

Synthesis and Characterization of Red Light-Emitting Random Copolymers

Yeong-Beom Lee¹ and Hong-Ku Shim²

¹LCD Division, Samsung Electronics Co. Ltd.

¹LCD Division, Device Solution Business, Samsung Electronics Co. Ltd. #200 Myeongam-Ri, Tangjeong-Myeon, Asan-City, Chungcheongnam-Do, 336-841

TEL: +82-41-535-5378, e-mail: yeongbeom.lee@samsung.com.

²Department of Chemistry, Korea Advanced Institute of Science and Technology

373-1 Guseong-dong, Yuseong-ku, Daejeon, 305-701, Korea

TEL:+82-42-350-2867, e-mail: hkshim@mail.kaist.ac.kr

Abstract

A series of new light-emitting random copolymers with fully conjugated structure was prepared, for the first time through the well-known Gilch polymerization between 1,4-bis(chloromethyl)-2-ethylhexyloxy-5-methoxybenzene and 2,5-bis(bromomethyl)thiophene monomers in different ratios. The synthesized polymers (on thin film) showed the maximum wavelength of UV-visible absorbance and photoluminescence (PL) near 500 nm and near 600 nm, respectively. A single-layer light-emitting diode device, which has a simple ITO (indium-tin oxide)/polymer/Al configuration, was fabricated by spin-coating of polymers and then vacuum evaporation of Al metal. The threshold bias of PMEHPVTVs was in the range of 3.5-10 V. As in the PL spectra, the maximum wavelength of light emission near 600 nm was also shown in electroluminescence (EL) spectra of PMEHPVTVs when the operating voltage was about 7 - 14 V.

1. Introduction

Electroluminescent (EL) devices based on polymer materials have attracted much attention in the past ten years due to their potential applicability in display industry [1]. Polymer light emitting diodes (PLEDs) have many advantages for the development of a large-area light-emitting display, such as good processibility, low operating voltage, fast response time and color tunability over the full visible range by control of the HOMO-LUMO band gap of the emissive layer [2,3]. Dialkoxy-PPV such as MEH-PPV shows an efficient electroluminescence, good processibility and good mechanical properties, but its EL emission corresponds to orange red region (ca. 580 nm) [4]. The introduction of substituents is allowing solubility and enhancing the EL quantum efficiency. The cyclohexyl side chain was adopted firstly in polythiophene(PT) as a bulky substituent to achieve spectral blue shift due to steric hindrance [5]. Shim *et al.* reported poly[2-(5-cyclohexylmethoxy)pentyl-5-methoxy-1,4-phenylene-

vinylene] *via* dehydrohalogenation polymerization. The polymer showed about 6 times higher than that of MEH-PPV in the measured relative EL quantum efficiency and 15% higher than that of MEH-PPV in the PL quantum efficiency [6]. By the way, poly(thienylenevinylene) (PTV) shows an EL emission in pure red region (around 670 nm) but its luminescence efficiency is very low [7]. Shim *et al.* reported the synthetic routes and electrical conductivity of a series of random poly(1,4-phenylenevinylene-co-2,5-thienylenevinylene)s (dark red color solid) *via* the Wessling and Zimmerman's procedure [8], and the synthesis and EL devices ($\lambda_{em} = 616$ nm in photoluminescent emission and $\lambda_{em} = 630$ nm in electroluminescent emission) of an alternating copolymer of PPV-PTV, poly[2-methoxy-5-(3,7-dimethyloctyloxy-1,4-phenylenevinylene-*alt*-2,5-thienylenevinylene] *via* Wittig condensation polymerization [7], and the synthesis and light emitting properties of a series of poly(1,4-phenylenevinylene-*alt*-3-alkyl-2,5-thienylenevinylene)s ($\lambda_{em} = 620, 605$ nm in photoluminescent emission) *via* the Heck coupling reaction [9]. Moratti *et al.* reported the synthesis of an alternating phenylenevinylene and thienylenevinylene copolymer *via* the Knoevenagel condensation polymerization and its infrared light emitting properties ($\lambda_{em} = 850$ nm in photoluminescent emission and $\lambda_{em} = 730$ nm in electroluminescent emission) [10].

Recently, we have synthesized novel light-emitting random copolymers of fully conjugated structure with 2-ethylhexyloxy-5-methoxyphenylenevinylene (MEHPV) unit and thienylenevinylene (TV) unit which have heteroaromatic ring, poly[2-ethylhexyloxy-5-methoxy-1,4-phenylenevinylene-co-2,5-thienylenevinylene] (PMEHPVTV)s, for the first time through Gilch polymerization. Dialkoxy-PPV shows efficient electroluminescence, good processibility and good mechanical property, but the EL emission is shown at orange red region (ca. 580 nm). By the way, poly(thienylenevinylene) (PTV)

shows EL emission in pure red region (around 670 nm) through the luminescence efficiency of PTV is very low. So we attempted to obtain red light emission by controlling the feed ratio of 2,5-bis(bromomethyl)thiophene monomer on the polymerization and high molecular weights by Gilch method. In this research, we report the synthesis and properties of PMEHPVTVs, and characteristics of the single layer EL devices of the polymers.

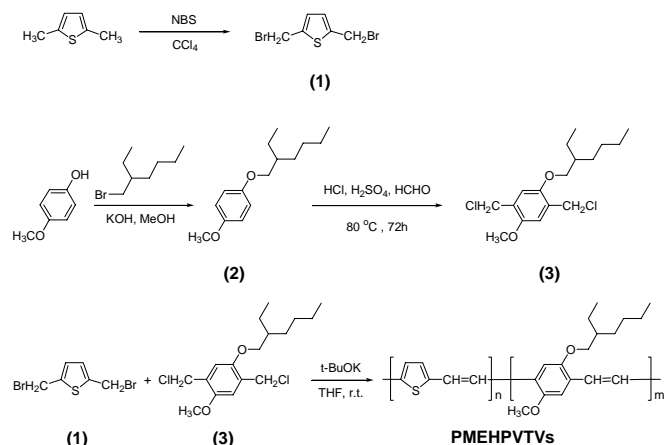


Fig. 1. Synthetic routes of PMEHPVTVs and their monomers.

2. Experimental Section

2.1. Synthesis The synthetic routes of PMEHPVTVs and their monomers are shown in Scheme 1. 2,5-bis(bromomethyl)thiophene (1) was obtained by halogenation of 2,5-dimethylthiophene with *N*-bromosuccinimide (NBS) in tetrachloromethane without a catalyst, and 1 was very unstable in the air. 4-(2-Ethylhexyloxy)-1-methoxybenzene (2) was synthesized by alkylation of 4-methoxyphenol with 2-ethylhexyl bromide. 1,4-Bis(chloromethyl)-5-(2-ethylhexyloxy)-2-methoxybenzene (3) was prepared by chloromethylation of 2 with excess hydrochloric acid and formaldehyde in 1,4-dioxane. Some intermediates, including the monomers, were characterized by elemental analysis, and melting point measurements and common spectroscopic techniques such as $^1\text{H-NMR}$, FT-IR, and UV-visible spectroscopies. Their results are in good agreement with the structures obtained in each step of the synthetic routes. The PMEHPVTVs were synthesized by Gilch polymerization between 2,5-bis(bromomethyl)thiophene and 1,4-dis(chloromethyl)-5-(2-ethylhexyloxy)-2-methoxybenzene using tert-butoxide as a base in an anhydrous THF solvent at room temperature for 8 h. Then, the final

PMEHPVTVs were purified by Soxhlet extraction in methanol for 2 days. The yields of PMEHPVTVs were 80 % (dark red solid, 57 % after Soxhlet extraction), 69 % (dark red solid, 65 % after Soxhlet extraction) and 64 % (light red solid, 50 % after Soxhlet extraction) for PMEHPVTV81, PMEHPVTV41, and PMEHPVTV21, respectively. The PMEHPVTVs were soluble in aprotic polar solvents such as THF, 1,2-dichloroethane, chloroform, and cyclohexanone because of interaction between polar solvents and alkoxide parts of MEHPV in the main chain. Their solubility was especially good in 1,2-dichloroethane and cyclohexanone. The molecular weights were obtained from gel permeation chromatography (GPC) analysis using polystyrene as standard and THF as eluant. The weight average molecular weights of the polymers were determined to be 743,200 ($M_w/M_n=15.9$) for PMEHPVTV81 (monmer (3):(1) = 8:1), 268,000 ($M_w/M_n=16.9$) for PMEHPVTV41 and 448,100 ($M_w/M_n=57.5$) for PMEHPVTV21.

2.2. Chemical structure characterization Figure 2 is the $^1\text{H-NMR}$ spectra of the polymers, which show signal broadening caused by polymerization, which the chemical shifts are well consistent with the proposed polymer structures. After purification of the polymers, Two small broad peaks between $\delta = 7.1$ and $\delta = 6.5$ were originated from the protons of the thienylene and vinylene group in the polymer backbone. The sizable peak at 7.24 ppm comes from chloroform and the peak at 1.53 ppm originates from H_2O molecules in CDCl_3 solvent.

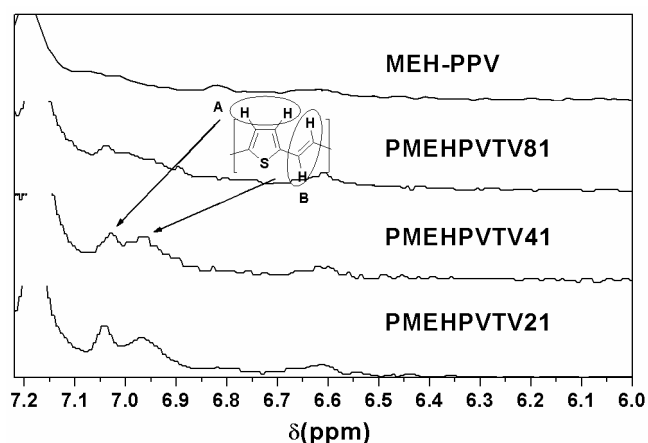


Fig. 2. $^1\text{H-NMR}$ characterization of thienylenevinylene group in PMEHPVTVs

The FT-IR spectra of PMEHPVTVs showed the bands at $3062\text{--}3075\text{ cm}^{-1}$, together with that at $\text{ca. } 780\text{ cm}^{-1}$, were assigned to being the stretching vibration of C-H

in the heteroaromatic ring at the positions 3 and 4 to the in plane ($\nu\text{C-H}_{\text{ip}}$) and out-of-plane ($\delta\text{C-H}_{\text{op}}$) bending vibration, respectively. The bands at 1430-1442 cm^{-1} were attributed to the stretching vibration of C=C in the heteroaromatic ring ($\nu\text{C}=\text{C}_{\text{Ar}}$). The weak and sharp band corresponding to the out-of-plane bending mode of the *trans*-vinylene system conjugated with the aromatic ring ($\nu\text{C}=\text{C}_{\text{vi}}$) appeared at ca. 960 cm^{-1} . This proves that the vinylene double bond formation and consequently the polymerization reaction have been successful. In the UV-visible spectra, all PMEHPVTVs showed similar absorption maxima at $\lambda_{\text{max}} = 500$ nm (on solution and on thin film on ITO glass substrate) respectively and these absorption peaks originated from the $\pi\text{-}\pi^*$ transition of the conjugated main chain.

2.3. Thermal characterization Thermal characterization of the PMEHPVTVs was carried out using TGA and DSC instruments. TGA studies indicated that the first decomposition (at 5% weight loss) of all polymers occurred around 380 °C (under nitrogen atmosphere), originating from breaking of the alkyloxy group from polymer backbone. In DSC thermograms, the polymers did not show melting endothermic peaks, indicating that they represent a noncrystalline phase, but showed relatively high glass transition temperatures; Tg values are around 150-160 °C for all PMEHPVTVs because of the rigidity of the heteroaromatic backbone in the polymer chain.

3. Results and discussion

Optical and electrical characteristics The final PMEHPVTVs were dissolved in 1,2-dichloroethane and were processed into optically good quality films by spin coating the polymer solution. In UV-visible absorption spectra of PMEHPVTVs in THF solution and on thin film of PMEHPVTVs coated onto a quartz plate, the similar maximum absorption near 500 nm was shown. The PL maxima of PMEHPVTVs are different between solution (560 nm) and thin film (600 nm) because of the solvatochromic effect. The maximum absorption of all PMEHPVTVs and maximum PL emission of PMEHPVTV21 showed ca. 500 nm and ca. 600 nm in wavelength, respectively. In PL spectra, the emission maximum wavelength of PMEHPVTV21 have red-shifted about 20 nm than that of MEH-PPV.

A single-layer light-emitting diode was fabricated by using ITO as an anode and Al as a cathode,

respectively. The PMEHPVTV polymers described above were deposited onto indium-tin oxide-covered glass substrates by spin-casting the polymers dissolved in 1,2-dichloroethane. The Al electrode (cathode) was then evaporated onto this in vacuum with thickness of about 110 nm.

Fig. 3 shows the current-voltage (I-V) characteristics of the single-layer light-emitting diode of ITO/PMEHPVTVs/Al. The forward bias current was obtained when the ITO electrode was positively biased and the Al electrode negatively biased. The current increased with increasing forward bias voltage, indicating typical rectifying characteristics.

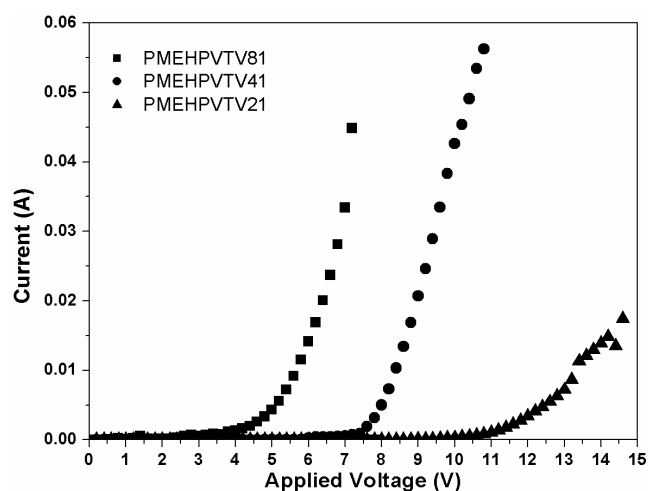


Fig. 3. Current vs. voltage curves of PMEHPVTVs

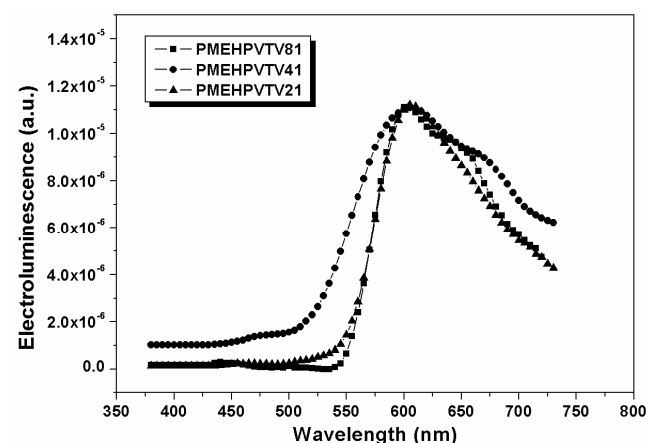


Fig. 4. Electroluminescent spectra of PMEHPVTVs

The threshold voltages of PMEHPVTV polymers were in the range of 3.5-10 V, which was low or similar, compared with that of other red light emitting PPV-based polymers. The PMEHPVTV polymer films showed maximum EL emission at 600 nm, which was similar to that of the PL spectrum of PMEHPVTV21,

corresponding to the orange-red region. The electroluminescence spectra of PMEHPVTVs exhibited similar EL emissive wavelength at 596 and 615 nm in Figure 4, which were orange red and red, on the operating voltage of 7-11 V, respectively.

4. Conclusion

We have prepared novel light-emitting random copolymers containing thienylenevinylene units in the main chain, for the first time through Gilch polymerization. The PMEHPVTV polymers were obtained with high molecular weights in the range of 743,000-268,000. The resulting polymers showed good solubility in common organic solvents and good thermal stability. They could spin-cast onto various substrates to give highly transparent homogeneous thin films without heat treatment. In the UV-visible and photoluminescence spectra, the maximum absorption of PMEHPVTVs and PL emission spectra of PMEHPVTV21 showed orange red emission at ca. 500 and ca 600 nm, respectively. Single-layer light-emitting diodes of ITO/PMEHPVTVs/Al were fabricated. The threshold voltages of PMEHPVTVs were in the range of 3.5-10 V. The EL spectra of PMEHPVTVs gave similar maximum peaks at 596 and 615 nm, which were orange red and red, on the operating voltage of 7-14 V.

5. References

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