Macromolecules **2004,** *37,* 7123−7131

A New Route to Organoboron Polymers via Highly Selective Polymer Modification Reactions

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Received December 11, 2003; Revised Manuscript Received June 9, 2004

ABSTRACT: We have developed a highly efficient new method for the introduction of Lewis acidic boron centers into the side chains of organic polymers. Our methodology involves three steps: (i) the controlled polymerization of the functional monomer 4-trimethylsilylstyrene (**S−Si**), (ii) the exchange of the silyl groups in poly(4-trimethylsilylstyrene) (**PS−Si**) with BBr_3 to give the reactive polymer poly(4-dibromoborylstyrene) (**PS−BBr**), and (iii) the fine-tuning of the Lewis acidity of the individual boron centers through substituent exchange reactions with nucleophiles. Treatment of **PS−BBr** with ethoxytrimethylsilane and THF respectively yields the moderately Lewis acidic poly(arylboronate)s **PS−BOR** (R = Et, 4-bromobutyl). The alkoxy groups in **PS−BOR** have been exchanged with pinacol to form the air-stable polymer **PS−BPin** (Pin = pinacolato). Treatment of **PS−BBr** with 2-thienyltrimethyltin and pentafluorophenylcopper respectively gives the well-defined highly Lewis acidic triarylborane polymers **PS−BTh** and **PS−BPf** (Th = 2-thienyl, Pf = 2,3,4,5,6-pentafluorophenyl), which contain triarylborane moieties at every repeat unit along the polymer chain. All polymers have been studied by multinuclear NMR spectroscopy and differential scanning calorimetry. The molecular weights of the arylboronate polymers **PS−BOR** have been determined by gel permeation chromatography, and the highly selective formation of polymer **PS−BPin** has been confirmed by static light scattering.

Introduction

Inorganic and organometallic polymers have over the past two decades emerged as an important area of research in the field of materials chemistry. New devices have, for example, been developed based on polysiloxanes and polysilanes, new advances in medical research have been triggered by the discovery of polyphosphazenes, and, more recently, transition-metal-containing polymers have been developed for nanoscience applications.[1]

The incorporation of electron-deficient boron centers into polymer structures is particularly intriguing as it, for example, provides an opportunity to take advantage of the facile and reversible formation of donor acceptor bonds for the further manipulation and functionalization of the polymers.[2] Indeed, the binding of nucleophiles to organoboron polymers has resulted in the design and development of new supported reagents and immobilized catalysts[3] and of highly selective sensor materials.[4,5] Boron-containing polymers also play a major role as intermediates in the synthesis of functionalized polymers with polar side groups[6−8] and are used as polymeric electrolytes for batteries,[9] sophisticated flame retardants,[10] and preceramic[11] and photoluminescent materials.[12,13]

However, the selective incorporation of highly Lewis acidic boron centers into polymer structures remains a challenging task. While organoboron polymers can be prepared from organoboron monomers using a variety of polymerization techniques including condensation and addition polymerization,[11,12] standard free radical polymerization,[5,14] metathesis polymerization,[15] and Ziegler−Natta polymerization,[6] the polymerization of monomers bearing strongly Lewis acidic moieties has been largely restricted to Ziegler−Natta polymerization procedures[6] due to the high reactivity of the monomers. Notably, Chung and co-workers have recently reported the homo- and copolymerization of a boron-functionalized styrene monomer with styrene using a titanium catalyst, which yields syndiotactic boron-functionalized random copolymers with molecular weights ranging from M_n = 28 000 to 83 000 and polydispersities between 2.0 and 2.9.[16] The functionalization of organic polymers or resins in a postpolymerization modification step represents an alternative to the polymerization of borylated monomers. Early studies by Paetzold showed that the direct borylation of polystyrene with haloboranes X_2BH under forcing conditions occurs with relatively low selectivity.[17] In a recent development, transition-metal-catalyzed borylation of polyolefins has been reported by Hartwig and Hillmyer to yield boronate-functionalized polymers in one step.[8] Moreover, Chung and co-workers showed that the olefin-functionalized copolymers poly(ethylene-*co*-1,4-hexadiene) and poly(propylene-*co*-1,4-hexadiene) can be efficiently converted to boron-functionalized polymers via hydroboration reactions.[18] However, in most instances multistep polymer modification reactions need to be used to introduce the boron moiety, and often only low degrees of functionalization are realized.[19]

Our research in this area is aimed at the development of well-defined soluble organoboron polymers and copolymers 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 (Figure 1). We give here full details on the synthesis and properties of a new family of well-defined boron-based polymeric Lewis acids.[20]

Results and Discussion

We have developed a new methodology for the synthesis of organoboron polymers that involves three

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10.1021/ma035880r CCC: $27.50

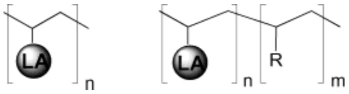
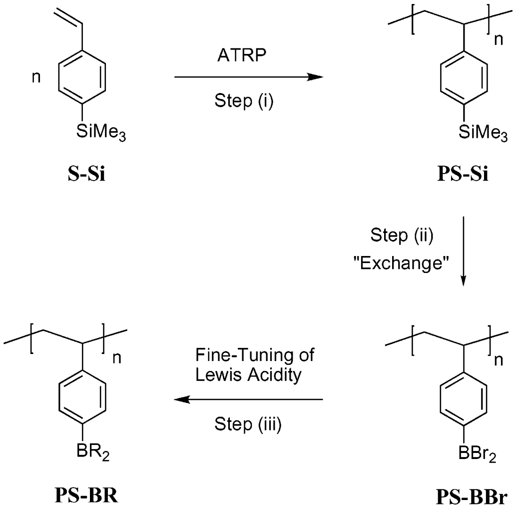


Figure 1. Schematic representation of Lewis acid functionalized homopolymers and block copolymers (LA represents a Lewis acid center and R corresponds to an organic group).

Scheme 1. General Method for the Synthesis of Organoboron Polymers of Varying Lewis Acidity



steps: (i) the controlled polymerization of the functional monomer 4-trimethylsilylstyrene (**S−Si**), (ii) the selective exchange of the functional group in poly(4-trimethylsilylstyrene) (**PS−Si**) with BBr_3 to give the borylated polymer **PS−BBr**, and (iii) the fine-tuning of the Lewis acidity of the individual Lewis acid centers through substituent exchange reactions with nucleophiles, which gives access to a series of new well-defined polymers **PS−BR** bearing Lewis acidic boron centers (Scheme 1).[20]

(i) Controlled Polymerization of 4-Trimethylsilylstyrene. Poly(4-trimethylsilylstyrene) (**PS−Si**)[21,22] of controlled molecular weight was synthesized according to a typical protocol for atom transfer free radical polymerization (ATRP)[23] in anisole (50 wt %) at 110 °C initiated with 1-phenylethyl bromide (1-PEBr) and catalyzed by CuBr/*N*,*N*,*N*′*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA). Different ratios of 4-trimethylsilylstyrene to initiator were used to obtain polymers with molecular weights ranging from 5000 to 30 000. The polymer solutions thus obtained were passed through a column of neutral alumina and isolated by repeated precipitation into methanol. Molecular weights were determined by GPC analysis using a refractive index and light scattering detector. GPC relative to polystyrene standards can provide a rough estimate of the molecular weight but slightly underestimates the actual molecular weight by ca. 10−15% as shown by a comparison with static light scattering data. For example, a sample of **PS−Si** of $M_n = 27\,120$ according to static light scattering measurements (GPC-LS) gives a molecular weight of $M_n = 24\,200$ when determined by GPC detection vs polystyrene standards.

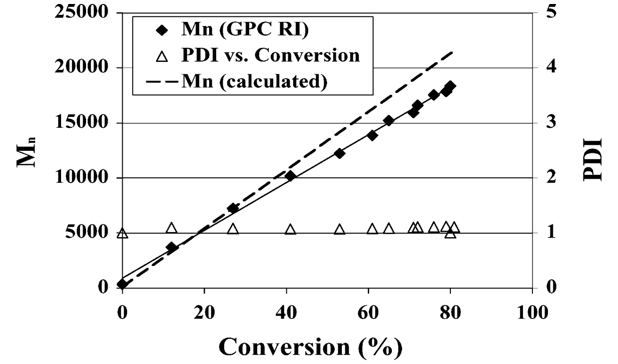


Figure 2. Dependence of M_n and PDI on monomer conversion for atom transfer radical polymerization (ATRP) of 4-(trimethylsilyl)styrene in anisole (50 wt %) at 110 °C as determined by GPC relative to polystyrene standards using a refractive index detector. $[M]_0 = 2.6$ M and $[M]_0:[1\text{-PEBr}]_0:[CuBr]_0:[PMDETA]_0 = 150:1:1:1$.

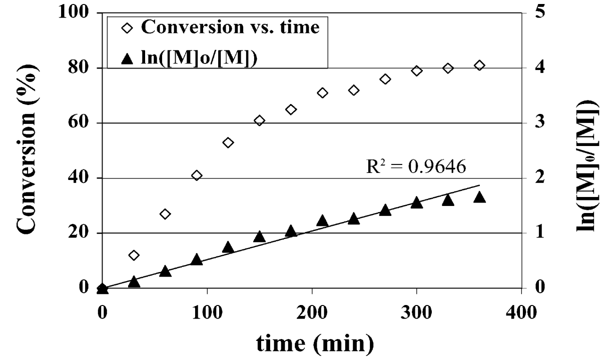


Figure 3. Kinetic data for atom transfer radical polymerization (ATRP) of 4-(trimethylsilyl)styrene in anisole (50 wt %) at 110 °C as determined by ^{1}H NMR spectroscopy. $[M]_0 = 2.6$ M and $[M]_0:[1\text{-PEBr}]_0:[CuBr]_0:[PMDETA]_0 = 150:1:1:1$.

A kinetic analysis of the polymerization reaction was performed using a molar ratio of 4-trimethylsilylstyrene:1-PEBr:CuBr:PMDETA = 150:1:1:1. The molecular weight of the active propagation chains increases linearly with increase in monomer conversion, and the polydispersity remains narrow throughout the polymerization (PDI < 1.2), as shown in Figure 2. The slightly lower molecular weights determined for **PS−Si** in comparison to the calculated molecular weights are due to the difference in hydrodynamic volume between **PS−Si** and the polystyrene standards. The initial linearity of $\ln([M]_0/[M])$ vs time (t) in the pseudo-first-order kinetic plot (Figure 3) indicates that the number of active species remains constant during this part of the polymerization reaction, and thus chain termination is insignificant; i.e., $k_p[P^*] = \text{constant}$, where k_p stands for the rate constant and $[P^*]$ stands for the concentration of active propagation chains.[24] However, while the polydispersity remains low and the molecular weight continues to increase linearly, a deviation from linearity of $\ln([M]_0/[M])$ with time is evident at longer reaction times. This effect indicates a decrease in active propagation chains and could be due to chain transfer or termination by radical coupling or elimination reactions.[25] A linear dependence of $\ln([M]_0/[M])$ vs $t^{2/3}$ for living free radical polymerizations as a result of the persistent radical effect has been derived by Fischer and has in some instances been experimentally verified.[26] In the case of ATRP, typically a linear dependence on t is observed, which is attributed at least in part to a decrease in the termination rate constant k_t with increase in chain length and viscosity.[26d] However, this effect is less pronounced in solution polymerizations. Indeed, our data for $\ln([M_0]/[M])$ give a significantly better correlation with $t^{2/3}$ ($R^2 = 0.9902$) than with t ($R^2 = 0.9646$).

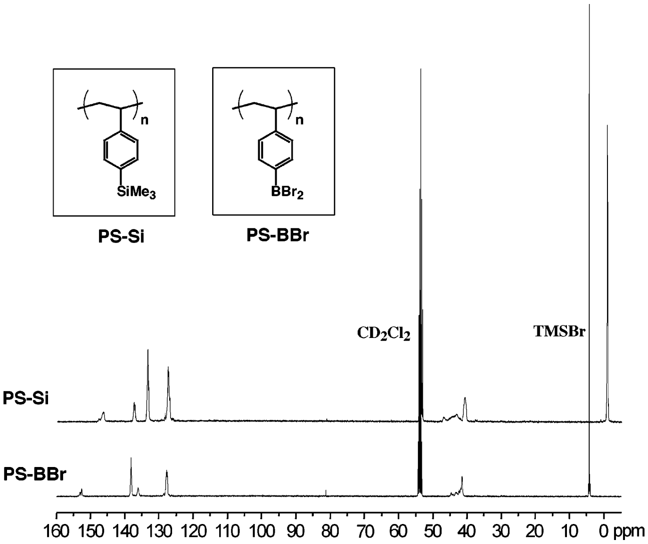


Figure 4. Comparison of the ^{13}C NMR spectra of **PS−Si (**M_n = 5750, PDI = 1.13**)** and the resulting **PS−BBr** in CD_2Cl_2.

To confirm the compatibility of the silyl functional groups with the catalyst system, a model reaction was performed, in which the compound 4-trimethylsilylcumene was treated with the ATRP components in a 1:1 molar ratio and the resulting mixture heated to 110 °C for 3 h. Analysis of the reaction mixture by GC-MS showed coupling products of the initiator as previously reported by Matyjaszewski[25a] but did not reveal any products resulting from C−Si bond cleavage. The observed good control of the polymerization and lack of side reactions with the silyl functional groups thus indicate the potential applicability of our methodology to the preparation of a wide variety of well-defined polymers of different molecular weight and architecture, including copolymers.[27]

(ii) Borylation of Poly(4-trimethylsilyl)styrene. A solution of the silylated polymer **PS−Si** in CH_2Cl_2 was treated with a slight excess of BBr_3 (*caution*! BBr_3 is toxic and highly corrosive), a strong Lewis acid that cleaves Si−C(sp^2) bonds under mild conditions with nearly quantitative yields, and high selectivity.[28] Selective cleavage of the Si−C(sp^2) bonds in **PS−Si** (>97%) to form **PS−BBr** occurred over a period of ca. 12−24 h at room temperature as confirmed by multinuclear NMR spectroscopy.[29] The signal due to the trimethylsilyl substituents of **PS−Si** in the ^{29}Si NMR spectrum at $\delta = -4.4$ completely disappeared, and a new sharp resonance that may be assigned to Me_3SiBr developed at $\delta = 28.0$. At the same time a new broad resonance grew in the ^{11}B NMR spectrum at $\delta = 54$ in a region typical of arylboron dibromides. The chemical shift of $\delta = 54$ compares favorably with that of $\delta = 55.8$ found for the molecular model compound 4-dibromoborylcumene ($4\text{-}Br_2BC_6H_4{}^iPr$; see Supporting Information). The presence of strongly electron-withdrawing substituents on the phenyl rings is further reflected in the ^{1}H and ^{13}C NMR spectra of **PS−BBr**. Upon borylation, the protons in the *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−BBr** (for 4-dibromoborylcumene: $\delta = 8.08$). A similar trend is observed for the carbon atoms in the *ortho*-position to the boryl groups which resonate at $\delta = 138.5$ (**PS−Si**: $\delta = 133.8/133.5$) (Figure 4). A broad resonance at $\delta = 136.4$ can be attributed to the carbon atom bearing the boryl substituent, and two closely spaced signals ($\delta = 153.3$, 152.9) are observed for the *ipso*-carbon atom closest to the polymer backbone. Again, these data correlate well with those of the molecular model compound 4-dibromoborylcumene, which shows signals at $\delta = 157.2$ and 138.5 for the C4 and C2,6 carbons of the phenyl group, respectively. 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.

The soluble borylated polymer **PS−BBr** can be isolated in ca. 80% yield as a white solid material after precipitation into hexanes. However, because of the extreme sensitivity to moisture, the polymer is most conveniently used in situ for further exchange of the bromide substituents with nucleophilic reagents.

(iii) Fine-Tuning of Lewis Acidity. The dibromoborylated polymer **PS−BBr** is ideally suited as a precursor to other polymers with boron centers of varying Lewis acidity. While the introduction of alkoxy substituents on boron should yield moderately Lewis acidic arylboronate polymers, the exchange of the bromide substituents for aryl groups should provide access to highly Lewis acidic triarylborane polymers.

(a) Synthesis and Characterization of Poly(styreneboronate)s. Initially we studied the reactivity of **PS−BBr** toward alcohols such as methanol or ethanol. However, better exchange selectivity is achieved with silyl ethers or cyclic ethers, which do not produce hydrogen bromide upon reaction with **PS−BBr**.[30] Thus, the polymeric boronate **PS−BOEt** readily formed upon treatment with excess of Me_3SiOEt and was isolated as a white solid in ca. 90% yield upon freeze-drying from benzene (Scheme 2). Similarly, **PS−BBr** smoothly reacted with an excess of tetrahydrofuran to give the gummy polymer **PS−BOBuBr** in ca. 83% yield upon precipitation into hexanes. The isolated yield of ca. 83% for the gummy polymer **PS−BOBuBr** is slightly lower due to losses during precipitation into hexanes.[31] The alkoxy substituents in **PS−BOEt** are readily replaced upon reaction with pinacol at ambient temperature in toluene to yield the air-stable pinacol polymer **PS−BPin**, which was isolated by precipitation into methanol (Scheme 2). A relatively high glass transition temperature of $T_g = 228$ °C was observed for **PS−BPin** (M_n = 12 690) in comparison to poly(4-trimethylsilystyrene) ($T_g = 132$ °C, M_n = 27 120), which may be attributed to the bulky and rigid nature of the five-membered boronate ring. The gummy appearance of **PS−BOBuBr** suggested a significantly lower glass transition temperature relative to that for **PS−BPin**. Indeed, DSC analysis revealed $T_g = -52$ °C for **PS-BOBuBr** and $T_g = 20$ °C for **PS-BOEt**. As expected from the high flexibility of the alkoxy side chains attached to these polymers, the glass transition temperatures are significantly lower than that for **PS-BOPin**.

All arylboronate polymers **PS−BOR** (R = Et, 4-bromobutyl, pinacolato) were fully characterized by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopy, and the selective attachment of pinacol substituents in **PS−BPin** was further confirmed by elemental analysis. Formation of the arylboronate polymers is reflected in a pronounced upfield shift of the ^{11}B NMR resonance at $\delta = 26$ relative to the precursor polymer **PS−BBr** ($\delta = 54$), which is indicative of significant π-overlap between the alkoxy substituents and the boron centers (Table 1). The

Scheme 2. Formation of Arylboronate Polymers PS-BOR (R = Et, 4-Bromobutyl, Pinacolato) from PS−BBr

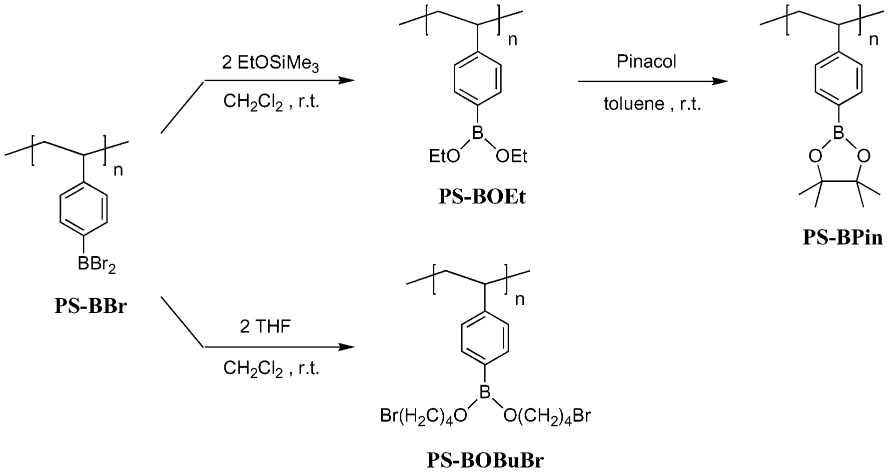
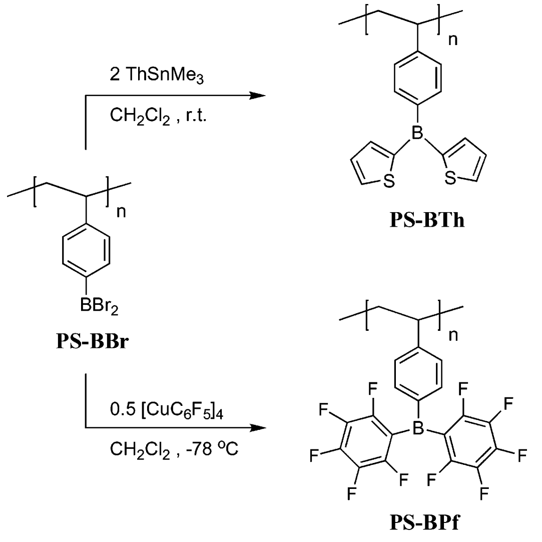


Table 1. ^{11}B NMR Data of Polymeric Lewis Acids PS-BR and the Respective Model Compounds M-BR[a]

R groups[b]	Br	Pf	Th	OEt	OBuBr	Pin
PS-BR	54 (2800)	56 (2500)	47 (2500)	26 (1400)	26 (1700)	26 (1600)
M-BR	56 (300)	62 (1100)	55 (1000)	28 (450)	28 (550)	31 (400)

[a] Chemical shifts are given in ppm relative to $BF_3{\cdot}OEt_2$; the width of the signal at half-height (reported in Hz) is given in parentheses. [b] Pf = 2,3,4,5,6-pentafluorophenyl, Th = 2-thienyl, BuBr = 4-bromobutyl, Pin = pinacolato.

Scheme 3. Selective Formation of Triarylborane Polymers via Tin−Boron and Copper−Boron Exchange Reactions (Th = 2-Thienyl)



chemical shifts observed are at slightly higher field in comparison to those recorded for the related model compounds. This effect, however, is not significant as the signal is strongly broadened as a result of the incorporation of the boron centers into the polymer structure.

(b) Synthesis and Characterization of Triarylborane Polymers. Triarylborane polymers are readily accessible from **PS−BBr** via tin−boron exchange reactions. Treatment of a solution of **PS−BBr** in dichloromethane with a slight excess of the highly selective aryl transfer reagent 2-trimethylstannylthiophene yielded polymer **PS−BTh** (Scheme 3). The polymer thus formed was obtained as a white solid material in 80% isolated yield after repeated precipitation from dichloromethane into hexanes. The glass transition temperature for the triarylborane polymer **PS−BTh** (prepared from **PS−Si** of M_n = 27 120, PDI = 1.11) was determined to be 148 °C (onset), which compares favorably with that of the structurally related triarylamine polymer poly(vinyltriphenylamine) (T_g = 136 °C for M_n = 26 200).[32]

We were interested in attaching electron-withdrawing pentafluorophenyl (Pf) substituents to boron in order to access even more highly Lewis acidic polymers such as **PS−BPf**. Tin−boron exchange cannot, however, be applied to the synthesis of **PS−BPf** because the methyl group in the respective organotin reagent $C_6F_5SnMe_3$ is transferred more readily than the pentafluorophenyl group.[33,34] The arylcopper reagent pentafluorophenylcopper, $[C_6F_5Cu]_4$,[35] provides a solution to this problem. We have recently shown that this crystalline, readily isolable organometallic reagent selectively transfers the C_6F_5 moiety to boron halides at low temperature in aromatic or chlorinated solvents.[36] Indeed, treatment of **PS−BBr** with 0.5 equiv of $[C_6F_5Cu]_4$ yielded the highly Lewis acidic polymer **PS−BPf**. We found that it is important in this reaction to avoid any excess of the copper reagent. We thus applied a slight deficiency of $[C_6F_5Cu]_4$ (95−97%) and then treated the crude product with a small amount of $ThSnMe_3$ (Th = 2-thienyl) in order to quench any unreacted B−Br groups.[37] The polymer **PS−BPf** was obtained as a white solid in ca. 74% yield after repeated precipitation into hexanes (Scheme 3). The glass transition temperature for **PS−BPf** (prepared from **PS−Si** of M_n = 27 120, PDI = 1.11) of 134 °C (onset) is similar to that of **PS−BTh** and the previously reported nitrogen analogue poly(vinyltriphenylamine) of T_g = 136 °C.[32]

The triarylborane polymers **PS−BAr** (Ar = Th, Pf) were fully characterized by multinuclear NMR spectroscopy, and the selective attachment of the aryl groups was further confirmed by elemental analysis. The large chemical shifts of δ = 47 for **PS−BTh** and of δ = 56 for **PS−BPf** confirm the expected high Lewis acidity of these triarylborane polymers (Table 1). Similar to our observations with the arylboronate polymers, the ^{11}B NMR resonances appear slightly upfield-shifted and strongly broadened in comparison to the signals for the cumene model compounds. While the ^{1}H NMR spectra for polymers **PS−BAr** typically show broad signals that

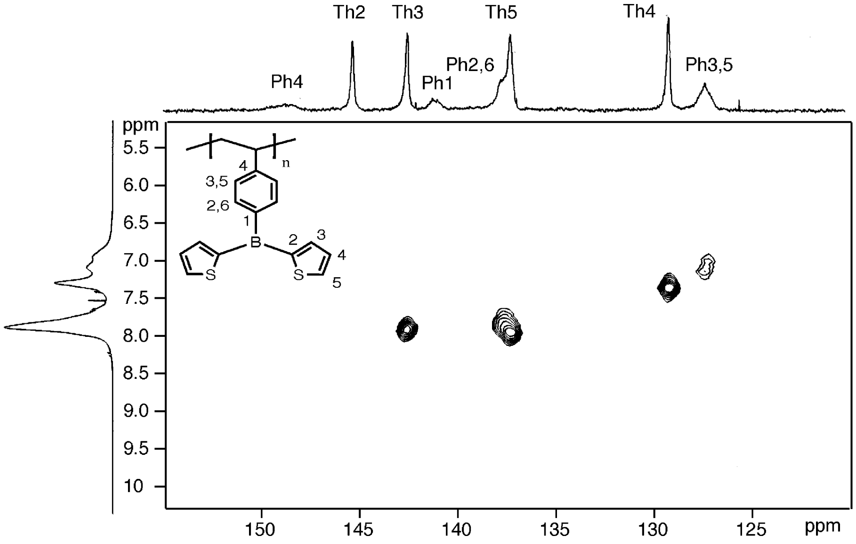


Figure 5. Aromatic region of the HMQC spectrum of **PS−BTh**.

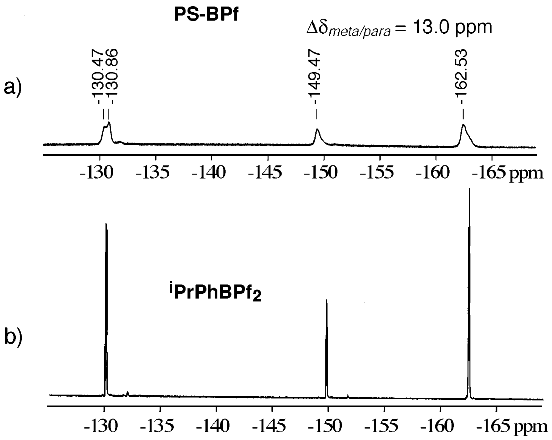


Figure 6. (a) ^{19}F NMR spectrum of **PS−BPf** (Pf = 2,3,4,5,6-pentafluorophenyl) in CD_2Cl_2; $\Delta\delta_{\text{meta/para}}$ represents the chemical shift difference between the *meta*- and *para*-fluorine atoms. (b) ^{19}F NMR spectrum of 4-isopropylphenylbis(pentafluorophenyl)borane in C_6D_6.

do not provide much information, the ^{13}C NMR signals are distinct and can readily be assigned through two-dimensional NMR spectroscopy as shown for the polymer **PS−BTh**. The HMQC (heteronuclear multiple quantum correlation) spectrum of **PS−BTh** shows in the aromatic region one set of four relatively sharp peaks assigned to the pending thienyl substituents and one set of resonances for the phenyl groups that is strongly broadened due to the atactic nature of the polystyrene backbone (Figure 5).

The ^{13}C NMR chemical shifts of the phenyl groups of the polystyrene backbone also demonstrate the high Lewis acidity of polymers **PS−BAr**. For instance, the carbon atoms in the *ortho*-position to the boryl group resonate at $\delta = 140.0$ and 137.4 for **PS−BPf** and **PS−BTh**, respectively. The chemical shifts are close to that of the parent compound **PS−BBr** at $\delta = 138.5$ and significantly downfield-shifted relative to the signals observed for the arylboronate polymers in the range from $\delta = 133.8$ to 135.2.

The attachment of pentafluorophenyl groups in **PS−BPf** was conveniently followed by ^{19}F NMR spectroscopy. A large chemical shift difference of $\Delta\delta_{m,p} = 13.0$ (Figure 6a) between the *meta*- and *para*-fluorine atoms at $\delta_p = -149.5$ and $\delta_m = -162.5$, respectively, is indicative of highly Lewis acidic centers attached to the pentafluorophenyl groups.[34,38] The resonance due to the *ortho*-fluorine atoms is split into two signals at $\delta_o = -130.5/-130.9$ as a result of the atactic nature of the polystyrene backbone. The chemical shifts compare favorably with those of the molecular model compound 4-isopropylphenylbis(pentafluorophenyl)borane (Figure 6b).[36,39]

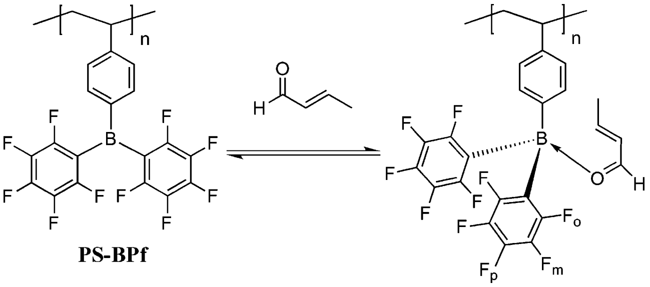


Figure 7. Estimation of Lewis acidity of **PS−BPf** through formation of crotonaldehyde complex in CD_2Cl_2.

Estimation of Lewis Acidity According to Childs' Method. The relative Lewis acidity of the boron centers in **PS−BPf** was estimated by complexation with crotonaldehyde in CD_2Cl_2 at −20 °C according to Childs' method (Figure 7).[40] On a scale from 0 to 1.0 (BBr_3 = 1.0) a relative Lewis acidity of 0.60 was determined for **PS−BPf** based on the ^{13}C NMR shifts of the complexed crotonaldehyde relative to those of the free aldehyde. The determined relative Lewis acidity of **PS−BPf** is pronounced, but slightly lower than that found for $B(C_6F_5)_3$ (values ranging from 0.68 to 0.77 have been reported)[41,42] as is expected since the phenyl groups of the polystyrene are not fluorinated. A pronounced Lewis acidity of **PS−BPf** is further confirmed by a characteristic large chemical shift difference between the *meta*- and *para*-fluorine atoms of $\Delta\delta_{m,p} = 13.0$ for the free acid (see Figure 6) that significantly decreases to $\Delta\delta_{m,p} = 6.4$ in the polymeric crotonaldehyde adduct.

Molecular Weight Determination of Boron-Containing Polymers. The molecular weights of the alkoxy-substituted polymers were determined by GPC measurements relative to polystyrene standards.[43] The molecular weight and polydispersity of all polymers were found to be very close to those of the precursor polymer **PS−Si**. Static light scattering measurements

Table 2. Comparison of GPC and Light Scattering Data for PS-Si and PS-BPin in THF[a]

polymer	dn/dc (mL/g)	M_w	PDI	DP	A_2 (mol·mL/g^2)	R_H (nm)
PS-Si	0.157	10 140	1.08	51	8.774×10^{-4}	2.2
PS-BPin	0.138	13 830	1.09	53	4.772×10^{-4}	2.4

[a] Differential refractive index (dn/dc) from batch measurements, molecular weight (M_w), degree of polymerization (DP), and second virial coefficient A_2 from batch mode static light scattering, polydispersity (PDI) from GPC (LS detector), and hydrodynamic radius (R_H) from dynamic light scattering.

were performed on polymer **PS−BPin** in order to further confirm the high selectivity and absence of cross-linking upon borylation and subsequent functionalization of **PS−Si**. Again, both the experimentally determined average degree of polymerization and the polydispersity of **PS−BPin** were similar to those of the precursor polymer **PS−Si** (Table 2). This clearly confirms that the borylation and subsequent substituent exchange occur without significant cross-linking or cleavage of the polymer backbone.

Conclusions

We have developed a highly efficient new method for the attachment of Lewis acidic boron centers to the side chains of organic polymers. The borylation of the silylated polymer **PS−Si** with BBr_3 occurs nearly quantitatively and with very good selectivity. The resulting reactive polymer **PS−BBr** serves as a highly versatile precursor to a family of new boron-containing polymeric Lewis acids. Facile substituent exchange reactions on boron provide access to various poly(arylboronates) **PS−BOR** and highly Lewis acidic polymeric triarylboranes **PS−BAr**. For example, the introduction of pentafluorophenyl substituents on boron resulted in formation of **PS−BPf**, the first polymeric analogue of the important class of highly Lewis acidic fluorinated arylboranes, which play a major role as catalysts in organic synthesis[44] and as cocatalysts in olefin polymerization.[41,45,46] The organoboron polymers also lend themselves to further studies with regard to the formation of polymeric complexes with nucleophiles and their assembly with donor-functionalized polymers, which is currently underway in our laboratory.

Experimental Section

Materials and General Methods. The compounds 4-chlorostyrene (99%), Mg (turnings, 99.9%), Me_3SiCl (98%), BBr_3 (99.9%), CuBr (98%), 1-bromo-1-phenylethane (97%), anisole (99%), pinacol (99%), and crotonaldehyde (99+%) were purchased from Acros. The compounds Me_3SiOEt (98%) and N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA; 99%) were purchased from Aldrich, and 4-bromocumene (97%) was obtained from Lancaster. BBr_3 was distilled under vacuum, and Me_3SiCl, Me_3SiOEt, PMDETA, anisole, and 1-bromo-1-phenylethane were distilled from CaH_2 prior to use; CuBr was purified according to a literature procedure.[47] All other chemicals were used as received without further purification. The compounds 4-trimethylsilylstyrene,[48] 2-trimethylstannylthiophene,[49] and $[C_6F_5Cu]_4(\text{toluene})_2$[35] were prepared according to literature procedures. Reactions and manipulations involving boron species were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Innovative Technologies). Ether solvents were distilled from Na/benzophenone prior to use. Hydrocarbon and chlorinated solvents were purified using a solvent purification system (Innovative Technologies; alumina/copper columns for hydrocarbon solvents), and the chlorinated solvents were subsequently distilled from CaH_2 and degassed via several freeze−pump−thaw cycles.

The 399.952 MHz ^{1}H and 100.564 MHz ^{13}C NMR spectra were recorded at ambient temperature on a Varian VXR-S 400 MHz and the 499.893 MHz ^{1}H and 125.681 MHz ^{13}C NMR spectra on a Varian INOVA 500 MHz spectrometer. The 79.4 MHz ^{29}Si (DEPT mode) and the 376.263 MHz ^{19}F spectra were recorded on the Varian VXR-S 400 spectrometer, and the 160.4 MHz ^{11}B NMR spectra were recorded on the Varian INOVA 500 spectrometer equipped with a boron-free probe using boron-free quartz NMR tubes. All solution ^{1}H and ^{13}C NMR spectra were referenced internally to the solvent peaks. ^{29}Si and ^{11}B NMR spectra were referenced externally to $SiMe_4$ ($\delta = 0$) and $BF_3{\cdot}Et_2O$ ($\delta = 0$) in C_6D_6, respectively, and ^{19}F NMR spectra were referenced to α,α',α''-trifluorotoluene (0.05% in C_6D_6; $\delta = -63.73$). GPC analyses were performed in THF (1 mL/min) using a Waters Breeze system equipped with a 717plus autosampler, a 1525 binary HPLC pump, a 2487 dual λ absorbance detector, and a 2414 refractive index detector. A series of styragel columns (Polymer Laboratories; 5 μm Mix-D, 5 μm Mix-C, and 10 μm Mix-B), which were kept in a column heater at 35 °C, were used for separation. The columns were calibrated with polystyrene standards (Polymer Laboratories). Multiangle laser light scattering (MALLS) experiments were performed at 690 nm (30 mW linear polarized GaAs laser) using a Wyatt Dawn EOS instrument either in a batch mode or in-line with the GPC as specified; differential refractive indices dn/dc were determined using a Wyatt Optilab at 690 nm. Dynamic light scattering (DLS) studies were performed using the Wyatt Dawn EOS modified with a Wyatt QELS attachment. Data were collected at an angle of 108° using an avalanche photodiode and an optical fiber and processed with the Wyatt QELS software (regularization analysis). GC-MS spectra were acquired on a Hewlett-Packard HP 6890 series GC system equipped with a series 5973 mass selective detector and a series 7683 injector. A temperature profile with a heating rate of 20 °C/min from 50 to 280 °C was used. Mass spectral data (EI mode; direct probe) were obtained at the Michigan State University Mass Spectrometry Facility which is supported, in part, by a grant (DRR-00480) from the Biotechnology Research Technology Program, National Center for Research Resources, National Institutes of Health. DSC measurements were performed on a Perkin-Elmer differential scanning calorimeter Pyris 1 system with ca. 20 mg of polymer using the specified scan rate. Elemental analyses were performed by Quantitative Technologies Inc. Whitehouse, NJ.

Caution! BBr_3 is toxic and highly corrosive and should be handled appropriately with great care. Fluorinated grease was used for ground glass joints in all reactions involving boron tribromide.

Representative Procedure for the Synthesis of Poly(4-trimethysilylstyrene) (PS−Si). 4-Trimethylsilylstyrene was distilled from CaH_2 and degassed via several freeze−pump−thaw cycles prior to use. In a glovebox, 4-trimethylsilylstyrene (50 g, 0.284 mol), 1-bromo-1-phenylethane (0.26 g, 1.42 mmol), copper(I) bromide (0.20 g, 1.42 mmol), and PMDETA (0.25 g, 1.42 mmol) were charged into a 250 mL Schlenk flask, and 50 g of anisole were added. The flask was then taken out of the glovebox, degassed by three freeze−pump−thaw cycles, and subsequently immersed in an oil bath preset at 110 °C. After stirring for 5 h the flask was cooled to room temperature, and the reaction mixture was precipitated into methanol (1 L). The precipitate was collected by filtration and redissolved in THF. The THF solution was then passed through a short column packed with ca. 5 g neutral alumina and concentrated to ca. 15 mL. Poly(4-trimethylsilylstyrene) (**PS−Si**) was recovered by precipitation into methanol (1 L) and dried under vacuum at 50 °C for 24 h (yield: 32.2 g, 64%). For **PS−Si**: ^{1}H NMR (399.952 MHz, CD_2Cl_2) $\delta = 7.31$, 7.17, 7.04 (br m, 2H, Ph−H2,6), 6.58, 6.38, 6.18 (br m, 2H, Ph−H3,5), 2.0−1.2 (br, 3H, $C\boldsymbol{H}_2C\boldsymbol{H}$), 0.24 (s, 9H, $Si[C\boldsymbol{H}_3]_3$). ^{1}H NMR (399.952 MHz, $CDCl_3$) $\delta = 7.25$, 7.11, 6.97 (br m, 2H, Ph−H2,6), 6.54, 6.33, 6.10 (br m, 2H, Ph−H3,5), 2.0−1.2 (br, 3H, $C\boldsymbol{H}_2C\boldsymbol{H}$), 0.21 (s, 9H, $Si[C\boldsymbol{H}_3]_3$). ^{1}H NMR (399.952 MHz, C_6D_6) $\delta = 7.45$, 7.37, 7.29 (br m, 2H, Ph−H2,6), 6.81, 6.63, 6.54 (br m, 2H, Ph−H3,5), 2.27, 2.10 (br m, 1H, $\mathrm{CH_2C}\boldsymbol{H}$]), 1.63 (br, 2H, $\mathrm{C}\boldsymbol{H}_2\mathrm{CH}$), 0.31 (br s, 9H, $\mathrm{Si[C}\boldsymbol{H}_3]_3$). ^{13}C NMR (100.564 MHz, CD_2Cl_2) δ = 146.8 (br, Ph−C4), 137.8, 137.5, 137.3 (Ph−C1), 133.8, 133.5 (Ph−C2,6), 128.0, 127.8, 127.7, 127.3, (Ph−C3,5), 48−42 (br, $\mathrm{CH_2}\boldsymbol{C}\mathrm{H}$), 41.2 ($\boldsymbol{C}\mathrm{H_2CH}$) −0.8 ($\mathrm{Si[}\boldsymbol{C}\mathrm{H_3]_3}$). ^{13}C NMR (100.564 MHz, C_6D_6) δ = 146.7 (Ph−C4), 137.4 (Ph−C1), 133.7 (Ph−C2,6), 128.0 (Ph−C3,5), 48−42 (br, $\mathrm{CH_2}\boldsymbol{C}\mathrm{H}$), 41.2 ($\boldsymbol{C}\mathrm{H_2CH}$), −0.5 ($\mathrm{Si[}\boldsymbol{C}\mathrm{H_3]_3}$). ^{29}Si NMR (79.4 MHz, CD_2Cl_2) $\delta = -4.4$. GPC-LS (in THF): M_n = 27 120, M_w = 30 100, PDI = 1.11; refractive index increment at 25 °C in THF: d*n*/d*c* = 0.161 mL/g; DSC (second heating curve; M_n = 27 120): T_g = 132 °C (onset, 20 °C/min). Polymers of different molecular weight were obtained by variation of the ratio of initiator to monomer.

General Procedure for Kinetic Analysis of Atom Transfer Radical Polymerization of PS−Si. 4-Trimethylsilylstyrene, 1-bromo-1-phenylethane, CuBr, PMDETA (150/1/1/1), and anisole (50 wt %; used as both solvent and internal NMR standard) were charged in a glovebox into a Schlenk flask with a rubber septum, which was then immersed in an oil bath at 110 °C. At predetermined times, a small amount of sample was withdrawn from the flask with a nitrogen-flushed syringe for GPC and NMR analysis.

Reaction of PS−Si with BBr_3: Synthesis of Poly(4-dibromoborylstyrene) (PS−BBr). *Caution*: BBr_3 is toxic and highly corrosive! A solution of BBr_3 (0.31 mL, 3.3 mmol) in 5 mL of CH_2Cl_2 was added dropwise under stirring to **PS−Si** (0.48 g; ca. 2.7 mmol repeat units; M_n = 5750; PDI = 1.13) in 10 mL of CH_2Cl_2. After completion of the addition the mixture was stirred for 24 h. Complete replacement of the silyl substituents for dibromoboryl groups was confirmed by ^{1}H NMR spectroscopy. The reaction solution was concentrated under high vacuum to ca. 2 mL and then precipitated into a large volume of hexanes (ca. 200 mL). The hexane solution was decanted from a white precipitate. The solid was washed with hexanes and dried under high vacuum for 12 h to give 0.60 g (81%) of **PS−BBr**. More conveniently, the polymer solution may be used directly for further reactions with nucleophiles. ^{1}H NMR (399.952 MHz, CD_2Cl_2): δ = 8.2−7.6 (br m, 2H, Ph−H2,6), 7.2−6.4 (br m, 2H, Ph−H3,5), 2.4−1.4 (br m, 3 H, $\mathrm{C}\boldsymbol{H}_2\mathrm{C}\boldsymbol{H}$). ^{1}H NMR (399.952 MHz, $CDCl_3$) δ = 8.2−7.6 (br m, 2H, Ph−H2,6), 7.2−6.4 (br m, 2H, Ph−H3,5), 2.4−1.4 (br m, 3 H, $\mathrm{C}\boldsymbol{H}_2\mathrm{C}\boldsymbol{H}$). ^{13}C NMR (100.564 MHz, CD_2Cl_2): δ = 153.3, 152.9 (Ph−C4), 138.5 (Ph−C2,6), 136.4 (Ph−C1), 128.1, 127.9 (Ph−C3,5), 45−42 (br, $\mathrm{CH_2}\boldsymbol{C}\mathrm{H}$), 42.1, 41.7 ($\boldsymbol{C}\mathrm{H_2CH}$). ^{11}B NMR (160.370 MHz, $CDCl_3$): δ = 54 ($w_{1/2}$ = 2800 Hz). Note: The crude mixture shows the following additional signals due to Me_3SiBr: ^{1}H NMR (399.952 MHz, CD_2Cl_2): δ = 0.59 (s, 9 H, $\mathrm{BrSi(C}\boldsymbol{H}_3)_3$). ^{13}C NMR (100.564 MHz, CD_2Cl_2): δ = 4.5 ($\mathrm{BrSi(}\boldsymbol{C}\mathrm{H_3)_3}$). ^{29}Si DEPT NMR (79.4 MHz, CD_2Cl_2): δ = 28.0 ppm; the NMR data for Me_3SiBr were confirmed by comparison with those of a sample of commercial Me_3SiBr (Aldrich) in CD_2Cl_2.

Treatment of PS−BBr with Me_3SiOEt: Synthesis of Poly(4-diethoxyborylstyrene) (PS−BOEt). A solution of **PS−BBr** prepared from BBr_3 (0.86 g, 3.4 mmol) and **PS−Si** (0.50 g, ca. 2.8 mmol repeat units; M_n = 5750; PDI = 1.13) in 15 mL of CH_2Cl_2 was treated with Me_3SiOEt (1.3 mL, 8.3 mmol) and stirred for 12 h. All volatile material was removed under high vacuum, and the oily residue was redissolved in benzene (10 mL). After freeze-drying **PS−BOEt** was isolated as a white solid (0.52 g, 90%). ^{1}H NMR (399.952 MHz, CD_2Cl_2): δ = 7.6−7.0 (br m, 2H, Ph−H2,6), 7.0−6.4 (br m, 2H, Ph−H3,5), 4.13 (br, 4H, $\mathrm{OC}\boldsymbol{H}_2\mathrm{CH_3}$), 2.2−1.4 (br m, 3H, $\mathrm{C}\boldsymbol{H}\mathrm{C}\boldsymbol{H}_2$), 1.33 (br, 6H, $\mathrm{OCH_2C}\boldsymbol{H}_3$). ^{1}H NMR (399.952 MHz, $CDCl_3$): δ = 7.5−7.1 (br m, 2H, Ph−H2,6), 6.8−6.2 (br m, 2H, Ph−H3,5), 4.00 (br, 4H, $\mathrm{OC}\boldsymbol{H}_2\mathrm{CH_3}$), 2.0−1.4 (br m, 3H, $\mathrm{C}\boldsymbol{H}\mathrm{C}\boldsymbol{H}_2$), 1.23 (br, 6H, $\mathrm{OCH_2C}\boldsymbol{H}_3$). ^{1}H NMR (399.952 MHz, C_6D_6): δ = 7.8−7.4 (br m, 2H, Ph−H2,6), 7.1−6.5 (br m, 2H, Ph−H3,5), 4.07 (br, 4H, $\mathrm{OC}\boldsymbol{H}_2\mathrm{CH_3}$), 2.6−1.4 (br m, 3H, $\mathrm{C}\boldsymbol{H}\mathrm{C}\boldsymbol{H}_2$), 1.21 (br, 6H, $\mathrm{OCH_2C}\boldsymbol{H}_3$). ^{13}C NMR (100.564 MHz, CD_2Cl_2): δ = 148.0, 147.1 (Ph−C4), 133.8 (Ph−C2,6), 131.0 (Ph−C1), 127.4 (Ph−C3,5), 60.4 ($\mathrm{O}\boldsymbol{C}\boldsymbol{H}_2\mathrm{CH_3}$), 48−42 (br, $\mathrm{CH_2}\boldsymbol{C}\mathrm{H}$]), 41.0 ($\boldsymbol{C}\mathrm{H_2CH}$), 17.8 ($\mathrm{OCH_2}\boldsymbol{C}\mathrm{H_3}$). ^{11}B NMR (160.370 MHz, CD_2Cl_2): δ = 26 ($w_{1/2}$ = 1400 Hz). GPC (in THF against PS standards): M_n = 5470, PDI = 1.14; DSC (second heating curve): T_g = 20 °C (onset, 20 °C/min); repeated elemental analyses showed consistently low carbon content, which is likely due to partial hydrolysis of the boronic ester linkages during analysis.

Treatment of PS−BBr with THF: Synthesis of Poly[4-bis(4′-bromobutoxy)borylstyrene] (PS−BOBuBr). A solution of **PS−BBr** prepared from BBr_3 (0.60 g, 2.4 mmol) and **PS−Si** (0.35 g, ca. 2.0 mmol repeat units; M_n = 5750; PDI = 1.13) in 15 mL of CH_2Cl_2 was treated with THF (0.40 g, 5.5 mmol) and stirred for 12 h. The reaction solution was concentrated under high vacuum to ca. 2 mL and then precipitated into a large volume of hexanes (ca. 200 mL). The hexane solution was decanted from a gummy precipitate. After freeze-drying, **PS−BOBuBr** was isolated as a colorless gummy material (0.69 g, 83%). ^{1}H NMR (399.952 MHz, C_6D_6): δ = 7.8−7.2 (br m, 2H, Ph−H2,6), 7.1−6.4 (br m, 2H, Ph−H3,5), 3.92 (br, 4H, $\mathrm{OC}\boldsymbol{H}_2$), 3.10 (br, 4H, $\mathrm{C}\boldsymbol{H}_2\mathrm{Br}$), 2.6−1.4 (br m, 14H, $\mathrm{C}\boldsymbol{H}_2\mathrm{C}\boldsymbol{H}_2\mathrm{CH_2Br}$, $\mathrm{C}\boldsymbol{H}_2\mathrm{C}\boldsymbol{H}$). ^{1}H NMR (399.952 MHz, $CDCl_3$): δ = 7.8−7.0 (br m, 2H, Ph−H2,6), 7.0−6.2 (br m, 2H, Ph−H3,5), 3.99 (br, 4H, $\mathrm{OC}\boldsymbol{H}_2$), 3.41 (br, 4H, $\mathrm{C}\boldsymbol{H}_2\mathrm{Br}$), 2.1−1.0 (br m, 14H, $\mathrm{C}\boldsymbol{H}_2\mathrm{C}\boldsymbol{H}_2\mathrm{CH_2Br}$, $\mathrm{C}\boldsymbol{H}_2\mathrm{C}\boldsymbol{H}$). ^{13}C NMR (100.564 MHz, C_6D_6): δ = 147.7 (Ph−C4), 134.3 (Ph−C2,6), 130.7 (Ph−C1), 128 (Ph−C3,5), 63.7 ($\mathrm{O}\boldsymbol{C}\mathrm{H_2}$), 50−42 (br, $\mathrm{CH_2}\boldsymbol{C}\mathrm{H}$), 41.2 ($\boldsymbol{C}\mathrm{H_2CH}$), 33.7 ($\boldsymbol{C}\mathrm{H_2Br}$), 30.5, 29.7 ($\boldsymbol{C}\mathrm{H_2}\boldsymbol{C}\mathrm{H_2CH_2Br}$). ^{11}B NMR (160.370 MHz, C_6D_6): δ = 26 ($w_{1/2}$ = 1700 Hz). GPC (in THF against PS standards): M_n = 6300, PDI = 1.14; DSC (second heating curve): T_g = −52 °C (onset, 20 °C/min); elemental analysis for **PS−BOBu** (153 repeat units): calcd: C, 45.99; H, 5.54; found: C, 46.36; H, 5.75.

Treatment of PS−BOEt with Pinacol: Synthesis of PS−BPin. Neat pinacol (1.04 g, 8.77 mmol) was added to **PS−BOEt** (1.47 g, 7.3 mmol; synthesized from **PS−Si** of M_n = 9390, PDI = 1.08 by GPC-LS) in 20 mL of toluene and stirred for 12 h. The resulting clear solution was then concentrated to ca. 5 mL under vacuum and precipitated into methanol (500 mL). The white solid thus obtained was dissolved in 20 mL of benzene and freeze-dried to give a white powdery material (1.27 g, 77%). ^{1}H NMR (399.952 MHz, C_6D_6): δ = 8.2−7.8 (br m, 2H, Ph−H2,6), 6.9−6.4 (br m, 2H, Ph−H3,5), 2.4−1.2 (br m, 3H, $\mathrm{C}\boldsymbol{H}\mathrm{C}\boldsymbol{H}_2$), 1.4−1.0 (br, 12H, $\mathrm{OC}\boldsymbol{Me}_2\mathrm{C}\boldsymbol{Me}_2\mathrm{O}$). ^{13}C NMR (100.564 MHz, CD_2Cl_2): δ = 149.1 (Ph−C4), 135.2 (Ph−C2,6), 127.8 (Ph−C3,5), 127.0 (Ph−C1), 84.0 ($\mathrm{O}\boldsymbol{C}\mathrm{Me_2}\boldsymbol{C}\mathrm{Me_2O}$), 48−42 (br, $\mathrm{CH_2}\boldsymbol{C}\mathrm{H}$), 41.1 ($\boldsymbol{C}\mathrm{H_2CH}$), 25.3 ($\mathrm{OC}\boldsymbol{Me}_2\mathrm{C}\boldsymbol{Me}_2\mathrm{O}$). ^{11}B NMR (160.370 MHz, CD_2Cl_2): δ = 26 ($w_{1/2}$ = 1600 Hz). GPC (in THF against PS standards): M_n = 10 100, PDI = 1.10; refractive index increment at 25 °C in THF: d*n*/d*c* = 0.138 mL/g; static light scattering (Zimm plot): M_w = 13 830; $A_2 = 4.772 \times 10^{-4}$ mol·mL/g^2; dynamic light scattering: R_H = 2.4 nm (average); DSC (second heating curve): T_g = 228 °C (onset, 40 °C/min); TGA (20 °C/min; under N_2): 98% weight loss between 360 °C and 560 °C; elemental analysis for **PS−BPin** (51 repeat units): calcd: C, 72.75; H, 8.27; found: C, 72.63; H, 8.36.

Treatment of PS−BBr with 2-(Trimethylstannyl)thiophene: Synthesis of Poly(4-(di-2-thienylboryl)styrene) (PS−BTh). A solution of **PS−BBr** prepared from BBr_3 (3.11 g, 12.4 mmol) and **PS−Si** (2.0 g, ca. 11.3 mmol repeating units; M_n = 27 120; PDI = 1.11) in 20 mL of CH_2Cl_2 was treated with a solution of 2-(trimethylstannyl)thiophene (6.1 g, 28.3 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred for 12 h. The reaction solution was concentrated under high vacuum to ca. 5 mL, and the polymer was recovered by repeated precipitation into hexanes. The resulting white solid was washed with hexanes and dried under high vacuum for 24 h at 50 °C to give 2.5 g (80%) of **PS−BTh**. ^{1}H NMR (499.893 MHz, $CDCl_3$): δ = 8.0−7.4 (br, 6H, Ph−H2,6 and Th−H3,5), 7.08 (br, 2H, Th−H4), 6.9−6.7 (br, 2H, Ph−H3,5), 2.6−1.4 (br m, 3H, $\mathrm{C}\boldsymbol{H}_2\mathrm{C}\boldsymbol{H}$). ^{13}C NMR (125.681 MHz, $CDCl_3$): δ = 149.2, 148.4 (br, Ph−C4), 145.1 (Th−C2), 142.3 (Th−C3), 140.9 (br, Ph−C1), 137.4 (br, Ph−C2,6), 137.0 (Th−C5), 129.0 (Th−C4), 127.1 (br, Ph−C3,5), 47−42 (br, $\mathrm{CH_2}\boldsymbol{C}\mathrm{H}$), 41 (br, $\boldsymbol{C}\mathrm{H_2CH}$). ^{11}B NMR (160.370 MHz, $CDCl_3$): δ = 47 ($w_{1/2}$ = 2500 Hz). DSC (second heating curve): T_g = 148 °C (onset, 40 °C/min); elemental analysis for **PS−BTh** (153 repeat units): calcd: C, 68.51; H, 4.68; S, 22.79; found: C, 68.17; H, 4.50; S, 21.96.

Treatment of PS−BBr with CuC_6F_5: Synthesis of Poly[4-bis(pentafluorophenyl)borylstyrene] (PS−BPf). A solution of **PS−BBr** prepared from BBr_3 (0.78 g, 3.1 mmol) and **PS−Si** (0.50 g, ca. 2.8 mmol repeat units; $M_n = 27\,120$; PDI = 1.11) in 15 mL of CH_2Cl_2 was treated at −78 °C with a solution of $[CuC_6F_5]_4(toluene)_2$ (1.80 g, 1.6 mmol) in 10 mL of CH_2Cl_2. The mixture was kept stirring for 1 h at −78 °C and then allowed to slowly warm to room temperature and stirred for 3 h. A solid precipitate (CuBr) formed and was removed by filtration through a fritted glass disk. A small amount of $ThSnMe_3$ was added in order to quench any unreacted B−Br groups. The reaction solution was concentrated under high vacuum to ca. 3 mL and then precipitated repeatedly into a large volume of hexanes (ca. 200 mL). The hexane solution was decanted from a white precipitate. The solid was washed with hexanes and dried under high vacuum for 24 h to give 0.94 g (74%) of **PS−BPf**. ^1H NMR (399.952 MHz, CD_2Cl_2): δ = 7.3 (br m, 2H, Ph−H2,6), 6.6 (br m, 2H, Ph−H3,5), 2.2−1.2 (br m, 3H, $C\boldsymbol{H}_2C\boldsymbol{H}$). ^{13}C NMR (125.7 MHz, CD_2Cl_2): δ = 154.5 (br, Ph−C4), 147.2 (d, $^1J_{CF}$ = 248 Hz, Pf-C2,6), 143.6 (d, $^1J_{CF}$ = 256 Hz, Pf-C4), 140.0 (br, Ph−C2,6), 138.1 (d, $^1J_{CF}$ = 254 Hz, Pf-C3,5), 137.1 (br, Ph−C1), 128.3, 127.9 (br, Ph−C3,5), 114.2 (br, Pf-C1), 46−42 (br, $\boldsymbol{C}H[\boldsymbol{C}H_3]_2$). ^{19}F NMR (376.263 MHz, CD_2Cl_2): δ = −130.5, −130.8 (4F, Pf-F2,6), −149.5 (2F, Pf-F4), −162.5 (4F, Pf-F3,5). ^{11}B NMR (160.370 MHz, CD_2Cl_2): δ = 56 ($w_{1/2}$ = 2500 Hz); DSC (second heating curve): T_g = 134 °C (onset, 20 °C/min); elemental analysis for **PS−BPf** (153 repeat units): calcd: C, 53.61; H, 1.58; found: C, 53.33; H, 1.75. A sulfur content of 0.14% was found by elemental analysis, indicating the attachment of a small number of thiophene groups (average of ca. 3 thiophene groups per polymer).

Determination of the Relative Lewis Acidity of PS−BPf. A solution of **PS−BPf** (ca. 0.3 M) in CD_2Cl_2 was treated with a deficiency of crotonaldehyde (ca. 50%) according to Childs' method.[40] The relative Lewis acidity of the boron centers was estimated to 0.60 (BBr_3 = 1.0) by comparison of the chemical shift of the olefinic carbon NMR signals for the free aldehyde and the Lewis acid complex. (Reliable ^1H NMR data could not be obtained due to signal overlap; furthermore, neighboring group effects in the polymer may influence the ^1H NMR chemical shifts.) Similar treatment of **PS−BPf** with a slight excess of crotonaldehyde (1.3 equiv) gave the following NMR data for the fully complexed polymeric Lewis acid: ^{19}F NMR (376.263 MHz, C_6D_6): δ = −133.0 (4F, Pf-F2,6), −159.4 (2F, Pf-F4), −165.8 (4F, Pf-F3,5).

Acknowledgment is made to the National Science Foundation (CAREER award CHE-0346828 to F.J.), to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Rutgers Research Council for support of this research. We thank the National Science Foundation for GPC and LS instrumentation provided through the NSF-MRI program (MRI 0116066). We are grateful to Dr. Lazaros Kakalis for acquisition of 2D NMR spectra.

Supporting Information Available: Data for model compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA035880R