

# Polythiophenes with Carbazole Side Chains: Design, Synthesis and Their Application in Organic Solar Cells

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A series of polythiophene derivatives **P1-P5** containing carbazole side chains were designed and synthesized via the Stille polymerization. All carbazole containing polymers showed broad absorption in the visible region. The power conversion efficiencies of solar cells based on blends of two component copolymers and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM) were determined to be 0.29 and 0.56% for **P1** and **P5**, respectively. For solar cells fabricated with the three component copolymers and PC<sub>61</sub>BM, the efficiencies were 0.56% for **P2**, 0.86% for **P3**,

and 0.70% for **P4**. The introduction of electrondonating carbazole side chains can broaden the absorption in the visible region and meanwhile reduce phase separation due to the steric hinderance of the carbazole moiety to the conjugated main chain. Improving efficiency needs a balance of broad absorption and ordered packing of polymer chains in the solid state.



# Introduction

Since the seminal work of Tang<sup>[1]</sup> in 1986, organic solar cells (OSCs) have attracted considerable scientific attention for their potential use in low-cost, light weight, solution-processable, and flexible large-area panels.<sup>[2,3]</sup> Among various optoelectronic active materials for polymer solar cells, regioregular poly(3-hexylthiophene) (rr-P3HT) is widely used for its excellent light absorption and electronic conductivity. The power conversion efficiency (PCE) has reached about 5% based on the blend of rr-P3HT and phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM), the so-called bulk heterojunction (BHJ) solar cell.<sup>[4,5]</sup>

However, it is calculated that P3HT is only capable of absorbing about 46% of the available solar photons,  $^{[6]}$  namely, photons in the wavelength range from 350 to

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Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China Fax: +86 10 8261 8587; E-mail: zsbo@iccas.ac.cn 650 nm. To better harvest the solar energy and further improve PCE, novel low band gap polymers were designed, synthesized, and applied to fabricate polymer solar cells, in which PCEs of 5–6.5% have been achieved.<sup>[7–13]</sup> Strategies for decreasing the band gap of conjugated polymers include: (1) designing conjugated polymers with a main chain alternating donor-acceptor structure;<sup>[14,15]</sup> and (2) using conjugated functional groups as side chains of polythiophene.<sup>[16–22]</sup>

Carbazole-containing polymers are a type of important organic semiconductors used as hole transporting materials in thin layer optoelectronic devices such as organic lightemitting diodes,<sup>[23]</sup> organic field effect transistors,<sup>[24,25]</sup> and OSCs.<sup>[12,13,26]</sup> Herein, we designed and synthesized a series of polythiophenes carrying various amounts of carbazole vinylene side chains. The incorporation of electron donating carbazole vinylene side chains can broaden the absorption of the thiophene polymers in the visible region. However, the high density of lateral bulk *N*-alkyl carbazole groups make the polythiophene main chains less conjugated by generating a large dihedral angel between the



adjacent thiophene rings, which decreases the ordered packing of polymer chains in solid state and is a negative effect for the charge transport. The copolymerization of carbazole-based thiophene monomer 3 and 2,5-dibromo-3-hexylthiophene (4) with 2,5-bis(tri-*n*-butylstannyl)thiophene (5) can probably relieve the steric hinderance generated by the adjacent N-alkyl substituted carbazole groups, and thus make polythiophene main chains for a better packing in solid state. Improving the power conversion efficiency needs a balance of broad absorption and ordered packing of polymer chains in the solid state. With this idea in mind, a series of polythiophene copolymers were prepared and their optical and photovoltaic properties were also investigated. Solar cells using three component copolymer P3 and  $PC_{61}BM$  blends as the active layer gave the best performance with  $V_{\rm oc} = 0.49$  V,  $J_{\rm sc} = 5.19 \, {\rm mA} \cdot {\rm cm}^{-2}$ , FF = 0.34, and PCE = 0.86%.

# **Experimental Part**

#### **Materials and Instruments**

All chemicals were purchased from commercial suppliers and used without further purification. THF and Et<sub>2</sub>O were distilled from sodium with benzophenone as an indicator under nitrogen atmosphere. Hexane and CH<sub>2</sub>Cl<sub>2</sub> were distilled from CaH<sub>2</sub>. Chloroform was distilled before use. 2,5-dibromo-3-hexylthiophene,<sup>[27]</sup> 2,5-bis(tri-*n*-butylstannyl)thiophene,<sup>[28]</sup> diethyl (2,5-dibromothiophen-3-yl)methylphosphonate,<sup>[16]</sup> 9-hexyl-9H-carbazole-3-carbaldehyde,<sup>[29]</sup> phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM),<sup>[30]</sup> and Pd(PPh<sub>3</sub>)<sub>4</sub><sup>[31]</sup> were prepared according to the literature procedures. All reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200–300 mesh).

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DM 300 or AV 400 spectrometer in CDCl<sub>3</sub>. The gel permeation chromatography (GPC) measurements were performed on a Waters chromatography connected to a Water 410 differential refractometer with THF as an eluent. The electrochemical behavior of the compounds was investigated using cyclic voltammetry (CHI 630A Electrochemical Analyzer) with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium tetrafluoroborate solution in CH<sub>3</sub>CN at room temperature under an atmosphere of nitrogen with a scanning rate of 30 mV · s<sup>-1</sup>. A glassy carbon working electrode, a Pt wire counter electrode, and an Ag/AgNO<sub>3</sub> (0.01 M in CH<sub>3</sub>CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc) redox system and assumption that the energy level of Fc is 4.8 eV below vacuum. Electronic absorption spectra were obtained on a SHIMADZU UV-vis spectrometer model UV-1601PC. Fluorescence spectra were recorded on a Varian FLR025. Elemental analyses were performed on a Flash EA 1112 analyzer. TGA (Pyris 1 TGA) and DSC (TA 2910) measurements were carried out under a nitrogen atmosphere at a heating rate of  $10 \,^\circ C \cdot min^{-1}$  to record the thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Atomic force microscopy (AFM) measurements were performed under



#### Fabrication and Characterization of Polymer Solar Cells

Polymer solar cells (PSCs) were fabricated with the device configuration of ITO/PEDOT:PSS/polymer:PC<sub>61</sub>BM(1:4, wt.-%)/Al. The ITO glass was pre-cleaned and modified by a thin layer of PEDOT:PSS (Bayer) which was spin-cast from a PEDOT:PSS aqueous solution on the ITO substrate, and was dried subsequently at 140 °C for 20 min in a vacuum oven. The thickness of the PEDOT:PSS layer was about 40 nm. The active layer was prepared by spin-coating the chlorobenzene solution of the polymers and PC<sub>61</sub>BM (1:4, wt.-%) with the polymer concentration of  $3 \text{ mg} \cdot \text{mL}^{-1}$  on the ITO/PEDOT:PSS electrode. The resulting film was coated by thermal evaporated of a 100 nm Al layer at a pressure of  $1 \cdot 10^{-4}$  Torr at room temperature. For each polymer sample five devices were fabricated. The effective area of one cell is 4 mm<sup>2</sup>.

The current-voltage (I-V) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. A xenon lamp with AM 1.5 filter was used as the white light source, and the optical power at the sample was  $100 \text{ mW} \cdot \text{cm}^{-2}$ . The light intensity was calibrated with a standard single-crystal Si photovoltaic cell.

### Synthesis of 3-((E)-2-(2,5-dibromothiophen-3yl)vinyl)-9-hexyl-9H-carbazole (3)

To a solution of diethyl (2,5-dibromothiophene-3-yl)methylphosphonate (1.40 g, 3.58 mmol) and 9-hexyl-9H-carbazole-3-carbalde-hyde (1.00 g, 3.58 mmol) in dry THF (50 mL), was added dropwise a solution of *t*-BuOK (0.80 g, 7.16 mmol) in THF (20 mL). After 1 h, the mixture was poured into water and extracted with chloroform. The organic layer was collected, washed with water, dried over anhydrous  $Na_2SO_4$ , filtered, and evaporated to dryness. The residue was chromatographically purified on silica gel column eluting with  $CH_2Cl_2$ /hexane (1:1) to afford **3** as a yellow solid (1.48 g, 80%).

 $^1\mathrm{H}$  NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.19 (s, 1H), 8.15 (d, 1H), 7.63 (d, 1H), 7.51 (t, 1H), 7.42 (d, 1H), 7.35 (d, 1H), 7.30 (t, 1H), 7.26 (s, 1H), 7.05 (m, 2H), 4.26 (t, 2H), 1.87 (m, 2H), 1.35 (m, 6H), 0.92 (t, 3 H).  $^{13}\mathrm{C}$  NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 141.1, 140.7, 139.9, 132.7, 127.8, 127.6, 126.1, 124.6, 123.4, 123.0, 120.7, 119.3, 119.2, 117.4, 111.8, 109.1, 108.8, 43.4, 31.8, 29.2, 27.2, 22.8, 14.3. (C<sub>24</sub>H<sub>23</sub>Br<sub>2</sub>NS): Calcd. C 55.75, H 4.54; Found: C 55.72, H 4.48.

# General Procedure for the Synthesis of Copolymers (P1-5)

A mixture of **3**, 2,5-dibromo-3-hexylthiophene (**4**), and 2,5bis(tributylstannyl)thiophene (**5**) in 20 mL toluene was carefully degassed before and after  $Pd(PPh_3)_4$  was added. The mixture was heated at reflux, stirred under nitrogen for 24 h, and then allowed to cool to room temperature. The mixture was poured into a large amount of methanol, and the resulted precipitate was collected by filtration. The crude polymer was subjected to Soxhlet extraction with methanol, acetone, hexane, and chloroform, successively. The chloroform fraction (150–170 mL) was reduced to 20–25 mL under reduced pressure, precipitated in methanol, filtered, and dried under high vacuum for 1 d to afford the final product as a dark solid.

Polymer **P1**. Monomer **3** (159 mg, 0.3 mmol), **5** (203 mg, 0.3 mmol), toluene (20 mL), and Pd(PPh<sub>3</sub>)<sub>4</sub> (3.5 mg,  $3.0 \cdot 10^{-3}$  mmol) mmol) were used. **P1** (103 mg, 74%) was obtained.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.35–6.51 (broad), 4.27–4.00 (broad), 1.84–1.81 (broad), 1.40–1.21 (broad), 0.98–0.81 (broad). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.22, 137.44, 135.45, 128.46, 124.86, 122.95, 120.54, 119.08, 108.87, 96.23, 43.02, 31.60, 28.91, 26.95, 22.61, 14.10.

Polymer **P2**. Monomer **3** (185 mg, 0.356 mmol), **4** (28 mg, 0.084 mmol), **5** (293 mg, 0.442 mmol), toluene (20 mL), and Pd(PPh<sub>3</sub>)<sub>4</sub> (5.1 mg,  $4.4 \cdot 10^{-3}$  mmol) were used. **P2** (133 mg, 77%) was obtained.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.63–7.21 (broad), 4.41–4.16 (broad), 2.78–2.50 (broad), 1.78–1.60 (broad), 1.35–1.29 (broad), 1.0–0.8 (broad). <sup>13</sup>C NMR (100 MHz, CDCl3):  $\delta$  = 140.81, 140.23, 137.10, 135.24, 128.41, 126.74, 125.74, 124.41, 122.90, 120.54, 119.00, 109.44, 108.87, 43.46, 43.12, 31.56, 30.45, 29.39, 28.97, 27.94, 26.96, 26.92, 22.59, 17.65, 14.09, 13.69.

Polymer **P3**. Monomer **3** (130 mg, 0.252 mmol), **4** (82 mg, 0.252 mmol), **5** (334 mg, 0.504 mmol), toluene (20 mL), and Pd(PPh<sub>3</sub>)<sub>4</sub> (5.8 mg,  $5.0 \cdot 10^{-3}$  mmol) were used. **P3** (90 mg, 52%) of was obtained.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.08–7.91 (broad), 7.46–7.27 (broad), 7.25–6.98 (broad), 4.10–3.86 (broad), 2.63–2.47 (broad), 1.75–1.58 (broad), 1.39–1.28 (broad), 1.17–0.86 (broad). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.82, 140.27, 137.12, 128.41, 126.74, 125.82, 124.38, 123.19, 122.87, 120.51, 119.06, 108.86, 43.16, 31.60, 30.37, 29.65, 29.37, 28.99, 27.90, 26.99, 26.90, 22.59, 17.57, 14.17, 14.07, 13.66.

Polymer **P4**. Monomer **3** (65 mg, 0.125 mmol), **4** (204 mg, 0.624 mmol), **5** (496 mg, 0.749 mmol), toluene (20 mL) and Pd(PPh<sub>3</sub>)<sub>4</sub> (8.7 mg,  $7.5 \cdot 10^{-3}$  mmol) were used. **P4** (63 mg, 29%) was obtained.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.18–8.09 (broad), 7.65–7.31 (broad), 7.15–6.94 (broad), 4.30–4.15 (broad), 2.80–2.58 (broad), 1.85–1.60 (broad), 1.34–1.18 (broad), 0.98–0.87 (broad). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.99, 140.49, 134.94, 125.95, 124.51, 123.00, 120.64, 119.19, 109.00, 43.33, 31.85, 31.73, 30.56, 29.47, 29.13, 27.12, 22.80, 22.71, 14.28, 14.18, 13.76.

Polymer **P5. 4** (131 mg, 0.402 mmol), **5** (266 mg, 0.402 mmol), toluene (20 mL), and Pd(PPh<sub>3</sub>)<sub>4</sub> (4.6 mg, 4.0  $\cdot 10^{-3}$  mmol) were used. **P5** (47 mg, 47%) was obtained. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.10–6.80 (broad), 2.77–2.60 (broad), 1.69–1.60 (broad), 1.42–1.26 (broad), 1.01–0.91 (broad). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 140.47, 134.79,



*Scheme 1.* Synthesis of monomer **3** by the Horner-Emmons reaction.

129.68, 126.39, 124.43, 68.01, 31.73, 30.45, 29.62, 29.33, 25.65, 22.68, 14.16.

### **Results and Discussion**

#### Synthesis and Characterization of Polymers

The synthetic route of monomer 3 carrying carbazole vinylene side group is shown in Scheme 1. The Horner-Emmons reaction of diethyl (2,5-dibromothiophen-3-yl)methylphosphonate (1) and 9-hexyl-9H-carbazole-3carbaldehyde (2) afforded monomer 3 in a yield of 80% in exclusively trans form, which was confirmed by its <sup>1</sup>H NMR spectrum. N-hexyl substituted carbazole could increase the solubility of the targeted polymers in common organic solvents. All these copolymers were synthesized by the Stille polymerization. The polymerization of monomers 3, 4 and 5 under Stille polymerization conditions at different feed ratios afforded a series of polymers (P1-5), as shown in Scheme 2. The chemical structures of copolymers were characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. The molecular weights of copolymers measured by gel permeation chromatography (GPC) calibrated with polystyrene standards are summarized in Table 1. The weight average molecular weight  $(\overline{M}_w)$  of polymers ranged from 7.4 to  $18.7 \text{ kg} \cdot \text{mol}^{-1}$  and the polydispersity indexes (PDI) were in the range of 1.9 to 3.7. The three component copolymers (P2-4) displayed lower molecular weight compared to the two component copolymers (P1 and P5).

The feeding molar ratios of monomers **3**, **4** and **5** used for the preparation of copolymers (**P1–5**) and the ratios of units **3** to **4** in copolymers (denoted as m:n) determined by the



Scheme 2. Synthesis of polymers (P1-5) by the Stille cross-coupling reaction.



Polymers	Amounts of monomers			m:n <sup>a</sup>	$\overline{M}_{ m w}$	PDI	$T_{\rm d}{}^{\rm b}$
		mmol					°C
	3	4	5				
P1	0.307	0	0.307	1:0	18000	3.3	416
P2	0.356	0.084	0.442	5:1	10400	2.4	287
Р3	0.252	0.252	0.504	5:4	11900	2.2	371
P4	0.125	0.624	0.749	1:3	7 400	1.9	350
P5	0	0.402	0.402	0:1	18700	3.7	426

*Table 1.* Monomers, molar ratios (m:n) of monomer **3** to **4** determined by NMR integration, molecular weights ( $\overline{M}_w$ ), polydispersities (PDI) and decomposition temperatures ( $T_d$ ) of polymers.

<sup>a</sup>Ratios determined by NMR integration; <sup>b</sup>The temperature at which 5% weight loss occurred based on the initial weight.

integration of <sup>1</sup>H NMR spectra of polymers are summarized in Table 1. The chemical shift of methylene group connected to N in carbazole is about 4.1 ppm; the chemical shift of the methylene group connected to thiophene ring is about 2.7 ppm. Therefore, the ratios of m:n in copolymers could be calculated from the integration of these two peaks in their <sup>1</sup>H NMR spectra. The molar ratios of fraction **3** and **4** (m:n) in copolymers determined by the <sup>1</sup>H NMR integration were 5:1 for P2, 5:4 for P3, 1:3 for P4. It is notable that some small declination was observed between the feeding molar ratios and the molar ratios determined by NMR integration. Thermal properties of copolymers were investigated by thermogravimetric analysis (TGA), which showed that the two component copolymers (P1 and P5) had better thermal stability than the three component copolymers (P2-4), as shown in Table 1.

#### **Optical Properties**

UV-vis spectra of monomer 3 and polymers (P1-5) in dilute THF solution and films are shown in Figure 1 and the wavelengths of absorption peaks are summarized in Table 2. Monomer 3 exhibited an absorption band in the ultraviolet region ranging from 290 to 390 nm with two peaks at 307 and 342 nm, respectively. In THF solution, the two component polymer P1 showed a broad absorption ranging from 250 to 650 nm with three peaks at 297, 347, and 535 nm. The two peaks at 297 and 347 nm were attributed to the absorption of the carbazole-vinylenethiophene units; the absorption band from about 400 to 650 nm with the absorption maximum at 535 nm was attributed to the absorption of the polythiophene main chain. The two component polymer P5, which did not contain the carbazole-vinylene-thiophene units, displayed only one absorption band in the visible region ranging from 320 to 630 nm with the maximum at 475 nm. The absorption peak of P1 is red shifted about 60 nm compared

to that of **P5**, indicating the introduction of carbazolevinylene functional groups to 3-position of thiophene could effectively broaden the absorption of polymers in the visible region. In solution, the three component copolymers (**P2-4**) also exhibited a broad absorption in the range of 270 to 650 nm, but all of them show a great blue shift



*Figure 1.* UV-vis absorption spectra of **3** and **P1–5** in THF solution  $(1.6 \cdot 10^{-3} \text{ mg} \cdot \text{mL}^{-1})$  (a) and in film (b).

Polymer	Absorption $\lambda_{max}$		Emission $\lambda_{\max}$ nm in THF	$\varphi_{ox}$ (V vs Ag/Ag <sup>+</sup> )/E <sub>HOMO</sub>	Band gap	
	Solution	Film				
	nm	nm	nm	eV	eV	
P1	530	556	600	0.35/-5.06	1.85	
P2	482	536	590	0.54/-5.25	1.88	
P3	475	529	580	0.48/-5.19	1.89	
P4	464	518	575	0.48/-5.19	1.92	
P5	474	518	565	0.51/-5.22	1.92	

Table 2. Optical and electrochemical properties of polymers.

compared to copolymer P1, which displays the important influence of 3-hexylthiophene to polymers. With the decrease of the content of the conjugated side chains in polymers (P2-4), the relative absorbance in the region of 300-400 nm decreased. The same trend was also observed for absorption spectra of polymers (P1-5) in films as shown in Figure 1(b). Compared to the absorption in THF solution, polymers (P1-5) show a red shift absorption in films, which to some extent reflects the aggregation in solid state. For regioregular polymers such as P3HT, in going from solution to film the red-shift value of absorption maximum can be up to 110 nm. The maximum absorption red-shift values of polymers P1, P2, P3, P4, and P5 were 26, 54, 54, 54, and 44 nm, respectively, as shown in Table 2. Polymer P1 displayed the smallest red-shift of absorption, reflecting that the larger carbazole-vinylene side groups could significantly influence the packing of polythiophene main chains in solid state. The incorporation of 3-hexylthiophene units into the polymer main chain has to some extent weakened the steric hinderance of the adjacent carbazolevinylene side chains, and thus decreased the dihedral angel of thiophene rings in the polymer main chain.

Photoluminescent (PL) spectra of polymers (P1-5) in dilute THF solution with a concentration of  $1.6 \cdot 10^{-3} \text{ mg} \cdot \text{mL}^{-1}$ excited at 470 nm are shown in Figure 2 and the emission maximum are summarized in Table 2. In THF solution, all polymers exhibited weak fluorescence in the range of 500 to 700 nm. With the increase of carbazole vinylene substituted thiophene fraction, the fluorescence intensities of polymers decreased as shown in Figure 2. This result indicated that the incorporation of carbazole vinylene functional group could significantly quench the fluorescence of polythiophene main chain, which may be originated from internal charge transfer.<sup>[32]</sup> A similar result was observed by excitation of the carbazole vinylene side chains at the wavelength of 370 nm. The relative ratio of quantum yields of polymers (P1-5) was determined, according to equation 1, to be  $\phi_{P5}$ :  $\phi_{P4}$ :  $\phi_{P3}$ :  $\phi_{P2}$ :  $\phi_{P1} = 1:0.94:0.66:0.38:0.28$ . In this equation  $I_1$  and  $I_2$  are the integrated emission

intensities of samples;  $A_1$  and  $A_2$  are the absorbance of samples at the desired wavelength  $\lambda_{max}$ ; and  $n_1$  and  $n_2$  are the index of refraction of the samples solution.<sup>[33]</sup>

$$\phi_1 = \phi_2 \left(\frac{I_1}{I_2}\right) \left(\frac{A_2}{A_1}\right) \left(\frac{n_1^2}{n_2^2}\right) \tag{1}$$

#### **Electrochemical Properties**

The electrochemical properties of polymers (**P1–5**) were characterized with cyclic voltammetry using  $Bu_4NF_4B$  as supporting electrolyte in acetonitrile solution with a platinum button working electrode, a platinum wire counter electrode, and an Ag/AgNO<sub>3</sub> reference electrode. The irreversible cyclic voltammetry diagrams of the polymers are shown in Figure 3. The film of polymer **P1** showed two oxidation peaks at 0.60 and 0.92 V in the redox cycle in the range of 0 and 1.4 V. Polymer **P5** exhibited only one oxidation peak at 0.48 V in the same scanning range. The onset oxidation potentials ( $E_{Ox}^{onset}$ ) of the polymers were



Figure 2. Emissin spectra of polymers (P1-5) in THF solution  $(1.6 \times 10^{-3} \text{ mg} \cdot \text{mL}^{-1})$  excited at 470 nm.





*Figure 3.* Cyclic voltammograms of the five polymers on a platinum electrode in  $0.1 \text{ MBu}_4 \text{BF}_4$ , acetonitrile solution.

in the range of 0.35 and 0.54 V, and the data are also listed in Table 2. In comparison with the  $E_{Ox}^{onset}$  of P3HT (0.348 V),<sup>[30]</sup> these polymers showed higher air-stability than P3HT. The HOMO energy levels of polymers were calculated according to the following equation.<sup>[34]</sup>

$$E_{\rm HOMO} = -(\varphi_{ox(\rm Ag/AgCl)} + 4.71) eV \tag{2}$$

The optical band gaps ( $\Delta E$ ) of polymers (**P1–5**) calculated from the UV-vis absorption onsets of films are also listed in Table 2. These results indicated that the introduction of carbazole vinylene functional group as the side chains could decrease the optical band gap of polythiophenes and hence broaden the absorption range.

#### **Photovoltaic Properties**

Photovoltaic properties of polymers were investigated with the device configuration of ITO/PEDOT:PSS/ polymer:PC<sub>61</sub>BM/Al. The ratio of polymer to PC<sub>61</sub>BM in the active layer was carefully optimized and a ratio of 1:4 gave the best device performance. Figure 4 displayed the *I-V* characteristics of devices under the illumination at AM 1.5 G (100 mW  $\cdot$  cm<sup>-2</sup>), and the results are listed in Table 3. A photovoltaic device of P3HT:PC<sub>61</sub>BM was also fabricated for comparison. The two component polymers



*Figure 4.* Current density-voltage characteristics of illuminated (AM 1.5G, 100 mW  $\cdot$  cm<sup>-2</sup>) polymer solar cells based on the blends of **P1–5** and P3HT with PC<sub>61</sub>BM.

(P1 and P5) showed the low short circuit current density  $(J_{sc})$ of 1.72 and 2.37 mA  $\cdot$  cm<sup>-2</sup>; whereas P3HT showed a high  $J_{\rm sc}$  of 9.1 mA  $\cdot$  cm<sup>-2</sup>. The great declination of  $J_{\rm sc}$  should be due to the irregularity of P1 and P5. It is notable that no improvement was achieved for devices based on these five polymers (P1-5) after annealing at 150 °C for 30 min. Moreover, the  $J_{sc}$  of **P1** is even lower than that of **P5** despite of the broad absorption of **P1**. The low  $J_{sc}$  of **P1** is probably due to the steric hinderance of carbazole side chain which prevents the polymer main chains from ordered packing in solid state. Polymers (P1-5) showed the fill factors (FF) in the range of 0.3 to 0.44. The low FF of 0.30 for P1 reflects the unbalanced charge transportation, resulted by the unordered packing of polymer chains. Combined with the low  $J_{\rm sc}$  and FF, polymer **P1** gave the lowest PCE of 0.29% among these polymers. When introducing 3-hexylthiophene into the conjugated main chain, three component

Table 3. Photovoltaic properties of the polymer solar cells.

Blend films	$V_{\rm oc}$	J <sub>sc</sub>	FF	PCE
	v	$mA \cdot cm^{-2}$		%
<b>P1</b> :PC <sub>61</sub> BM = 1:4	0.57	1.72	0.30	0.29
<b>P2</b> :PC <sub>61</sub> BM = 1:4	0.46	2.87	0.42	0.56
$P3:PC_{61}BM = 1:4$	0.49	5.19	0.34	0.86
<b>P4</b> :PC <sub>61</sub> BM = 1:4	0.53	3.56	0.37	0.70
$P5:PC_{61}BM = 1:4$	0.54	2.37	0.44	0.56
$P3HT:PC_{61}BM = 1:0.8^{a}$	0.57	9.08	0.47	2.4

<sup>a</sup>Device was thermally annealed at 150  $^\circ\text{C}$  for 30 min before measurement.

polymers (**P2-4**) gave slightly increased J<sub>sc</sub> and FF compared to P1. Therefore, combined with the reduced steric hinderance of carbazole and the broad absorption, P3 demonstrated the highest  $J_{\rm sc}$  of 5.19 mA  $\cdot$  cm<sup>-2</sup> and PCE of 0.86% among these polymers. It is important for polymer donor and PC<sub>61</sub>BM acceptor to form a thermally stable interpenetrating network to achieve higher PCE. The morphology of the blend films was therefore investigated by atomic force microscopy (AFM) in tapping mode. As shown in Figure 5, the polymer and  $PC_{61}BM$  blend films exhibited smooth surface without obvious phase separation. The root-mean-square (RMS) roughness of polymer:PC<sub>61</sub>BM (1:4) blend films are 0.44, 0.60, 0.52, 0.77, and 0.62 nm for P1, P2, P3, P4, and P5, respectively. The height image of blend film of P3HT/PCBM annealed at 150 °C for 30 min was also listed in Figure 5, with RMS value of 2.5 nm. The lower rms is probably due to the low regioregularity and the lateral large carbazole functional side chains of these polymers, which prohibits the ordered packing of polymer chains in solid state.

## Conclusion

In conclusion, a set of thiophene copolymers carrying carbazole vinylene side chains was designed and synthesized via the Stille polymerization. The incorporation of the lateral carbazole vinylene functional groups could significantly broaden the absorption spectra of polymers. On one hand, the N-alkyl substituted carbazole-vinylene side chains endowed polymers with good solubility in common organic solvents. On the other hand, these bulk side groups can decrease the conjugation of the polymer main chain by inducing a larger dihedral angel between the adjacent thiophene rings. Optical property investigation showed that the steric hinderance caused by the bulky carbazole vinylene side chains could be weakened in some extent by the copolymerization with 2,5-dibromothiophene as the third monomer. Three-component copolymer P3 showed a better absorption spectrum and a larger red-shift value on going from solution to film. Therefore, the threecomponent copolymers P3 exhibited the highest energy

conversion efficiency of 0.86% in these polymer:  $PC_{61}BM$  photovoltaic devices.

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Figure 5. AFM images (5  $\mu$ m  $\times$  5  $\mu$ m) of the surface morphology of blend polymer films spin-coated from chlorobenzene solution. Note: blend film of P3HT/PC<sub>61</sub>BM was annealed at 150 °C for 30 min before measurement.



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