Macromolecules **1999,** *32,* 1476−1481

Statistical Copolymers for Blue-Light-Emitting Diodes

H. N. Cho, J. K. Kim, D. Y. Kim, and C. Y. Kim*

Polymer Materials Laboratory, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

N. W. Song and D. Kim

National Creative Research Initiatives Center for Ultrafast Optical Properties Characterization and Spectroscopy Laboratory, Korea Research Institute of Standards and Science, P.O. Box 102, Yusung, Taejon 305-600, Korea

Received August 26, 1998; Revised Manuscript Received December 28, 1998

ABSTRACT: Fluorene-based statistical copolymers with *m*- and *p*-divinylbenzene were synthesized by the Heck reaction to fabricate blue-light-emitting diodes (LEDs). Photoluminescence (PL) spectra of the copolymers showed the maximum at 475 nm regardless of the concentration ratios between *m*- and *p*-divinylbenzene to reveal the complete energy transfer from the chromophore with the meta unit to the fluorophore of the para unit while 100% of the meta unit exhibited the emission maximum at 430 nm. The highest PL intensity was obtained with the ratio of 7/3 between the meta and para units. However, the time-resolved picosecond fluorescence study on the polymer solution revealed that the intramolecular energy transfer alone in the copolymers was incomplete to suppress the emission at 430 nm. The electroluminescence (EL) center of the copolymers was the same as that of the PL to show the maximum at 475 nm. The highest quantum efficiency of a single-layered LED fabricated with the light emissive copolymer with 30% of the para unit was observed to be 0.04%, which would be improved by optimization of the device characteristics.

Introduction

Significant progress in light-emitting diodes (LEDs) based on polymers has been made since poly(*p*-phenylenevinylene) was introduced as an electroluminescent (EL) material.[1] Polymers or their precursors are made soluble in organic solvents for easy processibility, and the strength of the polymer films makes flexible LEDs possible.[2] The most important advantage of using polymers as light-emitting materials in LEDs is to synthesize the polymers as designed for specific purpose.[3]

A few polymers[4−7] have been proved to be suitable for fabricating prototypes of LEDs which emit green, orange, or red color. The polymers show good processibility, high quantum efficiency, and long lives of shelf and stress. However, a reliable blue-light-emitting polymer has yet to be developed.

A few attempts have been made to synthesize polymers with a large band gap to emit blue color. Polydialkylfluorene (PDAF) was the first one introduced as a blue-emitting polymer[8] followed by poly(*p*-phenylene) (PPP).[9] PPP was modified to be soluble in organic solvents while keeping the band gap intact for blue emission.[10−13] Twisting of the PPP backbone by attaching side groups to enhance the solubility blue-shifted the emission maximum with a decrease in fluorescence quantum yield.[10] The twist was prevented by making the PPP backbone planar by partially incorporating the benzene units into a stepladder structure.[14] Poly(*p*-pyridine)[15] and poly(methylcyclohexylthiophene)[16] LEDs also emitted blue light.

Blue-color emission by a polymer LED was observed when the conjugation length of the fluorophore was shortened by the inclusion of an ether linkage in the polymer backbone.[17] Another approach toward well-defined fluorophores was based on polymers with luminescent conjugated side chains.[18−21]

A few random[22] and alternating[23−25] copolymers were identified as blue-light emitters, of which LEDs showed an increase in the external quantum efficiency by blending with other emitting polymers.[26] A significant enhancement of the quantum efficiency was also observed when poly(methoxyethylhexoxy−phenylenevinylene) (MEH−PPV) was blended either with poly(3-hexylthiophene)[27] or with a partially conjugated blue-emitting copolymer.[28] The enhancement of the quantum efficiency by blending is attributed to exciton confinement in the fluorophores of the polymers.[29]

In the present work, we have tried to optimize molecular structure for blue-color emission with high quantum efficiency. Statistical copolymers are designed to maximize the energy transfer between two chromophore units with different band gaps and the confinement of the singlet excitons in the chromophore with the lower band gap. The statistical copolymers bearing only carbon and hydrogen elements and conjugation throughout the molecular chain are soluble in organic solvents and show high glass transition temperature (T_g). The energy-transfer mechanism is also studied by employing time-resolved picosecond fluorescence spectroscopy.

Results and Discussion

The statistical copolymers with fluorene as one unit and a mixture of *m*- and *p*-divinylbenzene as the other were synthesized by employing the Heck reaction as shown in Scheme 1. All the copolymers were soluble in chloroform, THF, and chlorobenzene. The average synthesis yields of the statistical copolymers were 96.0%, and the number-average molecular weight (M_n) and molecular weight distribution (MWD) were around

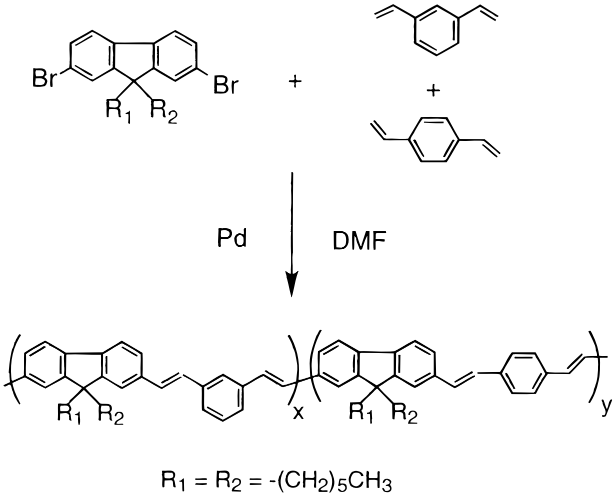
10.1021/ma981340w CCC: $18.00

Table 1. Synthesis Yields and Characteristics of the Resulting Polymers

	DBDHF[a] (g)	*m*-DVB[b] (g)	*p*-DVB[c] (g)	polymer yield (g)	polymer yield (%)	M_n (g/mol)	MWD
P-0	1.97	0.52		1.75	93.5	11 600	2.43
P-1	1.97	0.47	0.05	1.81	98.4	12 600	2.20
P-3	1.97	0.36	0.16	1.72	93.5	11 000	2.95
P-5	1.97	0.26	0.26	1.78	96.7	11 800	1.95
P-10	1.97		0.52	1.80	97.8	10 300	2.31

[a] DBDHF = 2,7-dibromo-9,9′-di-*n*-hexylfluorene. [b] *m*-DVB = *m*-divinylbenzene. [c] *p*-DVB = *p*-divinylbenzene.

Scheme 1. Synthesis Route to the Statistical Copolymers; Ratios between *m*- (*x*) and *p*-Divinylbenzene (*y*) Were 10:0 (P-0), 9:1 (P-1), 7:3 (P-3), 5:5 (P-5), and 0:10(P-10), Respectively



11 000 and 2.4, respectively, as shown in Table 1. T_g of the copolymers was around 125 °C, and the weight decrease was less than 5% on heating to 400 °C in air or in a nitrogen atmosphere.

The optical absorption (AB) spectrum of the statistical copolymer with the meta and para unit concentration of 1:1 (P-5) was compared to those of the fluorene-based copolymers[25] consisting of either a meta (P-0) or a para (P-10) unit (Figure 1a). The AB spectrum of P-5 with the maximum at 405 nm was a superposition of those of P-0 and P-10 with the maxima at 380 and 430 nm, respectively. However, as shown in Figure 1b, the normalized PL spectrum of P-5 showed the maximum at 475 nm, the same maximum as that of P-10 on the photoexcitation at 365 nm. The PL maximum of P-0 at 430 nm was not detected in P-5. It is apparent that the meta-structured chromophore was excited at 365 nm, but the electronic excitation energy was transferred to the para-structured one before the development of a radiative singlet exciton decay of the meta-structured one.[26] It seems that only the fluorophores of P-10 showed the singlet exciton decay although the chromophores of P-0 were mostly excited.

The PL intensity at 475 nm on photoexcitation at 365 nm seemed to be closely related to the concentration ratios between the para and meta units in the statistical copolymers as shown in Figure 2. The PL intensity was enhanced with an increase of the concentration of *p*-divinylbenzene to be maximized at the concentration of 30% and decreased with a further increase of the concentration of the para unit.

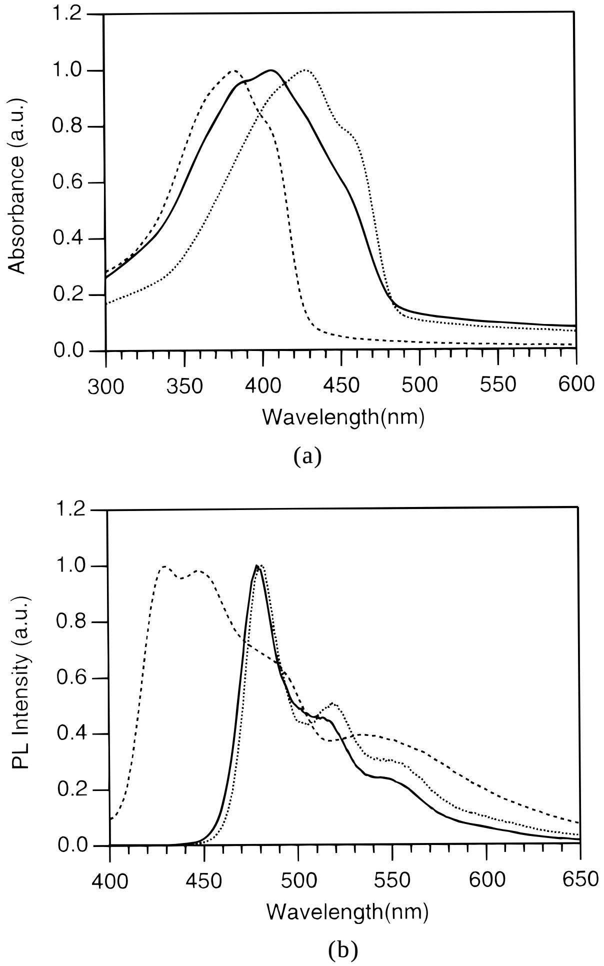


Figure 1. AB (a) and PL (b) spectra of P-10 (···), P-5 (—), and P-0 (- - -) on photoexcitation at 365 nm.

The enhancement of the PL intensity with lower concentrations of the para unit in the copolymers may be explained by the dilution effect for reducing the concentration quenching which results in weak emission.[30] The excitons formed in the meta-structured fluorophore with a larger band gap might migrate to the para-structured one with a smaller band gap before the intramolecular exciton annihilation or the exciton migration to the quenching sites. There is a possibility that the migrated excitons were confined in the para-structured fluorophores before the singlet exciton decay, and the confinement probability might be high when the fluorophores were isolated from each other by the meta-structured units in the statistical copolymers. The energy transfer from the meta- to the para-structured chromophores must be efficient to show little trace for the meta-structured fluorophores in the PL spectra of the statistical copolymers. The energy transfer is more favorable as the PL emission spectrum by the meta-structured unit closely matches the absorption spectrum of the para-structured one.[31]

The PL spectra of all the statistical copolymers showed the shoulder and the bump at 500 and 550 nm, respectively. It is interesting to note that the shoulder and the bump grew proportionally to the intensity of the main peak at 475 nm. The shoulder at 500 nm

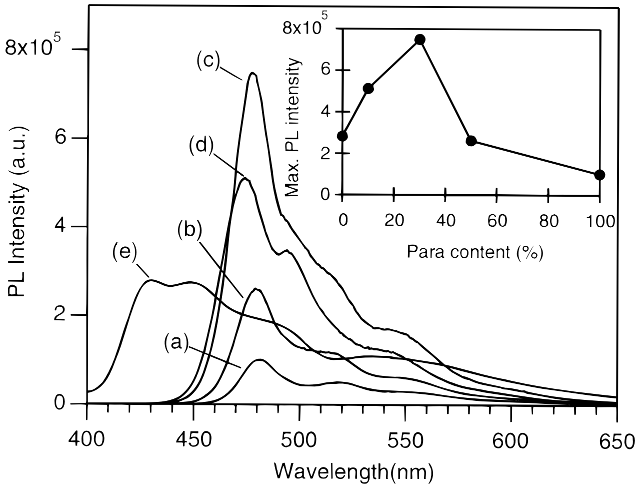


Figure 2. PL spectra of the statistical copolymers with different para contents on photoexcitation at 365 nm: (a) P-10, (b) P-5, (c) P-3, (d) P-1, and (e) P-0. Inset shows the plot of the PL intensity at 475 nm vs para content in the statistical copolymers.

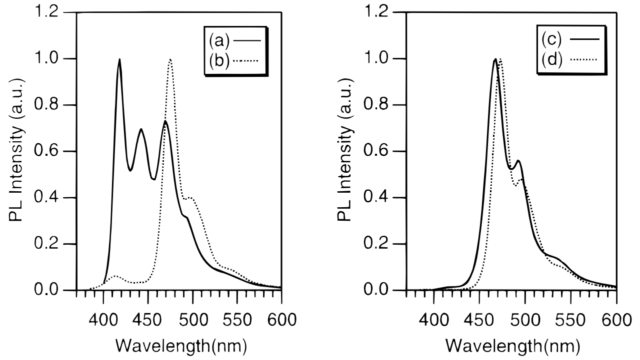
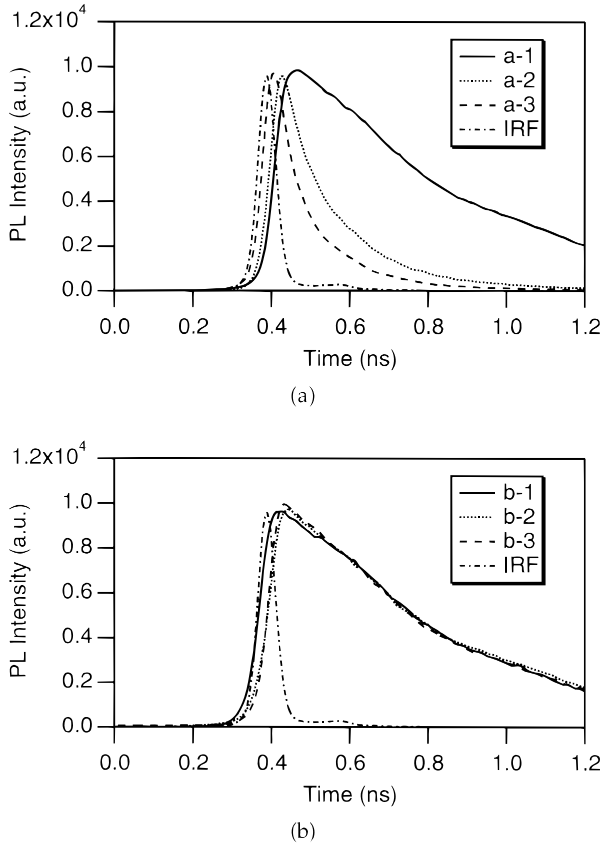


Figure 3. PL spectra of the solutions of 1:1 blend of P-0 and P-10 in the concentration of 10^{-5} (a) and 5×10^{-2} mol/L (b), and the statistical copolymer (P-5) in 10^{-5} (c) and 5×10^{-2} mol/L (d).



(a)

(b)

Figure 4. Time-resolved PL decay profiles of the blends of P-0 and P-10 in the concentration of 5×10^{-2} (a) and 10^{-5} (b) mol/L, respectively. The blend ratios between P-0 and P-10 were 10/0 (1), 9/1 (2), and 5/5 (3).

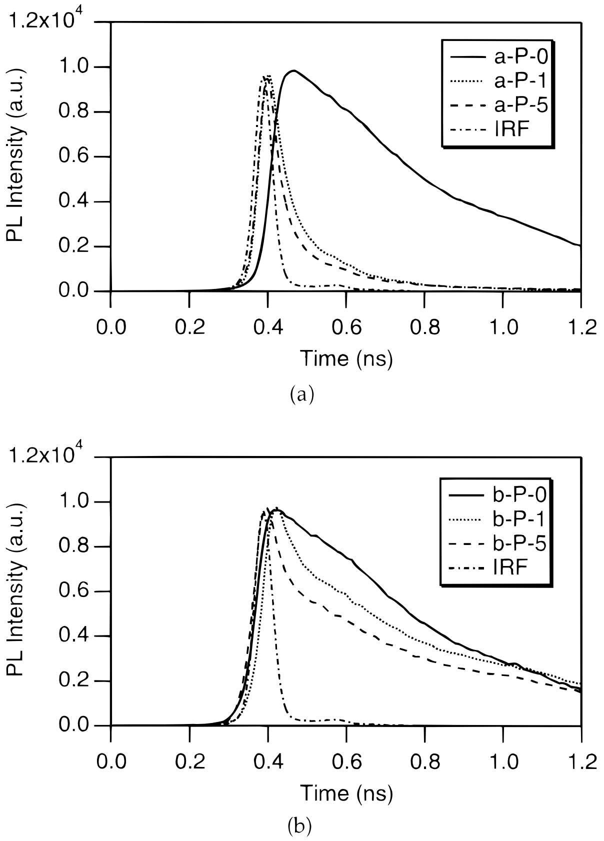
seemed to be the vibronic progression while the bump at 550 nm might be an excimer emission or an independent singlet exciton decay with a much lower band gap. There is a possibility that a fluorophore with a low band gap might exist inherently in the copolymer or develop after the $\pi-\pi^*$ electronic transition of the main chromophore.

Figure 3 shows the normalized PL spectra of solutions of 1:1 blend between P-0 and P-10 and P-5 of 5×10^{-2} and 10^{-5} mol/L in chloroform on photoexcitation at 365 nm. The blend solution of 5×10^{-2} mol/L exhibited the main peak at 475 nm with a weak bump at 430 nm while the diluted solution of 10^{-5} mol/L did the two strong peaks at 430 and 475 nm with the vibronic shoulders. It is apparent that the critical concentration of the blend in chloroform for the full energy transfer from P-0 to P-10 lay between the two concentrations. However, no decomposition of the PL spectrum was observed from the P-5 solution of either 5×10^{-2} or 10^{-5} mol/L as was as the statistical copolymers with the meta and para unit concentration of either 7:3 (P-3) or 9:1(P-1) on the same dilutions. This seems to prove that the intramolecular energy transfer from the meta unit chlorophore to the para unit fluorophore was complete to suppress the PL emission of the former at 430 nm.

It is noteworthy that the bump at 550 nm in the PL spectra of the films shrank but failed to disappear on dilution to 10^{-5} mol/L. It is difficult to expect that the excimer-forming sites still remained in the condition. Singlet exciton units of long conjugation segments with the emission at 550 nm might exist originally in the copolymer, but the concentration of the long segments decreases by losing the coplanarity of the unit due to the enhanced molecular mobility in the dilute solution to result in the reduction of the intensity at 550 nm.

The energy-transfer dynamics between the two chromophores was examined by employing the time-resolved picosecond fluorescence spectroscopy as shown in Figures 4 and 5 and in Table 2. The dotted-dashed curve in Figures 4 and 5 is the instrumental response function (IRF) of the time-correlated single-photon counting method.[32] When the polymer solution was excited by 398 nm pulses which were generated by frequency doubling of a Ti:sapphire pulsed laser, the PL decay from the fluorophores in the P-0 solution of 5×10^{-2} mol/L at 430 nm exhibited approximately the single-exponential decay with a time constant of 476 ps.

However, the blend solutions of P-0 and P-10 with ratios of 9:1 and 1:1, respectively, revealed double-exponential decay curves at 430 nm (Figure 4a-1). The fast decay components of the blend solutions of 9:1 and 1:1 were 131 and 25 ps, respectively. It is apparent that a portion of the energy received by the chromophores in P-0 (donor) of the 1:1 blend solution of 10^{-2} mol/L on the photoexcitation was transferred to those in P-10 (acceptor) before the singlet exciton decay of P-0. However, the intermolecular distance between the two fluorophores in the 9:1 blend solution of 10^{-2} mol/L seemed to be large enough to inhibit the full energy



(a)

(b)

Figure 5. Time-resolved PL decay profiles of the copolymers in the concentration of 5×10^{-2} (a) and 10^{-5} (b) mol/L, respectively.

Table 2. Time-Resolved PL Spectral Data of Light-Emissive Polymers

sample (concn)	D/A[a]	τ_{DA} (ps)	E_τ[b]
P-0/P-10 blends (0.05 mol/L)	100/0	476	0.00
	90/10	131	0.72
	50/50	25	0.95
P-0/P-10 blends (10^{-5} mol/L)	100/0	387	0.00
	90/10	388	0.00
	50/50	405	0.00
copolymers (0.05 mol/L)	P-0	476	0.00
	P-1	25	0.95
	P-3	24	0.95
	P-5	21	0.96
copolymers (10^{-5} mol/L)	P-0	387	0.00
	P-1	86	0.78
	P-3	18	0.95
	P-5	14	0.96

[a] D/A = the concentration ratio of P-0 (donor) to P-10 (acceptor). [b] $E_\tau = 1 - \tau_{DA}/\tau_D$, where E_τ is the energy-transfer efficiency, and τ_D and τ_{DA} are the lifetime of donor emission in the absence and in the presence of acceptor, respectively.

transfer (Figure 4a-2). When the concentration of the blend solution was as low as 10^{-5} mol/L, no energy transfer was observed (Figure 4b), and the decay time at 430 nm was around 400 ps regardless of the blend ratios.

The statistical copolymers of P-5 and P-1 also exhibited the fast PL decay characteristics at 430 nm when the solution concentration was 5×10^{-2} mol/L (Figure 5a and Table 2). The PL decay time of all the copolymers was around 20 ps, indicating a fast energy transfer. It is interesting to note that the energy transfer in the statistical copolymer P-1 with the P-0 component of 90% was much faster (25 ps) than that in the polymer blend with P-0 component of 90% (131 ps). It is clear that the intramolecular energy transfer from the meta unit chromophore to the para unit one was significant to complete the energy transfer when the solution concentration was 5×10^{-2} mol/L. However, it must be noted that the energy transfer between the two chromophores in the concentration of 10^{-2} mol/L was carried out both intramolecularly and intermolecularly as proved in the further diluted solution.

The nature of the intramolecular energy transfer between the two fluorophores in the statistical copolymers was understood when the copolymer was diluted to 10^{-5} mol/L in chloroform (Figure 5b). The fast PL decay times at 430 nm due to the energy transfer between the two chromophores of the P-3 and P-5 solutions with the concentration of 10^{-5} mol/L were 18 and 14 ps, respectively, while that of P-1 was 86 ps, but still a large drop from 388 ps of the 9:1 blend solution of 10^{-5} mol/L (Table 2). It is important to note that the PL decay time of P-1 was 3 times longer than that of P-3. The poor energy transfer in P-1 compared to that in P-3 or P-5 might be due to the longer average distance between the two kinds of the fluorophores in an isolated single chain of P-1 in the diluted solution. The average center-to-center distances between meta and para units in the statistical copolymer were calculated to be approximately 89, 23, and 18 Å for P-l, P-3, and P-5, respectively.

It is important to observe the significant contribution of the slow decay component to the PL decay spectra (Figure 5b). The fast decay time of P-5 was 14 ps (Table 2), but the PL intensity at 430 nm had sustained longer after the fast decay contribution (Figure 5b-P-5). The fast decay contribution was even lower for the P-1 solution of 10^{-5} mol/L, and the PL intensity was sustained much longer than that for the P-5 solution (Figure 5b-P-1). It indicated that the excitons formed in the meta unit chromophores adjacent to the fluorophores in the para unit ones transferred energy immediately to the para unit ones on the photoexcitation while the meta unit excitons formed at several monomer units away from the fluorophore of P-1 performed the radiative singlet decay before the energy transfer. It is speculated that when an exciton with lower energy was confined in a para fluorophore unit, a meta unit exciton with higher energy exhibited the radiative singlet decay before heterogeneous singlet–singlet annihilation between the excitons of the para and the meta units.

It is clear that the intramolecular energy transfer is incomplete in the lifetime of the singlet exciton generated in the meta unit chromophore. The intermolecular energy transfer must be supplemented to complete the energy transfer between the two chromophores in the lifetime of the chromophore with the higher energy. The solid blends between P-0 and P-10 demonstrated an efficient energy transfer between the two chromophores.[26] However, there is a possibility of singlet–singlet annihilation in the P-0 chains, which favors the statistical copolymers over the polymer blends for a high PL quantum efficiency.

The PL decay time (86 ps) of the 10^{-5} mol/L P-1 solution at 430 nm was more than 4 times longer than that of P-3 or P-5, which indicated an incomplete energy transfer compared to that of P-3 or P-5. However, the PL intensity of solid P-1 was higher than that of solid P-5 at 475 nm, and the highest PL intensity was observed from solid P-3 (Figure 2). It is probable that there is more than one exciton in a single polymer chain

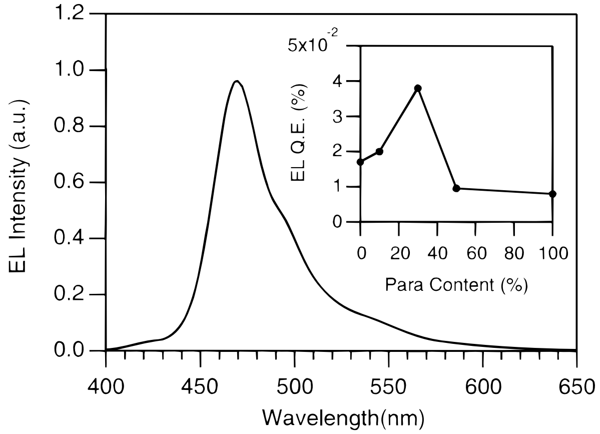


Figure 6. EL spectrum of LED fabricated with the blend of P-3/PVK = 2/8. Inset shows the maximum quantum efficiency of LEDs prepared by compolymers/PVK = 2/8 blends vs para content of copolymers.

on photoexcitation. The excitons have a good chance to experience the exciton−exciton annihilation process in a single chain when the fluorophore concentration is high. P-5 has a higher probability of a long para linkage block compared to that of P-1. P-1, on the contrary, has a low concentration of the block of the para unit to confine excitons effectively. It is apparent that the para units in P-1 do not accommodate all the energy transferred from the meta units but confine excitons to show a higher PL intensity than P-5. The optimum concentration ratio for the highest PL intensity is 30% of the para unit in the statistical copolymer. It is assumed that the concentration of the block of the para unit in P-3 is low.

Electroluminescence (EL) of a blend between P-3 and poly(vinylcarbazole) (PVK) with a concentration ratio of 1:4 sandwiched between aluminum and indium−tin oxide (ITO) glass showed almost the same spectrum as the PL spectrum of P-3, indicating the same emissive centers for the PL and EL emission as shown in Figure 6. The EL emission maximum was 470 nm, and the full width at the half-maximum (fwhm) was less than 50 nm. The radiative singlet exciton decay was observed only from the excitons formed in the para unit in the copolymer. The EL quantum efficiency of the copolymers with the emitter thickness of around 93 nm was highest for P-3 followed by P-1 as shown in the inset.

The current−bias potential−luminescence (*I*−*V*−*L*) curve from an LED fabricated with the blend of P-3 and PVK is drawn in Figure 7. The onset potential for the light emission was around 12 V when the thickness of the emissive layer was around 93 nm. The onset potential was reduced to less than 10 V for the emissive layer thickness of 54 nm. The potential was increased to 15 V for the thickness of 127 nm. The EL quantum efficiency was 0.04% for the emissive layer thickness of 93 nm while those of 54 and 127 nm thick layers were 0.02 and 0.06%, respectively. The onset potential and quantum efficiency are expected to be lowered and enhanced, respectively, by optimization of the device characteristics.

Conclusion

Fluorene-based statistical copolymers with different ratios of *m*- and *p*-divinylbenzene synthesized by employing the Heck reaction showed fair thermal properties and good processibility. The PL spectrum originated from the emissive centers in the para-linked unit of the statistical copolymers. A complete energy transfer from the high-band gap chromophores to the low-band gap ones was observed from the bulk statistical copolymers. However, it was proved that the intramolecular energy transfer through the conjugation was considerable but incomplete in the lifetime of the meta unit excitions. The statistical copolymer with the meta−para ratio of 7:3 has the optimum condition for a high concentration of singlet excitons confined in the para units to emit strong and clean blue color with the fwhm of 50 nm. Single-layered LEDs fabricated with the statistical copolymers showed blue color without much tail in the yellow emission region with a reasonably good quantum efficiency of 0.04%.

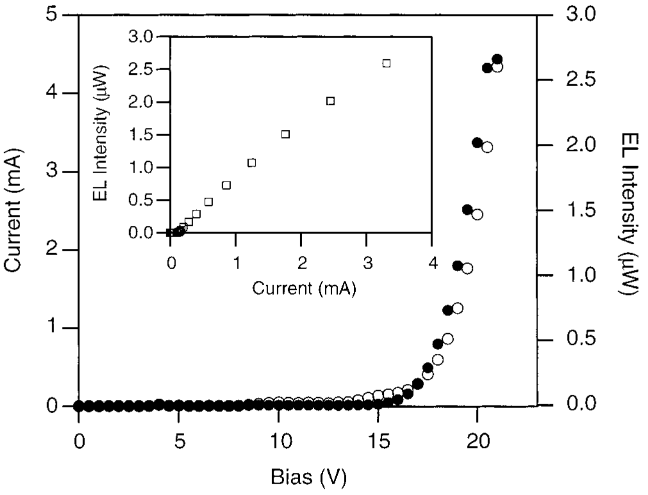


Figure 7. Voltage−current (○) and luminescence (●) characteristics of LED prepared by the blend of P-3/PVK = 2/8. Inset shows the current−luminescence characteristics of the device.

Experimental Section

Materials. Fluorene, 1-bromohexane, and *n*-butyllithium (2.5 M in hexane) were purchased from Aldrich and used without further purification. Tetrahydrofuran (THF) was purified by distillation from sodium in the presence of benzophenone. Dimethylformamide (DMF) was purified by distillation under reduced pressure after drying over calcium hydride (CaH_2). Other chemicals were used as received unless otherwise specified. Divinylbenzene (Aldrich, 80%, mixture of isomers) was purified by passing it through the inhibitor remover column (Aldrich) and separated into the two isomers of *m*- and *p*-divinylbenzene (*m*-DVB and *p*-DVB) by the literature procedure.[33]

Monomer Synthesis. The starting material, 9,9′-di-*n*-hexylfluorene, was synthesized by the reaction of fluorene and 1-bromohexane using *n*-butyllithium in THF according to the literature procedure[34] and purified by recrystallization from *n*-hexane (89% yield, mp 30−31 °C). 2,7-Dibromo-9,9′-di-*n*-hexylfluorene (DBDHF) was synthesized as follows: to solution of 66.8 g (0.2 mol) of 9,9′-di-*n*-hexylfluorene and a catalytic amount of iodine (0.2 g) in CH_2Cl_2 (500 mL) at 0 °C was added dropwise 67.2 g (0.42 mol) of bromine in CH_2Cl_2 (150 mL) over 1 h under rigorous exclusion of light. The reaction mixture was then allowed to warm to room temperature and stirred for 18 h. A 20% aqueous KOH solution (150 mL) was added to the resulting mixture until the red color disappeared. The organic layer was separated, washed with water, and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure to afford light yellow solid. The white crystalline product was obtained by twice recrystallization from *n*-hexane (89.5 g, 91%, mp 61−62 °C). ^{13}C NMR: δ 152.55, 139.06, 130.15, 126.16, 121.50, 121.12, 55.58, 40.11, 31.36, 29.48, 23.53, 22.48, 13.90. ^{1}H NMR: δ 0.58−0.81 (m, 10H, $-CH_2$ and $-CH_3$), 1.06−1.14 (m, 12H, $-CH_2$), 1.87−1.96 (m, 4H, α-CH_2), 7.43−7.54 (m, 6H, aromatic). Anal. Calcd for $C_{25}H_{32}Br_2$: C, 60.99; H, 6.55. Found: C, 61.39; H, 6.64.

Polymerization. The polymerization with the reaction scheme as shown in Scheme 1 was carried out under an argon atmosphere employing the Heck reaction. Five samples were synthesized with the repeating unit ratios between fluorenedivinylene-*p*-phenylene and fluorenedivinylene-*m*-phenylene of 0/10, 1/9, 3/7, 5/5 and 10/0, denoted as P-0, P-1, P-3, P-5, and P-10, respectively. A typical procedure was described as follows: to a 100 mL Schlenk flask equipped with a stirring bar and containing 1.97 g (4 mmol) of 2,7-dibromo-9,9′-di-*n*-hexylfluorene, 0.59 g (4.05 mmol) of a divinylbenzene mixture with the ratio of 1 to 1 between *m*- and *p*-divinylbenzene, 36.4 mg of palladium(II) acetate, and 248 mg of tri-*o*-tolylphosphine was added 40 mL of DMF via a syringe. After a homogeneous solution was obtained, 3.0 mL of tri-*n*-butylamine was added to the reaction solution. The reaction mixture was stirred vigorously at 100 °C for 24 h. The vinyl chain ends due to the excess feeding of the divinylbenzene were capped with 0.5 mL of bromotoluene in 10 mL of DMF at the end of the polymerization for 6 h at 100 °C and then poured slowly into an excess amount of methanol (500 mL). The precipitated material was recovered by filtration. It was redissolved in chloroform and microfiltered followed by precipitation again into methanol. Filtration and drying under vacuum at 40 °C for 24 h afforded 1.78 g (96.7% yield) of a final statistical copolymer (P-5) as light-yellow solid (M_n = 11 800, MWD = 1.95). ^{1}H NMR: δ 0.77 (br, 10H, $-CH_2$ and $-CH_3$), 1.08 (br, 12H, $-CH_2$), 2.05 (br, 4H, α-CH_2), 7.23−7.78 (m, 14H, vinyl and aromatic). The characteristics of the polymers were described in Table 1.

Instrumentation. A Waters GPC 150 was employed to deduce a number-average molecular weight (M_n) and molecular weight distribution (MWD) based on polystyrene as standards. The thermal properties were determined by using a Perkin-Elmer DSC-7 for T_g and a Du Pont TGA 951 for degradation. Specimens for PL measurement were spin-cast from 2 wt % solution of each copolymer in chlorobenzene. Liquid cells for PL measurement of the solution were fabricated with two glass plates separated by 75 μm thick spacers. LEDs were assembled with one of the 100 nm thick spin-cast copolymers on ITO glass followed by thermal evaporation of aluminum. UV−visible absorption spectra were recorded with a HP 8452A diode array spectrophotometer. The copolymers were photoexcited at 365 nm generated by a xenon lamp, and PL and EL spectra were recorded with an ISS PL-1 fluorometer. $I-V-L$ characteristics were recorded on a Keithley 236 source/measure unit for voltage−current relationship and by a Newport 818-SL photodiode for voltage−electroluminescence intensity.

Time-Resolved PL Spectroscopy. A time-correlated single photon counting (TCSPC) system has been described in detail elsewhere,[32] and a brief description is given here. The excitation laser is a femtosecond Ti:sapphire laser (Tsunami, Spectra-Physics) pumped by a CW argon ion laser (BeamLok 2060, Spectra-Physics). The mode-locked laser pulse (796 nm) from the Ti:sapphire laser has an 80 fs pulse width and the averaging power of 200 mW at a 82 MHz repetition rate. The laser pulse was frequency-doubled by using a β-BBO crystal to give a 398 nm excitation source. The emission was collected at a 90° angle to the excitation laser beam by 10 and 15 cm focal length lenses, focused onto a Jobin-Yvon HR320 monochromator, and detected with a microchannel plate photomultiplier tube (Hamamatsu R2809U). The signal was amplified by a wide-band amplifier (Philips Scientific), sent to a Quad constant fraction discriminator (Tennelec), a time-to-amplitude converter (Tennelec), a photon counter (Ortec), and a multichannel analyzer (Tennelec/Nucleus), and finally stored in a computer.

Acknowledgment. This work is a part of K-2000 Project, KIST. This work has also been financially supported by the Ministry of Science and Technology of Korea (N.W.S. and D.K.).

References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(2) Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* **1992**, *357*, 477.

(3) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 402.

(4) Burn, P. L.; Holmes, A. B.; Kraft, A. J.; Bradley, D. D. C.; Friend, R. H.; Brown, A. R. *J. Chem. Soc., Chem. Commun.* **1992**, 32.

(5) Braun, D.; Heeger, A. J. *Appl. Phys. Lett.* **1991**, *58*, 1982.

(6) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993,** *365*, 628.

(7) Braun, D.; Staring, E. G. J.; Demandt, R. C. J. E.; Rikken, G. L. J.; Kessener, Y. A.; Venhuizen, R. R. *Synth. Met.* **1994**, *66*, 75.

(8) Ohmori, Y.; Uchida, M.; Muro, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1991,** *30*, L 1941.

(9) Grem, G.; Leditzky, G.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992,** *4*, 36.

(10) Vahlenkamp, T.; Wegner, G. *Macromol. Chem. Phys.* **1994**, *195*, 1933.

(11) Hamaguchi, M.; Sawada, H.; Kyokane, J.; Yoshino, K. *Chem. Lett.* **1996**, 527.

(12) Yang, Y.; Pei, Q.; Heeger, A. J. *J. Appl. Phys.* **1996**, *79*, 934.

(13) Remmar, M.; Neher, D.; Grüner, J.; Friend, R. H.; Gelinck, G. H.; Warman, J. M.; Quattrocchi, C.; dos Santos, D. A.; Brédas, J.-L. *Macromolecules* **1996**, *29*, 7432.

(14) Huber, J.; Müllen, K.; Salbeck, J.; Schenk, H.; Scherf, U.; Stehlin, T.; Stern, R. *Acta Polym.* **1994,** *45*, 244.

(15) Gebler, D. D.; Wang, Y. Z.; Blatchford, J. W.; Jessen, S. W.; Lin, L. B.; Gustafsson, T. L.; Wang, H. L.; Swager, T. M.; MacDiarmid, A. G.; Epstein, A. J. *J. Appl. Phys.* **1995,** *78*, 4264.

(16) Berggren, M.; Inganäs, O.; Gustafsson, G.; Andersson, M. R.; Hjertberg, T.; Wennerström, O. *Nature.* **1994,** *372*, 444.

(17) Yang, Z.; Sokolik, I.; Karasz, F. E. *Macromolecules.* **1993,** *26*, 1188.

(18) Li, X. C.; Cacialli, F.; Giles, M.; Grüner, J.; Friend, R. H.; Holmes, A. B.; Moratti, S. C.; Yong, T. M. *Adv. Mater.* **1995,** *7*, 898.

(19) Lee, J.-K.; Schrock, R. R.; Baigent, D. R.; Friend, R. H. *Macromolecules* **1995**, *28*, 1966.

(20) Aguiar, M.; Karasz, F. E.; Akcelrud, L. *Macromolecules* **1995**, *28*, 4598.

(21) Chung, S.-J.; Jin, J.-I.; Kim, K.-K. *Adv. Mater.* **1997**, *9*, 551.

(22) Kreyenschmidt, M.; Klaerner, G.; Fuhrer, T.; Ashenhurst, J.; Karg, S.; Chen, W. D.; Lee, V. Y.; Scott, J. C.; Miller, R. D. *Macromolecules* **1988**, *31*, 1099.

(23) Hilberer, A.; Brouwer, H.-J.; van der Scheer, B.-J.; Wildeman, J.; Hadziioannou, G. *Macromolecules* **1995,** *28*, 4525.

(24) Tanigaki, N.; Masuda, H.; Kaeriyama, K. *Polymer* **1997**, *38*, 1221.

(25) Cho, H. N.; Kim, D. Y.; Kim, Y. C.; Lee, J. Y.; Kim, C. Y. *Adv. Mater.* **1997,** *9*, 326.

(26) Kim, D. Y.; Kim, J. K.; Cho, H. N.; Kim, C. Y. *Proc. SPIE* **1998**, *3148*, 151.

(27) Yu; G.; Nishino, H.; Heeger, A. J.; Chen, T.-A.; Rieke, R. D. *Synth. Met.* **1995**, *80*, 125.

(28) Lee, J.-I.; Kang, I.-N.; Hwang, D.-H.; Shim, H.-K.; Jeoung, S. C.; Kim, D. *Chem. Mater.* **1996**, *8*, 1925.

(29) Baigent, D. R.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. *Synth. Met.* **1996**, *8*0, 119.

(30) Zhang, C.; Seggern, H.; Pakbaz, K.; Kraabel, B.; Schmidt, H. W.; Heeger, A. J. *Synth. Met.* **1994**, *62*, 35.

(31) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983; Chapter 10.

(32) Lee, M. Y.; Kim, D. *J. Opt. Sci., Korea* **1990**, *1*, 52.

(33) Storey, B. T. *J. Polym. Sci., Part A* **1965**, *3*, 265.

(34) Fukuda, M.; Sawada, K.; Yoshino, K. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2465.

MA981340W