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Synthesis and characterization of fluorene-based electroluminescent polymers containing silyl groups

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Summary

Two types of fluorene-based copolymers, poly(9,9'-di-n-hexyl-2,7-fluorenediylethynylene-alt-9-trimethylsilyl-2,7-fluoreneethynylene[P-1], poly(9,9'-di-n-hexyl-2,7-fluorenediylethynylene-alt-9,9'-bis-trimethylsilyl-2,7-fluoreneethynylene[P-2] were synthesized by employing palladium catalyzed polycondensation. Resulting polymers showed a good solubility in various organic solvents such as THF, chloroform, dioxane etc. and could be easily spin-coated onto an ITO glass plate to make a fine thin film. Characterization of these polymers includes FT-IR, UV-vis., ^{1}H and ^{13}C-NMR, was conducted. Thermal properties were also investigated by DSC and TGA as well as molecular weight studies. The present polymers exhibited emission of blue-white color. The photoluminescence (PL) spectrum of the polymers showed two peaks at 490 and 540 nm and it was found that electroluminescence (EL) spectra of the polymer [P-2] was very similar to its PL spectrum.

Introduction

A light emitting diode (LED) has been fabricated with various organic materials and showed a great possibility of application in display system [1]. Photoluminescent (PL) π-conjugated polymers such as the poly(alkylthiophene) [2], poly(p-phenylene) (PPP) [3], and poly(p-phenylenevinylene) (PPPV) [4] etc. have been extensively studied as the emissive layer of a LED. Recently, poly(alkylfluorene) [5] has been the subject of intensive study since it showed a blue-color emission. However, there was few report of attempts to prepare its derivatives and no improvement was achieved about emissive organic materials conjugated by carbon-carbon triple bond [6] and introduced fluorene moiety. Therefore, the present work has been focused on the new series of synthesis and characterization of fluorene-based monomers and polymers which was accomplished by attaching side chains [7] and inserting solubility groups [8] on the back bone of them to enhance processability [1].

Experimental

Synthesis of monomers

The sequences of synthesis of the monomers are shown in. Fig.1.
9,9'-di-n-hexylfluorene was synthesized by the reaction of fluorene and n-hexyl bromide using n-butyllithium in THF according to the literature procedure [9].

9-trimethylsilyl fluorene (1a) 33.2g(0.2mol) of fluorene and 400ml of THF in 1L-two-neck flask were stirred and purged with argon at room temperature and then chilled by acetone/dry-ice. 84ml(0.21mol) of 2.5M n-BuLi/hexane was added slowly into the flask through the syringe. The reaction mixture was stirred for 1h at 25°C and again cooled by acetone/dryice. 25.6ml(0.2mol) of chlorotrimethylsilane was added slowly through syringe and kept stirring for 12h at room temperature. After complete reaction, the reactant was hydrolyzed with water and extracted with ether. The extracted organic solution was then dried with anhydrous $MgSO_4$ and filtered. Yellow solid obtained on evaporation of the solvent. This solid was recrystallized with ethanol and dried in a vacuum oven at 40°C. White solid of 9-trimethylsilyl fluorene with melting temperature range of 97 ~ 98°C was obtained. Yield : 40.6g(87.5%), ^{1}H-NMR($CDCl_3$), δ(ppm) : -0.55~0.03(m, 9H, $SiMe_3$), 3.88(s, 1H, C_{quat}), 7.35~7.96(m, 8H, Aromatic) , ^{13}C-NMR, δ(ppm) : -2.81($SiMe_3$), 42.63(C_{quat}), 119.91, 124.00, 125.19, 125.96, 140.42, 145.72(Aromatic)

9,9'-bis-trimethylsilyl fluorene (1b) 400ml of dried THF in 1L-two-neck-flask was purged with argon and then 33.2g(0.2mol) of fluorene was added into the flask with stirring. The reaction mixture was chilled by acetone/dry ice and 84ml(0.21mol) of 2.5M n-BuLi/hexane was added slowly through the syringe. The reactant was stirred for over 1h and then cooled again with acetone/dry ice, which was added by 25.6ml(0.2mol) of chloromethylsilane, followed by warming up to room temperature and stirred for 3h. After stirring, the same amount of 2.5M n-BuLi/hexane and chlorotrimethylsilane was used to repeat one more reaction and the organic mixture was stirred for 24h. Distilled water was poured into the flask and extracted several times with ethyl ether. The extracted organic solution was then dried with anhydrous $MgSO_4$ and filtered. White solid was remained on evaporation of the solvent. White transparent solid with melting temperature range of 110°C~111°C was obtained by recrystallization with ethanol. Yield : 51.5g(79%), ^{1}H-NMR($CDCl_3$), δ(ppm) : -0.16~0.03(m, 18H, $SiMe_3$), 7.35~7.96(m, 8H, Aromatic) , ^{13}C-NMR, δ(ppm) : -1.60~-0.55($SiMe_3$), 43.92(C_{quat}), 119.78, 124.24, 124.46, 125.65, 140.26, 147.46(Aromatic)

2,7-di-bromo-9,9'-di-n-hexylfluorene(1c) 66.8g(0.2mol) of 9,9'-di-n-hexylfluorene, 500ml of methylenechloride, and 0.1g of iodine were stirred in a 1-L-three-neck flask at room temperature. The reaction mixture was cooled to 5°C by ice/water and 67.2g(0.42mol) of bromide diluted with 150ml of methylenechloride was added slowly. The reactant was warmed to 25°C and then kept for 24h to complete reaction. 10% KOH aqueous solution was added slowly into the flask until the red color was disappeared. The reaction mixture was extracted several times with H_2O, dried with anhydrous $MgSO_4$ and filtered. Pale yellow viscous liquid was obtained on evaporation of the solvent and turned into white crystal after recrystallization several times with hexane. Yield : 89g(90%), ^{1}H-NMR($CDCl_3$), δ(ppm) : 0.59(br, s, 6H, CH_3), 0.73~1.13(m, 16H, CH_2), 1.87~1.96(m, 4H, CCH_2), 7.45~7.49(m, 6H, Aromatic) , ^{13}C-NMR, δ(ppm) : 13.90(CH_3), 22.48, 23.53, 29.48, 31.35, 40.02(CH_2), 55.58(C_{quat}), 121.12, 121.49, 126.15, 130.15, 139.06, 152.55(Aromatic)

2,7-Dibromo-9,9'-di-n-hexylfluorene To a solution of 66.8g(0.2 mol) of 9,9'-di-n-hexylfluorene and catalytic amount of iodine(0.2g) in CH_2Cl_2 (500 mL) at 0°C was added dropwise 67.2g(0.42 mol) of bromine in CH_2Cl_2(150 mL) over 1h under rigorous exclusion of light. The reaction mixture was then allowed to warm to room temperature and was stirred for 18h. 20% aqueous KOH solution(150mL) 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 obtain light yellow solid.

The white crystalline product was obtained by twice recrystallization from n-hexane. Yield:(89.5g,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).

2,7-di-bromo-9-trimethylsilyl fluorene(1d) 20g(0.0832mol) of 9-trimethylsilyl fluorene, 250ml of methylenechloride and 0.1g of iodine was stirred in 500ml-two-neck flask and then cooled to 5°C by ice water. 29.28g(0.18mol) of bromide was diluted with 50ml of methylenechloride and dropped slowly into the flask and kept for 24h. After the reaction was completed, The reaction mixture was added by 10% aqueous solution of KOH until the red color was turned into transparent one and extracted thoroughly with distilled water ,which was dried with anhydrous $MgSO_4$ and filtered. Pale yellowish solid was left when the solvent was evaporated in a vacuum oven, and recrystallized with ethyl acetate to get white solid with the range of melting temperature from 151°C~153°C. Yield : 23.28g(70%), ^{1}H-NMR($CDCl_3$), δ(ppm) : -0.13~0.05(m, 9H, $SiMe_3$), 3.81(s, 1H, CH), 7.45~7.66(m, 6H, Aromatic) , ^{13}C-NMR, δ(ppm) : -2.88($SiMe_3$) 42.84(C_{quat}), 120.25, 121.20, 126.92, 128.58 ,138.26, 147.54(Aromatic)

2,7-di-bromo-9,9'-bis-trimethylsilyl fluorene(1e) In 500ml-two-neck flask, 10g (0.032mol) of 9,9'-bis-trimethylsilyl fluorene, 200ml of methylenechloride and 0. 1g of iodine was stirred and then cooled to 5°C by ice water. 11.26g (0.07mol) of bromide diluted with 50ml of methylenechloride was added dropwise into the flask and kept for 24h. 10% aqueous solution of KOH was added into the flask until red color was disappeared and the mixture was extracted thoroughly with distilled water, dried with anhydrous $MgSO_4$ and then filtered. The resulting organic solution was evaporated to get pale yellowish solid in a vacuum oven, which was recrystallized with ethyl acetate and then white solid was obtained. The melting temperature of 2,7-di-bromo-9,9'-bis-trimethylsilyl fluorene is from 123°C~124°C. Yield : 21.73g(85%), ^{1}H-NMR($CDCl_3$), δ(ppm) : -0.08~0.004(m, 18H, $SiMe_3$), 7.27~7.77(m, 6H, Aromatic) , ^{13}C-NMR, δ(ppm) : -1.08($SiMe_3$) 44.92(C_{quat}), 120.00, 121.15, 127.25, 127.76, 138.16, 149.63(Aromatic)

2,7-bis-[(trimethylsilyl)ethynyl]-9,9'-di-n-hexylfluorene(1f) 49.2g(0.1mol) of 2,7-di-bromo-9,9'-di-n-hexylfluorene, 3.95g(5mmol) of bis-triphenylphosphinepalladium dichloride [$(PPh_3)_2PdCl_2$], 0.95g(5mmol) of CuI were dissolved in 400ml of piperidine in 1L three-neck flask under argon atmosphere. In the flask, 21.6g(0.22mol) of trimethylsilyl acetylene was added dropwise and heated to reflux for 3h with stirring. The reactant was cooled to room temperature, removed the solvents, and extracted three times with benzene. The extracted solution was washed thoroughly with distilled water and dried with anhydrous $MgSO_4$, which was then filtered. The obtained solid was recrystallized with ethanol. White solid was remained with filtration. (melting temperature: 126~128°C) Yield : 42g(80%), ^{1}H-NMR($CDCl_3$), δ(ppm) : 0.28(s, 18H, $SiMe_3$), 0.53(br, s, 6H, CH_3), 0.74~1.30(m, 16H, CH_2), 1.94~1.98(m, 4H, CCH_2), 7.43~7.62(m, 6H, Aromatic) , ^{13}C-NMR, δ(ppm) : 0.05($SiMe_3$), 13.92(CH_3), 22.55, 23.54, 29.62, 31.49, 40.33(CH_2), 55.18(C_{quat}), 94.26(C≡), 106.09(≡$CSiMe_3$), 119.86, 121.75, 126.24, 131.26, 140.90, 150.99(Aromatic)

2,7-diethynyl-9,9'-di-n-hexylfluorene(1g) 27.4g(52mmol) of 2,7-bis-[(trimethylsilyl) ethynyl]-9,9'-di-n-hexylfluorene, 4.53g (78mmol) of potassiumfluorene were dissolved in a mixture of 5ml of H_2O and 150ml of dimethylformamide in a 250ml-two-neck flask and reacted for 6hours at room temperature. The reaction mixture was poured into 500ml of ice water and extracted three times with ethyl ether, which was then dried with anhydrous $MgSO_4$ and filtered. The obtained liquid was purified by silica gel column using a solvent mixture of ethyl acetate and hexane with a ratio of 1 to 10 as an eluant. The resulting product was evaporated to get 17.1g(86% yield) of yellowish luminescent liquid. The melting temperature is 36~37°C. ^{1}H-NMR($CDCl_3$), δ(ppm) : 0.57~0.62(br, 6H, CH_3), 0.77~1.15(m, 16H, CH_2), 1.93~1.96(m, 4H, CCH_2), 3.14(s, 2H, CH) 7.46~7.65(m, 6H, Aromatic) , ^{13}C-NMR, δ(ppm) : 13.90(CH_3), 22.53, 23.66, 29.62, 31.46, 40.22(CH_2), 55.23(C_{quat}), 77.27(≡CH), 84.54(C≡), 119.95, 120.91, 126.58, 131.26, 141.00, 151.09(Aromatic)

Synthesis of polymers

Poly(9,9'-di-n-hexyl-2,7-fluorenediylethynylene-alt-9-trimethylsilyl-2,7-fluoreneethynylene)[P-1] In a 100ml flask, 0.76g (2mmol) of 2,7-diethynyl-9,9'-di-n-hexylfluorene, 0.716g (1.8mmol) of 2,7-di-bromo-9-trimethylsilyl fluorene, 81.6mg (0.4mmol) of iodobenzene, 92.4mg (0.08mmol) of tetrakistriphenylphosphinepalladium and 15.2mg(0.08mmol) of CuI were added to a mixture of 50ml of toluene and 20ml of diisopropylamine. The mixture was refluxed at 70°C for 12h. 0.2g (1.2mmol) of bromobenzene was added into the flask to terminate the reaction and kept for 2hours. The reaction mixture was cooled to room temperature, precipitated dropwise into a 1L of methanol and filtered. The resulting product, yellowish solid, was dissolved in chloroform and then precipitated again with methanol. The purified yellowish solid was washed thoroughly with methyl alcohol

and dried in a vacuum oven at 40°C.
Yield : 1.11g(99%), ^{1}H-NMR(CDCl$_3$), δ(ppm) : 0.045(s, SiMe$_3$), 0.67~1.09(br, m, CH$_2$ or CH$_3$), 2.04~2.36(br, s, CCH$_2$), 3.91~3.94(br, s, CH), 7.26~7.88(m, Aromatic) , ^{13}C-NMR, δ(ppm) : -2.80(SiMe$_3$) 13.96(CH$_3$), 22.57, 23.58, 29.56, 31.37, 40.29(CH$_2$), 42.69, 55.06(C$_{quat}$), 90.42, 90.78(C≡C), 120.04~151.19(Aromatic)

Poly(9,9'-di-n-hexyl-2,7-fluorenediylethynylene-alt-9,9'-bis-trimethylsilyl-2,7-fluoreneethynylene)[P-2] 0.76g (2mmol) of 2,7-diethynyl-9,9'-di-n-hexylfluorene, 0.84g (1.8mmol) of 2,7-dibromo-9-trimethylsilyl fluorene, 81.6mg (0.4mmol) of iodobenzene, 92.4mg (0.08mmol) of tetrakistriphenylphosphinepalladium and 15.2mg (0.08mmol) of CuI were added to a mixture of 50ml of toluene and 20ml of diisopropylamine in a 100ml flask purged with argon. The mixture was refluxed at 70°C for 12hours and 0.2g (1.0mmol) of bromobenzene was added into the flask to complete the reaction. After cooled to 25°C, the reaction mixture was precipitated dropwise into a 1L of methanol and filtered. The remained yellowish solid was dissolved in chloroform, precipitated again in methanol, and washed thoroughly with methyl alcohol. 1.18g(98%) of yellowish solid was obtained in a vacuum oven at 40°C. ^{1}H-NMR(CDCl$_3$), δ(ppm) : 0.03(s, SiMe$_3$), 0.65~1.90(br, m, CH$_2$ or CH$_3$), 2.01(s, CCH$_2$), 7.26~7.91(m, Aromatic) , ^{13}C-NMR, δ(ppm) : -0.89(SiMe$_3$) 13.94(CH$_3$), 22.54, 23.67, 29.62, 31.47, 40.32(CH$_2$), 44.71, 55.23(C$_{quat}$), 90.29, 91.03(C≡C), 119.93~151.36(Aromatic)

Results and discussion

The heck reaction has been applied to synthesize [P-1] and [P-2] functionalized with n-hexyl and trimethylsilyl side groups. From the ^{1}H and NMR ^{13}C-NMR spectra of soluble polymers, it was shown that acetylenic proton peaks of monomer, was not detected and the acetylenic carbon peaks, 77.27 and 84.54 ppm of monomer were disappeared and new acetylenic carbon peaks were appeared. Whereas, the peaks from IR spectra of trimethylsilyl groups in monomer and polymer were similar. This confirms that polymerization has been completed. The two polymers were soluble in various organic solvents such as CHCl$_3$, THF, and dioxane etc and easily spin-coated to make thin films. Gel permeation chromatography(GPC) using polystyrene standards indicated number average molecular weights($\overline{M}_n$) of ca. 3800 and 4500 (Table 1.) with polydispersities ($\overline{M}_w/\overline{M}_n$) of 2.9 and 3.1 for [P-1] and [P-2].
In thermogravimetric analysis (TGA; N$_2$; 10°C/min), the polymer [P-1] showed the slow onset of 4% weight loss on heating to 325°C and a fast decomposition of weight as shown in fig. 5 and also [P-2] showed essentially the similar curve of [P-2], the slight weight loss at about 300°C and maximum decrease in weight at around 374°C(Fig 5.). For comparison, [P-1] appears to be a little bit more thermally stable than [P-2]. There must be the weight loss on the thermal treatment at the low temperature due to evaporation of the oligomers which might exist since Mw and MWD were low and broad.

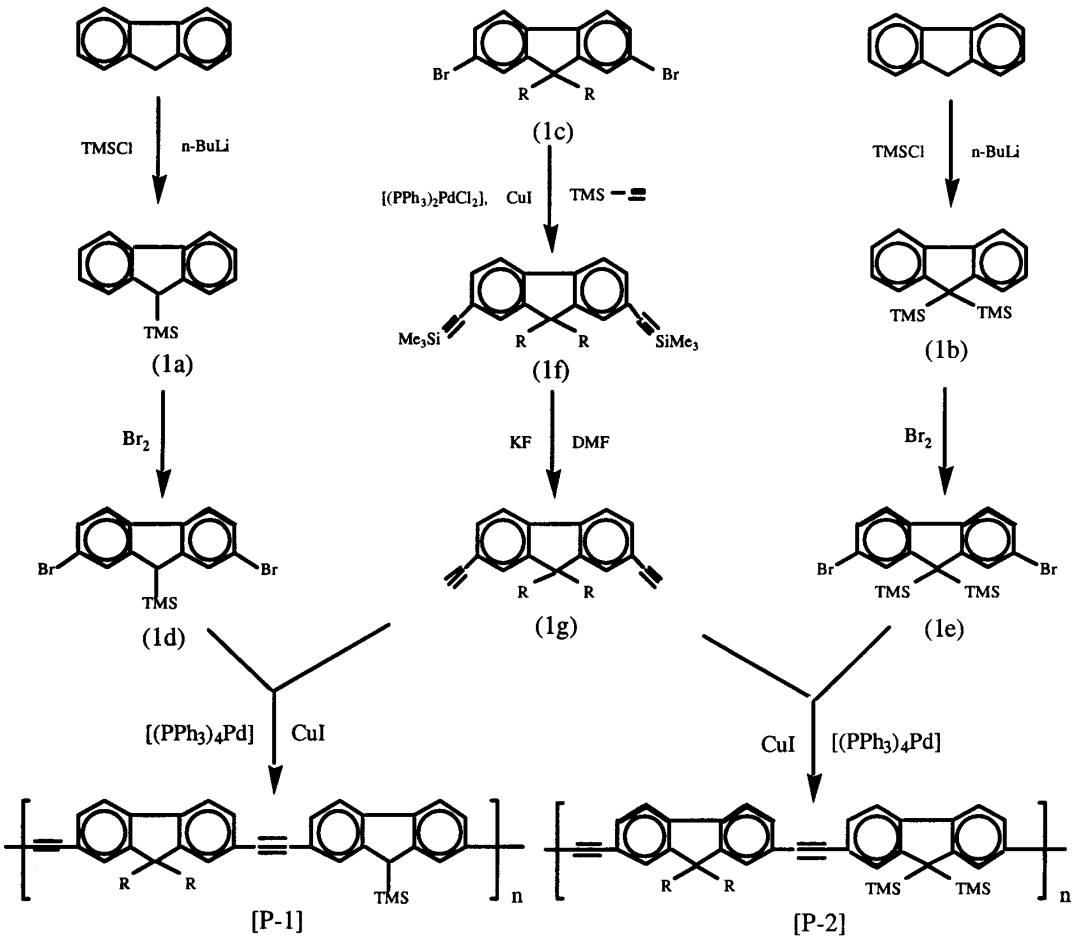
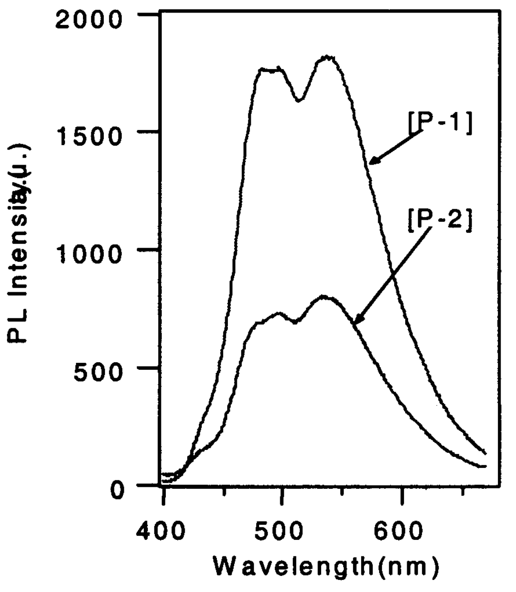


Fig 1. Synthetic routes to polymers

Table 1. UV-Vis. Characterization of luminescence polymers

polymer	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	λ_{max}, nm	band gap (eV)	
				(a)	(b)
[P-1]	3800	2.9	388	3.19	2.76
[P-2]	4500	3.1	385	3.22	2.69

calculated from λ_{max}
calculated from band-edge



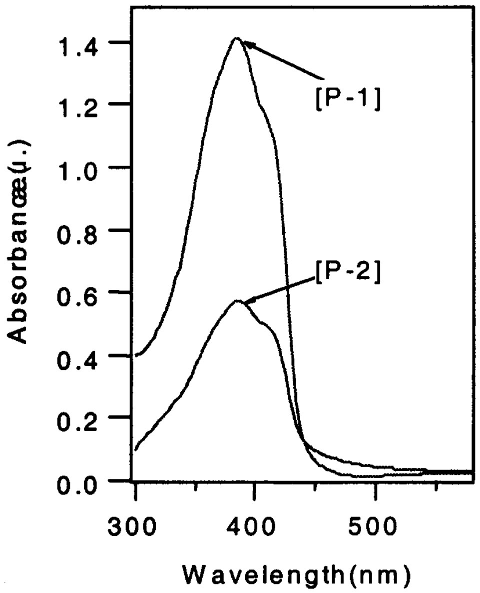
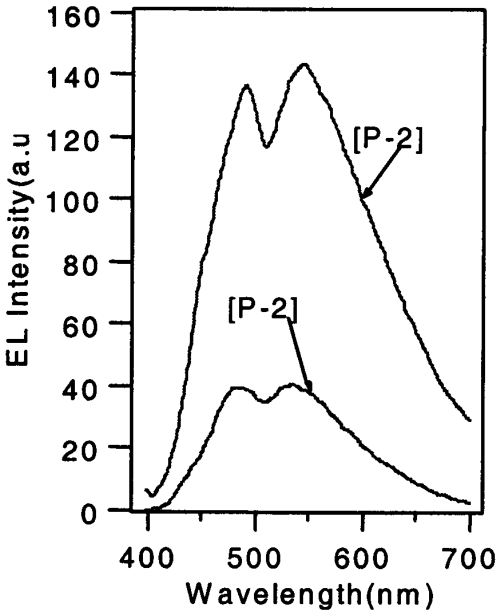


Fig 2. PL spectra of [P-1] and [P-2]

Fig 3. AB spectra of [P-1] and [P-2]

The PL spectrum of the polymers, [P-1] and [P-2] are shown in Fig 2. with the full width at half maximum (FWHM) of 150nm and two peaks at 490nm and 540nm. The EL spectrum (Fig. 4) covers almost full color range of visible light. Judging from the absorption spectra of these polymers,(Fig. 3) there must be two emission center in the polymers.



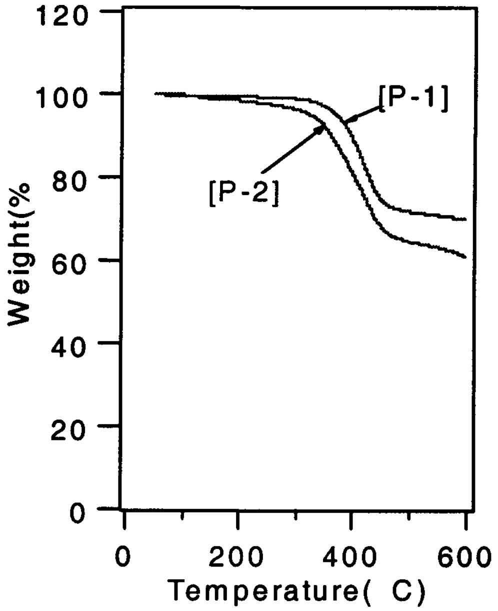


Fig 4. EL spectra of [P-1] and [P-2]

Fig 5. TGA thremograms of [P-1] and [P-2]

Conclusion

Two alternating copolymers, [P-1] and [P-2], having two different monomeric units, were easily synthesized by Heck reaction. The initial aim to synthesize these materials was to study luminescent polymers containing carbon-carbon triple bond in the main chain and introduce side groups such as hexyl and trimethylsilyl to produce good solubility in common organic solvent and improve high processibility to be used in LED devices. The PL spectra shows similarity from each other. The EL spectrum of [P-2] becomes almost identical to the PL spectrum, generating a blue-white emission.

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