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# **Supporting Information for**

### Enabling Ammonia-Borane: Copolymerization of ammonia-borane and amine-boranes yield liquid products

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# General

All reactions were performed under an inert atmosphere, using standard Schlenk line and glovebox techniques. Ethereal solvents and toluene were distilled from Na/benzophenone ketyl radical. <sup>1</sup>H, <sup>13</sup>C (75 MHz), and <sup>11</sup>B (96 MHz) NMR spectra were recorded at room temperature (unless otherwise noted) on a Bruker AVANCE 300 MHz spectrometer. <sup>1</sup>H and <sup>13</sup>C spectra were referenced to the residual <sup>1</sup>H protons/carbons in the deuterated solvent. <sup>11</sup>B NMR was referenced externally to BF<sub>3</sub> • ether. Hexylamine and 3-methoxypropylamine were distilled from CaH<sub>2</sub>. 2.0 M BH<sub>3</sub>•SMe<sub>2</sub> in THF (Acros) was used as received. Ammonia borane (AB, 99%) was used as received from JSC Aviobor. All other reagents were used as received from Acros and Aldrich Chemical Company.

#### Synthesis of 3-Methoxyamineborane (D):

A solution of hexylamine (4.05 g, 40.0 mmol) in THF (20 mL) was chilled to -20 °C. A separate solution of 2.0M BH<sub>3</sub>-SMe<sub>2</sub> in THF (20.0 mL) was also chilled to -20 °C. The two solutions were slowly added together under stirring and allowed to warm ca. 30 min. The volatiles were then removed by vacuum to yield a colorless oil (4.56 g, 99%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.16 (b s, 2H, *N*-H), 2.38 (p, 2.5H), 1.12 (m, 2.1H), 1.00 (m, 4H), 0.82 (m, 5.3H). <sup>1</sup>H{<sup>11</sup>B} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  2.61 (b s, 2H, *N*-H), 2.24 (p, 2.3H), 2.18 (t, 2.57H, *B*-H) 1.10 (p, 1.88H), 0.94 (p, 2.22H), 0.82 (m, 5.3H), 0.73 (p, 1.7H). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -17.65 (q, J<sub>B-H</sub> = 92 Hz). <sup>13</sup>C DEPT135 (C<sub>6</sub>D<sub>6</sub>):  $\delta$  13.77 (CH<sub>3</sub>), 22.36 (CH<sub>2</sub>), 25.91 (CH<sub>2</sub>), 28.64 (CH<sub>2</sub>), 31.15 (CH<sub>2</sub>).

#### Synthesis of Hexylamineborane (E):

A solution of 3-methoxypropylamine (3.57 g, 40.0 mmol) in THF (20 mL) was chilled to -20 °C. A separate solution of 2.0M BH<sub>3</sub>-SMe<sub>2</sub> in THF (20.0 mL) was also chilled to -20 °C. The two solutions were slowly added together under stirring and allowed to warm ca. 30 min. The volatiles were then removed by vacuum to yield a colorless oil (4.04 g, 98%). <sup>1</sup>H{<sup>11</sup>B} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.51 (b s, 2H, *N*-H), 2.78 (m, 5H), 2.53 (m, 2.3H), 2.23 (s, 2.8H, *B*-H), 1.13 (m, 2H). <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  -17.80 (q, J<sub>B-H</sub> = 92 Hz). <sup>13</sup>C DEPT135 (C<sub>6</sub>D<sub>6</sub>):  $\delta$  27.87 (CH<sub>2</sub>), 48.13 (CH<sub>2</sub>), 58.22 (CH<sub>3</sub>), 71.92 (CH<sub>2</sub>).

# TGA/DSC

Thermogravimetrics were performed on a Mettler Toledo  $851^{\text{e}}$  TGA. All measurements were performed under inert (N<sub>2</sub>) atmosphere at 40 sccm. To determine stability of **D** (methoxy), **E** (hexyl), and **D/AB** mixture at ambient temperature, their percent mass loss at 30 °C was monitored over 24 h.



D: 0.137/26.383 \* 100 = 0.52% loss E: 0.0641/26.8401 \* 100 = 0.24% loss

Percentage of stored H<sub>2</sub> (assuming all mass loss is H2) D (3.88% stored): 13.3% E: (3.48% stored): 6.9%



DSC of run #6 (1:1 hexylAB:AB) spent fuel cooled to -60 °C (2°/min), held for 10 min, and warmed to 30 °C (2°/min). No visible events suggest the material does not readily crystalize

#### Table 1

AmineBorane, instrument	1 <sup>st</sup> event onset Temp	1 <sup>st</sup> event max Temp	Integrated Heat kJ/mol H <sub>2</sub>	2 <sup>nd</sup> event onset Temp	2 <sup>nd</sup> event max Temp	Integrated Heat kJ/mol H <sub>2</sub>
AB <sup>1</sup> , C80	105*	113	-21.7	-	-	-
EDAB <sup>2</sup> , DSC	-	123	-10.1	-	160	-5.5
'D', methoxyAB	95.2	122.5	-22.9	137.3	165.2	-2.7
'E', hexylAB	90.6	107.7	-26.8	162.8	170.4	-6.61

DSC runs were performed on a recently calibrated Mettler Toledo, ramped from  $30-200 \,^{\circ}C @ 1^{\circ}/min$ . Runs were blank corrected and processed on version X of Calisto software using the baseline integration function.

1 Wolf, G.; Baumann, J.; Baitalow, F.; Hoffmann, F. P. *Thermochim. Acta*, 2000, **343**, 19-25. 2 Neiner, D.; Karkamkar, A.; Bowden, M.; Choi, Y. J.; Luedtke, A.; Holladay, J.; Fisher, A.; Szymczak, N.; Autrey, T. *Envery Environ. Sci.*, 2011, **4**, 4187-4193. Personal communication with the authors established that the reported DSC values are peak temperatures observed.

\*present authors estimate



Example DSC of 'D', blank corrected and integrated

## **Gaseous Impurity Measurements**

Gaseous Impurity Analysis: using Parr's Multi-Reactor System, samples of amineboranes **D** and **E**, as well as blends with AB were loaded into the reaction vessel, pressurized with inert gas ( $N_2$ , 10 bar), then heated through a temperature profile (soaked at 25 °C 1 minute, ramped from 25-110 °C over 10 min, soaked at 110 °C 5 min, ramped from 110-130 °C over 5 min, and then held at 130 °C for 10 h). Gas products were diluted with N<sub>2</sub> before flowing thru a Nicolet Avatar 380 FTIR. All gases were metered with mass flow controllers and diluted such that the resulting signal was within the linear region of our calibration curves. Omnic and TQ Analyst software (ver 7.3, 7.2 respectively) was used to quantify the products against calibration standards of diborane (2% in Ar, Electronic Fluorocarbons, LLC., Warminster, PA) and ammonia (93.25 and 930.6 ppm, Airgas, Port Allen, LA). Pulsed injections of gaseous borazine (Gelest, Morrisville, PA) were used to make a calibration curve with the area response of a chemigram within Omnic (1445-1482 cm<sup>-1</sup>, 800-3950 cm<sup>-1</sup> baseline). High standards had concentrations of 2000 ppm for diborane, 1000 ppm for ammonia, 1000 ppm for methane, and 933 ppm for borazine. Reported values are corrected for mass flow dilution.

Run	Loading	AB	mmols	Ammonia	Borazine	Diborane	Methane	
	(mmol)	(mmol)	Loading	(ppm/	(ppm/	(ppm/	(ppm/	
			+ AB	mmol*)	mmol*)	mmol*)	mmol*)	
	3-Methoxypropylamineborane							
1	20.0	-	20.0	<1	<1	78	$2.6 \times 10^{2}$	
2	6.0	2.0	8.0	<1	30	7.5	$2.5 \times 10^{2}$	
2b**	6.0	2.0	8.0	<1	6.5	<1	$2.1 \times 10^{2}$	
3	10.8	10.8	21.6	-	-	-	-	
	Hexylamineborane							
4	20.0	-	20.0	<1	<1	20	9.3	
5	3.0	1.0	4.0	<1	$1.9 \times 10^{2}$	<1	11	
5b**	3.0	1.0	4.0	<1	$2.3 \times 10^{2}$	<1	21	
6	7.9	7.9	15.8	-	-	-	-	
	Ammonia borane							
	-	1.0	1.0	$2.0 \times 10^{1}$	$2.5 \times 10^{3}$	$5.4 \times 10^{2}$	<1	
	Ethylenediamine borane							
	40.0***	-	40.0***	<1	<1	$1.9 \times 10^{2}$	<1	

Table 2.

\*corresponds to total loading of alkylamineborane and ammonia borane

\*\*fuel blend consisting of low density ammonia borane instead of the as received variety

\*\*\*total mmoles of ethylenediamine borane are reported as mmols B-N functionalities.

# **Characterization of Liquid-Phase Decomposition Products**

FTIR and <sup>1</sup>H, <sup>11</sup>B, <sup>1</sup>H{<sup>11</sup>B}, and <sup>11</sup>B{<sup>1</sup>H} NMR were used to characterize the liquid phase products of thermolytic decomposition.  $C_6D_6$  was the solvent used unless otherwise noted

















# **GPC/SEC Measurements**

An Agilent 1100 LC was equipped with two PLgel 5µm (50Å 300 x 7.5mm) columns kept at constant temperature (30 °C) and an RID kept at 40 °C. Distilled or anhydrous grade THF (Mettler-Toledo Coulumbic Karl Fisher titrator measurements are below detection limit [1 ppm]

with 4-5 g samples), kept under a constant UHP Ar purge, was used as the mobile phase. Calibration was performed with Agilent polystyrene standards prepared with dry THF at ~2 mg/mL. The following is representative calibration curve generated from Agilent's Chemstation GPC data analysis add-on (revision B.01.02):



A flow rate of 0.5 mL/min was used for known/unknown sample evaluation. All samples were prepared in dry THF and filtered through a 0.2  $\mu$ m filter prior to data collection.

				Molar Masses of Selected Peaks			
Run	M <sub>p</sub>	M <sub>w</sub>	M <sub>n</sub>	M <sub>1</sub>	M <sub>2</sub>	M <sub>3</sub>	M <sub>4</sub>
1 'G'	350	340	340	350			
2	350	440	392	350			
3	360	550	433	360	310	260	200
4 'H'	470	460	460	470			
5	490	630	570	490			
6	490	710	592	490	390	290	

Table 3

Run #1: evaluation yielded a unimodal product. Example trace below.  $M_p$  = 350 amu,  $M_w$  = 340 amu,  $M_n$  = 340.



Run #2: evaluation yielded a multimodal product with one predominant peak. Example trace below.  $M_p$  = 350,  $M_w$  = 440,  $M_n$  = 392.



Run #3: evaluation yielded a multimodal product. Example trace below.  $M_p = 360$ ,  $M_w = 550$ ,  $M_n = 433$ . Molar masses corresponding to the four most clearly defined peaks are 200, 260, 310 and 360 amu.



Run #4: evaluation yielded a unimodal product. Example trace below.  $M_p$  = 470,  $M_w$  = 460,  $M_n$  = 460.



Run #5: evaluation yielded a multimodal product with one predominant peak. Example trace below.  $M_p = 490$ ,  $M_w = 630$ ,  $M_n = 570$ .



Run #6: evaluation yielded a multimodal product. Example trace below.  $M_p$  = 490,  $M_w$  = 710,  $M_n$  = 592. Molar masses corresponding to the three most clearly defined peaks are 290, 390, and 490 amu.



### **DLS Measurements**

Measurements were performed on a Melvern Zetasizer Nano ZS at  $\lambda = 633$  nm. Each measurement consisted of six 15 s scans. The sample was thermostated to 25 °C. The sample RI was set to 1.586. Averages of hydrodynamic radii were compared to an Aldrich Technologies certified 550 Mp poly(methylmethacrylate) (PMMA) standard and a Varian certified 5000 Mp PMMA standard. All samples were prepared under inert atmosphere and in anhydrous grade THF. Cuvettes with gas-tight apertures were used, which were rinsed 2X with 0.2 µm filtered THF prior to sample addition. Samples were prepared at 10 wt% in THF. After being vigorously shaken ca. 30 s, they were passed through a 0.2 µm syringe filter directly into a cuvette and analyzed by DLS.





### **ESI-MS** Measurements

A Varian 500 series ESI-MS instrument was used. The mass range is 50-2000 amu and the resolution is <0.5 amu Samples were prepared at 1 mg/mL in either anhydrous grade MeCN or anhydrous grade THF (Mettler-Toledo Coulumbic Karl Fisher titrator measurements are below detection limit [1 ppm] with 4-5 g samples), and passed through a 0.2  $\mu$ m syringe filter.

Run #1: mass-spectrum. The base peak corresponds to tris(3-methoxypropyl)borazine plus sodium (residual in MeCN).



Run #4: mass-spectrum. The base peak corresponds to trishexylborazine  $(M - 1)^+$ , while the peak at m/z = 372.3 corresponds to trishexylborazine plus potassium (from Fischer Scientific 3A molecular sieves).





monia Borane Optical View. Top = As Received, Bottom = Precipitated



#### Hydrogen Storage Center of Excellence

Flow through reactor experiments were performed using a helical flow reactor and a packed-bed reactor. All reactor experiments were performed in the downward flow orientation.



Flow-through reactor setup employed for thermal dehydrogenation of **D** 

<sup>11</sup>B NMR of spent reactor fuel

