

## Regioregular Electroactive Polyolefins with Precisely Sequenced $\pi$ -Conjugated Chromophores

Jianguo Mei, Brian S. Aitken, Kenneth R. Graham, Kenneth B. Wagener,\* and John R. Reynolds\*

The George and Josephine Butler Polymer Research Laboratory,  
Department of Chemistry and Center for Macromolecular  
Science and Engineering, University of Florida, Gainesville,  
Florida 32611-7200

Received April 19, 2010

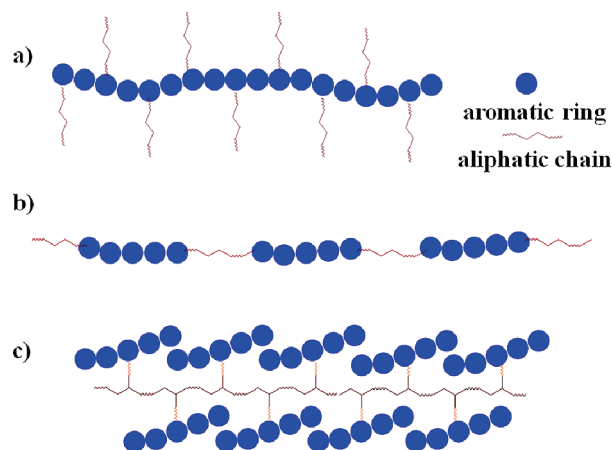
Revised Manuscript Received June 14, 2010

Polymeric  $\pi$ -conjugated materials have emerged as electroactive components in a wide range of organic optoelectronic devices.<sup>1–4</sup> On the basis of the location of conjugated segments, these polymers can be classified into three categories: conjugated polymers as well as main-chain and side-chain  $\pi$ -electron functional polymers. In a conjugated polymer, as shown in Figure 1a,  $\pi$ -electrons are delocalized along the backbone and not confined to individual repeat units or chromophores, therefore, its optical and electronic properties are significantly different from those of the monomers from which it was made. A variety of polymerization methods have been applied to prepare conjugated polymers, including Grignard metathesis,<sup>5,6</sup> oxidation polymerization,<sup>7,8</sup> the Gilch reaction,<sup>9</sup> and various cross-coupling reactions (Stille, Suzuki, Yamamoto, Hiyama, Negishi, Heck, Sonogashira, etc.).<sup>10–16</sup> As electroactive materials in the field of organic electronics, conjugated polymers have garnered the most attention and success to date. For example, power conversion efficiencies of organic solar cells based on these materials have reached over 6%.<sup>17,18</sup>

Main chain  $\pi$ -electron functional polymers consist of well-defined conjugated building blocks connected by electrically insulating flexible aliphatic or oligoether chains, as shown in Figure 1b. In contrast to conjugated polymers,  $\pi$ -electrons are localized on the conjugated segments of these materials. Furthermore, the alternating rigid-flexible arrangement often imparts liquid crystallinity to these copolymers.<sup>19</sup> They can be obtained either by step-growth polycondensations to form ester, ether, amide linkages or C–C bonds<sup>20–26</sup> or by cross-coupling reactions of flexible monomers terminated with aromatic rings.<sup>27,28</sup>

Side-chain  $\pi$ -electron functional polymers, as their name implies, contain  $\pi$ -electron functional moieties pendant to an electrically insulating backbone, (see Figure 1c). These polymers may be regarded as reversed conjugated polymers, where the aliphatic backbone serves to provide solubility and mechanical flexibility, with pendant electroactive components.<sup>29–32</sup> Here, we report on  $\pi$ -electron functionalized materials containing linear hydrocarbon backbones, thus they may be appropriately named electroactive polyolefins, in contrast with the conventional role of polyolefins as insulators.

Interest in electroactive polyolefins lies primarily in two aspects. First, they effectively combine electronic and optical properties (high quantum efficiencies, narrow and well-resolved emission bands, etc.) of molecular species with the solution processability and capability to form thin-films inherent to polymers. Second, various functional units separated by insulating spacers can be incorporated into a single polymer chain to serve their purposes



**Figure 1.** Three types of polymeric  $\pi$ -conjugated materials: (a) conjugated polymers, (b) main-chain  $\pi$ -electron functional polymers, and (c) side-chain  $\pi$ -electron functional polymers.

cooperatively.<sup>33,34</sup> Electroactive polyolefins have previously been obtained by radical initiated polymerization of styrene or acrylate monomers bearing the desired functional moieties.<sup>31,32,35,36</sup> Hirao and Chen et al. have recently reported living anionic polymerization of styrene monomers *para*-substituted with  $\pi$ -conjugated oligo(fluorene) derivatives. In addition, postfunctionalization of precursor polymers (e.g., bromo- or borylated polystyrenes, etc.) provides an alternative route to electroactive polymers of this type.<sup>37–43</sup> Jäkle et al. have demonstrated such an approach to a great extent using borylated polystyrenes.<sup>39–41,43</sup> Synthesis of electroactive polyolefins with more than one methylene spacer between adjacent  $\pi$ -conjugated chromophores, however, is currently undeveloped as compared to the aforementioned polymer architectures. Indeed, methods to access this class of electroactive polyolefins are rather limited. Ring-opening metathesis polymerization (ROMP) of cyclopentene-based or norbornylogous monomers is one of the few or perhaps the only known pathway to this type of electroactive polyolefin, with presumably four or five carbon spacers between each electroactive unit, respectively.<sup>29,44–50</sup> A wide range of electroactive polyolefins based on ROMP have been prepared and applied for a set of applications such as nanolithography, hole-transporting materials, organic light emitting diodes and electrochromic devices, as demonstrated by Marder, Sotzing, and others.<sup>46,47,49,50</sup> However, strictly speaking, when there is only one substitution on norbornene, cyclopentene or another cyclic monomer, as is most often practiced, the resultant electroactive polymer obtained by ROMP is generally not regioregular. As a matter of fact, polymerization of 2-substituted-5-norbornene monomers, which are overwhelmingly the most common, can occur in a head-to-head or head-to-tail fashion, resulting in a material containing a statistical mixture of 4, 5, or 6 carbon atoms between each chromophore.

The use of acyclic diene metathesis (ADMET) to create perfectly regioregular polyethylenes with precisely placed hydrophobic, hydrophilic, or ionic branches has been extensively researched by the Wagener group.<sup>51–53</sup> In this communication, we extend this area of research by preparing polymers containing borylated-fluorene moieties precisely placed along a polyolefin backbone, followed by Suzuki cross-coupling with aryl bromides, to produce fluorene-based regioregular electroactive polyolefins. To the best of our knowledge, these regioregular electroactive

\*Corresponding authors. E-mail: (K.B.W.) wagener@chem.ufl.edu; (J.R.R.) reynolds@chem.ufl.edu.

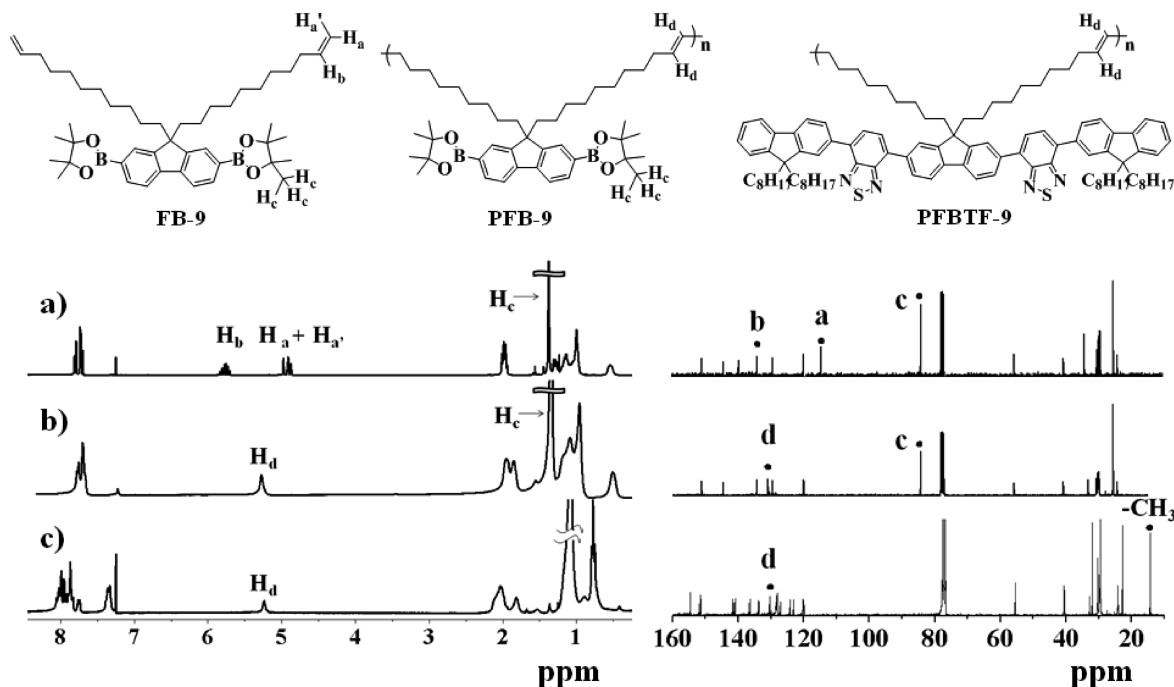
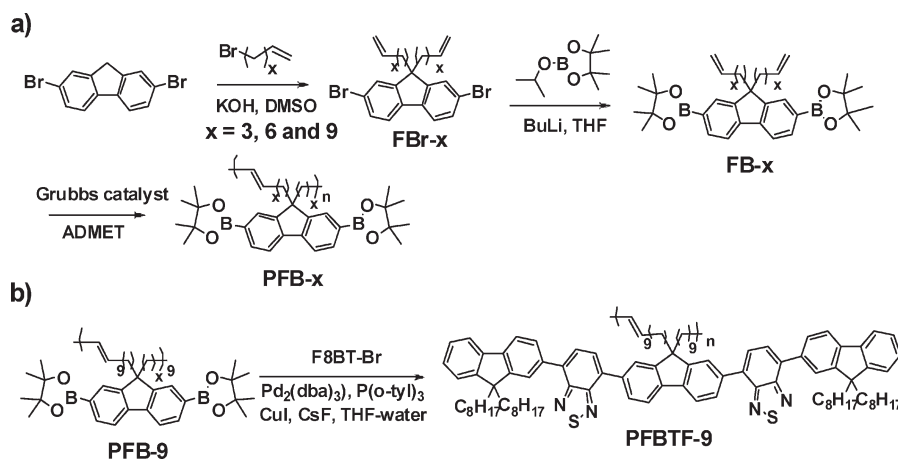


Figure 2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of (a) **FB-9**, (b) **PFB-9**, and (c) **PFBTF-9**.

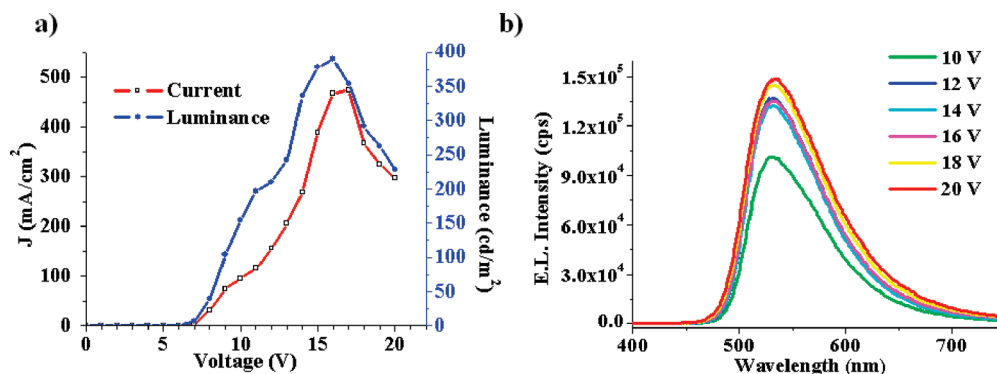
Scheme 1. Synthesis of (a) Borylated Polyolefins via ADMET and (b) a Green Light-Emitting Regioregular Polyolefin by Post-Functionalization through the Suzuki–Miyaura Reaction



polyolefins are the first of their kind. Owing to the precisely controllable spacing of electroactive moieties along their polyolefin backbones, these materials are not only of potential importance for the study of fundamental structure–property relationships (e.g., energy and charge transfer among adjacent electroactive sites), but are also of particular interest as active materials in optoelectronic devices. Indeed, fluorene-based oligomers and polymers have shown good performance in blue, green, red, and white organic light-emitting diodes.<sup>54–57</sup>

The synthesis of fluorene-based borylated polyolefins and the green light-emitting regioregular polyolefin **PFBTF-9** is illustrated in Scheme 1a. Starting from commercially available 2,7-dibromo-9H-fluorene, two olefinic arms were installed through simple alkylation using potassium hydroxide as a base in dimethyl sulfoxide (DMSO) at 60 °C to give compounds **FBr-x** ( $x = 3, 6$ , and  $9$ ) in excellent yields. Monomer **FB-x** can be easily obtained via lithiation and borylation of **FBr-x** in a one-pot reaction in THF. Because of their relatively high melting points, these monomers are not suitable for bulk polymerization as is most often practiced for ADMET. Instead, polymerizations were

performed in 1,2-dichlorobenzene (bp, 180.5 °C) under dynamic vacuum using argon as the makeup gas (see the Supporting Information). Polymerization of monomer **FB-9**, as a 50 wt % solution in 1,2-dichlorobenzene proceeded smoothly with Grubbs' first-generation catalyst at 45 °C, yielding unsaturated polymer **PFB-9**. Figures 2a and 2b show the  $^1\text{H}$  and  $^{13}\text{C}$  NMR of **FB-9** and **PFB-9**, respectively. In the  $^1\text{H}$  NMR of **FB-9**, the characteristic signals from the terminal alkenes are well resolved into  $\text{H}_b$  (5.82–5.65 ppm) and  $\text{H}_a/\text{H}_a'$  (4.98–4.85 ppm) with the expected 1:2 integration ratio; these are accompanied by signals at 133.9 (b) and 114.2 ppm (a) in the  $^{13}\text{C}$  NMR. The methyl groups on the pinacolboron ester yield an intense signal at 1.38 ppm ( $\text{H}_c$ ) in  $^1\text{H}$  NMR and 83.9 ppm (c) in  $^{13}\text{C}$  NMR, as shown in Figure 2a. After polymerization, there are no detectable terminal alkene signals and a new internal alkene signal,  $\text{H}_d$  (5.17–5.42 ppm) appears (see Figure 2b), thus indicating high polymerization conversion. A similar analysis can be carried out for the  $^{13}\text{C}$  NMR spectra shown in Figure 2, parts a and b. We are also pleased to find that the boronic ester groups are unaffected by the polymerization conditions, as the integral of internal



**Figure 3.** (a) Current density and luminance as a function of driving voltage for a **PFBTF-9** PLED pixel. (b) Electroluminescence spectra of **PFBTF-9** PLED at varying driving voltages.

olefinic protons ( $H_d$ ) in **PFB-9** is about 1:12 relative to that of the methyl groups ( $H_c$ ) on the pinacolatoboron esters and the signal at 83.9 ppm (c) in the  $^{13}\text{C}$  NMR remains intact. The number-average molecular weight ( $M_n$ ) of **PFB-9**, from gel permeation chromatography (GPC, using polystyrene standards for calibration), is  $\sim 39$  kDa, with a polydispersity index (PDI) of 1.8; this roughly corresponds to 50–55 repeat units. By following a similar polymerization protocol, **PFB-6** and **PFB-3** were prepared with  $M_n$  of 30 and 11 kDa, and PDI of 2.0 and 1.4, respectively. The lower molecular weight for **PFB-3** is likely due to its reduced solubility, which results in precipitation during polymerization, however, owing to its lighter repeat unit, its number-average degree of polymerization is only slightly lower (approximately 40).

To investigate the possibility of introducing  $\pi$ -conjugated chromophores through Suzuki–Miyaura cross-coupling, 4-bromo-7-(9,9-dioctyl-9H-fluorene-2-yl)benzo[c][1,2,5]thiadiazole (**F8BT-Br**) was chosen as an aryl halide source, as its corresponding oligomers and polymers have been well-documented as electroactive materials in organic light-emitting diodes and photovoltaic devices. An unexpected event, however, was encountered in postfunctionalization of **PFB-9** when classical Suzuki catalytic systems were used (such as  $\text{Pd}_2(\text{dba})_3$ , tri-*o*-tolylphosphine,  $\text{K}_2\text{CO}_3/\text{NaOH}/\text{Et}_4\text{NOH}$ , water and toluene); the polymer solution gelled shortly after addition of the base. As it is known that polymeric ionic species (ionomers) are poorly soluble in nonpolar organic solvents such as toluene, we suspected that the aforementioned gel was the result of an ionomer formed by activation of the pinacolboronate ester in basic media, a prerequisite step for the Suzuki reaction. Interestingly, this problem was not observed in the course of postfunctionalization of borylated polysulfones or polystyrenes.<sup>37,38</sup> Low contents of pinacolboronate ester groups in such polymers may account for this difference. Nevertheless, we were pleased to find that the use of cesium fluoride as an activator overcame the precipitation problem and the addition of copper iodide facilitated the overall transformation.<sup>58</sup> Compared to aqueous hydroxide base, activation of the boronic ester by fluoride ion is much slower, while copper iodide is believed to speed up the transmetalation step. The net result is that accumulation of ionic species during the reaction does not occur, hence the lack of precipitation.

NMR analysis of **PFBTF-9** from the Suzuki–Miyaura reaction revealed that the signal from the methyl groups on the pinacolboronate ester moieties (1.38 ppm ( $H_c$ ) in  $^1\text{H}$  NMR and 83.9 ppm (c) in  $^{13}\text{C}$  NMR) almost completely disappeared, and a new set of signals in the aromatic region from fluorene–benzothiadiazole appeared with proper integrations relative to other protons. Further evidence of successful coupling is the appearance of terminal methylic carbons from the octyl solubilizing groups (14.4 ppm) in  $^{13}\text{C}$  NMR, as shown in Figure 2c. In addition, IR spectra collected both before and after functionalization

of **PFB-9** are rather complicated, however, it is clear that the B–O stretching frequencies present in the borylated polymer are completely diminished in **PFBTF-9** polymers; thus also indicating a clean Suzuki–Miyaura reaction. Finally, the high conversion yields ( $>95\%$  based on isolated mass) also indirectly support the nearly complete transformation of boronic ester functional groups. After optimization and Soxhlet purification of the final product polymer, we determined that the resultant material had a number-average molecular weight ( $M_n$ ) of 56 kDa with a PDI of 1.6.

Solution and solid-state UV–vis absorption and fluorescence emission measurements of **PFBTF-9** were carried out. **PFBTF-9** shows a two-band absorption with maxima at 321 and 437 nm in chlorobenzene, as shown in Figure S1 (see the Supporting Information). A broadening and red-shift of the second band can be observed upon film formation, which leads to an absorption maximum at 445 nm in the pristine film. This trend is similar to the broadening in **F8BT** [poly(9,9'-dioctylfluorene-*alt*-benzothiadiazole)].<sup>59</sup> Interestingly, the spectral broadening and red-shift were much less pronounced in the photoluminescence spectra. Only minor broadening and almost no red-shift in emission were observed, with emission maxima at 541 nm in solution and 543 nm in the solid state. This is in sharp contrast with **F8BT** in which a large red-shift in emission exists between solution (538 nm) and the pristine film (550 and 580 nm).<sup>59</sup> These differences conceivably result from the different interchain interactions in **PFBTF-9** and **F8BT**. In conjugated polymers, interchain interactions are usually enhanced on moving from solution to the solid state, leading to aggregates in the ground state and excimers in excited states, hence long-lived emission and a red shift is observed.<sup>60,61</sup> At this point, we are not able to explain the absence of these photophysical phenomena, thus, further studies on the nature and mechanism of emission in **PFBTF-9** are needed.

To test whether **PFBTF-9** is able to operate as the active material in solid state electronic devices, polymer light-emitting diodes (PLEDs) were fabricated using a simple sandwich configuration of ITO/PEDOT:PSS/**PFBTF-9**/LiF/Ca/Al. The devices displayed bright green emission with a maximum radiant emittance of  $145 \mu\text{W}/\text{cm}^2$  at relatively high currents ( $750 \text{ mA}/\text{cm}^2$ ). The luminance of the **PFBTF-9** device and its electroluminescent spectra at varying driving voltages are displayed in Figure 3a. The spectra in Figure 3b indicate that the device shows stable emission with no red or blue shift as the drive voltage is increased; an important fact for their practical applications. The minimally optimized **PFBTF-9** based device shows a turn on voltage of 7 V with a maximum luminance of approximately  $400 \text{ cd}/\text{m}^2$  and a luminous efficiency of  $0.15 \text{ cd}/\text{A}$ . It should be mentioned that the conjugated polymer **F8BT** PLED, as a control experiment in our hands, has a maximum luminance of  $\sim 5000 \text{ cd}/\text{m}^2$  and a



luminous efficiency of 1.0 cd/A. We are intrigued to further explore this difference, and in particular the relationship between structure (spacer length) and property (device performance).

Having confirmed **PFBTF-9** as an electroactive material, we were encouraged to prepare blue, red, and white light-emitting fluorene-based regioregular electroactive polyolefins (structures shown in Figure S2 in Supporting Information). Under the same Suzuki coupling reaction conditions, a vibrant blue light-emitting polyolefin (**PFFF-9**) was prepared by reacting **PFB-9** with blue chromophore 2-bromo-9,9-dioctyl-9H-fluorene, yielding a number-average molecular weight ( $M_n$ ) of 51 kDa and a polydispersity index (PDI) of 1.6. Attempts to prepare red-emitting polymer (**PFTBTFF-9**) were complicated by its relatively poor solubility. Full conversion of **PFB-9** was not achieved, as suggested by  $^1\text{H}$  NMR of the resulting precipitates (about 50% conversion). This is not completely surprising, as the corresponding conjugated polymer also exhibits reduced solubility. We are currently exploring the possibility of using an alternative red chromophore to overcome this solubility issue.

Single-component white light-emitting polymers have recently drawn a great deal of attention as active emitting materials for PLEDs.<sup>32,34,62–64</sup> Toward this end, we have been able to prepare a white light photoluminescent polyolefin using an optimized mole feed ratio (99.5:0.4:0.1) of the aforementioned blue, green, and red chromophores by applying a one-pot postfunctionalization strategy. Efficient energy transfer processes from the blue emitting chromophore to those at lower energies allow for only small amounts of the green, and red components to be included. The molecular weight ( $M_n$ ) and polydispersity index (PDI) of the resulting polymer are 51 kDa and 1.7 respectively.<sup>65</sup> Under UV illumination at 365 nm, the four fluorene-based polyolefins in solution emit vivid blue, green, red, and white light, as shown in Figure S2 (see the Supporting Information). It is important to note that the regioregularity refers only to the placement of chromophores equally spaced along the polymer chain. In the white light emitting copolymer, the various chromophores are randomly incorporated relative to one another.

In summary, we have demonstrated a new protocol for the preparation of regioregular electroactive polyolefins. Blue, green, red, and white light-emitting polymers can be prepared from a single borylated precursor polymer. Since both ADMET and Suzuki coupling chemistries are highly functional group tolerant, this method can be considered as a generic approach to various regioregular electroactive polyolefins. Demonstration of the ability to fabricate PLEDs from these electroactive materials indicates their potential usefulness in other types of organic electronic devices, such as solar cells and field effect transistors. Current efforts are underway to prepare variable spacer-length structurally precise fluorene-based electroactive polyolefins and to illustrate spacer-length effects in energy/charge transfer, crystallization behaviors, and their performance in solid state devices.

**Acknowledgment.** We are grateful to AFSOR (FA9550-09-1-0320) for financial support.

**Supporting Information Available:** Text giving synthetic details, characterization, and device fabrication; figures showing normalized UV–vis absorption and photoluminescence spectra of **PFBTF-9**; chemical structures of blue, green, red and white-light emitting polymers; chloroform solutions of the aforementioned materials under UV illumination. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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