Synthesis and Characterization of New Orange-Red Light-Emitting PPV Derivatives with Bulky Cyclohexyl Groups†

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A series of 2,5-dialkoxy substituted poly(1,4-phenylenevinylene) derivatives containing a rigid and bulky cyclohexyl group in the side chain, poly[2-(7-cyclohexylheptyloxy)-5-butoxy-1,4-phenylenevinylene] (PBCyHpPV), Poly[2-(6-cyclohexylmethoxyhexyloxy)-5-butoxy-1,4-phenylenevinylene] (PBCyHxPV), Poly[2,5-di-(6-cyclohexylmethoxy-hexyloxy)-1,4-phenylenevinylene] (PDCyHxPV) were synthesized *via* the Gilch polymerization. The synthesized polymers were soluble in common organic solvents and showed good thermal stability up to 370 °C. The maximum absorption of PBCyHpPV, PBCyHxPV and PDCyHxPV as thin films was at 513 nm, 515 nm, 511 nm, respectively. Photoluminescence maximum emission of above polymers appeared at 590 nm, 597 nm, 590 nm, respectively. The electroluminescence (EL) maxima of the polymers appeared around 585-590 nm, and also showed another shoulder around 630 nm strongly. PDCyHxPV showed the highest EL efficiency and EL power than those of other polymers due to the dilution effect of the two rigid and bulky cyclohexyl groups.

Key Words : Electroluminescence, Poly(*p*-phenylenevinylene), Cyclohexyl

Introduction

Since the discovery of electroluminescence (EL) from poly(*p*-phenylenevinylene) (PPV),[1] PPV and its derivatives have been extensively studied due to their potential applications as emissive layers in light-emitting diodes (LED)s.[2,3] EL devices based on organic thin layers are of great interest because of their possible application as large-area light-emitting displays which are operative at low driving voltage, good processibility, fast response time and color tunability over the full visible range by control of the HOMO-LUMO energy band gap of the emissive layer.[4-12] However, the final conjugated PPV is insoluble and infusible, so that the processibility is very poor.[13-15] Braun and Heeger *et al.*[16-18] have reported that they used a soluble PPV derivative with bulky alkoxy side group, poly [2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV), as an emissive layer and used lower work function metal, particularly calcium (Ca), as an electron injecting contact. Since MEH-PPV was synthesized, many researching groups tried to synthesize the PPV derivatives with dialkoxy substituents for enhancement of the quantum efficiency and solubility. The choice of substituents is allowing solubility and enhancing the EL quantum efficiency. Yoshino *et al.*[19,20] reported the increment of PL and EL efficiency as increasing the side chain length of light-emitting polythiophene and PPV. This may imply that conjugated EL polymers with long interchain distance due to the long alkyl side chain can reach high PL and EL efficiencies caused by confinement of excitons on a main chain and preventing exciton-exciton collisions in the alkyl side chain. A cyclohexyl side chain was adopted firstly in polythiophene as a bulky substituent to achieve spectral blue shift due to steric hindrance.[21,22] For the case of PPVs, Jang *et al.*[23] reported that the dialkoxy substituted PPV derivative containing a rigid and bulky cyclohexyl group in the side chain, poly[2-(5-cyclohexylmethoxypentoxy)-5-methoxy-1,4-phenylenevinylene] (PMCYHPV), showed good solubility in common organic solvents and about 6 fold higher EL external quantum efficiency than that of MEH-PPV with almost the same operation voltage and EL color. In the present study, we report the synthesis of three new PPV derivatives containing a cyclohexyl group in the side chain: poly[2-(6-cyclohexylmethoxyhexyloxy)-5-butoxy-1,4-phenylenevinylene] (PBCyHxPV), poly[2,5-di-(6-cyclohexyl methoxy hexyloxy)-1,4-phenylenevinylene] (PDCyHxPV), poly[2-(7-cyclohexylheptyloxy)-5-butoxy-1,4-phenylenevinylene] (PBCyHpPV). In addition, we investigate the effect of the cyclohexyl group on the physical and electrochemical properties of above three polymers, as well as the performance of these polymers as emissive layers in LEDs.

Experimental Section

Instrumentation. NMR spectra were recorded using a Bruker AVANCE 400 spectrometer with tetramethylsilane as the internal reference. The number and weight average molecular weights of polymers were determined by gel permeation chromatography (GPC) analysis on a Waters GPC-150C instrument, using THF as eluent and polystyrene as standard. TGA was performed under nitrogen atmosphere at a heating rate of 10 °C/min with a DuPont 9900 analyzer.

†Dedicated with admiration and respect to Professor Sang Chul Shim in honor of his scientific achievements.

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UV-visible and photoluminescence spectra were measured using a Jasco V-530 UV/vis spectrometer and a Spex Fluorolog-3 spectrofluorometer, respectively. The configuration of the EL device was ITO/PEDOT/polymer/LiF/Al. The PEDOT [poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene)] employed as the hole-injection layer was spin coated onto precleaned ITO/glass substrate at a spin speed of 2500 rpm for 40 s. Thin polymer films with a thickness of approximately 100 nm were then spin coated onto the PEDOT layer from a 0.5 wt% polymer solution in chloroform. LiF and Al were deposited onto the polymer films using the vacuum evaporation method at a pressure of 10^{-6} Torr. Electroluminescence spectra were measured with a Minolta CS-1000. The current/voltage and luminescence/voltage characteristics were measured using a current/voltage source (Keithley 238) and a luminescence detector (Minolta LS-100). Cyclic voltammetry was performed on an AUTOLAB/PGSTAT12 with a three-electrode cell in a solution of Bu_4NBF_4 (0.10 M) in acetonitrile at a scan rate of 50 mV/s. All measurements were performed at room temperature under ambient atmosphere.

Materials. All reagents were purchased from Aldrich and used without further purification. PEDOT was purchased from Bayer. Tetrahydrofuran (THF) was dried over sodium/benzophenone.

7-Cyclohexylheptyl bromide (1). A 2 mL of (bromomethyl)cyclohexane (35.6 g, 0.2 mol) was added to a suspension containing Mg (4.7 g, 0.2 mol) in THF (40 mL). After stirring for 5 minutes, the mixture started to reflux. The rest of (bromomethyl) cyclohexane was then added to the mixture in such a rate to maintain the refluxing. The resulting Grignard reagent was transferred into an addition funnel and added dropwise into a mixture containing an excess of 1,6-dibromohexane (61 g, 0.25 mol), Li_2CuCl_4 (25 mL of 0.1 M THF solution, 2.5 mmol), and 40 mL of THF at 0 °C. The resulting mixture was stirred overnight at room temperature and then poured into water. The mixture was extracted with methylene chloride. Pure product was obtained by vacuum distillation. The product yield was 42%. ^{1}H NMR ($CDCl_3$, ppm) δ 3.3 (t, 2H), 1.8 (m, 2H), 1.6 (m, 5H), 1.5-1.0 (m, 14H), 0.8 (m, 2H).

(6-Bromo-hexyloxymethyl)cyclohexane (2). Cyclohexylmethanol (46 g, 0.4 mol) was dissolved in 300 mL of anhydrous tetrahydrofuran, and 60 wt% sodium hydride (24.3 g, 0.6 mol) was added to the solution at room temperature. And then the solution was refluxed under nitrogen atmosphere. After 4 hours, 1,6-dibromohexane (152 g, 0.6 mol) was slowly added to the solution and the solution was refluxed for 24 hours. The reaction was quenched by addition of water, and then extracted with methylene chloride. The colorless liquid product was obtained by vacuum distillation. The product yield was 45%. ^{1}H-NMR ($CDCl_3$, ppm) δ 3.3 (m, 4H), 3.1 (d, 2H), 1.8 (m, 2H), 1.7-1.2 (m, 15H), 0.8 (m, 2H).

1-(7-Cyclohexylheptyloxy)-4-butoxybenzene (3). Compound **3** was prepared by reacting 16.7 g (0.1 mol) of 4-butoxyphenol, 26.2 g (0.1 mol) of compound **1** and 7.3 g (0.11 mol) of potassium hydroxide in 200 mL methanol. The reaction solution was heated at 80 °C for 24 hours. The resulting mixture was extracted with methylene chloride and dried over anhydrous magnesium sulfate. The pure white solid product was acquired by precipitated from methanol. The product yield was 80%. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.8 (s, 4H), 3.9 (m, 4H), 1.7 (m, 10H), 1.5-1.3 (m, 15H), 1.0-0.8 (m, 5H).

1-Butoxy-4-(6-cychlohexylmethoxy-hexyloxy)-benzene (4). Compound **4** was prepared following the procedure described above for compound **3**. The product yield was 83%. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.8 (s, 4H), 3.8 (t, 4H), 3.2 (t, 2H), 3.1 (d, 2H), 1.8-0.8 (m, 25H).

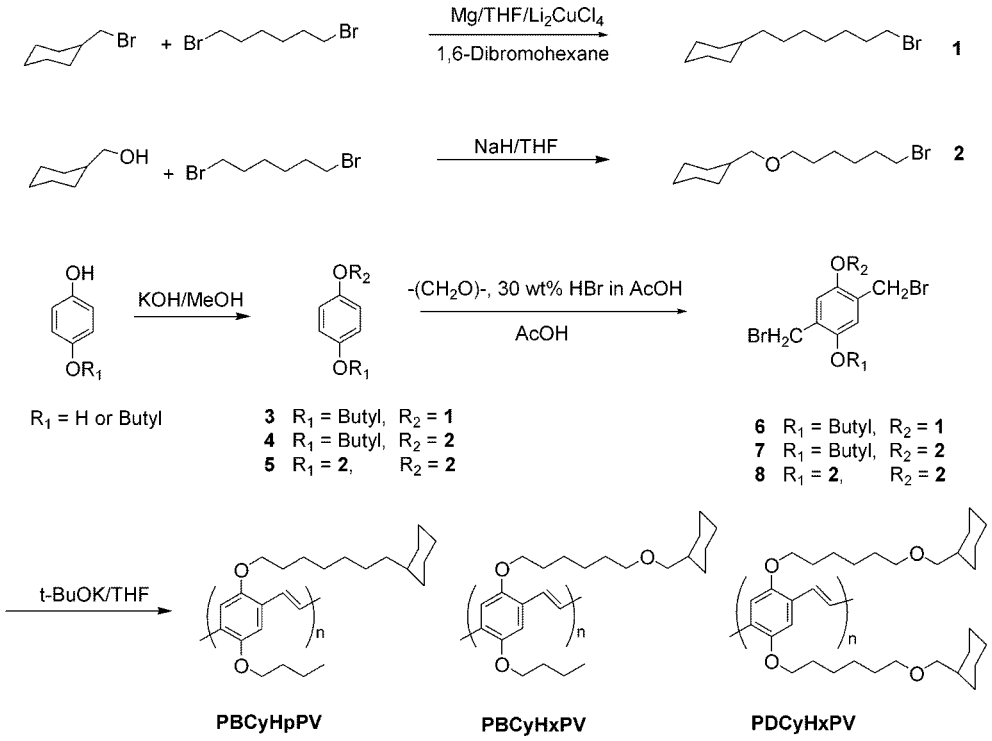
1,4-Bis-(6-cyclohexylmethoxy-hexyloxy)-benzene (5). Compound **5** was prepared following the procedure described above for compound **3**, starting from hydroquinone. The product yield was 63%. ^{1}H-NMR ($CDCl_3$, ppm): δ 6.8 (s, 4H), 3.8 (t, 4H), 3.3 (t, 4H), 3.1 (d, 4H), 1.8-0.8 (m, 38H).

1,4-Bisbromomethyl-2-butoxy-5-(7-cyclohexyl-heptyloxy)-benzene (6). To a solution of compound **3** (17.3 g, 50 mmol) and paraformaldehyde (7.5 g, 250 mmol) in 100 mL of acetic acid was added dropwise 20 mL of 30 wt% HBr solution in acetic acid at room temperature. A nitrogen atmosphere was established followed by heating the mixture to 70 °C for 4 hours. After allowing the mixture to cool to ambient temperature, the mixture was diluted with chloroform followed by extraction with water and $NaHCO_3$ (aq). The chloroform solution was dried over anhydrous magnesium sulfate followed by removal of the solvent under reduced pressure. Purification by recrystallization from hexane afforded 21 g (80%) of compound **6**. ^{1}H-NMR ($CDCl_3$, ppm): δ 6.9 (s, 2H), 4.6 (s, 4H), 4.0 (m, 4H), 1.7 (m, 10H), 1.5-1.3 (m, 15H), 1.0-0.8 (m, 5H).

1,4-Bisbromomethyl-2-butoxy-5-(6-cyclohexylmethoxy-hexyloxy)-benzene (7). To a solution of compound **4** (7.0 g, 20 mmol) and paraformaldehyde (3.0 g, 100 mmol) in 30mL of acetic acid was added dropwise 10 mL of 30 wt% HBr solution in acetic acid at room temperature. The following experimental procedures were the same as above described. The product yield was 62% (6.8 g). ^{1}H-NMR ($CDCl_3$, ppm): δ 6.8 (s, 2H), 4.5 (s, 4H), 3.9 (t, 4H), 3.4 (t, 2H), 3.2 (d, 2H), 1.8-0.8 (m, 26H).

1,4-Bisbromomethyl-2,5-bis(6-cyclohexylmethoxy-hexyloxy)-benzene (8). To a solution of compound **5** (6.0 g, 12 mmol) and paraformaldehyde (2.0 g, 67 mmol) in 30 mL of acetic acid was added dropwise 7 mL of 30 wt% HBr solution in acetic acid at room temperature. The following experimental procedures were the same as above described. The product yield was 59% (4.9 g). ^{1}H-NMR ($CDCl_3$, ppm): δ 6.8 (s, 2H), 4.6 (s, 4H), 3.9 (t, 4H), 3.4 (t, 4H), 3.1 (d, 4H), 1.8-0.8 (m, 38H).

Poly[2-(7-cyclohexyl-heptyloxy)-5-butoxy-1,4-phenylenevinylene] (PBCyHpPV). The compound **6** (1.06 g, 2 mmol) was dissolved in 80 mL of anhydrous tetrahydrofuran, and 12 mL of potassium *t*-butoxide (1 M in THF) in 60 mL anhydrous tetrahydrofuran was slowly added dropwise to the solution under nitrogen atmosphere. The reaction



Scheme 1. Synthetic pathways to the monomers and polymers.

was let to proceed for 24 hours at room temperature. The completed reaction mixture was slowly added to an excess amount of methanol while stirring it. The crude polymer was precipitated two times in methanol/acetone cosolvent for removal of low-molecular weight products. The polymer yield was 40%. The synthetic routes and polymer structure are shown in Scheme 1. ^{1}H-NMR ($CDCl_3$, ppm): δ 7.48 (s, 2H), 7.12 (s, 2H). 4.08 (s, 4H), 1.88-0.79 (m, 30H). PDI: 2.33, *Mn*: 243,000, *Mw*: 567,000.

Poly[2-(6-cyclohexylmethoxy-hexyloxy)-5-butoxy-1,4-phenylenevinylene] PBCyHxPV. The compound **7** (1.1 g, 2 mmol) was dissolved in 80 mL of anhydrous tetrahydrofuran, and 12 mL of potassium *t*-butoxide (1 M in THF) in 60 mL anhydrous tetrahydrofuran was slowly added dropwise to the solution under nitrogen atmosphere. The following procedures were the same as above described. The polymer yield was 59% (0.46 g). ^{1}H-NMR ($CDCl_3$, ppm): δ 7.49 (s, 2H), 7.15 (s, 2H). 4.06 (s, 4H), 3. 44 (t, 2H), 3.17 (d, 2H), 1.90-0.80 (m, 26H). PDI: 3.57, *Mn*: 174,000, *Mw*: 622,000.

Poly[2,5-bis-(6-cyclohexylmethoxy-hexyloxy)-1,4-phenylenevinylene] PDCyHxPV. The compound **8** (1.37 g, 2 mmol) was dissolved in 80 mL of anhydrous tetrahydrofuran, and 12 mL of potassium *t*-butoxide (1 M in THF) in 60 mL anhydrous tetrahydrofuran was slowly added dropwise to the solution under nitrogen atmosphere. The following procedures were the same as above described. The polymer yield was 52% (0.55 g). ^{1}H-NMR ($CDCl_3$, ppm): δ 7.47 (s, 2H), 7.14 (s, 2H). 4.05 (s, 4H), 3. 42 (t, 4H), 3.15 (d, 4H), 1.90-0.80 (m, 38H). PDI: 3.29, *Mn*: 121,000, *Mw*: 398,000.

Results and Discussion

PPV derivatives with bulky cyclohexyl groups as substituents, PBCyHpPV, PBCyHxPV and PDCyHxPV, were prepared by the Gilch polymerization with potassium *tert*-butoxide in THF. The monomer and polymer syntheses are shown in Scheme 1. The chemical structures of the three polymers were confirmed by ^{1}H NMR. The ^{1}H NMR spectra of the polymers in $CDCl_3$ showed vinylene peaks at 7.0-7.1 ppm, but did not contain the benzylic proton peaks at 4.5-4.6 ppm of the monomers. All other peaks showed good correspondence with the chemical structures of the polymers. The number-average molecular weights and weight-average molecular weights of the polymers were 121,000-243,000 and 389,000-622,000 with a polydispersity of 2.33-3.57, as determined by GPC using THF as eluent and polystyrene as standard.

PBCyHxPV and PDCyHxPV, which have the ether linkage in the side chain, were completely soluble in common organic solvents such as chloroform, THF, methylene chloride, dichloroethane at room temperature. But PBCyHpPV, which has not the ether linkage in the side chain, showed the selective solubility to some solvents. For example, this polymer was completely soluble in chloroform and nitrobenzene at room temperature. On the other hand, PBCyHpPV was partially soluble at room temperature and completely soluble when slightly heated to around 40-60 ^{o}C in xylene, THF and methylene chloride. The selective solubility of PBCyHpPV is very useful for the fabrication of multilayer PLEDs without any damages of the polymer layers.

Thermogravimetric analysis (TGA) was performed under

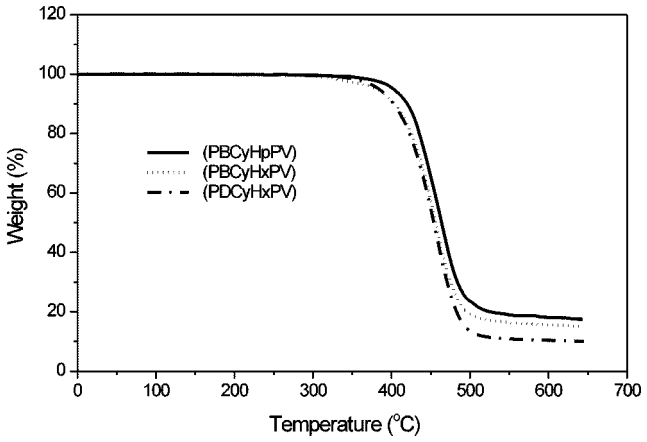


Figure 1. TGA thermograms of PBCyHpPV, PBCyHxPV, and PDCyHpPV.

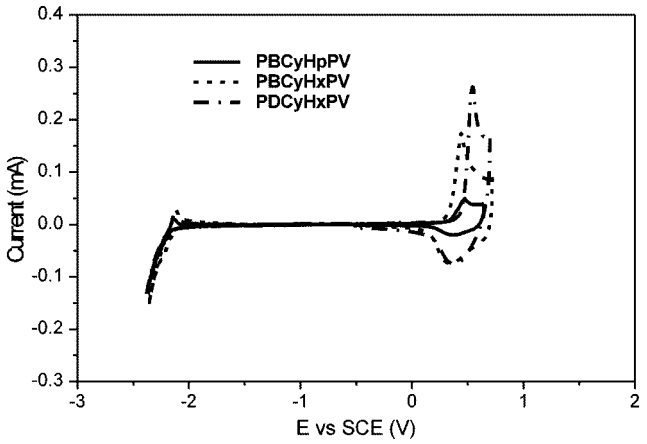


Figure 3. Cyclic voltamograms of PBCyHpPV, PBCyHxPV and PDCyHpPV.

nitrogen atmosphere at heating rate of 10 °C/min. Figure 1 shows that the synthesized polymers lose less than 5% of their weight on heating to 370 °C. This excellent thermal stability of the newly synthesized polymers can prevent the deformation of the EL emissive layer from the heat produced during operation of the device.

The thin films of the polymers were prepared on quartz plates by spin-coating the polymers from their solution in chloroform (10 mg polymer/3 mL solvents). All of the films made from above polymers showed the red color with naked eye. The UV-visible absorption and photoluminescence (PL) spectra of the polymers as thin films are shown in Figure 2. The UV-vis absorption maxima of PBCyHpPV, PBCyHxPV and PDCyHxPV as thin films were at 513 nm, 515 nm, 511 nm, respectively. PL spectra of PBCyHpPV, PBCyHxPV and PDCyHxPV as thin films showed well-resolved maxima at 590 nm, 597 nm and 590 nm, respectively. These PL emission maxima are similar with those of MEH-PPV and PMCYHPV.[23]

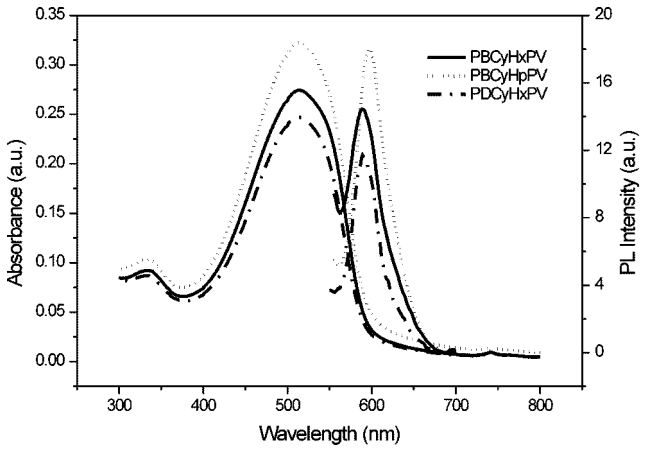


Figure 2. UV-visible absorption and photoluminescence spectra of PBCyHpPV, PBCyHxPV and PDCyHpPV.

Cyclic voltammetry (CV) was employed to investigate the redox behavior of the polymers and to estimate their HOMO and LUMO energy levels. The polymer films were coated onto a Pt electrode and scanned positively and negatively at a scan rate 50 mV/s in a 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in anhydrous acetonitrile. All measurements were calibrated using ferrocene (Fc) as the standard.[24] Figure 3 shows the CV curves of the *p*- and *n*-doping processes of the polymers. Both the oxidation and reduction processes of polymers were reversible. In the anodic scan, the onset of oxidation (*p*-doping) of the polymers occurred around 0.58-0.69 V (*vs* SCE), corresponding to HOMO energy levels of -4.97 ~ -5.08 eV. On sweeping the polymers cathodically, the onsets of reduction (*n*-doping) began around -1.72 ~ -1.76 V, corresponding to LUMO energy levels of 2.63 ~ -2.67 eV. These HOMO and LUMO energy levels of the polymers are almost same as the energy levels reported for MEH-PPV.[25] The electrochemical data of the polymers obtained from their cyclic voltammograms are summarized in Table 1.

Devices with the configuration of ITO/PEDOT/polymer/LiF/Al were fabricated to investigate the electroluminescent properties and the current-voltage-luminance characteristics of the polymers. Polymer films of thickness approximately

Table 1. Electrochemical properties and energy levels of the polymers

Polymer	*p*-Doping (V)[a]			*n*-Doping (V)[a]			Energy levels (eV)		
	E_{onset}	E_{pa}	E_{pc}	E_{onset}	E_{pc}	E_{pa}	HOMO[b]	LUMO[b]	E_g
PBCyHpPV	0.62	0.83	0.72	-1.76	-1.84	-1.77	-5.01	-2.63	2.38
PBCyHxPV	0.58	0.80	0.51	-1.72	-1.78	-1.88	-4.97	-2.67	2.30
PDCyHxPV	0.69	0.90	0.75	-1.75	-1.81	-1.76	-5.08	-2.64	2.44

[a]E_{onset}, E_{pa} and E_{pc} stand for onset potential, anodic peak potential, and cathodic peak potential, respectively. [b]Calculated using the empirical equation: $E = -(E_{onset} + 4.39)$.

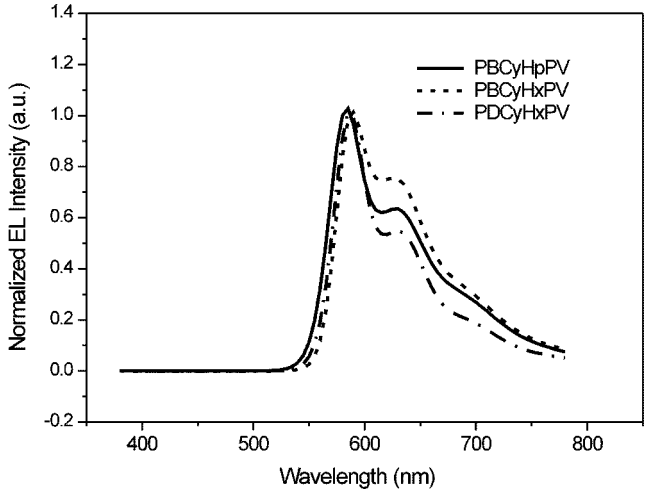


Figure 4. Electroluminescence spectra of PBCyHpPV, PBCyHxPV and PDCyHxPV in devices of configuration ITO/PEDOT/polymer/LiF/Al.

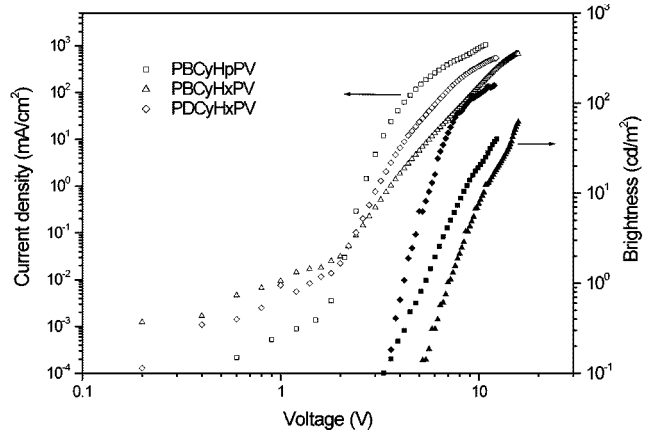


Figure 5. The current density-voltage and brightness-voltage characteristics of PBCyHpPV, PBCyHxPV and PDCyHxPV.

100 nm were spin-coat onto a PEDOT layer of thickness approximately 30 nm, which had been precast on the ITO substrate. The electroluminescence (EL) from the polymers in the devices was orange-red. As shown in Figure 4, the EL spectra of the polymers showed maxima around 585-590 nm, and shoulder peaks around 630-635 nm, respectively. These features are similar to those observed in the PL spectra of the corresponding polymer films.

The current density-voltage-luminance characteristics (*I-V-L*) of the devices fabricated from the polymers are shown in Figure 5. In the forward bias, the turn-on voltages (V_T) of the polymers are between 1.7-1.9 V. PL and EL emission peaks, turn-on voltages and EL external quantum efficiencies of the polymers are listed in Table 2. EL emission intensity and efficiency are depending on the substituent structures on the arylene ring and PDCyHxPV shows the lowest turn-on voltage and highest EL external quantum efficiency. These results can be accounted for by the dilution effect of two rigid and bulky cyclohexyl groups in the side chains of PDCyHxPV. This better dilution effect makes excitons created by hole-electron collision in polymer main chain to undergo radiative pathway rather than non-radiative pathway.

Table 2. Comparison of turn-on voltages and EL external quantum efficiencies of PBCyHpPV, PBCyHxPV and PDCyHxPV

Polymer	PL/EL maximum (nm)	Turn-on voltage (V)	External quantum efficiency (%)	Relative quantum efficiency
PBCyHpPV	590 / 585, 630(s)[a]	1.9	3.6×10^{-3}	1
PBCyHxPV	597 / 590, 635(s)[a]	1.9	5.5×10^{-3}	1.5
PDCyHxPV	590 / 590, 630(s)[a]	1.7	1.6×10^{-2}	4.4

(s)[a] means shoulder peak

Conclusions

The new orange-red light-emitting PPV derivatives containing the rigid and bulky cyclohexyl groups in the side chains, PBCyHpPV, PBCyHxPV and PDCyHxPV, were synthesized by the Gilch polymerization. A rigid and bulky substituent on an arylene ring is an important factor on the solubility, thermal stability and EL efficiency in the polymer LEDs. PBCyHpPV showed the selective solubility to the organic solvents, but PBCyHxPV and PDCyHxPV were completely soluble in common organic solvents at room temperature and all of the polymers showed the good thermal stability up to 370 under nitrogen atmosphere. PDCyHxPV showed 4.4 times higher EL external quantum efficiency than that of PBCyHpPV due to the dilution effect of two cyclohexyl groups.

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