“$AB_2 + AB$” Approach to Hyperbranched Polymers Used as Polymer Blue Light Emitting Materials

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Received November 20, 2003
Revised Manuscript Received February 3, 2004

Introduction. Because of their potential applications in large-area flat-panel displays, polymer light emitting materials have received remarkable scientific and industrial attention.[1] Three primary colors, i.e., blue, green, and red emitting materials, are essential for full-color displays. Green and red light emitting materials have been already achieved with high brightness and efficiency. However, as yet, no example of blue light emitting polymers fully meets requirements for commercially feasible light emitting diodes.[2] A challenging goal in this area is to achieve blue light emitting materials with long-term stability, high efficiency, and free of blue-green emission. Highly soluble poly(2,7-(9,9-dialkyl)fluorene)s (PFs) and their copolymers are considered as very promising blue light emitting materials because of their excellent chemical and thermal stabilities and exceptionally high solid-state quantum yields not reached with other conjugated polymers.[3] Problems encountered with these rodlike PFs and their copolymers are their tendency to aggregate. Formation of excimers in the solid state leads to blue-green emission and fluorescence quenching.[4] Some attempts were done to avoid this detrimental excimer emission, for example, the use of longer and branched side chains or bulky groups,[4e,5] the copolymerization of 9,9-dialkyl-2,7-dibromofluorene with appropriate comonomers,[6] the end-capping of PFs with bulky groups,[7] the cross-linking of PFs,[8] and the encapsulation of polyfluorene backbones into dendritic envelopes.[9]

Recently dendrimers[10] and hyperbranched polymers[11] have received considerable attention due to their unusual molecular structures and properties. There are two types of dendrimers reported as light emitting materials.[12] One is dendrimers with conjugated skeletons; the other is chromophore(s) embedded in the dendritic architectures, e.g., in the core, branching units, and/or periphery. Highly branched and globular features improve the light emitting efficiencies and also make the materials form good quality amorphous films.[12f] Comparing with the large number of publications on light emitting dendrimers, hyperbranched polymers as light emitting materials are limited.[13] The concept in our work is to introduce branching units into the PFs to make the polymers of a hyperbranched structure, which helps to depress the aggregation and excimer formation.

In this paper we described the synthesis and properties investigation of a new family of hyperbranched fluorene copolymers. A novel “$AB_2 + AB$” approach based on Suzuki polycondensation (SPC) was developed for the polymer synthesis. The obtained hyperbranched polymer **P40** exhibited very good luminescent stabilities and did not show any green-blue emission even after annealing at 200 °C for 30 min in air. To the best of our knowledge, this is the first example of hyperbranched polymers used as blue light emitting materials.

Results and Discussion. a. Polymer Synthesis and Characterization. The hyperbranched polymers were obtained from Suzuki polycondensation (SPC) of **1** and **2** (Scheme 1).[14] Two monomers 7-bromo-9,9-dioctylfluorene-2-boronic acid (**1**)[15] and 3,5-dibromobenzeneboronic acid (**2**)[16] were synthesized according to literature procedures. Originally Muellen and Kim used them for preparation of luminescent rod−coil block copolymers and hyperbranched polyphenylenes, respectively. The polymerizations were done under different feed ratios between **1** and **2** in toluene with freshly prepared $Pd(PPh_3)_4$ (0.7 mol %) as catalyst precursor.[17] Because random hyperbranched polymer synthesized by one-pot SPC has a large number of bromo end groups that are detrimental for light emitting applications, monofunctional monomer 9,9-dioctylfluorene-2-boronic acid (**3**) was therefore used to cap the end groups. The reaction mixture was stirred and refluxed for 7 days at the first stage of polymerization. Compound **3** was then added to the reaction mixture together with additional $Pd(PPh_3)_4$ (0.7 mol %). The reaction was continued for a further 3 days. Three polymers **P5**, **P15**, and **P40** were obtained by taking **1** and **2** in molar ratios of 100:5, 100:15, and 100:40, respectively. Standard workup afforded slightly yellowish amorphous materials. All polymers are soluble in common organic solvents, e.g., toluene, THF, chloroform, and methylene chloride. The molecular structure of the polymers was characterized with high-resolution NMR spectroscopy and elemental analysis (see Supporting Information). In the proton NMR spectra, the characteristic signals of the branching units and fluorene units were observed at around $\delta = 7.35$ and 7.80 ppm, respectively. In comparison with polymers **P5**, **P15**, and **P40**'s spectra, it was found that the integration of the signals of the branching units increased with more amount of monomer **2** added. This indicates that the content of branching units increased. For polymer **P40**, the amount of branching units is approximately 27%. The average molecular weights were determined by gel permeation chromatography (GPC) against polystyrene standard. The molecular weight values were merely estimates due to the differences in hydrodynamic radius between the hyperbranched polymers and the polystyrene standard. The maximum apparent weight-average molecular weights (M_w) for **P5**, **P15**, and **P40** were found to be 40, 128, and 114 kg/mol, respectively. The thermal properties of the hyperbranched polymers **P5**, **P15**, and **P40** were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All these polymers **P5**, **P15**, and **P40** exhibit good thermal stabilities. They show less than 5% decomposition up to 400 °C under nitrogen but lose about 50% of their weights at about 450 °C. No distinct glass transitions were observed for all polymers **P5**, **P15**, and **P40** in their DSC curves of the second heating (10 °C/min).

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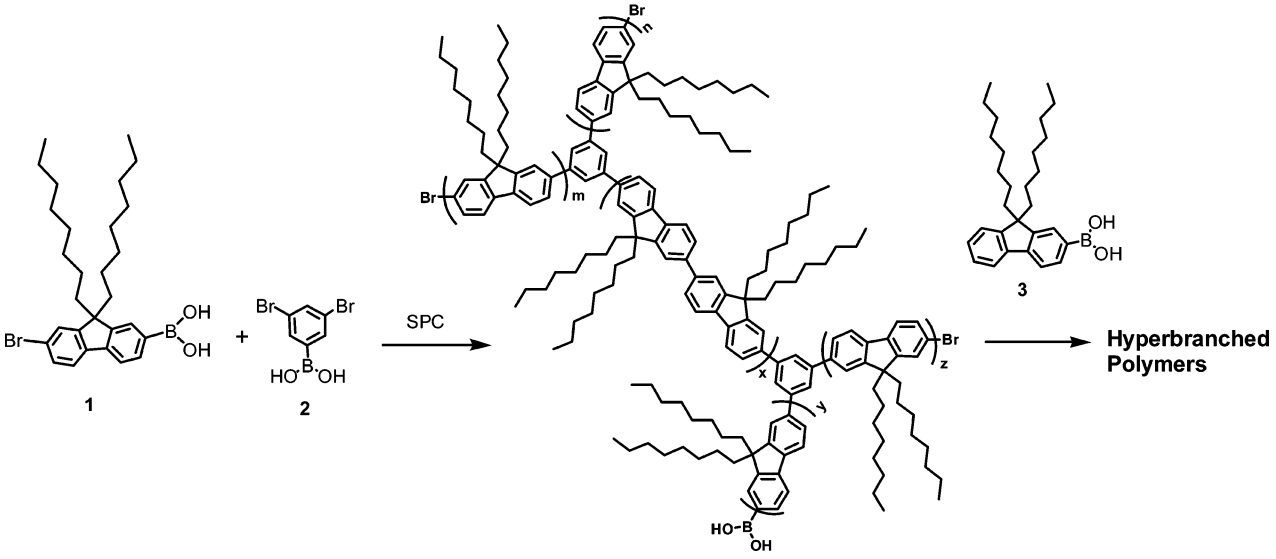
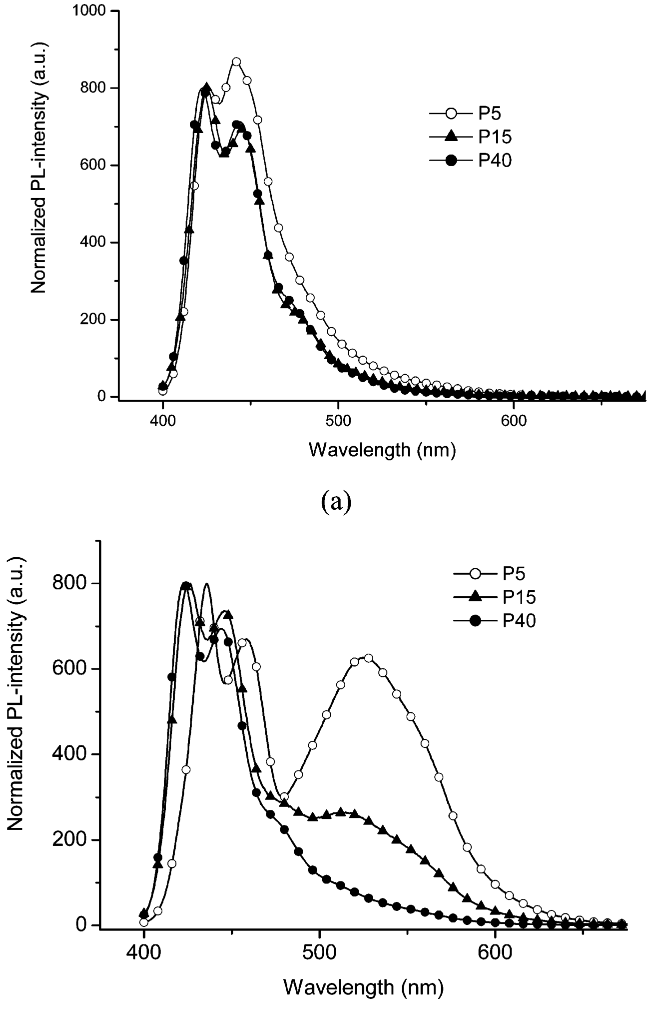
10.1021/ma0357422 CCC: $27.50

Scheme 1



b. Optical Properties. In the absorption and photoluminescent (PL) spectra of **P5**, **P15**, and **P40** in dilute toluene solution, the absorption maxima are blue-shifted with the increasing content of 1,3,5-substituted benzene rings. This indicates that the introduction of branching units interrupts the linear π-system to some extent. Comparing with the absorption spectra of monodisperse oligofluorenes reported in the literature,[18] the average conjugated length between two branching units of the hyperbranched polymers can be estimated. The average conjugated lengths (numbers of fluorene units between two branching units) for **P5**, **P15**, and **P40** are 8, 6, and 4, respectively. These results are roughly consistent with the feed ratios of monomers in the polymerization. In toluene solution, the PL spectrum of **P5** is almost identical to that of PFs with an emission maximum at 440 nm. **P15** and **P40** exhibit two emission peaks at 420 and 440 nm. The PL quantum yields (Φ_F) of samples **P5**, **P15**, and **P40** in toluene were measured with 9,10-diphenylanthracene as a reference standard (cyclohexane solution, $\Phi_F = 0.9$).[19] The highest quantum efficient yield reaches 0.65, which is smaller than that of poly(2,7-(9,9-dioctyl)-fluorene)s ($\Phi_F = 0.78$).

Solid films on quartz plates used for UV–vis, fluorescence, and polarized light microscope characterization were prepared by spin-coating with 1% toluene solution at 1500 rpm. After thermal treatment of the solid films at 200 °C for 30 min in air, a weak long wavelength absorption tail appeared at 450 nm in the absorption spectrum of **P5** film. This long wavelength tail became smaller with the increasing content of branching units. It cannot be observed in the spectrum of annealed **P40** film. The PL spectra of pristine **P5**, **P15**, and **P40** films are shown in Figure 1a. All polymers emit blue light; no green-blue emission can be detected. The PL spectrum of annealed **P5** film exhibits a new band at around 525 nm, which is typical for linear PF films after annealing (Figure 1b). This low-energy long wavelength emission band in green-blue region might be due to the aggregation and formed excimers of polymer chains. In the case of **P40** film, the thermal treatment did not make any effect on the PL spectrum. No green-blue band emission was observed even after the film was annealed at 200 °C for 30 min in air. This result indicated that hyperbranched structure could prevent the aggregation and crystallization of the rigid polymer chains. Formation of good quality amorphous films for **P40** was also confirmed by polarized light micrography.



(a)

(b)

Figure 1. Photoluminescent spectra of **P5**, **P15**, and **P40** solid films: (a) before annealing; (b) after annealing at 200 °C for 30 min in air.

In conclusion, an "$AB_2 + AB$" approach was developed to synthesize conjugated hyperbranched polymers, which can be used as highly efficient blue light emitting materials. The hyperbranched polymers synthesized via one-pot SPC are of high molecular weights and good solubilities in common organic solvents. **P40** film exhibited very good luminescent stabilities; blue-green emission band was completely suppressed in its annealed film.

Acknowledgment. Financial support from The Chinese Academy of Sciences (Hundred Talents Program), the National Natural Science Foundation of China (the Outstanding Youth Fund No. 20225415), and the Major State Basic Research Development Program (No. 2002CB613401) is greatly acknowledged.

Supporting Information Available: Detailed experimental procedures, characterization of all compounds, and their spectra. This material is available free of charge via Internet at http://pubs.acs.org.

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MA0357422