

Weakly Coordinating Amphiphilic Organoborate Block Copolymers

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Organoborates are widely used as counterions to stabilize main group and transition metal complexes.¹ They also serve important roles as electrolytes in lithium ion batteries² and electrochemical redox processes,³ as components of ionic liquids,⁴ and as membrane materials.⁵ The protection of highly reactive cationic species from attack by nucleophiles with subsequent degradation and/or deactivation is of particular importance in the area of olefin polymerization, where borates have been extensively used as counterions to active cationic transition metal complexes.⁶ Fluorinated derivatives are attractive because of their weakly coordinating and chemically more inert nature. To incorporate these borate counterions into polymeric structures is an intriguing premise, since beneficial effects can be expected from the improved processability and anticipated stabilizing effect of the polymer chain.⁷ One approach that has been successfully employed involves noncovalent anchoring of molecular organoborate anions to cationic polymers.⁸ The alternative method of covalent functionalization of polymers with weakly coordinating organoborate moieties is less developed, and especially reports of fluorinated organoborate polymers remain scarce.^{9,10}

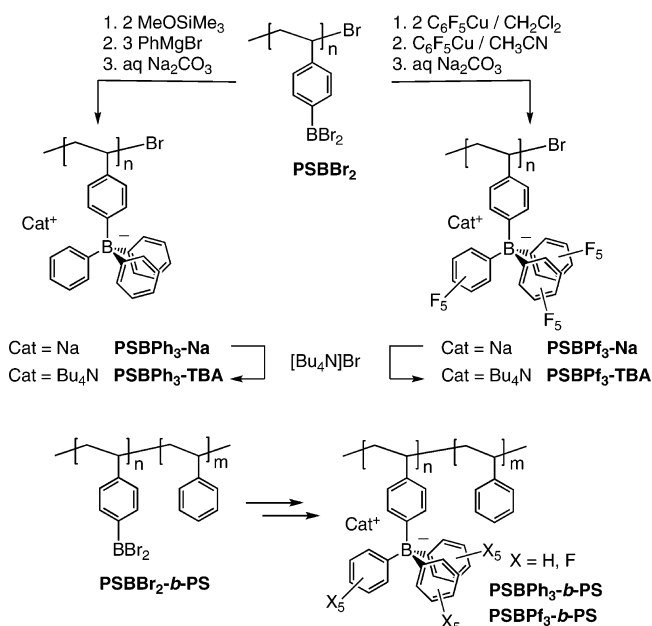
We became interested in the incorporation of organoborate functionalities into amphiphilic block copolymers¹¹ for their well-known ability to form interesting micellar aggregates. Organometallic block copolymers have received tremendous interest in recent years.¹² However, organoborate block copolymers have to the best of our knowledge not been reported to date and new controlled synthesis routes to these types of materials are needed.^{13–15} We describe here a versatile new method for the preparation of organoborate polymers and report the first block copolymers, in which one of the constituent blocks is functionalized with weakly coordinating organoborate moieties, while the other block (polystyrene, PS) is unfunctionalized and thus provides solubility in nonpolar solvents. Studies on their self-assembly in solvents that selectively dissolve one of the constituent copolymer components are also presented.

Poly(4-trimethylsilylstyrene) (PSSiMe₃; *n* = 93) and the corresponding block copolymers with styrene as a second block (PSSiMe₃-*b*-PS; *n* = 33, *m* = 120 or *n* = 29, *m* = 238) are readily accessible via atom transfer radical polymerization (ATRP) according to published procedures.^{15,16} Exchange of the SiMe₃ groups with a slight excess of BBr₃ results in the selective and essentially quantitative formation of the boron-functionalized homopolymers and block copolymers, PSBBr₂ and PSBBr₂-*b*-PS, based on multinuclear NMR studies.^{15,16}

There are several possible approaches for the conversion of these BBr₂-functionalized polymers to the desired organoborate polymers. One method that was applied to the triphenylborate-modified polymer PSBPh₃ is based on the treatment of boronates with an excess of organolithium or Grignard reagents.¹⁷ Hence, we first converted the BBr₂ groups to B(OMe)₂ moieties with

the mild reagent Me₃SiOMe, and the resulting boronate polymer was then reacted with PhMgBr at 85 °C in THF for 3 h (Scheme 1). An alternative route involves initial formation of the triorganoborane intermediate which, if it is readily available,¹⁸ can be very selectively and under mild conditions converted to the organoborate. This method¹⁹ was successfully applied to the preparation of PSBPf₃ (Pf = C₆F₅). PSBBr₂ was first reacted with the organocopper reagent C₆F₅Cu in CH₂Cl₂ to give PSBPf₂, which was in turn converted *in situ* to the desired borate polymer by addition of a third equivalent of C₆F₅Cu in acetonitrile. Acetonitrile coordinates to copper and, thereby, promotes formation of the [Cu(CH₃CN)_{*x*}][PSBPf₃] polymeric complex. The organoborate polymers were isolated in the form of their sodium derivatives after addition of the reaction mixture into an aqueous sodium carbonate solution, extraction into acetone, and subsequent dialysis against acetone. The amphiphilic block copolymers PSBR₃-*b*-PS (R = Ph, Pf) were prepared from PSBBr₂-*b*-PS using similar methods.

Scheme 1. Synthesis of Organoborate-Functionalized Homopolymers and Block Copolymers; Cat⁺ = Na⁺, Bu₄N⁺



The sodium borate homopolymers are water-soluble, while the block copolymers are soluble in either polar (e.g., THF, acetone, MeOH, DMF, DMSO, water) or nonpolar solvents (e.g., toluene). For dissolution in block-selective solvents such as MeOH, water, or toluene, the block copolymers were first taken up in a common solvent and then dialyzed. Conversion to the Bu₄N derivatives was achieved by dissolution in water and subsequent addition into a

solution of $[\text{Bu}_4\text{N}]\text{Br}$. The products were obtained as white solids that are readily isolated and well soluble in a range of polar organic solvents.

Table 1. Results for Polymer Modification Procedures

	M_n ($\times 10^3$) ^a	M_w ($\times 10^3$) ^a	PDI ^a	DP_n ^b	Yield (%) ^c
PSSiMe ₃	16.4	18.4	1.11	93	
PSBPh ₃	60.1	70.3	1.17	102	54
PSBPf ₃	52.1	59.7	1.14	61	69
PSSiMe ₃ - <i>b</i> -PS	18.3	19.5	1.07	33/120	
PSBPh ₃ - <i>b</i> -PS	28.9	34.5	1.20	28/120 ^d	70
PSBPf ₃ - <i>b</i> -PS	28.2	32.7	1.16	18/120 ^d	66

^a Relative to PS standards based on GPC-RI detection of the ammonium salts in DMF/20 mM LiBr at 40 °C and the silylated precursor polymers in THF at 35 °C; the Bu_4N counterions are included in the calculations. ^b DP_n = number average degree of polymerization of the first and second block, respectively, based on GPC analysis. ^c Isolated yield of the sodium derivative. ^d Calculated assuming that the MW of the PS block remains constant.

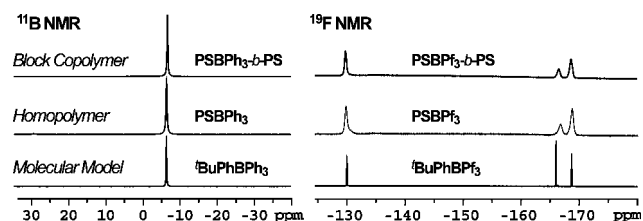


Figure 1. Comparison of selected ^{11}B and ^{19}F NMR spectra of homo- and block copolymers with those of the respective molecular species $\text{Na}[(\text{C}_6\text{H}_4)_3\text{BAr}_3]$; cation = Na^+ , solvent = acetone- d_6 .

Formation of the borate polymers was confirmed by multinuclear NMR spectroscopy.²⁰ The phenylborate homopolymers and block copolymers show slightly broadened ^{11}B NMR resonances at ca. -6 ppm ($w_{1/2} = 30$ Hz), a chemical shift that is identical to that of the related molecular model compound $\text{Na}[(\text{C}_6\text{H}_4)_3\text{BPh}_3]$ ($w_{1/2} = 10$ Hz) (Figure 1). In comparison, the fluorinated derivatives PSBPf_3 and PSBPf_3 -*b*-PS feature slightly more upfield shifted signals at ca. -13 ppm, again consistent with the chemical shift of the molecular species $\text{Na}[(\text{C}_6\text{H}_4)_3\text{B}(\text{C}_6\text{F}_5)_3]$. The fluorinated polymers are also conveniently analyzed by ^{19}F NMR; three broad resonances at -129.7 , -166.6 , and -168.7 ppm are found for the *ortho*, *para*, and *meta*-fluorines of PSBPf_3 , and essentially identical shifts are observed for the respective block copolymer (Figure 1). The absence of any other signals in the ^{11}B and ^{19}F NMR spectra supports selective borate formation.²¹

While the ^1H NMR data are less informative due to the broad nature of the signals, ^{13}C NMR spectroscopy proved useful, and the downfield region of the spectra that shows the *ipso*-carbon atoms is most instructive (Figure S3).²⁰ For the molecular model $\text{Na}[(\text{C}_6\text{H}_4)_3\text{BPh}_3]$, a large and a small quartet are found for the boron-bound carbons of the phenyl and *tert*-butylphenyl groups, respectively, as a result of coupling to ^{11}B . The same pattern is found in the spectra for PSBPh_3 and PSBPh_3 -*b*-PS, except that the signals are slightly broadened, thus confirming selective attachment of the tetraarylborate functionalities to the polymers. For the block copolymer, a second set of resonances that match those of PS is also apparent.

The molecular weight of the organoborate homopolymers and block copolymers was estimated by gel permeation chromatography (GPC-RI) relative to PS standards in DMF using 20 mM LiBr as an additive. For all polymers well-defined monomodal elution profiles were observed with polydispersities in the range of $\text{PDI} =$

1.14 to 1.20 (Table 1). The bands are only slightly broadened relative to those of the silylated precursor polymers, thereby further confirming the high selectivity of the polymer modification reactions. The molecular weights are generally in the expected range, but those of the fluorinated polymers are similar to or even lower than those for the phenylborate polymers. This may be the result of a relatively more compact conformation of the fluorinated polymers in the presence of LiBr (more effective shielding of the charges).

We then carried out studies on the assembly behavior of the organoborate block copolymers in solvents that selectively dissolve one of the constituent blocks. Dynamic light scattering (DLS) was performed on toluene solutions of the sodium and TBA salts of PSBPh_3 -*b*-PS and PSBPf_3 -*b*-PS (derived from PSSiMe_3 -*b*-PS with $n = 33$; $m = 120$), which were obtained by dialysis from acetone to toluene. The results from regularization analysis (DYNALS algorithm) suggest the presence of aggregates with an average apparent hydrodynamic radius, $R_{h,\text{app}}$, of ca. 15 nm, independent of the particular aryl substituents on boron or the counterion employed (Figure 2). It is reasonable to assume that the PS block forms the corona of the micellar structures in toluene as the solvent. Conversely, when the ammonium borate block copolymer PSBPf_3 -*b*-PS is dissolved in (hot) MeOH, the polystyrene should form the core, leaving the organoborate functionalities exposed to the polar solvent. Slightly larger aggregates with $R_{h,\text{app}}$ of ca. 20 nm and a somewhat broader distribution were observed in this case.

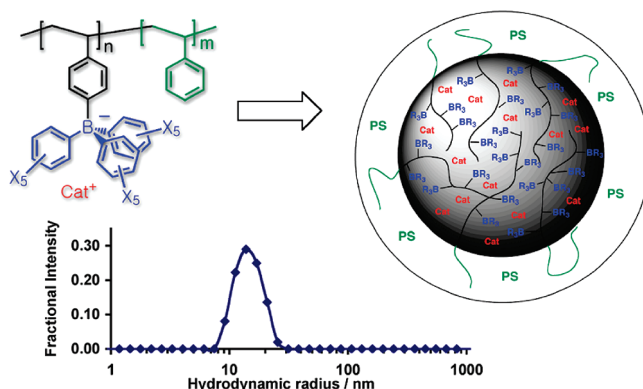


Figure 2. Top: Schematic illustration of the block copolymer assembly of PSBR_3 -*b*-PS in toluene ($R = \text{Ph}$, Pf ; $\text{Cat} =$ counterion (Na^+ , Bu_4N^+); $\text{PS} =$ polystyrene). Bottom: Size distribution histogram of a solution of the sodium salt of PSBPf_3 -*b*-PS in toluene; $n = 33$, $m = 120$.

To demonstrate the ability of the reverse micelles to accept cationic transition metal complexes, we treated the sodium salt of another sample of block copolymer PSBPf_3 -*b*-PS ($n = 29$; $m = 238$) with $[\text{Rh}(\text{cod})(\text{dppb})]^+(\text{OTf})^-$.^{22,23} By ^1H NMR integration, the degree of loading was estimated to be $>85\%$. Micellization was then induced by (a) addition of MeOH as a borate-selective solvent to a solution of the block copolymer in THF as a common solvent and (b) dialysis of the block copolymer in THF to toluene as a PS selective solvent. As expected, formation of regular micelles in MeOH could be confirmed by DLS and TEM analysis (Supporting Information). Interestingly, TEM analysis of the unstained samples prepared in toluene revealed the formation of reverse micelles, which contained dark cores as a result of the rhodium metal loading (Figure 3). The size of these micellar structures was in reasonably good agreement with data derived from DLS ($R_{h,\text{app}}$ ca. 19 nm). This is slightly larger than what we found for the Na precursor ($R_{h,\text{app}} = 16$ nm) prior to reaction with the Rh complex, suggesting a modest expansion of the micellar core upon loading with the transition metal complex.

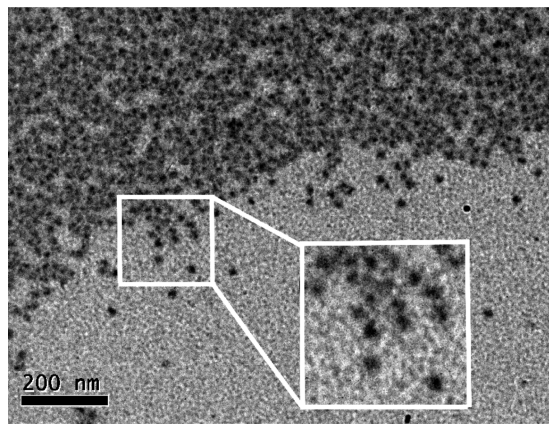


Figure 3. TEM image of PSBPf₃-b-PS ($n = 29$; $m = 238$) after loading with [Rh(cod)(dppb)]⁺ and subsequent micellization in toluene.

In conclusion, we report a new method for the preparation of organoborate polymers. Both homopolymers and the first examples of organoborate block copolymers are readily accessible through selective postmodification procedures. These weakly coordinating polyanions, and in particular the self-assembled block copolymer micelles, are promising candidates as supports for reactive cationic metal complexes, where the “inert” PS corona can not only promote solubility of charged species [ML_n]⁺[BR₄][−] in nonpolar solvents but also possibly act as a protective layer. Further studies in this regard and on their use in catalysis are in progress.

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

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- (18) The phenyl derivative PS-BPh₂ is not readily accessible from PSBBR₂.
- (19) Another possible advantage is that mixed-substituted organoborate polymers PSBR¹R²R³ could become available through selective stepwise introduction of the organic substituents. While not further explored in this work, such an approach could prove highly useful for the development of other functional organoborate polymers.
- (20) Further experimental details are provided in the Supporting Information.
- (21) No difference in the efficiency of the polymer modification reactions for the block copolymers in comparison to the homopolymers was observed. According to the ¹¹B and ¹⁹F NMR data the boron-pendant groups consist of >95% tetrarylborate functionalities; moreover, the extent of borylation of the functional block is >95% based on NMR analysis after the initial Si/B exchange reaction. However, a small amount of deborylation in subsequent steps cannot be completely ruled out since these defects would not be visible in the ¹¹B and ¹⁹F NMR data and may be masked in the ¹H and ¹³C NMR data.
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