Poly[2-(4'-decyloxylphenyl)-1,4-phenylenevinylene]: A Novel Soluble Phenyl-Substituted Poly(*p*-phenylenevinylene) Derivative as Electroluminescent Material

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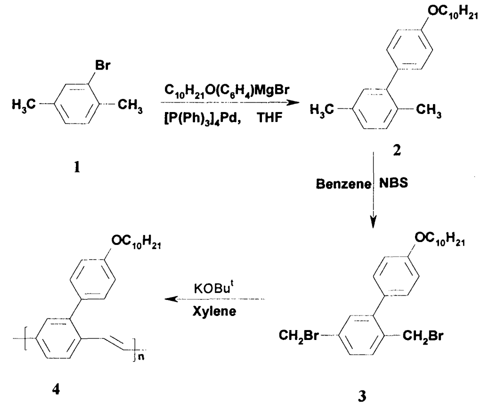
A novel soluble phenyl-substituted PPV derivative, poly[2-(4'-decyloxylphenyl)-1,4-phenylenevinylene (DOP-PPV), is synthesized, which has PL quantum efficiency of 40% and emits bright green light from single layer light-emitting diode devices (ITO/DOP-PPV/Ca or Al) with the emission maximum at 520 nm and external quantum efficiency of *ca.* 0.3%.

Enormous efforts have been devoted to the development of conjugated polymers as eletroluminescent (EL) materials since the first discovery of electroluminescence in poly(1,4-phenylenevinylene) (PPV).[1] Among the EL polymers that have been developed, PPV and derivatives still remain as the most popular class. Different functional groups have been attached to the backbone of PPV as substituents on the benzene ring or/and the vinylene band to improve the processability and quantum yields and to tune the HOMO-LUMO bandgap, which results in different emissive wavelength, of the resultant polymers.[2] Overview the substituents in PPV derivatives, phenyl substituted groups are hardly found, except the recent contributions from Nishide[3], Hseieh et al[4] and Spreitzer et al.[5] This is partially owing to the poor solubility of such PPV derivatives.[6] Hseieh et al firstly prepared the insoluble thin films of poly(2,3-diphenyl-p-pheneylene vinylene) (DP-PPV) and its derivatives via a chlorine precursor route.[4] Soluble DP-PPV derivatives were then synthesized via a versatile synthetic steps involving Diels-Alder reaction in the preparation of monomers and a Gilch synthetic route in polymerization.[4] In order to ensure the solubility of the polymers, a nonpolymerizable acidic additive has to be used in the polymerization process to limit the molecular weight of the resultant polymers. In the work of Spreitzer et al, soluble phenyl-substituted PPVs were obtained by copolymerizing different phenyl-substituted monomers via a Gilch route in dioxane.[5] All the phenyl-substituted PPVs exhibit attractive properties either in high photoluminescence (PL) efficiency or in good EL performance. Phenylene is an interesting substituent in EL polymers, as demonstrated in polythiophene derivatives.[7] In order to understand the effects of phenylene substituents on the electronic and optical properties of PPV, it is essential to synthesize soluble phenyl-substituted PPVs with well structure definition. We report here the successful synthesis of a soluble phenyl-substituted homopolymer with a modified Gilch route.

As shown in Scheme 1, the new polymer, poly[2-(4'-decyloxylphenyl)-1,4-phenylenevinylene] (DOP-PPV), was obtained by a dehydrohalogenation condensation polymerization from the corresponding monomer, 1,4-bis(bromomethyl)-2-(4-decyloxy)benzene **3**. The monomer **3** was synthesized from the starting material of 2-bromo-*p*-xylene **1** through a Grignard coupling reaction with 4-decyloxyphenylmagnisium bromide catalysed by Pd(PPh$_3$)$_4$, which afforded 2-(4'-decyloxyphenyl)-1,4-xylene **2**, and then followed by a dibromonation with NBS in benzene. The base used in the polymerization is KOBu^t. The solvent used in the polymerization is an important factor for the solubility of the resultant polymers. When THF was used, the polymers obtained always had very poor solubility in common organic solvents. When xylene was employed as the solvent, a soluble polymer was afforded. This may be attributed to the lower polarity of xylene, which reduces the reactivity in the polymerization and results in lower molecular weight of the resultant polymer.



The crude polymer was purified by dissolving in THF and then precipitating from methanol. The process was repeated twice. After being dried under vacuum, DOP-PPV **4** was obtained as yellow solid with the yield of ~ 32% for polymerization. The chemical structure and purify of the polymer were confirmed by NMR and elemental analysis.[8] DOP-PPV **4** is completely soluble in common organic solvents such as THF, chloroform, toluene, and xylene with the concentration up to 3% (w/v). Thermogravimetric analysis (TGA) reveals that the polymer is stable up to 300 °C without decomposition in air.

Uniform and transparent solid film of DOP-PPV **4** on substrate could be obtained by spin-coating its solutions in above solvents. The UV-visible and PL spectra of the DOP-PPV **4** film on micro slide are shown in Figure 1. All the spectra were measured at room temperature. The absorption maximum and edge of the DOP-PPV **4** are at 398 and 489 nm, respectively. The HOMO-LUMO band gap could be estimated to be 2.54 eV from the absorption edge wavelength. The absorption spectrum is blue-shifted by about 30 nm compared with that of unsubstituted PPV. This could be attributed to the large steric effect of the 4-decyloxybenzene substituent. The emission spectrum shows its maximum at ~ 515 nm, corresponding to the green region. The difference between the absorption and emission maxima is 117 nm, it is larger than those of PPV (110 nm)[1a] and DMOS-PPV (106 nm),[9] which

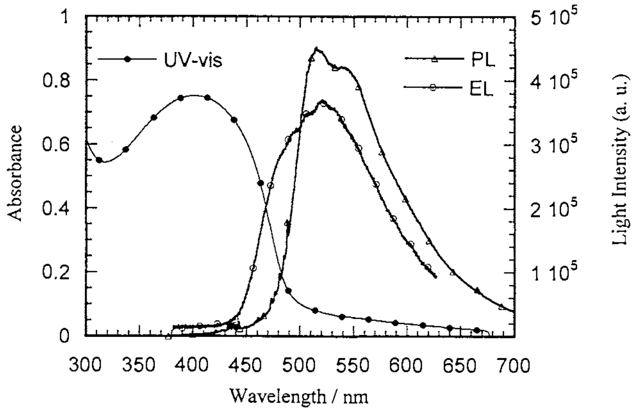


Figure 1. Absorption, photoluminescent and electroluminescent spectra of polymer 4, DOP-PPV.

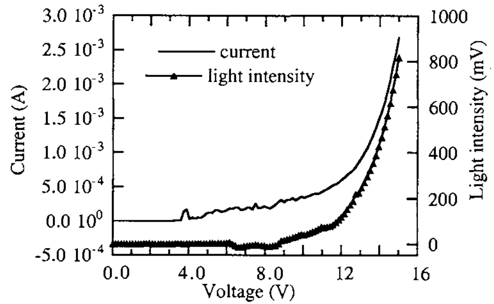


Figure 2. Current and light intensity vs. bias voltage of an ITO/DOP-PPV/Al devices.

are all green light-emitting polymers. This implies that the overlap between absorption and emission spectra is smaller in the DOP-PPV **4** than those in PPV and DMOS-PPV, which is good for decreasing the self-absorption while used as light-emitting materials. The absolute PL quantum efficiency of DOP-PPV in neat film was measured to be ~ 40% at room temperature under air followed the procedure demonstrated by Greenham et al.[10]

The light-emitting diodes were fabricated with the configurations of ITO/DOP-PPV/Ca (or Al). The thickness of the polymer films is in the range of about 100 nm without optimization. The devices with both calcium and aluminum as cathode all emit visible green light under the forward bias above ~ 8 V. Bright green light could be seen in day light when the forward bias is over 11 V. Figure 2 shows the current-voltage (*I-V*) and output light intensity-voltage characteristic measured from a device with aluminum as cathode. The turn on voltages for both current and emissive light are around 7 V. The external EL quantum efficiency of the device was measured to be ~ 0.03%. The relatively low quantum efficiency may be attributed to the unbalanced injection between electrons and holes. The electrochemical measurement (cyclic voltammetry) reveals that the oxidative onset potential and reductive onset potential are 1.05 and -1.58 V (*vs.* Ag wire quasi-reference electrode) respectively, which correspond to the estimated HOMO and LUMO levels of 5.44 and 2.81 eV respectively.[10] The electrochemical band gap is also close to the optical band gap. This means that electrons are much easy to be injected if calcium was employed as cathode. As excepted, when calcium was used as cathodic material, the EL external quantum efficiency was increased by one order to about 0.3%. An EL spectrum recorded from an ITO/DOP-PPV/Al device is also given in Figure 1.

In conclusion, a soluble phenyl-substituted PPV homopolymer was successfully synthesized via a modified Gilch route. The good processability, reasonably high PL efficiency, and good EL performance indicate that it may be a good candidate for the application in polymer LEDs. Also it provides an opportunity to study the effect of phenylene substituents on the optical and electronic properties of PPV series polymers.

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8 Selected spectroscopic data: Monomer **3**, ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48-7.51 (1H, d, *J* = 7.9 Hz, Ar-H), 7.34-7.38 (3H, m, Ar-H), 7.26-7.7.28(1H, m, Ar-H), 6.96-6.99 (2H, d, *J* = 8.7 Hz, Ar-H), 4.48 (2H, s, CH_2Br), 4.44 (2H, s, CH_2Br), 3.99-4.03 (2H, t, *J* = 6.6 Hz, CH_2O), 1.82-1.88 (2H, m, CH_2), 1.29-1.79 (16H, m, CH2), 0.87-0.91 (3H, t, *J* = 6.8 Hz, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz) δ 158.73, 142.23, 137.89, 135.46, 131.58, 131.38, 131.01, 129.92, 128.10, 114.29, 68.02, 32.65, 31.80, 31.70, 29.49, 29.46, 29.30, 29,21, 25.98, 22.57, 14.00 ppm. MS (EI, m/e): 498, 496, 494 (M^+), 196 (100%). DOP-PPV **4**, ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27-7.62 (2H, b), 6.70-7.25 (7H, b), 4.00 (2H, b), 1.82 (2H, b), 1.11-1.55 (16H, b), 0.88 (3H, b) ppm. Anal. Found: C, 84.85; H, 8.15%. Calcd. for $C_{24}H_{30}O$: C, 86.18; H, 9.04%. FT-IR (KBr) ν_{max}/cm^{-1}: 2945, 2860, 1705, 1650, 1610, 1523, 1460, 1180, 833. M_n (relative to polystyrene in THF): 2.04×10^5; Polydisperity: 2.91.

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