

Министерство науки и высшего образования Российской Федерации

Федеральное государственное бюджетное учреждение науки
Институт проблем химико-энергетических технологий
Сибирского отделения Российской академии наук

УТВЕРЖДАЮ

Директор


С.В. Сысолятин

« 04 » июня 2024 г.

ПРОГРАММА КАНДИДАТСКОГО ЭКЗАМЕНА по дисциплине «Иностранный язык» (английский язык)

1. Естественные науки

(код и наименование области наук)

1.4. Химические науки


(код и наименование группы научных специальностей)


1.4.3. Органическая химия

(код и наименование научной специальности)


Программа кандидатского экзамена рассмотрена и одобрена на заседании Ученого совета ИПХЭТ СО РАН, протокол от 31.05.2024 № 7.

Составители:


Преподаватель отдела аспирантуры, канд. психол. наук  Ю.В. Клюева
Доцент кафедры социально-гуманитарных дисциплин
Бийского технологического института (филиала)

ФГБОУ ВО «Алтайский государственный технический
Университет им. И.И. Ползунова», канд. филол. наук  Е.С. Замашанская

Согласовано:

Зам. директора по научной работе, канд. хим. наук  В.В. Малыхин

Ученый секретарь, канд. хим. наук  А.Г. Суханова

Заведующая отделом аспирантуры, канд. экон. наук  Н.В. Волкова

Бийск 2024

Введение

Настоящая программа кандидатского экзамена разработана для научной специальности 1.4.3 Органическая химия в соответствии с Положением о перечне кандидатских экзаменов, процедуре сдачи кандидатских экзаменов и прикреплении лиц для сдачи кандидатских экзаменов, утвержденном приказом от 19.12.2022 № 15365-484.

Кандидатский экзамен представляет собой форму оценки степени подготовленности соискателя ученой степени кандидата наук к проведению научных исследований по конкретной научной специальности и отрасли науки, по которой подготавливается или подготовлена диссертация.

Соискатель ученой степени кандидата наук должен показать высокий уровень сформированности знаний, умений и навыков самостоятельного поиска, анализа и переработки зарубежной литературы по тематике диссертационного исследования; способности к выступлению с докладами на иностранном языке и участию в международных конференциях, школах-семинарах.

Процедура проведения кандидатского экзамена

Кандидатский экзамен проводится в форме сочетания устной и письменной форм.

Кандидатский экзамен по иностранному языку проводится в два этапа:

1) аспирант выполняет письменный перевод научного текста по специальности на русский язык. Объем текста – 5000 печатных знаков; время выполнения работы – 45–60 минут. Успешное выполнение письменного перевода является условием допуска ко второму этапу экзамена;

2) аспирант выполняет три задания (устно):

- изучающее чтение оригинального текста по специальности (объем текста: 2500–3000 печатных знаков; время выполнения работы – 45–60 минут; передача извлеченной информации осуществляется на русском языке);

- беглое чтение оригинального текста по специальности (объем текста – 1000–1500 печатных знаков; время выполнения – 2–3 минуты); для проверки беглого чтения допускается использовать текст первого этапа экзамена;

- беседа с экзаменаторами на иностранном языке по вопросам, связанным со специальностью и научной работой аспиранта.

Качество перевода, выполненного аспирантом в рамках первого этапа кандидатского экзамена, оценивается по зачетной системе. Перевод должен быть представлен в виде рукописного текста.

Перечень заданий для кандидатского экзамена (промежуточного контроля)

Первый этап экзамена – образец текста для письменного перевода – представлен в Приложении 1.

Критерии оценки первого этапа экзамена:

- «зачтено» – выполнен весь объем перевода, отобранные языковые средства соответствуют поставленной задаче, наблюдается оправданное, последовательное и логичное изложение мысли, отсутствие повторов и нарушения стилового единства текста, вариативность используемых лексико-синтаксических единиц; отсутствуют грубые грамматические, орфографические и лексические ошибки в языковом материале;

- «не зачтено» – выполнен не весь объем перевода, имеются грамматические, орфографические и лексические ошибки в языковом материале, перевод выполнен неадекватно.

Задания второго этапа экзамена оцениваются по четырехбалльной шкале: «отлично», «хорошо», «удовлетворительно», «неудовлетворительно».

Второй этап экзамена – образец текста для изучающего чтения – представлен в Приложении 2.

Критерии оценки текста для изучающего чтения:

- «отлично» – представлен полный перевод, адекватный смысловому содержанию текста на русском языке. Текст грамматически корректен, лексические единицы и синтаксические структуры, характерные для научного стиля речи, переведены адекватно;

- «хорошо» – представлен полный перевод, но встречаются лексические, грамматические и стилистические неточности, которые не препятствуют общему пониманию текста, однако не согласуются с нормами языка перевода и стилем научного изложения;

- «удовлетворительно» – фрагмент текста переведен не полностью или с большим количеством лексических, грамматических и стилистических ошибок, которые препятствуют общему пониманию текста;

- «неудовлетворительно» – представлен неполный перевод; аспирант демонстрирует непонимание содержания текста, большое количество смысловых и грамматических ошибок.

Второй этап экзамена – образец текста для беглого чтения – представлен в Приложении 3.

Критерии оценки текста для беглого чтения:

- «отлично» – чтение корректное, лексические единицы и синтаксические структуры, характерные для научного стиля речи, прочитаны правильно;

- «хорошо» – встречаются неточности в произношении, которые не препятствуют общему пониманию текста;

- «удовлетворительно» – фрагмент текста, предложенного на экзамене, прочитан с большим количеством ошибок, которые препятствуют общему пониманию текста;

- «неудовлетворительно» – абсолютно неверное прочтение текста, большое количество ошибок в произношении.

Второй этап экзамена – перечень вопросов для беседы с экзаменаторами на иностранном языке по вопросам, связанным с научной специальностью и научной работой аспиранта:

1. When did you first think of becoming a scientist?
2. Why did you decide to enter the post-graduate courses?
3. Do members of your family have science degrees?
4. Who is your research advisor?
5. What is the subject of your research?
6. Is the topic of your research connected with your graduate work?
7. What is the motive force of scientific progress?
8. Can science do without theories and hypotheses?
9. Do you think you could make a discovery?
10. Could you describe the present state of research in your sphere?
11. What latest discoveries in your field of research do you know?
12. What characteristics should a scientist have nowadays? Why do you think so?
13. What scientists in your field of research do you know?
14. Who do you think is the founder in your field of research?
15. Did you take part in any international conferences in English?
16. How often are international conferences held in your field?
17. Have you got any published articles?
18. Are you satisfied with your level of English?

19. Do you think it is important for a scientist to communicate in English? Why do you think so?

20. Do you think it is important for a scientist to translate English texts?

Критерии оценки беседы с экзаменаторами на иностранном языке по вопросам, связанным с научной специальностью и научной работой аспиранта:

- «отлично» – аспирант способен вести беседу на иностранном языке, не допустил существенных ошибок в построении предложений, правильно употребил видовременные формы глагола;

- «хорошо» – аспирант в целом способен вести беседу на иностранном языке, аспирант допустил незначительные ошибки в построении предложений либо в употреблении видовременных форм глагола;

- «удовлетворительно» – ведение беседы вызывает у аспиранта существенные затруднения, допустил ошибки в построении предложений либо в употреблении видовременных форм глагола;

- «неудовлетворительно» – аспирант не способен вести беседу на иностранном языке, ответы не соответствуют лексико-грамматическим нормам иностранного языка.

Итоговая оценка по кандидатскому экзамену выводится как средняя оценка членов комиссии за все задания второго этапа экзамена.

Конкретные задания к кандидатскому экзамену подбираются преподавателем в соответствии с тематикой научных исследований аспиранта.

Кандидатский экзамен проводится в смешанной форме: задание первого этапа кандидатского экзамена выполняется письменно, задания второго этапа – устно. Для подготовки соискатель использует экзаменационные листы.

Рекомендуемая литература

Основная литература:

1. Басова, О.В. Английский язык для аспирантов и соискателей естественно-научных специальностей: учебное пособие / О.В. Басова, О.С. Дворжец. – Омск: Омский государственный университет им. Ф.М. Достоевского (ОмГУ), 2019. – 138 с. – Режим доступа: по подписке. – URL: <https://biblioclub.ru/index.php?page=book&id=613822> (дата обращения: 19.02.2024).

2. Основы перевода, аннотирования и реферирования научно-технического текста: учебное пособие / Е.А. Чигирин, Т.Ю. Чигирина, Я.А. Ковалевская, Е.В. Козыренко; науч. ред. Е.А. Чигирин. – Воронеж: Воронежский государственный университет инженерных технологий, 2019. – 157 с. – Режим доступа: по подписке. – URL: <https://biblioclub.ru/index.php?page=book&id=601568> (дата обращения: 19.02.2024).

3. Стрельцов, А.А. Практикум по переводу научно-технических текстов: English ↔ Russian / А.А. Стрельцов. – Москва; Вологда: Инфра-Инженерия, 2019. – 381 с. – Режим доступа: по подписке. – URL: <https://biblioclub.ru/index.php?page=book&id=564673> (дата обращения: 19.02.2024).

Дополнительная литература:

1. Данилова, С.В. Английский язык для академических целей=Academic Listening and Watching: учебное пособие по развитию навыков аудирования для магистрантов естественно-научных дисциплин / С.В. Данилова. – Омск: Омский государственный университет им. Ф.М. Достоевского (ОмГУ), 2019. – 90 с. – Режим доступа: по подписке. – URL: <https://biblioclub.ru/index.php?page=book&id=613819> (дата обращения: 19.02.2024).

2. Кисель, Л.Н. Английский язык. Интенсивный курс обучения чтению=English. Intensive Reading Training Course: учебное пособие / Л.Н. Кисель, Д.Г. Панасюк. – Минск: РИПО, 2021. – 108 с. – Режим доступа: по подписке. – URL: <https://biblioclub.ru/index.php?page=book&id=697398> (дата обращения: 19.02.2024).

3. Тихонов, А.А. Английский язык: теория и практика перевода: учебное пособие / А.А. Тихонов. – Москва: ФЛИНТА, 2019. – 120 с. – Режим доступа: по подписке. – URL: <https://biblioclub.ru/index.php?page=book&id=611202> (дата обращения: 19.02.2024). – ISBN 978-5-9765-4143-6.

4. Фролова, В.П. Век химии=Age of Chemistry (English for students of chemical direction): английский язык для студентов химического профиля: учебное пособие / В.П. Фролова, Л.В. Кожанова, Т.Ю. Чигирин; науч. ред. Е.А. Чигирин. – 3-е изд., перераб. и доп. – Воронеж: Воронежский государственный университет инженерных технологий, 2019. – 201 с. – Режим доступа: по подписке. – URL: <https://biblioclub.ru/index.php?page=book&id=601455> (дата обращения: 19.02.2024).

5. Чигина, Н.В. Деловое общение на иностранном языке: учебное пособие / Н.В. Чигина, Е.Г. Бухвалова, С.В. Сырескина; Самарский государственный аграрный университет. – Кинель: Самарский государственный аграрный университет, 2020. – 113 с. – Режим доступа: по подписке. – URL: <https://biblioclub.ru/index.php?page=book&id=611425> (дата обращения: 19.02.2024).

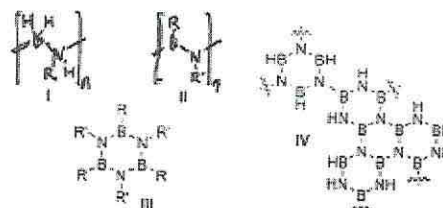
Poly(iminoborane)s: An Elusive Class of Main-Group Polymers?

Ozan Ayhan, Thomas Eckert, Felix A. Plamper, and Holger Heltgen*

Dedicated to Professor Peter Pätzold

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 organoboron polymers and BN-doped polycyclic aromatic hydrocarbons are currently attracting considerable attention. Surprisingly, poly(iminoborane)s (PIBs; $[\text{BRNR}]_n$), 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.^[2–5] 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.^[6–8] Potential applications suggested for such compounds include their utilization as polymeric precursors to shaped BN ceramics^[9] or as piezoelectric materials.^[40] 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.^[24–26] Against this background, it seems surprising that the current state of knowledge on polymers with unsaturated BN units is rather limited.^[24–26,31] 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, $[\text{BHNH}]_n$.^[12,29]

The term “polyiminoborane” has occurred frequently in the literature in the context of dehydrogenation studies of ammonia borane (NH_2BH_2 , 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,41] 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 $[\text{BHNH}]_n$.^[12(a),13(a),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 $[\text{BHNH}]_n$,^[13(a)] state-of-the-art solution- and solid-state ^{11}B and ^{15}N NMR studies have revealed the presence of N_2B and B_2N in addition to N_2BH and B_2NH sites.^[11,22(a),42] Therefore, it was recently proposed

* O. Ayhan, Dr. H. Heltgen
Institut für Anorganische Chemie, RWTH Aachen University
Landoltweg 1, 52056 Aachen (Germany)
E-mail: holger.heltgen@ac.rwth-aachen.de
Homepage: <http://www.ac.rwth-aachen.de/extern/heltgen/index.html>

Dr. T. Eckert, Priv.-Doz. Dr. F. A. Plamper
Institut für Physikalische Chemie, RWTH Aachen University
Landoltweg 2, 52056 Aachen (Germany)

Supporting information for this article can be found under:
<http://dx.doi.org/10.1002/anie.201607131>.

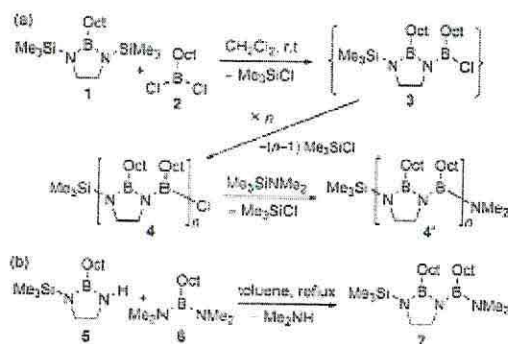
that the structure of this material should better be described as a polyborazylene (IV), that is, a poorly-defined macromolecular network of partially fused borazine rings.^[13a,b] In fact, the provided NMR data are remarkably similar to those of a polyborazylene sample prepared through a different route.^[14]

Thermolysis of Manners' poly(*N*-methylaminoborane) (I, R = CH₃) 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.^[15] In the 1980s, Paetzold and co-workers reported on the isolation of waxy materials for which a constitution of linear poly(iminoborane) (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]₂ transformed into hexaethylborazine upon heating above 150 °C. An analogous transformation of the derivative [PrBN⁺Pr]₂, however, was not achieved.^[16b]

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.^[13] 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 2a). *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 2b).

Monitoring of the reaction of **1** with **2** in CD₂Cl₂ at ambient temperature by ¹¹B{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 ¹¹B resonance for the B–Cl end groups of the growing chain (at around 44.5 ppm) continuously decreased



Scheme 2. a) Synthesis of oligo(iminoborane) **4** and end-capped derivative **4'**. b) Synthesis of model compound **7** (Oct-*n*-C₄H₁₁).

in intensity. One broad signal remained in the ¹¹B{¹H} NMR spectrum for the bulk boron atoms of the oligomer **4**, which in the course of the reaction was shifted slightly upfield to $\delta = 31$ ppm. In the ¹H NMR spectrum, a common signal appeared for the protons of the ethylene bridge, centered at $\delta = 3.32$ ppm. Small peaks at $\delta = 3.00$ –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 SiMe₃ end group was detected at $\delta = 0.15$ ppm, and concomitant formation of the volatile condensation byproduct Me₂SiCl was evidenced by its ¹H resonance at $\delta = 0.45$ 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 ≈ 7. Then, Me₂SiNMe₂ (5 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.

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 1a), 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 1b). 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 1d). Fitting to a worm-like chain model gave a rigid rod with 2.7 nm for the extended chain length together with

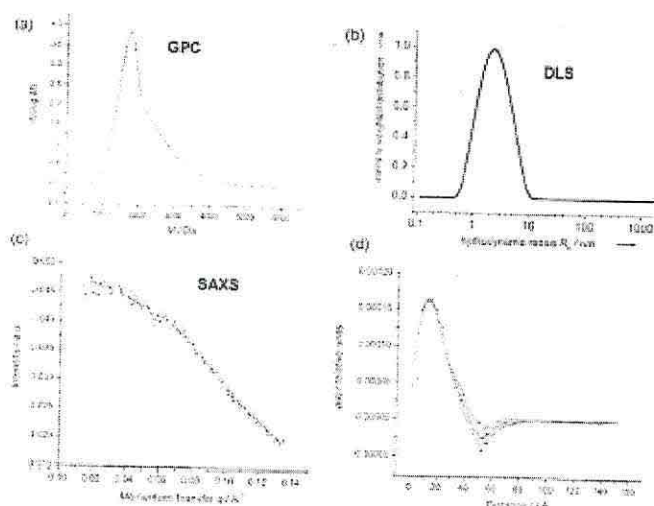


Figure 1. a) Molar-mass distribution of **4** as determined by GPC (in THF, versus polystyrene standards). b) Intensity-weighted size distribution of **4** in *n*-pentane by DLS ($\theta = 30^\circ$). c) SAXS profile of **4** in *n*-pentane, fitted with a worm-like chain model. d) Bayesian-weighted distance 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 $T_g = -71^\circ\text{C}$. 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 $\lambda_{\text{abs,max}} = 269\text{ nm}$, that is, slightly red-shifted with respect to that of the molecular model **7** ($\lambda_{\text{abs,max}} = 248\text{ nm}$).

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 $p(\text{N}) \rightarrow p(\text{B})^*$ 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(aminoborane). 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 approach by which this unwanted side reaction was effectively suppressed through the introduction of an ethylene bridge between two N atoms of

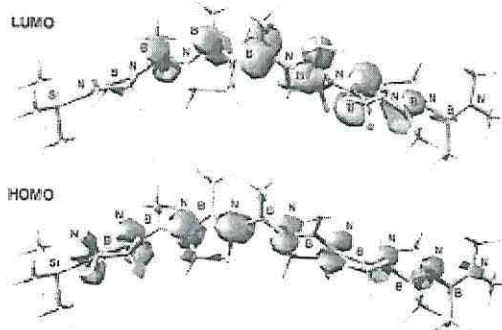


Figure 2. Calculated frontier orbitals (isovalue: 0.032) of an *n*-4 (B3LYP-D3/def2-SVP) model for **4**.

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(aminoborane)s, and we are probing the potential of these materials for potential application as electronic materials and ceramic precursors.

Acknowledgements

Funding by the German Research Foundation (DFG) through the Emmy Noether Programme and support by the COST action CM1302 (SIPs) is gratefully acknowledged. We

Приложение 2
(обязательное)

Образец текста для изучающего чтения

**SYNTHESIS OF SILYLANILINE PRECURSORS TO ORGANIC-INORGANIC
HYBRID POLYMERS**

by

Samuel Floren

Submitted in partial fulfillment of the
requirements for Departmental Honors in
the Department of Chemistry and Biochemistry

Texas Christian University

Fort Worth, Texas

May 2, 2016

INTRODUCTION

The polymer industry has catapulted our civilization to new heights of productivity and leisure, producing many of the household and industry standards for our way of life. Most tools, games, utilities, and necessities either contain or are made entirely out of one or more different kinds of polymers. Traditional polymers that one would usually encounter are typically organic polymeric systems developed for their utility. However, the chemical intrigue of polymeric systems lies outside of the practicality of these plastics. The nature of the polymeric backbone and testing the possibilities of replacing organic moieties with their inorganic analogues is the basis of the work presented here.

Typically, polymer synthesis falls under the realm and classification of organic chemistry, as most polymers involve a stable carbon-carbon backbone. Well-developed examples include polyethylene¹, polyvinylchloride¹ (PVC), or polystyrene¹ (Styrofoam).

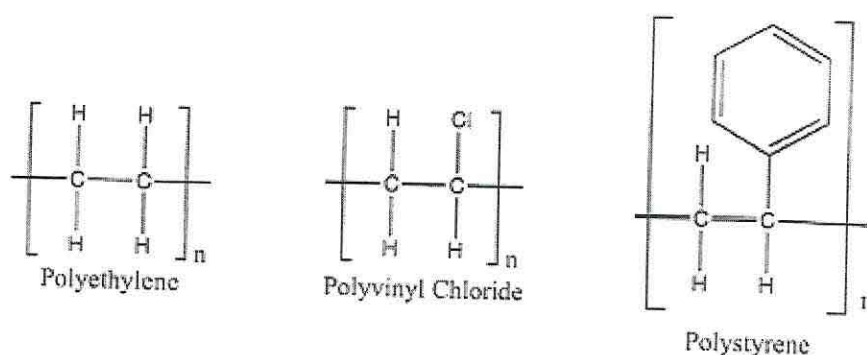


Figure 1. Common Organic Polymers

These polymers are all important and have been designed to display specific characteristics, such as structural integrity, flexibility, chemical and thermal stability, and

a lack of toxicity to humans. During recent decades, inorganic chemists have been interested in the development of new polymers, both as scaffolds for inorganic reactions, and in synthesizing polymers with an inorganic backbone. Inorganic polymers have sometimes displayed enhanced properties over organic polymers. These properties include bonds that are more resistant to free radical cleavage and the incorporation of elements with different valencies than carbon, which would affect the compound's flexibility, reactivity, thermal stability, and solvent interactions.²

A common backbone of an organic polymer consists of carbon atoms with tetravalency, containing eight valence electrons for every two carbon atoms. If, instead of carbon, alternating boron-nitrogen bonds were to be incorporated, the result would be an identical number of valence electrons. This indicates that the boron-nitrogen bond is isoelectronic to the carbon-carbon bond. This supports the hypothesis that a polymer consisting of an alternating boron-nitrogen structure would behave similarly to its carbon-carbon analogue.

The boron-nitrogen bond shares many of the same characteristics of a carbon-carbon bond. As stated above, the number of valence electrons is the same. In addition, the boron-nitrogen analogues of alkanes (amine-boranes, X_3B-NR_3), alkenes (aminoboranes $X_2B=NR_2$), and alkynes (iminoboranes, $XB\equiv NR$) share similar bond distances and properties.³ This suggests that a polymeric system consisting of a boron-nitrogen backbone is possible.

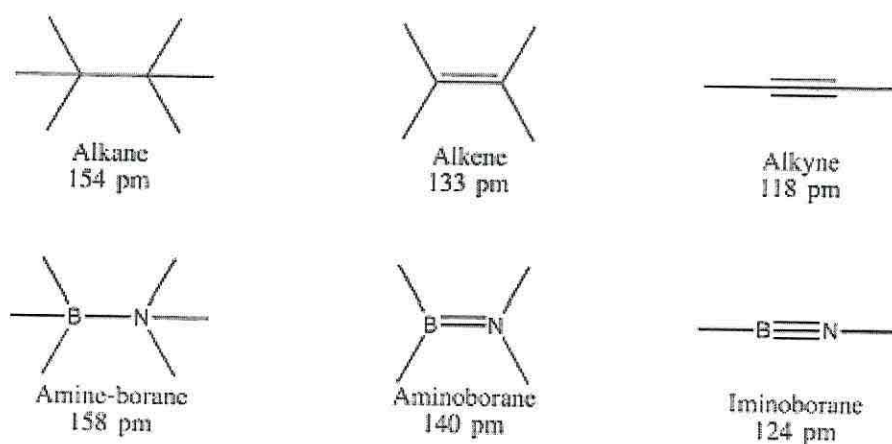


Figure 2. Comparative Structures and Bond Lengths of C-C and B-N Moieties

One of the problems associated with producing polymers with a boron-nitrogen backbone, is the generation of a cyclic trimeric by-product called borazine.⁴ Borazine is such a stable structure that its formation acts as a thermodynamic sink. With this in mind, a different synthetic technique was necessary in order to design a polymer that did not degenerate into borazine. Understanding this challenge, the Neilson group has spent a number of years investigating various synthetic strategies in order to develop potential precursors to boron-nitrogen polymeric systems.

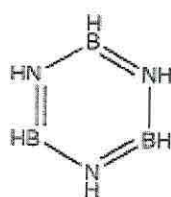


Figure 3. The Cyclic Boron-Nitrogen Trimer: Borazine

Приложение 3
(обязательное)

Образец текста для беглого чтения

Borates in Industrial Use

David M. Schubert

U.S. Borax Inc., 26877 Tourney Road, Valencia, California 91355, USA
e-mail: dave.schubert@borax.com

Boron compounds find extensive use in a wide range of industrial applications, nearly all involving boron-oxygen compounds. Although quite diverse, these end uses depend on the same fundamental aspects of the structure and bonding patterns of boron. The most important industrial uses of boron compounds are discussed along with recent developments in the understanding of fundamental chemistry of crystalline and vitreous borates that underlie these applications. The formation of ester linkages to boron leads to industrial uses and provides a basis for the biological interactions of boron. Full recognition of the essential role that boron plays in biological systems has only come about in the last few years. The use of boron in the manufacture of glass and other vitreous products accounts for more than one half of all boron use. Perborates, agriculture, wood preservation, and fire retardancy are also important application areas. New applications are being developed for the use of borates in the pulp and paper and ceramics industries, among others.

Keywords: Boron, Borate, Glass, Ester, Bioessentiality

1	Introduction	2
2	Aqueous Chemistry	5
3	Crystalline Borates	6
4	Vitreous Borates	15
5	Organic Ester Formation	17
6	Biological Aspects of Boron	20
6.1	Natural Products	20
6.2	Bioessentiality	20
6.2.1	Plants	21
6.2.2	Animals	23
6.3	Toxicity	24
7	Industrial Boron Products	25
7.1	Refined Borates	25
7.1.1	Borax Pentahydrate	25
7.1.2	Borax Decahydrate	26

7.1.3	Boric Acid	26
7.1.4	Anhydrous Borax	27
7.1.5	Boric Oxide	27
7.1.6	'Disodium Octaborate'	28
7.1.7	Zinc Borates	28
7.2	Beneficiated Mineral Borates	29
7.2.1	Colemanite	29
7.2.2	Tincal	29
7.2.3	Kernite	30
7.2.4	Ulexite	30
7.2.5	Hydroboracite	30
7.2.6	Metamorphic Borates	31
8	Major Industrial Uses of Borates	31
8.1	Vitreous Applications	31
8.1.1	Fiberglass	31
8.1.2	Specialty Glass	32
8.1.3	Ceramic Glazes/Porcelain Enamels	33
8.2	Agricultural Use	33
8.3	Biostatic Use	33
8.3.1	Wood Preservation	34
8.4	Fire Retardants	34
8.5	Perborates	35
8.5.1	Detergency - Consumer Bleaching	36
8.5.2	Detergency - Laundry Builder	37
8.6	Emerging Applications of Borates	37
9	References	38

1 Introduction

Boron finds use in a wide range of industrial applications, the vast majority of which involve boron-oxygen compounds. This class exhibits a rich structural chemistry, featuring both crystalline and non-crystalline solids of industrial importance, and complex solution chemistry. The full extent of the role of boron as an essential element in fundamental life processes has only become clear during the past decade. The emerging biological roles of boron are relevant to both the commercial and environmental aspects of boron science. Although boron-oxygen chemistry is diverse and complex, it is ultimately based on the electrophilic character of trivalent boron. This review explores the chemistry of boron as it relates to its large-scale technological roles.

Although boron has a relatively low natural abundance (ca. 0.001% of the earth's crust) it is widely dispersed in the environment, occurring in rocks, soils, and natural waters at low but significant levels [1]. Owing to boron's unique

properties, it is more susceptible to fractionation by geological processes and can become concentrated to a greater extent than other elements of similar natural abundance. With the exception of a few rare fluoride minerals, boron always occurs on the earth in combination with oxygen, either in crystalline borate minerals or in water, primarily in the form of naturally occurring boric acid, $B(OH)_3$. Boron is found in sea water at an average level of 4.6 ppm. This level is too low to permit economical extraction of industrial quantities. Thus, commercial supplies of boron are derived from mineral deposits, which are found as alkali or alkaline earth metal borates and borosilicates, with sodium and calcium borates being the most important. Although borate minerals are numerous, large commercially exploitable borate ore deposits are rare. However, when such deposits occur they can be vast. Owing to the relatively high water solubilities of borate minerals, these deposits are always found in arid regions. Most borates are produced in California and Turkey, with the rest coming from Russia, China, and the Andean regions of South America [2].

An estimated 1.25×10^6 metric tons of B_2O_3 is currently consumed annually in the form of the various borate products. Fig. 1 shows the approximate proportions of boron consumed by various large industries. It is notable that the use of borates in the manufacture of various types of vitreous materials, particularly fiberglass, ceramic glazes, and specialty borosilicate glasses, accounts for more than half of all boron used by industry. The uses of borates in peroxygen bleaching systems for household laundry detergents, micronutrient fertilizers, cellulose insulation (fire retardant), and cleaning products are also important. Following these applications there are hundreds of other minor uses of borates, a small selection of which are listed in Table 1.

For the most part, these other applications utilize boron oxides, but a small fraction of uses involves non-oxide materials such as boron hydrides and engineering ceramics. Although these non-oxide materials have received great attention in academic circles in recent decades, they are yet to gain much industrial significance in the overall scheme of the borate industry.

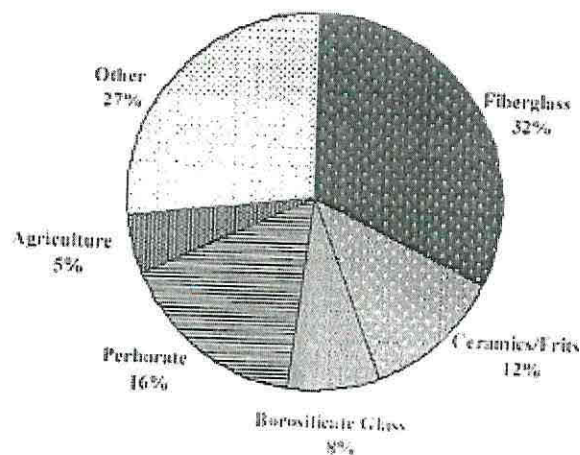


Fig. 1. Estimated total borate use by major industrial applications in B_2O_3 equivalents for the year 2001