Macromolecules **2007,** *40,* 1413−1420

Silylated Initiators for the Efficient Preparation of Borane-End-Functionalized Polymers via ATRP

Yang Qin, Chengzhong Cui, and Frieder Jäkle*

Department of Chemistry, Rutgers University Newark, 73 Warren Street, Newark, New Jersey 07102

Received July 26, 2006; Revised Manuscript Received December 13, 2006

ABSTRACT: Borane-end-functionalized polymers have been prepared through (i) atom transfer radical polymerization (ATRP) of styrene using a silylated initiator, 1-bromo-1-(4-trimethylsilylphenyl)ethane (PEB-$SiMe_3$), (ii) exchange of the $SiMe_3$ end groups with BBr_3, and (iii) modification of the Lewis acidic boron centers with nucleophiles. Ditelechelic α,ω-borane-functionalized polymers were obtained through atom transfer radical coupling (ATRC) of the silane-end-functionalized polymers followed by exchange with BBr_3 and subsequent reaction with nucleophiles. Self-assembly of the borane-functionalized mono- and ditelechelic polymers into supramolecular structures by means of reversible noncovalent and covalent interactions including Lewis acid−base complexation and boroxine formation has been explored.

Introduction

Boron-containing polymers continue to attract much attention due to their potential use in catalysis, sensor applications, and material science.[1] Research in these areas has been mainly focused on the incorporation of boron moieties into the main chain and the attachment as side groups of polymeric structures. The preparation of polymers containing borane moieties as end groups, on the other hand, is intriguing since boron-end-functionalized polymers may serve as precursors to various other telechelic polymers using well-established functional group conversion techniques and can also be advantageously used as building blocks for the formation of block or graft copolymer architectures.[2]

The methods that are most commonly applied for the preparation of boron-end-functionalized polymers involve (i) the use of borane initiators, (ii) the addition of borane chain transfer agents in olefin polymerization, and (iii) the functional group conversion of suitable preformed telechelic polymers with a borane source. (i) Living cationic polymerizations are frequently initiated with boron halides and thus represent a facile method for the incorporation of boron moieties at the termini of polymer chains.[3−5] For instance, Faust and co-workers have studied the living cationic polymerization of isobutylene and α-methylstyrene initiated with BCl_3. The resulting telechelic polymers bear a Cl atom at one chain end and a BCl_2 group at the other, which then can be further transformed to other borane functionalities such as $B(OMe)_2$ and $B(OH)_2$. Another methodology that takes advantage of boron initiators is the polyhomologation of organoboranes, which has been pioneered by Shea and co-workers.[6−8] The living polymerization of an ylide such as dimethylsulfoxonium methylide is catalyzed/initiated by trialkylboranes, resulting in well-defined organoboron star polymers that subsequently are converted into linear polymethylenes through oxidative B−C bond cleavage. (ii) In a different approach, the incorporation of borane moieties at the polymer chain ends by using borane chain transfer agents in metallocene-mediated olefin polymerizations has been demonstrated by Chung and co-workers.[9,10] With 9-BBN and $HB(Mes)_2$ (9-BBN = 9-borabicyclononane; Mes = 2,4,6-trimethylphenyl) as chain transfer agents in the polymerization of ethylene, the respective borane-terminated polyethylenes were obtained, while the bulkier borane $HB(Trip)_2$ (Trip = 2,4,6-triisopropylphenyl) did not get incorporated due to increased steric hindrance of the Trip groups. The terminal borane groups were further transformed to hydroxyl groups by oxidative cleavage with H_2O_2 under basic conditions. Interestingly, the 9-BBN borane end groups can also react with limited amount of oxygen to form peroxide (B−O−O−C) species, and the resulting polymers were used in turn as macroinitiators for the free radical chain extension with other monomers such as methyl methacrylate.[9] (iii) Finally, functional group conversion by hydroboration of vinyl-terminated polymers also gives straightforward access to borane-end-functionalized polymers. For instance, Katayama and co-workers showed that hydroboration of vinyl-terminated poly(norbornene)s with 9-BBN led to borane-terminated poly(norbornene)s which were later transformed to hydroxyl-terminated polymers.[11] Similarly, hydroboration of vinyl-terminated polypropylene was used by Chung and co-workers for the synthesis of maleic anhydride-modified polypropylene.[12] Moreover, Chujo and co-workers studied the hydroboration polymerization of α,ω-vinyl-terminated polymers with bifunctional boranes for the synthesis of organoboron segmented block polymers.[13] In recent work, Ohno and co-workers introduced 9-BBN moieties at both ends of poly(propylene oxide) (PPO) through either hydroboration or dehydrocoupling reactions.[14] The borane end groups served as anion traps, and high ion conductivity and transference were observed for the borane-terminated PPO.

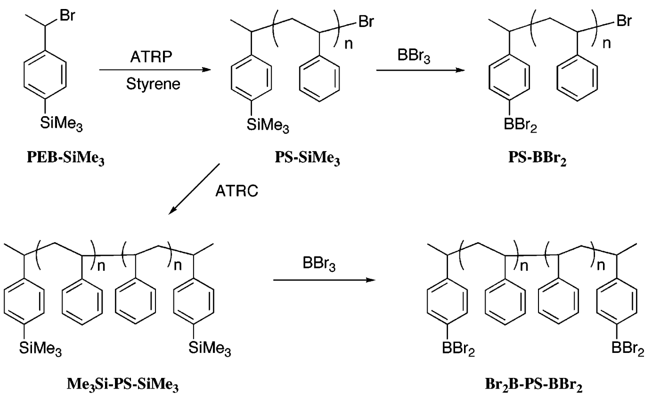
Herein we report a new synthetic route to borane-end-functionalized polymers, in which the use of functional initiators in a controlled polymerization protocol is combined with facile and high yielding polymer modification procedures. We have previously described a straightforward methodology for the incorporation of boron moieties into the side chains of well-defined polystyrenes through highly selective exchange of trimethylsilyl substituents with boron halides.[15,16] We have also demonstrated that the halide substituents on boron can easily be exchanged, and the properties of these polymers can thus readily be fine-tuned. We show here that controlled free radical polymerization of olefins with silyl-functionalized initiators can serve as an excellent tool for the preparation of well-defined polymers, in which either one or both chain ends are function-

---

* Corresponding author. E-mail: fjaekle@rutgers.edu.

10.1021/ma061704h CCC: $37.00

Scheme 1. Synthesis of Dibromoboryl-End-Functionalized Polymers by Atom Transfer Radical Polymerization and Subsequent Silicon−Boron Exchange



alized with boranes. We further describe how these borane moieties reversibly bind to nucleophiles and can be advantageously used in supramolecular polymer chemistry. In this context, the self-assembly of polymers through donor−acceptor interaction and reversible boroxine ring formation[17−19] is discussed.

Results and Discussion

Synthesis of Silane-End-Functionalized Polymers. Silane-terminated polystyrene (PS-SiMe$_3$) was obtained by atom transfer radical polymerization (ATRP)[20,21] using the silane-functionalized initiator 1-bromo-1-(4-trimethylsilylphenyl)ethane (PEB-SiMe$_3$, Scheme 1),[22] which is an analogue of the commonly used ATRP initiator 1-bromo-1-phenylethane (PEB).[20] A typical ATRP protocol was used with CuBr/*N*,*N*′,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the catalyst system in anisole (50% w/w) at 110 °C and ratios of St:PEB-SiMe$_3$:CuBr:PMDETA of 50:1:1:1 and 40:1:1:1, respectively. The polymerization was stopped at about 40−50% conversion to ensure preservation of the bromine end groups. According to gel permeation chromatography (GPC) and GPC with in-line multiangle laser light scattering detector (GPC-MALLS) analysis, the polymers show narrow molecular weight distributions (PDI $<$ 1.2), indicative of a controlled polymerization process. The polymers were used in the preparation of monotelechelic organoboron polymers as described below.

The bromine end groups of the silane-functionalized polymer PS-SiMe$_3$ can be further manipulated through atom transfer radical coupling (ATRC)[23] to form the ditelechelic α,ω-silane-functionalized polymer, Me$_3$Si-PS-SiMe$_3$ (Scheme 1). The sample of PS-SiMe$_3$ ($M_n = 3358$, GPC-RI) used for ATRC was prepared in bulk, and the polymerization was stopped at an early stage (∼30% conversion) to ensure full coverage of the bromine end groups. As previously described by Matyjaszewski and coworkers for the coupling of bromine-terminated PS,[23] CuBr/PMDETA and activated Cu powder[24] were used as the catalyst system. The Cu powder was added in order to reduce the amount of CuBr$_2$, which acts as a deactivator during the coupling process. A slightly modified procedure with a ratio of PS-SiMe$_3$:CuBr:PMDETA:Cu of 1:2:10:5 at 90 °C was applied in order to maximize the coupling efficiency. The coupling reaction was monitored by GPC analysis, as shown in Figure 1.

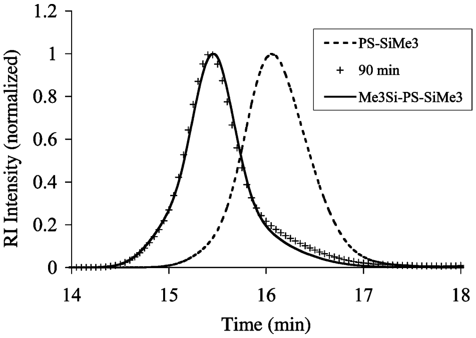


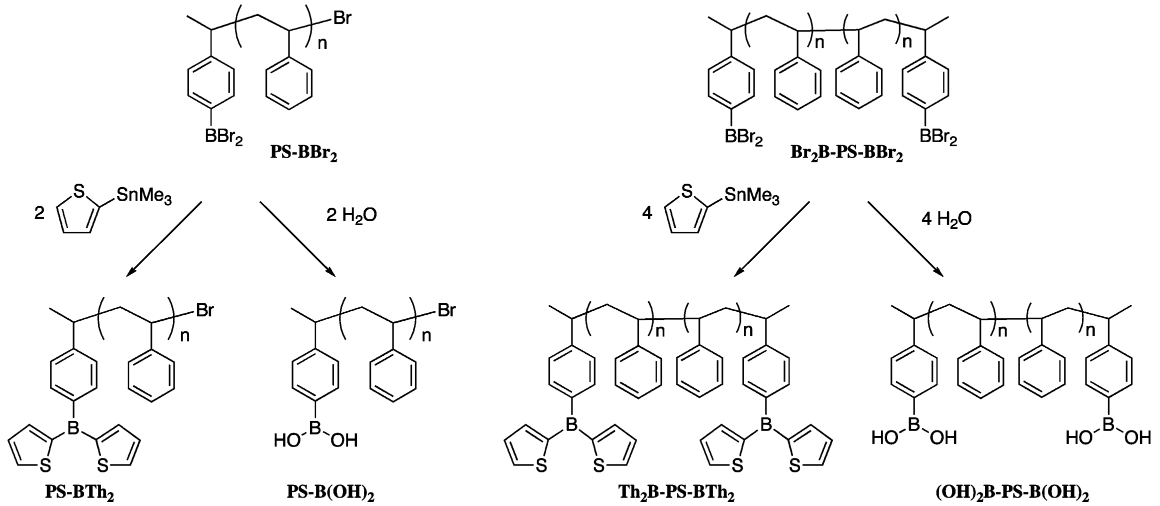
Figure 1. Gel permeation chromatography (GPC) traces for the atom transfer radical coupling (ATRC) process of PS-SiMe$_3$ (THF, 1 mL/min, refractive index detector; - - -, PS−SiMe$_3$ precursor; +, crude product after 90 min reaction time; —, isolated product after precipitation).

According to the GPC results, the coupling reaction reaches about 90% after 30 min and 94% after 90 min. The extent of coupling was calculated from the equation $\chi_c = 2(1 - M_{n,0}/M_n)$, where χ_c is the extent of coupling, $M_{n,0}$ is the initial molecular weight, and M_n is the molecular weight after coupling reaction.[23] Further reaction was not observed with extended reaction time based on GPC analyses. As shown in Figure 1, only a small low molecular weight tail can be seen in the trace after 90 min, indicating an efficient coupling reaction. The coupling product Me$_3$Si-PS-SiMe$_3$ was purified by precipitation from THF into methanol/hexanes (50/50). Polymer chains with lower molecular weight did not as effectively precipitate under these conditions and were decanted with the supernatant. The low molecular weight fraction significantly reduces in the trace of Me$_3$Si-PS-SiMe$_3$ after precipitation and the extent of coupling was calculated to be 96%. Accordingly, the multiplet resonances at ca. 4.4 and 4.5 ppm for the proton of the −CPh(H)Br end group of PS-SiMe$_3$ are not observed in the ^{1}H NMR spectrum of the coupled product Me$_3$Si-PS-SiMe$_3$ (see Figure S1 in the Supporting Information). Moreover, a significantly higher glass transition temperature was observed for Me$_3$Si-PS-SiMe$_3$ (T_g (onset) = 95 °C) relative to PS-SiMe$_3$ (T_g(onset) = 80 °C), consistent with the increased molecular weight of Me$_3$Si-PS-SiMe$_3$ ($M_n = 6439$ for Me$_3$Si-PS-SiMe$_3$ vs $M_n = 3358$ for PS-SiMe$_3$).

Functionalization of PS-SiMe$_3$ and Me$_3$Si-PS-SiMe$_3$. The trimethylsilyl groups in PS-SiMe$_3$ and Me$_3$Si-PS-SiMe$_3$ were exchanged for BBr$_2$ groups through reaction with a slight excess of BBr$_3$ in CH$_2$Cl$_2$ over a period of 12−24 h (Scheme 1). The dibromoborylated polymer, PS-BBr$_2$, was isolated by precipitation into cold hexanes followed by freeze-drying from benzene. The ^{11}B NMR spectrum of the product shows a broad peak at 56 ppm, which is in the range of typical dibromoarylboranes. In the ^{1}H NMR spectrum, the resonance at 0.3 ppm due to the trimethylsilyl groups completely disappeared, and a new resonance in the aromatic region at 8.04 ppm evolved, which corresponds to the protons at the *ortho* positions of the phenyl end group (see Figure 5).[25] The multiplet structure of this signal reflects the atactic nature of the PS chain. The molecular weight derived from ^{1}H NMR end-group analysis matched very well with that obtained from GPC analysis for the starting material, indicating that the boron−silicon exchange reaction proceeded smoothly. Ditelechelic α,ω-borane-functionalized polymers are obtained in a similar procedure by reaction of Me$_3$Si-PS-SiMe$_3$ with BBr$_3$ (Scheme 1). The NMR spectra of Br$_2$B-PS-BBr$_2$ are identical to those of PS-BBr$_2$, except for the lack of signals for the Br terminus observed for monotelechelic PS-BBr$_2$ (see Figure S2 in the Supporting Information).

The polymers PS-BBr$_2$ and Br$_2$B-PS-BBr$_2$ are highly reactive toward air and moisture and therefore most conveniently used in situ for further reaction with nucleophiles. Scheme 2 describes the functionalization of PS-BBr$_2$ with different nucleophiles. The functionalization of Br$_2$B-PS-BBr$_2$ follows the same methodology, and the resulting ditelechelic borane polymers

Scheme 2. Functionalization of PS-BBr$_2$ and Br$_2$B-PS-BBr$_2$



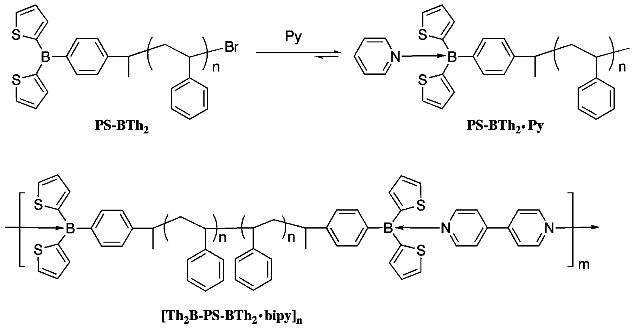
show similar features in the NMR spectra as their monofunctionalized counterparts.

As shown in Scheme 2, the polymeric Lewis acid PS-BTh$_2$ was obtained by treatment of PS-BBr$_2$ with 2-(trimethylstannyl)-thiophene under inert atomsphere. The product was isolated in high yield (81%) by precipitation into hexanes and dried under high vacuum. The ^{11}B NMR spectrum of PS-BTh$_2$ shows a broad peak at 50 ppm, which is in the range of typical triarylboranes and similar to that of the bis(thienyl)boryl homopolymer ($\delta = 47$) and the related molecular species (4-*t*-BuPh)BTh$_2$ ($\delta = 55$).[15b] According to GPC analysis of PS-BTh$_2$ in THF, the molecular weight ($M_n = 3517$) and polydispersity (PDI = 1.09) are similar to those of the starting material PS-SiMe$_3$ ($M_n = 3688$, PDI = 1.10), indicating that no cross-linking or degradation of the polymer occurred during the boron−silicon and boron−tin exchange reactions. The polymer slowly degrades under ambient conditions and was therefore handled under an inert atmosphere. A hydrolytically stable boronic acid-end-functionalized polymer, PS-B(OH)$_2$, was obtained simply by hydrolysis of PS-BBr$_2$ (Scheme 2). The formation of a boroxine linkage and self-assembly of the polymers through the boronic acid end groups will be discussed in the next section.

Self-Assembly of Polymers through the Borane End Groups. Supramolecular chemistry has become a basic concept and an expanding area of today's chemical research since Lehn, Pederson, and Cram received the Nobel prize in 1987.[26−28] Supramolecular polymers, assembled from traditional polymers through noncovalent interactions including complementary hydrogen bonding and metal−ligand complexation, are especially intriguing for the combination of novel structures and features of supramolecular species and the well-known polymeric properties.[29,30] These noncovalent interactions allow for establishment of a stimuli-responsive equilibrium between the supramolecular structures and the polymeric building blocks. We studied the possibility of using the borane-end-functionalized and ditelechelic polymers as building blocks toward supramolecular polymer structures through (i) the reversible formation of Lewis acid−base complexes[31] and (ii) the reversible construction of boroxine rings.

(i) Assembly through Lewis Acid−Base Complexes. We have shown previously that for bis(thienyl)borane side-group functionalized polystyrene the boron centers are highly Lewis acidic, and it is therefore possible to form isolable complexes with pyridine bases.[32] Indeed, the pyridine complex of PS-BTh$_2$, PS-BTh$_2$·Py, was readily obtained by stirring PS-BTh$_2$ with excess pyridine in CH$_2$Cl$_2$ followed by removal of volatile materials under vacuum (Scheme 3). A sharp signal at 0 ppm in the ^{11}B NMR spectrum confirmed the tetracoordinated nature of the boron centers. Moreover, integration of the ^{1}H NMR spectrum is in agreement with one pyridine molecule bound to each polymer chain.[33]

Scheme 3. Formation of Polymeric Lewis Acid−Base Complexes



Treatment of the ditelechelic polymer Th$_2$B-PS-BTh$_2$ with 1 equiv of 4,4′-dipyridyl (bipy) provides an opportunity for the self-assembly of longer polymer chains [Th$_2$B-PS-BTh$_2$·bipy]$_n$ through donor−acceptor interactions (Scheme 3).[33] Under relatively concentrated conditions (15.5 mM boryl groups and 7.7 mM 4,4′-dipyridyl in CDCl$_3$), the ^{11}B NMR spectrum shows a single peak at 0 ppm consistent with pyridine-coordinated boron centers. The ^{1}H NMR spectra of PS-BTh$_2$·Py and [Th$_2$B-PS-BTh$_2$·bipy]$_n$ show very similar patterns and further indicate complexation of the Lewis acidic boron centers (Figure 3). Integration confirms the presence of one 4,4′-dipyridyl molecule per polystyrene chain. DSC studies revealed a glass transition temperature of $T_g = 105$ °C for [Th$_2$B-PS-BTh$_2$·bipy]$_n$, which is similar to that of high-MW PS and significantly higher than that of the low-MW starting material Th$_2$B-PS-BTh$_2$ ($T_g = 88$ °C) (Figure 2), thus confirming assembly of Th$_2$B-PS-BTh$_2$ through 4,4′-dipyridyl into a polymer with considerably higher molecular weight.

To further investigate the formation of the extended structure in solution, we monitored the titration of Th$_2$B-PS-BTh$_2$ with 4,4′-dipyridyl in anhydrous CDCl$_3$ using ^{1}H NMR spectroscopy. The original concentration of Th$_2$B-PS-BTh$_2$ was ca. 15.5 mM boryl groups, and upon addition of 4,4′-dipyridyl only one set of averaged signals was observed. The chemical shifts

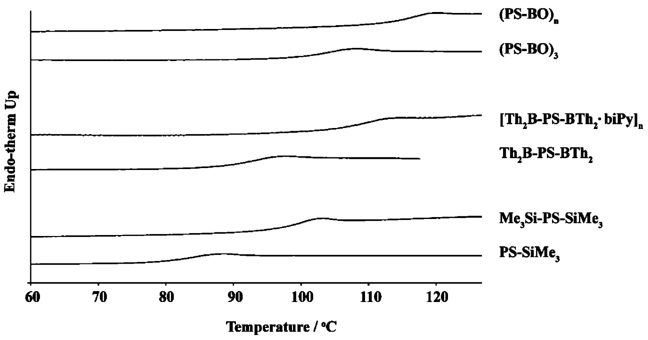


Figure 2. Differential scanning calorimetry (DSC) plots of the end-functionalized polymers and their self-assembled aggregates (onset, second heating curve, 20 °C/min).

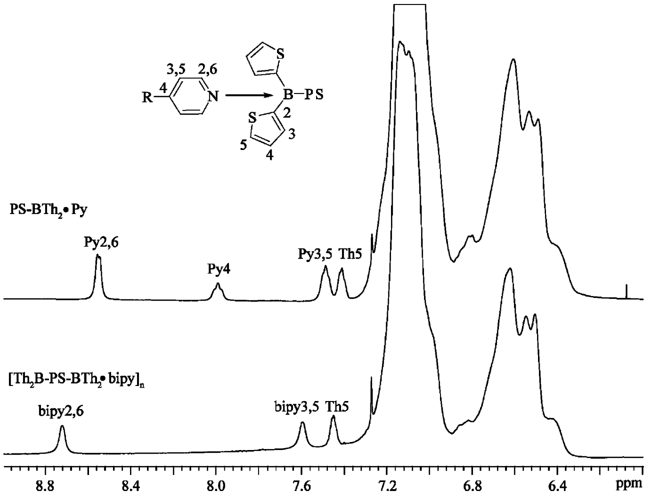


Figure 3. ^{1}H NMR spectra of PS-BTh·Py (R=H) and [Th$_2$B-PS-BTh$_2$·bipy]$_n$ (R = pyridyl) in CDCl$_3$ (ca. 15.5 mM functional group).

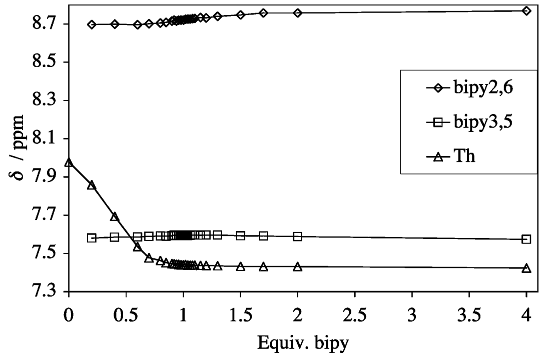


Figure 4. ^{1}H NMR titration of Th$_2$B-PS-BTh$_2$ with 4,4′-dipyridyl in CDCl$_3$ (ca. 15.5 mM boryl group).

changed gradually, as shown in Figure 4. The signal for the thiophene protons Th-H5 shifted from the initial value of 7.98 to 7.44 ppm upon addition of 1 equiv of bipy per polymer chain and leveled off at higher bipy concentration, indicating that the boryl groups were essentially fully coordinated in the presence of 1 equiv of bipy. The signal for bipy-H3,5 did not experience a significant change, and the bipy-H2,6 resonance remained at ca. 8.70 ppm up to equimolar bipy to polymer ratio. However, the chemical shift gradually increased to 8.75 ppm when up to 2 equiv of bipy was added. Averaged ^{1}H NMR signals for dicoordinated and monocoordinated bipy groups are apparently observed in this regime. The data presented thus further support the formation of [ThB-PS-BTh·bipy]$_n$ in solution at a ratio of bipy to organoboron polymer of 1:1.

(ii) Assembly through Boroxine Linkages. Boronic acids[34] and polymer-supported boronic acids have found applications as scaffolds for the solid-phase synthesis of carbohydrates,[35] sensors and stimuli responsive polymers including the sensing of sugars,[36−38] and separation media in biochemical applications.[39,40] Boroxines, the cyclic anhydrides of boronic acids formed by elimination of three molecules of water, have found commercial use as flame retardants,[41] dopants that enhance lithium ion transference in polymer electrolyte,[42] and boronic acid alternative in Suzuki−Miyaura coupling reactions.[43]

PS-BBr$_2$ was treated with water to give PS-B(OH)$_2$, which was then subjected to azeotropic distillation in benzene. Upon elimination of water, (PS-BO)$_3$, a triarm star with boroxine core is expected to form. The ^{1}H NMR signals of the two protons at the ortho positions of the phenyl ring attached to boron are used to monitor the process. As shown in Figure 5, the signal of PS-B(OH)$_2$ at 7.7 ppm disappeared upon azeotropic distillation and a new peak formed at 8.1 ppm. These chemical shifts are very similar to those reported in the literature for phenylboroxine and phenylboronic acid derivatives,[18] respectively, suggesting the transformation into a boroxine-centered star polymer. Moreover, DSC analysis of the product (PS-BO)$_3$ showed a significantly higher glass transition temperature ($T_g = 101$ °C) over that of the starting material PS-SiMe$_3$ ($T_g = 80$ °C) (Figure 2), which indicates a significant increase of molecular weight and thus provides further evidence for the assembly of PS-B(OH)$_2$ through boroxine linkages. Importantly, the boroxine can readily be transformed back to boronic acid functionalities by hydrolysis in the presence of a small amount of D$_2$O as shown by ^{1}H NMR spectroscopy (Figure 5). Thus, the formation of the star polymer is a reversible process.

When the ditelechelic polymer Br$_2$B-PS-BBr$_2$ was similarly subjected to hydrolysis, the bis(boronic acid) polymer (HO)$_2$B-PS-B(OH)$_2$ was obtained (Scheme 2). Upon azeotropic distillation of a benzene solution of (HO)$_2$B-PS-B(OH)$_2$ a white precipitate formed, which was isolated by removal of benzene under high vacuum. The resulting white solid was found to be insoluble in anhydrous acetone.[44] Presumably, instead of a triarm star-like structure as in the case of (PS-BO)$_3$, a network-like structure with boroxine cross-links was formed, as illustrated in Figure 6.[45] We performed DSC and TGA measurements to further confirm the formation of the boroxine network and to investigate its properties. Indeed, a significantly higher glass transition temperature ($T_g = 112$ °C) was observed compared to the starting material Me$_3$Si-PS-SiMe$_3$ ($T_g = 95$ °C), consistent with a more rigid structural framework (Figure 2). In the TGA measurements, both Me$_3$Si-PS-SiMe$_3$ and the boroxine network showed a similar decomposition onset of ca. 400 °C. No residue was found for Me$_3$Si-PS-SiMe$_3$, and only 3% weight retained in the case of (PS-BO)$_n$, presumably due to residual boron oxide.

When a drop of D$_2$O was added to a suspension of (PS-BO)$_n$ in dry acetone-d_6, a clear solution was obtained. The ^{1}H NMR spectrum was similar to that of PS-B(OH)$_2$ in acetone-d_6/D$_2$O (Figure 5), indicating the breakup of the boroxine network and re-formation of the boronic acid-functionalized polymer, (HO)$_2$B-PS-B(OH)$_2$. Thus, the formation of boroxine cross-links is reversible, and the polymer properties can be modified by the presence or absence of water.[46]

Conclusions

We have developed a modular synthetic methodology for the preparation of borane-end-functionalized polymers through ATRP of styrene using a silylated initiator, followed by exchange with BBr$_3$ and modification through treatment with nucleophiles. Our methodology is highly versatile since various

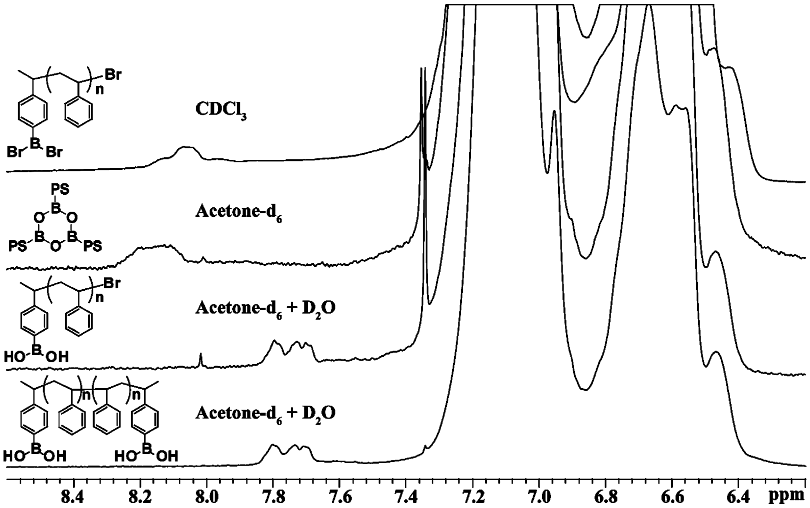


Figure 5. Reversible interconversion of PS-B(OH)$_2$/(PS-BO)$_3$ and (HO)$_2$B-PS-B(OH)$_2$/(PS-BO)$_n$ (insoluble in acetone) as monitored by ^{1}H NMR spectroscopy.

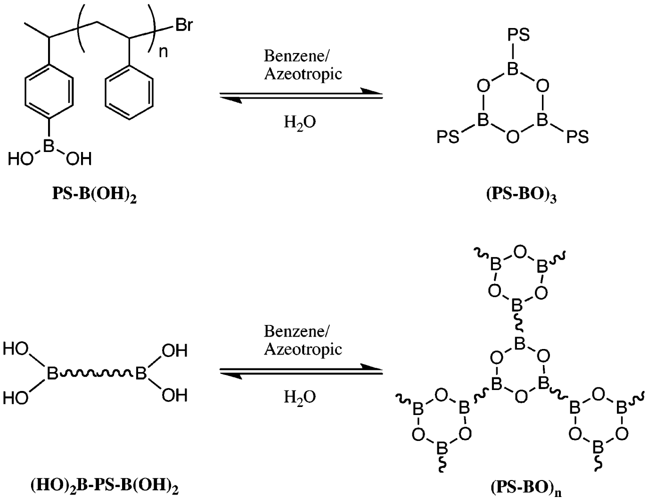


Figure 6. Schematic representation of the formation of the triarm star structure of (PS-BO)$_3$ with a boroxine core and the boroxine cross-linked polystyrene (PS-BO)$_n$ (the structural representation is idealized as a few non-cross-linked -PS-B(OH)$_2$ and -PS-B(OH)-PS- moieties likely also exist).

substituents can be introduced to the borane end groups, which can serve as precursors to other end-functionalities and be used for the construction of polymer assemblies. In pursuit of these goals, we have shown that the bis(thienyl)boryl- and boronic acid-end-functionalized polymers can be reversibly converted to supramolecular polymer structures through Lewis acid−base interactions and boroxine linkages, respectively. Thus, new methodologies for the reversible assembly of supramolecular polymer structures in addition to traditional hydrogen bonding and metal−ligand interactions are provided. Especially the reversible assembly of polymers through strong covalent B−O bonds in an equilibrium that is easily shifted by addition or removal of water, and can be influenced by the presence of Lewis bases,[47] is expected to provide new opportunities in the field.

Experimental Section

Materials and General Methods. The compounds 1-bromo-4-ethylbenzene, Mg (turnings), Me$_3$SiCl, *N*-bromosuccinimide, BBr$_3$, CuBr, CuBr$_2$, Cu (electrical dust), pyridine, 4,4′-dipyridyl (bipy), and anisole were purchased from Acros. *N,N′,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA) was purchased from Aldrich. BBr$_3$ was distilled under vacuum, and Me$_3$SiCl, PMDETA, anisole, and pyridine were distilled from CaH$_2$ prior to use; CuBr was purified according to a literature procedure.[48] Cu powder was activated according to a literature procedure[24] and used immediately. The synthesis of 2-trimethylstannylthiophene was reported previously.[16a] All other chemicals were used as received without further purification. Reactions and manipulations involving reactive 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 499.893 MHz ^{1}H and 125.681 MHz ^{13}C NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer. The 399.844 MHz ^{1}H and 100.541 MHz ^{13}C NMR spectra were recorded on a Varian VXR-S 400 MHz spectrometer. 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. ^{11}B NMR spectra were referenced externally to BF$_3$·Et$_2$O ($\delta = 0$) in C$_6$D$_6$. 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. Two Styragel columns (Polymer Laboratories; 5 μm Mix-C), 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 in-line with the GPC; differential refractive indices d*n*/d*c* were calculated from in-line GPC-MALLS mode with Wyatt Astra software assuming 100% mass recovery. DSC measurements were performed on a Perkin-Elmer differential scanning calorimeter Pyris 1 system with ca. 10 mg of the polymer and at a scan rate of 20 °C/min. The results reported correspond to the onset from the second heating cycle. TGA measurements were performed on a Perkin-Elmer Pyris 1 thermogravimetric analyzer at a scan rate of 20 °C/min and up to 800 °C.

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.

Synthesis of 1-Ethyl-4-trimethylsilylbenzene.[22] To a suspension of magnesium (7.0 g, 0.29 mol) in 300 mL of THF was added slowly 20 mL of 1-bromo-4-ethylbenzene (26.9 g, 0.145 mol). The reaction mixture was subsequently heated to reflux under nitrogen for 2 h and cooled down to 0 °C. Chlorotrimethylsilane (25 mL, 21.4 g, 0.197 mol) was added slowly, and the reaction mixture was stirred at room temperature overnight. After standard aqueous workup, the product 1-ethyl-4-trimethylsilylbenzene was distilled (31 °C, 10^{-2} Torr) and collected as a colorless liquid (22.8 g, 88.3%). ^{1}H NMR (399.851 MHz, C_6D_6): $\delta = 7.45$ (d, $^3J = 8$ Hz, 2H, Ph-H2,6), 7.12 (d, $^3J = 8$ Hz, 2H, Ph-H3,5), 2.47 (q, $^3J = 7.6$ Hz, 2H, CH_2CH$_3$), 1.10 (t, $^3J = 7.6$ Hz, 3H, CH$_2$CH_3), 0.23 (s, 9H, SiMe$_3$).

Synthesis of 1-Bromo-1-(4-trimethylsilylphenyl)ethane (PEB-SiMe$_3$).[22] 1-Ethyl-4-trimethylsilylbenzene (22.5 g, 0.126 mol) was dissolved in 300 mL of CCl_4, and benzoyl peroxide (0.2 g) and *N*-bromosuccinimide (22.3 g, 0.126 mol) were added in one portion. The reaction mixture was heated to reflux for 12 h while being irradiated by a 450 W Hanovia medium-pressure Hg broadband UV lamp through standard Pyrex glassware. After cooling, the solid succinimide was removed by filtration, and the filtrate was washed with saturated aqueous $NaHSO_3$. The organic layer was dried over Na_2SO_4 and concentrated. The remaining oil was distilled (56 °C, 10^{-2} Torr) to give the product as a colorless liquid (22.7 g, 70.0%). ^{1}H NMR (499.893 MHz, C_6D_6): $\delta = 7.34$ (d, $^3J = 8$ Hz, 2H, Ph-H2,6), 7.21 (d, $^3J = 8$ Hz, 2H, Ph-H3,5), 4.81 (q, $^3J = 7.0$ Hz, 1H, CHBr), 1.71 (d, $^3J = 7.0$ Hz, 1H, CHCH_3), 0.17 (s, 9H, SiMe$_3$). ^{13}C NMR (125.698 MHz, C_6D_6): $\delta = 144.1$ (Ph-C1), 140.6 (Ph-C4), 133.9 (Ph-C2,6), 126.5 (Ph-C3,5), 49.5 (***C***HBr), 26.8 (CH***C***H$_3$), −1.2 (SiMe$_3$).

Solution Polymerization of Styrene with PEB-SiMe$_3$: Synthesis of PS-SiMe$_3$. Styrene (57 g, 0.547 mol), 1-bromo-1-(4-trimethylsilylphenyl)ethane (2.80 g, 10.9 mmol), CuBr (1.57 g, 10.9 mmol), and PMDETA (1.90 g, 10.9 mmol) were dissolved in 57 g of anisole, and the mixture was degassed by three freeze−pump−thaw cycles. The reaction mixture was then heated to 110 °C under nitrogen for 90 min and precipitated into methanol (1 L). The precipitate was redissolved in THF and passed through a short plug of neutral alumina gel. Precipitation into methanol gave a white solid, which was collected by filtration and dried under vacuum at 60 °C overnight (24 g, 42%). ^{1}H NMR (499.893 MHz, $CDCl_3$): $\delta = 7.4−6.3$ (all aromatic H's), 4.6−4.3 (m, CHBr), 2.6−1.2 (polymer backbone), 1.05 (m, 3H, CHCH_3), 0.26 (9H, SiMe$_3$). ^{13}C NMR (125.698 MHz, C_6D_6): $\delta = 145.7$ (br, styrene Ph-C1), 133.7 (SiPh-C2,6), 126.8 (SiPh-C3,5), 126.1 (br, styrene Ph-C's), 47−40 (polymer backbone), −0.95 (SiMe$_3$). GPC-RI: $M_n = 4038$, $M_w = 4469$, PDI = 1.11. GPC-MALLS (THF): $M_n = 4256$, $M_w = 4653$, PDI = 1.09, d*n*/d*c* (25 °C in THF) = 0.179 mL/g. DSC (onset): $T_g = 80$ °C; TGA (onset): $T_{dec} = 409$ °C, 100% weight loss. Another sample was obtained under similar conditions with similar molecular weight. GPC-RI: $M_n = 3688$, $M_w = 4051$, PDI = 1.10. Both samples were used to prepare monotelechelic organoboron polymers as described below.

Bulk Polymerization of Styrene with PEB-SiMe$_3$: Synthesis of PS-SiMe$_3$(b). 1-Bromo-1-(4-trimethylsilylphenyl)ethane (1.76 g, 6.85 mmol), CuBr (0.98 g, 6.85 mmol), $CuBr_2$ (0.077 g, 0.34 mmol), and PMDETA (1.25 g, 7.2 mmol) were dissolved in styrene (71.4 g, 0.69 mol); the mixture was purged with N_2 for 0.5 h and then immersed into an oil bath preset at 80 °C. After 1 h the polymer was recovered by precipitation into methanol (∼1 L), redissolved in THF, and passed through a short plug of neutral alumina gel. Precipitation into methanol gave a white solid, which was collected by filtration and dried under vacuum at 60 °C overnight (19.6 g, 28%). GPC-RI: $M_n = 3358$, $M_w = 3919$, PDI = 1.17. The sample was used to prepare the ditelechelic polymer Me$_3$Si-PS-SiMe$_3$ via ATRC.

Synthesis of Me$_3$Si-PS-SiMe$_3$. PS-SiMe$_3$(b) ($M_n = 3358$ by GPC-RI, 3.0 g, 0.76 mmol end group units), CuBr (0.11 g, 0.76 mmol), PMDETA (0.66 g, 3.8 mmol), Cu metal (0.19 g, 3.0 mmol), and 20 g of anisole were charged into a Schlenk flask; the mixture was degassed by three freeze−pump−thaw cycles and then immersed into an oil bath preset at 90 °C. The reaction was monitored by GPC analysis and stopped after 3 h by cooling down to room temperature and passing through a short plug of neutral alumina gel. The solution was then concentrated and precipitated into methanol. The solid obtained was further purified by precipitation from THF into methanol/hexanes (50/50) to remove uncoupled low molecular weight material and finally into methanol and dried at 60 °C under high vacuum overnight (1.8 g, 60%). GPC-RI: $M_n = 6439$, $M_w = 7532$, PDI = 1.17. DSC (onset): $T_g = 95$ °C; TGA (onset): $T_{dec} = 405$ °C, 100% weight loss.

Synthesis of PS-BTh$_2$. To a solution of PS-SiMe$_3$ ($M_n = 3688$ by GPC-RI, 4.0 g, 1.14 mmol) in ∼40 mL of CH_2Cl_2 was added slowly a solution of BBr_3 (0.32 g, 1.26 mmol) in ∼10 mL of CH_2Cl_2. The reaction mixture was kept stirring overnight, and 2-trimethylstannylthiophene (0.78 g, 3.16 mmol) in ∼10 mL of CH_2Cl_2 was added slowly. The mixture was stirred for another 12 h and concentrated to about 5 mL before precipitation into cold hexanes (∼500 mL, −30 °C). The hexanes were decanted, and the precipitate was dried under vacuum to give 3.24 g of white powdery material (81%). ^{1}H NMR (399.844 MHz, $CDCl_3$): $\delta = 7.99$ (Th-H5), 7.83 (Th-H3), 7.70 (BPh-H2,6), 7.40 (Th-H4), 7.3−6.3 (all other aromatic H's), 2.4−1.2 (polymer backbone), 1.12 (CHCH_3). ^{13}C NMR (125.698 MHz, $CDCl_3$): $\delta = 145.9$ (br, styrene Ph-C1), 142.6 (Th−C3/5), 137.5 (BPh-C2,6), 137.2 (Th-C3/5), 129.1 (Th-C4), 128.1, 125.9 (m, styrene Ph−C's), n.o. (BPh-C1), 47−40 (polymer backbone). ^{11}B NMR (160.380 MHz, $CDCl_3$): $\delta = 50$ ($w_{1/2} = 3800$ Hz). GPC-RI: $M_n = 3517$, $M_w = 3828$, PDI = 1.09.

Synthesis of Th$_2$B-PS-BTh$_2$. To a solution of Me$_3$Si-PS-SiMe$_3$ ($M_n = 6439$ by GPC-RI, 0.30 g, 0.093 mmol) in ∼10 mL of CH_2Cl_2 was added slowly a solution of BBr_3 (45 mg, 0.18 mmol) in ∼10 mL of CH_2Cl_2. The reaction mixture was kept stirring overnight, and 0.14 g of 2-trimethylstannylthiophene (0.56 mmol) in ∼5 mL of CH_2Cl_2 was added slowly. The mixture was stirred for another 12 h and concentrated to about 1 mL before precipitation into cold hexanes (∼100 mL, −30 °C). The precipitate was isolated by filtration and dried under vacuum to give 0.25 g of a white powdery material (83%). ^{1}H NMR (499.893 MHz, $CDCl_3$): $\delta = 7.97$ (Th-H5), 7.80 (Th-H3), 7.63 (BPh-H2,6), 7.38 (Th-H4), 7.3−6.2 (all other aromatic H's), 2.4−1.2 (polymer backbone). GPC-RI: $M_n = 6270$, $M_w = 7311$, PDI = 1.17. DSC (onset): $T_g = 88$ °C; TGA (onset): $T_{dec} = 400$ °C, 97% weight loss.

Complexation with Pyridine: Synthesis of PS-BTh$_2$·Py. PS-BTh$_2$ ($M_n = 3517$ by GPC-RI, 0.50 g, 0.143 mmol) was dissolved in 10 mL of CH_2Cl_2, and pyridine (13.6 mg, 0.171 mmol) was added. The mixture was stirred for 1 h, and all volatile material was removed under high vacuum. PS-BTh$_2$·Py was recovered quantitatively as a white solid. ^{1}H NMR (399.844 MHz, $CDCl_3$, ca. 10 mM boryl groups): $\delta = 8.55$ (Py-H2,6), 7.80 (Py-H4), 7.49 (Py-H3,5), 7.42 (Th-H5), 7.3−6.3 (all other aromatic H's), 2.5−1.2 (polymer backbone), 1.07 (CHCH_3). ^{13}C NMR (100.541 MHz, $CDCl_3$): $\delta = 154.4$ (Th-C2), 147.4 (Py-C2,6), 145.8 (styrene Ph-C1), 140.8 (Py-C4), 133.3 (BPh-C2,6), 132.4 (Th-C3), 127.5 (Th-C5), 125.7 (Th-C4), 125.1 (Py-C3,5), 128.1, 126.2 (all other aromatic C's), n.o. (BPh-C1), 47−40 (polymer backbone). ^{11}B NMR (160.380 MHz, $CDCl_3$): $\delta = 0$ ($w_{1/2} = 800$ Hz). GPC-RI: $M_n = 2379$, $M_w = 2905$, PDI = 1.22.

Complexation with 4,4′-Dipyridyl (bipy): Synthesis of [Th$_2$B-PS-BTh$_2$·bipy]$_n$. Th$_2$B-PS-BTh$_2$ (50 mg, 15.5 μmol) and 4,4′-dipyridyl (1.2 mg, 7.7 μmol) were dissolved in 1 mL of benzene, and [Th$_2$B-PS-BTh$_2$·bipy]$_n$ was recovered by freeze-drying. ^{1}H NMR (399.844 MHz, $CDCl_3$, ca. 15.5 mM boryl groups): $\delta = 8.72$ (bipy-H2,6), 7.59 (bipy-H3,5), 7.45 (Th-H5), 7.3−6.3 (all other aromatic H's), 2.4−1.2 (polymer backbone). ^{11}B NMR (160.380 MHz, $CDCl_3$): $\delta = 1$ ($w_{1/2} = 1370$ Hz). GPC-RI: $M_n = 6144$, $M_w = 7092$, PDI = 1.15. DSC (onset): $T_g = 105$ °C; TGA (onset): $T_{dec} = 400$ °C, 100% weight loss.

General Procedure of the Titration of Th$_2$B-PS-BTh$_2$ with 4,4′-Dipyridyl. Th$_2$B-PS-BTh$_2$ (50 mg, ca. 15.5 μmol boryl groups) was dissolved in 1 mL of $CDCl_3$ and charged into a NMR tube equipped with a rubber septum. A solution of 4,4′-dipyridyl (ca. 77 mM in $CDCl_3$) was added in predetermined increments using a microliter syringe. ^{1}H NMR measurements were performed after each addition of the base solution.

Synthesis of (PS-BO)$_3$. To a solution of BBr_3 (72 mg, 0.29 mmol) in 20 mL of CH_2Cl_2 was added dropwise a solution of PS-SiMe$_3$ ($M_n = 4038$ by GPC-RI, 1.0 g, 0.23 mmol end groups) in 10 mL of CH_2Cl_2, and the mixture was stirred for 12 h. The solution was then concentrated to ~2 mL and precipitated into cold hexanes (−30 °C) to give the intermediate PS-BBr_2 as a gummy material. PS-BBr_2 was freeze-dried from benzene and dried under high vacuum at 50 °C for 12 h. ^1H NMR (399.844 MHz, $CDCl_3$): δ = 8.04 (BPh-H2,6), 7.4−6.4 (other aromatic H's), 2.6−1.0 (polymer backbone). ^{11}B NMR (160.380 MHz, $CDCl_3$): $\delta = 56$ ($w_{1/2} = 1850$ Hz). PS-BBr_2 was then dissolved in benzene (50 mL), and water (0.5 mL) was added. After azeotropic distillation until no more water separated, the product was isolated by freeze-drying and dried under high vacuum at 60 °C overnight (0.80 g, 80%). ^1H NMR (499.893 MHz, $CDCl_3$): δ = 8.05 (m, BPh-H2,6), 7.6−6.4 (other aromatic H's), 2.6−1.0 (polymer backbone). ^1H NMR (499.893 MHz, d_6-acetone/D_2O): δ = 7.80−7.71 (m, BPh-H2,6), 7.4−6.4 (other aromatic H's), 2.5−1.0 (polymer backbone). ^{11}B NMR (160.380 MHz, $CDCl_3$): $\delta = 22$ ($w_{1/2} = 2840$ Hz). GPC-RI: $M_n = 3771$, $M_w = 5219$, PDI = 1.38. DSC (onset): T_g = 101 °C; TGA (onset): T_{dec} = 394 °C, 98.5% weight loss.

Formation of Boroxine Cross-Linked PS: Synthesis of (PS-BO)$_n$. Me_3Si-PS-$SiMe_3$ (M_n = 6439 by GPC-RI, 0.50 g, 0.063 mmol) was dissolved in 10 mL of CH_2Cl_2, and a solution of BBr_3 (63 mg, 0.25 mmol) in 10 mL of CH_2Cl_2 was added dropwise. The reaction mixture was stirred overnight and concentrated to ~1 mL. Br_2B-PS-BBr_2 was recovered by precipitation into cold hexanes and redissolved in ~20 mL of benzene. Water (1 mL) was added to the benzene solution, and the mixture was subjected to azeotropic distillation for 6 h until no more water separated and a white precipitate formed. Benzene was then removed under vacuum, and the remaining white solid was dried at 60 °C under high vacuum for 12 h (0.31 g, 62%). ^1H NMR (499.893 MHz, d_5-pyridine): δ = 8.33 (br, BPh-H2,6), 7.5−6.6 (other aromatic H's), 2.6−1.0 (polymer backbone). ^{11}B NMR (160.380 MHz, d_5-pyridine): δ = 15. ^1H NMR (499.893 MHz, d_6-acetone/D_2O): δ = 7.80−7.71 (m, BPh-H2,6), 7.4−6.4 (other aromatic H's), 2.5−1.2 (polymer backbone). DSC (onset): T_g = 112 °C; TGA (onset): T_{dec} = 395 °C, 97% weight loss.

Acknowledgment. We thank the National Science Foundation (NSF CAREER award CHE-0346828 to F.J. and instrumentation grant MRI-0116066), the Alfred P. Sloan foundation (research fellowship to F.J.), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Supporting Information Available: ^1H NMR plots of PS-$SiMe_3$, Me_3Si-PS-$SiMe_3$, PS-BBr_2, and Br_2B-PS-BBr_2. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Jäkle, F. *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 293−307. (b) Jäkle, F. *Coord. Chem. Rev.* **2006**, *250*, 1107−1121.
(2) Goethals, E. J. *Telechelic Polymers: Synthesis and Application*; CRC Press: Boca Raton, FL, 1989.
(3) Balogh, L.; Wang, L.; Faust, R. *Macromolecules* **1994**, *27*, 3453−3458.
(4) Balogh, L.; Fodor, Z.; Kelen, T.; Faust, R. *Macromolecules* **1994**, *27*, 4648−4651.
(5) Koroskenyi, B.; Wang, L.; Faust, R. *Macromolecules* **1997**, *30*, 7667−7672.
(6) Shea, K. J.; Walker, J. W.; Zhu, H.; Paz, M.; Greaves, J. *J. Am. Chem. Soc.* **1997**, *119*, 9049−9050.
(7) Shea, K. J. *Chem.−Eur. J.* **2000**, *6*, 1113−1119.
(8) Wagner, C. E.; Rodriguez, A. A.; Shea, K. J. *Macromolecules* **2005**, *38*, 7286−7291.
(9) Xu, G.; Chung, T. C. *J. Am. Chem. Soc.* **1999**, *121*, 6763−6764.
(10) Chung, T. C.; Xu, G.; Lu, Y.; Hu, Y. *Macromolecules* **2001**, *34*, 8040−8050.
(11) Katayama, H.; Fukuse, Y.; Nobuto, Y.; Akamatsu, L.; Ozawa, F. *Macromolecules* **2003**, *36*, 7020−7026.
(12) Lu, B.; Chung, T. C. *Macromolecules* **1998**, *31*, 5943−5946.
(13) Miyata, M.; Meyer, F.; Chujo, Y.; Groh, P. W.; Ivan, B. *Polym. Bull.* **2004**, *52*, 25−31.
(14) Mizumo, T.; Sakamoto, K.; Matsumi, N.; Ohno, H. *Electrochim. Acta* **2005**, *50*, 3928−3933.
(15) (a) Qin, Y.; Cheng, G.; Sundararaman, A.; Jäkle, F. *J. Am. Chem. Soc.* **2002**, *124*, 12672−12673. (b) Qin, Y.; Cheng, G.; Achara, O.; Parab, K.; Jäkle, F. *Macromolecules* **2004**, *37*, 7123−7131. (c) Qin, Y.; Sukul, V.; Pagakos, D.; Cui, C.; Jäkle, F. *Macromolecules* **2005**, *38*, 8987−8990.
(16) (a) Qin, Y.; Pagba, C.; Piotrowiak, P.; Jäkle, F. *J. Am. Chem. Soc.* **2004**, *126*, 7015−7018. (b) Qin, Y.; Kiburu, I.; Shah, S.; Jäkle, F. *Macromolecules* **2006**, *39*, 9041−9048. (c) Parab, K.; Venkatasubbaiah, K.; Jäkle, F. *J. Am. Chem. Soc.* **2006**, *128*, 12879−12885.
(17) Tokunaga, Y.; Ueno, H.; Shimomura, Y.; Seo, T. *Heterocycles* **2002**, *57*, 787−790.
(18) (a) Perttu, E. K.; Arnold, M.; Iovine, P. M. *Tetrahedron Lett.* **2005**, *46*, 8753−8756. (b) Kua, J.; Fletcher, M. N.; Iovine, P. M. *J. Phys. Chem. A* **2006**, *110*, 8158−8166.
(19) Frohn, H.-J.; Adonin, N. Y.; Bardin, V. V.; Starichenko, V. F. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2827−2833.
(20) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921−2990.
(21) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689−3745.
(22) Drumm, J. E., III.; Lett, R. M.; Stevenson, T. M. DuPont de Nemours, E. I. Co. US 5378708, 1995.
(23) Sarbu, T.; Lin, K.-Y.; Ell, J.; Siegwart, D. J.; Spanswick, J.; Matyjaszewski, K. *Macromolecules* **2004**, *37*, 3120−3127.
(24) Fuson, R. C.; Cleveland, E. A.; Bachmann, W. E.; Wilds, A. L.; Korman, A. L. *Org. Synth. Collect.* **1995**, *3*, 339−340.
(25) As expected, the multiplet resonances at 4.5 and 4.4 ppm for the proton of the −CPh(H)Br end group of PS-$SiMe_3$ do not change position upon borylation. However, if a larger excess of BBr_3 is used, the signals move to 4.3 and 4.1 ppm. This is tentatively attributed to BBr_3-promoted intramolecular Friedel−Crafts alkylation of the second to last phenyl group under loss of the bromine and formation of an indane ring (formation of cis and trans isomers of 1-polystyryl-3-phenylindane). The latter is a well-known termination reaction in the cationic polymerization of styrene. See: (a) Taylor, A. R.; Keen, G. W.; Eisenbraun, E. J. *J. Org. Chem.* **1977**, *42*, 3477−3480. (b) Matyjaszewski, K.; Lin, C.-H.; Pugh, C. *Macromolecules* **1993**, *26*, 2649−2654.
(26) Lehn, J.-M. *Angew. Chem., Int. Ed.* **1988**, *27*, 89−112.
(27) Pedersen, C. J. *Angew. Chem., Int. Ed.* **1988**, *28*, 1009−1020.
(28) Cram, D. J. *Angew. Chem., Int. Ed.* **1988**, *27*, 1021−1027.
(29) Recent reviews of supramolecular polymers: (a) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071−4097. (b) Schubert, U. S.; Eschbaumer, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 2892−2926. (c) Lehn, J.-M. *Science* **2002**, *295*, 2400−2403. (d) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373−399. (e) Pollino, J. M.; Weck, M. *Chem. Soc. Rev.* **2005**, *34*, 193−207. (f) Amstrong, G.; Buggy, M. *J. Mater. Sci.* **2005**, *40*, 547−559. (g) Lehn, J. M. *Prog. Polym. Sci.* **2005**, *30*, 814−831. (h) Ciferri, A., Ed. *Supramolecular Polymers,* 2nd ed.; 2005, p 761.
(30) Recent examples of supramolecular polymers: (a) Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. *Adv. Mater.* **2000**, *12*, 874−878. (b) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W. *MRS Bull.* **2000**, *25*, 49−53. (c) Kato, T. *Science* **2002**, *295*, 2414−2418. (d) Cate, A. T.; Sijbesma, R. P. *Macromol. Rapid Commun.* **2002**, *23*, 1094−1112. (e) Calzia, K. J.; Tew, G. N. *Macromolecules* **2002**, *35*, 6090−6093. (f) Simic, V.; Bouteiller, L.; Jalabert, M. *J. Am. Chem. Soc.* **2003**, *125*, 13148−13154. (g) Messmore, B. W.; Hulvat, J. F.; Sone, E. D.; Stupp, S. I. *J. Am. Chem. Soc.* **2004**, *126*, 14452−14458. (h) Bodenthin, Y.; Pietsch, U.; Mohwald, H.; Kurth, D. G. *J. Am. Chem. Soc.* **2005**, *127*, 3110−3115. (i) Sivakova, S.; Bohnsack, D. A.; Mackay, M. E.; Suwanmala, P.; Rowan, S. J. *J. Am. Chem. Soc.* **2005**, *127*, 18202−18211. (j) Gorczynski, J. L.; Chen, J.; Fraser, C. L. *J. Am. Chem. Soc.* **2005**, *127*, 14956−14957. (k) Dobrawa, R.; Lysetska, M.; Ballester, P.; Grüne, M.; Würthner, F. *Macromolecules* **2005**, *38*, 1315−1325. (l) Hofmeier, H.; Hoogenboom, R.; Wouters, M. E. L.; Schubert, U. S. *J. Am. Chem. Soc.* **2005**, *127*, 2913−2921. (m) Park, T.; Zimmerman, S. C.; Nakashima, S. *J. Am. Chem. Soc.* **2005**, *127*, 6520−6521. (n) Kolomiets, E.; Buhler, E.; Candau, S. J.; Lehn, J.-M. *Macromolecules* **2006**, *39*, 1173−1181.
(31) The reversible assembly of polymers from molecular bifunctional Lewis acids and bifunctional Lewis bases has been well documented: (a) Fontani, M.; Peters, F.; Scherer, W.; Wachter, W.; Wagner, M.; Zanello, P. *Eur. J. Inorg. Chem.* **1998**, 1453−1465. (b) Grosche, M.; Herdtweck, E.; Peters, F.; Wagner, M. *Organometallics* **1999**, *18*, 4669−4672.
(32) (a) Qin, Y.; Parab, K.; Cheng, G.; Achara, O.; Jäkle, F. *Polym. Prepr.* **2003**, *45*, 513−514. (b) Qin, Y.; Jäkle, F. *J. Inorg. Organomet. Polym. Mater.*, in press.
(33) The anticipated binding constant of pyridine molecules to triarylboron moieties is ca. 10^6−10^7 M^{-1}. See: Sundararaman, A.; Victor, M.; Varughese, M.; Jäkle, F. *J. Am. Chem. Soc.* **2005**, *127*, 13748−13749.

(34) Hall, D. G., Ed. *Boronic Acids: Preparation, Application in Organic Synthesis and Medicine*; Wiley-VCH: Weinheim, 2005.

(35) Belogi, G.; Zhu, T.; Boons, G.-J. *Tetrahedron Lett.* **2000**, *41*, 6965−6968.

(36) Elmas, B.; Onur, M. A.; Senel, S.; Tuncel, A. *Colloids Surf., A* **2004**, *232*, 253−259.

(37) Appleton, B.; Gibson, T. D. *Sens. Actuators, B* **2000**, *65*, 302−304.

(38) Sano, M.; Okamura, J.; Kanekiyo, Y.; Shinkai, S. *Colloids Surf., A* **2000**, *169*, 131−136.

(39) Stolowitz, M. L.; Ahlem, C.; Hughes, K. A.; Kaiser, R. J.; Kesicji, E. A.; Li, G.; Lund, K. P.; Torkelson, S. M.; Wiley, J. P. *Bioconjugate Chem.* **2001**, *12*, 229−239.

(40) Senel, S. *Colloids Surf., A.* **2003**, *219*, 17−23.

(41) Morgan, A. B.; Jurs, J. L.; Tour, J. M. *J. Appl. Polym. Sci.* **2000**, *76*, 1257−1268.

(42) Mehta, M. A.; Fujinami, T. *Chem. Lett.* **1997**, 915−916.

(43) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.

(44) The material could be solubilized upon treatment with d_5-pyridine at 60 °C over an extended period of time. The similarity of the ^{1}H NMR data of the resulting solution to those of 4-*tert*-butylphenyl boroxine in d_5-pyridine suggests the presence of pyridine-bound boroxine rings.

(45) The concept of using boroxine linkages to construct large and complex structures has attracted recent interest; for instance, the use of boroxine linkages for the immobilization of stable blue-light-emitting oligofluorene networks and the construction of porous, crystalline covalent organic frameworks with high surface area have been reported. See: (a) Li, Y.; Ding, J.; Day, M.; Tao, Y.; Lu, J.; D'iorio, M. *Chem. Mater.* **2003**, *15*, 4936−4943. (b) Côté, A. P.; Benin, A. I.; Ockwig, N. W.; O'keeffe, M.; Matzger, A. J.; Yaghi, O. M. *Science* **2005**, *310*, 1166−1170. (c) See also related work on boronate esters: Tilford, R. W.; Gemmill, W. R.; zur Loye, H. C.; Lavigne, J. J. *Chem. Mater.* **2006**, *18*, 5296−5301.

(46) GPC measurement of $[\mathrm{Th_2B\text{-}PS\text{-}BTh_2{\cdot}bipy}]_n$ and $(\mathrm{PS\text{-}BO})_3$ in THF gave molecular weights corresponding to the starting materials $\mathrm{Th_2B\text{-}PS\text{-}BTh_2}$ and $\mathrm{PS\text{-}SiMe_3}$, respectively, presumably due to decomplexation of the bipy molecules caused by interaction with the column material and hydrolysis of the boroxine linkages. See Experimental Section for details.

(47) Iovine, P. M.; Fletcher, M. N.; Lin, S. *Macromolecules* **2006**, *39*, 6324−6326.

(48) Whitesides, G. M.; Sadowski, J. S.; Lilburn, J. *J. Am. Chem. Soc.* **1974**, *96*, 2829−2835.

MA061704H