# New Quinoline-Based Alternating Copolymers Containing a Fluorene Unit

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**Introduction.** Optical and electronic properties of polyquinolines have been studied extensively for their potential use in photonics and electronic applications. Some wholly aromatic polyquinolines, which are normally excellent electrical insulators, were reported to exhibit electrical conductivity as high as 10 S/cm when doped either with electron donors or by electrochemical reduction.[1] Certain fluorinated polyquinolines were also shown to be feasible for their use in the emissive layer in blue LED.[2] Third-order nonlinear optical properties of conjugated polyquinolines,[3] as well as photovoltaic and photoconducting properties[4] of polyquinoline, have been reported previously.

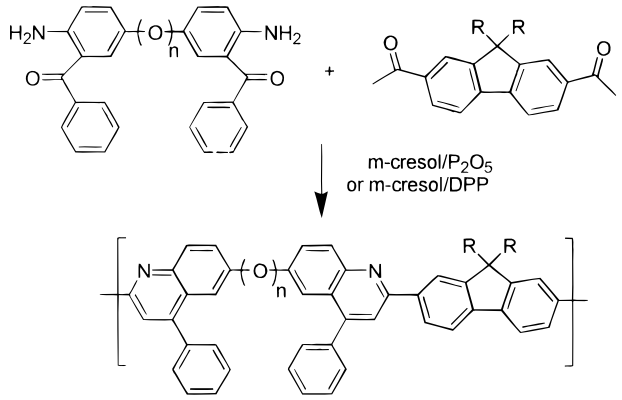
Blue-emitting polymer LED, difficult to achieve with inorganic materials, was first prepared by Yoshino et al.[5] using poly(9,9-dihexylfluorene) by oxidative coupling. The peak emission wavelength was 470 nm with blue visible light. Solid-state light-emitting electrochemical cells based on polyfluorene-containing bis(3,6-dioxaheptyl) side groups and a dissolved lithium salt emitted bright blue light at low operating voltages.[6] Recently reported fluorene-based alternating copolymers[7] showed stable blue and green emissions with good processibility.

In this report, we report characteristics of new polyquinolines having a 9,9-di-*n*-hexylfluorene moiety in the main chain prepared by Friedländer quinoline synthesis in an attempt to combine excellent thermal stability of polyquinolines with light-emitting properties of polyfluorenes.

**Monomer Synthesis.** 4,4′-Diamino-3,3′-dibenzoyldiphenyl ether[8] and 3,3′-dibenzoylbenzidine[9] were synthesized according to the literature. 2,7-Diacetyl-9,9-di-*n*-hexylfluorene was synthesized by general Friedel Craft acylation[10] of 9,9-di-*n*-hexylfluorene:[11] mp 53−55 °C; $^1$H NMR: $\delta$ 7.83−8.02 (m, 6H, aromatic), 2.70 (s, 6H, acetyl), 2.06 (m, 4H, $-OCH_2-$), 0.74−1.29 (m, 16H, $-CH_2-$), 0.56 (br, 6H, $-CH_3$). IR (KBr window, cm$^{-1}$): 2960, 2932, 2862, 1682, 1602, 1580, 1354, 1242, 826. Anal. Calcd for $C_{29}H_{38}O_2$: C, 83.21; H, 9.15. Found: C, 83.0; H, 9.37.

**Polymerization.[12] (1) POF66.** In a completely dried reactor, 5.1 g of phosphorus pentoxide were mixed in 12 mL of freshly distilled *m*-cresol. The mixture was heated to 140 °C for 2.5−3.5 h with continuous stirring under a nitrogen gas flow. This reaction mixture was prepared just before polymerization. The solvent in a polymerization medium was cooled to room temperature, followed by the addition of 0.6127 g (1.5 mmol) of 4,4′-diamino-3,3′-dibenzolydiphenyl ether and 0.6279 g (1.5 mmol) of 2,7-diacetyl-9,9-di-*n*-hexylfluorene. The reaction was stirred under a nitrogen gas flow at 140 °C for 60 h. The deep red polymerization solution was poured slowly into 500 mL of ethanol containing 50 mL of triethylamine and then continuously extracted with ethanol for 24 h. After drying 1.10 g (89%) of POF66 was obtained. Anal. Calcd for $(C_{55}H_{50}N_2O)_n$: C, 87.5; H, 6.67; N, 3.71. Found: C, 86.7; H, 6.65; N, 4.04.

**Scheme 1. Synthesis of POF66 and P1F66**




**POF66** n=1, R = hexyl
**P1F66** n=0, R = hexyl

**(2) P1F66.** Because of the rigid rod structure of P1F66, commercially available diphenyl phosphate was chosen as the catalyst to increase molecular weight.[13] A solution containing 0.3952 g (1 mmol) of 3,3′-dibenzoylbenzidine, 0.4186 g (1 mmol) of 2,7-diacetyl-9,9-di-*n*-hexylfluorene, 5 mL of *m*-cresol, and 7.5 g of diphenyl phosphate was heated to 140−142 °C for 2−3 h under a nitrogen gas flow. After 60 h, the same procedure as described in POF66 yielded 0.68 g (84%) of P1F66. Anal. Calcd for $(C_{55}H_{50}N_2)_n$: C, 89.39; H, 6.82; N, 3.79. Found: C, 89.0; H, 6.79; N, 4.15.

**Characterization.** IR spectra were recorded from a NaCl window on a Midac FT-IR spectrophotometer and a Varian 200 (200 MHz) was used for NMR measurements. GPC analyses of polymers were performed on a Waters HPLC component system equipped with five ultra-$\mu$-styragel columns ($10^5$, $10^4$, $10^3$, 500 Å) using THF as a solvent. DSC analyses were performed on a Perkin-Elmer DSC7 at a heating rate of 10 °C/min and TGA analyses were conducted with a Du Pont 2950 at a heating rate of 10 °C/min under a nitrogen gas flow. UV−vis spectra were recorded with a HP 8452A diode array spectrophotometer. Photoluminescence (PL) spectra and electroluminescence (EL) spectra were obtained using an ISS K2 multifrequency phase fluormeter equipped with a 300 W xenon arc lamp.

**Results and Discussion.** The new polymer POF66 and P1F66 were synthesized successfully according to Scheme 1 with good yields of >84%. The molecular weights of these polymers are $M_w = 6.01 \times 10^4$, $M_n = 2.73 \times 10^4$ and $M_w = 2.57 \times 10^4$, $M_n = 1.41 \times 10^4$, respectively. POF66 and P1F66 were soluble in common organic solvents such as $CHCl_3$ and THF. Figure 1 shows the $^1$H NMR and FT-IR spectra of POF66. The disappearance of the characteristic doublet absorption bands of amine (3450, 3350 cm$^{-1}$), carbonyl stretchings

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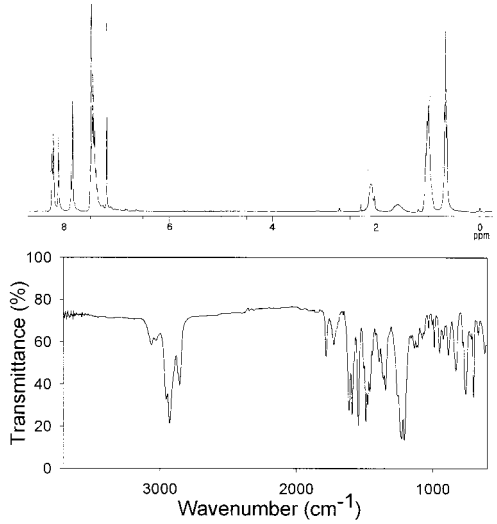


**Figure 1.** $^1$H NMR and FT-IR spectra of POF66.

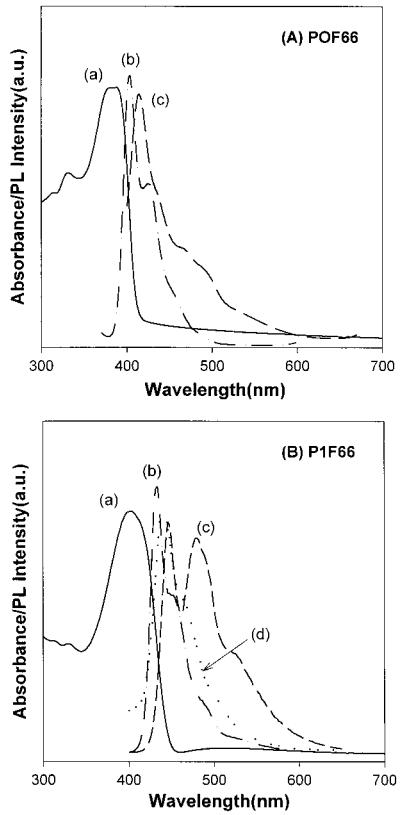


**Figure 2.** (A) POF66: (a) UV absorption spectrum (film), (b) PL spectrum of solution (in a $CHCl_3$, $10^{-5}$ M), and (c) PL spectrum of film of POF66. (B) P1F66: (a) UV absorption spectrum (film), (b) PL spectrum of solution (in a $CHCl_3$, $10^{-5}$ M), (c) PL spectrum of film of P1F66, and (d) PL spectrum of P1F66/PVK blend (20/80 by weight).

of acetyl (1682 $cm^{-1}$), and benzophenone (1625 $cm^{-1}$) units of the monomers and appearance of new strong bands near 1500 $cm^{-1}$ confirmed the complete polymerization.

Compared with typical polyfluorene,[11] POF66 and P1F66 showed highly thermal stabilities with initial decomposition temperatures of 425 and 420 °C, and retained 66% and 74% of their mass up to 600 °C under a nitrogen gas flow. The two polymers had $T_g$'s of 204 and 210 °C, respectively.

Figure 2 presents the absorption and emission spectra of POF66 and P1F66, and their intensities were normalized. The UV−visible maximum absorption peak of POF66 was 388 nm, which is attributed to the $\pi-\pi^*$ transition, and the PL spectra of POF66 showed emission maxima at 404 nm for solution and 414 nm for thin film when excited at 365 nm. The absorption maximum of P1F66 was 404 nm, which is red-shifted by 16 nm compared to POF66 because of its fully aromatic structure. The dilute solution PL spectrum (excited at 365 nm) of P1F66 showed a maximum peak at 434 nm and a minor shoulder at 450 nm, with blue emission. The PL spectrum of the thin film had two peaks at 446 and 480 nm and showed green emission. This broad peak around 480 nm and shoulder around 525 nm were likely due to interchain excimer emission.[14] To investigate the excimer formation of P1F66 in the solid state, P1F66 was blended with PVK.[15] A broad peak around 480 nm and shoulder around 525 nm disappeared in the P1F66/PVK blend film (20/80 by weight, excited at 340 nm), which is originated from the dilution effect of PVK. The dilute solution emission spectrum can be attributed to the singlet excited states of the single chain, but thin film emission of the conjugated polymer is originated from mainly singlet excimers. In contrast to P1F66, POF66 showed no additional broad emission peak in its thin film state, since the ether linkage of POF66 suppressed the chain packing in the solid state.

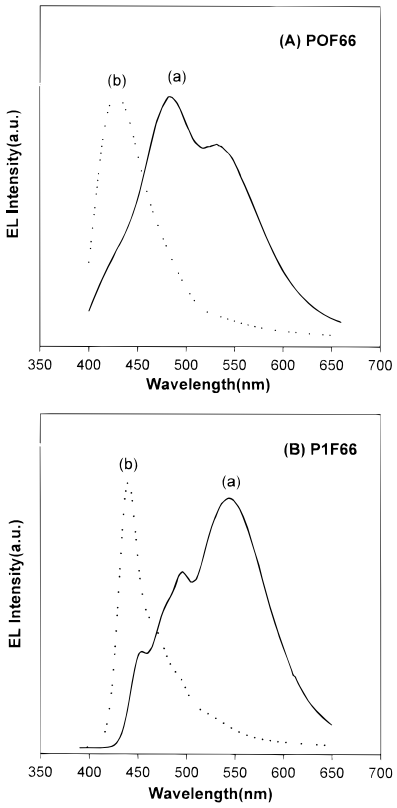


**Figure 3.** Normalized EL spectra of (A) POF66 and (B) P1F66: (A) (a) POF66 and (b) POF66/PVK blend (20/80 by weight); (B) (a) P1F66 and (b) P1F66/PVK blend (20/80 by weight).

Figure 3 shows electroluminescence (EL) spectra of POF66 and P1F66. When excited at 365 nm, the emission maximum for POF66 occurred around 480 nm in the blue region and P1F66 showed green emission with emission maximum around 544 nm. Both the polymers showed blue shift and sharpening of electroluminescence (EL) spectra when blended with PVK (20/

80 by weight, excited at 340 nm) because of dilution effect.

In summary, we report synthesis and characterization of two new polyquinolines (POF66, P1F66) containing a 9,9-di-*n*-hexylfluorene unit in the main chain using Friedländer quinoline synthesis. These two polymers were found to be thermally stable with initial decomposition temperatures over 420 °C. POF66 showed emission maxima at 404 nm in dilute solution and at 414 nm in thin film. P1F66 showed blue fluorescence in the dilute solution state ($\lambda_{max} = 434$ nm) and green fluorescence in the solid state ($\lambda_{max} = 446$, 480 nm) because of interchain excimer formation. EL spectra of POF66 and P1F66 lie in the blue region ($\lambda_{max} = 480$ nm) and the green region ($\lambda_{max} = 544$ nm), respectively.

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