# Allylboration Polymerization. 1. Synthesis of Boron-Containing Polymers by the Reaction between Triallylborane and Dicyano Compounds

# Yoshiki Chujo,\* Ikuyoshi Tomita,<sup>1</sup> and Takeo Saegusa<sup>2</sup>

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-01, Japan

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Boron-containing polymers containing borazine, phosphinoborane, and decarborane monomer units3 have been of interest as polymeric materials or as precursors for the production of inorganic materials.4 Recently, we reported a novel methodology for the preparation of organoboron polymers.<sup>5</sup> Hydroboration polymerization of nonconjugated diolefins with thexylborane gave organoboron polymers that contained carbon-boron bonds in the main chains. These polymers can be used as reactive polymers to produce poly(alcohol)s<sup>6</sup> or poly(ketone)s.<sup>7</sup> On the other hand, in the case of hydroboration polymerization of dicyano compounds, boron-containing polymers having cyclodiborazane backbones were obtained.8 These cyclodiborazane polymers were stable against air and water. As another method for the preparation of cyclodiborazane polymers, we describe here an allylboration polymerization system using triallylborane (1) and bifunctional dicyano compounds (2a-h).

The reactions between nitriles and allylboranes such as triallylborane<sup>9</sup> and allyl(dialkyl)boranes<sup>10</sup> were reported to produce derivatives of cyclodiborazanes in quantitative yields. Mikhailov and his co-workers have shown that these compounds are air stable. Thus, this allylboration reaction of nitrile groups was first applied to the polymerization system using triallylborane and dicyano compounds (Scheme I).

Two molar equivalents of triallylborane (1) was added to isophthalonitrile (2a) without solvent at 0 °C under nitrogen, and the reaction mixture was stirred at room temperature. 2a dissolved at the early stage, where monomeric iminoborane species might be produced. Within a few hours, the reaction mixture became viscous and a colorless glassy product was formed. After dissolving in THF, polymer 3a was purified by reprecipitation into EtOH/H<sub>2</sub>O (1/1, v/v) (78% yield). The molecular weight of the polymer was measured by GPC on the basis of polystyrene calibration curves. From this result,  $\bar{M}_n$  and  $\bar{M}_w$  of 3a were found to be 14 000 and 25 700, respectively.

The structure of 3a was confirmed by  $^1\text{H}$  and  $^{11}\text{B}$  NMR and IR analyses. In its  $^1\text{H}$  NMR spectrum (Figure 1), the peaks assignable to methylene protons adjacent to the boron atom, methylenes adjacent to the imino carbon, vinyl protons, and aromatic protons were observed at  $\delta$  0.58–2.26, 3.41, 4.46–6.30, and 6.88–7.62 ppm, respectively. The integral ratios of these peaks were in good agreement with those for the expected structure.

In the <sup>11</sup>B NMR spectrum of 3a, a broad peak at 3.7 ppm accompanying small peaks at 33.2 and 38.1 ppm was observed (Figure 2). As a model compound for 3a, an iminoborane dimer (4) was prepared by an allylboration reaction between benzonitrile and 1 (Scheme II) according to the method reported by Mikhailov.<sup>9</sup> The <sup>11</sup>B NMR spectrum of 4 showed a single peak at 5.0 ppm, which was characterized as a four-coordinated boron atom.<sup>12</sup> The main peak at 3.7 ppm for 3a, thus, supported the formation

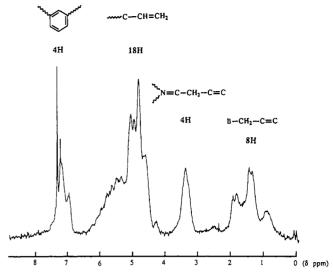


Figure 1. <sup>1</sup>H NMR spectrum of 3a.

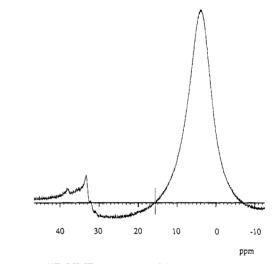


Figure 2. 11B NMR spectrum of 3a.

# Scheme I 2 $B(CH_2CH=CH_2)_3$ + $N\equiv C-R-C\equiv N$ 1 2 $C_3H_5$ $C_$

of a four-membered structure. The small peaks at 33.2 and 38.1 ppm might be ascribed to three-coordinated monomeric iminoborane species<sup>13</sup> or some impurities.

In its IR spectrum, a strong peak due to the C=N stretching band was observed at 1659 cm<sup>-1</sup>. No peak was observed at 2240 cm<sup>-1</sup>, which demonstrated the complete conversion of C≡N.

Polymerizations of various dicyano compounds with 1 were examined under the same conditions. The results are summarized in Table I. Aliphatic dicyano compounds (2c-h) as well as aromatic dicyano compounds (2a,b) resulted in the formation of the corresponding boron-containing polymers in good yields. All polymers obtained here were soluble in common organic solvents such as THF, CHCl<sub>3</sub>, and benzene.

Thermogravimetric analyses (TGA) of 3a were carried out under nitrogen and under air (Figure 3). In both cases,

### Scheme II

Table I Allylboration Polymerization of Various Dicyano Compounds with Triallylboranes

run	dicyano compd	yield <sup>b</sup> (%)	$ar{M}_{ m n}{}^{ m c}$	$ar{M}_{\mathbf{w}^c}$	$ar{M}_{\mathbf{w}}/ar{M}_{\mathbf{n}}$
1	m-NCC <sub>6</sub> H <sub>4</sub> CN (2a)	78	14000	25 700	1.84
2	$p\text{-NCC}_6\text{H}_4\text{CN}$ (2b)	89	5900	11 000	1.86
3	$NC(CH_2)_2CN(2c)$	79	4500	9 200	2.04
4	$NC(CH_2)_3CN(2d)$	78	5500	12000	2.18
5	$NC(CH_2)_4CN$ (2e)	81	6300	13 600	2.16
6	$NC(CH_2)_5CN(2f)$	93	8900	18 000	2.02
7	$NC(CH_2)_6CN(2g)$	85	9000	20 400	2.27
8	$NC(CH_2)_8CN(2h)$	89	11900	24 600	2.07

<sup>a</sup> Polymerizations were carried out in bulk at 0 °C. <sup>b</sup> Isolated yields after precipitation into EtOH/H<sub>2</sub>O (1/1). <sup>c</sup> GPC (THF), polystyrene standard.

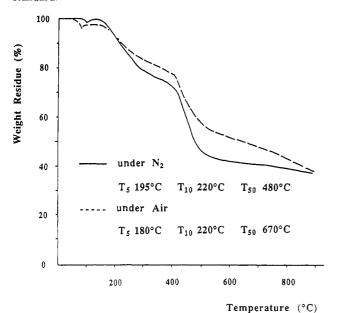


Figure 3. Thermogravimetric analysis of 3a.

a black solid was left in 38 wt % after pyrolysis at 900 °C. This result might be taken that 3a can be expected as a precursor for boron-containing inorganic materials. The remaining solid after pyrolysis, however, has not been characterized at present.

Differential scanning calorimetric analysis (DSC) of 3a gave significant information about the thermal reaction of 3a. At the first scan of 3a, a strong exothermic peak at 140 °C was recognized. At the second scan, however, the corresponding peak was not observed. The samples after DSC measurement were insoluble in THF, CHCl<sub>3</sub>, or benzene. From the results of IR measurement, no peak for iminoborane species was detected.<sup>14</sup> It is known that 4 is converted to 5 by the further intramolecular allylboration reaction upon heating at 100 °C for 1 h9b (Scheme II). These facts suggest that the thermal treatment of 3a caused the further allylboration reaction to form a polymer consisting of new B-N four-membered rings. The low solubility of the polymer obtained after heating might be caused by some intermolecular cross-linking reactions via a thermal allylboration reaction.

The air stability of 3a was monitored by tracing the change of its molecular weight in GPC on exposure to air for the appropriate time. When the sample was kept under air for several days, it became less soluble, and the molecular weight of the THF-soluble part was lower in comparison with that of the sample freshly prepared. An example of an air-exposure experiment for 17 days showed a decrease of the molecular weight  $(\bar{M}_n)$  of 3a from 8800

## References and Notes

- (1) Present address: Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Midori-ku, Yokohama 227, Japan.
- (2)Present address: KRI International, Inc., Chudoji, Shimogyoku, Kyoto 600, Japan.
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- The IR spectrum of this liquid (after reaction for 5 min) indicated almost complete conversion of nitrile groups. The formation of monomeric iminoborane species was supported by the peak at 1814 cm<sup>-1</sup>, which was converted gradually to the iminoborane dimer species (1659 cm<sup>-1</sup>) after the longer reaction time.
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- (14) IR (KBr): 3596, 3040, 2998, 2920, 1636, 1472, 1391, 998, 918, 717 cm<sup>-1</sup>.