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Preparation of Organoboron Block Copolymers via ATRP of Silicon and Boron-Functionalized Monomers

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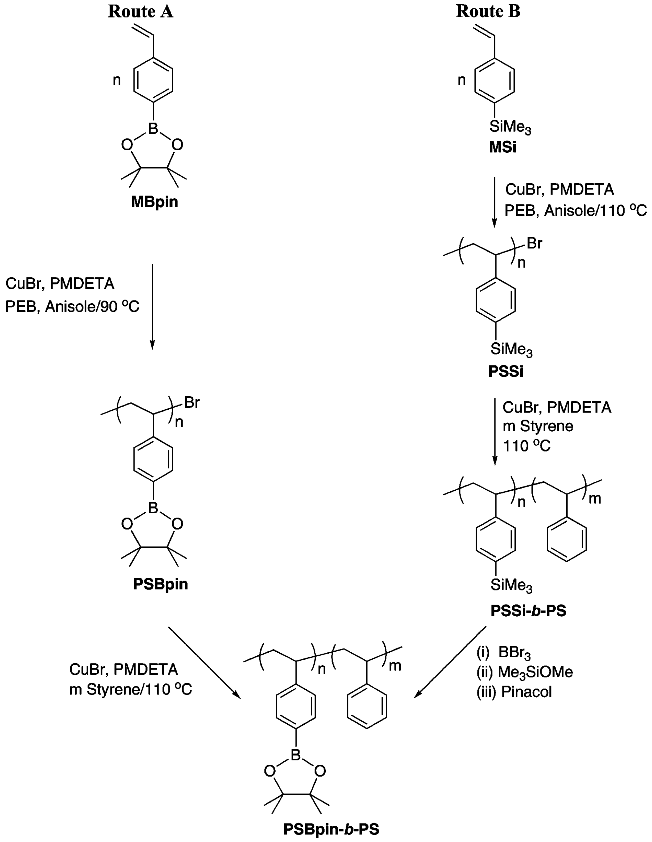
Boron-containing polymers represent an important class of materials that are extensively used, for example, as intermediates in the synthesis of functionalized polymers with polar side groups,[1] supported reagents and immobilized catalysts,[2] scaffolds for the solid-phase synthesis of carbohydrates,[3] sensors and stimuli responsive polymers including the sensing of sugars,[4,5] separation media in biochemical applications,[6] polymeric electrolytes for batteries,[7] flame retardants,[8] ceramic precursors,[9,10] and luminescent and other electronically interesting materials.[11] Their preparation generally involves either direct polymerization of boron-functionalized monomers or functionalization of polymers with boron groups. Polymerization of boron monomers has overall received more attention for the placement of boron substituents in the side chains of non-cross-linked polyolefins. The method of choice usually is standard free radical polymerization due to the reasonably good compatibility with boron−carbon bonds and the relatively straightforward synthetic procedures involved. Thus, heat-induced or AIBN (2,2′-azobis(2-methylpropionitrile)) initiated free radical polymerization has been applied to the homo- and copolymerization of olefins containing boronic acid and boronic ester,[5,12] borazine,[13] and polyborane and carborane[14] moieties. Ring-opening metathesis polymerization (ROMP)[10,15] and Ziegler−Natta techniques[16,17] have also commonly been employed, and the latter are especially useful for the polymerization of more highly reactive and more strongly Lewis acidic organoboron species. A recent example is the polymerization of a boron-functionalized styrene monomer with a titanium catalyst, which yields syndiotactic boron-functionalized polymers.[17] Postpolymerization modification procedures represent an interesting alternative that sometimes can circumvent commonly encountered issues with compatibility of certain organoboron monomers with given polymerization procedures.[18] Recent advances in this field have led to the successful application of hydroboration chemistry to vinyl group containing polyolefins,[19] and even unfunctionalized polyethylethylene (PEE) and polypropylene have been successfully borylated through a novel transition-metal-catalyzed process.[20] We have shown that well-defined fully functionalized borylated polystyrene is readily accessible through facile and high yield polymer modification reactions using silylated polystyrene as the precursor.[21]

While all these methods are extensively used in the preparation of boron-containing homo- and random copolymers, despite potentially intriguing possibilities, reports on the incorporation of boron into well-defined block copolymers are rare.[22] Controlled free radical polymerization methods such as atom transfer radical polymerization (ATRP)[23] have become an important tool for the preparation of block copolymers and other polymer architectures. Since ATRP tolerates various functionalities,[23] we studied the suitability of ATRP for the controlled polymerization of boron-containing monomers and the formation of block copolymers.

Scheme 1. Synthesis of the Organoboron Block Copolymer PSBpin-*b*-PS; 1-PEB = 1-Phenylethyl Bromide and PMDETA = *N,N′,N′,N″,N″*-Pentamethyldiethylenetriamine



Two different routes for the preparation of boron-containing block copolymers were investigated (Scheme 1). In the direct polymerization method, route A, we attempted the first controlled polymerization of a boron-containing monomer via ATRP. The resulting well-defined organoboron polymer should in turn be able to serve as a macroinitiator in the chain extension with styrene or other monomers. We have previously shown that trimethylsilyl-functionalized polystyrene (PSSi) can be used as an efficient precursor to boron-modified styrenic polymers.[21] Thus, postpolymerization modification (route B) represents an interesting alternative method that entails controlled polymerization of a trimethylsilyl-functionalized monomer and subsequent chain extension with styrene, followed by highly selective boron−silicon exchange with BBr_3.

The direct polymerization method (route A) starts from the organoboron monomer MBpin, which was obtained in moderate yield ($\sim$50%) through treatment of styreneboronic acid with pinacol followed by high-vacuum distillation. The polymerization behavior of this

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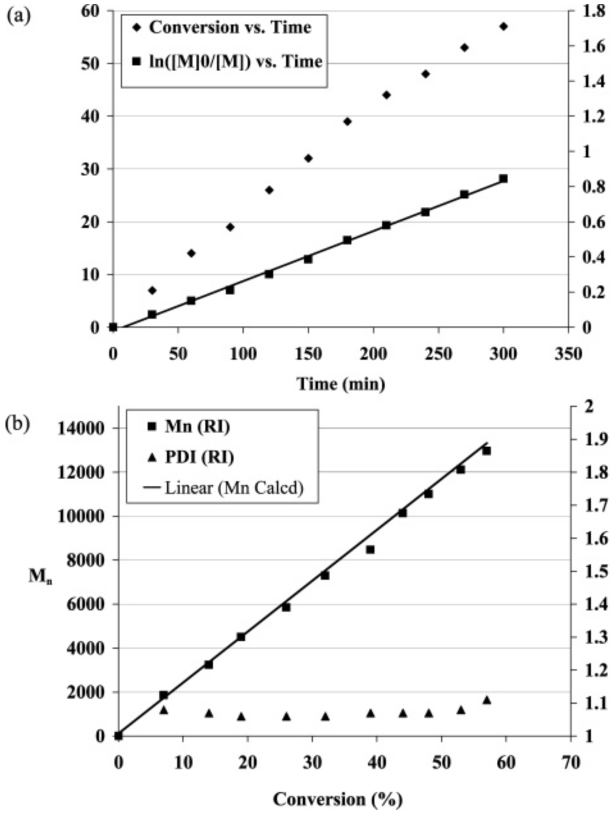

Figure 1. (a) Kinetic data for atom transfer free radical polymerization (ATRP) of 4-pinacolatoborylstyrene (MBpin) in anisole (50 wt %) at 90 °C as determined by ^{1}H NMR spectroscopy. (b) Dependence of number-average molecular weight (M_n) and polydispersity index (PDI) on conversion based on gel permeation chromatography with refractive index detector (GPC-RI) relative to polystyrene standards. $[M]_0 = 4.3$ M and $[M]_0:[1\text{-PEB}]_0:[CuBr]_0:[PMDETA]_0 = 100:1:2:4$ (1-PEB = 1-phenylethyl bromide; PMDETA = *N,N′,N′,N″,N″*-pentamethyldiethylenetriamine).

organoboron monomer was studied using a typical protocol for ATRP[24] with 1-phenylethyl bromide (PEB) as the initiator and *N,N′,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA)/CuBr as the catalyst system. The polymerization conditions were optimized by varying monomer concentration, temperature, initiator-to-catalyst ratio, and ligand-to-catalyst ratio. The best results were obtained with a ratio of monomer:initiator:catalyst:ligand of 100:1:2:4 at 90 °C. Under these conditions the polymerization was well controlled, and a pseudo first-order kinetic behavior was observed up to ca. 60% conversion, as shown in Figure 1a. The monomer reactivity was found to be similar to that of styrene, though MBpin polymerized at a considerably slower rate than 4-trimethylsilylstyrene (MSi).[25] At higher conversion deviations from ideal behavior were found, which are likely due to increased significance of chain transfer events.[26]

Consistent with these observations is that the molecular weight increases linearly with conversion up to about 60% conversion, while the polydispersity index (PDI) remains low in this regime (Figure 1b). Again, deviations from linearity were observed at higher conversions with values of the number-average molecular weight (M_n) lower than expected, but with only slightly higher dispersities. Thus, the polymerization of MBpin can be considered a controlled process before it reaches 60% conversion.

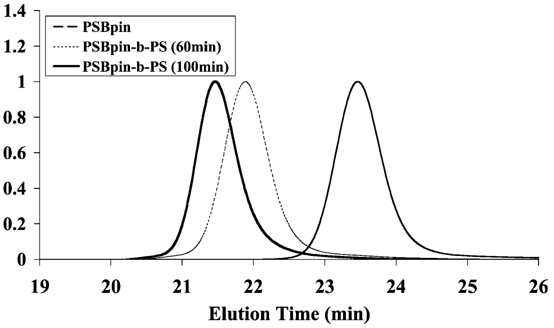

Figure 2. Gel permeation chromatography (refractive index detector) traces of PSBpin and PSBpin-*b*-PS (see Scheme 1) during the chain extension reaction.

Chain extension of the resulting organoboron polymer PSBPin was attempted by ATRP with styrene in bulk at 110 °C (Scheme 1). To ensure full coverage of the polymer with Br end groups, a sample that was obtained at low conversion of MBPin was used as the macroinitiator ($M_w = 8540$). The polymerization was monitored by gel permeation chromatography (GPC) analysis of samples withdrawn at predetermined time intervals. The GPC traces in Figure 2 clearly show that the molecular weight increases with time and the dispersity remains narrow (PDI = 1.04). This indicates that thermally induced polymerization is insignificant. Moreover, in the traces for PSBpin-*b*-PS, no low molecular weight shoulders are observed. The absence of any detectable amount of the starting block, PSBpin, suggests close to quantitative initiation and provides further evidence for the quasi-living nature of the polymerization of MBpin. The composition of the copolymer after a reaction time of 100 min was studied by a combination of GPC, ^{1}H NMR, and elemental analysis. All three methods gave the same ratio of PS repeat units relative to PSBpin repeat units (ca. 5:1). Thus, the chain extension of PSBpin with styrene can at least during the early stages also be considered a quasi-living process, and the molecular weight can be controlled based on the reaction time (see Supporting Information).

As mentioned above, postpolymerization modification of silylated polymers provides an alternative route to boron-containing polymers (route B, Scheme 1). This method is particularly attractive since we could previously show that very good control is possible in ATRP even at relatively high conversions of 4-trimethylsilylstyrene and that the silyl groups can be quantitatively replaced with boryl moieties.[21] A trimethylsilyl-functionalized polymer (PSSi) of low molecular weight ($M_w = 6243$) was used as the macroinitiator for the polymerization of styrene under ATRP conditions (Scheme 1). A kinetic analysis of the chain extension of PSSi with styrene showed a linear dependence of $\ln([M]_0/[M])$ vs time and indicated that the molecular weight of the block copolymer can be controlled and the dispersity remains narrow (see Supporting Information). The block copolymer PSSi-*b*-PS was recovered by precipitation into hexanes/ethanol (1:2) and studied by gel permeation chromatography with in-line light scattering detector (GPC-LS) (Table 1). Treatment of PSSi-*b*-PS with (i) BBr_3 in CH_2Cl_2, (ii) Me_3SiOMe, and (iii) pinacol gave the organoboron block copolymer PSBpin-*b*-PS, which was isolated by precipitation into methanol. We have previously shown for the synthesis of the respective homopolymer PSBPin that this procedure leads to

Table 1. GPC-LS (Gel Permeation Chromatography with in-Line Light Scattering Detector) and ^{1}H NMR Analysis of Polymers from Route B (Scheme 1)

polymer	M_w (GPC-LS)	mole fraction of functional block by GPC-LS	mole fraction of functional block by ^{1}H NMR
PSSi[a]	6243	1, DP[b] = 34	1
PSSi-*b*-PS[a]	19480	0.21	0.19[c]
PSBpin-*b*-PS[a]	21530	0.21	0.19[d]

[a] See Scheme 1 for polymer labeling. [b] Average degree of polymerization based on weight-average molecular weight (M_w). [c] Derived from integration of corresponding signals of PSSi and PS. [d] Derived from integration of corresponding signals of PSBpin and PS.

highly selective polymer modification.[21] The individual reactions were followed by NMR spectroscopy and the NMR spectra of the final product were found to be nearly identical to those for the block copolymer obtained through the direct polymerization route (see Supporting Information). GPC-LS analysis was performed before and after postpolymerization modification, and the results are summarized in Table 1. The GPC-LS and ^{1}H NMR data confirm that the copolymer composition remains almost constant throughout the postpolymerization modification process. Elemental analyses for the two block copolymers from route A and route B matched well with the individual molecular weights and mole fractions determined by GPC-LS of the homopolymers and block copolymers.

The thermal properties of the boron-containing block copolymer PSBpin-*b*-PS were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The block copolymer prepared through route B gave almost identical result as that from route A. Two glass transitions are observed in the DSC trace of PSBpin-*b*-PS at ca. 110 and 201 °C (onset). These data correlate well with those of the respective homopolymers, PS ($T_g = 107$ °C) and PSBpin ($T_g = 197$ °C). The latter is indicative of phase separation of the two blocks in the solid state. Good thermal stability of the block copolymer was confirmed by TGA. A decomposition temperature close to that of PS and somewhat higher than for the homopolymer PSBPin was observed.

In conclusion, we have successfully prepared the new organoboron block copolymer, PSBpin-*b*-PS. Direct polymerization of the boron monomer MBPin provides rapid access to the desired boron-containing block copolymer in only two reaction steps. While the postpolymerization modification route through the respective silicon-functionalized block copolymer PSSi-*b*-PS involves one additional step, especially at higher conversions control over the polymerization process can more easily be achieved. Another benefit of the polymer modification route is that the bromine substituents on boron can very easily be modified by reaction with other nucleophiles.[21] However, the use of the highly reactive reagent BBr_3 may somewhat limit the variety of monomers that can be incorporated into organoboron block copolymers. In this respect, the direct polymerization method will likely prove more versatile. Preliminary studies indicate that the respective boronic acid-functionalized block copolymers are accessible in a similar fashion and undergo micellization upon addition of water to a THF solution, which is consistent with the formation of a novel amphiphilic block copolymer (see Supporting Information). The boronic acid block copolymers are also promising precursors to various other boron polymers through straightforward esterification reactions. The results described herein thus open up new possibilities in the various application fields that involve organoboron polymers including organic/inorganic hybrid materials, polymer electrolytes, polymer-supported catalysts, polymeric sensors, and separation media.

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Supporting Information Available: Experimental procedures and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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