

## Blue light-emitting polyalkylfluorene copolymers for LEDs

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### Abstract

Blue light-emitting polyfluorene derivatives, poly[9,9-bis(4'-*n*-octyloxyphenyl) fluorene] (PBOPF), poly[9,9-bis(2'-ethylhexyl)]fluorene (PBEHF) and copolymers of PBOPF and PBEHF were synthesized through Ni(0) mediated polymerization and their light-emitting properties were investigated. The PBEHF thin film showed significant excimer band in PL spectra after thermal annealing at 100 °C for 2h. But no significant excimer emission was observed in the PL spectra of the PBOPF and the copolymers even after thermal annealing suggesting that BOPF unit effectively suppressed the excimer emission.

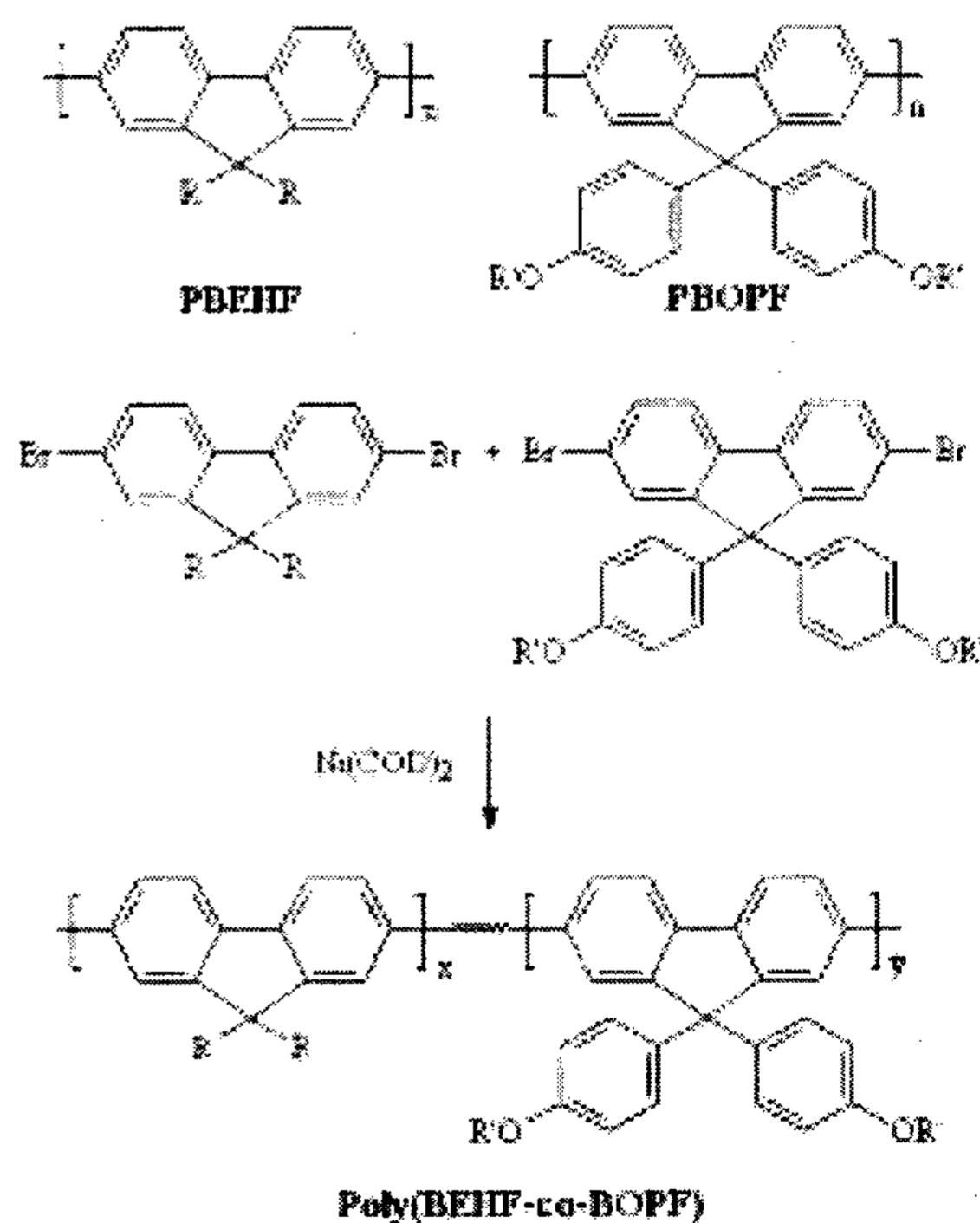
### 1. Introduction

A number of polyfluorene (PF) polymers and their derivatives have been studied since poly(9,9-di-*n*-hexylfluorene) (PDHF) was first reported as a blue-light emitting polymer [1]. The interest in these polymers arose because they show highly efficient photoluminescence (PL) and electroluminescence (EL), excellent thermal and oxidative stability, and good solubility in common organic solvents [2-4]. A major drawback of PFs, however, is that they show excimer and/or aggregate formation upon thermal annealing or the passage of current, leading to red-shifted emission. Continuing efforts have been made to suppress the excimer formation in PFs, including copolymerization with anthracene, end-capping with a sterically hindered group [5], and introducing sterically hindered substituents at the 9-position of fluorene [6].

Recently we synthesized a new PF derivative with two alkyloxyphenyl groups at the 9-position of fluorene, poly[9,9-bis(4'-*n*-octyloxyphenyl)]fluorene

(PBOPF). PBOPF showed stable and efficient blue light emission and no significant excimer emission was observed. In this paper, we suggest a new approach to suppress the excimer emission by introducing the BOPF in PFs as a comonomer. PBOPF, poly(9,9-bis(2'-ethylhexyl))fluorene (PBEHF) and copolymers of BEHF and BOPF, poly(BEHF-co-BOPF)s were prepared and their light-emitting properties were investigated. The chemical structures of the polymers are shown in Scheme 1.

Scheme 1



## 2. Experimental

UV-visible and PL spectra were recorded on Jasco V-530 and Spex Fluorolog-3 spectrofluorometers. The number and weight average molecular weight of polymers were determined by gel permeation chromatography (GPC) on a Waters GPC-150C instrument. The polymer film was prepared by spin casting the blend solutions containing 1 % by weight in chlorobenzene. Uniform and pinhole free films with a thickness around 80 nm were easily obtained from the polymer solution. For the double layer device, a modified water dispersion of PEDOT [poly(3,4-ethylenedioxy-thiophene)] doped with poly(styrene sulfonate) (PSS) was used as a hole-injection/transport layer. Metal contact (Ca) was deposited on the top of the polymer film through a mask by vacuum evaporation at pressure below  $4 \times 10^{-6}$  Torr, yielding active areas of  $4 \text{ mm}^2$ . In the case of Ca cathode ( $\sim 50 \text{ nm}$ ), an additional encapsulating layer of Al ( $\sim 200 \text{ nm}$ ) was thermally evaporated. For the measurements of device characteristics, current-voltage (I-V) changes were measured using a current/voltage source (Keithley 238) and an optical power meter (Newport 818-SL). Bright and 1931 CIE chromaticity of the EL devices were recorded by a PR-650 SpectraScan colorimeter. All processes and measurements mentioned above were carried out in air at room temperature.

## 3. Results and discussion

PBHEF, PBOPF, and two random copolymers of PBEHF and PBOPF were prepared through Yamamoto coupling reaction. The actual compositions of the poly(BEHF-co-BOPF)s were determined by  $^1\text{H-NMR}$  spectra. The feed mol ratios of the BOPF were 5 and 25 mol% of the total amount of monomers, and the determined actual BOPF mole ratios of the corresponding copolymers were 4 mol % and 24 mol %, respectively. The reactivity of the two monomers to the coupling polymerization reaction is supposed to be similar from the results.

The weight average molecular weight ( $M_w$ ) of the polymers ranged from 24,000 to 79,000 with a polydispersity index ranging from 2.0 to 4.0. All the synthesized polymers were soluble in common organic solvents, and formed transparent and smooth film after spin coating.

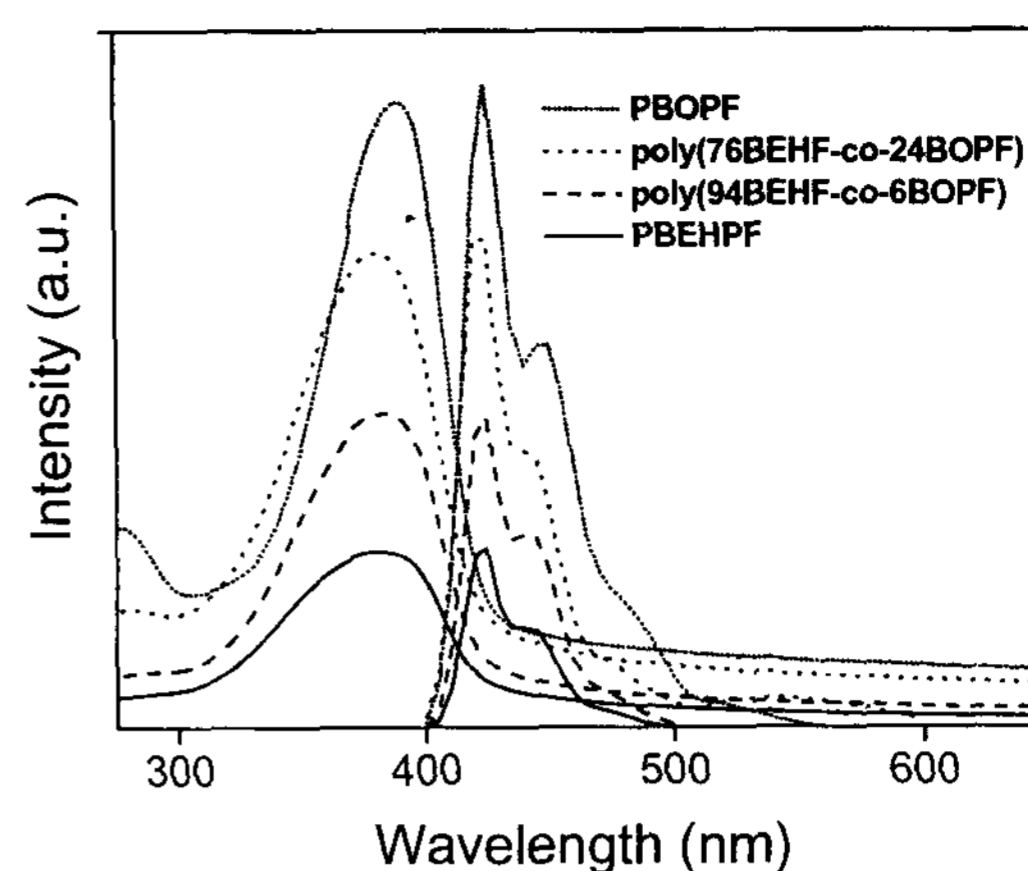


Figure 1. UV absorption and PL emission spectra of the polymers.

Figure 1 shows the UV-visible absorption and PL spectra of the thin films of the polymers coated onto fused quartz plates. The maximum UV absorption of PBOPF, PBEHF and copolymers are almost similar within 10 nm variation, and all the polymers showed peak PL emission at about 420 nm. In general, polyfluorenes are promising new materials for blue light emitting diodes, because of their high photoluminescence (PL) quantum efficiencies and thermal stability. In polymer film of polyfluorenes, however, troublesome long wavelength emission by excimer formation on heating during device formation or operation has been the crucial serious problem for practical applications.

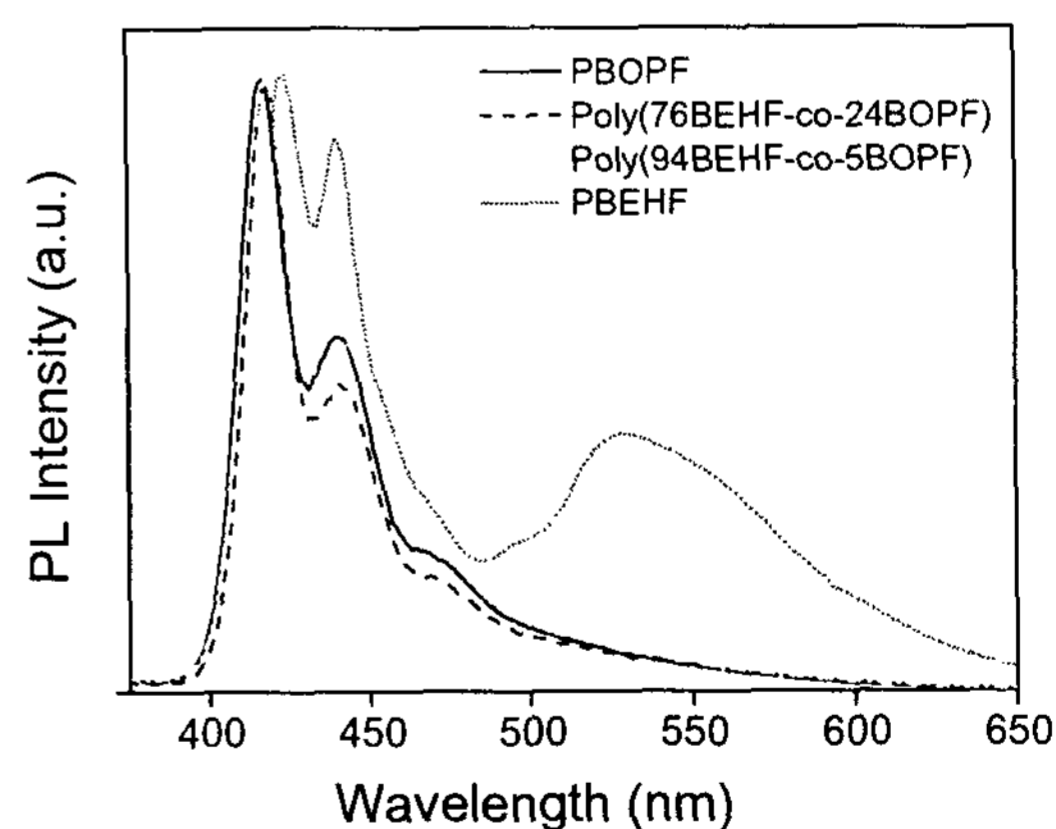


Figure 2. PL emission spectra of the polymer films after annealing at  $100 \text{ }^\circ\text{C}$  for 2h.

PBOPF was designed and synthesized to suppress the excimer emission by introducing long alkyloxyphenyl groups in 9-position of fluorene.

Figure 2 shows the PL spectra of the polymers after thermal annealing at 100 °C for 2h. In the PL spectra PBEHF thin film shows the significant excimer emission in 500~600 nm region. On the contrary, PBOPF and poly(BEHF-co-BOPF) films show the temperature independent stable PL emission. No significant excimer emission was observed in long wavelength region even after thermal annealing. Therefore, we believe that BOPF could be used as a useful comonomer in PFs for stable blue light emission because BOPF units effectively suppress the excimer emission and also improve the color purity of the EL device.

The EL devices with ITO/PEDOT(50 nm)/Polymer(80 nm)/Ca(50 nm)/Al(200 nm) configuration were fabricated according to the procedures described in experimental section. The EL spectra of the devices are almost similar to the PL spectra of the corresponding polymers, except for the peak intensities of the phonon side bands changed slightly. No significant excimer emission was also observed in EL spectra of the devices using PBOPF and the copolymers as in PL spectra. The forward current was increased with increasing the forward bias and showed typical diode characteristics. All the EL devices using the polymers showed observable blue light emission at about 3~4V. Especially, the device using PBOPF showed the best performance among the EL devices using the polymers. The maximum brightness was 375 cd/m<sup>2</sup> with luminous efficiency of 0.15 lm/W at 9V.

#### 4. Conclusion

In conclusion, we successfully synthesized

stable blue light-emitting polyfluorene derivatives, PBOPF and poly(BOPF-co-BEHF)s through Ni(0) mediated coupling reaction. The PBOPF and BOPF containing copolymers were showed no significant excimer emission in their PL and EL spectra, suggesting that alkyloxyphenyl group could effectively suppress the long wavelength excimer emission. The EL devices were fabricated in an ITO/PEDOT/polymer/Ca/Al configuration. The EL spectra showed similar emissions to the PL results, and the EL device using PBOPF showed best performance among the devices using the polymers.

#### 5. Acknowledgements

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#### 6. References

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