Polymers *Very Important Paper*

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Polyboramines for Hydrogen Release: Polymers Containing Lewis Pairs in their Backbone

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***Abstract:** The one-step polycondensation of diamines and diboranes triggered by the in situ deprotonation of the diammonium salts and concomitant reduction of bisboronic acids leads to the assembly of polymer chains through multiple Lewis pairing in their backbone. These new polyboramines are dihydrogen reservoirs that can be used for the hydrogenation of imines and carbonyl compounds. They also display a unique dihydrogen thermal release profile that is a direct consequence of the insertion of the amine–borane linkages in the polymeric backbone.*

Boron-based polymers have been the focus of growing attention because they exhibit outstanding properties such as photoluminescence, electroluminescence, nonlinear optical properties, and n-type semiconductivity that make them well-suited as materials for organic electronics, imaging, or ion and molecule sensing.[1] A vast majority of these polymers are derived from boron-containing monomers polymerized by free-radical additions, or organometallic coupling reactions;[1,2] that is, their main chain contains only covalent bonds. In addition, polymeric boron nitrides are obtained from the dehydrogenation of ammonia borane ($NH_3{\cdot}BH_3$), and are thus crucial materials for dihydrogen-storage purposes.[3,4] Indeed, the storage and controlled release of dihydrogen has become an essential area of research to address the ever-growing energetic demand. While ammonia borane was identified early on as an ideal candidate to constitute a H_2 reservoir because of its maximal storage capacity (19.6 wt%. H_2),[3–5] its shortcomings such as poor processability, foaming, corrosive or toxic emissions, as well as troublesome material recycling have been identified. As part of our program devoted to the use of Lewis bases to access new reactivities at boron,[6] we set out to investigate the properties of new long-chain boron polymers built from monomers assembled through Lewis pairs. We selected N and B hydrogen-disubstituted amine boranes (ABs) in poly-Lewis paired polymers as a starting point (see Figure 1). There are very few reports on the synthesis of poly(amine-borane)s or polyboramines, and examples are limited to the use of bipyridines or pyrazines with aryl/aliphatic bisborane monomers.[7] The target application of these systems is essentially the elaboration of dynamic polymers[7] that have potentially interesting fluorescent properties.[1,2f] Most of these polymers are synthesized by precipitation methods and have poor stability in solution. Therefore, none of them was extensively characterized. Moreover, substituted ABs were employed in those cases.[7] Thus, none of the few materials obtained could be engaged in further reactions. A report by Manners et al. mentions the Ir-catalyzed synthesis of polyaminoboranes which are covalently bonded polymers, that is, analogues of polyolefins, but high temperatures are required to achieve the dehydrogenation of polyaminoboranes.[8]

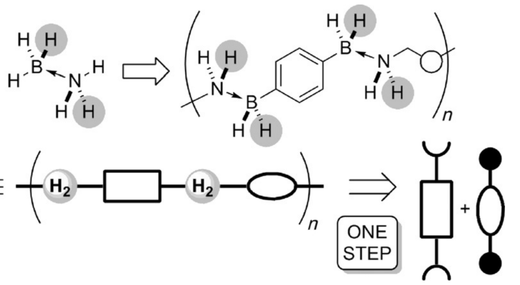

Figure 1. General strategy for the synthesis of H_2-releasing polyboramines.

Herein we report a new type of polyboramines, comprising bis-hydrogenated N and B atoms, obtained in one step from commercially available simple monomers by using unusual heterogeneous conditions (Figure 1). The polymer is soluble and stable in THF and DMSO. This new type of boron-based polymer was evaluated as a reactive material in hydrogen-transfer reactions based on ammonia borane chemistry. We also investigated the potential of these polyboramines as dihydrogen-storage materials, in particular the influence of the polymer chains on the dehydrogenation profile (Figure 1).

To access the polymers, an AA/BB type polycondensation strategy was selected (Figure 1), using simple bisboronic acids or esters and diammonium chlorides as difunctional monomers, starting from a heterogenous suspension of insoluble starting materials in THF.[9] This approach is versatile and

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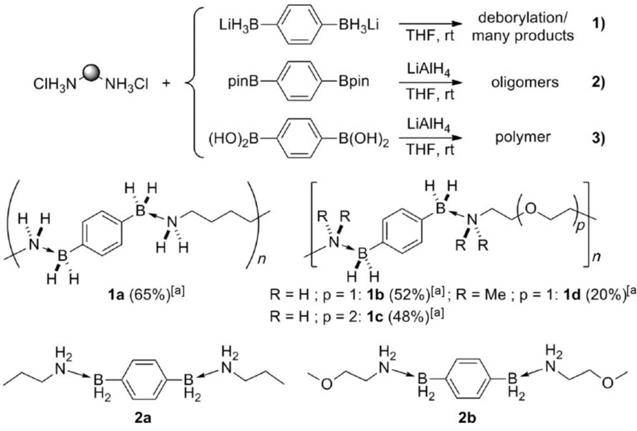
uses readily accessible building blocks.[10] However it requires a precise stoichiometry to achieve high molar masses. Aliphatic diamines were chosen based on electronic considerations. As good Lewis bases, they provide increased stability for the amine–borane bond. Bisboronic species with a *para*-phenylene motif were selected to avoid potential oxidative deborylation and provide rigidity to the polymer.

The polymerization relies on the formation of the key Lewis pairs. We chose to develop a simple, ideally one-step, synthetic route.[9] The reaction had to be 100% selective and quantitative for an efficient polycondensation. The acid/base reaction of borohydrides and ammonium salts releases dihydrogen gas as a side-product. We hoped to harness this favorable entropic driving force toward the formation of the polymer.

We first attempted to generate the desired borohydrides in a separate flask from the bisboronic acid (or pinacol ester) precursor and to mix the resulting crude product with the diammonium salt. This procedure, however, led to only minute amounts of polymers (reaction 1, Scheme 1). Various side-reactions occurred, among which significant deborylation, which is likely due to the prolonged exposure of the boron-containing molecules to the hydride, leading to a stoichiometric imbalance that is detrimental to the polycondensation. We therefore decided to trigger the reduction of the diboronic acid precursor with $LiAlH_4$ in THF in the presence of the diammonium salt by a one-pot procedure (reactions 2–3, Scheme 1). Indeed, we surmised that the direct deprotonation of the ammonium by the basic hydride ($LiAlH_4$) would take place first to generate an amine–alane in situ,[11] which would lead to the ABs by reduction of the boronic acids. This step also generates insoluble aluminum oxides. When using this procedure, deborylation was largely avoided, but the bisboronic pinacol ester precursors gave only short-chain oligomers (reaction 2, Scheme 1).



Scheme 1. Synthesis of the polyboramines. [a] Yield of isolated product after precipitation and filtration.

By switching to the *para*-phenylene-bisboronic acid as bisborane precursor, we were able to generate longer polymer chains (reaction 3, Scheme 1, $M_n > 10^5\, g\,mol^{-1}$, see Figure 2). The polymer was isolated from the insoluble precipitated fraction by filtration followed by several washes. Part of the product remained trapped in the filter cake, thus decreasing the yield of isolated material. A white powder was obtained after evaporation of the volatile components. However, even after 2 days under high vacuum (10^{-5} mbar), the material still retained some THF. TGA analyses indicated that the vast majority of the lithium and aluminum salts remained in the insoluble fraction (less than 4% residues, after heating the polymer to 900 °C). In contrast, when *para*-phenylenebisboronic pinacol ester was used as a precursor, a large amount of salts was detected (up to 30%), together with residual pinacol. In the latter case, AB oligomers were isolated as a white solid.

We synthesized four polymers by using our method. Polymers **1a**, **1b**, and **1c** have respectively zero, one, and two oxygen atoms in the aliphatic fragment. They were obtained in 65%, 52%, and 48% yields, respectively. Starting from a tertiary diammonium salt, polymer **1d** was isolated in 20% yield. We believe this behavior is due to the increased steric hindrance on the nitrogen atom, which lowers the stability of the Lewis pair, and thus of the polymer. The presence of diborylaryl chromophores in the polymer main chain means that the products are fluorescent white powders (see the Supporting Information for **1a** and **1b**).[1] Compounds **1a** and **1b** both exhibit a glass transition temperature (T_g) of about 60 °C (63 °C and 60 °C, respectively, see Figures S43, S44, and S52). These average values might be a consequence of rigidity induced by the aromatic linker and flexibility by the aliphatic one. However, after solvent removal, the crude **1a** becomes poorly soluble in THF. The extra oxygen atoms in **1b** significantly enhanced the solubility of the material at low temperatures in THF. This behavior led us to develop conditions for SEC characterization. We used THF with 1 wt% tetra *n*-butyl ammonium bromide (TBAB) as eluent. TBAB is a salt that shields the chains from intermolecular dipolar interactions, thus breaking up the aggregates and enabling total elution of the polymers. The molar mass could thus be estimated ($> 10^5\, g\,mol^{-1}$, based on polystyrene standards).

The ^{11}B NMR spectra of polymers **1a–d** display a broad singlet from $\delta = -3$ to around -12.0 ppm. The B−H bonds were identified by ^1H NMR (broad singlet at $\delta = 2.36$ ppm) and IR spectroscopy ($\nu(B\text{–}H) = 2313\ cm^{-1}$, see pp. S19–23 and S46 in the Supporting Information).

We next investigated the thermal behavior of the boron-containing materials, and particularly their dehydrogenation profile. Polyboramines **1a** and **1b** can liberate H_2 at 96 °C and 95 °C, which was evidenced by temperature-programmed desorption (TPD) measurements, on an apparatus specifically set up to evidence H_2 desorption from materials. This result was further supported by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC, Figure 2, and pp. S35–S42 in the Supporting Information). These H_2 release temperatures are lower than that of any of the ABs reported to date for H_2 storage,[4] and is also much lower than the dehydrogenation temperature of the isolated molecular analogues (see pp. S44–S45 in the Supporting Information), without catalysis.[12] The polyaminoboranes[8] generated after dehydrogenation retain a partial solubility in THF. They

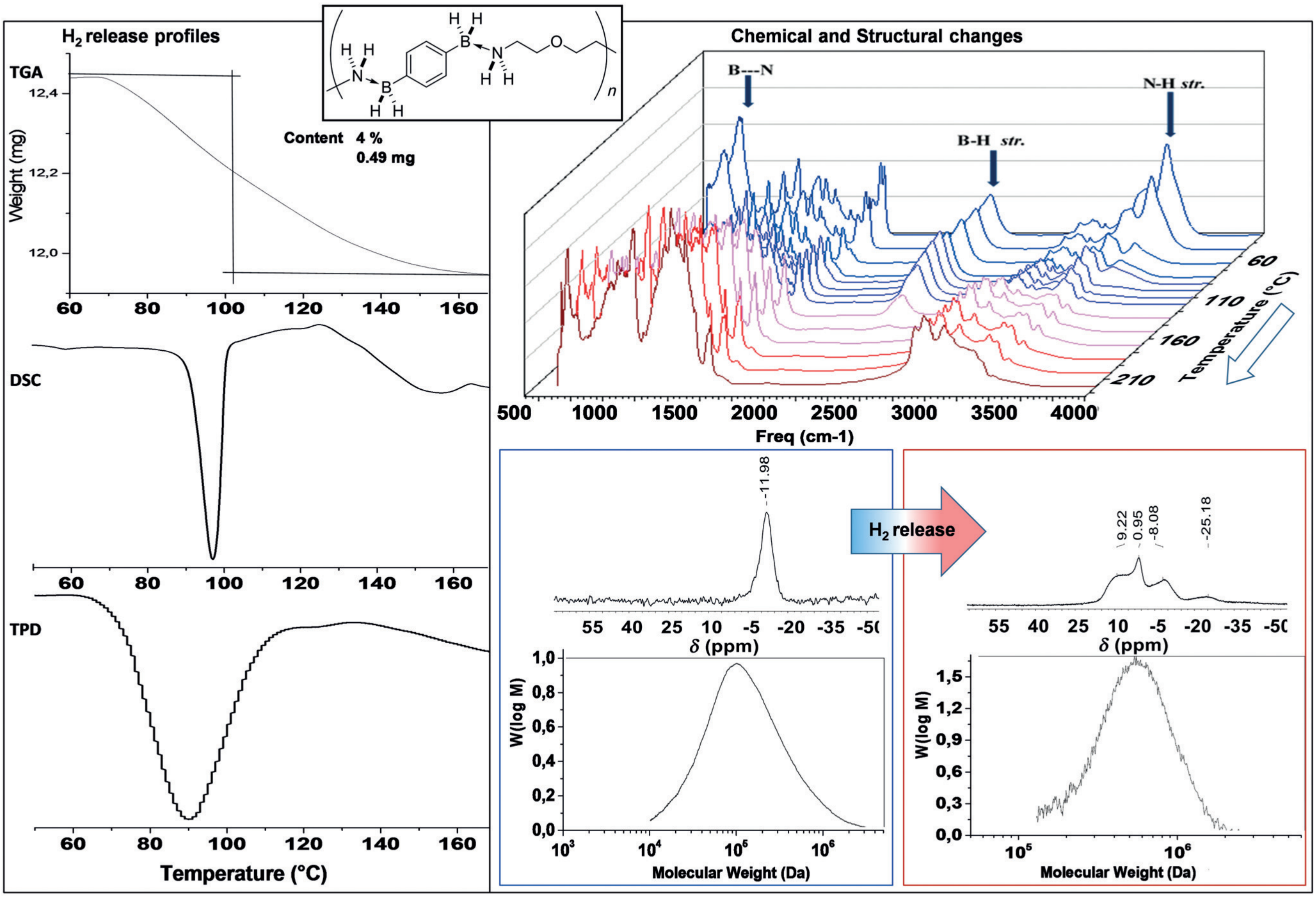


Figure 2. Dehydrogenation profile of polyboramine **1b** with multiple characterization techniques: TGA, DSC, and TPD analyses (left), VTIR (top-right corner), and ^{11}B NMR and SEC analyses associated with H_2 release (2 equivalents, bottom-right corner).

undergo a second dehydrogenation to form the fully dehydrogenated polyborimines at around 160 °C. The latter products are soluble in LiBr-containing DMF (0.5 wt%) at 60 °C to prevent significant aggregation. SEC analysis showed that much higher molar masses than those of the starting polyboramines were present ($>10^5$ g mol^{-1}; Figure 2). The dehydrogenation appears to increase the molar masses rather than induce chain scissions. This behavior is likely due to the intermolecular interactions between the borimines.[13]

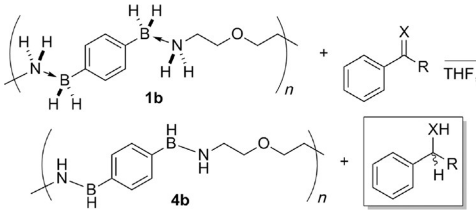
The DSC profiles of polyboramines **1a** and **1b** showed an endothermic peak below 100 °C. This phenomenon has been attributed to dehydrogenation (as evidenced by comparison of DSC, TGA, TPD, in situ variable-temperature IR data and recrystallization studies of **1b**, see Figure 2 (left and top-right) and Figure S49) rather than melting as observed in **2a** (Figures S48, S50, S51). The H_2-release profiles of the polyboramines are endothermic (Figure S43–S44), and are exothermic for the molecular analogues (Figure S45). This feature will be discussed below.

The combined analyses show that the insertion of ABs into polymeric chains completely changes their behavior and generates properties that are distinct from those of their molecular analogues.[12] In order to establish further the scope of this reactivity change, we examined the transfer hydrogenation of imines, ketones, and aldehydes. For this purpose, we selected the most soluble polymer **1b** (Table 1).

The polymer was first mixed with diphenylimine at 40 °C in THF (Table 1, entry 1). This led to a conversion of 52 % into the desired amine. The selectivity (against tetrachloroethane as internal standard) was 100 %, thus suggesting that no decomposition occurred.

By increasing the stoichiometry of **1b**, the reduction proceeded smoothly and quantitatively at room temperature (Table 1, entry 2). Use of different *N*-alkyl imines resulted in equally high yields; however, in these cases, the temperature had to be slightly increased (40 °C, entries 5–8). In contrast, the more activated *N*-phenylsulfonyl phenylimine reacted very efficiently at lower stoichiometry and at room temperature (entry 9). The polymer was also able to hydrogenate benzaldehyde (entry 11) and acetophenone (entry 12) in equally high yields at the lower polymer stoichiometry. As expected, the ketone reacted less rapidly and required heating, however, its use resulted in the direct formation of alcohols as reduction products. We next carried out control experiments. Almost no imine reduction took place with borazane $NH_3{\cdot}BH_3$ at 40 °C (9 % conv., entry 4).[14] Benzaldehyde was consumed, but no free alcohol was observed, thus suggesting the product remains bound to boron in this case (entry 12). No reactivity difference was observed when the

Table 1: Transfer hydrogenation from polyboramine **1b** as H_2 donor.



Entry[a]	X	R	T [°C]	Conv. [%][b]	Yield [%][b]
1	–NPh	H	40	52	52
2[c]	–NPh	H	RT	> 99	> 99
3[d]	–NPh	H	40	79	39
4[e]	–NPh	H	40	9	9
5	–NMe	H	40	77	77
6[c]	–NMe	H	40	> 99	> 99
7	–N*t*Bu	H	40	65	63
8[c]	–N*t*Bu	H	40	> 99	> 99
9	–NSO_2Ph	H	RT	> 99	> 99
10	O	Me	40	> 99	> 99
11	O	H	RT	> 99	> 99
12[e]	O	H	RT	80	0

[a] Conditions: **1b** (0.04 mmol/unit), imine (0.08 mmol), $[D_8]$THF (0.6 mL), 12 h; [b] determined by ^{1}H NMR with $C_2H_2Cl_4$ as internal standard (4.7 μL, 0.045 mmol); [c] **1b** (0.08 mmol/unit); [d] **2b** was used (0.04 mmol); [e] borazane was used (0.08 mmol).

reactions were performed in the presence of LiCl as additive (see the Supporting Information). Thus, the residual salts in polyboramines do not influence the reactivity.

With a molecular equivalent of the polymer (**2b**, see Scheme 1), the reduction was faster than with borazane or **1b** (79% conversion; Table 1, entry 3), but it was accompanied by a great deal of degradation. Finally, the polymer resulting from the reduction was characterized by NMR spectroscopy, which showed that only the first equivalent of H_2 was transferred to the substrates.[15]

The polyboramines are thus more than the sum of their monomeric equivalents. The polymer chains seem to have a specific effect that is especially marked for the thermal dehydrogenation. To understand better the phenomena linked to H_2 release, we carried out theoretical modeling. The mechanisms of the thermal dehydrogenation of AB systems involve multiple pathways.[16–18] A selection of four energetically favored pathways for $[PhBH_2{-}NH_2(nPr)]$ was thus computed by using DFT calculations (Figure 3). This model fragment was chosen because it was closest to our real system. We used the B97D3 functional, which has been employed by Grimme et al. to compute frustrated Lewis pairs,[19] to best depict the Lewis base/acid adducts.

Our starting point is the AB dimer **dim** involving dihydrogen-bonding interactions (DHB) between the N–H and B–H moieties (Figure 3), since it is lower in energy than the monomeric form.[16–18]

An intramolecular reaction leads to molecular hydrogen formation via **TS-dim** ($\Delta H = 40.6$ kcal mol^{-1}). Alternatively, the loss of DHB interactions to form monomeric **AB-mon** will lead to **TS-uni** (see the Supporting Information) for H_2 release ($\Delta H = 50.6$ kcal mol^{-1}). Taking into account the barrier heights, these two pathways are thus unlikely. Therefore, the plausible pathway involves the cleavage of a N–B bond (**TS-I**; see the Supporting Information), thus leading to key intermediate **I** (Figure 3), which contains both a three-center two-electron B–H–B bond and an NH–N hydrogen bond. From there one can envisage two pathways, which start from conformers **I** and **I′**, evidenced by Dixon et al. as the two reactive conformers that lead to dehydrogenation.[17] From **I**, **TS-II** features a six-membered transition state ($\Delta H = 30.2$ kcal mol^{-1}), which leads to H_2 release and formation of aminoborane **II** (see the Supporting Information). Intermediate **II** promptly dimerizes through **TS-II-dim**, leading to the thermodynamic product **II-dim**. Alternatively, conformer **I′** produces an ionic diammoniate of diborane ion-pair species (**DADB**) through **TS-II′** ($\Delta H = 34.8$ kcal mol^{-1}; see the Supporting Information). From **DADB**, H_2 release is subsequently achieved by **TS-III′** ($\Delta H = 25.3$ kcal mol^{-1}; see the Supporting Information).

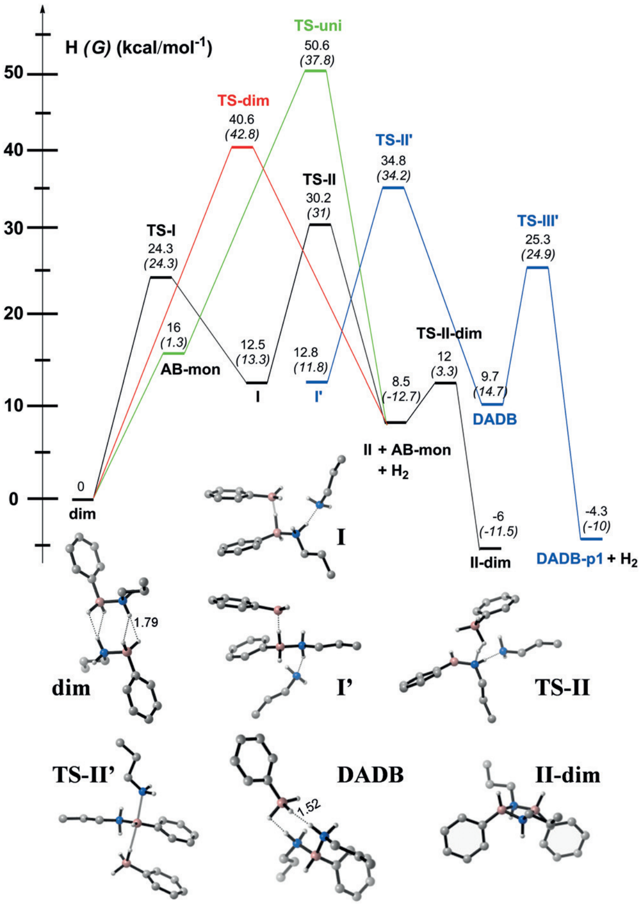


Figure 3. Comparison of the energy profiles leading to H_2 release. Selected intermediates of the two lower energetic pathways (black and blue) are represented. Only H atoms linked to N (blue) and B (red) are shown for clarity.

It is crucial to use a functional such as B97D3 that properly takes in account dispersion contributions (D3BJ).[19] This correction led us to obtain energetic barriers for the H_2 release ($\Delta H = 30$–34 kcal mol^{-1}) which are consistent with the experimental observations. DSC and TPD analyses of the molecular AB showed that the polymer has a higher propensity to dehydrogenate compared to its molecular analogue (see above). We believe that the polymer chains favor the initial cleavage of the N−B bond because of entropic effects. Then, it is unlikely that ion pairing can occur in the polymer, since this would require substantial, energetically unfavorable chain rearrangements. Thus, it is likely that **TS-II** is substantially lower in energy in the polymers. Conversely, a cooperative ziplike behavior arising from the intermolecular polymer chain entanglement, which preorganizes the AB pairs might also be at play. In that case, direct hydrogen release via a neutral intermediate would be again favored. This specificity of the polymer chains is the reason for the lower dehydrogenation temperature. Similarly, the final pseudodimerization leading to **II-dim** is likely to be strongly affected by the polyboramine macromolecular nature (long chains, entanglement), which conceivably would lower the associated energetic gain. This would result in an overall endothermic process, with **II-dim** higher in energy, in contrast to the molecular case. The entropic factor for the polymer is also likely to disfavor dimerization.[20]

To conclude, we have synthesized polyboramine polymers by simple treatment of bisboronic building blocks and bisammonium salts with $LiAlH_4$. This procedure allowed us to access Lewis pair assembled H_2-storing polymers with molar masses high enough for entanglement. The polymers retained a solubility in polar organic solvents and are amorphous ($T_g \approx 60\,°C$), potentially enabling their processability. They hydrogenate imines, aldehydes, and ketones under mild conditions, and perform better than their molecular analogues. Furthermore, the polyboramines displayed unique thermal behavior. The thermal dehydrogenation occurs below 100 °C and is endothermic, in stark contrast to the regular ABs used for this purpose. This is a direct consequence of the incorporation of the ABs into polymeric chains. We believe that this effect should be of interest for other areas in boron, polymer, and dihydrogen-storage chemistry.

Acknowledgements

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[1] a) F. Jäkle, *Chem. Rev.* **2010**, *110*, 3985; b) C. D. Entwistle, T. B. Marder, *Angew. Chem. Int. Ed.* **2002**, *41*, 2927; *Angew. Chem.* **2002**, *114*, 3051; c) C. D. Entwistle, T. B. Marder, *Chem. Mater.* **2004**, *16*, 4574.

[2] a) Y. Qin, C. Cui, F. Jäkle, *Macromolecules* **2008**, *41*, 2972; b) F. Cheng, E. M. Bonder, F. Jäkle, *J. Am. Chem. Soc.* **2013**, *135*, 17286; c) W. Wan, F. Cheng, F. Jäkle, *Angew. Chem. Int. Ed.* **2014**, *53*, 8934; *Angew. Chem.* **2014**, *126*, 9080; d) F. Guo, X. Yin, F. Pammer, F. Cheng, D. Fernandez, R. A. Lalancette, F. Jäkle, *Macromolecules* **2014**, *47*, 7831; e) F. Cheng, W.-M. Wan, Y. Zhou, X.-L. Sun, E. M. Bonder, F. Jäkle, *Polym. Chem.* **2015**, *6*, 4650; f) A. W. Baggett, F. Guo, B. Li, S.-Y. Liu, F. Jäkle, *Angew. Chem. Int. Ed.* **2015**, *54*, 11191; *Angew. Chem.* **2015**, *127*, 11343.

[3] a) M. Zahmakiran, T. Ayvalı, K. Philippot, *Langmuir* **2012**, *28*, 4908; b) C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2003**, *125*, 9424; c) T. B. Marder, *Angew. Chem. Int. Ed.* **2007**, *46*, 8116; *Angew. Chem.* **2007**, *119*, 8262.

[4] a) A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners, *Chem. Rev.* **2010**, *110*, 4023; b) C. W. Hamilton, R. T. Baker, A. Staubitz, I. Manners, *Chem. Soc. Rev.* **2009**, *38*, 279.

[5] a) B. Carboni, L. Monnier, *Tetrahedron* **1999**, *55*, 1197; b) D. J. Heldebrant, A. Karkamkar, J. C. Linehan, T. Autrey, *Energy Environ. Sci.* **2008**, *1*, 156.

[6] a) S.-H. Ueng, M. Makhlouf Brahmi, É. Derat, L. Fensterbank, E. Lacôte, M. Malacria, D. P. Curran, *J. Am. Chem. Soc.* **2008**, *130*, 10082; b) J. Lalevée, S. Telitel, M.-A. Tehfe, J. P. Fouassier, D. P. Curran, E. Lacôte, *Angew. Chem. Int. Ed.* **2012**, *51*, 5958; *Angew. Chem.* **2012**, *124*, 6060; c) S. Telitel, A.-L. Vallet, S. Schweizer, B. Delpech, N. Blanchard, F. Morlet-Savary, B. Graff, D. P. Curran, M. Robert, E. Lacôte, J. Lalevée, *J. Am. Chem. Soc.* **2013**, *135*, 16938.

[7] a) S. Itsuno, T. Sawada, T. Hayashi, K. Ito, *J. Inorg. Organomet. Polym.* **1994**, *4*, 403; b) Y. Chujo, I. Tomita, N. Murata, H. Mauermann, T. Saegusa, *Macromolecules* **1992**, *25*, 21; c) N. Matsumi, Y. Chujo, *Macromolecules* **1998**, *31*, 3802; d) M. Grosche, E. Herdtweck, F. Peters, M. Wagner, *Organometallics* **1999**, *18*, 4669; e) E. Sheepwash, V. Krampl, R. Scopelliti, O. Sereda, A. Neels, K. Severin, *Angew. Chem. Int. Ed.* **2011**, *50*, 3034; *Angew. Chem.* **2011**, *123*, 3090.

[8] a) A. Staubitz, A. P. Soto, I. Manners, *Angew. Chem. Int. Ed.* **2008**, *47*, 6212; *Angew. Chem.* **2008**, *120*, 6308; b) J. R. Vance, A. P. M. Robertson, K. Lee, I. Manners, *Chem. Eur. J.* **2011**, *17*, 4099; c) E. M. Leitao, T. Jurca, I. Manners, *Nat. Chem.* **2013**, *5*, 817.

[9] a) G. W. Schaeffer, E. R. Anderson, *J. Am. Chem. Soc.* **1949**, *71*, 2143; b) P. Veeraraghavan Ramachandran, B. C. Raju, P. D. Gagare, *Org. Lett.* **2012**, *14*, 6119.

[10] a) C.-T. Yang, Z.-Q. Zhang, H. Tajuddin, C.-C. Wu, J. Liang, J.-H. Liu, Y. Fu, M. Czyzewska, P. G. Steel, T. B. Marder, L. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 528; *Angew. Chem.* **2012**, *124*, 543; b) H. Chen, S. Schlecht, T. C. Semple, J. F. Hartwig, *Science* **2000**, *287*, 1995; c) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890.

[11] a) J. K. Ruff, M. F. Hawthorne, *J. Am. Chem. Soc.* **1960**, *82*, 2141; b) B. Németh, J.-P. Guégan, T. Veszprémi, J.-C. Guillemin, *Inorg. Chem.* **2013**, *52*, 346.

[12] a) A. J. V. Marwitz, M. H. Matus, L. N. Zakharov, D. A. Dixon, S.-Y. Liu, *Angew. Chem. Int. Ed.* **2009**, *48*, 973; *Angew. Chem.* **2009**, *121*, 991; b) W. Luo, P. G. Campbell, L. N. Zakharov, S.-Y. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 19326; c) L. Zhang, S. Li, Y. Tan, Z. Tang, Z. Guo, X. Yu, *J. Mater. Chem. A* **2014**, *2*, 10682; d) C. C. Chong, H. Hirao, R. Kinjo, *Angew. Chem. Int. Ed.* **2014**, *53*, 3342; *Angew. Chem.* **2014**, *126*, 3410; e) G. Chen, L. N. Zakharov, M. E. Bowden, A. J. Karkamkar, S. M. Whittemore, E. B. Garner, T. C. Mikulas, D. A. Dixon, T. Autrey, S.-Y. Liu, *J. Am. Chem. Soc.* **2015**, *137*, 134.

[13] The polymers may crosslink, see some proposed structures in the Supporting Information (p. S53, Figure S66).

[14] X. Yang, L. Zhao, T. Fox, Z.-X. Wang, H. Berke, *Angew. Chem. Int. Ed.* **2010**, *49*, 2058; *Angew. Chem.* **2010**, *122*, 2102.

[15] ^{11}B NMR spectroscopy showed that after 50 min, polyboramine **1b** was converted into **4b**. See Figure S39.
[16] a) B. L. Dietrich, K. I. Goldberg, D. M. Heinekey, T. Autrey, J. C. Linehan, *Inorg. Chem.* **2008**, *47*, 8583; b) T. Kakizawa, Y. Kawano, K. Naganeyama, M. Shimoi, *Chem. Lett.* **2011**, *40*, 171; c) T. Banu, K. Sen, D. Ghosh, T. Debnath, A. K. Das, *RSC Adv.* **2014**, *4*, 1352; d) K. Sen, T. Banu, T. Debnath, D. Ghosh, A. K. Das, *RSC Adv.* **2014**, *4*, 21924.
[17] a) M. T. Nguyen, V. S. Nguyen, M. H. Matus, G. Gopakumar, D. Dixon, *J. Phys. Chem. A* **2007**, *111*, 679; b) R. G. Potter, D. M. Camaioni, M. Vasiliu, D. Dixon, *Inorg. Chem.* **2010**, *49*, 10512; c) D. Dixon, M. Gutowski, *J. Phys. Chem. A* **2005**, *109*, 5129.
[18] a) E. M. Leitao, N. E. Stubbs, A. P. M. Robertson, H. Helten, R. J. Cox, G. C. Lloyd-Jones, I. Manners, *J. Am. Chem. Soc.* **2012**, *134*, 16805; b) A. Staubitz, M. Besora, N. J. Harvey, I. Manners, *Inorg. Chem.* **2008**, *47*, 5910.
[19] S. Grimme, H. Kruse, L. Goerigk, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 1402; *Angew. Chem.* **2010**, *122*, 1444.
[20] The transition states of the dehydrogenation of the molecular model are barely affected by the entropy (S), since they maintain the same molecularity. See Figure 3, where the $\Delta H^{\neq}$ and $\Delta G^{\neq}$ values are similar.

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