Decreased Aggregation Phenomena in Polyfluorenes by Introducing Carbazole Copolymer Units

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ABSTRACT: To decrease aggregation phenomena and improve the luminescence of the blue-light-emitting polymer polyfluorene, carbazole units were copolymerized to introduce disorder in the polymer backbone. A "kink" linkage was introduced into the polyfluorene chain by forming a 9:1 and 7:3 copolymer with the carbazole group at the 3,6 positions. The disordered polyfluorene was made though a Ni-catalyzed reaction, which resulted in high yield and high molecular weight polymers. The structure and physical properties were confirmed by NMR, SEC, UV absorption, photoluminescence, elemental analysis, and quantum yield measurements. The copolymers exhibited better spectral properties both in solution and in film compared to previously synthesized polyfluorene homopolymers. Annealing studies showed both improved thermal and UV stability of the copolymer over previously reported homopolymers. Cyclic voltammetry studies showed a slightly lower highest occupied molecular orbital (HOMO) than the homopolymer.

Introduction

From the first demonstration of polymer light-emitting diodes (PLED)s in the 1990s,¹ the work on conjugated polymer materials has intensified.² Conjugated polymers with different chemical structures emitting different colors in the whole visible range have been designed, and devices based on these materials have been fabricated.^{3,4} The structure of a polymer lightemitting diode is simple. The emitting layer is sandwiched between two electrodes, a transparent anode (normally ITO) and a low-work function metal cathode, such as Ca and Al. Applying a voltage bias results in electroluminescence, which is mainly due to electron and hole charge carrier recombination. The balance of charge injection is very important in achieving high efficiency.⁵ Poor interfacial contact between the polymer and anode interface and chain aggregation can also lead to poor performance of a polymer light-emitting diode.^{6,11}

A stable blue polymer light-emitting diode is still a challenge for polymer scientists. Because of the large band gap between the LUMO and HOMO energy levels, it is hard to achieve a balanced charge injection. Polyfluorene, as a blue light emitter, is a promising material due to its high efficiency and good thermal stability.^{7–12} However, chain aggregation tends to de-grade the device performance.^{11,12} This physical degradation usually results to a red-shifted fluorescence and reduced intensity by exciton migration and relaxation through lower energy excimer traps.¹¹ Excimers are known to provide nonradiative relaxation pathways in conjugated polyfluorenes which lead to reduced emission efficiency relative to exciton luminescence.¹¹ Rigid-rod polyfluorenes have a tendency toward a nematic type of packing arrangement in the bulk and thus are inherently prone to chain aggregation.^{6c,11} To depress chain aggregation and increase quantum efficiency, the introduction of disorder to the conjugated system seemed to be a good route. Son et al.¹³ engineered the distribution of cis linkages in poly(phenylenevinylene) (PPV) chains. The cis linkages interrupt conjugation and interfere with the packing order of the polymer chains. The devices fabricated on this material performed significantly better. Another problem for polyfluorene is its poor hole-transporting abilities.¹⁴ Carbazole derivatives are widely used as hole-transporting materials between the emitting layer and the anode to balance the charge injection.¹⁵ Incorporating them in the polyfluorene structures seemed to be another route in improving the energy level mismatch between the anode and polyfluorenes. Recently, the molecular design and characterization of thiophene copolymer derivatives of polyfluorenes have been reported.¹⁶ Interesting thermochromic and solvatochromic properties were reported on the basis of disordered structures due to alternation of the chain planarity. However, the excitonic effects were not investigated in detail.

In this paper, we outline our strategies in improving the material properties of polyfluorenes, which can eventually be useful for PLED device applications. We have introduced the carbazole unit linkage through the 3,6 positions into poly(2,7-9,9-dioctylfluorene) polymers. The linear structure of the polyfluorene is interrupted by the linkages to the carbazole units. We intend to introduce a "kink" disorder on the conjugated polymer chain, to depress the aggregation phenomena and its effect on the excimer formation. The introduction of carbazole units may also influence the HOMO energy level, resulting in better hole-transporting ability for polyfluorene. Different minimal carbazole unit ratios in the polymer composition were incorporated to study the trend of the properties. The schematic illustration for this strategy is shown in Scheme 1.

Experimental Section

Materials. The commercial products fluorene, ethylcarbazole, bromine, bromooctane, *N*-bromosuccinamide (NBS), bis-(cyclooctadiene)nickel(II) or Ni(COD)₂, cyclooctadiene, and 2,2'bipyridyl were purchased from Aldrich and used as received. Tetrahydrofuran (THF) and toluene were purchased from Fisher and distilled over sodium and benzophenone ketyl prior

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Scheme 1. Schematic Illustration of Disorder in Polyfluorene



to use. Dimethylformamide (DMF) was purchased from Fisher and distilled over calcium hydride.

Instrumentation. NMR spectra were collected on a Bruker ARX 300 spectrometer with chloroform-d as solvent and TMS as internal standard. UV-vis and fluorescence spectra were obtained on a Perkin-Elmer Lambda 20 spectrometer and Perkin-Elmer LS50B spectrometer, respectively. Quantum efficiencies of each polymer in solution were determined using a dilute diphenylanthracene solution in cyclohexane (with PL efficiency of 0.90) as the standard.¹⁷ The polymer film (yield) efficiencies were also measured using diphenylanthracene, dispersed in PMMA spin-coated film with concentration less than 10⁻³ M with PL efficiency of 0.83) as the standard.¹⁸ Size exclusion chromatography (SEC) data were measured on a Waters chromatography setup using polystyrene as standard. A cyclic voltammogram was obtained on a Amel 2049 potentiostat and Power lab system (4sp) with a three-electrode cell in a solution of tetrabutylammonium tetrafluoroborate (0.1 M) in acetonitrile at a scan rate of 20 mV/s. A Mettler DSC30 and TG50 were used to record the differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), respectively. The ellipsometric film thickness was measured using a Multiskop instrument from Optrel GbR at 70° incidence and 632.8 nm HeNe light source.

Synthesis of 2,7-Dibromofluorene. Fluorene (2.493 g, 15 mmol), NBS (10.68 g, 60 mmol), ferric chloride (0.1 g), and DMF (60 mL) were mixed and heated to reflux for 5 h under darkness. The resulting mixture was then poured into water and extracted with methylene chloride. The organic layer was washed extensively with dilute hydrochloric acid, sodium bicarbonate, and water and dried over magnesium sulfate. The solvent was evaporated under vacuum. The residue was recrystallized from ethanol, and 3.9 g of the product was obtained (yield 81%). ¹H NMR: δ (ppm) 7.66 (d, 2H), 7.60 (d, 2H), 7.50 (dd, 2H), 3.86 (s, 2H). ¹³C NMR: δ (ppm) 144.6, 139.5, 130.0, 128.2, 121.0, 120.1, 36.4. Elem. Anal. Calcd: C, 48.19; H, 2.49; Br, 49.32. Found: C, 48.39; H, 2.53.

Synthesis of 2,7-Dibromo-9, 9-dioctylfluorene. 2,7-Dibromofluorene (3.00 g, 9.26 mmol) was reacted with *n*-bromooctane (4.46 g, 23.1 mmol) in a two-phase system composed of toluene (20 mL) and sodium hydroxide (50% w/w) aqueous solution using tetrabutylammonium bromide (0.3 g, 0.9 mmol) as the phase transfer catalyst at 60 °C for 4 h. After diluting the reaction mixture with ethyl acetate, the organic layer was washed with water. The separated organic layer was

dried over magnesium sulfate, and the solvent was evaporated. The crude product was recrystallized from ethanol to give 4.20 g of pale yellow needle crystals (yield 83%). ¹H NMR: δ (ppm) 7.52 (d, 2H), 7.45 (d, 2H), 7.43 (d, 2H), 1.90 (p, 4H), 1.26–1.05 (m, 20H), 0.83 (t, 6H), 0.58 (m, 4H). ¹³C NMR: δ (ppm) 152.4, 138.9, 130.0, 126.1, 121.4, 121.0, 55.6, 40.0, 31.6, 29.8, 29.0, 23.5, 22.5, 13.9. Elem. Anal. Calcd: C, 63.51; H, 7.35; Br, 29.14. Found: C, 63.33; H, 7.33.

Synthesis of 3,6-Dibromo-9-ethyl-9H-carbazole. Bromine (3.52 g, 22.0 mmol) was added very slowly to a solution of 9-ethylcarbazole (2.00 g, 10.2 mmol) in chloroform with 20 mg of ferric chloride as the catalyst at 0 °C. After addition, the mixture was warmed to room temperature for another 3 h. The resulting mixture was then poured into water. The excess of bromine was washed away by sodium sulfite solution. The organic layer was washed by brine and water, dried over magnesium sulfate, and the solvent was evaporated. The crude product was run through a column using hexanes as eluent. 1.8 g of title compound was obtained (yield 48%). 0.6 g of monosubstituted bromide compound was also separated.¹H NMR: δ (ppm) 8.12 (d, 2H), 7.55(dd, 2H), 7.26(d, 2H), 4.29 (q, 2H), 1.39 (t, 3H). ¹³C NMR: δ (ppm) 138.8, 129.0, 123.5, 123.3, 111.9, 110.1, 37.8, 13.7. Elem. Anal. Calcd: C, 47.63; H, 3.14; Br, 45.26; N, 3.97. Found: C, 47.69; H, 3.24.

Synthesis of P9F1C and P7F3C. In a Schlenk tube was place Ni(COD)₂ (0.619 g, 2.20 mmol), 2,2'-dipyridyl (0.243 g, 2.20 mmol), cyclooctadiene (0.352 g, 2.20 mmol), and DMF (5 mL). After three freezing-thaw cycles, the catalyst was heated to 80 °C for half an hour to form the purple complex. 2,7-Dibromo-9,9-octylfluorene (0.494 g, 0.90 mmol) and 3,6dibromo-9-ethylcarbazole (0.0353 g, 0.1 mmol) in toluene (6 mL) were added to the solution and heated at 80 °C for another 4 days. The ratio of the monomers was varied for the different copolymer compositions. After cooling to room temperature, the reaction mixture was poured into 100 mL of HCl, 100 mL of acetone, and 100 mL of methanol and stirred for 2 h. The solid was filtered, redissolved in chloroform, and precipitated in large amount methanol. The pale yellow solid was dried in a vacuum at 60 °C for 48 h (0.320 g, yield 87%). ¹H NMR: δ (ppm) 8.51 (b, 0.21H), 7.86-7.7.34 (m, 6.4H), 4.48 (b, 0.22H), 2.21(b, 4H), 1.14(b, 24H), 0.81(t, 6H). ¹³C NMR: δ (ppm) 152.0, 140.7, 140.2, 126.3, 121.7, 120.2, 55.6, 40.6, 32.0, 30.3, 29.5, 24.1, 22.8, 14.3. Elem. Anal. Calcd: C, 89.44; H, 10.18; N, 0.38. Found: C, 88.42; H, 10.10; N, 0.39. The synthesis of P7F3C was also done in a similar manner with spectrochemical characteristics similar to P9F1C. Elem. Anal. Calcd: C, 89.11; H, 9.62; N, 1.27. Found: C, 88.82; H, 9.58; N, 1.23.

Results and Discussion

Synthesis. Scheme 2 shows the synthetic route for the monomer synthesis and polymerization. NBS was used to brominate the 2,7 position of fluorene with a relatively high yield. This method is simpler compared with the copper bromide method.¹⁹ NBS is a good reagent for nucleophilic substitution in DMF.²⁰ At room temperature, even an excess of NBS gave the monosubstituted product of 2-bromofluorene. However, by varying the temperature, most of the product resulted in 2,7-dibromofluorene.

The polymer was synthesized by a well-known method, the so-called Yamamoto coupling reaction.²¹ For this study, the feed mole ratio of the fluorene and carbazole were varied to 9:1 and 7:3 for **P9F1C** and **P7F3C**, respectively. A polyfluorene homopolymer, **PFO**, was also made through this method for control experiment. The rationale for this 9:1 ratio is in trying to obtain polyfluorene-like properties for comparison with minimum doping of carbazole units. The **P7F3C** was made to compare the properties derived from increased carbazole content. The copolymers are statistical random copolymers containing both of the components. The introduction of the 3,6-substituted carbazole offers a

Scheme 2. Synthetic Route of the Monomers and the Polyfluorene Copolymer



disorder in the linear polyfluorene chain (Scheme 1). The structure of the polymer was confirmed by NMR and elemental analysis. Figure 1 shows the ¹H NMR of **P9F1C** and **P7F3C**. The polymer composition can be estimated by the integration area of the peaks from the ¹H NMR. The peak at 4.48 ppm is attributed to the protons connected to nitrogen in the carbazole unit. The peak at 2.12 ppm is attributed to the protons adjacent to the ninth position in the fluorene unit. The area ratios for the two polymers are 1:18.22 and 1:5.33, respectively, and the calculated fluorene content for the copolymers



(b)

Figure 1. (a) $^1\mathrm{H}$ NMR spectra of P-9F-1C. (b) $^{13}\mathrm{C}$ NMR spectra of P-9F-1C.

Table 1. Structural and Thermal Properties of the Polymers

		-		
M _n	$M_{ m w}$	DPI	<i>T</i> g (°C)	TGA (5 wt % loss)
1 600 6 200 7 000	69 700 88 700 48 700	1.68 1.92 1.80	113 79	418 412 408
	M _n 1 600 6 200 7 000	$ \begin{array}{cccc} M_{\rm n} & M_{\rm w} \\ 1 600 & 69 700 \\ 6 200 & 88 700 \\ 7 000 & 48 700 \\ \end{array} $	M _n M _w DPI 1 600 69 700 1.68 6 200 88 700 1.92 7 000 48 700 1.80	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

are 90% and 73%, which are quite consistent with the monomer feed ratios. Elemental analysis results also confirmed the fluorene content in the copolymers by calculation from the nitrogen content in the polymers. The molecular weight of the polymers was determined by size exclusion chromatography (SEC) and calibrated by polystyrene standards. This polymerization process gave quite high molecular weight values. The initial results showed the number-average molecular weights are higher than 10 000 (Table 1). This high value is typical of what has been reported for polyfluorenes synthesized using this method, as determined by SEC.²² Absolute molecular weight determination is needed in order to assign the degree of polymerization. The molecular weight of the polymer can be controlled by the amount of the nickel catalyst, reaction temperature, and reaction time. By using more than 2-fold of the nickel catalyst, higher molecular weight products could be obtained. In addition, excess of nickel catalyst can reduce the terminal halogen content. The terminal unit is regarded to be a fluorene or carbazole group, which is considered to originate from the intermediate Nifluorene-polymer or Ni-carbazole-polymer species, giving octylfluorene-polymer or carbazole-polymer species during workup after polymerization.²¹ The elemental analysis results showed no halogen content in the polymers, which supports the suggested termination mechanism.

P9F1C has a glass transition temperature (T_g) at about 79 °C as determined by DSC. This is lower than the fluorene homopolymer (113 °C) and most of the previously reported values for polyfluorenere and verifies the effect of the carbazole in introducing disorder. No discernible glass transition temperature was ob-



Figure 2. TGA trace of P-9F-1C.

tained for **P7F3C**. The thermal stability of these polymers was studied by TGA. Like other polyfluorene derivatives, these polymers also exhibit a high thermal stability, showing 5% weight loss at higher than 400 °C. The thermal decomposition curve of **P9F1C** is shown in Figure 2. The decomposition of the polymer involves two steps. The first step starts from 357 °C and has a sharp loss until 51% of the mass. The second one starts from 678 °C. The first step may be assigned to the side chain decomposition and the second one to the main chain. Both PFO and P7F3C showed similar results (Table 1).

Spectroscopic Properties. The absorption and emission spectra of the polymers are shown in Figure 3, and the results are summarized in Table 2. P9F1C has an absorption maximum at 384 nm and an onset at 427 nm. Miller et al.23 studied the absorption maximum related to different oligomer chain lengths, which reflects the conjugation length. An oligomer with 10 fluorene units has absorption at 384 nm. Compared with their results, the polymer made here should have comparable persistent conjugation lengths to that of an oligomer with 10 fluorene units. As the carbazole content in the copolymer increases, the conjugated length decreases, which can be seen from the absorption spectra of **P7F3C**. This polymer shows an absorption peak at 374 nm and an onset at 413 nm. It is reasonable that the 3,6-substitution of the carbazole decrease the conjugation, since the linear π -system was interrupted. As shown in Figure 3, all the polymers in THF solution have emission peaks at around 417 and 440 nm, which is typical for polyfluorene. The absorption of the films spin-coated from 1% xylene solution at 2000 rpm has a small shift to short wavelength. Unlike the polyfluorene film, which has an aggregation peak at around 520 nm besides two excitonic emission peaks, the photoluminescence of the copolymer films only show peaks at around 424 and 447 nm. Both polyfluorene homopolymer and the copolymers exhibit very high quantum efficiencies (yield) in solution. A typical value for these polymers is higher than 0.70. As has been studied before, polyfluorene film exhibits a form of intermolecular aggregation, resulting in long wavelength featureless emission. The aggregation is also molecular weight dependent in which a higher molecular weight gives less aggregation.²⁴ The polyoctylfluorene homopolymer **PFO** made in this report is among the highest molecular weights that have been reported, but the aggregation peak at around 520 nm can still be observed. The lack



Figure 3. Absorption and photoluminescence spectra of the polymers.

Table 2. Spectra Properties and Quantum Yield

	solution			film		
	Ab (nm)	PL (nm)	φ	Ab (nm)	PL (nm)	φ
PFO	389	417, 439	0.78	383	425, 447, 520	0.40
P9F1C	384	417, 438	0.74	383	424, 447	0.71
P7F3C	374	417, 440	0.81	370	424, 447	0.50

of the excimer emission on the **P9F1C** (and **P7F3C**) films proves that even introducing a 10% amount of carbazole linkage can influence the packing of the polymer chains in a film, greatly enhancing the quantum efficiency, which is almost doubled compared with the polyfluorene homopolymer (Table 2).

Annealing Studies. To study the structural and conformational changes of the polymer in the film state, annealing experiments were performed on **P9F1C**. The film was spin-coated on a quartz substrate and then annealed at 200 °C at various durations. Figure 4a shows the absorption spectra upon annealing. No change was observed for the absorption spectra compared to the unannealed state. All the films annealed for different times showed similar spectra, with a maximum at 384 nm, which is also identical with the absorption of the polymer in THF solution.

However, the emission peaks of polyfluorene copolymer at around 420 and 447 nm decreased rapidly upon annealing at 200 °C under air, while the excimer peak around 520 nm increased. Annealing results in a



Figure 4. Absorption and photoluminescence changes under annealing different times: (a) Ab, (b) PL.

progressive growth and alignment of aggregate regions or domains in the film. These regions tend to trap and quench the energy of the exciton population mainly due to excimer formation and delocalization. Previous studies have also shown that this broad peak, attributed to a polymer ordering rearrangement, can be deconvoluted to three excimer peaks located at 491, 524, and 562 nm.¹¹ Unlike the polyfluorene homopolymer, the photoluminescence of these copolymers is more stable upon annealing. The excimer peak increases very slowly at around 520 nm up to 30 min. For previously reported homopolymers the observed increase was much faster.¹¹ Annealing at such temperatures, which is much higher than the glass transition temperature, can cause movement of the chain segments and increase the packing order. However, the disorder introduced through the cabazole unit depresses this tendency toward π -stacking and nematic arrangement.^{6c} Similar observations on the effect of disorder to chromic behavior of other polyfluorene copolymers have been reported by Leclerc.¹⁶ They have attributed this to the increased conformational flexibility of the copolymers to interchain interaction resulting in the incorporation of nonfluorene comonomer units.

Band Gap Studies. The redox behavior of the polymers were investigated by cyclic voltammetry (CV) with a standard three-electrode electrochemical cell in a 0.10 M tetrabutylammonium tetrafluoroborate solution in



Figure 5. Cyclic voltammogram of the polymer films. Scan rate: 20 mV/s.

Table 3. Band Gap Characteristics of the Polymers As Determined from CV Data and Absorption Onset

	absorption onset (nm)	band gap (eV)	$\begin{array}{c} \text{oxidation onset} \\ V \ (vs \\ Ag/Ag^+(0.01 \ M)) \end{array}$	HOMO (eV)	LUMO (eV)
PFO P9F1C P7F3C	427 427 413	2.9 2.9 3.0	1.09 0.93 0.84	$-5.8 \\ -5.6 \\ -5.5$	$-2.9 \\ -2.7 \\ -2.5$

actonitrile at room temperature under nitrogen with a scanning rate of 20 mV/s. A platinum working electrode, counter electrode, and an Ag/Ag⁺ (0.01 M in ACN) reference electrode were used. This reference electrode potential was calibrated to be 0.32 V higher than Ag/AgCl (3 M NaCl) electrode that was used to calculate the HOMO and LUMO. The anodically scanned cyclic voltammograms are shown in Figure 5. The oxidation process of **P9F1C** has an onset at 0.93 V (vs Ag/Ag⁺-(0.01 M)) and gives a peak at 1.28 V (vs Ag/Ag⁺(0.01 M)). The oxidation is pseudoreversible and gives the corresponding reduction peak at 0.93 V (vs Ag/Ag⁺(0.01 M)). As shown in Figure 6, the fluorene homopolymer has an onset at 1.09 V (vs Ag/Ag⁺(0.01 M)) and a peak at 1.56 V (vs Ag/Ag⁺(0.01 M)), which is slightly higher than the copolymer. An interesting phenomenon was observed for **P7F3C** during the electrochemical study. A small peak at around 0.83 V (vs Ag/Ag⁺(0.01 M)) emerged from the second cycle that was not observed in the first cycle. This peak could be attributed to the carbazole dimer formed during the first oxidation process.^{25,26} This is consistent with some of the polymer chains terminated with carbazole units which are still electrochemically active especially at the 3,6 positions. This probability is certainly higher for the P73FC compared to **P9F1C** because of the higher carbazole content. The cathodic wave was not observed from all of the polymers beyond the solvent limit. The energy levels of the HOMO and the LUMO were thus estimated from the cyclic voltammograms and the onset of the absorption spectra. The results are summarized in Table 3. The copolymers with carbazole units have slightly lower energy levels than that of the polyfluorene homopolymer, which means that a better hole transporting ability can be expected. PLED devices will be prepared in collaboration with another group to verify electroluminescence behavior compared to polyfluorene homopolymers.

Conclusions

Our results show that carbazole units can be incorporated to polyfluorene derivatives in a statistical manner using the Yamamoto coupling method of synthesis. The minimum carbazole unit in the polymer backbone was designed to introduce disorder in the linear polyfluorene chain. The polymers exhibit blue emission upon excitation. Annealing at 200 °C under air produced a smaller change in the luminescence up to 30 min, showing greater stability than the polyfluorene homopolymer toward aggregation. The introduction of the disorder into the conjugated polymer backbone also enhanced the quantum yield of the film. CV studies showed that the oxidation potential of the copolymer decreased as the carbazole content increased compared to the alkyl fluorene homopolymer. This has important implications on chemical tuning of hole-transport properties for these materials. Thus, the possibility of improved polyfluorene materials and luminescence properties through carbazole copolymerization has been demonstrated.

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