

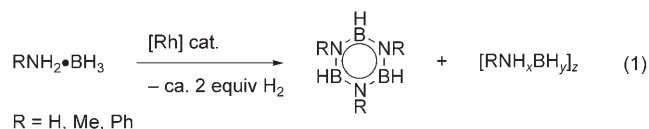
Iridium-Catalyzed Dehydrocoupling of Primary Amine–Borane Adducts: A Route to High Molecular Weight Polyaminoboranes, Boron–Nitrogen Analogues of Polyolefins**

Anne Staubitz, Alejandro Presa Soto, and Ian Manners*

Despite the historic analogy between boron–nitrogen compounds and those of carbon^[1] and the expanding interest in polymeric materials based on main-group elements,^[2] macromolecular chemistry based on boron–nitrogen linkages is extremely limited.^[3] In particular, high molecular weight boron–nitrogen analogues of polyolefins ($[\text{R}_2\text{N}-\text{BR}'_2]_n$) have never been convincingly characterized,^[4] although such structures have attracted attention with respect to computational studies.^[5] Herein we report a catalytic route to the first, soluble macromolecular examples of these materials.

We have previously reported the catalytic formation of phosphorus–boron bonds from phosphine–borane adducts through dehydrocoupling/dehydrogenation mediated by a variety of late-transition-metal (e.g. Ru, Rh, Ir, Pd, Pt) precatalysts.^[6] The use of secondary phosphine–borane adducts $\text{R}_2\text{PH}-\text{BH}_3$ as substrates was found to give linear or cyclic oligomers. In addition, the Rh-catalyzed dehydrocoupling of less sterically encumbered primary phosphine–borane adducts RPH_2-BH_3 led to the elimination of a single equivalent of H_2 and afforded high molecular weight polyphosphinoboranes $[\text{RPH}-\text{BH}_2]_n$. We also found that secondary amine–borane adducts $\text{R}_2\text{NH}-\text{BH}_3$ yield cyclic oligomers $(\text{R}_2\text{N}-\text{BH}_2)_x$ ($x=2$ or 3).^[7] However, our initial attempts to extend this catalytic dehydrocoupling chemistry to the formation of polyaminoboranes with a boron–nitrogen backbone from primary amine–borane adducts RNH_2-BH_3 and ammonia–borane NH_3-BH_3 with Rh precatalysts were unsuccessful. Instead, we observed the elimination of up to approximately two equivalents of H_2 to yield mixtures of borazines $[\text{RNBH}]_3$ and poorly defined (and presumably branched or cyclic) insoluble oligomeric material [Eq. (1)].^[7]

The recent intense interest in amine–boranes as hydrogen-storage materials^[8] has led to a series of new and in several cases improved dehydrocoupling catalysts for amine–borane adducts based on a variety of early and late transition



metals.^[9] In particular, the report by Goldberg, Heinekey, and co-workers^[9a] that Brookhart's Ir catalyst **1**^[10] successfully and rapidly dehydrocouples $\text{NH}_3\cdot\text{BH}_3$ in dilute solution with the elimination of a single equivalent of H_2 to yield a product that is believed to be the pentamer $[\text{NH}_2\text{BH}_2]_5$ prompted us to re-explore the synthesis of polyaminoboranes.

When a concentrated solution of *N*-methylamine–borane ($\text{MeNH}_2\cdot\text{BH}_3$) in THF was treated with 0.3 mol % of **1** at 0°C , we observed vigorous bubbling. As the solution became increasingly viscous, the reaction mixture was allowed to stir at 20°C for about 20 minutes [Eq. (2)]. The resulting product was then isolated and purified by precipitation into *n*-alkane as a nonsolvent to give a white solid (Figure 1 a), which was subsequently characterized as the polypropylene analogue **2a** by NMR spectroscopy, elemental analysis (EA), IR spectroscopy, and in terms of molecular weight by gel permeation chromatography (GPC) and dynamic light scattering (DLS) measurements.

Structural characterization was consistent with the formation of a poly(*N*-methylaminoborane) (**2a**). The ^{11}B NMR

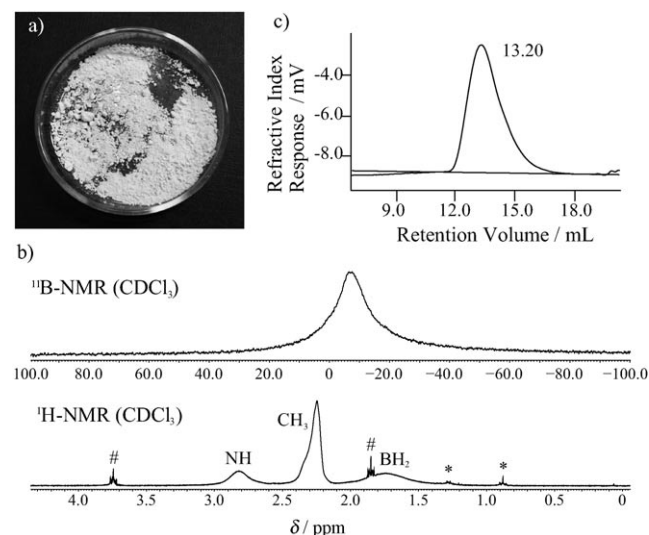
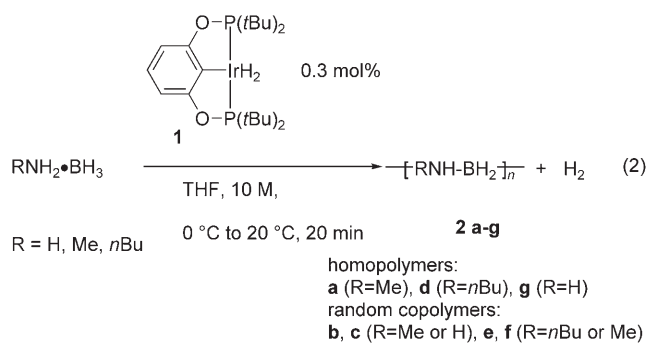


Figure 1. a) Poly(*N*-methylaminoborane) (**2a**). b) ^{11}B and ^1H NMR spectra. # = THF, * = butane. c) GPC trace (THF with 0.1 % w/w $n\text{Bu}_4\text{NBr}$).

[*] Dr. A. Staubitz, Dr. A. Presa Soto, Prof. Dr. I. Manners
School of Chemistry
University of Bristol
Cantock's Close, Bristol, BS8 1TS (UK)
Fax: (+44) 117-929-0509
E-mail: ian.manners@bristol.ac.uk
Homepage: <http://www.inchm.bris.ac.uk/people/manners/home.html>

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spectrum of this polymer (Figure 1b) showed a very broad single peak at $\delta = -6.7$ ppm and no detectable splitting in the proton-coupled spectrum.^[11]

The ^{13}C NMR spectrum shows a very broad *N*-Me peak at $\delta = 36.8$ ppm and also a more narrow peak at $\delta = 35.8$ ppm. Presumably this pattern arises from the tacticity effects of the diastereomeric nitrogen center. The ^1H NMR spectrum (Figure 1b) showed three broad singlets at $\delta = 2.75$ ppm (NH), $\delta = 2.18$ ppm (CH_3), and $\delta = 1.68$ ppm (BH_2). Despite prolonged exposure to a vacuum (ca. 10^{-3} mmHg), residual solvent (THF, alkanes) was still detectable, which suggested that it is confined by the 3D arrangement of polymer chains. Residual *n*-alkane was even detected when *n*-butane was used as the nonsolvent. Taking the ^1H NMR integrations of residual solvent into account, a satisfactory C, H, and N elemental analysis was obtained. In the IR spectrum (Figure 2d), we identified a band for the N–H stretch ($\tilde{\nu} = 3256 \text{ cm}^{-1}$), a cluster of bands for the methyl group ($\tilde{\nu} = 2985 \text{ cm}^{-1}$), and a very distinctive cluster of bands for the B–H stretches ($\tilde{\nu} = 2366 \text{ cm}^{-1}$). Significant broadening of the N–H stretch caused by hydrogen bonding with residual THF was not observed, which is consistent with the assertion that solvent is essentially physically trapped in the polymer matrix. The GPC trace (in THF with 0.1 % w/w *n*Bu₄NBr, calibrated with polystyrene standards) revealed that the product was of high molecular weight ($M_w = 160\,000$) and had a fairly high polydispersity index (PDI, 2.9) (Figure 1c). Results consistent with a high molecular weight polymer were obtained by DLS in THF; an average hydrodynamic radius of 3 nm, (with very small amounts of aggregated products) was determined (Table 1).

When a concentrated solution of ammonia–borane ($\text{NH}_3 \cdot \text{BH}_3$) in THF (10 M) was treated with 0.3 mol % **1**, only insoluble material **2g** was obtained. To facilitate characterization, we attempted to form a soluble random

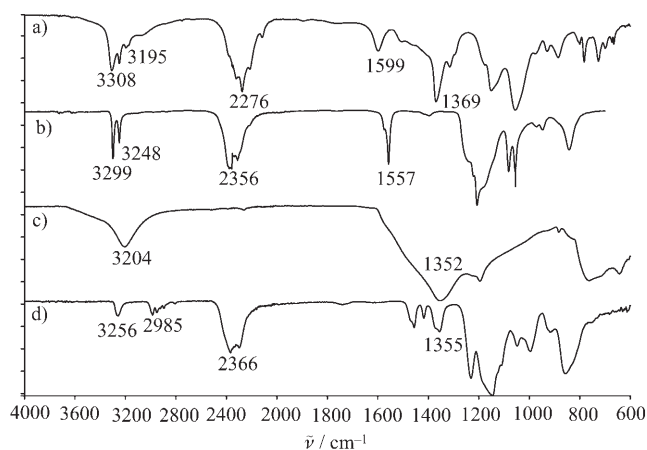


Figure 2. IR spectra of a) ammonia–borane ($\text{NH}_3 \cdot \text{BH}_3$), b) polyamino–borane (**2g**), c) pyrolyzed **2g** (900 °C), d) poly(*N*-methylaminoborane) (**2a**).

copolymer **2b** (R=H or Me) by copolymerization of a mixture of $\text{MeNH}_2 \cdot \text{BH}_3$ and $\text{NH}_3 \cdot \text{BH}_3$. When a ratio of *N*-methylamine–borane to ammonia–borane of 3:1 was used, a soluble polymeric product was indeed obtained (Table 1, entry 2). In analogous experiments we then attempted to increase the relative amount of $\text{NH}_3 \cdot \text{BH}_3$ to identify the minimum ratio that still generates a soluble random copolymer. When the reaction was performed with a ratio of 1:1 (Table 1, entry 3), the resulting polymer was sufficiently soluble in THF (with 0.1 % w/w *n*Bu₄NBr) to obtain GPC results and for DLS (in DMSO). However, the THF/*n*Bu₄NBr solution was already slightly opaque so that it seems unlikely that the ratio can be lowered much further.

To explore the generality of the polymerization further, we explored the use of other amine–borane adducts as potential polymer precursors. The use of *n*BuNH₂·BH₃ is interesting as the *n*-butyl group is bulkier than methyl and also because the use of this liquid adduct allows the catalytic reaction with **1** to be performed in the absence of added solvent. The reaction proceeded smoothly, but the product **2d** was very soluble in most solvents, so that instead of purifying the material by precipitation, a solution of the polymer in hexanes was filtered through a pad of alumina to remove residual catalyst.

As the *N*-methylamine–borane had led to polymer **2a**, which was much easier to purify by precipitation, we also copolymerized this species with *N*-*n*-butylamine–borane in different ratios (Table 1, entries 5 and 6). For a *n*BuNH₂·BH₃/MeNH₂·BH₃ ratio of the monomer precursors of 3:1, the

Table 1: Synthesis and characterization data for polyaminoboranes **2a–2f**.

Entry	Monomer precursors (ratio)	Polyaminoborane	Yield [%]	M_w (GPC)	PDI (GPC)	R_h [nm] ^[c] (DLS)
1	MeNH ₂ ·BH ₃	[MeNHBH ₂] _n	2a 60	160 000	2.9	3 ^[a]
2	MeNH ₂ ·BH ₃ /NH ₃ ·BH ₃ (3:1)	[MeNHBH ₂] _{3n} - <i>r</i> -[NH ₂ BH ₂] _n	2b 72	156 000	11.0	3 ^[a]
3	MeNH ₂ ·BH ₃ /NH ₃ ·BH ₃ (1:1)	[MeNHBH ₂] _n - <i>r</i> -[NH ₂ BH ₂] _n	2c 91	47 000	3.9	4 ^[b]
4	<i>n</i> BuNH ₂ ·BH ₃	[<i>n</i> BuNHBH ₂] _n	2d 82	405 000	1.6	5 ^[a]
5	<i>n</i> BuNH ₂ ·BH ₃ /MeNH ₂ ·BH ₃ (3:1)	[<i>n</i> BuNHBH ₂] _{3n} - <i>r</i> -[MeNHBH ₂] _n	2e 18	183 000	1.9	4 ^[a]
6	<i>n</i> BuNH ₂ ·BH ₃ /MeNH ₂ ·BH ₃ (1:1)	[<i>n</i> BuNHBH ₂] _{2n} - <i>r</i> -[MeNHBH ₂] _n	2f 48	244 000	2.2	4 ^[a]

[a] Measured in THF; [b] measured in DMSO; [c] R_h = hydrodynamic radius.

polymer yield obtained by precipitation was still low, but could be increased by using a ratio of 1:1. Again, all materials were characterized using GPC, DLS, NMR spectroscopy, EA, IR spectroscopy, and thermogravimetric analysis (TGA). These methods led to analogous results to those discussed for poly-(*N*-methylaminoborane), but the ^1H and ^{13}C NMR spectra were, as expected, much more complicated.^[12]

Because the unsubstituted polyaminoborane (**2g**) is isoelectronic with polyethylene, the simplest polyolefin, we characterized this insoluble material in more detail. The IR spectrum (Figure 2b) of **2g** was similar to that reported by Kim et al.,^[4c] who obtained their material in low yield by a thermal reaction between NaBH_4 and $(\text{NH}_4)_2\text{SO}_4$.

A striking difference, however, is that we observed two sharp bands for **2g** in the region for the symmetric and asymmetric N–H stretches (Figure 2b), whereas Kim et al. found two much more poorly resolved bands with a considerable shoulder at higher wavenumber. Likewise, the B–H stretches for **2g** consist of two distinctive bands (Figure 2b), whereas Kim's material showed only one broad band. We also compared WAXS (wide-angle X-ray scattering) patterns for the two materials. A WAXS analysis of **2g** confirmed that it was different from that obtained by Kim and co-workers. The WAXS pattern for their material suggests amorphous character, whereas our polyaminoborane **2g** showed sharp peaks, suggesting semicrystallinity.^[13] The WAXS pattern of **2g** is also different from the cyclic pentamer characterized by Shore and co-workers.^[14] Taken in conjunction with the fact that we obtained high molecular weight (co)polymers with solvating substituents such as **2c** by using the described method, this result is an indication that **2g** is indeed polymeric, although it is not possible to exclude that **2g** is cyclic or merely oligomeric.

As the novel polyaminoboranes are of potential interest as precursors to boron–nitride-based ceramics, we studied their thermal decomposition behavior by TGA and by pyrolysis in a tube furnace (10°Cmin^{-1} gradient to 900°C). Another difference between our polyaminoborane and Kim's material is the ceramic yield obtained after pyrolysis. Polyaminoborane **2g** gave a ceramic yield of 36 % at 900°C in the tube furnace (46 % by TGA) compared with 75 % at 1400°C in the tube furnace for the material obtained by Kim from the thermal reaction between NaBH_4 and $(\text{NH}_4)_2\text{SO}_4$. These combined observations (IR, WAXS, and TGA) are consistent with the hypothesis that the polymer described by Kim and co-workers may have been already cross-linked to some extent, whereas our material **2g** is predominantly linear. The ceramic yield of the pyrolysis of **2g** was independent of its formulation (powder or pellet). In the case of the pellet, we observed substantial shrinkage during pyrolysis, although the shape was retained (Figure 3). IR analysis of this material obtained from **2g** in the tube furnace (Figure 2c) showed only a broad band in the N–H stretching region, but no B–H stretch. However, even heating to 1200°C for 3 hours did not change the IR spectrum significantly. Powder X-ray diffraction of the ceramic product showed a semicrystalline material with two major peaks, the first at $2\theta = 14.9^\circ$, d-spacing $6.0 \text{ \AA}$, and the second at $2\theta = 28.21^\circ$, d-spacing $3.16 \text{ \AA}$. The latter peak could be identified as a peak for boron nitride.^[4c]

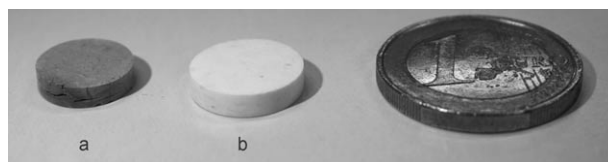


Figure 3. Pellet of **2g** after (a) and before (b) pyrolysis. Euro coin shown for sense of scale.

The moderate ceramic yield for the pyrolysis of polyaminoborane **2g** is presumably due to depolymerization and loss of low molecular weight oligomers. We therefore attempted to increase the ceramic yield by copolymerizing ammonia–borane with the cross-linker hydrazine–diborane ($\text{H}_3\text{B}\cdot\text{NH}_2\text{NH}_2\cdot\text{BH}_3$) in a ratio of 9:1 to give copolymer **2h**, which was isolated in 69 % yield.^[15]

When this material was pyrolyzed as a pellet in the tube furnace (10°Cmin^{-1} gradient to 900°C), we found an improved ceramic yield of 52 %. This result suggests that with careful polymer design, useful precursors for boron–nitride ceramics should be accessible.

In summary, well-characterized examples of a new class of inorganic polymers have been prepared from readily available precursors. They contain an essentially linear nitrogen–boron polymer backbone and are isoelectronic with polyolefins such as polyethylene and polypropylene. Detailed studies of the properties of the new polyaminoborane materials are in progress. We are also exploring a variety of synthetic strategies designed to increase ceramic yields and hydrogen content further and to permit convenient polymer functionalization.

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