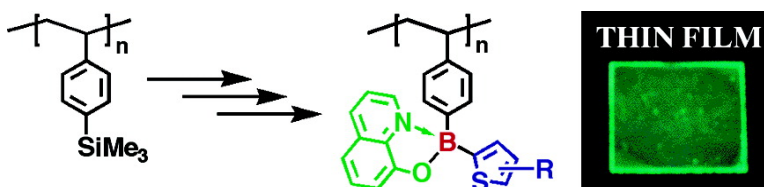


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Luminescent Organoboron Quinolates Polymers

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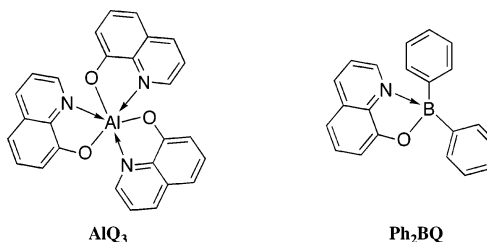
Abstract: The synthesis of well-defined luminescent organoboron polymers via a novel three-step procedure starting from silylated polystyrene is reported. Highly selective borylation of poly(4-trimethylsilylstyrene) (**PS-Si**), followed by replacement of the bromine substituents in poly(4-dibromoborylstyrene) (**PS-BBr**) with substituted thienyl groups (R = H, 3-hexyl, 5-hexyl), and final introduction of the 8-hydroxyquinolato moiety yields a series of new organoboron quinolate polymers in 67–83% isolated yield. The hexyl-substituted polymers are highly soluble and solution-processable yielding thin films that efficiently emit light at 513–514 nm upon excitation at 395 nm.

Introduction

Organoboron quinolates are an important class of compounds that have found widespread applications in the identification of chiral boron catalysts,¹ in trace metal analysis via fluorescent response,² and as fungicides, bacteriocides, and antibiotics.³ However, it is their luminescence that has recently attracted a great deal of interest. Aluminum quinolates (AlQ₃, Chart 1) and related derivatives were first reported by Tang and VanSlyke in 1987 to possess electroluminescent properties and are currently widely used as materials for emission and electron-conduction layers in organic light-emitting devices (OLEDs).⁴ The recent discovery by Wang and co-workers⁵ that certain organoboron quinolates such as Ph₂BQ show efficient luminescence while at the same time providing good stability revitalized research into boron quinolates and related species.^{6–8}

Boron and aluminum quinolates are currently applied in device fabrication via vacuum deposition techniques. Solution processing methods including ink-jet printing techniques, on the other hand, receive more and more attention as a potential low-cost alternative.⁹ Incorporation of the inorganic component into

Chart 1

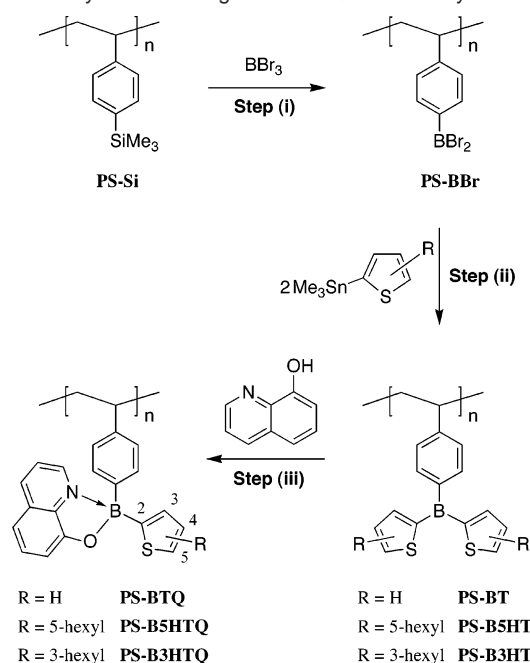


polymer structures may therefore provide new possibilities. However, only recently have the first reports on the synthesis of AlQ₃- and RAlQ₂-substituted polymers appeared in the literature,¹⁰ and boron quinolate polymers have to our knowledge not been described previously.

Several methods for the synthesis of organoboron quinolates are available. Most commonly used are the exchange of an alkoxy substituent OR' in diorganoalkoxyboranes R₂BOR' and the ester formation from organoboronic acids R₂BOH.¹¹ Alternatively, alcoholysis of a triorganoborane R₃B may be performed, upon which one of the organic substituents R is cleaved selectively by the 8-hydroxyquinoline (HQ) to yield the desired product R₂BQ.^{3a,5b} This approach is particularly useful when diorganoalkoxyboranes or organoboronic acids are not readily available, and we thus decided to apply it to the synthesis of organoboron quinolate polymers from organoboron polymers. We report here on the facile synthesis of the first organoboron quinolate polymers via a novel modular approach that will allow

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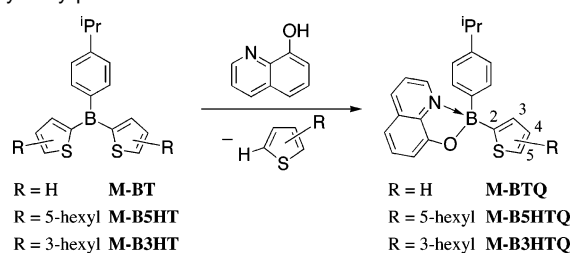
Scheme 1. Synthesis of Organoboron Quinolone Polymers

the fine-tuning of the polymer properties and emission characteristics through the substitution pattern on boron as well as the quinolate moiety.

Results and Discussion

We have recently reported a new method for the selective synthesis of the reactive polymer poly(4-dibromoborylstyrene) (**PS-BBr**) via treatment of poly(4-trimethylsilylstyrene) with boron tribromide in CH_2Cl_2 at ambient temperature.¹² The **PS-BBr** solution thus obtained was reacted in a second step in-situ with a slight excess of the organotin reagents 2-trimethylstannylthiophene, 2-trimethylstannyl-5-hexylthiophene, and 2-trimethylstannyl-3-hexylthiophene, respectively (Scheme 1).¹³ Highly selective transfer of the aryl groups to **PS-BBr** resulted in formation of the novel mixed-substituted triarylborane polymers **PS-BT**, **PS-B5HT**, and **PS-B3HT**, respectively. For characterization purposes, polymer **PS-BT** was isolated by repeated precipitation from dichloromethane into hexanes, and the selective formation of **PS-BT** was confirmed by ^1H , ^{13}C , and ^{11}B NMR spectroscopy and elemental analysis. However, the triarylboranes polymers are more conveniently used directly in the next step. Thus, isolation and purification of the highly soluble hexyl-substituted intermediates, the triarylborane polymers **PS-B5HT** and **PS-B3HT**, was not attempted. However, their formation was confirmed by multinuclear NMR spectroscopy.

The final step of the reaction sequence involves the alcoholysis of one of the B-aryl substituents with 8-hydroxyquinoline. This transformation must occur with high selectivity at the thienyl–boron rather than the phenyl–boron bond, because the boryl substituents would otherwise be cleaved from the polymer backbone. To study the selectivity of this reaction, we

Scheme 2. Reaction of Triarylborane Model Compounds with 8-Hydroxyquinoline

decided to use cumene derivatives as model compounds, which represent one monomer unit along the polystyrene backbone. Treatment of **M-BT** with 1 equiv of 8-hydroxyquinoline at room temperature in dichloromethane indeed led to highly selective formation of **M-BTQ** as a result of exclusive cleavage of the thienyl–boron bond (Scheme 2). Cumene would be expected to form upon cleavage of the phenyl group, but was neither detected by ^1H NMR spectroscopy nor by GC-MS analysis of the crude reaction mixture.

The triarylborane polymers were accordingly treated in-situ with 8-hydroxyquinoline to form the desired yellow-colored luminescent organoboron quinolate polymers **PS-BTQ**, **PS-B5HTQ**, and **PS-B3HTQ**, respectively (Scheme 1). Following purification by precipitation into hexanes and subsequently into methanol, the polymers were isolated as yellow solids in 78%, 83%, and 67% overall yield, respectively. While the unsubstituted parent polymer **PS-BTQ** exhibits low solubility, the *n*-hexyl-substituted derivatives **PS-B5HTQ** and **PS-B3HTQ** are readily soluble in typical organic solvents such as THF, toluene, chloroform, and dichloromethane. Further studies therefore focused on the hexyl-substituted polymers.

The chemical nature and the degree of functionalization of **PS-B5HTQ** and **PS-B3HTQ** were investigated by multinuclear NMR spectroscopy, static light-scattering measurements, and elemental analysis. A single resonance at $\delta = 5$ in the ^{11}B NMR spectra, which is in a region typical of tetracoordinate boron centers, confirms the binding of the quinolate moiety to boron. The ^1H NMR spectra feature very broad overlapping signals in the aromatic region and somewhat sharper resonances in the aliphatic region that are assigned to the pendant hexyl groups. The aromatic region of the ^{13}C NMR spectra is better resolved, and a comparison of the spectrum of **PS-B5HTQ** and the model compound **M-B5HTQ** is shown in Figure 1. The carbon resonances for the quinolate and thiophene groups are virtually unchanged in the polymer relative to those of the model compound. The signals for the phenyl group, on the other hand, are slightly shifted and strongly broadened due to the atactic nature of the polystyrene backbone. The absence of signals for unreacted triarylborane moieties in the NMR spectra suggests a high degree of functionalization (>95%).¹⁴ This is further confirmed by elemental analyses, which are in excellent agreement with the predicted data for complete functionalization.

A comparison of static light-scattering data derived from Zimm plots of **PS-B5HTQ**, **PS-B3HTQ**, and **PS-Si** shows that the average number of polymer repeat units (DP) for the quinolate polymers is essentially identical to that of the starting polymer (Table 1). Moreover, GPC-LS analyses reveal a low

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(13) Thiophene substituents were chosen, because selective and quantitative substitution of **PS-BBr₂** can easily be achieved, while the subsequent reaction with 8-hydroxyquinoline occurs selectively at the thienyl–boron bond rather than the phenyl–boron bond. Any other (hetero)aromatic group that satisfies these requirements may also be applied.

(14) A degree of functionalization >95% is also evident from the close similarity of the calculated absorption coefficients for the polymers and model compounds.

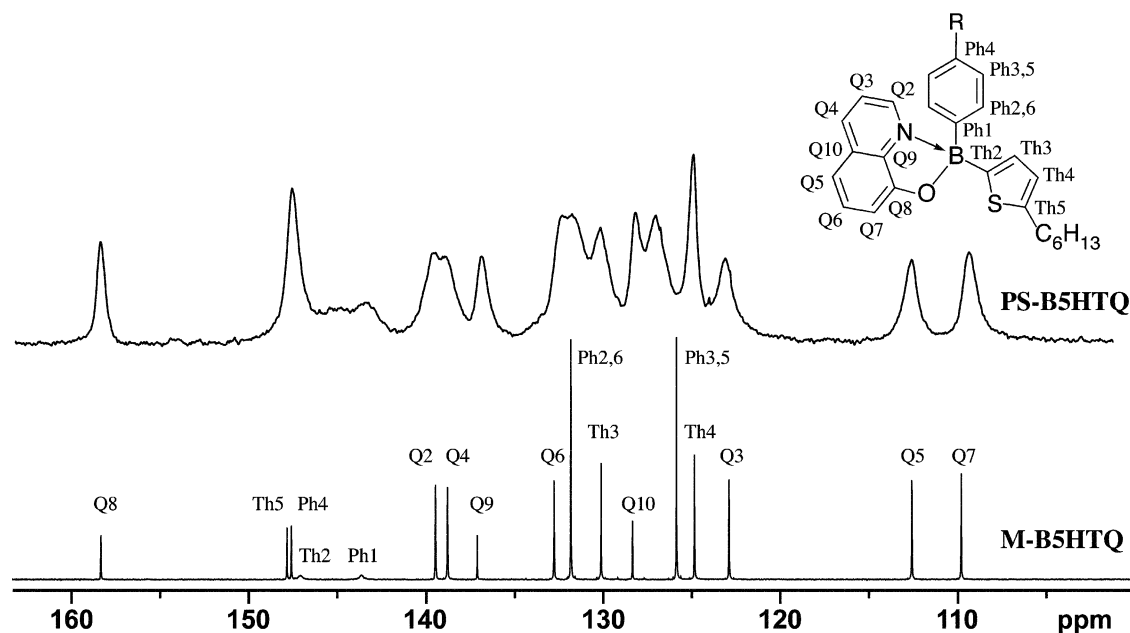


Figure 1. Aromatic region of the ^{13}C NMR spectra of PS-B5HTQ and M-B5HTQ.

Table 1. Comparison of GPC and Static Light-Scattering Data for PS-Si, PS-B5HTQ, and PS-B3HTQ

polymer ^a	dn/dc^b (mL/g)	M_w^c	DP^c	PDI^d
PS-Si	0.157	26 000	147	1.13
PS-B5HTQ	0.205	62 000	146	1.04
PS-B3HTQ	0.201	64 000	150	1.06

^a Measurements were performed in THF. ^b The differential refractive indices (dn/dc) were determined in THF at 35 °C. ^c The molecular weight average M_w and the average degree of polymerization (DP) were derived from Zimm plots. ^d The polydispersity index (PDI) was estimated from inline GPC-LS detection.

polydispersity of the quinolate polymers ($PDI = 1.04\text{--}1.06$).¹⁵ The three reaction steps, the borylation, the aryl transfer to boron, and the final alcoholysis with 8-hydroxyquinoline, thus occurred without cleavage of the backbone or significant cross-linking.

The thermal characteristics of the organoboron quinolate polymers were studied by differential scanning calorimetry (DSC), and their stability in the solid state and in solution was examined by NMR spectroscopy. While PS-BTQ exhibits a relatively high glass transition temperature of $T_g = 221$ °C, the hexyl-substituted derivatives PS-B5HTQ and PS-B3HTQ show a significantly lower T_g of ca. 146 °C (onset). In the solid state, all three polymers are perfectly stable for several months under nitrogen atmosphere and show less than 5% decomposition over a period of 1 week under air. Comparable stability was also found in aromatic solvents such as benzene or toluene.

The most exciting property of the new organoboron polymers certainly is their apparent strong luminescence observed in solution and in thin films. The optical properties of the polymers PS-B5HTQ and PS-B3HTQ were thus studied by absorption and emission spectroscopy. Both polymers form yellow solutions as a result of an absorption band at $\lambda = 392$ nm ($\epsilon = 2900$) and $\lambda = 394$ nm ($\epsilon = 3000$), respectively. Excitation at the absorption maxima gives rise to green fluorescence (Figure 2) with emission maxima of $\lambda = 508$ nm and $\lambda = 509$ nm and

(15) These experiments indicated that a significant amount of polymer was retained on the separation columns.

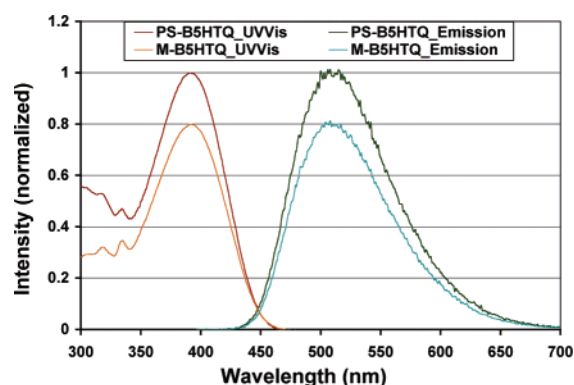


Figure 2. Absorption and emission spectra of PS-B5HTQ and M-B5HTQ in THF. The absorption and emission intensities of the polymer are normalized to 1.0, and those of the model compound are adjusted to 0.8.

Table 2. Photophysical Properties of Organoboron Quinolate Polymers and Model Compounds in Solution

compound ^a	λ_{\max} (nm)	ϵ ($\text{L mol}^{-1} \text{cm}^{-1}$)	λ_{exc} (nm)	λ_{em} (nm)	quantum yield
M-BTQ	391	2900	391	509	0.14
PS-BTQ	391	2650	391	509	0.12
M-B5HTQ	392	3000	392	509	0.14
PS-B5HTQ	392	2900	392	508	0.12
M-B3HTQ	394	3100	394	508	0.16
PS-B3HTQ	394	3000	394	509	0.14

^a Concentrations were ca. 3×10^{-5} M in THF. For the polymers, the concentration of the chromophore was estimated on the basis of the repeating units assuming 100% functionalization.

quantum yields of 0.12 and 0.14 for PS-B5HTQ and PS-B3HTQ, respectively. A comparison with cumene model compounds revealed nearly identical absorption and emission spectra and only slightly lower quantum yields for the polymeric materials relative to the molecular compounds (Table 2). The absence of a bathochromic shift suggests that there is no significant delocalization of the excited state along the polymer chain despite the high concentration of chromophores. Thin films of polymers PS-B5HTQ and PS-B3HTQ that were cast from toluene solution showed similar photophysical characteristics

with absorption bands at $\lambda = 395$ nm and $\lambda = 396$ nm and emission maxima at 513 and 514 nm for **PS-B5HTQ** and **PS-B3HTQ**, respectively. The slight bathochromic shift in both the absorption and the emission spectra of the films may tentatively be attributed to interchain interactions.¹⁶

Luminescence lifetime measurements were performed on THF solutions of **PS-B5HTQ** and the related model compound **M-B5HTQ** to further investigate the luminescent properties and to address the question whether the individual chromophores attached to the polymer chains indeed act independently. For both **PS-B5HTQ** and **M-B5HTQ**, a single exponential decay was observed (see Supporting Information). However, in the case of the polymer solution, a significantly shorter lifetime of 24–25 ns was observed in comparison to that of the molecular compound with 32–33 ns.¹⁷ This result is in agreement with the slightly lower quantum yield for the polymer **PS-B5HTQ** (0.12) relative to **M-B5HTQ** (0.14). Enhanced exciton diffusion to randomly distributed traps within the polymer chains is therefore likely to be responsible for the lower luminescence lifetime and quantum yield in the case of the polymer.

In summary, we have developed a novel modular synthetic route to the first luminescent organoboron quinolate polymers. The polymers **PS-B5HTQ** and **PS-B3HTQ** were obtained through a straightforward procedure starting from the silylated precursor **PS-Si**. Successive treatment of **PS-Si** with (i) BBr₃, (ii) a thienyltrimethyltin derivative, and (iii) 8-hydroxyquinoline provides a facile and high-yield route to organoboron quinolate polymers. Solutions and thin films of **PS-B5HTQ** and **PS-B3HTQ** show luminescent properties similar to those of the respective molecular model compounds with bright green

emission upon excitation at the wavelength for the absorption maximum λ_{max} . A markedly shorter luminescence lifetime for polymer **PS-B5HTQ** in comparison to the model compound **M-B5HTQ** in THF solution may be attributed to enhanced exciton diffusion to randomly distributed traps within the polymer chains. Our new approach is highly versatile because the polymer properties can readily be fine-tuned. Thus, we have shown that substitution of the pendant aryl rings with hexyl groups leads to enhanced polymer processability. Future work will focus on further improvement of the stability of the polymers and the fine-tuning of the emission characteristics through variation of the substitution pattern of the chelating ligand as was previously described for molecular boron and aluminum compounds.^{4b,6,8,18}

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

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