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Spectrum-stable hyperbranched polyfluorene with photocrosslinkable group

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Abstract

Two kinds of blue light-emitting hyperbranched crosslinkable polyfluorene P1 and P2 with different contents of branch unit were synthesized via the palladium-catalyzed Suzuki coupling reaction, and the linear crosslinkable polyfluorene P0 was also prepared for comparison. The molecular weight and thermal behavior of the polymers were measured by GPC, DSC and TGA. Compared with uncrosslinked P0, P1 and P2, the photoluminescence spectra of crosslinked P0, P1 and P2 were little influenced. After annealing for 3 h at 200 °C in air, the photoluminescence spectrum of P2 with higher contents of branch unit showed more excellent stability compared with that of P1 and P0. The spectrum-stable hyperbranched polyfluorene can be used in multilayer and multicolor PLED.

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Keywords: Hyperbranched; Polyfluorene; Photocrosslink

1. Introduction

The discovery of electroluminescent poly(*p*-phenylene vinylene) (PPV) in 1990 has attracted considerable interest of the development of conjugated polymers for their application in flat-panel-display technology [1]. Although monochromatic polymer light-emitting diodes (PLEDs) have been studied extensively, multicolor PLED devices could greatly enhance their technological impact and satisfy commercial full-color display applications. So far, multicolor OLED can be realized by the fabrication of multilayer devices with consecutive evaporations of different emitting materials. However, the fabrication of PLEDs by wet methods such as spin-coating is often complicated because the lower layers are usually soluble in the solvents used for casting subsequent layers. To circumvent this problem, crosslink technique is believed to be a promising approach [2,3]. Initiated with the UV light, heat, and electronic beam etc., soluble polymers can be crosslinked into insoluble network structure.

Polyfluorene (PF) derivatives are promising blue light-emitting materials candidates due to high quantum yields, excellent solubility, film-formation ability and ease in controlling their properties via substitution in the 9,9-position of the fluorene unit [4]. However, it is difficult for PF to obtain pure and stable blue light emission due to the presence of undesirable green emission under high temperature or device operation. Two explanations have been given for the green emission: one was the keto defect [5], and the other was excimer or aggregate emission [6].

Highly branched and globular molecular features improve the light-emitting efficiencies and also make the materials to form good quality amorphous films. Recently, there have been several attempts to achieve stable luminescent spectra via hyperbranched molecular structure [7]. In these researches, the formed hyperbranched molecular structure improves the spectrum stability.

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In this contribution, three blue light-emitting crosslinkable polyfluorenes with hyperbranched and linear structure have been synthesized successfully via Suzuki coupling reaction. The formed polymer can be crosslinked photochemically by the crosslinkable group and the photocrosslink has little influence on the photoluminescence (PL) spectra of the polymer. The hyperbranched crosslinkable polyfluorene P2 with higher content of branch unit has more stable photoluminescence spectrum than the lower branch unit content hyperbranched crosslinkable polyfluorene P1 and linear crosslinkable polyfluorene P0, even after annealing for 3 h at 200 °C in air after crosslink.

2. Experimental section

Generally all reagents were purchased from Acros, Fluka or Aldrich Chemical Co. and were used without further purification. All solvents were dried under standard procedure.

NMR spectra were recorded on Varian Mercury plus 400 at 295 K. GPC results were obtained on Shimadzu LC-VP. The DSC and TG scans were done on Shimadzu DSC-60A and DTG-60A equipment, respectively. The heating rate was 10 K/min. Nitrogen was used as the protective and purge gas. UV−vis absorption spectra were recorded on Shimadzu UV-3150. Fluorescence spectra were measured on Shimadzu RF-5300PC.

2.1. Monomer synthesis

Monomers **1** and **3** were synthesized according to the Refs. [7b,8]. The procedure is shown in Scheme 1.

*2.1.1. Monomer **1***

Into a solution of 2,7-dibromo-9,9-dioctylfluorene (5.05 g, 9.22 mmol) in anhydrous THF (70 ml) *n*-BuLi was added (1.6 M in hexane, 19.5 ml, 31.2 mmol) drop wise at −78 °C. The reaction mixture was stirred for 2 h before tri-isopropyl borate (8.3 ml, 6.72 g, 35.75 mmol) was added in one portion. The mixture was recovered to room temperature, stirred overnight and then 2 M HCl was added (30 ml) with stirring. The mixture was extracted with ether and the combined extracts were evaporated to give a white solid. Then the solid was refluxed with 1,3-propanediol (1.6 ml, 1.68 g, 22.13 mmol) in toluene for another 10 h. After the solvent was evaporated, the crude product was purified by re-crystallization with hexane to afford **1** (4.16 g, 81%) as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.71 (m, 6H), 4.20 (t, 8H), 2.09 (m, 4H), 1.98 (m, 4H), 1.21−0.91 (m, 20H), 0.80 (t, 6H), 0.53 (m, 4H).

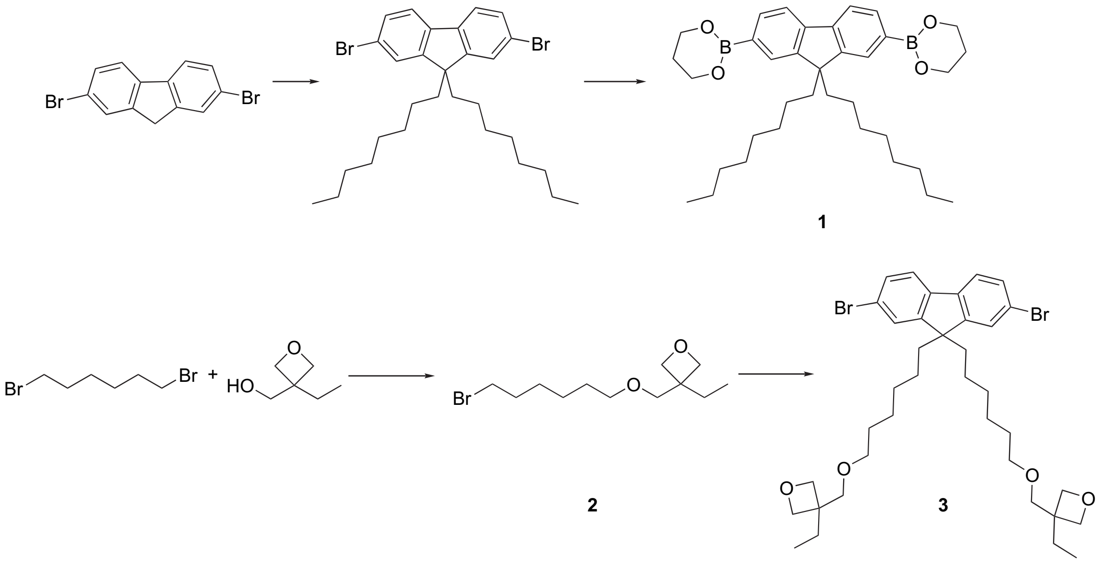
*2.1.2. Monomer **3***

After degassing, the mixture of **2** (11.2 g, 40 mmol), 2,7-dibromo-fluorene (3.2 g, 10 mmol), tetra-*n*-butylammonium chloride, DMSO (70 ml) and 50% aqueous NaOH solution (5 ml) were stirred at 60 °C for 8 h. The reaction mixture was allowed to cool at room temperature and extracted with ethyl acetate. The extract was washed with water and dried over anhydrous magnesium sulfate overnight. After condensation using a rotary evaporator, it was purified by column chromatography on silica gel with petroleum ether:ethyl acetate (10:1) as the eluent to afford **3** as light yellow solid (yield: 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.47 (d, 6H), 4.38 (m, 8H), 3.46 (s, 4H), 3.33 (t, 4H), 1.90 (m, 4H), 1.68 (m, 4H), 1.36 (m, 4H), 1.08 (m, 8H), 0.82 (t, 6H), 0.56 (m, 4H).

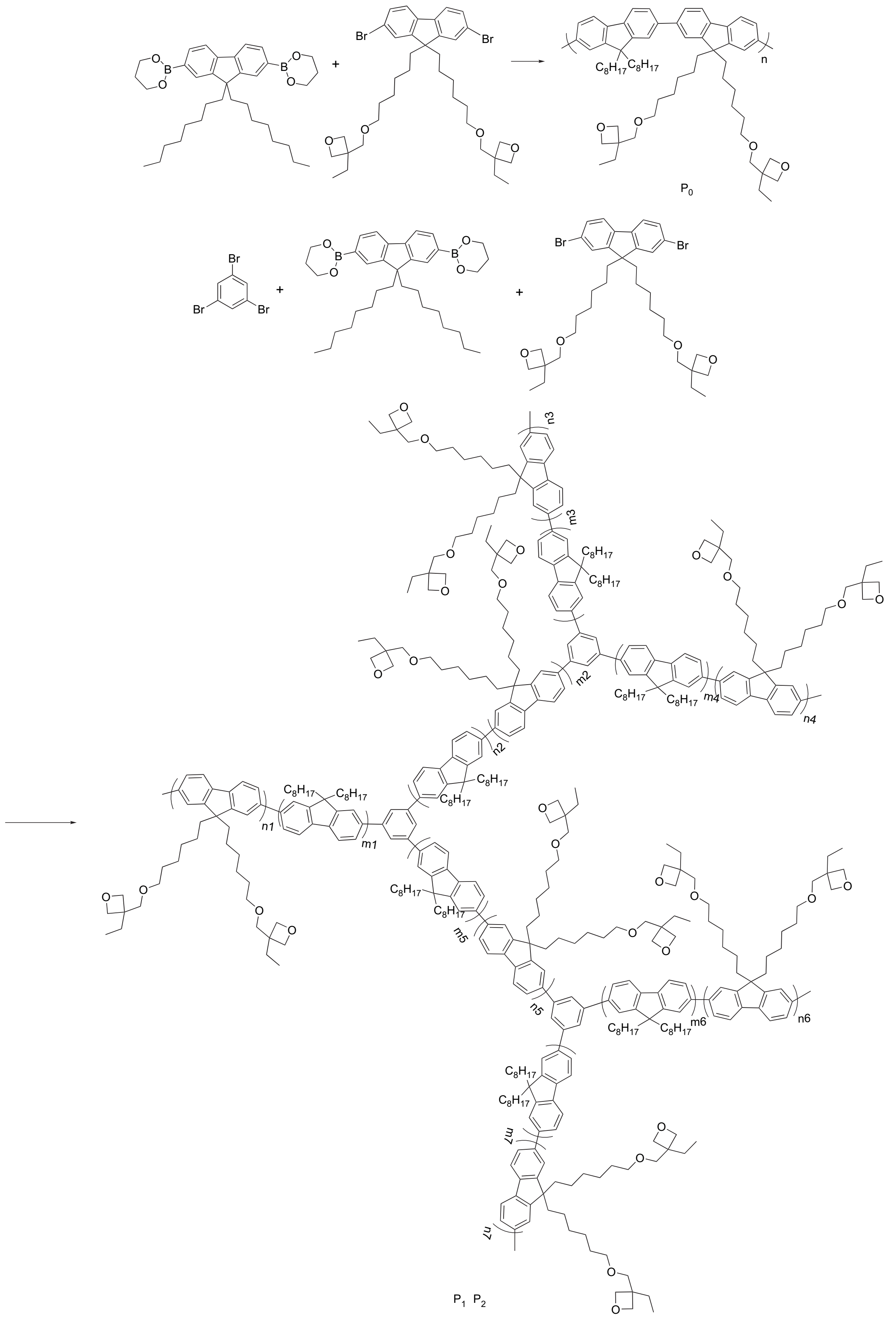
2.2. Polymerization

In Scheme 2, the linear crosslinkable polymer P0 and hyperbranched crosslinkable polymers P1 and P2 were synthesized via palladium-catalyzed Suzuki coupling [9].

Hyperbranched crosslinkable polymer (P1, P2), monomers **1** and **3**, 1,3,5,-tribromobenzene, K_2CO_3 and tetrakis-(triphenylphosphine)palladium(0) were put in a flask. After degassed and filled with nitrogen, the degassed toluene and water were



Scheme 1. Synthetic routes of the monomers **1** and **3**.



Scheme 2. Synthetic routes of polymers P0, P1 and P2.

Table 1
Monomer molar feeding ratio in polymer

Monomer	P0 (%)	P1 (%)	P2 (%)
9,9-Dioctylfluorene-2,7-bis(trimethylene boronate)	50.00	48.74	55.00
9,9-Di(6-(2-(3-oxetanyl)butoxyl)hexyl)-2,7-dibromofluorene	50.00	46.26	15.00
1,3,5,-Tribromobenzene		5.00	30.00

added. The mixture was stirred at 75 °C for 72 h under a nitrogen atmosphere. After that, the reaction mixture was purified by column chromatography on silica gel first with petroleum ether:ethyl acetate (1:1) and followed with toluene plus THF as eluent. After condensation with rotary evaporator, it was added drop wise into methanol to give a light color precipitate.

Linear crosslinkable polymer P0 was synthesized in the same procedure.

The monomer feeding ratio of P0, P1 and P2 is listed in Table 1.

2.3. Crosslink procedure

The crosslink procedure was done according to Ref. [3].

Thin film was prepared by spin-coating the polymers from THF solution (10 mg ml^{-1}) with 1 wt% (relative to the polymer) of triphenylsulfonium hexafluoroantimonate as initiator for the cationic polymerization of the oxetane units. The films were irradiated (standard UV lamp, $\lambda = 302$ nm) for about 3 s in inert gas atmosphere at room temperature, then the film were annealed at 90 °C for 30 s. Afterwards, the films were rinsed with THF and finally heated to 180 °C for 5 min to remove the radical cations formed upon polymerization.

3. Results and discussions

3.1. Design and synthesis

A different way was chosen to synthesis monomer **3** compared to Ref. [10]. As a convenient synthesis procedure, monomer **3** was obtained in 80% yield. In the experiment, interestingly, monomer **3** is a light yellow solid at room temperature rather than a yellow oil-like compound [10]. In Fig. 2, DSC has been applied to analysis the melting point and enthalpy which are 63.98 °C and 86.82 J/g, respectively. But monomer **3** was hard to condense so that the melting peak cannot be found in the second cycle of the analysis, neither is the crystallization peak.

For hyperbranched polymers, the conventional synthesis methods are the AB2 and A2 + B3 approaches [7a,7c,11]. As a useful way, CMM method can be used for multi-monomer couple [11]. Based on our experience in hyperbranched polymer, the A2 + B2 + C3 method is a competitive way for the introduction of multi-component and easy to control the content of the monomer. In these experiments, the polymers were obtained in about 50% yield.

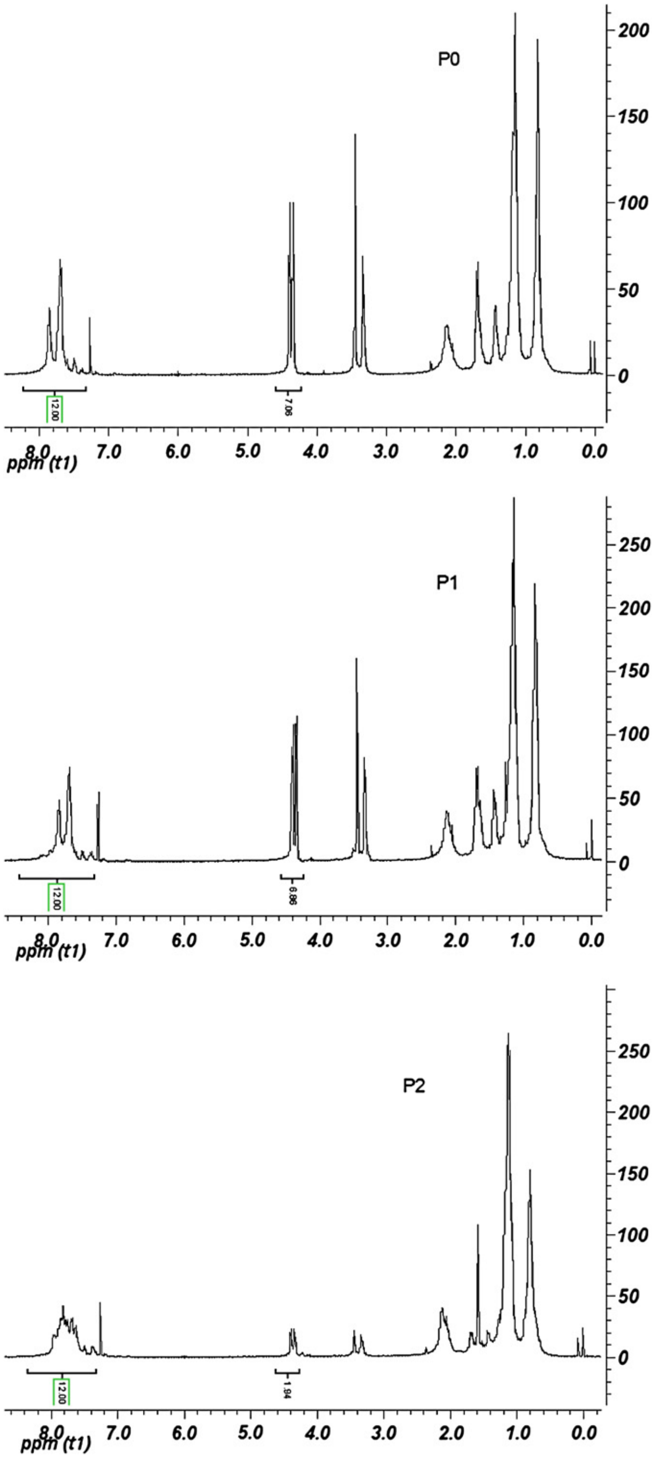


Fig. 1. ^{1}H NMR of P0, P1, and P2.

P0, P1, and P2 can be easily dissolved in $CHCl_3$, THF, and toluene. The ^{1}H NMR is shown in Fig. 1. The ^{13}C NMR data are listed as follows.

P0: ^{13}C NMR (100 MHz, CDCl3): δ (ppm) = 151.8, 151.6, 140.4, 140.0, 132.1, 128.8, 127.2, 126.2, 121.4, 120.0, 78.6, 73.3, 71.5, 55.3, 43.3, 40.4, 31.8, 30.0, 29.5, 29.2, 26.7, 25.9, 23.9, 22.6, 14.1, 8.2.

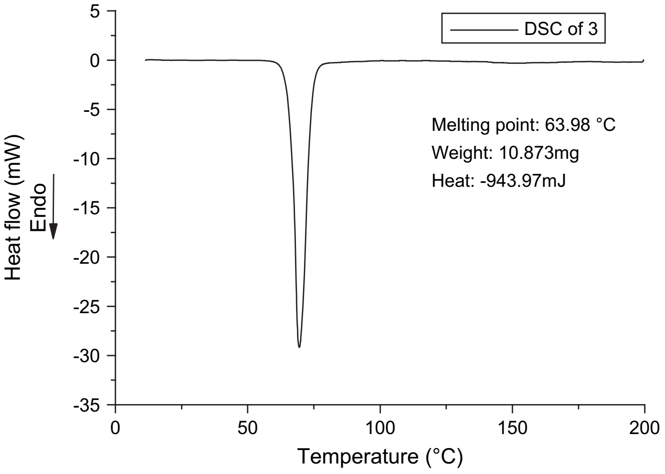


Fig. 2. DSC analysis of monomer 3.

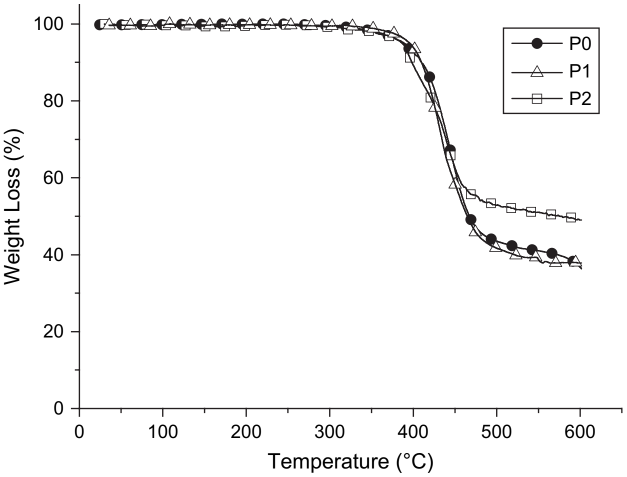


Fig. 3. TG analysis of polymers P0, P1 and P2.

P1: ^{13}C NMR (100 MHz, CDCl3): δ (ppm) = 151.8, 151.6, 140.4, 140.0, 128.8, 127.2, 126.2, 121.4, 120.0, 78.6, 73.3, 71.5, 55.3, 43.3, 40.4, 31.8, 30.0, 29.5, 29.2, 26.7, 25.9, 23.9, 22.6, 14.1, 8.2.

P2: ^{13}C NMR (100 MHz, CDCl3): δ (ppm) = 151.9, 151.0, 144.2, 142.9, 141.2, 140.8, 140.4, 138.9, 128.8, 127.2, 126.3, 125.0, 123.3, 121.7, 120.2, 78.6, 73.3, 55.3, 43.3, 40.4, 31.8, 30.0, 29.5, 29.2, 26.7, 25.8, 23.9, 22.6, 14.1, 8.2.

In ^{1}H NMR spectrum, the peak around 4.36 is the hydrogen of oxetane that indicates the relative amounts of monomer **3** while the peak above 7.26 is the hydrogen of aromatic ring. The integration area shown in Fig. 1 indirectly reflects the content of the core. From the spectrum, we can find that the content of monomer **3** in P2 is much less than that in P1 and P0, which indicates the higher content of the core in P2.

3.2. Molecular weight and thermal properties

The molecular weights and thermal properties of the polymer are listed in Table 2. The number-averaged molecular weights and polydispersity indices (M_n, PDI) of the polymers P0, P1, and P2 are (12,600; 1.76), (17,200; 2.79) and (10,200; 2.70), respectively. The polydispersity indices are close to that reported previously [7].

In DSC measurement, no distinct glass transitions were observed for P0, P1 and P2 before 200 °C. Fig. 3 is the TG analysis of the polymers P0, P1 and P2. From the curve, it is known that the thermal decomposition temperature of P0, P1 and P2 all exceeds 350 °C, which indicates that the thermal stability of the polymer is very well.

Table 2
Molecular weights and thermal properties of polymers

Polymer	M_n	M_w	PDI	T_g (°C)	T_d (°C) (by 5% decomposition)
P0	12,600	22,200	1.76	–	389
P1	17,200	48,000	2.79	–	395
P2	10,200	27,500	2.70	–	387

3.3. Spectroscopic properties

Fig. 4 displays the UV–vis spectra of P0, P1 and P2 in solid film (a) and in toluene solution (b). In solid film, P0, P1 and P2 exhibit the maximum absorption peaks at 386, 377, 344 nm while in toluene solution at 384, 376, 342 nm, respectively. Compared with P0 and P1, shorter wavelength absorption is observed for P2 both in film and solution.

Compared with P0, the relatively lower content of the core in P1 has less effect on the UV–vis absorption spectrum. For P2, with the large increase of the content of the core, the polymer exhibits different spectrum.

Fig. 5 is the photoluminescence (PL) spectra of the polymers P0, P1 and P2 in toluene (a) and in film state before crosslink (b) and after crosslink (c) and annealing for 3 h at 200 °C in air after crosslink (d).

In Fig. 5 (a), the maximum emission peaks of P0, P1 and P2 in toluene are at 415, 414, 407 nm, respectively. The maximum emission peak of P1 is quite similar to that of P0, which indicates that less content of the core executes less influence on the PL spectra. For P2, the obvious hypsochromic shift of the maximum emission peak shows the influence of relatively higher content of the core.

In Fig. 5(b) and (c), the maximum emission peaks of P0, P1 and P2 in film state locate at 448, 452, 418 nm before crosslink, respectively, and at 448, 450, 419 nm after crosslink, respectively. This indicates that the crosslink procedure has little effect on the PL spectra of linear and hyperbranched polymers. On the other hand, as indicated in Ref. [4d], the agglomeration of the polyfluorene molecular chain will cause bathochromic shift in PL spectrum. Compared to the solution state, the relatively less bathochromic shift of the maximum emission peak of P2 than those of P0 and P1 also means the less agglomeration among molecules of P2.

After annealing, the PL spectra of P0 and P1 in Fig. 5(d) all show the longer wavelength emission around 540 nm, in which the change of the PL spectra of the linear polyfluorene P0 is similar to that of previously reported [5c–e], while the maximum emission peaks of P2 are still around 418 nm. This

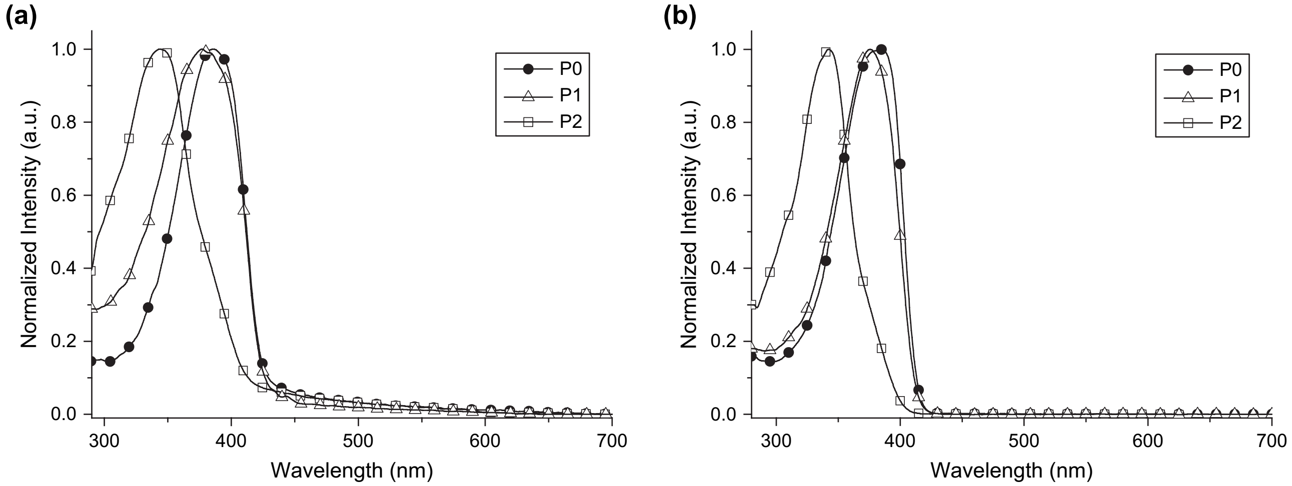


Fig. 4. UV–vis spectra of polymers in film state (a) and in toluene solution (b).

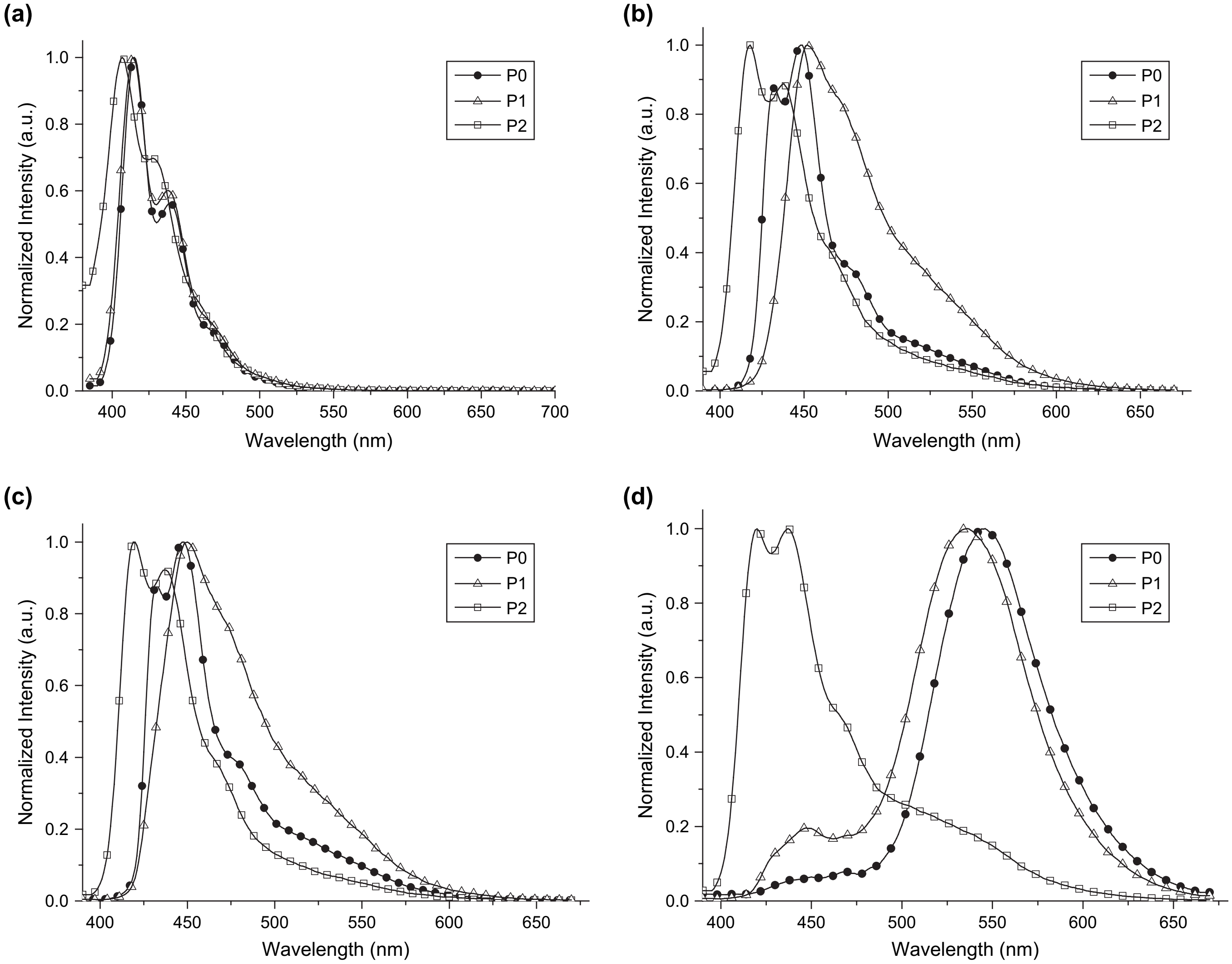


Fig. 5. PL spectra of polymers in toluene solution (a) and in film state before crosslink (b) and after crosslink (c) and annealing for 3 h at 200 °C in air after crosslink (d).

indicates that the hyperbranched polyfluorene P2 has a more stable photoluminescence spectrum.

From Fig. 5, it can be clearly seen that the annealing strongly influences the photoluminescence spectra of polymer even after crosslink. But with the increase of the content of the core, the hyperbranched polymer P2 exhibits stable PL spectrum at higher temperature.

4. Conclusion

A series of linear and hyperbranched crosslinkable polyfluorene with good solubility in common solvent were synthesized via Suzuki coupling reaction. In this report, the melting point of monomer 3 is analyzed with DSC. The data of DSC and TGA show that the synthesized polymers possess no distinct glass transition temperature before 200 °C and exhibit good thermal stability higher than 350 °C. The introduction of the crosslinkable group has little influence on the photoluminescence spectra of the polymer. The hyperbranched polyfluorene P2 with higher content of the core exhibits stable photoluminescence spectra even after annealing at higher temperature. Research of the reported blue light-emitting hyperbranched crosslinkable polyfluorene in multilayer and multicolor PLED is under way.

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