

Polymers | Hot Paper |

BN- and BO-Doped Inorganic–Organic Hybrid Polymers with Sulfoximine Core Units

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In memory of Professor Dr. Dieter Enders

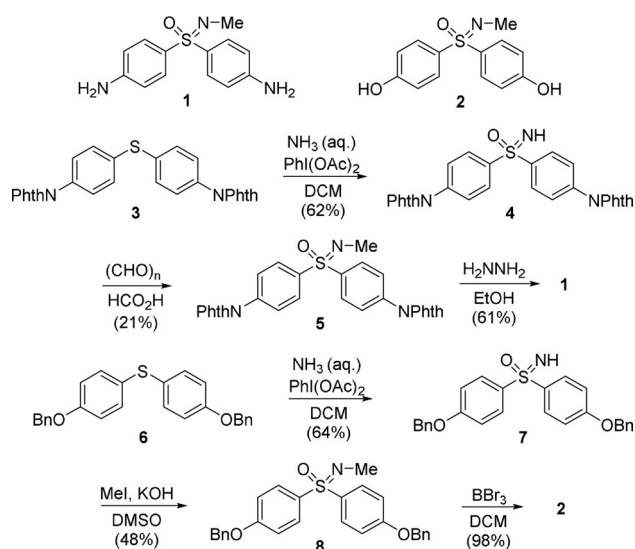
Abstract: While polysulfones constitute a class of well-established, highly valuable applied materials, knowledge about polymers based on the related sulfoximine group is very limited. We have employed functionalized diaryl sulfoximines and a *p*-phenylene bisborane as building blocks for unprecedented BN- and BO-doped alternating inorganic–organic hybrid copolymers. While the former were accessed by a facile silicon/boron exchange protocol, the synthesis of polymers with main-chain B–O linkages was achieved by salt elimination.

Polysulfones are a family of plastic materials that are noted for their high thermal and oxidative stability.^[1] They are being used within fluid handling components, steam sterilizable biomedical moldings as well as in a range of chemical process and automotive applications.^[2] Some of us recently reported a series of BN-doped inorganic–organic hybrid polymers,^[3–6] including the first poly(*p*-phenylene iminoborane), which can be regarded as a BN-analogue of poly(*p*-phenylene vinylene) (PPV).^[3d] A dapson-type diaryl sulfone was also incorporated into a polymeric material.^[3e]

Formal exchange of a sulfonyl oxygen by a nitrogen atom converts a sulfone into a sulfoximine. The latter compounds are relevant in asymmetric synthesis^[7] and applications in medicinal^[8] and crop protection chemistry.^[9] Functionalizing the sulfoximine nitrogen allows a fine-tuning of physicochemical

properties, which proved useful in drug design and bioactivity adjustment.^[10] Surprisingly, sulfoximines have only once been applied as building blocks in polymers.^[11] In that study, Takata et al. used Friedel–Crafts reactions to prepare polysulfoximines with molecular weights (M_n) of approximately 13 000. Herein, we describe the synthesis and characterization of the first inorganic–organic hybrid polysulfoximines.

In light of previous work,^[12] sulfoximines **1** and **2** were identified as suitable organic starting materials. Both compounds were N-methylated, thereby confining the reactive anchor sites of the molecules to the free aryl amino and hydroxyl groups. With the vision to allow future variations of the N-substituent, phthalimid- and benzyl-protected NH-sulfoximines **4** and **7**, respectively, were targeted first. The synthetic sequences are shown in Scheme 1. The preparation of **1** started from known



Scheme 1. Syntheses of key intermediates **1** and **2**.

diarylsulfide **3**,^[12] which was imidated and oxidized by adopting a protocol reported by Luisi, Bull, and others^[13] to give **4** in 62% yield. Noteworthy, we applied aqueous ammonia as a nitrogen source instead of the originally suggested ammonium carbamate.

N-Methylation under standard Eschweiler–Clark conditions afforded sulfoximine **5** (21%), which was deprotected with hydrazine in ethanol to give **1** in 61% yield. Following an analogous reaction sequence, sulfoximine **2** was prepared by imida-

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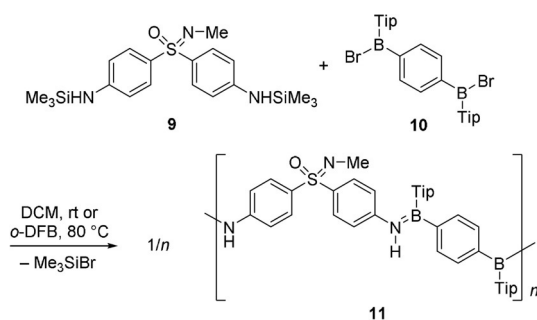
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tion/oxidation of **6**^[14] to give **7** (64%) followed by N-methylation with MeI in KOH/DMSO^[15] providing **8** in 48% yield and sequential debenzoylation with BBr₃ (98%).

Targeting a polymer formation by silicon/boron exchange, bis(silylated) sulfoximine **9** was prepared, in analogy of literature precedence,^[16] by treatment of **1** with a mixture of Me₃SiCl and Et₃N in THF at 45 °C for 24 h. The coupling partner for **9** was bis(bromoborane) **10**^[3d] (Tip = 2,4,6-triisopropylphenyl). Two co-polycondensation reactions were performed (Scheme 2). In both cases, a 1:1 ratio of **9** and **10** was applied.



Scheme 2. Polycondensation reaction of sulfoximine **9** and bisborane **10** to give alternating copolymer **11**.

In the first experiment (trial 1), the mixture was kept in dichloromethane for 3 days at ambient temperature. Trial 2 involved *o*-difluorobenzene (*o*-DFB) as the solvent and heating the mixture to 80 °C for 24 h. The resulting alternating copolymers **11** were then purified by precipitation from concentrated solution with hexane and subsequent drying in vacuo. The identities of copolymers **11**, which were obtained as off-white solids, were unambiguously ascertained by NMR spectroscopy. Their molecular mass distributions were determined by gel permeation chromatography (GPC, Table 1). For both samples, the ¹H NMR spectrum showed a shift of the NH-Signal from $\delta = 3.77$ ppm in **9** to the aromatic region in **11** ($\delta = 7.25$ ppm), which was also observed in previously prepared related BN polymers.^[3d]

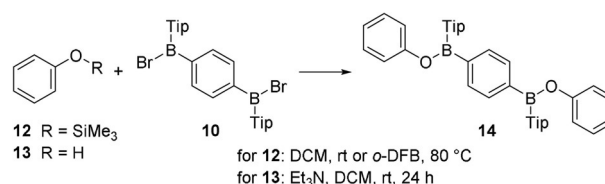
Table 1. GPC data of polymers **11** and **15** (against polystyrene standards).

| | M_n | M_w | PDI | DP_n |
|------------------------------------|--------|--------|------|--------|
| 11 (trial 1) ^[a] | 9 750 | 18 600 | 1.91 | 13 |
| 11 (trial 2) ^[b] | 11 830 | 28 900 | 2.44 | 15 |
| 15 (trial 1) ^[a] | 2400 | 2970 | 1.52 | 3 |
| 15 (trial 2) ^[b] | 5300 | 9740 | 1.84 | 7 |

[a] Prepared in dichloromethane (DCM), rt, 3 d. [b] Prepared in *o*-difluorobenzene (*o*-DFB), 80 °C, 24 h.

The GPC analyses revealed number average molecular weights of $M_n = 9\,750$ (trial 1) and $11\,830$ (trial 2), according to polymerization degrees of $DP_n = 13$ and 15 , respectively. The polydispersity indices were close to 2, as expected for step-growth polycondensation processes.

Next, copolymers with main-chain B–O linkages^[17] were targeted. Hypothesizing that such products could be accessed by analogous Si/B exchange reactions as applied before in the synthesis of **11**, organic starting materials with silylated phenolic hydroxyl groups became of interest. In order to get an estimate of the feasibility of such an approach, a prior model reaction between **10** and trimethylsilylated phenol **12** was performed (Scheme 3). In the first experiment, the reaction was



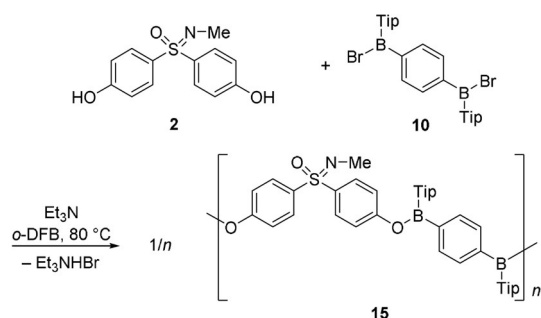
Scheme 3. Model reactions testing the feasibility of Si/B exchange and salt elimination reactions in the formation of alternating copolymers with B–O linkages.

run in dichloromethane at room temperature. As hypothesized, product **14** was indeed formed as revealed by ¹H and ¹¹B NMR spectroscopy. The initial presence of two doublets ($\delta = 8.04$ and 7.88 ppm) in the ¹H NMR spectrum suggested a stepwise formation of **14**. However, the entire process was very slow, and even after four weeks the conversion was not yet complete. A similar outcome resulted when *o*-difluorobenzene was used as a solvent at a reaction temperature of 80 °C. Also in this case, the conversion was slow, taking five weeks in total. Although these results showed that a Si/B exchange could, in principle, be applied to accomplish a B–O bond formation starting from **10**, the slow rate of this process proved unfavorable for its application to co-polycondensation reactions. Therefore, we decided to investigate B–O bond formation between **10** and the parent free phenol (**13**).

While initial attempts without base remained unsatisfying, the presence of triethylamine had a tremendously positive effect, leading to a clean and quantitative coupling providing **14** within 24 hours at room temperature. Compound **14** was then isolated by filtration and characterized by multinuclear NMR spectroscopy. The ¹¹B{¹H} NMR spectrum showed a resonance at $\delta = 47.3$ ppm, which is in the expected range for the suggested constitution.

Encouraged by this result, the aforementioned conditions were applied in the copolymerization of sulfoximine **2** with bisborane **10** (Scheme 4). Within three days in the presence of Et₃N, the dichloromethane solution became highly viscous (trial 1). However, after work-up the GPC analysis revealed that the product was of relatively low molecular weight ($M_n = 2\,400$, $DP_n = 3$; Table 1). Consequently, in the next experiment (trial 2) the solvent was changed to *o*-DFB, and then the reaction temperature was raised to 80 °C. Pleasingly, in this manner, after 24 h the molecular weight (M_n) of the resulting polymer **15** was increased to $5\,300$, revealing an average chain length of $DP_n = 7$ (Table 1).^[18]

In summary, we have prepared the first inorganic–organic hybrid sulfoximine-containing polymers as alternating copoly-



Scheme 4. Polycondensation reaction of sulfoximine **2** and bisborane **10** to give alternating copolymer **15**.

mers with B=N and B–O linkages. While our Si/B exchange polycondensation protocol was successful in the former case, for the synthesis of polymers with B–O linkages in the main chain a salt elimination approach proved to be favorable. In view of the recently demonstrated advantageous effect of the formulation of dapson-type drugs into polymer conjugates for anti-inflammatory purposes^[19] on the one hand, and the well-established biomedical activity of many boron-containing polymers^[20] on the other hand, we are currently exploring the biomedical potential of our novel sulfoximine-B=N/B–O hybrids in detail.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: boron · hybrid materials · polymers · sulfoximines · sulfur

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