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Poly(fluorenevinylene) Derivative by Gilch Polymerization for Light-Emitting Diode Applications

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Electroluminescence (EL) devices have been extensively studied due to the their potential application to full-color flat panel displays since the first observation of EL in anthracene in 1965.[1] In the late 1980s, a high-performance device fabricated by Tang and VanSlyke using the two-layer light-emitting diodes (LEDs) with organic fluorescent dyes was a breakthrough in the field.[2] Then a variety of organic materials have been developed as luminescent materials including small molecular systems and π-conjugated polymers. Among the π-conjugated polymers, poly(*p*-phenylenevinylene) (PPV)[3] and poly(9,9-dialkylfluorene) (PF)[4] derivative systems are considered to be promising candidate materials for polymer LEDs. For the synthesis of PPV-based polymers, it is well-known that Gilch polymerization is widely used with several advantages, yielding high molecular weight, low polydispersity, reproducibility, and easy design of the monomers. Recently, poly(9,9-dialkylfluorene-2,7-vinylene) was prepared by acyclic diene metathesis (ADMET) polymerization[5] and the Heck reaction.[6] However, this is the first paper reporting the synthesis of poly(9,9-di-*n*-octylfluorene-2,7-vinylene) (PFV) via Gilch polymerization together with its characterization and purification using membrane technology. Scheme 1 shows the synthetic route for the monomer and polymer. 9,9-Di-*n*-octylfluorene was prepared with 1-bromooctane and fluorene in a two-phases system composed of DMSO and sodium hydroxide (50% w/w) aqueous solution using tetrabutylammonium bromide (TBAB) as a phase transfer catalyst at room temperature for 12 h. The introduction of a chloromethyl group into the 2- and 7-position in 9,9-di-*n*-octylfluorene was carried out in a mixture of aqueous formaldehyde (39%, 100 mL), 9,9-di-*n*-octylfluorene (34 g, 86 mmol), and 80 mL of 1,4-dioxane with gaseous HCl at 80 °C for 5 h.[7] The structure and purity of monomer were confirmed by ^{1}H NMR, ^{13}C NMR, and elemental analyses.[8] The overall yield of the monomer synthesis was about 40%. The polymerization of the monomer was performed with an excess of potassium *tert*-butoxide in THF at room temperature for 24 h under a N_2 atmosphere.[9] The key factor for obtaining the high molecular weight of the PFV by Gilch polymerization is the introduction of a chloromethyl group into the 9,9-di-*n*-octylfluorene unit. However, the polymerization of fluorene-based monomer with bromomethyl group gave a relatively low molecular weight of the PFV due to the synthesis of 2,7-bis(*tert*-butoxymethyl)-9,9-di-*n*-octyl-9*H*-fluorene. The drawback of Gilch polymerization is the difficulty in controlling the polymerization rate and formation of the insoluble gel portion during the reaction.[10] However, we did not observe any gel formation during the polymerization. The PFV was completely soluble in various organic solvents such as chloroform, chlorobenzene, toluene, and xylene. The molecular structures of the monomer and the PFV were identified by ^{1}H NMR and UV−vis spectroscopy. Figure 1 shows the ^{1}H NMR spectra of the monomer (a) and the PFV (b) in $CDCl_3$. The absence of the characteristic chloromethyl proton peaks at 4.6 ppm of monomer and appearance of new vinylic proton peaks at 7.1 ppm with aromatic proton peaks in PFV confirms the polymerization reaction, and all other peaks are in good agreement with the chemical structure of the polymer. Recently, one significant defect structure was detected in the main chain of Gilch-polymerized PPV derivatives as reported by Becker et al.[11] This defect can be easily explained by head-to-head formation instead of regular head-to-tail polymerization reaction. The interpretation of the broad ^{1}H NMR signal at 3.0 ppm is consistent with the 2-{2-[9,9-di-*n*-octyl-9*H*-fluoren-2-yl]ethyl}-9,9-dioctyl-9*H*-fluorene moiety in PFV similar to the tolane−bisbenzyl (TBB) in PPV derivatives. The amount of defect structure in PFV is roughly estimated to be 10−15%. To improve the device performance, the PFV was further purified by multiple precipitations into the different solvents such as methanol and isopropyl alcohol, and then the purified PFV was finally dialyzed

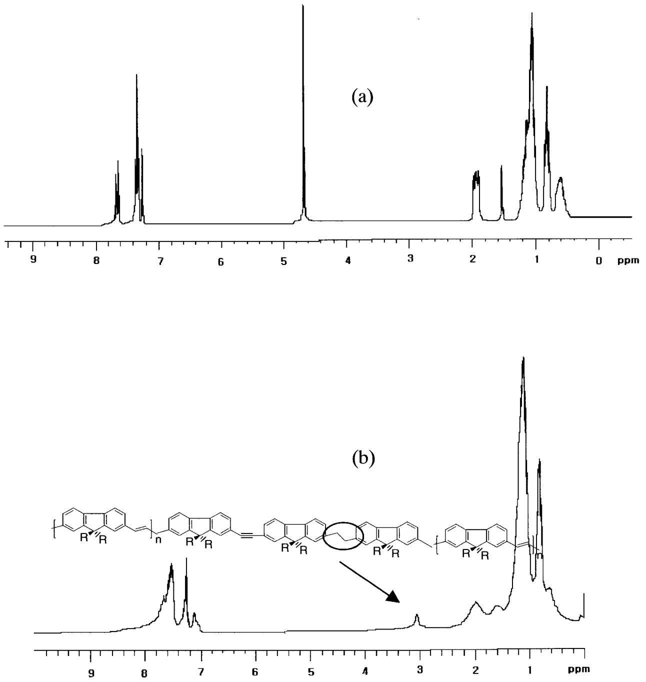

Figure 1. ^{1}H NMR spectra of monomer (a) and PFV (b) in $CDCl_3$.

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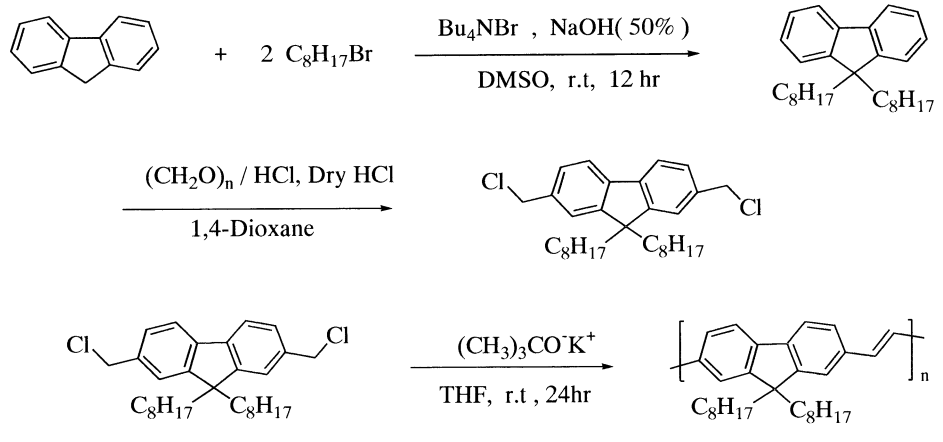
Scheme 1



PFV

against chloroform solvent with dialysis membrane (Spectrum Co.) for 3 days to remove the medium molecular weight polymer (weight-average molecular weight cutoff, 80 000). The remaining solution in dialysis membrane was poured into methanol and then filtered and dried under vacuum. The weight-average molecular weight (M_w) and polydispersity of the PFV were estimated to be 13.9 × 10^4 and 18.4, respectively, as measured prior to the molecular fractionation experiment. However, after removing the medium molecular weight portion in the bimodal GPC curve, the PFV exhibits a narrow polydispersity (~2.1) and unimodal GPC curve with a M_w value of 22.2 × 10^4. In previous work synthesized by ADMET polymerization,[5] however, the molecular weight of poly(9,9-di-*n*-octylfluorene-2,7-vinylene) was 6.9 × 10^4. PFV has a glass transition temperature at 173 °C as determined by DSC. This value is higher than those of poly(9,9-dialkylfluorene)s (75−113 °C).[12,13] PFV exhibits a higher thermal stability than that of poly(9,9-dialkylfluorene) derivatives, showing 5% weight loss at 415 °C. The high thermal stability of the PFV prevents the deformation and degradation of the emitting layer from current-induced heat during the operation of the EL devices. The PEDOT:PSS was spin-coated from aqueous solution with isopropyl alcohol (10 wt %) on the surface-treated ITO substrate and cured for 30 min. The emissive layer was deposited on top of the PEDOT film. After that, the aluminum cathode was thermally evaporated at ~10^{-6} mbar. Optical absorption (Abs) and photoluminescence (PL) spectra of the thin PFV film are shown in Figure 2 together with the EL spectrum of the ITO/PEDOT/PFV/Al device. The absorption peak is located around 420 nm due to the $\pi-\pi^*$ transition of the conjugated polymer backbone with a shoulder at 377 nm, which corresponds to the characteristic peak of the fluorene unit. The absorption of PFV is approximately 40 nm red-shifted relative to that of poly(9,9-dialkylfluorene) derivatives.[14] The maximum emission peak is at 507 nm, which corresponds to greenish-blue light. The EL spectrum was almost identical to the PL spectrum. Energy band diagrams of the PFV and poly(9,9-dihexylfluorene) for comparison were determined from the optical absorption spectrum for the band gap and the cyclic voltammogram for the HOMO energy level. The band gap and HOMO level are 2.6 and 5.3 eV for PFV and 2.9 and 5.7 eV for poly(9,9-di-*n*-hexylfluorene), respectively.[15] The barrier heights were found to be 0.6 and 1.0 eV at the interface of the ITO (4.7 eV)/HOMO state for hole injection and 1.6 and 1.5 eV at the interface of the Al (4.3 eV)/LUMO state for electron injection of the PFV and poly(9,9-di-*n*-hexylfluorene), respectively. Both polymers show that the major carrier is the holes rather than electrons, due to the lower band offset between the anode and HOMO energy level. Figure 3 shows the current−voltage−luminescence (*I*−*V*−*L*) characteristics of the ITO/PEDOT/PFV/Al device. The turn-on voltage is approximately 2.5 V, and the current density increases in an exponential manner with increasing forward bias, which is typical of diode characteristic. However, the turn-on

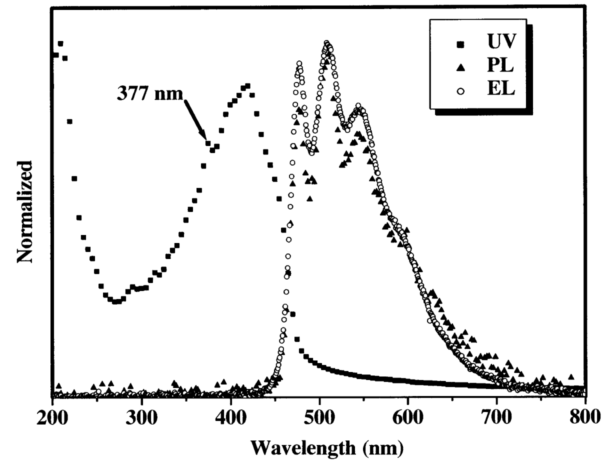


Figure 2. UV−vis absorption (a) and PL spectra (b) in the solid state and EL spectrum of the ITO/PEDOT/PFV/Al device.

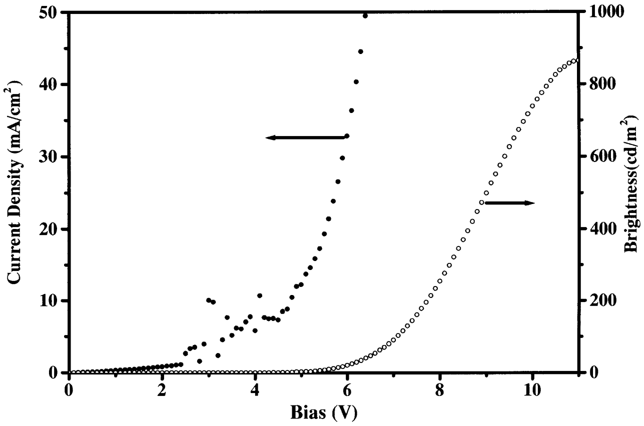


Figure 3. Current−voltage−luminescence (*I*−*V*−*L*) characteristics of the ITO/PEDOT/PFV/Al device.

voltage of the poly(9,9-di-*n*-octylfluorene) is about 4 V with the ITO/PEDOT/poly(9,9-di-*n*-octylfluorene)/Ca/Al device.[16] The relatively lower turn-on voltage of the PFV even though Al electrode than that of poly(9,9-dioctylfluorene) may be due to the introduction of vinylene unit into the fluorene backbone which usually lowers the HOMO binding energy. The polymer LED emits bright greenish-blue light at room temperature. The maximum luminescence and luminescence efficiency were about 870 cd/m^2 at 10 V and 0.16 Cd/A, respectively. Further optimization of molecular structure and detailed EL properties are under investigation.

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