

# Molecular Weight Tuning and Spectral Studies of Novel CN-PPVs via Gilch Reaction Route

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**ABSTRACT:** Two novel cyano-containing PPVs (CN-PPVs) with different solubilizing alkyloxy groups were synthesized through Gilch reaction from the monomer 2-cyano-5-(4'-alkoxyphenyl)-1,4-bisbromomethylbenzene. The structures of the polymers were determined by NMR, FTIR, and elemental analysis (EA). The results show that the solubility, thermal stability, and fluorescence properties of CN-PPVs vary with differing molecular weight. The relationship between the molecular weight of the polymers and the amount of 4-methoxyphenol used was consistent with anionic polymerization, of which the molecular weight is known to be inversely related to the amount of the

initiator. When the number-average molecular weight ( $M_n$ ) is in the range of 30,000–100,000, the solubility of the polymers was very good in chloroform, tetrahydrofuran, and toluene, and have good film properties. The fluorescence emission maxima range from 457 to 520 nm, exhibiting appreciable red-shift with the increase of the molecular weight. This series of novel CN-PPVs also bear high thermal stability. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 4124–4130, 2007

**Key words:** cyano; PPV; CN-PPV; molecular weight; photoluminescence

## INTRODUCTION

Since poly(*p*-phenylene vinylene) (PPV) was used in light-emitting diodes by Cambridge University in 1990,<sup>1</sup> its derivatives have attracted increasing academic and commercial interests because of their superior properties such as low cost, high photoluminescent efficiency, easy processibility, and long device lifetime.<sup>2–5</sup> Nevertheless, there are current needs in gaining more understandings of the correlation between the polymer structures and device functions. PPVs but it has been found that their hole mobilities ( $\mu^+$ ) are one to three orders of magnitude higher than their electron mobilities ( $\mu^-$ ).<sup>6</sup> Many efforts have been taken to overcome this shortcoming, the most often practices have been to use an electron transporting material to block the hole. On the other hand, electron-withdrawing group, such as

cyano, fluorine, and nitrogen-containing heterocycles, may improve the ability of electron transport,<sup>7,8</sup> tune the balance of electron and hole fluxes, thus enhance the quantum efficiency. Many reports suggested to introduce cyano groups to the aromatic ring or vinyl unit of PPV to tune the balance of electron and hole transport.<sup>9–15</sup> Secondly, processing has much to do with the solubility of the material in common solvents as well as the viscosity of the solution, which generally favors moderate molecular weight and bulky substituent group or long side chain on the polymers. The molecular weight could be tuned by changing polymerization conditions.<sup>16,17</sup> Thirdly, the introduction of bulky aromatic ring and cyano groups to conjugated polymers usually helps to enhance the stability, especially the thermal stability.<sup>18–20</sup>

Herein, two novel series of cyano-containing PPV derivatives (CN-PPVs) were designed and successfully synthesized through Gilch<sup>18</sup> reaction from the monomers of 2-cyano-5-(4'-alkoxyphenyl)-1,4-bisbromomethylbenzenes. The molecular weights of the polymers are successfully controlled, by using 4-methoxyphenol as the modifying agent. The results were consistent with the reported anionic initiation. When the molecular weights are varied between 30,000 and 100,000 the solubility of the polymers was very good in chloroform, tetrahydrofuran (THF), and toluene. The  $\lambda_{\max}$  of PL ranged from 457 to 520 nm,

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exhibiting an appreciable red-shift with the increase of the molecular weight. This series of CN-PPVs bears high thermal stability, which is attributed to biphenyl and cyano groups.

## EXPERIMENTAL

### Measurements

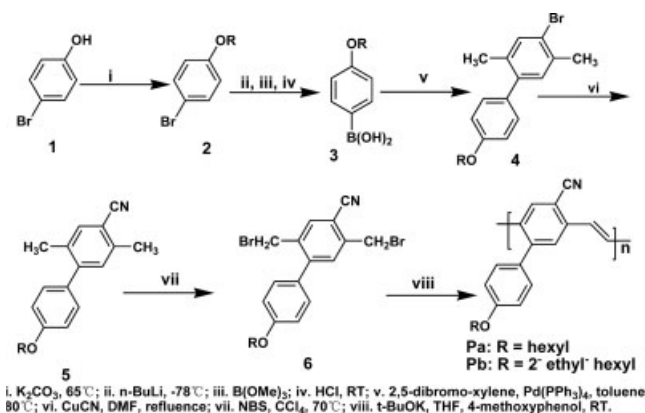
The  $^1\text{H}$  NMR spectra were collected on a Varian Mercury Plus 400 spectrometer with tetramethylsilane as the internal standard. FTIR spectra were recorded on a Shimadzu IR Prestige-21 FTIR-8400s spectrophotometer by drop-casting sample solution on KBr substrates. Mass spectra (MS) were obtained using a HP 5973 MS mass spectrometer at an ionizing voltage of 70 eV. UV-Vis spectra were recorded on a Shimadzu 3150 PC spectrophotometer. The concentrations of polymer solutions were about 0.01 mg/mL or less. Fluorescence measurement was carried out on a Shimadzu RF-5301 PC spectrofluorophotometer with a xenon lamp as a light source. Thermogravimetric analysis (TGA) was performed on a Shimadzu thermogravimetry and differential thermal analysis. DTG-60H at a heating rate of  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$ . Elemental microanalysis was carried out on a Vario EL III CHNOS Elemental analyzer. Gel permeation chromatography (GPC) analysis was conducted with a HP1100 HPLC system equipped with 7911GP-502 and GP NXC columns, using polystyrenes as the standard and THF as the eluent at a flow rate of 1.0 mL/min and  $35^\circ\text{C}$ .

### Materials

All chemical reagents used were purchased from Aldrich Chemical. THF was purified by distillation from sodium in the presence of benzophenone. Toluene was purified by distillation from sodium. Other organic solvents were used as received. The polymers were synthesized by Gilch reaction using potassium *tert*-butoxide (*t*-BuOK) as the catalyst and using 4-methoxyphenol as the molecular weight modifying agent according to Scheme 1. The monomers and the polymers were characterized by  $^1\text{H}$  NMR and elemental analysis (EA). Compounds **4a**, **4b**, **5a**, and **5b** were characterized by GC-MS, and polymers were characterized by FTIR.

### Synthesis

These two novel series of CN-PPVs were synthesized according to Scheme 1 from the starting material 4-bromo-phenol. The monomer was obtained through five steps of reaction, and was polymerized via Gilch reaction with *t*-BuOK and 4-methoxyphenol as initia-



Scheme 1 Synthetic route of the monomers and polymers.

tor and molecular weight modifying agent to yield the title polymers (apply to Scheme 1).

### 4-(2'-Ethylhexyloxy)benzene bromide<sup>15</sup> (**2b**)

About 17.30 g (100 mmol) 4-bromo-phenol and 39.2 g (285 mmol) dried  $\text{K}_2\text{CO}_3$  were added into a 250 mL dried three-neck flask under  $\text{N}_2$  condition, 150 mL dried DMF were injected into the sealed flask, and 19.2 g (18.0 mL, 100 mmol) 2-ethylhexyl bromide was added dropwise, the reaction mixture was stirred for 18 h at  $60$ – $65^\circ\text{C}$ , and then quenched with HCl (1.0M, 260 mL) and 200 mL hexane, the water phase was extracted with hexane, and the organic phase was eluted with HCl (1.0M, 130 mL  $\times$  3), combined the organic phase, and it was washed with NaOH (2.0M, 130 mL) and water (twice), dried over  $\text{Na}_2\text{SO}_4$ . Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with hexane to yield colorless liquid product **2b** (18.46 g, 61.6%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.34 (d,  $J = 8.8$  Hz, 2H, Ar H), 6.78 (d,  $J = 8.8$  Hz, 2H, Ar H), 3.80 (d,  $J = 5.6$  Hz, 2H,  $-\text{OCH}_2-$ ), 1.76 (m, 1H,  $-\text{OCH}_2-\text{CH}-$ ), 1.58–1.32 (m, 8H,  $-\text{CH}_2-$ ), 0.93 (m, 6H,  $-\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{21}\text{BrO}$ : C, 58.95; H, 7.42. Found: C, 59.20; H, 7.47.

### 4-Hexyloxybenzene bromide (**2a**)

According to the method as described for **2b**, we obtained colorless liquid product **2a** (59.62%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.369 (d,  $J = 8.8$  Hz, 2H, Ar H), 6.787 (d,  $J = 8.8$  Hz, 2H, Ar), 3.911 (t,  $J = 6.8$  Hz, 2H,  $\text{OCH}_2-$ ), 1.784 (m, 2H,  $-\text{OCH}_2\text{CH}_2-$ ), 1.474 (m, 2H,  $-\text{OCH}_2\text{CH}_2\text{CH}_2-$ ), 1.335 (m, 4H,  $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ ), 0.909 (t,  $J = 6.8$  Hz, 3H,  $-\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{12}\text{H}_{17}\text{BrO}$ : C, 56.04; H, 6.66. Found: C, 56.32; H, 6.43.

4-(2'-Ethylhexyloxy)benzene boronic acid (**3b**)

To a solution of **2b** (8.6 g, 30 mmol) in anhydrous THF (100 mL) was added 18 mL *n*-BuLi solution (45 mmol, 2.5M in hexane) at  $-78^{\circ}\text{C}$  under  $\text{N}_2$ . The reaction mixture was stirred for 1 h before trimethyl borate (10 mL, 9.27 g, 89.0 mmol) was added in one portion. The mixture was warmed to room temperature, stirred overnight and then quenched with HCl (2.0M, 150 mL) before adding a large amount of water for extraction of ethyl ether. The organic phase was washed with brine and water, and dried over  $\text{MgSO}_4$ . Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether/ethyl acetate (2 : 1) as the eluent to yield light brown viscous liquid product **3b** (6.68 g, 89.04%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 8.106 (d,  $J = 8.8$  Hz, 2H, Ar H), 7.018–6.996 (d, 2H,  $J = 8.8$  Hz, Ar H), 4.133 (s, 2H,  $-\text{B}(\text{OH})_2$ ), 3.941 (d, 2H,  $J = 5.6$  Hz,  $-\text{OCH}_2-$ ), 1.787–1.756 (m, 1H,  $-\text{OCH}_2-\text{CH}-$ ), 1.546–1.281 (m, 8H,  $-\text{CH}_2$ ), 0.923–0.905 (m, 6H,  $-\text{CH}_3$ ).

4-Hexyloxybenzene boronic acid (**3a**)

According to the method as described for **3b**, we obtained light brown viscous liquid product **3a** (5.02 g, 75.43%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.763 (d,  $J = 8.8$  Hz, 2H, Ar H), 6.969 (d, 2H,  $J = 8.8$  Hz, Ar H), 5.538 (s, 2H,  $-\text{B}(\text{OH})_2$ ), 4.016 (t, 2H,  $J = 6.0$  Hz,  $-\text{OCH}_2-$ ), 1.806 (m, 2H,  $-\text{OCH}_2-\text{CH}_2-$ ), 1.474 (m, 2H,  $-\text{OCH}_2\text{CH}_2\text{CH}_2-$ ), 1.344 (m, 4H,  $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ ), 0.909 (t,  $J = 6.8$  Hz, 3H,  $\text{CH}_3$ ).

2-Bromide-5-[4'-(2''-ethylhexyloxy)benzene]-*p*-xylene (**4b**)

A mixture of 6.30 g (25.2 mmol) **3b**, and 5.26 g (20.0 mmol) 2,5-dibromo-xylene (**4**) in a 250 mL three-neck flask was degassed, and then 692 mg  $\text{Pd}(\text{PPh}_3)_4$  (0.6 mmol), 100 mL toluene, and 20.0 mL  $\text{Na}_2\text{CO}_3$  solution (2.0 mol/L, 40 mmol) was added under  $\text{N}_2$ . The reaction mixture was stirred at  $80^{\circ}\text{C}$  for 48 h. After the mixture was cooled to the room temperature, diethyl ether was added. The organic layer was separated and washed with brine for drying over  $\text{MgSO}_4$ . Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether to yield a colorless oily liquid product (**4b**) 4.42 g (56.96%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.426 (s, 1H, Ar H), 7.277 (d,  $J = 8.8$  Hz, 2H, Ar H), 7.109 (s, 1H, Ar H), 6.950 (d,  $J = 8.8$  Hz, 2H, Ar H), 3.896 (d,  $J = 5.6$  Hz, 2H,  $-\text{OCH}_2-$ ), 2.383 (s, 3H,  $-\text{CH}_3$ ), 2.223 (s, 3H,  $-\text{CH}_3$ ), 1.768–1.723 (m, 1H,  $-\text{OCH}_2-$

$\text{CH}-$ ), 1.558–1.317 (m, 8H,  $-\text{CH}_2$ ), 0.956–0.938 (m, 6H,  $-\text{CH}_3$ ). MS:  $\text{M}^+$  388 (48%), 390 (48%), 276 (100%), 278 (98%). Anal. Calcd for  $\text{C}_{22}\text{H}_{29}\text{BrO}$ : C, 67.86; H, 7.51. Found: C, 69.03; H, 7.53.

2-Bromide-5-(4'-hexyloxybenzene)-*p*-xylene (**4a**)

According to the method as described for **4b**, we obtained colorless oily liquid product **4a** (3.93 g, 54.60%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.378 (s, 1H, Ar H), 7.266 (d,  $J = 8.8$  Hz, 2H, Ar H), 7.009 (s, 1H, Ar H), 6.759 (d,  $J = 8.8$  Hz, 2H, Ar H), 3.913 (d,  $J = 5.6$  Hz, 2H,  $-\text{OCH}_2-$ ), 2.375 (s, 3H,  $-\text{CH}_3$ ), 2.215 (s, 3H,  $-\text{CH}_3$ ), 1.760–1.715 (m, 2H,  $-\text{OCH}_2-\text{CH}_2-$ ), 1.550–1.309 (m, 8H,  $-\text{CH}_2$ ), 0.928–0.926 (m, 3H,  $-\text{CH}_3$ ). MS:  $\text{M}^+$  360 (48%), 362 (48%), 276 (100%), 278 (98%). Anal. Calcd for  $\text{C}_{20}\text{H}_{25}\text{BrO}$ : C, 66.48; H, 6.97. Found: C, 66.61; H, 7.04.

2-Cyano-5-[4'-(2''-ethylhexyloxy)benzene]-*p*-xylene (**5a**)

To a solution of 3.60 g **4a** (10.0 mmol) in 20 mL of DMF was added 1.33 g  $\text{CuCN}$  (15.0 mmol), and the mixture was refluxed 48 h. The reaction mixture was cooled to room temperature and poured into 50 mL of 15% ammonia and 50 mL chloroform. The organic phase was washed with ammonia and water several times, washed with brine twice for drying over  $\text{MgSO}_4$ . Upon evaporating off the solvent, the residue was purified with column chromatography on silica gel with petroleum ether/chloroform (3 : 1) to yield brown oily liquid product **5a** 2.24 g (72.90%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.461 (s, 1H, Ar H), 7.150 (s, 1H, Ar H), 7.201 (d,  $J = 8.8$  Hz, 2H, Ar H), 6.960 (d,  $J = 8.8$  Hz, 2H, Ar H), 3.981 (t,  $J = 5.6$  Hz, 2H,  $-\text{OCH}_2$ ), 2.514 (s, 3H,  $\text{CH}_3$ ), 2.248 (s, 3H, Ar  $\text{CH}_3$ ), 1.790 (m, 2H,  $-\text{OCH}_2\text{CH}_2-$ ), 1.5–1.2 (m, 8H,  $\text{CH}_2$ ), 0.965 (t,  $J = 5.6$  Hz, 3H,  $-\text{CH}_2\text{CH}_3$ ). MS: 307 ( $\text{M}^+$ , 33.43%), 223 (100%). Elemental Anal. for  $\text{C}_{21}\text{H}_{25}\text{NO}$  Calcd: C, 82.04; H, 8.22; N, 4.56. Found: C, 82.24; H, 8.34; N, 4.65.

2-Cyano-5-(4'-hexyloxybenzene)-*p*-xylene (**5b**)

According to the method as described for **5a**, we obtained brown oily liquid product **5b** (2.10 g, 62.7%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm): 7.470 (s, 1H, Ar H), 7.151 (s, 1H, Ar H), 7.207–7.185 (d,  $J = 8.8$  Hz, 2H, Ar H), 6.969–947 (d,  $J = 8.8$  Hz, 2H, Ar H), 3.891–3.877 (d,  $J = 5.6$  Hz, 2H,  $-\text{OCH}_2-$ ), 2.515 (s, 3H, Ar  $\text{CH}_3$ ), 2.252 (s, 3H, Ar  $\text{CH}_3$ ), 1.752 (m, 1H,  $-\text{OCH}_2\text{CH}-$ ), 1.461–1.256 (m, 8H,  $\text{CH}_2$ ), 0.916 (m, 6H,  $-\text{CH}_3$ ). MS: 335 ( $\text{M}^+$ , 15.71%), 223 (100%). Elemental Anal. for  $\text{C}_{23}\text{H}_{29}\text{NO}$  Calcd: C, 82.34; H, 8.71; N, 4.18. Found: C, 82.56; H, 8.78; N, 4.03.



2-Cyano-5-(4'-hexyloxybenzene)-*p*-bisbromomethylbenzene (**6a**)

To a solution of **5a** (0.615 g, 2.0 mmol) in carbon tetrachloride (60 mL), *N*-Bromosuccinimide (0.712 g, 4.0 mmol) and azobis(isobutyronitrile) were added as initiator. The reaction mixture was heated to reflux for about 4 h under N<sub>2</sub>. The completion of the reaction was indicated by the appearance of succinimide on the surface of the reaction solution and determined by thin layer chromatogram. The succinimide was filtered and the filtrate was concentrated. The concentrate was purified with column chromatography on silica gel, using petroleum ether/methylene dichloride (3 : 1) as the eluent to yield brown viscous liquid product **6a** (385.0 mg, 41.6%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.818 (s, 1H, Ar H), 7.425 (s, 1H, Ar H), 7.351–7.329 (d, *J* = 8.8 Hz, 2H, Ar H), 7.008–6.986 (d, *J* = 8.8 Hz, 2H, Ar H), 4.620 (s, 2H, –CH<sub>2</sub>Br), 4.408 (s, 2H, –CH<sub>2</sub>Br), 4.014 (t, *J* = 6.8 Hz, 2H, –OCH<sub>2</sub>), 1.853 (m, 2H, –OCH<sub>2</sub>CH<sub>2</sub>–), 1.468 (m, 2H), 1.364–1.251 (m, 4H), 0.901 (t, *J* = 7.2 Hz, 3H, –CH<sub>3</sub>). Elemental Anal. for C<sub>21</sub>H<sub>23</sub>Br<sub>2</sub>NO Calcd: C, 54.22; H, 4.98; N, 3.01. Found: C, 54.52; H, 5.21; N, 3.32.

2-Cyano-5-[4'-(2''-ethylhexyloxy)benzene]-*p*-bisbromomethylbenzene (**6b**)

According to the method as described for **6a**, we obtained brown viscous liquid product **6b** (390.5 mg, 39.6%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.813 (s, 1H, Ar H), 7.425 (s, 1H, Ar H), 7.355–7.334 (d, *J* = 8.4 Hz, 2H, Ar H), 7.009–6.987 (d, *J* = 8.8 Hz, 2H, Ar H), 4.612 (s, 2H, –CH<sub>2</sub>Br), 4.409 (s, 2H, –CH<sub>2</sub>Br), 3.910–3.896 (d, *J* = 6.5 Hz, 2H, –OCH<sub>2</sub>), 1.815 (m, 1H, OCH<sub>2</sub>CH–), 1.469 (m, 2H, –CH<sub>2</sub>), 1.354–1.255 (m, 6H, CH<sub>2</sub>), 0.934 (m, 6H, –CH<sub>3</sub>). Elemental Anal. for C<sub>23</sub>H<sub>27</sub>Br<sub>2</sub>NO Calcd: C, 56.00; H, 5.52; N, 2.84. Found: C, 56.32; H, 5.28; N, 3.10.

Poly-[2-cyano-5-(4'-hexyloxybenzene)-*p*-phenylene vinylene] (**Pa**<sub>1</sub>–**Pa**<sub>4</sub>)

A 100 mL three-neck flask with stirrer and reflux condenser was flushed with nitrogen gas for about 30 min. The solvent THF (20 mL) was degassed by bubbling N<sub>2</sub> through it for another 20 min. Another 10 mL of dry THF was used to rinse in the mixture of the monomer **6a** and 4-methoxyphenol (0, 1, 2, 5 wt %, in weight percent of the monomer, and the polymers were denoted **Pa**<sub>1</sub>, **Pa**<sub>2</sub>, **Pa**<sub>3</sub>, and **Pa**<sub>4</sub>, respectively). Polymerization of 0.232 g (0.50 mmol) of **6a** was initiated by addition of 0.65 mL (0.65 mmol, 1.0 mol/L in THF) of potassium *t*-BuOK in THF. In most cases the viscosity increased significantly while the reaction mixture turned from trans-

parent light brown to deep blue-orange. After 15 min, 1.65 mL (1.65 mmol, 1.0 mol/L in THF) of potassium *t*-BuOK in THF was added to start termination. Stirring was continued for 12 h. In some case, precipitate was observed during the anaphase of polymerization. For workup the solution was poured into ice-water under vigorous stirring. Aqueous hydrochloric acid (10 mL of 1.0 mol/L) and methanol (50 mL) were added, and the precipitated polymer was recovered by filtration over a glass filter. The polymer was washed with methanol and dried under reduced pressure at room temperature to yield brown solid product **Pa**<sub>1</sub> (79 mg, 52.0%). **Pa**<sub>1</sub> does not dissolve again in common organic solvents.

Element Anal. for (C<sub>21</sub>H<sub>21</sub>NO)<sub>*n*</sub> Calcd: C, 83.13; H, 6.98; N, 4.62. Found: C, 83.86; H, 6.42; N, 4.51. FTIR: 2215 cm<sup>-1</sup> (CN).

Respectively, we obtained **Pa**<sub>2</sub>, **Pa**<sub>3</sub>, and **Pa**<sub>4</sub>. The polymers were purified through dissolved-precipitated in chloroform and methanol.

Green fibrillar product **Pa**<sub>2</sub> (88 mg, 57.8%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.68–7.28 (m, 4H), 7.24–6.83 (m, 4H), 4.02 (t, 2H, –OCH<sub>2</sub>), 1.95 (m, 2H, –OCH<sub>2</sub>CH<sub>2</sub>), 1.51–1.23 (m, 6H, CH<sub>2</sub>), 0.895 (m, 3H, CH<sub>3</sub>). Element Anal. for (C<sub>21</sub>H<sub>21</sub>NO)<sub>*n*</sub> Found: C, 83.21; H, 6.74; N, 4.51. FTIR: 2214 cm<sup>-1</sup> (–CN).

Green powder product **Pa**<sub>3</sub> (62.4 mg, 41.0%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.78–7.36 (m, 4H), 7.28–6.89 (m, 4H), 4.08 (t, 2H, –OCH<sub>2</sub>), 1.97 (m, 2H, –OCH<sub>2</sub>CH<sub>2</sub>), 1.521–1.266 (m, 6H, CH<sub>2</sub>), 0.913 (m, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 155.4, 139.2, 138.4, 132.7, 128.9, 127.6, 125.3, 124.8, 122.8, 118.2, 115.4, 113.5, 110.8, 108.5, 67.9, 30.4, 28.7, 27.8, 25.1, 22.8, 14.5. Element Anal. for (C<sub>21</sub>H<sub>21</sub>NO)<sub>*n*</sub> Found: C, 82.78; H, 6.86; N, 4.83. FTIR: 2212 cm<sup>-1</sup> (–CN).

Green powder product **Pa**<sub>4</sub> (68.9 mg, 45.3%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.71–7.30 (m, 4H), 7.25–6.85 (m, 4H), 3.95 (t, 2H, –OCH<sub>2</sub>), 1.93 (m, 2H, –OCH<sub>2</sub>CH<sub>2</sub>), 1.52–1.25 (m, 6H, CH<sub>2</sub>), 0.895 (m, 3H, CH<sub>3</sub>). Element Anal. for (C<sub>21</sub>H<sub>21</sub>NO)<sub>*n*</sub> Found: C, 82.42; H, 7.06; N, 4.84. FTIR: 2218 cm<sup>-1</sup> (–CN).

Poly-[2-cyano-5-(4'-(2''-ethylhexyloxy)benzene)-*p*-phenylene vinylene] (**Pb**)

Polymerization was carried out as described for **Pa**<sub>3</sub>, with the molecular weight modifying reagent in an amount of 2 wt % of the monomer **6b**. **Pb** was isolated as powder (108.6 mg, 67.0%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 7.62–7.29 (m, 4H), 7.22–6.85 (m, 4H), 4.06 (t, 2H, –OCH<sub>2</sub>), 1.96 (m, 1H, –OCH<sub>2</sub>CH), 1.505–1.256 (m, 8H, CH<sub>2</sub>), 0.910 (m, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): 156.1, 138.8, 138.2, 133.5, 129.3, 128.1, 124.6, 124.1, 122.6, 117.8, 116.0, 112.8, 110.7, 108.1, 68.2, 40.3, 28.4, 27.2, 25.5, 22.3, 15.1, 12.7. Element Anal. for (C<sub>23</sub>H<sub>25</sub>

TABLE I  
Polymerization Results, Thermal and Spectral Data of Polymer

Polymer	4-Methoxyl-phenol (%)	$M_w$ ( $\times 10^4$ )	$M_n$ ( $\times 10^4$ )	PDI	$T_d$ ( $^{\circ}\text{C}$ )	$\lambda_{\text{max, abs}}$ (nm)	$\lambda_{\text{max, PL}}$ (nm)
<b>Pa<sub>1</sub></b>	0				426	374	569 <sup>a</sup>
<b>Pa<sub>2</sub></b>	1	15.6	7.3	2.1	415	319	520
<b>Pa<sub>3</sub></b>	2	11.9	5.3	2.2	412	319	487
<b>Pa<sub>4</sub></b>	5	9.7	2.8	3.5	386	319	457
<b>Pb</b>	2	12.3	6.4	1.9	405	377/316	495/518 <sup>b</sup>

$M_w$ , weight-average molecular weight;  $M_n$ , number-average molecular weight; PDI, polydispersity index.

<sup>a</sup> **Pa<sub>1</sub>** was not dissolved in THF,  $\text{CHCl}_3$ , the emission spectra was measured in powder excited by 374 nm. The emission spectra of **Pa<sub>2</sub>**, **Pa<sub>3</sub>**, and **Pa<sub>4</sub>**, excited by 319 nm in solid thin film also.

<sup>b</sup> The emission spectrum of **Pb** in  $\text{CHCl}_3$  solution, excited by 377 nm, and in solid thin film was excited by 317 nm.

$\text{NO})_n$  Calcd: C, 83.34; H, 7.60; N, 4.23. Found: C, 83.67; H, 7.84; N, 4.68. FTIR:  $2210\text{ cm}^{-1}$  ( $-\text{CN}$ ).

## RESULTS AND DISCUSSION

### Synthesis

The solubility, film property, thermal stability, as well as luminescence efficiency are essential for the application of luminescent polymers. These properties are closely dependent on the micro and macroscale structures of polymers and importantly,<sup>21</sup> the molecular weight that could be tuned by different polymerization conditions.<sup>17</sup> Two approaches are generally used for the synthesis of PPVs: the Wessling route and the Gilch route.<sup>3</sup> The Gilch route applies the treatment of  $\alpha,\alpha$ -dihalo-*p*-xylenes with potassium *t*-BuOK in organic solvents. In this way, the molecular weight of the polymer could be increased over 100,000 easily. The higher the molecular weight, the more insoluble the polymer. The mechanism of this polymerization process is not fully understood. Several reports have suggested a radical polymerization based on the decrease in molecular weight with the addition of chain transfer agent. In contrast, the addition of 4-*tert*-butylbenzyl chloride or 4-methoxyphenol resulted in a decrease of the molecular weight, indicating suggesting an anionic polymerization process. Also, both radical and anionic mechanisms have been observed for the polymerization. However, the nature of the propagating species, radical, or anionic, is not firmly established.<sup>16,17</sup> In the present work, using Gilch reaction alone to synthesize **Pa**, the resulting polymer was insoluble in common solvent. However, using 4-methoxyphenol as the molecular modifying agent, the molecular weight dropped with the increase of the load of 4-methoxyphenol, and the solubility was dramatically improved. The role of 4-methoxyphenol was as an anionic initiator. The number-average molecular weight ( $M_n$ ) of the polymers were measured by GPC against polystyrene standards, using THF as the eluting solvent (Table I). The results indicate that

when 4-methoxyphenol is introduced in 1–2 wt % (respectively, **Pa<sub>2</sub>**, **Pa<sub>3</sub>**) of the monomer, the polymer has a modest  $M_n$  of 53,000 and 73,000, respectively, and possess good solubility in common solvents. When the amount of 4-methoxyphenol is increased over 5 wt %, the  $M_n$  of the polymer dropped sharply to 28,000 (**Pa<sub>4</sub>**). The thermal stability is still good, but filming property is poor. Under the same condition, using 4-methoxyphenol by 2 wt % of the monomer **6b** to synthesize **Pb**, the  $M_n$  was measured to be 63,000 with a polydispersity index (PDI) of 1.96. **Pb** can be dissolved easily in common solvents (Table I). These results were consistent with anionic initiation since the  $M_n$  is known to be inversely related to the amount of initiator there (Table I).

### Characterization

All the monomers and polymers were characterized by <sup>1</sup>H NMR, and EA. Compounds **4a**, **4b**, **5a**, and **5b** were characterized by GC–MS, and polymers were characterized by FTIR. In GC–MS of Compound **4**, the isotopes of bromide were found. In <sup>1</sup>H NMR spectra, the chemical shift  $\delta = 3.80$ – $4.10$  was attributed to aliphatic hydrogen atoms adjacent to oxygen atom. The shift of the aromatic hydrogens was at about 6.8–7.6. Two  $-\text{CH}_3$  groups attached to the aryl cycle of Compounds **4** and **5** are not equivalent because of the structural asymmetry with, the chemical shifts were about 2.21, 2.37, and 2.25, 2.51 ppm, respectively. For the same reason, two  $-\text{CH}_2\text{Br}$  bonding to the aryl cycle of Compound **6** are asymmetry, the chemical shifts were about 4.62 and 4.42 ppm, respectively, and importantly, these peaks disappeared in <sup>1</sup>H NMR spectra of the polymers. It suggested that the polymerization was complete. The FTIR spectrum of polymers showed the absorption peak at about  $2210$ – $2220\text{ cm}^{-1}$ , which were attributed to the cyano group. The peaks at 2956, 2922, and  $2852\text{ cm}^{-1}$  were attributed to C–H flex vibration and at 1599, 1500,  $1450\text{ cm}^{-1}$  to aryl cycle backbone vibration, respectively (Fig. 1).

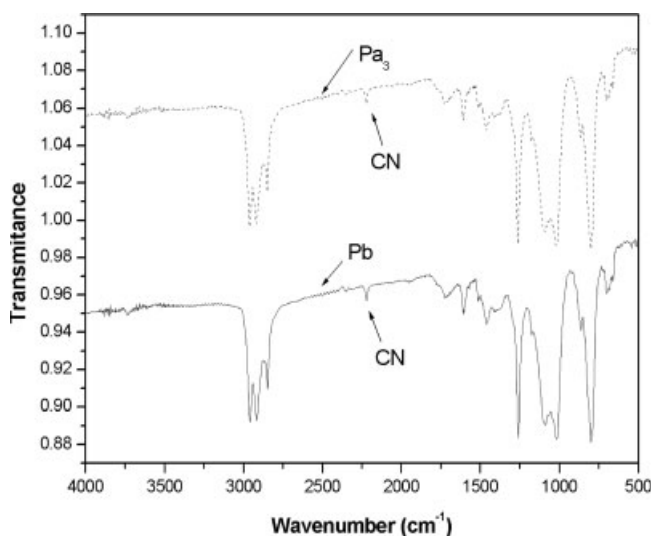


Figure 1 The FTIR Spectra of Pa<sub>3</sub> and Pb.

### Optical properties

Figure 2 shows the UV-Vis absorption and photoluminescence spectra of Pa<sub>2</sub>, Pa<sub>3</sub>, and Pa<sub>4</sub> in the solid films. There are nearly the same UV-Vis absorption spectra for Pa<sub>2</sub>, Pa<sub>3</sub>, and Pa<sub>4</sub> with an absorption band at about 319 nm, and the absorption band at 370–400 nm was not evident. The polymers exhibit bright fluorescence emission, with the emission peak red shifted upon the increase of molecular weight, using the same excitation wavelength of 319 nm. The maximal emission  $\lambda_{\text{max}}$  was at 520, 487, and 457 nm, corresponding to the molecular weight of Pa<sub>2</sub> (73,000), Pa<sub>3</sub> (53,000), and Pa<sub>4</sub> (28,000), respectively. As Pa<sub>1</sub> could not be well dissolved in THF and CHCl<sub>3</sub>, the emission spectra were measured in the powder form excited at 374 nm. The emission

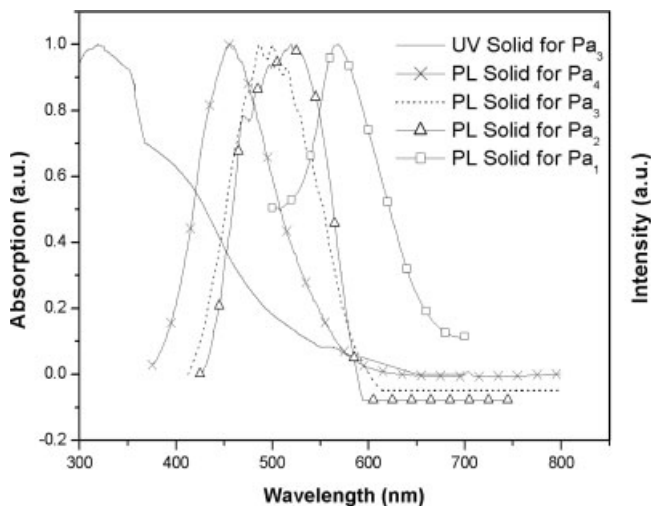


Figure 2 The UV-vis and PL spectra of Pa<sub>1</sub>, Pa<sub>2</sub>, Pa<sub>3</sub>, Pa<sub>4</sub>.

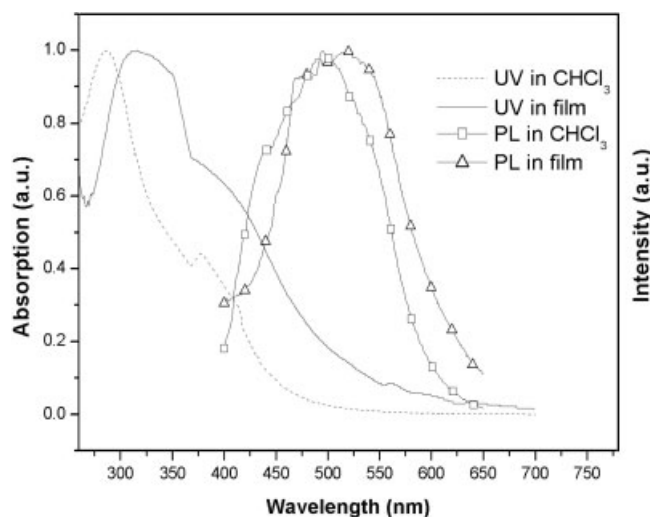


Figure 3 The UV-vis and PL spectra of Pb.

peak was found at 569 nm, which is attributed to the increased conjugation length of the polymers. As we know, the longer the conjugated length of the polymer, the more the  $\lambda_{\text{max}}$  (emission) will be red-shifted, and in the meantime, the worse the solubility (Figs. 2 and 3).

Figure 3 illustrates the UV-Vis absorption spectra of Pb in CHCl<sub>3</sub> solution and in the solid film. The absorption band at 317 nm in solid thin film is corresponding to the absorption band 286 nm in solution, and the absorption band at 377 nm in CHCl<sub>3</sub> solution is more evident than its counterpart in the solid film. In photoluminescence spectra the emission peak in the solution is blue-shifted and sharper than in the solid thin film, because the aggregation of the intermolecular in dilute solution is lower than that in the solid films.

### Thermal properties

The polymers of Pa<sub>1</sub>, Pa<sub>2</sub>, Pa<sub>3</sub>, Pa<sub>4</sub>, and Pb demonstrate high thermal stability. TGA reveals that the decomposition of these polymers starts over 426, 415, 412, 387, and 405°C, respectively, (Table I), and the decomposition temperature increases with the increase of the  $M_n$  of the polymers. This is attributed to the rod biphenyl structure and cyano group.<sup>15,18</sup> The thermal stability of the polymers are adequate as an electroluminescent material. No clear glass transition and melting were observed before thermal decomposition, which suggested that these polymers were amorphous.

### CONCLUSIONS

Through Gilch reaction we obtained two series of novel CN-PPV derivatives. It was found that the

molecular weight of the resulting polymers decreases with the increase of the loading of 4-methoxyphenol. The results are consistent with anionic initiation polymerization in terms of the inverse relationship between  $M_n$  and initiator of such process. When the load of 4-methoxyphenol is 1–2 wt % of the monomer, the polymers are soluble in common solvents. These polymers possess high thermal stability up to 412°C. With the modified electronic properties by the electron-withdrawing cyano functional moieties directly attached to the aromatic ring of polymer, these novel CN-PPVs may turn out to be appealing optoelectronic materials.

### References

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