

Synthesis and Properties of Partially Conjugated Hyperbranched Light-Emitting Polymers

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Received 17 December 2008; accepted 2 March 2009

DOI 10.1002/app.30359

Published online 22 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Via $A_2 + B_4$ and $A_2 + B_3$ [where A_2 is 1,4-distyrylol-2,5-butoxybenzene, B_3 is 1,1,1-*tris*-(*p*-tosyloxymethyl)-propane, and B_4 is pentaerythritol tetra(methyl benzene sulfonate)] approaches, we synthesized two kinds of partially conjugated hyperbranched polymers, hyperbranched polymer with 3 arms (HP1) and hyperbranched polymer with 4 arms (HP2), which had rigid conjugated segments [oligo-poly(phenylene vinylene)] and flexible, nonconjugated spacers arranged alternately through ether bonds in the skeleton. The conjugated segments were modified by pendant butoxy groups, which imparted the resulting polymers with excellent solubility in common organic solvents and excellent film-forming abilities. Fourier transform infrared and nuclear magnetic resonance spectroscopy were used to identify the structure of the monomers and polymers. Thermal property investigations showed that two poly-

mers both had good thermal stability with their decomposition temperatures in the range 396–405°C and high glass-transition temperatures, which are of benefit to the fabrication of high-performance light-emitting devices. The photophysical properties were studied, and the relative photoluminescence quantum efficiencies of HP1 and HP2 in dilute chloroform solution amounted to 56.8 and 49.3%, respectively. A brief light-emitting diode device with a configuration of indium tin oxide/HP1/Ca/Al was fabricated, and its electroluminescence performance was studied. The brightness of the device reached an optimistic maximum of 190 cd/m² at 8.2 V. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 517–523, 2010

Key words: hyperbranched; light-emitting diodes (LED); luminescence

INTRODUCTION

Since the first poly(*p*-phenylenevinylene) (PPV) was reported by the Cambridge group in 1990,¹ the synthesis and application of polymer light-emitting diodes (LEDs) of PPV derivatives have attracted more attention because of their easily adjustable structures, good processability and film-forming properties, thermal stability, and high luminescence efficiency.^{2,3}

Hyperbranched polymers have been used as electroluminescent materials because they have some beneficial properties, including low intermolecular interaction and good stability and solubility.^{4–7} However, their solubility and film-forming processability are still poor. In addition, strictly speaking, fully conjugated polymers are planar instead of three-dimensional structures, which are prone to self-aggregation

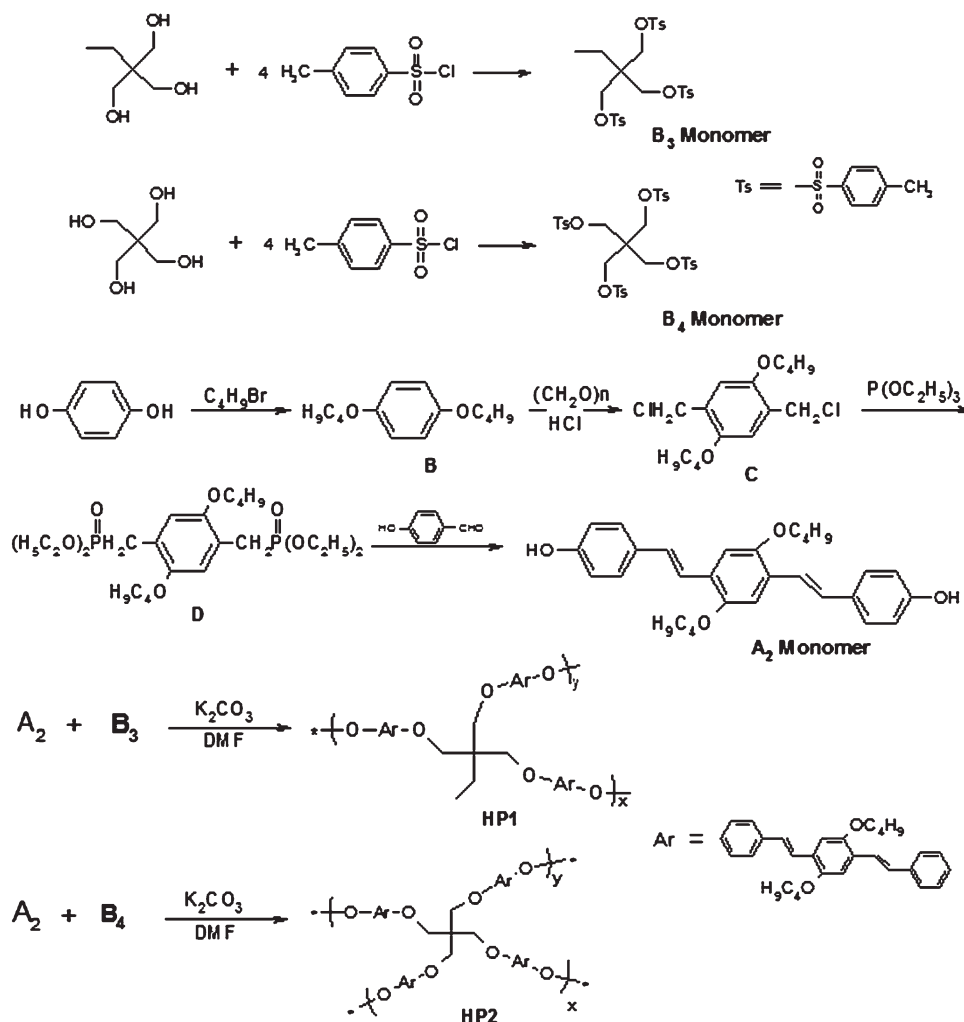
in the solid state and subsequently induce the generation of excimers and the quenching of electroluminescence.⁸ To overcome the problems mentioned previously, our group recently designed and synthesized some novel partially conjugated polymers and partially conjugated hyperbranched polymers.^{9–11} The interruption of the regular π -conjugated system was used to tailor the chromophore conjugation length, tune the emission spectra, and prevent the redshift of emission associated with the increase in conjugated length. Although the hyperbranched structure can greatly enhance the solubility of conjugated polymers, we found that the solubilities of either the fully conjugated hyperbranched light-emitting polymers or the partially conjugated hyperbranched ones without long flexible side chains attached to the conjugated fluorescent backbones were not good enough, and their film-forming abilities were limited somewhat accordingly, which resulted in unsatisfactory performance in the electroluminescent devices.¹²

In this study, we synthesized two kinds of partially conjugated hyperbranched polymers, HP1 and HP2, with genuine three-dimensional structures via $A_2 + B_3$ and $A_2 + B_4$ [where A_2 is 1,4-distyrylol-2,5-butoxybenzene, B_3 is 1,1,1-*tris*-(*p*-tosyloxymethyl)-propane, and B_4 is pentaerythritol tetra(methyl

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Contract grant sponsor: Natural Science Foundation of Beijing; contract grant number: 2062018.

Contract grant sponsor: Program of Introducing Talents of Discipline to Universities; contract grant number: B08003.



Scheme 1 Synthesis routes for the monomers and polymers.

benzene sulfonate)] approaches. In these two polymers, rigid conjugated segments, oligo-poly(phenylene vinylene) (oligo-PPV), and flexible nonconjugated spacers were arranged alternately through ether bonds in the skeleton. A three-dimensional structure in polymers can prevent the π - π^* stacking of chromophores and, thus, decrease the generation of excimers and the quenching of electroluminescence. To impart polymers with sufficient solubility in common organic solvents and better film-forming processability, two butoxy groups were introduced into the central benzene ring of oligo-PPV segments. The photophysical properties, the electrochemical properties of the polymers, and the performance of the relative LED devices were studied.

EXPERIMENTAL

Materials

Dimethylformamide (DMF) was used before anhydrous treatment. All other chemicals were reagent

grade and were used as purchased without further purification. All reactions were performed under a dry nitrogen atmosphere.

The synthesis routes for the monomers and HP1 and HP2 polymers are shown in Scheme 1.

Synthesis of monomer **B₃**

Monomer **B₃** was synthesized according to ref. 7.

¹H-NMR (CDCl₃, δ , ppm): 7.70–7.71 (d, 6H, Ar–H), 7.35–7.36 (d, 6H, Ar–H), 3.76 (s, 6H, OCH₂–), 2.47 (s, 9H, CH₃– Φ), 1.34–1.35 (m, 2H, CH₃CH₂), 0.62–0.65 (t, 3H, CH₃).

Synthesis of monomer **B₄**

B₄ was synthesized according to ref. 6.

Fourier transform infrared (FTIR; KBr, cm⁻¹): 2964, 1599, 1495, 1468, 1365, 1295, 1192, 1179, 1096, 976, 826, 811, 790. ¹H-NMR (CDCl₃, δ , ppm): 7.67–7.69 (d, 8H, Ar–H), 7.36–7.38 (d, 8H, Ar–H), 3.81 (s, 8H, OCH₂–), 2.47 (s, 12H, CH₃–Ar).

Synthesis of 1,4-bisbutoxy-benzene (B)

A solution of *p*-dihydroxybenzene (16.5 g, 0.15 mol) and ground potassium hydroxide (22 g, 0.39 mol) in dimethyl sulfoxide (DMSO; 225 mL) was stirred and heated to 70°C under a nitrogen atmosphere, and then, *n*-butyl bromide (45.6 g, 0.33 mol) was added slowly. When the addition was finished, the mixture was allowed to react at 70°C for 6 h. Then, the precipitate in the mixture was collected by filtration, washed with deionized water, and then dried *in vacuo* overnight. This crude product was purified by recrystallization from isopropyl alcohol.

Yield: 18.3 g (55%). FTIR (KBr, cm^{-1}): 2958, 2872, 1868, 1511, 1398, 1237, 1119, 1041, 829. $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 6.78–6.82 (s, 2H, Ar–H), 3.88–3.91 (t, 4H, OCH_2 –), 1.70–1.75 (t, 4H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.44–1.50 (q, 4H, CH_3CH_2), 0.94–0.97 (t, 6H, CH_3).

Synthesis of 1,4-bisbutyl-2,5-bis(chloromethyl)benzene (C)

A 100-mL, three-necked glass flask equipped with a reflux condenser, a hydrogen chloride (HCl) gas inlet, and a stirring rod was charged; then, **B** (13.26 g, 0.052 mol), 1,4-dioxane (40 mL), paraformaldehyde (4.53 g, 0.151 mol), zinc chloride (12.26 g, 0.09 mol), and saturated hydrochloric acid (20 mL) were added to the flask. The reaction mixture was stirred and heated at 65°C for 6 h under a HCl atmosphere. After the reaction was completed, 100 mL of deionized water was added to the solution to precipitate the crude product. The precipitate was collected by filtration and washed with deionized water, and then, the crude product was purified by recrystallization from acetone.

Yield: 17.97 g (94%). FTIR (KBr, cm^{-1}): 2957, 2868, 1613, 1469, 1409, 1312, 1220, 1130, 1043, 930, 867, 738. $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 6.90 (s, 2H, Ar–H), 4.62 (s, 4H, $-\text{CH}_2\text{Cl}$), 3.96–3.99 (t, 4H, OCH_2 –), 1.76–1.79 (t, 4H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.47–1.52 (q, 4H, CH_3CH_2), 0.6–0.98 (t, 6H, CH_3).

Synthesis of 1,4-bis(diethoxyphosphorylmethyl)-2,5-bisbutoxybenzene (D)

A 100-mL, three-necked glass flask equipped with a reflux condenser, a nitrogen inlet, and a stirring rod was charged under a nitrogen atmosphere; then, 33.3 g (0.2 mol) of triethyl phosphite and 25.1 g (0.1 mol) of **C** were added to the flask. The reaction mixture was stirred and heated at 140°C for 6 h. After cooling, the white solid mass was broken up and recrystallized with petroleum ether and dried *in vacuo*, and a white, needlelike crystal [4'-(diethoxyphosphorylmethyl)-phenyl-4-yl-methyl] phosphonic acid diethyl ester was obtained.

Yield: 41.77 g (92%). FTIR (KBr, cm^{-1}): 2962, 1510, 1473, 1392, 1254, 1212, 1030, 961. $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 6.89 (s, 2H, Ar–H), 3.99–4.01 (t, 8H, P-O-CH_2), 3.90–3.92 (t, 4H, Ar– OCH_2 –), 3.19–3.21 (d, 4H, Ar– CH_2 –P), 1.72–1.74 (t, 4H, $\text{CH}_3\text{CH}_2\text{CH}_2$), 1.46–1.47 (q, 4H, CH_3CH_2), 1.20–1.23 (t, 12H, $\text{P-O-CH}_2\text{CH}_3$), 0.93–0.96 (t, 6H, CH_3).

Synthesis of monomer A₂

To a 500-mL glass flask equipped with a nitrogen inlet and a stirring rod and flushed with nitrogen was added 5.0 g of sodium hydride (0.21 mol). Anhydrous DMF (30 mL) was added to the flask, and 0.5 h later, a solution of 4.41 g of **D** (0.009 mol) in anhydrous DMF (35 mL) was added over 15 min. After the mixture was stirred for 2 h, a solution of 3.1 g of *p*-hydroxybenzaldehyde (0.044 mol) in anhydrous DMF (30 mL) was added over 20 min. The reaction mixture was stirred for 20 h. Water was added dropwise into the mixture to neutralize the remaining sodium hydride. The reaction mixture was acidified with aqueous HCl (1N) to pH 5–6 and then dropped into cold water. The suspension was filtered, and the filter cake was recrystallized with an 80% ethanol–water solution and then dried *in vacuo*; a bright yellow solid, monomer A₂, was obtained.

Yield: 2.28 g (55.3%). FTIR (KBr, cm^{-1}): 3342, 2928, 2865, 1601, 1510, 1461, 1334, 1243, 1203, 1036, 966, 850, 814. $^1\text{H-NMR}$ (DMSO, δ , ppm): 9.54 (s, 2H, –OH), 7.37 (d, 2H, Ar–H), 7.22 (s, 2H, central Ar–H), 7.20 (d, 2H, $-\text{CH}=\text{CH}$ –central Ar), 7.19 (d, 2H, $-\text{CH}=\text{CH}$ –central Ar), 6.78–6.79 (d, 4H, Ar–H), 4.04–4.06 (t, 4H, $-\text{OCH}_2$ –), 1.77–1.79 (m, 4H, $-\text{OCH}_2-\text{CH}_2$ –), 1.50–1.54 (m, 4H, $-\text{CH}_2-\text{CH}_3$), 0.97–0.99 (t, 6H, $-\text{CH}_3$).

Synthesis of the hyperbranched polymer HP1

To a 50-mL, three-necked glass flask was added 0.198 g of B₃ (0.33 mmol), 0.229 g of A₂ (0.5 mmol), 1.98 g of anhydrous K₂CO₃ (10 mmol), and 40 mL of anhydrous DMF. The reaction mixture was stirred at 105°C for 72 h under a nitrogen atmosphere, then cooled to room temperature, dropped in deionized water, and filtered. The filtration was washed twice with deionized water and then dried *in vacuo*. The resulting solid was dissolved in chloroform, precipitated with alcohol, and dried *in vacuo*, and finally, the yellow powder of HP1 was obtained.

Yield: 0.28 g. FTIR (KBr, cm^{-1}): 3454, 2987, 2870, 1602, 1509, 1498, 1419, 1239, 1174, 1026, 964, 854. $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 7.45–6.92 (Ar–H), 4.04 ($-\text{OCH}_2$ –), 1.85 ($-\text{OCH}_2-\text{CH}_2$ –), 1.58 ($-\text{CH}_2$ –), 1.01 ($-\text{CH}_3$).

The weight-average molecular weight of HP1 measured by gel permeation chromatography (GPC) was near 24×10^3 with a polydispersity index of 2.22.

Synthesis of the hyperbranched polymer HP2

To a 50-mL, three-necked glass flask was added 0.344 g of B₄ (0.5 mmol), 0.229 g of A₂ (0.5 mmol), 1.98 g of anhydrous K₂CO₃ (10 mmol), and 40 mL of anhydrous DMF. The reaction mixture was stirred at 105°C for 72 h under a nitrogen atmosphere, then cooled to room temperature, dropped in deionized water, and filtered. The filtration was washed twice with deionized water and then dried *in vacuo*. The resulting solid was dissolved in chloroform, precipitated with alcohol, and dried *in vacuo*, and finally, the yellow powder of HP2 was obtained.

Yield: 0.35 g. FTIR (KBr, cm⁻¹): 2956, 2870, 2311, 1601, 1509, 1467, 1419, 1370, 1238, 1178, 1030, 972, 816. ¹H-NMR (CDCl₃, δ, ppm): 7.43–6.82 (Ar-H), 4.04 (—OCH₂—), 1.84–1.56 (—CH₂—), 1.01 (—CH₃).

The weight-average molecular weight of HP2 measured by GPC was near 10×10^3 with a polydispersity index of 2.03.

Characterization and instrumentation

NMR spectra were recorded on a Bruker Spectrospin AV 600-MHz spectrophotometer (Rheinstetten, Germany). FTIR spectra were obtained on a Bruker Tensor 37 spectrophotometer (Ettlingen, Germany). Ultraviolet-visible (UV-vis) spectra were recorded on a Shimadzu UV-3150 spectrophotometer (Tokyo, Japan). Photoluminescence (PL) spectra were measured with a Varian Cary Eclipse spectrophotometer (Varian, Australia). GPC was performed on a Waters 515-2410 apparatus (Milford Massachusetts) with tetrahydrofuran (THF) as the eluent and polystyrene as a reference. Thermogravimetric analysis (TGA) was carried out under nitrogen at a heating rate of 20°C/min with a Netzsch TG 209C instrument (Netasch, Germany). Differential scanning calorimetry (DSC) was carried out on a Netzsch DSC 204 F1 instrument under nitrogen at a heating rate of 10°C/min. Electrochemical measurement was carried out with a Zahner model IM6e instrument (Kansas City, Missouri). Cyclic voltammetry (CV) was performed on a CHI 600 electrochemical analyzer (Shanghai, China), with polymer-coated platinum as the working electrode, a Ag/Ag+ (0.01M AgNO₃/acetonitrile) electrode as a reference electrode, and a platinum wire electrode as an auxiliary electrode supported in a 0.1M Bu₄NClO₄/acetonitrile solution.

Fabrication of the light-emitting device

A brief LED device with a configuration of indium tin oxide (ITO)/HP1 (80 nm)/Ca (15 nm)/Al (100

nm) was fabricated. The device was prepared by the spin-coating of HP1 in a chloroform solution on the surface of ITO. The active metal electrode Ca was then thermally evaporated onto the surface of the polymer layer. Finally, a layer of Al (100 nm) was deposited on the surface to protect the active Ca.

RESULTS AND DISCUSSION

Synthesis of the hyperbranched polymers HP1 and HP2

Generally, the synthesis of conjugated light-emitting polymers has one crucial concern, solubility, which determines the film-forming ability and the film quality of the polymer layer in the polymer LED. Considering that hyperbranched polymers have a much better solubility than linear polymers because of their three-dimensional structure and large amount of end groups, we designed and synthesized a partially conjugated hyperbranched poly(p-phenylene vinylene) (HPV)¹¹ without long flexible side chains in the conjugated fluorescent segments. However, we found that the solubility and processability of HPV were not good enough to fabricate high-performance electroluminescent devices because of the poor solubility of the rigid chromophores. Here, two pendent butoxy groups were introduced into the central rings of the chromophores as soft side chains to improve the solubility of polymer HPV. Indeed, the solubilities of the two resulting polymers, HP1 (synthesized via the A₂ + B₃ approach) and HP2 (synthesized via the A₂ + B₄ approach), were much better than that of HPV. HP1 and HP2 dissolved completely in common organic solvents such as DMF, DMSO, THF, CHCl₃, CH₂Cl₂, and toluene, which also revealed that no crosslinked networks formed during the polymerization. The good solubility was probably due to two main reasons: the three-dimensional structure and the large amount of end groups of the hyperbranched polymers, which led to weak intermolecular interaction and strong interaction between the molecules and the solvent and, more importantly, the pendant alkoxy groups on the oligo-PPV moieties endowing the polymers with increased dissolution entropy and decreased interaction between the oligo-PPV segments. Furthermore, the polymer HP1, with a trihedral core structure, had a much better solubility and larger weight-average molecular weight than HP2, with a tetrahedral structure. Because the B₃ monomer has less steric hindrance than the B₄ monomer, the space between rigid chromophores in the resulting polymer HP1 was relatively bigger, and the molecule chain could move more easily so that the molecules had stronger interaction with solvents. In comparison, the HP2 molecules had denser rigid

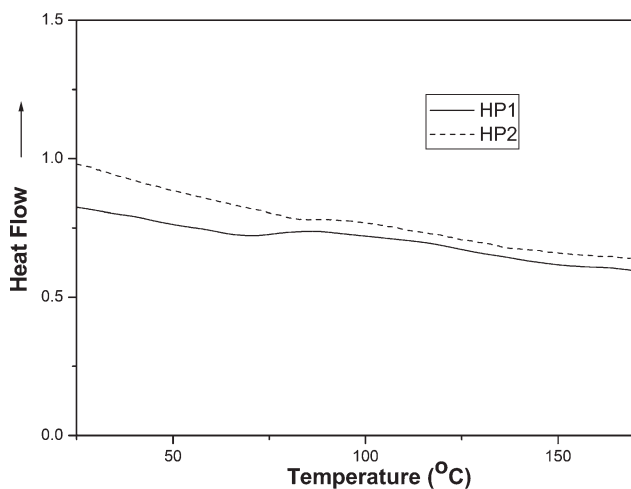


Figure 1 DSC curves of (—) HP1 and (- - -) HP2 at a heating rate of 20°C/min in nitrogen.

chromophores and a smaller porous structure than HP1. Therefore, HP1 demonstrated much a better solubility than HP2. As is well known, the molecular weight of synthesized polymers depends on their solubility during polymerization to a certain extent. Better solubility led to a higher molecular weight in the resulting polymers. As the reaction went on and the molecules grew, HP2 deposited earlier from the reaction solution because of its poorer solubility and stopped growing bigger, so it had a smaller molecular weight.

The thermal stability of the polymers, a critical factor influencing the lifetime of LED, was evaluated by TGA and DSC. As shown in Figure 1, the glass-transition temperatures (T_g 's) of HP1 and HP2 were 122 and 129°C, respectively. The high T_g 's were attributed to their near crosslinked hyperbranched molecular structures. Those T_g 's were also higher than that of HPV without alkoxy side chains in the

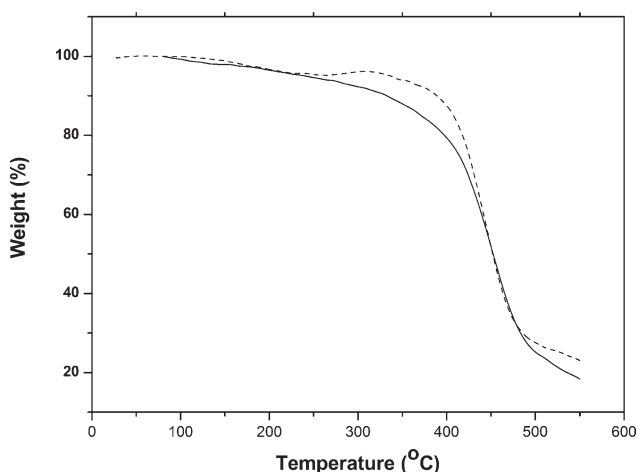


Figure 2 Thermogravimetric curves of (—) HP1 and (- - -) HP2 at a heating rate of 20°C/min in nitrogen.

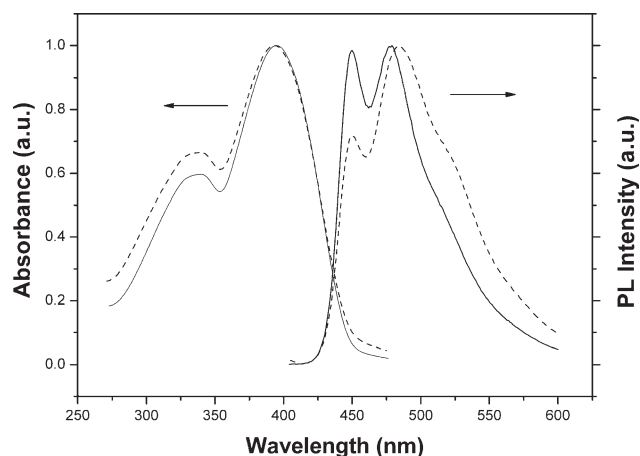


Figure 3 UV-vis and PL spectra of (—) HP1 and (- - -) HP2 in chloroform.

conjugated fluorescent segments (the T_g of HPV was 91°C). This was because, in HP1 and HP2, each repeating unit bearing two substituents on the rigid units made the repeating unit bulkier. This, in turn, reduced the segmental motions.¹³ The two polymers HP1 and HP2 displayed good thermal stability under a nitrogen atmosphere according to the TGA investigation. As shown in Figure 2, the decomposition temperatures of HP1 and HP2 began at 396 and 405°C, respectively, and no weight losses were observed at lower temperatures, which indicated that the two polymers were very stable.

Optical properties

Figures 3 and 4 show the UV-vis absorption and PL spectra of the hyperbranched polymers HP1 and HP2 in chloroform solutions and the film state, respectively. In solution state, the maximum absorption peaks of HP1 and HP2 were at 394 nm, and both showed a vibrational absorption peak at 339.5

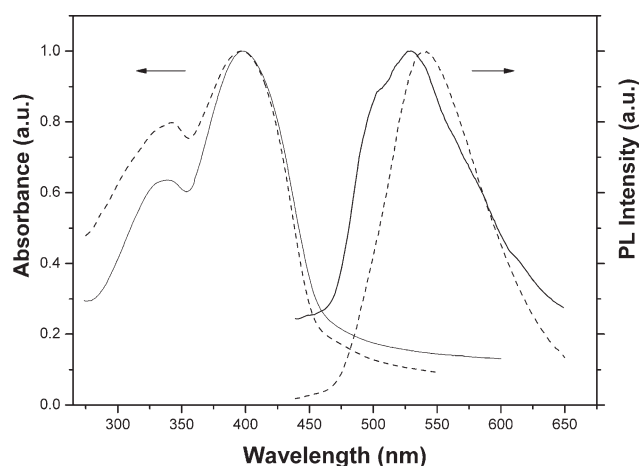


Figure 4 UV-vis and PL spectra of (—) HP1 and (- - -) HP2 films.

nm. The two absorption maxima corresponded to the π - π^* transition of the PPV moiety. In film state, the maximum absorption peaks of HP1 and HP2 were both located at 397 nm, which redshifted by 3 nm compared with that of HP1 and HP2 in chloroform. When the absorption maxima of HP1 and HP2 were normalized to an identical value, the vibrational absorption maximum of HP2 was larger than that of HP1, which was probably because of the lower time-average coplanarity of the chromophores in HP2 caused by its stronger steric hindrance. From the absorption onsets of the HP1 and HP2 films, the band gap energies were determined to be 2.68 and 2.69 eV, respectively. Moreover, after the incorporation of pendent alkoxy group into HPV, the absorption maxima of HP1 and HP2 in both solution and the film state shifted bathochromically to some degree compared with HPV. This was ascribed to the extended resonance in the distyrylbenzene segment caused by alkoxy groups.

The PL maxima of HP1 and HP2 in dilute chloroform solutions appeared at 478 and 483 nm, respectively. Both HP1 and HP2 showed a vibrational peak at 450 nm, whereas the emission intensity of HP2 was relatively weaker. HP2 showed a shoulder at 525 nm, and the full-width at half-maximum of HP2 was larger than that of HP1. These phenomena could be explained as follows: because intermolecular interaction could be omitted in dilute solution, the difference between the PL spectra of HP1 and HP2 was just caused by intramolecular interaction. In the HP2 molecule, the interchromophore distance was shorter than in HP1 because of its dense structure, which gave HP2 more opportunities to generate intramolecular excimers. Thus, the PL spectrum of HP2 showed a broader full-width at half-maximum and a redshifted maximum emission peak in comparison with that of HP1.

The relative PL quantum efficiencies of HP1 and HP2 in dilute chloroform solution were determined to be 56.8 and 49.3%, respectively (with the procedure published in literature¹¹); these were much larger than those in the fully conjugated hyperbranched PPV (48%) and linear PPV (35%).¹⁴ This was due to the introduction of nonconjugated spacers, which diluted the emitting chromophores and reduced self-quenching possibilities. In the solid state, both HP1 and HP2 displayed only one peak, occurring at 528 and 539 nm, respectively, which was redshifted slightly compared with the spectrum in solution. This phenomenon indicated that a hyperbranched structure could effectively reduce but not completely eliminate the generation of excimers.

Electrochemical properties

To gain information about the highest occupied molecular orbit (HOMO) and the lowest unoccupied

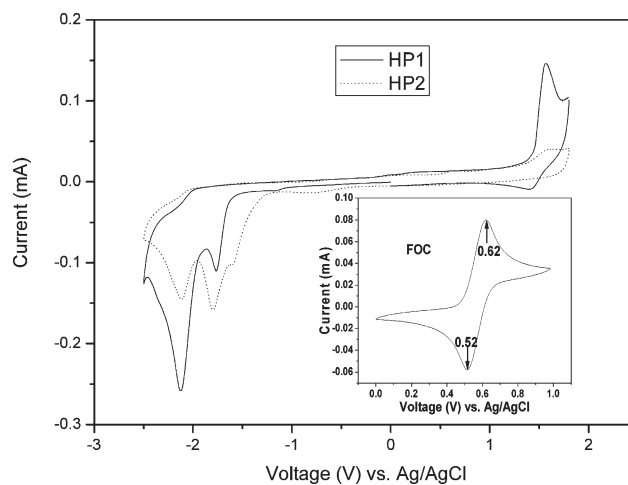


Figure 5 Cyclic voltammograms of HP1, HP2, and FOC.

molecular orbit (LUMO) energy levels of the hyperbranched polymer, we performed CV experiments. The potentials were referenced to Ag/AgCl and the arithmetic averages of the reduction and oxidation potentials of ferrocene/ferrocenium (FOC). As shown in Figure 5, in the cathodic and anodic scans, HP1 and HP2 showed irreversible n-doping and quasireversible p-doping processes. CV of both HP1 and HP2 showed two reduction peaks at -1.76 and -2.12 V, which corresponded to the reduction of the PPV chromophore. In the anodic scan, the oxidation potential of both HP1 and HP2 appeared at 1.56 V, which was attributed to the oxidation of the PPV chromophore.

The HOMO energy level (E_{HOMO}) of the two polymers was calculated from the onset potential of oxidation ($E_{\text{ox,on}}$) under the assumption that the absolute energy level of FOC was 4.8 eV below the vacuum level,^{15,16} and the LUMO energy level was calculated from E_{HOMO} and the absorption edge. To obtain E_{HOMO} , an empirical formula was used:¹⁷

$$E_{\text{HOMO}} = \text{IP}(\text{eV}) = -e(E_{\text{ox,on}} - E_{\text{foc}}) - 4.8$$

where IP is the ionization potential and E_{foc} is the arithmetic average of the reduction and oxidation potential of FOC versus Ag/AgCl.

According to our test, the value of E_{foc} was 0.57 eV. The HOMO and LUMO of HP1 were calculated to be -5.66 and -2.98 eV, respectively. The HOMO and LUMO energy levels of HP2 were -5.65 and -2.97 eV, respectively, almost the same as HP1. This was because HP1 and HP2 shared the fundamental chromophore, which dominated the electrochemical properties of the two polymers. The band gap of HP2 derived from the CV was 2.67 eV, which was very close to the optical band gap determined from the UV-vis spectra (2.69 eV). These data could be

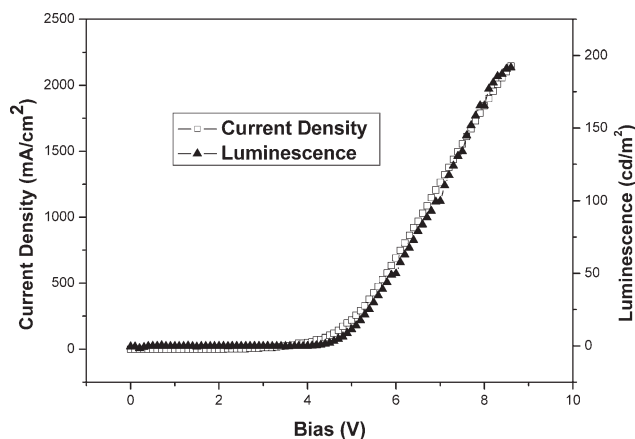


Figure 6 Current versus the voltage and luminance versus the voltage for ITO/polymer/Ca/Al devices.

used as a reference for the selection of the electrode and charge-transporting materials in LED fabrication.

Electroluminescent properties

Considering that HP1 had a much better solubility than HP2 and, in turn, had better film-forming abilities, we only took HP1 to investigate the electroluminescence performance. The solubility of HP1 was much better than HPV. Therefore, unlike the complicated fabrication process of the device made by HPV [because of HPV's poor solubility, we had to blend poly(ethylene oxide) (PEO) into the emitting layer to ensure a layer thick enough to make a LED device, and apart from that, we added a poly(3,4-ethylene dioxythiophene) layer to make the device achieve noticeable brightness], a brief LED device with the configuration of ITO/HP1 (80 nm)/Ca (15 nm)/Al (100 nm) was fabricated. The device showed typical LED behavior. As shown in Figures 4 and 6, the turn-on voltage was 4.8 V, which was much lower than that of HPV (36 V), and the brightness reached a maximum of 190 cd/m² at 8.2 V, enhanced greatly compared to that of HPV (25 cd/m² at 40 V). Although this LED device omitted the poly(3,4-ethylene dioxythiophene) layer to enhance the charge carrier efficiency compared to the device of HPV, the performance of the light-emitting device was greatly enhanced because we modified the polymer with pendent alkoxy groups. The maximum transfer efficiency of current density to brightness (i.e., the ratio of brightness to current density) of the device was 0.00932 cd/A at 8.1 V. Still, this was just an initial result; on the basis of our experience, much better performances can be expected after the configuration optimization of a device,¹⁸ and related work is in progress. In addition, we are working on modifying the polymers with electron-transport moieties to balance the injection and transport of holes and electrons, which

might bring a huge enhancement in the LED properties,¹⁹ and the stage achievement was satisfactory.

CONCLUSIONS

Two kinds of partially conjugated hyperbranched polymers were synthesized and confirmed by FTIR and ¹H-NMR spectroscopy. The synthetic procedure was relatively simple, and the yield was very high. The conformation of the polymers demonstrated a three-dimensional structure instead of an approximate planar structure of fully conjugated hyperbranched polymer. The two polymers had very good solubility in common organic solvents such as THF, CH₂Cl₂, CHCl₃, and DMF. Property investigations revealed that the two polymers had good thermal stability and high *T_g*'s. The HOMO and LUMO values of HP1 and HP2 determined from CV and UV-vis absorption were almost the same, just as we anticipated. A brief single-layer device (ITO/HP1/Ca/Al) reached an optimistic maximum brightness of 190 cd/m² at 8.2 V. Much better properties can be expected after the optimization of the LED or the modification of the light-emitting polymer with electron-transport moieties.

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