BN Polymers

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Poly(iminoborane)s: An Elusive Class of Main-Group Polymers?

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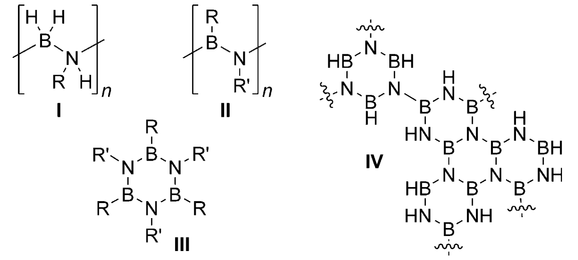
Dedicated to Professor Peter Paetzold

Abstract: *The significance of inorganic main-group polymers is demonstrated most clearly by the commercial relevance of polysiloxanes (silicones). Organoboron-based materials such as π-conjugated organoborane polymers and BN-doped polycyclic aromatic hydrocarbons are currently attracting considerable attention. Surprisingly, poly(iminoborane)s (PIBs; $[BRNR']_n$), that is, the parent unsaturated BN polymers, which are formally isoelectronic to polyacetylene, have not been convincingly characterized thus far. Herein, we present the synthesis and comprehensive characterization of a linear oligo(iminoborane), which comprises a chain of 12–14 BN units on average. With our synthetic approach, unwanted side reactions that result in borazine formation are effectively suppressed. Supporting DFT and TD-DFT calculations provide deeper insight into the microstructure and the electronic structure of the oligomer.*

Inorganic main-group polymers, that is, polymers with a backbone exclusively composed of main-group elements other than carbon, often show useful properties and functions that complement those of organic macromolecules.[1] Prominent examples are the well-known polysiloxanes (silicones). Organic–inorganic hybrid polymers with boron atoms incorporated into a π-conjugated organic framework are currently attracting considerable attention, particularly as a result of their great potential for application in organic optoelectronics or as sensory or imaging materials.[2,3] The development of purely inorganic boron-containing polymers, on the other hand, has proceeded at a markedly slower pace. Well-defined poly(aminoborane)s (PABs, **I**; Scheme 1), that is, polymers with a main chain of catenated σ-bonded boron and nitrogen atoms, became accessible only very recently through work by Manners and co-workers.[4,5] Potential applications suggested for such compounds include their utilization as polymeric precursors to shaped BN ceramics[6] or as piezoelectric materials.[4d] Boron-rich materials are also of interest for use in boron neutron capture therapy (BNCT) for cancer.[7]



Scheme 1. Poly(aminoborane)s (**I**), poly(iminoborane)s (**II**), borazines (**III**) (R, R′ = aryl, alkyl, or H), and an approximate structure of polyborazylene (**IV**).

The B–N bond of aminoboranes shows significant double-bond character. Substitution of C=C units with their isoelectronic and isosteric B–N units in mono- and polycyclic aromatic hydrocarbons (PAHs) has emerged as a viable strategy to produce novel molecular hybrid compounds that show structural similarities to their all-carbon congeners but in many cases fundamentally altered electronic properties.[2d,8,9] Against this background, it seems surprising that the current state of knowledge on polymers with unsaturated BN units is rather limited.[2d,10,11] Moreover, the inorganic parent unsaturated BN polymers, poly(iminoborane)s (PIBs, **II**), have never been convincingly characterized so far, although considerable theoretical interest has been devoted to such species.[12] Formally, PIBs are isoelectronic to polyacetylene, although a considerably larger band gap has been predicted for the parent system, $[BHNH]_n$.[12b]

The term "polyiminoborane" has occurred frequently in the literature in the context of dehydrogenation studies of ammonia borane ($NH_3{\cdot}BH_3$, AB). The solid-state pyrolysis of AB proceeds through a series of successive dehydrocoupling steps[13] to finally yield hexagonal boron nitride above around 1200 °C.[13b,k,l] The intermediate product formed besides the parent borazine (**III**, R = R′ = H) in the second dehydrogenation step has been described as an insoluble, intractable, amorphous solid of the approximate composition BNH_2. In various publications, this material has been termed "polyiminoborane (PIB)" and/or was referred to with the formula "$[BHNH]_n$".[12f,g,13g,j–l,n,o,14] However, whether it is actually a linear polymer that is formed under these conditions seems questionable. While IR spectroscopy, Raman spectroscopy, and solid-state ^{11}B NMR data for such partially pyrolyzed AB in some cases have been associated with the chemical name polyiminoborane or the formula $[BHNH]_n$,[13j,n,o] state-of-the-art solution- and solid-state ^{11}B and ^{15}N NMR studies have revealed the presence of N_3B and B_3N in addition to N_2BH and B_2NH sites.[13b,e,i,m,p] Therefore, it was recently proposed

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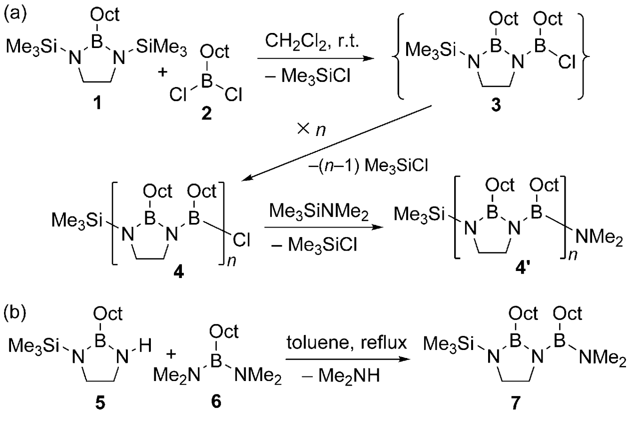
that the structure of this material should better be described as a polyborazylene (**IV**), that is, a poorly-defined macromolecular network of partially fused borazine rings.[13b,i,m,p] In fact, the provided NMR data are remarkably similar to those of a polyborazylene sample prepared through a different route.[15]

Thermolysis of Manners' poly(*N*-methylaminoborane) (**I**, R = CH_3) in solution resulted in depolymerization to give a mixture of low-molecular-weight oligomers and *N,N′N″*-trimethylborazine. The formation of a poly(iminoborane) has not been described.[4d] In the 1980s, Paetzold and co-workers reported on the isolation of waxy materials for which a constitution of linear poly(iminoborane)s (**II**, R = R′ = alkyl) was proposed.[16] These materials were obtained upon the generation of monomeric iminoboranes[17] in the gas phase and subsequent trapping at −196 °C. The products were found to be insoluble in common organic solvents, so their structural characterization was limited. Minor amounts of the corresponding borazines (**III**) additionally formed could be separated by extraction. The given assignment was based on elemental analysis and mass spectrometry data and on the observation that the compound identified as $[EtBNEt]_n$ transformed into hexaethylborazine upon heating above 150 °C. An analogous transformation of the derivative $[^{n}PrBN^{n}Pr]_n$, however, was not achieved.[16a]

Herein, we present the synthesis and comprehensive characterization of a processable oligo(iminoborane) with well-defined microstructure, composed of a chain of 12–14 BN units on average. For this purpose, the unwanted competing side reaction of potential BN monomers to give their cyclic trimers, that is, the respective borazine derivatives (**III**), seemed to be a major hurdle to overcome. We chose a strategy by which possible pathways leading to **III** should be prevented. For this purpose, we introduced an ethylene bridge to link the nitrogen atoms of the monomer. This steric constraint proved effective to preclude any borazine formation. Related approaches have been followed previously by Neilson and Retta, but, to the best of our knowledge, the identification of a poly- or an extended oligo(iminoborane) was not achieved in these studies.[18]

Recently, we presented a novel class of organic–inorganic hybrid polymers comprised of alternating diimidoborane and *para*-phenylene units.[11] The synthesis thereof was achieved using a facile polycondensation process through Si/B exchange with silazane Si−N bond cleavage. For the current study, we adopted this approach: we employed 1,3-bis(trimethylsilyl)-1,3,2-diazaborolidine **1** for polycondensation with dichloroborane **2** (Scheme 2 a). *n*-Octyl side chains (herein denoted as Oct) at boron were chosen in order to impart solubility. Additionally, we prepared compound **7** as a molecular model system (Scheme 2 b).

Monitoring of the reaction of **1** with **2** in CD_2Cl_2 at ambient temperature by $^{11}B\{^1H\}$ and ^1H NMR spectroscopy showed that both **1** and **2** were immediately consumed with initial selective formation of **3** (see Figure S27 in the Supporting Information). Even after short reaction times, the spectra revealed that further oligomerization had occurred. The ^{11}B resonance for the B−Cl end groups of the growing chain (at around 44.5 ppm) continuously decreased in intensity. One broad signal remained in the $^{11}B\{^1H\}$ NMR spectrum for the bulk boron atoms of the oligomer **4**, which in the course of the reaction was shifted slightly upfield to δ = 31 ppm. In the ^1H NMR spectrum, a common signal appeared for the protons of the ethylene bridge, centered at δ = 3.32 ppm. Small peaks at δ = 3.00–3.25 and 3.45–3.65 ppm remained, which we assign to the ethylene protons of the rings at the chain ends. The proton resonance for the $SiMe_3$ end group was detected at δ = 0.15 ppm, and concomitant formation of the volatile condensation byproduct Me_3SiCl was evidenced by its ^1H resonance at δ = 0.45 ppm. Quantitative evaluation of the signals over time revealed that conversion of the reactive groups leveled off at about 85 %, which may be associated with a rate reduction due to a marked increase in the viscosity of the solution. An estimation of the degree of polymerization after 14 days by using Carothers' equation yielded $DP_n \approx 7$. Then, Me_3SiNMe_2 (6 mol %) was added to deactivate the B−Cl end groups of **4**. The end-capped product **4′** was purified by adding the mixture to an excess amount of anhydrous acetonitrile, which resulted in separation of **4′** from solution. This afforded oligo(iminoborane) **4′** as a highly viscous amber fluid in 83 % yield.



Scheme 2. a) Synthesis of oligo(iminoborane) **4** and end-capped derivative **4′**. b) Synthesis of model compound **7** (Oct = *n*-C_8H_{17}).

The hydrolytically sensitive oligomer **4′** was characterized by multinuclear NMR spectroscopy, including ^1H DOSY (Figure S28), mass spectrometry (MS), elemental analysis, gel permeation chromatography (GPC), dynamic light scattering (DLS), small-angle X-ray scattering (SAXS), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA), as well as FTIR and UV/Vis spectroscopy. The GPC trace suggested molecular-weight averages of $M_n = 1800$ and $M_w = 1900$, respectively (Figure 1 a), which is consistent with the presence of a chain of about 6–7 repeat units, corresponding to 12–14 catenated BN units, on average. DLS gave a hydrodynamic radius (R_h) of 2.2 nm for particles of **4′** in *n*-pentane (Figure 1 b). The SAXS measurements revealed that **4′** adopts a slightly anisotropic structure with a small aspect ratio in *n*-pentane. The distance distribution indicates an ellipsoidal structure (prolate) with axes of inertia of 1.7 and 5.0 ± 1.0 nm and a radius of gyration (R_g) of 0.8 nm (Figure 1 d). Fitting to a worm-like chain model gave a rigid rod with 2.7 nm for the extended chain length together with

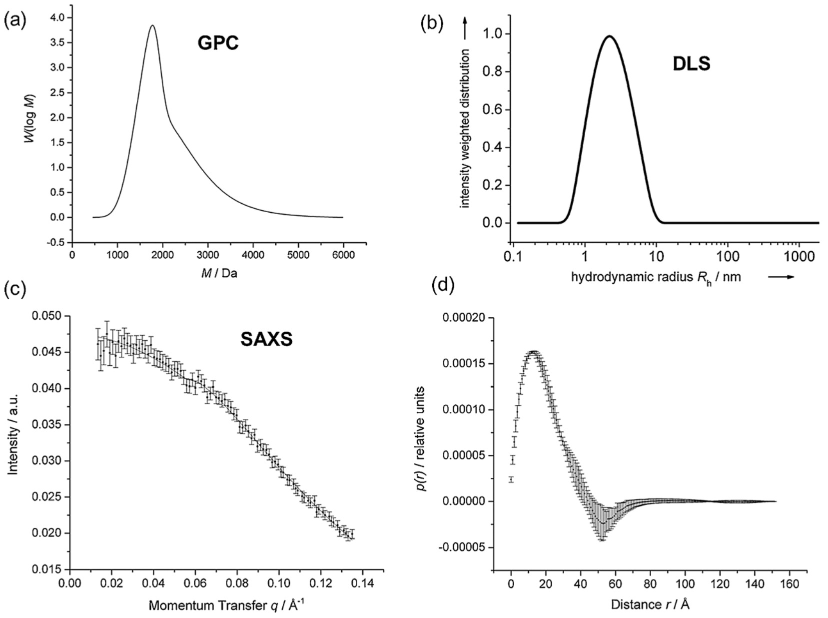


Figure 1. a) Molar-mass distribution of **4′** as determined by GPC (in THF, versus polystyrene standards). b) Intensity-weighted size distribution of **4′** in *n*-pentane by DLS ($\theta = 30°$). c) SAXS profile of **4′** in *n*-pentane, fitted with to worm-like chain model. d) Bayesian-weighted distance distribution function.

a 2.0 nm "worm" diameter (Figure 1c), thus indicating a slightly anisotropic structure due to the longer octyl side groups (contour length of octyl residue: ca. 1 nm) and the limited degree of polymerization (contour length along the backbone of a hexameric structure: ca. 3 nm). By DSC, a glass transition was observed at $T_g = -71\,°C$. The TGA showed that pyrolytic mass loss of **4′** occurs in basically two steps. At 350 °C, the sample loses 72.9 % of its weight, which points to an expulsion of the octyl side groups. In the second step, starting at about 450 °C, a further 9.0 % of mass is gradually lost. This correlates approximately with the mass of the ethylene bridges. The total ceramic yield obtained at 1000 °C amounts to 18.1 %, which is close to the fraction of BN in **4′** (16.3 %). This demonstrates that the ethylene bridges effectively stabilize the backbone of the oligomer. The UV/Vis spectrum of **4′** in THF displayed an absorption band in the UV spectral region at $\lambda_{abs,max} = 269$ nm, that is, slightly red-shifted with respect to that of the molecular model **7** ($\lambda_{abs,max} = 248$ nm).

To gain deeper insight into the geometric and electronic structure of **4′**, we carried out DFT calculations on model oligomers (with methyl instead of octyl groups on the boron) with chain lengths up to $n = 6$ repeat units. In the optimized structures, both the B and the N centers show trigonal planar coordination, with the mean angle sums of 360.0° (at B) and 359.9° (at N), respectively. The N-B-N and the B-N-B planes are not fully coplanar but have an average torsion angle of 19.5° (in the hexamer). This causes a helical structure with a translation of about 5 structural units (2.3 nm) as the most stable conformation.

Vertical singlet excitations were calculated by means of TD-DFT. This revealed a small but continuous red-shift with chain elongation, which levels off at about $n = 6$ to yield an absorption wavelength of 260 nm. This is in good agreement with the experimental absorption maximum of **4′**. The corresponding electronic transition from the HOMO to the LUMO can be classified as a p(N)→p(B)* process. The HOMO constitutes a combination of p orbitals of the nitrogen atoms, while the LUMO is composed of the vacant p orbitals of the boron atoms (for the tetramer, see Figure 2; see also Figures S45–S50). Both orbitals are extended over the entire molecular chain. Consequently, some degree of intramolecular charge transfer (ICT) character from nitrogen to boron is associated with this transition.

This work has provided access to the first well-defined oligo(iminoborane). Since the failure of previous attempts to prepare such species appeared to be ascribed to the facile formation of borazines from rational PIB monomers, we developed an aproach by which this unwanted side reaction was effectively suppressed through the introduction of an ethylene bridge between two N atoms of the monomer. The oligomer obtained comprises a chain of 12–14 BN units on average, which adopts a helical conformation in solution. It absorbs UV light due to an intramolecular charge transfer from nitrogen to boron. Currently, we are exploring routes to high-molecular-weight poly(iminoborane)s, and we are probing the potential of these materials for potential application as electronic materials and ceramic precursors.

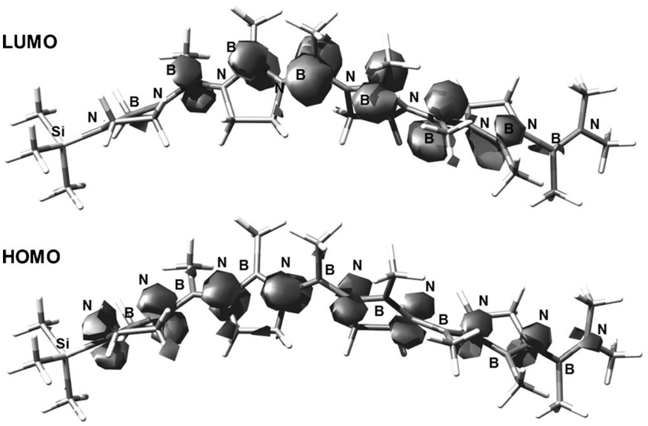


Figure 2. Calculated frontier orbitals (isovalue: 0.032) of an all-methyl-substituted model for **4′** with $n = 4$ (B3LYP-D3/def2-SV(P)).

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Keywords: B—N bonds · boron · hybrid materials · inorganic polymers · main-group polymers

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Communications

BN Polymers

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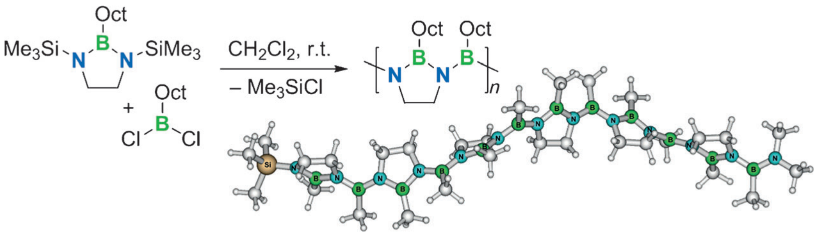
Poly(iminoborane)s: An Elusive Class of Main-Group Polymers?



B-N-B-N-B-N… : Poly(iminoborane)s are elusive inorganic-backbone polymers that are formally isoelectronic to polyacetylene. The first oligo(iminoborane) with a well-defined microstructure was synthesized through an approach that effectively prevents the formation of unwanted cyclic products. The essentially linear oligomer adopts a helical conformation in solution. UV irradiation is associated with N→B charge transfer.