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# Well-Defined Boron-Containing Polymeric Lewis Acids

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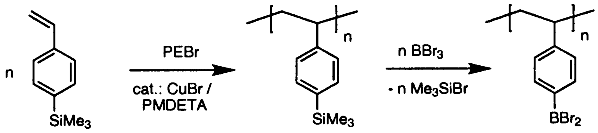
Organoboron compounds play a major role as catalysts and cocatalysts in organic transformation including polymerization reactions.[1] In a quest for superior catalysts, bifunctional organoboranes have been developed and, in several cases, have been shown to display enhanced reactivity and selectivity over their monofunctional counterparts.[2] However, the synthesis of organoboron polymers has been a challenging task that only recently was met with success leading to the discovery of new supported reagents and immobilized catalysts.[3] Boron-containing polymers also serve as intermediates in the synthesis of functionalized polymers with polar side groups[4−6] and are used as preceramic[7] and photoluminescent[8] materials.

Side-chain organoboron polymers have been prepared from organoboron monomers using a variety of polymerization techniques including standard free radical polymerization,[9] metathesis polymerization,[10] and Ziegler−Natta polymerization.[4] Alternatively, organic polymers or resins can be modified in a postpolymerization modification step. In this case, the boron centers are typically attached via multistep polymer modification reactions with low degrees of functionalization (<40%).[11] The direct borylation of polystyrene with $X_2BH$ under forcing conditions has been described, but occurs with low selectivity.[12] In an exciting new development, transition-metal-catalyzed borylation of polyolefins has been reported by Hartwig and Hillmyer to yield boronate-functionalized polymers in one step.[6]

However, a method for the synthesis of soluble boron polymers of controlled architecture, molecular weight, and degree of functionalization, in which the substituents on boron can be readily exchanged and consequently the strength of the Lewis acid centers can be fine-tuned, is currently not known. Such a process would provide an opportunity to investigate the binding behavior of nucleophiles to polymeric Lewis acids in depth. Moreover, studies of this type are likely to result in the discovery of new polymer-supported Lewis acid catalysts as well as cocatalysts for Ziegler−Natta polymerization. We report here a new route to well-defined polymeric Lewis acids via controlled radical polymerization of a silicon-functionalized monomer and subsequent borylation of the silylated polymer. The resulting reactive boron polymers serve as precursors to a family of well-defined polymers bearing Lewis acid centers.

4-Trimethylsilylstyrene was polymerized in anisole (50%) according to a typical protocol for atom transfer radical polymerization (ATRP)[13,14] initiated with 2 mol % 1-phenylethyl bromide (PEBr) and catalyzed by CuBr/pentamethyldiethylenetriamine (PMDETA) (68.5% conversion within 5 h at 110 °C). The molecular weight and dispersity of the resulting polymer **PS-Si** were determined by GPC analysis relative to polystyrene standards to be $M_w = 6500$ and PDI = 1.13. Molecular weight analysis by static light-scattering analysis gave similar results ($M_w = 6810$), indicating a close similarity of the hydrodynamic volume of polystyrene and **PS-Si**. A kinetic study of the polymerization reaction confirmed the "living" nature of the polymerization, thereby demonstrating the applicability of this methodology to the preparation of a wide variety of polymers of different molecular weight and architecture, including copolymers.

***Scheme 1.*** Synthesis of Dibromoborylated Polystyrene (**PS-B**)



The introduction of Lewis acidic boron centers into the polymer side chains was achieved by silicon boron exchange using $BBr_3$, a strong Lewis acid which is known to cleave Si−C(sp$^2$) bonds under mild conditions (ambient temperature) with nearly quantitative yields and high selectivity.[15] **PS-Si** was treated with a slight excess of $BBr_3$ (*Caution*! $BBr_3$ is toxic and highly corrosive) in $CH_2Cl_2$ at ambient temperature over a period of 12 h (Scheme 1). Importantly, this procedure did not lead to precipitation of the polymer. The soluble borylated polymer **PS-B** was isolated in 81% yield after precipitation into hexanes. Alternatively, the polymer may most conveniently be used in situ for further exchange of the bromide substituents with nucleophilic reagents.

Selective and quantitative cleavage of the Si−C(sp$^2$) bonds in **PS-Si** to form **PS-B** was confirmed by multinuclear NMR spectroscopy. Importantly, the signal due to the trimethylsilyl substituents of **PS-Si** in the $^{29}$Si ($\delta = -4.4$), $^{1}$H ($\delta = 0.24$), and $^{13}$C ($\delta = -0.5$) NMR spectra completely disappeared. A new set of sharp signals developed as a result of formation of $Me_3SiBr$ ($\delta(^{29}\mathrm{Si}) = 30.3$, $\delta(^{1}\mathrm{H}) = 0.59$, $\delta(^{13}\mathrm{C}) = 4.5$). Attachment of dibromoboryl groups to the side chains is evident from a broad signal in the $^{11}$B NMR spectrum at $\delta = 54$ ($h_{1/2} = 2800$ Hz), in a region typical of arylboron dibromides. The chemical shift favorably compares with that for the model compound 4-(dibromoboryl)cumene of $\delta = 55.8$. The attachment of a strongly electron-withdrawing substituent on the phenyl rings is further reflected in the $^{1}$H and $^{13}$C NMR spectra. Upon borylation, the protons in *ortho*-position to the functional group experience a pronounced downfield shift from $\delta = 7.4-7.0$ in **PS-Si** to $\delta = 8.2-7.6$ in **PS-B** (for 4-(dibromoboryl)cumene: $\delta = 8.07$). A similar trend is observed for the carbon atoms in *ortho*-position to the boryl groups which resonate at $\delta = 138.5$ (**PS-Si**: $\delta = 133.8/133.5$) (Figure 1). A broad signal at $\delta = 136.4$ can be attributed to the carbon atom bearing the boryl substituent, and two closely spaced resonances ($\delta = 153.3$, 152.9) are observed for the *ipso*-carbon atom closest to the polymer backbone. Importantly, our data do not show any sign of isomerization reactions at the phenyl rings or of polymer degradation, but rather indicate selective and quantitative borylation of **PS-Si** by $BBr_3$.

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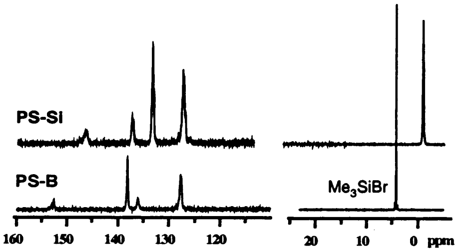


*Figure 1.* Phenyl/methyl regions of the $^{13}$C spectra of **PS-Si** and **PS-B**.

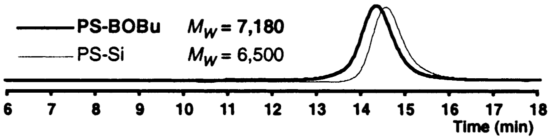
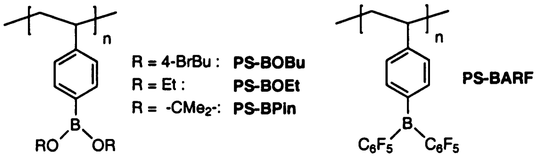


*Figure 2.* GPC traces for **PS-Si** and **PS-BOBu**.

**PS-B** readily reacts with nucleophiles, thereby serving as a precursor to a number of other polymers with boron centers of variable Lewis acidity. When **PS-B** was treated with $Me_3SiOEt$ or THF, the weakly Lewis acidic polymeric boronates, **PS-BOEt** and **PS-BOBu**, were obtained in 90 and 83% isolated yield, respectively. Interestingly, when **PS-BOEt** was subsequently reacted with pinacol in toluene at ambient temperature, the ethoxy substituents were readily replaced to yield the air-stable polymer **PS-BPin** containing a cyclic boronate moiety. **PS-BOEt** and **PS-BPin** were freeze-dried from benzene and readily isolated to give white solid materials. The isolated yield for the glassy polymer **PS-BOBu** is slightly lower due to losses during precipitation into hexanes.



An upfield-shifted $^{11}$B NMR signal for polymers **PS-BOR** ($\delta = 25$) confirms the introduction of alkoxy substituents on boron. The molecular weight was determined by GPC analysis to be in a similar range as that of the precursor **PS-Si**, whereas the polydispersity remained virtually identical (see Figure 2). This suggests that both the borylation and the subsequent substituent exchange occur without cleavage of the backbone or significant cross-linking.

Static light-scattering measurements were performed to further confirm the high selectivity and absence of cross-linking upon borylation of **PS-Si**. Comparative data as derived from Zimm plots of **PS-Si** and **PS-BPin** (see Table S2 of the Supporting Information) clearly show that the average number of polymer repeat units and the polydispersity remain unchanged.

The highly Lewis acidic polymer **PS-BARF** was obtained by reaction of **PS-B** with $Cu(C_6F_5)$ in 74% yield after precipitation into hexanes. The relative Lewis acidity of the boron centers was estimated by treatment with crotonaldehyde according to Childs' method[16] to 0.60 ($BBr_3 = 1.0$). A pronounced Lewis acidity of **PS-BARF** was further confirmed by a large chemical shift difference between the *meta*- and *para*-fluorine atoms of $\Delta\delta_{m,p} = 13.0$ for the free acid that significantly decreases to $\Delta\delta_{m,p} = 6.4$ in the polymeric Lewis acid-crotonaldehyde adduct. **PS-BARF** may be viewed as a polymeric analogue of the important Lewis acid tris(pentafluorophenyl)borane.[17]

In summary, we have developed an efficient new method for the introduction of Lewis acidic boron centers into the side chains of organic polymers. Facile substituent exchange reactions on boron lead to a new family of well-defined polymeric Lewis acids which lend themselves to further studies in catalysis and materials science.

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**Supporting Information Available:** Experimental procedures and data for all polymers described and for model compounds thereof. Kinetic plots for the polymerization of 4-trimethylsilylstyrene, Zimm plot for **PS-BPin**, and $^{19}$F NMR spectrum of **PS-BARF** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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