine complex gives soluble poly(cyclodiborazane)s in good yields(1a). Recently, hydroboration polymerization using mesitylborane(3) was found to proceed under fairly mild reaction conditions to give poly (cyclodiborazane)s with more regulated structure in relatively high molecular weights(4). Furthermore, this polymerization system was applicable to both of aliphatic and aromatic dicyano monomers.

Scheme 1



The availability of this system and high stability of the resulting polymers motivated us to try the variety of functionalization of poly(cyclodiborazane). For example, we have recently reported the polymerization of dicyanoanthracene (DCA)(5) and tetracyanoquinodimethane (TCNQ)(6). The obtained polymeric acceptors are expected as a polymer photocatalyst, electron transporting material or polymeric conductor.

In this paper, hydroboration polymerization of dicyano compounds using tripylborane(7) is described (Scheme 2). Tripylborane is a highly stable hydroborating agent which does not show any sign of decomposition even after 21 days (mesitylborane;

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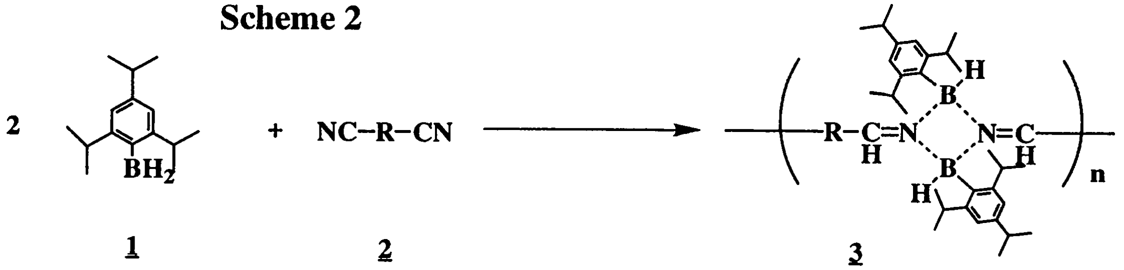
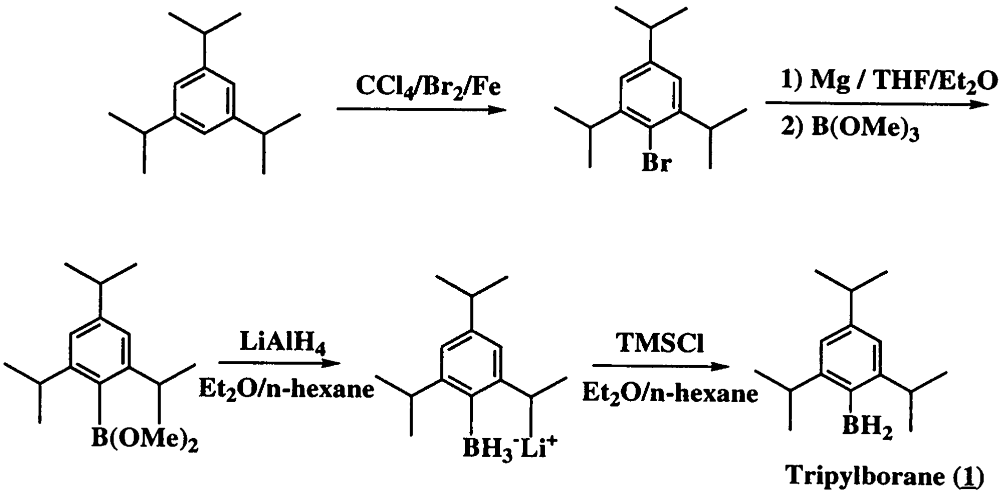
24h) when kept under nitrogen at room temperature. Since tripylborane is much easier to handle than thexylborane or mesitylborane, polymerization using tripylborane should be industrially more beneficial. Furthermore, more improved air stability of the resulting polymer is expected because of the severer steric hindrance around the boron atom.

Scheme 2





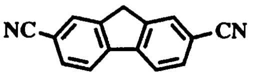
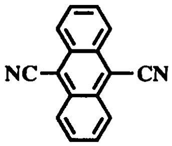
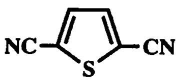
Scheme 3

Results and Discussion

Tripylborane (1) was prepared according to the reported procedure, as shown in Scheme 3. The hydroboration polymerization between 1 and adiponitrile was first examined as follows. To a THF solution of adiponitrile, a THF solution of 2 eq. of 1 was added dropwise under nitrogen atmosphere at room temperature. After stirring the reaction mixture for 12h, the polymerization was observed in the GPC (gel permeation chromatographic analysis) measurement. The polymer (3a) was purified by reprecipitating into MeOH and then freeze dried to afford a white powder in a good yield. 3a was quite soluble in common organic solvents such as THF, chloroform, benzene and so on. From the GPC measurement (THF, PSt standards), the number average molecular weight (*M*n) of 3a was estimated to be 3800.

The hydroboration polymerization of tripylborane with various dicyano compounds was examined, and the results are summarized in Table I. Except for 9, 10-dicyanoanthracene (2e), every monomer afforded the corresponding poly(cyclodiborazane) in good yield. However, in each case the *M*n of the polymer was relatively lower than the case where mesitylborane was employed, possibly due to lower reactivity or less solusbility of tripylborane.

Table I. Hydroboration Polymerization of Various Dicyano Compounds with Tripylborane [a]

Run	Dicyano Compounds		1/2	Mw [b]	Mn [b]	Mw/Mn [b]	Yield (%) [c]
1	$NC(CH_2)_4CN$	(2a)	1.9	9900	3800	2.6	86
2	$NC(CH_2)_8CN$	(2b)	2.2	11700	5500	2.2	90
3		(2c)	2.1	2700	1700	1.5	77
4		(2d)	1.7	4900	2800	1.7	91
5		(2e)	2.2	No Polymerization			
6		(2f)	2.1	3500	2300	1.5	45

(a) Reactions were carried out at room temperature under nitrogen atmosphere.
(b) GPC (THF), polystyrene standards.
(c) Isolated yields after reprecipitation into n-hexane.

The structures of the polymers were confirmed by ^{1}H-NMR, ^{11}B-NMR and IR spectra. In the ^{1}H-NMR spectrum of 3a, the peaks due to tripyl group were observed at 1.03-1.14, 2.31, 2.72 and 6.81 ppm respectively and the imine proton was observed at 7.19 ppm. All the peaks and their integration ratio were in good agreement with those for the expected structure. The ^{11}B-NMR spectrum of 3a showed the main peak at -0.21 ppm (Figure 1), which indicates the formation of four-membered cyclodiborazane structures. In the IR spectrum of 3a, the peaks attributable to B-H stretching and C=C stretching were observed at 1682 and 2420 cm^{-1}, respectively (Figure 2).

The UV-vis absorption spectrum was measured for the polymer (3f) prepared from 2,5-dicyanothiophene (in CHCl$_3$; at room temperature; Figure 3). Because of the alternating arrangement of donor and acceptor units, this polymer exhibited a relatively red-shifted absorption maximum (323 nm) owing to its intramolecular charge transferred structure.

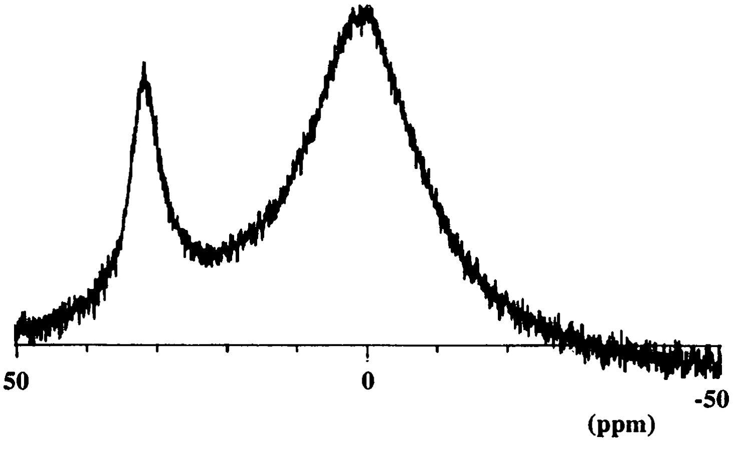


Figure 1. ^{11}B-NMR Spectrum of 3a in CDCl$_3$

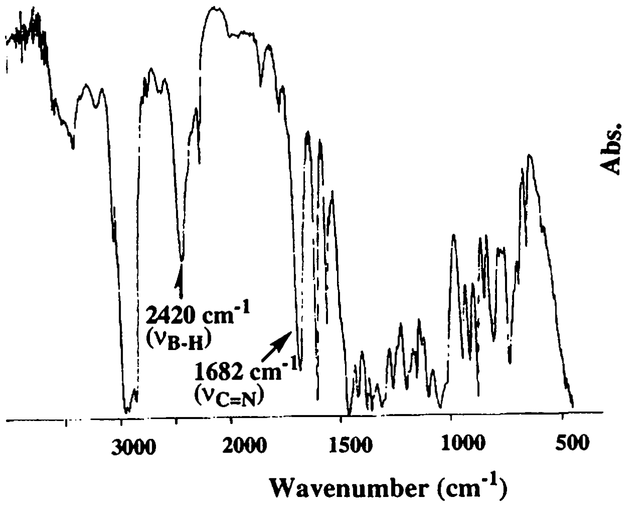


Figure 2. IR Spectrum of 3a

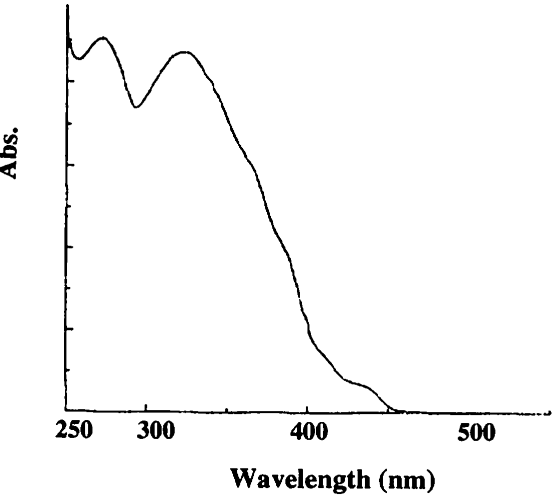


Figure 3. UV-vis Absorption Spectrum of 3f in $CHCl_3$ at Room Temp

The stability of 3a toward air and moisture was investigated by an air-bubbling experiment and treatment with water (Figure 4). To a THF solution of 3a, air was vigorously bubbled for 24h and the changes of molecular weights were monitored by GPC measurement. Similarly, a suspension of 3a in water was stirred for 24h and then characterized by GPC. In both cases, the GPC curves of polymers after each treatment were almost identical to the starting polymer, indicating fairly high stability of 3a.

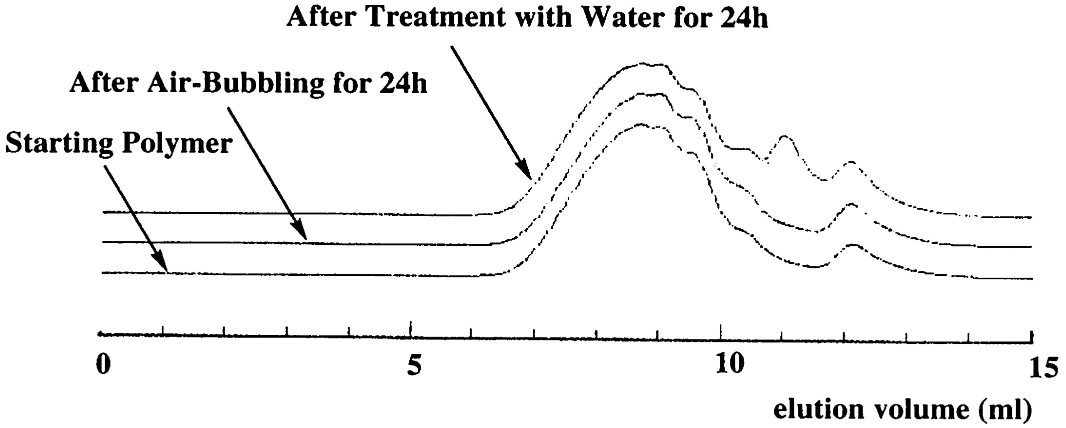


Figure 4. Stability of 3a toward Air and Moisture

Experimental Section

Materials and Instruments. Tetrahydrofuran was dried over sodium and distilled before use. Tripylborane was prepared according to the reported method(7). Adiponitrile and sebaconitrile were purchased from Tokyo Chemical Industry Co., Ltd. and purified by distillation. Terephthalonitrile was purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification. 2,7-Dicyanofluorene and 2,5-dicyanothiophene were prepared from the corresponding dibromides by the reaction with cuprous cyanide according to the reported procedure(8).

^1H- 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 G3000HXI by using THF 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.

Hydroboration Polymerization between 1 and 2. As a typical procedure, hydroboration polymerization of 1 with 2a was examined as follows. Under nitrogen atmosphere, **2a** (78.4 mg, 0.725 mmol) in 0.7 ml of THF was added dropwise to a THF solution (0.7 ml) of 2 eq. of **1** (303 mg, 1.401 mmol) at room temperature. After stirring the reaction mixture for 12h and the removal of solvent, the resulting polymer was purified by reprecipitation into MeOH and then freeze dried to afford **3a** as a white powder (325.5 mg, 0.602 mmol) in 86% yield. ^{1}H-NMR (δ, ppm) 1.03-1.14 (40H, N=CH-CH$_2$-CH_2, CH$_3$), 1.72 (4H, N=CH-CH_2), 2.31 (2H, CH), 2.72 (4H, CH), 6.81 (4H, Ar-H), 7.19 (2H, CH=N). ^{11}B-NMR (δ, ppm) -0.21. IR (cm^{-1}) 1682 ($\nu_{C=N}$), 2420 (ν_{B-H}).

3b-**d** and **3f** were prepared in a similar manner by using **2b**-**d** and **2f** instead of **2a**. **3b**; ^{1}H-NMR (δ, ppm) 1.01-1.18 (48H, N=CH-CH$_2$-CH_2-CH_2-CH_2, CH$_3$), 1.55 (4H, N=CH-CH$_2$), 2.16 (2H, CH), 2.77 (4H, CH), 6.83 (4H, Ar-H), 7.24 (2H, CH=N). IR (cm^{-1}) 1682 ($\nu_{C=N}$), 2422 (ν_{B-H}). yield 90%. **3c**; ^{1}H-NMR (δ, ppm) 1.18 (36H, CH$_3$), 2.55 (2H, CH), 2.78 (4H, CH), 6.85 [4H, Ar-H (tripyl)], 7.21 (4H, Ar-H), 7.61 (2H, CH=N). ^{11}B-NMR (δ, ppm) 3.03. IR (cm^{-1}) 1644 ($\nu_{C=N}$), 2404 (ν_{B-H}). yield 77%. **3d**; ^{1}H-NMR (δ, ppm) 1. 17 (36H, CH$_3$), 2.82 (6H, CH), 3.92 (2H, Ar-CH$_2$-Ar), 6.92 [4H, Ar-H (tripyl)], 7.41-7.55 (6H, Ar-H), 8.04 (2H, CH=N). IR (cm^{-1}) 1644 ($\nu_{C=N}$), 2406 (ν_{B-H}). yield 91%. **3f**; ^{1}H-NMR (δ, ppm) 1.20 (36H, CH$_3$), 2.57 (2H, CH), 2.83 (4H, CH), 6.89 [6H, Thi-H, Ar-H (tripyl)], 7.46 (2H, CH=N). IR (cm^{-1}) 1634 ($\nu_{C=N}$), 2408 (ν_{B-H}). yield 45%.

Stability of Organoboron Polymer. The stability of organoboron polymers toward air oxidation was examined by monitoring the change of the molecular weights by GPC curve during an oxidation experiment, in which a stream of air was bubbled into a THF solution of organoboron polymer. After the designated time, the resulting polymer was characterized by GPC.

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