

Scheme II

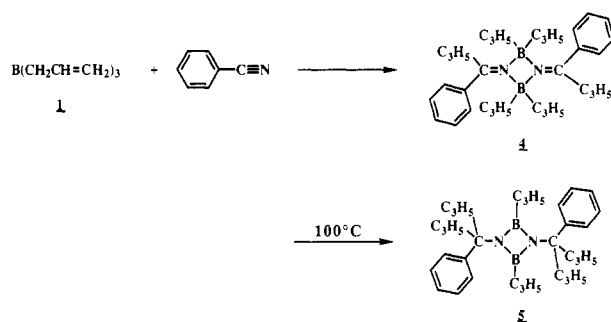


Table I
Allylboration Polymerization of Various Dicyano
Compounds with Triallylborane^a

run	dicyano compd	yield ^b (%)	\bar{M}_n^c	\bar{M}_w^c	\bar{M}_w/\bar{M}_n
1	<i>m</i> -NCC ₆ H ₄ CN (2a)	78	14000	25 700	1.84
2	<i>p</i> -NCC ₆ H ₄ CN (2b)	89	5900	11 000	1.86
3	NC(CH ₂) ₂ CN (2c)	79	4500	9 200	2.04
4	NC(CH ₂) ₃ CN (2d)	78	5500	12 000	2.18
5	NC(CH ₂) ₄ CN (2e)	81	6300	13 600	2.16
6	NC(CH ₂) ₅ CN (2f)	93	8900	18 000	2.02
7	NC(CH ₂) ₆ CN (2g)	85	9000	20 400	2.27
8	NC(CH ₂) ₈ CN (2h)	89	11900	24 600	2.07

^a Polymerizations were carried out in bulk at 0°C . ^b Isolated yields after precipitation into EtOH/H₂O (1/1). ^c GPC (THF), polystyrene standard.

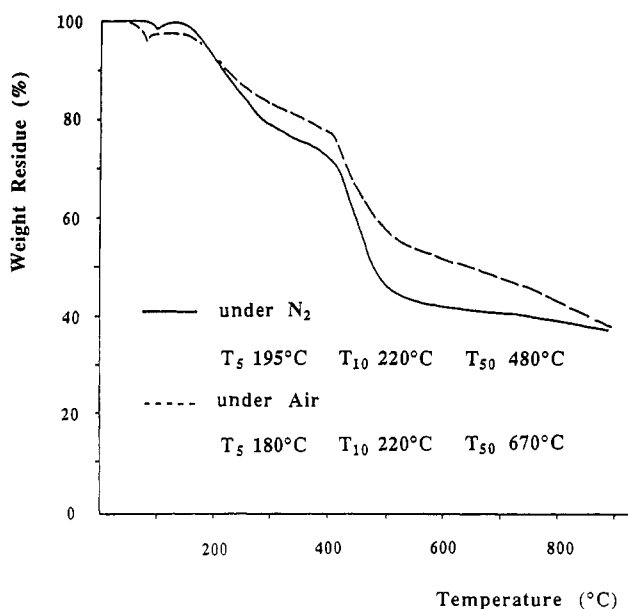


Figure 3. Thermogravimetric analysis of 3a.

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_3 , or benzene. From the results of IR measurement, no peak

for iminoborane species was detected.¹⁴ It is known that 4 is converted to 5 by the further intramolecular allylboration reaction upon heating at 100°C for 1 h^{9b} (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 to 1450.

References and Notes

- (1) Present address: Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Midori-ku, Yokohama 227, Japan.
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- (11) 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^{-1} , which was converted gradually to the iminoborane dimer species (1659 cm^{-1}) after the longer reaction time.
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- (13) In ^{11}B NMR, monomeric iminoborane species show their absorptions around 30–35 ppm. See, for example: (a) Mikhailov, B. N.; Ter-Sarkisyan, G. S.; Govorov, N. N.; Nikolaeva, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 1820. (b) Mikhailov, B. N.; Ter-Sarkisyan, G. S.; Govorov, N. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 1823.
- (14) IR (KBr): 3596, 3040, 2998, 2920, 1636, 1472, 1391, 998, 918, 717 cm^{-1} .