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Blue-light-emitting hyperbranched polyfluorenes with photocrosslinkable group

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The blue-light-emitting crosslinkable hyperbranched polyfluorene P2 with higher content of branched unit were synthesized by the palladium-catalyzed Suzuki coupling reaction. The molecular weight and thermal behavior was analysized by GPC, DSC and TG. By contrast with the lower branched unit content hyperbranched polyfluorene P1 and linear polyfluorene P0, the photoluminescence (PL) spectra of P2 shows excellent stability even annealing in air at 200 ^{o}C after 3 hours after crosslink. The stabilized hyperbranched polyfluorene can be used in multilayer and multicolor PLED.

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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, multi-color 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 [2]. To circumvent this problem, crosslinking technique is believed to be a promising approach [3]. Initiated with the UV light, heat, and electronic beam, etc., soluble polymers can be crosslinked into insoluble network structure. More recently, multicolor PLEDs with multi-type light-emitting polymers have been successfully fabricated with the technique.

Polyfluorene (PFs) derivatives are promising blue light-emitting materials due to their excellent chemical stabilities, high quantum yields, excellent solubility and film-formation ability, and ease in controlling their properties via facile substitution in the 9,9-position of the fluorene unit [4]. However, it is difficult for PFs to obtain pure and stable blue light emission due to the presence of undesirable green emission. 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 features improve the light emitting efficiencies and also make the materials form good quality amorphous films. Recently, there have been several attempts to achieve stable luminescent spectra via hyperbranched molecular structure [7].

In this contribution, a series of blue-light-emitting crosslinkable polyfluorenes with hyperbranched and linear structure have been synthesized successfully through facile approach. The formed soluble polymer via Suzuki polycondensation can be crosslinked photochemically. The introduction of crosslinkable group and the photocrosslinking for P2 has little effect on the photoluminescence (PL) properties even after annealing at 200℃ after 3 hours in air.

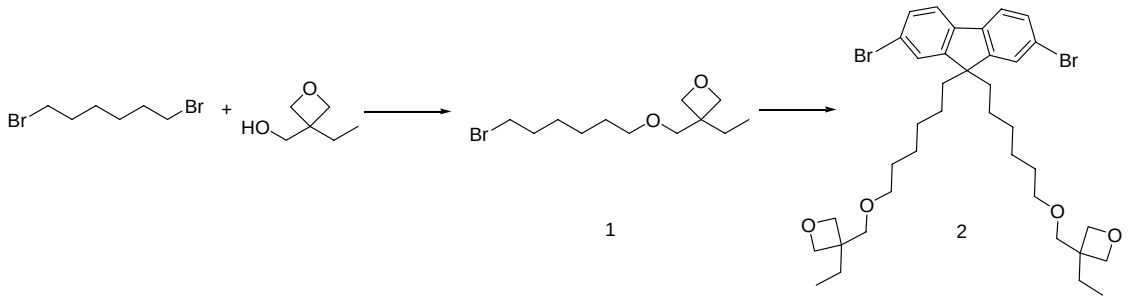
2. Experimental section

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

All NMR spectra were recorded on a Varian Mercury plus 400 at 295K. 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. In DSC, the polymer was heated to the maximum temperature and cooled to 30℃ in -10 K/min, and then re-heated in the rate of 10 K/min. UV-Vis absorption spectra were recorded on Shimadzu UV-3150. Fluorescence spectra were measured on Shimadzu RF-5300PC.

2.1 Monomer synthesis

In scheme 1, the 9,9-dioctylfluorene-2,7-bis(trimethylene boronate), 2,7-dibromo-9,9-dioctylfluorene, 9,9-di(6-(2-(3-oxetanyl) butoxyl)hexyl)-2,7-dibromofluorene, and 9,9-dioctyl-2-bromofluorene were synthesized according to the literature [7b,8].



Scheme 1. Crosslinkable monomer synthetic route.

9,9-di(6-(2-(3-oxetanyl)butoxyl)hexyl)-2,7-dibromofluore ne (2). After degassing, the mixture of 1 (11.2g, 40 mmol), 2,7-dibromofluorene (3.2g, 10 mmol), tetra-n-butylammonium chloride, DMSO (70ml) and 50% aqueous NaOH solution (4ml) were stirred vigorously at 60℃ for 8 hr. The reaction mixture was allowed to cool to room temperature and extracted with ethyl acetate. The extract was washed with water and dried over anhydrous magnesium sulfate overnight. After removing the solvent using a rotary evaporator, a yellow transparent liquid was collected by distillation under reduced pressure. It was purified by column chromatography on silica gel with petroleum ether: ethyl acetate (5:1) as the eluent to afford 4 as a light yellow solid (yield: 75%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.50 (d, 2H), 7.43 (d, 2H), 7.41 (s, 2H), 4.38 (m, 8H), 3.42 (s, 4H), 3.30 (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 two hyperbranched crosslinkable polymers P1, P2 and linear polymer P0 were synthesized via palladium-catalyzed Suzuki couplings [9]. The contents of the monomer in P0, P1 and P2 are listed in Table 1.

2.3 Crosslinking procedure

The crosslink procedure was done according to the literature [10].

Table 1. Monomer content in polymer.

Monomer	P0	P1	P2
9,9-dioctylfluorene-2,7-bis(trimethylene boronate)	50%	45%	7.5%
9,9-di(6-(2-(3-oxetanyl)butoxyl)hexyl)-2,7-dibromofluorene	50%	50%	62.5%
1,3,5,-tribromobenzene		5%	30%

3. Results and discussions

3.1. Design and synthesis

We choose a different way to synthesis the monomer 2 compared to the literature [10]. As a convenient synthesis procedure, the monomer 2 was obatained in high yield of 80%. In the experiment, interestingly, the monomer 2 is a light yellow solid compound rather than a yellow oil-like compound.

For hyperbranched polymers, the conventional synthesis methods are the AB2 and A2 + B3 approaches [7a, 11] As a useful way to synthesis hyperbranched polymer, CMM method can be used for multi-monomer couple [11]. Based on our experience in hyperbranched polymer, we think the A2 + B2 + B3' method [7b] is a competitive way for the introduction of multi-component and easy to control the content of the monomer. In P1 and P2, we change the relative content of the two kinds of

function group related to the different content of the core to make they are slightly unequal. In one hand, we need to avoid the gelation if the function group can react completely. On the other hand, the relatively large difference of the content of function group can lead to the lower molecular weight. The reaction condition of course executes influence which is very complicated. In our experiment, we got the polymer in 60% yield via Suzuki polycondensation. P0, P1, and P2 can be dissolved in $CHCl_3$, THF, and toluene. The NMR data are listed as follows.

P0: ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.85 (d), 7.70 (d), 7.59 (s), 7.49 (t), 4.40 (m), 3.45 (s), 3.33 (s), 2.13 (broad), 1.68 (m), 1.43 (broad), 1.14 (broad), 0.82 (m).

P1: ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.84 (broad), 7.69 (broad), 4.36 (m), 3.45 (s), 3.33 (s), 2.12 (broad), 1.68 (broad), 1.43 (broad), 1.14 (broad), 0.82 (s).

P2: ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.93-7.74 (broad), 7.37 (broad), 6.85 (broad), 4.36 (d), 3.44 (s), 3.32 (s), 2.13-2.03 (broad), 1.67 (broad), 1.12 (s), 0.80 (s).

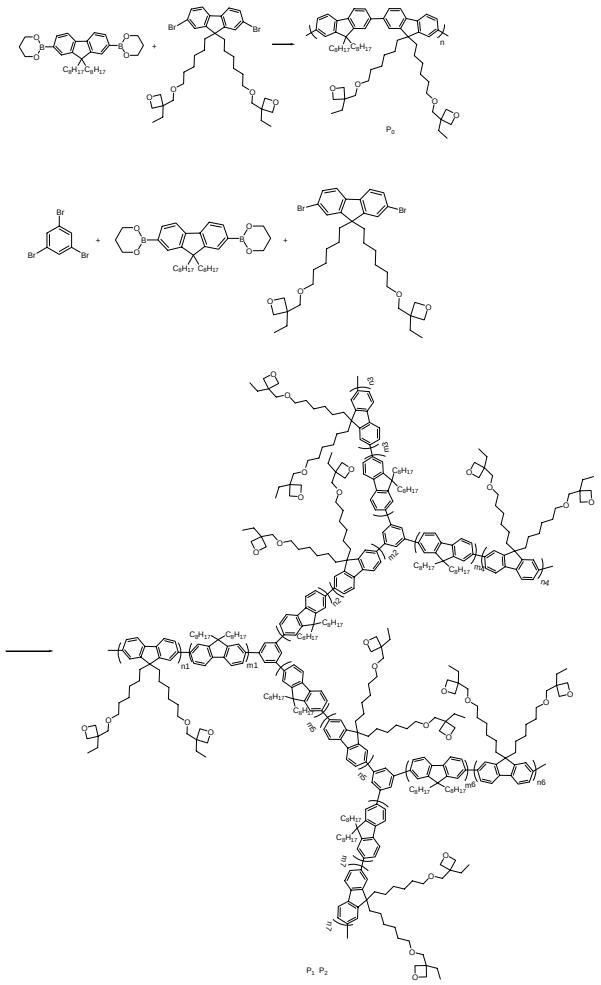
Compared to P0 and P1, the signal of hydrogen located in tribromobenzen appears around 6.85ppm for P2 while it is not obvious for P1 which indicates the variation of the content of the core. At the same time, the peak around 4.36ppm of P2 which represents the hydrogen in oxetane become smaller than that of P1 and P0 which indicates the less content of 2 in P2.

3.2. Molecular weight and thermal properties

The molecular weights and thermal properties of these polymers are listed in Table 2. The number-averaged molecular weights and polydispersity indices (Mn, PDI) of the P0, P1, P2 are (12000, 1.92), (216000, 1.30) and (10500, 1.24) respectively.

Table 2. Molecular weights and thermal properties of polymers.

polymer	Mn	Mw	PDI	Tg (℃)	Td (℃) (by 5% decomposition)
P0	12000	23000	1.92	-	378
P1	216000	280000	1.30	-	355
P2	10500	13000	1.24	-	359



Scheme 2. Polymers synthetic routes.

In DSC measurement, the P0, P1, P2 don't show distinct temperature of glass transition. Fig. 1 is the TG analysis of the polymer P0, P1, P2. From the thermogravimetric analysis, we can see that the thermal decomposition temperature all exceed 350 ℃ which indicates the thermal stability of the polymers is very good.

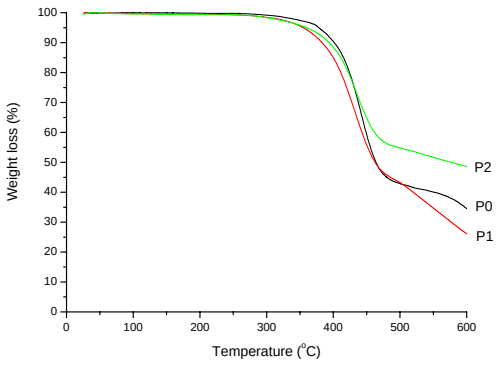


Fig. 1. TG analysis of polymer P0 P1 P2.

3.3 Spectroscopic properties

Fig. 2 displays the UV-Vis spectra of P0, P1 and P2 in solid film (a) and toluene solution (b). The maximum absorption peak of solid film of P0, P1, P2 are found as 386, 382, 345 nm respectively while in toluene solution are found as 383, 381, 340 nm separately. By comparison with the P0 and P1, the P2 shows the shorter wavelength absorption both in film and solution. For P1, the relatively less content of the core tribromobenzene has little effect on the UV-Vis absorption spectrum comparing to P0. For P2, with the large increase of the content of the core, the polymer exhibits different spectra behavior.

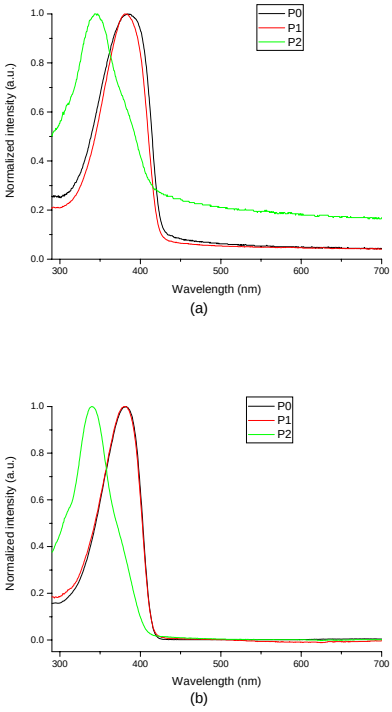


Fig. 2. UV-Vis spectra of polymers in film state (a) and toluene solution (b).

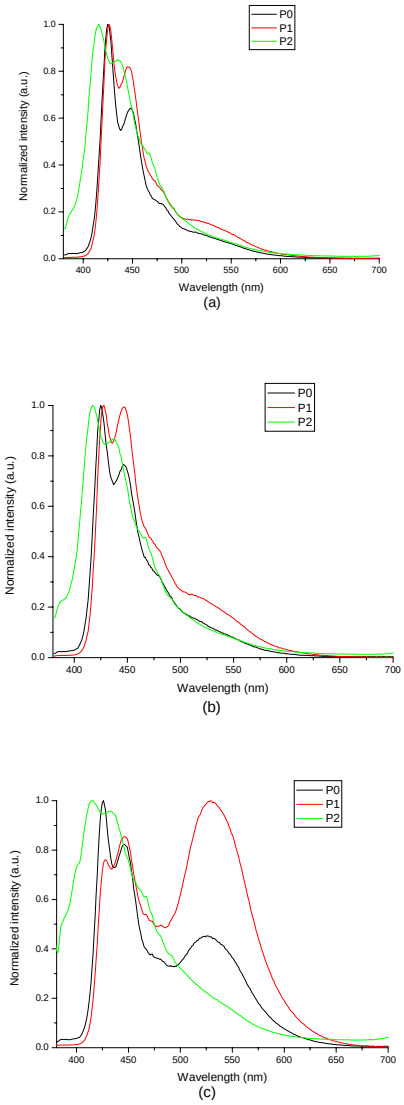


Fig. 3. PL spectra of polymers in film state before crosslink (a) and after crosslink (b) and annealing at 200℃ 3 hours after crosslink (c).

Fig. 3 shows the photoluminescence (PL) spectra of the polymer P0, P1, P2 in film state before crosslink (a) and after crosslink (b) and annealing at 200℃ 3 hours after crosslink (c).

The maximum emission peaks of P0, P1 and P2 before crosslink are located at 425, 426, 416 nm and after crosslink are at 425, 428, 417 nm. This indicates the crosslink procedure has little effect on the PL spectra.

After annealing, P0 and P1 all show the longer wavelength emission around 530 nm while the maximum emission peaks of P2 is still at 416 nm. This means the P2 is very stable in higher temperature.

From Fig. 3, it can be clearly seen that the annealing temperature strongly influence the photoluminescence spectra after crosslinking. Because the hyperbranched structure could prevent the aggregation and crystallization of the rigid polymer chains, it is reasonable that the P2 with higher core content exhibits stable spectra in elevated temperature.

4. Conclusion

We have synthesized a kind of new crosslinkable hyperbranched polyfluorene with the improved fluorescence spectra even anneal at high temperature. The introduction of the crosslinkable group has little influence

on the spectra. Research of the reported blue-light-emitting hyperbranched crosslinkable polyfluorene in multilayer and multicolor PLED is under way.

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