

Synthesis and Light-Emitting Properties of Phenyl-Thiophene-Based Alternating Copolymers Synthesized by Heck Coupling Reaction

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Abstract : A series of poly(1,4-phenylenevinylene-*alt*-3-alkyl-2,5-thienylenevinylene)s (alkyl = hexyl [PPV-*alt*-6-TV] and octyl [PPV-*alt*-8-TV] group) have been synthesized by the Heck coupling reaction. These polymers were characterized using ¹H-NMR, FT-IR spectroscopy, and thermogravimetric analysis (TGA). They are solvent processible and have obviously copolymeric structure. The photophysical properties of the polymers were investigated using UV-visible and steady-state photoluminescence (PL) spectroscopy. We studied the change of light-emitting properties by incorporating the thiophene group into the PPV polymer backbone using alternating copolymer system. The properties of two synthesized polymers are very similar, but they exhibited apparent changes of light-emitting properties compared with other PPV backbone based polymers. The broad absorption bands from 350 to 570 nm are due to π - π^* transitions of the polyconjugated systems. The absorption maxima of the two polymers were found at about 452 and 448 nm for PPV-*alt*-6-TV and PPV-*alt*-8-TV, respectively. The copolymers showed broad PL spectra between 550 and 700 nm without vibronic bands and PL emission maxima of PPV-*alt*-6-TV and PPV-*alt*-8-TV are about 620 and 605 nm, respectively. The copolymers exhibited the red emission (PPV-*alt*-6-TV), but more red shifted emissions are needed to obtain real red color.

Introduction

Since the successful fabrication of a polymer light emitting diode (PLED) using poly(*p*-phenylene vinylene) (PPV) as the active material,¹ there has been extensive research interest in conjugated polymers. The light weight, flexibility, ease of processing, and unique electrical and photonic semiconducting properties are among the most attractive characteristics of this class of materials. Although many polymers have been developed and studied²⁻⁸ since the discovery of electroluminescence (EL) in PPV, researchers still need materials which show better characteristics in terms of

efficiency, luminance, and color purity, *etc.*

Nominally fully conjugated PPV emits light in the green-yellow region of the visible spectrum.⁹ This color can be altered by incorporation of electron-donating and electron-withdrawing substituents on the polymer backbone or by limiting the conjugation length of the chromophore. With suitable change in molecular structure, one can control the color and efficiency of electroluminescence as well as solubility and processibility of the polymer.¹⁰ The dialkoxy substituted PPVs such as poly(2-methoxy-5-(2-ethylhexyloxy)phenylenevinylene) (MEH-PPV),¹¹ poly(2-methoxy-5-(3,7-di-methyloctyloxy)phenylenevinylene) (OC1C10-PPV)¹² exhibit longer wavelength emission than PPV. The trialkylsilyl or the alkoxyphenyl substituted PPVs such as poly(2-dimethyloctylsilyl-1,4-phenylenevinylene) (DMOS-PPV),¹³ poly(2-(4-(3,7-dimethyloctyloxy)

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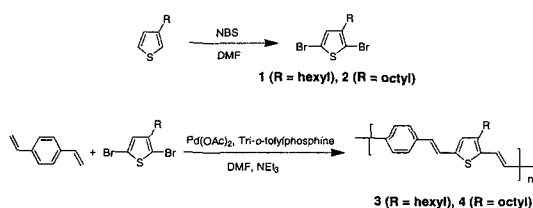
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phenyl)phenylenevinylene)^{14,15} are well processible due to the good solubility in various organic solvents as well as the similar emission to PPV.

Copolymerization is another way to control the polymer's characteristics. Introduction of carbazole or oxadiazole moiety, into polymer backbone can alter the electronic and photonic properties. We reported the carbazole or fluorene containing PPV copolymers which showed high photoluminescence efficiency with blue and greenish blue emission.¹⁶ We also studied the effect of kink structure in PPV derivatives on electronic and photonic properties.¹⁷ The conjugation breaker, meta linkage of vinylenes, led to blue shift of PL spectrum. In the same manner, low band gap comonomers can be introduced into PPV main backbone. The PPV copolymers containing low band gap comonomer, such as dialkoxy substituted comonomer, showed longer wavelength emission.¹⁴ Thiophene also has lower band gap than benzene and poly(2,5-thienylenevinylene) (PTV) has been found to have a 25% lower band gap than that of PPV.¹⁸ In this paper, we report the synthesis and luminance properties of the PPV copolymers containing thiophene to shift their emission to longer wavelength than that of PPV. We prepared alternating copolymers through Heck coupling polymerization¹⁹ using divinylbenzene and 2,5-dibromo-3-alkyl-thiophenes. The polymers synthesized are poly(1,4-phenylenevinylene-*alt*-3-hexyl-2,5-thienylenevinylene) (PPV-*alt*-6-TV) and poly(1,4-phenylenevinylene-*alt*-3-octyl-2,5-thienylenevinylene) (PPV-*alt*-8-TV). Hexyl and octyl side chain of thiophene monomers enable the polymers to be soluble in various organic solvents and processible. The synthetic route and polymer structures are shown Scheme I.

Experimental

Scheme I



Materials. *N,N*-Dimethylformaldehyde (DMF) was purified by distillation over phosphorous pentoxide (P_2O_5) and the triethylamine (NEt_3) was distilled over CaH_2 . 2-Hexyl thiophene and 2-octyl thiophene were purchased from the Acros Organics Co. and were used without further purification. Tri-*o*-tolylphosphine, palladium(II) acetate, *N*-bromosuccinimide (NBS), and all of the other chemicals were purchased from the Aldrich Chemical Co. and were used as received unless otherwise stated. The *p*-divinylbenzene was separated from a mixture of *p*-divinylbenzene and *m*-divinylbenzene according to the literature procedure.²⁰

Instrumentations. The synthesized compounds were identified by 1H - and ^{13}C -NMR spectra that obtained using a Bruker AM 200 spectrometer. FT-IR spectra were measured by a Bomem Michelson Series FT-IR spectrophotometer, and UV-visible spectra were obtained with as Shimadzu UV-3100S. Thermogravimetric analysis (TGA) of polymers was performed under nitrogen atmosphere at a heating rate of $10^\circ C/min$ with a Dupont 2200 analyzer. Elemental analyses were performed by the Analytical Laboratory of Korea Advanced Institute of Science and Technology using a Elemental Analyzer (EA1110-FISONs).

Steady-state PL spectra of the films were taken by pumping with 488 nm CW from argon ion laser. The fluorescence signal was dispersed by a 1-m scanning monochromator (Mcperson model 2061), a photomultiplier tube (Hamamatsu R928) and a lock in amplifier. Fluorescence decay was recorded by the time-correlated single-photon counting method. The light source was a high power Ti:sapphire laser system. The laser pulses with 150 fs and $300 \mu J/pulse$ at 800 nm and 1 kHz repetition rate was frequency-doubled by a β -BBO crystal (400 nm) to excite the samples. The fluorescence decay profiles were collected at the wavelength of interest using a microchannel plate PMT (Hamamatsu R2809U) and then fit to exponential decay functions using the previously described deconvolution technique to obtain a best fit. The sample was cooled down using a Janis C-210 head with a Leybold Heraeus helium compressor. The temperature was controlled by a Lakeshore 330 autotuning temperature controller. The temperature fluctuation during the measure-

ment was less than 1K and the cryostat was evacuated to 10^{-4} Torr. In order to avoid possible contamination by oxygen, the sample was kept in vacuum for all measurements.

Synthesis of Monomers (2,5-dibromo-3-hexylthiophene and 2,5-dibromo-3-octylthiophene) (1 and 2). Each of 4.0 g (23.8 mmol) of 3-hexylthiophene and 3.2 g (23.8 mmol) of 3-octylthiophene were reacted with 8.9 g (50.0 mmol) of *N*-bromosuccinimide (NBS) in 30 mL of *N,N*-dimethylformamide (DMF). The reaction mixtures were stirred and heated to 70°C for 6 hrs. Then the products were extracted with methylene chloride and washed sodium hydroxide solution and water. The organic layers were dried with anhydrous magnesium sulfate (MgSO_4) and the solvent was removed with rotary evaporator. Through column chromatography with silicagel and alumina, the product was purified and the colorless liquid was obtained. The yield was 7.8 g (90%) for 2,5-dibromo-3-hexylthiophene. $^1\text{H-NMR}$ (CDCl_3 , ppm): δ 6.75 (s, 1H), 2.46 (t, 2H), 1.52 (m, 2H), 1.28 (m, 6H), 0.87 (t, 3H). $^{13}\text{C-NMR}$ (CDCl_3 , ppm): δ 142.95, 130.92, 110.29, 107.91, 31.56, 29.54, 29.47, 28.78, 22.57, 14.09. Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{S}$: C, 71.36; H, 9.59; S, 19.05. Found: C, 72.65; H, 8.62; S, 18.73. And the yield was 5.7 g (90%) for 2,5-dibromo-3-octylthiophene. $^1\text{H-NMR}$ (CDCl_3 , ppm): δ 6.75 (s, 1H), 2.48 (t, 2H), 1.54 (m, 2H), 1.25 (m, 10H), 0.87 (t, 3H). $^{13}\text{C-NMR}$ (CDCl_3 , ppm): δ 142.97, 130.93, 110.26, 107.89, 31.84, 29.56, 29.45, 29.31, 29.19, 29.09, 22.65, 14.10. Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{S}$: C, 73.40; H, 10.27; S, 16.33. Found: C, 74.24; H, 9.72; S, 16.04.

Polymerization of PPV-*alt*-6-TV and PPV-*alt*-8-TV (3 and 4). A mixture of 0.52 g (4.0 mmol) of *p*-divinylbenzene, 1.3 g (4.0 mmol) of 2,5-dibromo-3-hexylthiophene, 0.036 g of palladium acetate and 0.24 g of tri-*o*-tolylphosphine was dissolved in 15 mL of DMF and 1.4 mL of triethylamine was added. And the reaction mixture was stirred and heated to 100°C for 48 hrs under nitrogen atmosphere. 2-Bromothiophene, 0.16 g (1.0 mmol) was added to reaction flask to end-cap the polymer and reacted for 12 hrs. 2,5-Dibromo-3-octylthiophene was also reacted in the same reaction condition as above reaction. The orange

brown solids were obtained by precipitation of the solution in methanol. The polymers were further purified by Soxhlet extraction with methanol. The yield was 0.8 g (67%) for poly(1,4-phenylenevinylene-*alt*-3-hexyl-2,5-thienylenevinylene) [PPV-*alt*-6-TV] (3). $^1\text{H-NMR}$ (CDCl_3 , ppm): δ 7.42 (m, 4H), 7.18 (m, 1H), 6.88 (d, 1H), 6.82 (d, 1H), 2.64 (t, 2H), 1.60 (m, 2H), 1.33 (m, 6H), 0.89 (t, 3H). $^{13}\text{C-NMR}$ (CDCl_3 , ppm): δ 142.06, 140.93, 140.22, 136.29, 135.57, 129.86, 129.50, 128.07, 127.36, 126.56, 121.65, 119.50, 31.67, 30.79, 29.05, 28.41, 22.59, 14.08. Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{S}$: C, 81.58; H, 7.53; S, 10.89. Found: C, 81.62; H, 7.91; S, 10.47. And the yield was 0.74 g (57%) for poly(1,4-phenylenevinylene-*alt*-3-octyl-2,5-thienylenevinylene) [PPV-*alt*-8-TV] (4). $^1\text{H-NMR}$ (CDCl_3 , ppm): δ 7.43 (m, 4H), 7.18 (m, 1H), 6.89 (d, 1H), 6.82 (d, 1H), 2.64 (t, 2H), 1.61 (m, 2H), 1.28 (m, 10H), 0.88 (t, 3H). $^{13}\text{C-NMR}$ (CDCl_3 , ppm): δ 142.14, 141.28, 140.71, 136.43, 135.71, 135.57, 135.43, 135.14, 129.64, 127.14, 126.55, 121.43, 31.87, 30.81, 30.14, 29.42, 29.24, 27.86, 22.64, 14.09. Anal. Calcd for $\text{C}_{22}\text{H}_{26}\text{S}$: C, 81.93; H, 8.13; S, 9.94. Found: C, 81.95; H, 8.49; S, 9.56.

Sample Fabrication. The synthesized polymers were dissolved in *p*-xylene, then the solutions were spin-coated onto quartz substrates for UV absorption and PL measurements.

Results and Discussion

Structure Characterization. The phenylenevinylene and thienylenevinylene alternating copolymers were prepared by Heck coupling reaction. The polymers were soluble in organic solvents such as methylene chloride, dichloroethane, and *p*-xylene. PPV-*alt*-8-TV showed slightly better solubility than PPV-*alt*-6-TV due to the longer alkyl chain. Heck reaction has various synthetic advantages over Wittig reaction on monomer preparation and reaction conditions. However, both Heck and Wittig reactions are not good polymerization method to obtain high molecular weight. The number average molecular weight (M_n) and the weight average molecular weight (M_w) of the PPV-*alt*-6-TV (PPV-*alt*-8-TV), determined by gel permeation chromatography

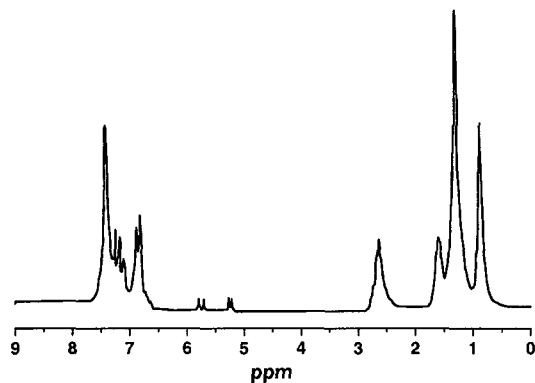


Figure 1. $^1\text{H-NMR}$ spectrum of poly(1,4-phenylenevinylene-*alt*-3-hexyl-2,5-thienylenevinylene), PPV-*alt*-6-TV, in CDCl_3 .

using polystyrene standards, were 8,000 (10,000) and 24,000 (26,000) with a polydispersity index (PDI) of 3.0 (2.6), respectively. Although the molecular weights of the polymers were somewhat low, they were high enough to fabricate the polymer films. The $^1\text{H-NMR}$ spectrum of the PPV-*alt*-6-TV is shown in Figure 1. The proton peaks of alkyl chain on thiophene appear at about 0.5~3.0 ppm and proton peaks of aromatic rings, benzene and thiophene appear at 7.0~8.0 ppm. The polymerization resulted in the appearance of vinylic proton peaks at about 6.8 ppm (broad doublet) along with aromatic protons of phenyl and thiophene in the $^1\text{H-NMR}$ spectra. The vinylic protons (5~6 ppm) indicate that a small amount of unreacted vinyl groups exist at the end of polymer chains though we tried to end-cap with 2-bromothiophene. PPV-*alt*-8-TV displayed the similar $^1\text{H-NMR}$ to PPV-*alt*-6-TV except the peaks from the alkyl chain on thiophene (not shown here). Figure 2 shows the FT-IR spectrum of PPV-*alt*-6-TV in KBr pellet. The strong peak appeared at about 970 cm^{-1} indicates that the vinylenes C=C bonds formed have the trans configurations. This proves the polymerization reactions have been successful. PPV-*alt*-8-TV also showed the similar FT-IR spectrum to PPV-*alt*-6-TV (not shown here). Thermal properties of the synthesized polymers were evaluated by the means of TGA under nitrogen atmosphere. Figure 3 shows that two polymers exhibited good thermal stability. The weight loss of the polymers was less than 5% on heating

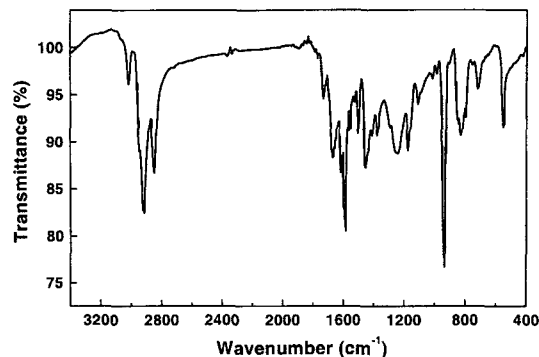


Figure 2. FT-IR spectrum of poly(1,4-phenylenevinylene-*alt*-3-hexyl-2,5-thienylenevinylene), PPV-*alt*-6-TV, in KBr pellet.

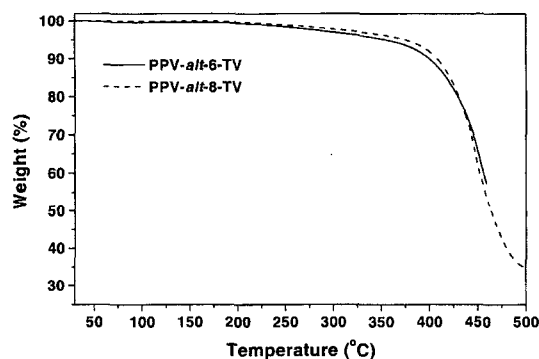


Figure 3. TGA thermograms of PPV-*alt*-6-TV and PPV-*alt*-8-TV.

up to about 300°C and above 400°C decomposition occurred. The polymerization results and thermal properties of PPV-*alt*-6-TV and PPV-*alt*-8-TV polymers are summarized in Table I.

Absorption and Photoluminescence Studies. Figure 4 shows the absorption spectra of PPV-*alt*-6-TV and PPV-*alt*-8-TV. The broad absorption bands from 350 to 570 nm are due to $\pi-\pi^*$ transitions of the polyconjugated systems.¹⁷ The maximum absorption peaks of the two polymers were found at about 452 and 448 nm for PPV-*alt*-6-TV and PPV-*alt*-8-TV, respectively, and the absorption edges were located at about 570 nm. As predicted from the absorption maxima and the edges of PPV (415 nm/530 nm) and PTV (540 nm/690 nm), the absorption maxima and the edges of the alternating copolymers of phenylenevinylene and thienylenevinylene, PPV-*alt*-

Table 1. Polymerization Results and Thermal Properties of PPV-*alt*-6-TV and PPV-*alt*-8-TV

polymers	polymer yield (%)	M_n^a	M_w^a	PDI ^a	T_{ID}^b (°C)
PPV- <i>alt</i> -6-TV	67	8,000	24,000	3.0	343
PPV- <i>alt</i> -8-TV	57	10,000	26,000	2.6	375

^a M_n , M_w , and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards.

^bTemperature at which initial loss of mass (5%) was observed.

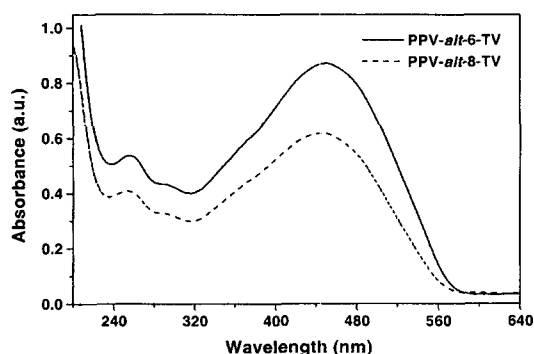


Figure 4. UV-visible spectra of PPV-*alt*-6-TV and PPV-*alt*-8-TV thin films coated on a quartz plate.

6-TV and PPV-*alt*-8-TV, are located between those of PPV and PTV. Therefore, we could successfully demonstrate the band gap control, especially lowering the band gap in PPV derivatives using copolymerization. Figure 5 shows the photoluminescence (PL) spectra of PPV-*alt*-6-TV and PPV-*alt*-8-TV. To compare the PL properties, PL spectra of PPV and MEH-PPV are also shown in Figure 5. The synthesized copolymers exhibited broad PL spectra between 550 and 700 nm and PL maxima of PPV-*alt*-6-TV and PPV-*alt*-8-TV are about 620 and 605 nm, respectively. As expected from absorption spectra of PPV and the copolymers, the copolymers also showed red shifted emission compared to PPV. Moreover, the PL spectra of the copolymers are located at longer wavelength than MEH-PPV. In terms of emission color, the copolymers showed the emission closed to red color, but still more red shifted of emissions are needed to obtain real red color. One possible approach may be the change of divinylbenzene monomer to alkoxy substituted divinylbenzene.

Figure 6 shows the temperature-dependent PL spectra of PPV-*alt*-6-TV. As the temperature increases, the PL intensity is lowered due to faster nonradiative decays. Similar temperature depen-

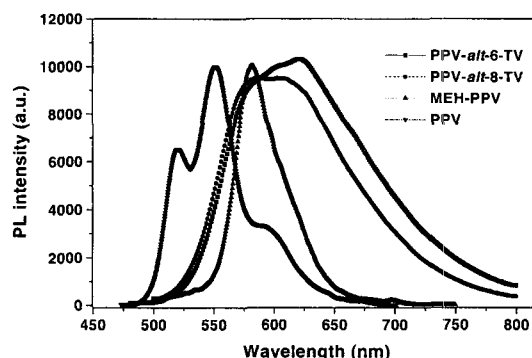


Figure 5. Photoluminescence (PL) spectra of PPV-*alt*-6-TV, PPV-*alt*-8-TV, MEH-PPV, and PPV thin films coated on a quartz plate.

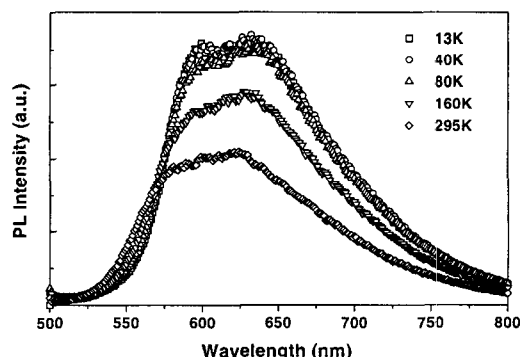


Figure 6. Temperature-dependent photoluminescence (PL) spectra of PPV-*alt*-6-TV.

dence of PL intensity was also observed in PPV-*alt*-8-TV. Time resolved PL were measured to obtain further information on the relaxation dynamics of PPV-*alt*-6-TV. Figure 7 shows the PL decay profiles of PPV-*alt*-6-TV at room temperature which were obtained at various wavelengths. PL decay profile shows that the average PL decay is faster at the high energy side of the PL band than that at the low energy side. The PL decay profiles of various conjugated polymers were

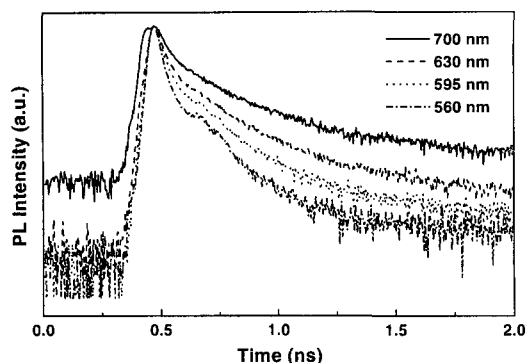


Figure 7. Photoluminescence (PL) decay profiles of PPV-alt-6-TV at 295 K at various wavelengths.

similar to the results of PPV-alt-6-TV.^{21,22} These observations were interpreted in terms of the random walk of excitations within the DOS (Density of States Distribution). The photoexcitation at shorter wavelengths produces excited states in the segments of the polymer chain within a range of conjugation lengths, and then the excitons readily migrate to the lower energy side.

Conclusions

PPV-alt-6-TV and PPV-alt-8-TV exhibited the absorption maxima near 452 and 448 nm, and PL emission maxima at about 620 and 605 nm, respectively, with 488 nm excitation. The copolymers showed red shifted emission compared to PPV and MEH-PPV, and we expect more red shifted emission from the copolymers of alkoxy substituted phenylenevinylene and thienylenevinylene, which is under investigation.

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References

- (1) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature*, **347**, 539 (1990).
- (2) A. Kraft, A. C. Grimsdale, and A. B. Holmes, *Angew. Chem. Int. Ed.*, **37**, 402 (1998).
- (3) W. J. Feast, J. Tsibouklis, K. L. Pouwer, L. Groenendaal, and E. W. Meijer, *Polymer*, **37**, 5017 (1996).
- (4) S. J. Lee, D. W. Kim, S. Y. Park, and S. I. Hong, *Korea Polymer Journal*, **5**, 52 (1997).
- (5) K. C. Fox, *New Sci.*, **141**, 33 (1994).
- (6) D. H. Hwang, S. D. Jung, L. M. Do, T. Ahn, H. K. Shim, and T. Zyung, *Bull. Korean Chem. Soc.*, **19**, 332 (1998).
- (7) R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdiund, and W. R. Salaneck, *Nature*, **397**, 121 (1999).
- (8) H. S. Kim, S. H. Noh, and T. Tsutsui, *Korea Polymer Journal*, **7**, 18 (1999).
- (9) T. A. Skotheim, R. L. Elsenbaumer, and J. R. Reynolds, *Handbook of Conducting Polymers*, 2nd ed., M. Dekker, New York, 1998, pp 1097.
- (10) A. Hilberer, P. F. vanHutten, J. Wildeman, and G. Hadziioannou, *Macromol. Chem. Phys.*, **198**, 2211 (1997).
- (11) D. Braun and A. J. Heeger, *Appl. Phys. Lett.*, **58**, 1982 (1991).
- (12) G. H. Gelinck, J. M. Warman, and E. G. J. Staring, *J. Phys. Chem.*, **100**, 5485 (1996).
- (13) D. H. Hwang, S. T. Kim, H. K. Shim, A. B. Holmes, S. C. Moratti, and R. H. Friend, *Chem. Commun.*, **19**, 2241 (1996).
- (14) H. Spreitzer, H. Becker, E. Kluge, W. Kreuder, H. Schenk, R. Demandt, and H. Schoo, *Adv. Mater.*, **10**, 1340 (1998).
- (15) H. Becker, H. Spreitzer, W. Kreuder, E. Kluge, H. Schenk, I. Parker, and Y. Cao, *Adv. Mater.*, **12**, 42 (2000).
- (16) T. Ahn, S. Y. Song, and H. K. Shim, *Macromolecules*, **33**, 6764 (2000).
- (17) T. Ahn, M. S. Jang, H. K. Shim, D. H. Hwang, and T. Zyung, *Macromolecules*, **32**, 3279 (1999).
- (18) A. J. Brassett, N. F. Colaneri, D. D. C. Bradley, R. A. Lawrence, and R. H. Friend, *Phys. Rev. B*, **41**, 10586 (1990).
- (19) Z. Bao, Y. Chen, R. Cai, and L. Yu, *Macromolecules*, **26**, 5281 (1993).
- (20) B. T. Storey, *J. Polym. Sci., Part A*, **3**, 265 (1965).
- (21) I. D. E. Samuel, B. Crystall, G. Rumbles, P. L. Burn, A. B. Holmes, and R. H. Friend, *Synth. Met.*, **54**, 281 (1993).
- (22) U. Lemmer, R. F. Mahrt, Y. Wada, A. Greiner, H. Bässler, and E. O. Göbel, *Appl. Phys. Lett.*, **62**, 2827 (1993).