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

Weiwei Li, Yang Han, Yulan Chen, Cuihong Li, Bingsong Li,* Zhishan Bo*

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-C61-butyric acid methyl ester (PC61BM) were determined to be 0.29 and 0.56% for P1 and P5, respectively. For solar cells fabricated with the three component copolymers and PC61BM, the efficiencies were 0.56% for P2, 0.86% for P3, and 0.70% for P4. The introduction of electron-donating carbazole side chains can broaden the absorption in the visible region and meanwhile reduce phase separation due to the steric hindrance 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[1] 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.[2,3] 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-C61-butyric acid methyl ester (PC61BM), the so-called bulk heterojunction (BHJ) solar cell.[4,5]

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 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.[7–13] Strategies for decreasing the band gap of conjugated polymers include: (1) designing conjugated polymers with a main chain alternating donor-acceptor structure,[14,15] and (2) using conjugated functional groups as side chains of polythiophene.[16–22]

Carbazole-containing polymers are a type of important organic semiconductors used as hole transporting materials in thin layer optoelectronic devices such as organic light-emitting diodes,[23] organic field effect transistors,[24,25] and OSCs.[12,13,26] 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 angle between the

W. W. Li, Y. Han, Y. L. Chen, C. H. Li, B. S. Li, Z. S. Bo
Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
Fax: +86 to 8261 8587; E-mail: zsbo@iccas.ac.cn
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 photo-voltaic properties were also investigated. Solar cells using three component copolymer P3 and PC61BM blends as the active layer gave the best performance with $V_{oc} = 0.49$ V, $I_{sc} = 5.19$ mA·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$_2$O were distilled from sodium with benzophenone as an indicator under nitrogen atmosphere. Hexane and CH$_2$Cl$_2$ were distilled from CaH$_2$. Chloroform was distilled before use. 2,5-dibromo-3-hexylthiophene$^{[27]}$, 2,5-bis(tri-n-butylstannyl)thiophene$^{[28]}$, diethyl (2,5-dibromo-3-yl)methylphosphonate$^{[29]}$, 9-hexyl-9H-carbazole-3-carbaldehyde$^{[30]}$, phenyl-C$_6$1-butyric acid methyl ester (PC$_{61}$BM)$^{[30]}$ and Pd(PPh$_3$)$_4$$^{[31]}$ were prepared according to the literature procedures. All reactions were performed under an atmosphere of nitrogen and 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 anhydrous Na$_2$SO$_4$, filtered, and evaporated to dryness. The residue was chromatographically purified on silica gel column eluting with CH$_2$Cl$_2$/hexane (1:1) to afford P3 with the polymer concentration of 3 mg·mL$^{-1}$ with the polymer concentration of 3 mg·mL$^{-1}$. The active layer was prepared by spin-coating the chlorobenzene solution of the polymers and PC$_{61}$BM (1:4, wt-%) with the polymer concentration of 3 mg·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 · 10$^{-10}$Torr at room temperature. For each polymer sample five devices were fabricated. The effective area of one cell is 4 mm$^2$.

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 mW·cm$^{-2}$. The light intensity was calibrated with a standard single-crystal Si photovoltaic cell.

**Synthesis of 3-((E)-2-(2,5-dibromotheophene-3-ylvinyl)-9-hexyl-9H-carbazole (3)**

To a solution of diethyl (2,5-dibromotheophene-3-yl)methylphosphonate (1.40 g, 3.58 mmol) and 9-hexyl-9H-carbazole-3-carbaldehyde (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$_2$SO$_4$, filtered, and evaporated to dryness. The residue was chromatographically purified on silica gel column eluting with CH$_2$Cl$_2$/hexane (1:1) to afford 3 as a yellow solid (1.48 g, 80%).

**General Procedure for the Synthesis of Copolymers (P1–5)**

A mixture of 3, 2,5-dibromo-3-hexylthiophene (4), and 2,5-bis(tri-n-butylstannyl)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(PPh3)4 (3.5 mg, 3.0 \times 10^{-3} \text{mmol}) were used. P1 (105 mg, 74%) was obtained.

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 8.35–6.51 \text{ (broad), } 4.27–4.00 \text{ (broad), } 1.84–1.61 \text{ (broad), } 1.40–1.21 \text{ (broad), } 0.98–0.81 \text{ (broad).} \)

\(^{13}\)C NMR (100 MHz, CDCl₃): \(\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, 104.41, 31.56, 30.45, 29.39, 28.97, 27.94, 26.96, 26.92, 22.59, 17.57, 14.17, 13.07, 13.66.

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(PPh3)4 (5.1 mg, 4.4 \times 10^{-3} \text{mmol}) were used. P2 (133 mg, 77%) was obtained.

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 8.63–7.21 \text{ (broad), } 4.41–4.16 \text{ (broad), } 2.78–2.50 \text{ (broad), } 1.78–1.60 \text{ (broad), } 1.35–1.29 \text{ (broad), } 1.0–0.8 \text{ (broad).} \)

\(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta = 140.81, 140.23, 137.10, 135.24, 128.41, 125.74, 124.41, 122.90, 120.50, 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(PPh3)4 (5.8 mg, 5.0 \times 10^{-3} \text{mmol}) were used. P3 (90 mg, 52%) of was obtained.

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 8.08–7.91 \text{ (broad), } 7.46–7.27 \text{ (broad), } 7.25–6.98 \text{ (broad), } 4.10–3.86 \text{ (broad), } 2.63–2.47 \text{ (broad), } 1.75–1.58 \text{ (broad), } 1.39–1.28 \text{ (broad), } 1.17–0.86 \text{ (broad).} \)

\(^{13}\)C NMR (100 MHz, CDCl₃): \(\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, 104.41, 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(PPh3)4 (8.7 mg, 7.5 \times 10^{-3} \text{mmol}) were used. P4 (63 mg, 29%) was obtained.

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 8.18–8.09 \text{ (broad), } 7.65–7.31 \text{ (broad), } 7.15–6.94 \text{ (broad), } 4.30–4.15 \text{ (broad), } 2.80–2.58 \text{ (broad), } 1.85–1.60 \text{ (broad), } 1.34–1.18 \text{ (broad), } 0.98–0.87 \text{ (broad).} \)

\(^{13}\)C NMR (100 MHz, CDCl₃): \(\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. Monomer 3 (131 mg, 0.402 mmol), 5 (266 mg, 0.402 mmol), toluene (20 mL) and Pd(PPh3)4 (4.6 mg, 4.0 \times 10^{-3} \text{mmol}) were used. P5 (47 mg, 47%) was obtained.

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 7.10–6.80 \text{ (broad), } 2.77–2.60 \text{ (broad), } 1.69–1.60 \text{ (broad), } 1.42–1.26 \text{ (broad), } 1.01–0.91 \text{ (broad).} \)

\(^{13}\)C NMR (100 MHz, CDCl₃): \(\delta = 140.47, 134.79, 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-3-carbaldehyde (2) afforded monomer 3 in a yield of 80% in exclusively trans form, which was confirmed by its \(^1\)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 \(^1\)H and \(^{13}\)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 (\(M_w\)) of polymers ranged from 7.4 to 18.7 kg \cdot 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
integration of $^1$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 $^1$H NMR spectra. The molar ratios of fraction 3 and 4 (m:n) in copolymers determined by the $^1$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-vinylene-thiophene 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 carbazole-vinylene 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.
compared to copolymer $P_1$, which displays the important influence of 3-hexylthiophene to polymers. With the decrease of the content of the conjugated side chains in polymers ($P_2$–$4$), the relative absorbance in the region of 300–400 nm decreased. The same trend was also observed for absorption spectra of polymers ($P_1$–$5$) in films as shown in Figure 1(b). Compared to the absorption in THF solution, polymers ($P_1$–$5$) 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 $P_1$, $P_2$, $P_3$, $P_4$, and $P_5$ were 26, 54, 54, 54, and 44 nm, respectively, as shown in Table 2. Polymer $P_1$ 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 carbazole-vinylene side chains, and thus decreased the dihedral angel of thiophene rings in the polymer main chain.

Photoluminescent (PL) spectra of polymers ($P_1$–$5$) in THF solution with a concentration of $1.6 \times 10^{-3}$ mg·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.$^{[32]}$ 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 ($P_1$–$5$) was determined, according to equation 1, to be $\phi_{P_5} : \phi_{P_4} : \phi_{P_3} : \phi_{P_2} : \phi_{P_1} = 1:0.94:0.66:0.38:0.28$. 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.$^{[33]}$

Electrochemical Properties

The electrochemical properties of polymers ($P_1$–$5$) were characterized with cyclic voltammetry using Bu$_4$NBF$_4$ as supporting electrolyte in acetonitrile solution with a platinum button working electrode, a platinum wire counter electrode, and an Ag/AgNO$_3$ reference electrode. The irreversible cyclic voltammetry diagrams of the polymers are shown in Figure 3. The film of polymer $P_1$ 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 $P_5$ exhibited only one oxidation peak at 0.48 V in the same scanning range.

![Figure 2](image-url)
in the range of 0.35 and 0.54 V, and the data are also listed in Table 2. In comparison with the \( E_{\text{ox}} \) of P3HT (0.348 V), these polymers showed higher air-stability than P3HT. The HOMO energy levels of polymers were calculated according to the following equation:

\[
E_{\text{HOMO}} = -\left(\varphi_{\text{ox}}(\text{Ag}/\text{AgCl}) + 4.71\right) \text{eV}
\] (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\(_{61}\)BM/Al. The ratio of polymer to PC\(_{61}\)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\(^{-2} \)), and the results are listed in Table 3. A photovoltaic device of P3HT:PC\(_{61}\)BM was also fabricated for comparison. The two component polymers (P1 and P5) showed the low short circuit current density (\( J_{\text{sc}} \)) of 1.72 and 2.37 mA \( \cdot \) cm\(^{-2} \), whereas P3HT showed a high \( J_{\text{sc}} \) of 9.1 mA \( \cdot \) cm\(^{-2} \). The great declination of \( J_{\text{sc}} \) 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 \( J_{\text{sc}} \) of P1 is even lower than that of P5 despite of the broad absorption of P1. The low \( J_{\text{sc}} \) of P1 is probably due to the steric hindrance 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 \( J_{\text{sc}} \) 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...
polymers (P2–4) gave slightly increased $J_{sc}$ and FF compared to P1. Therefore, combined with the reduced steric hinderance of carbazole and the broad absorption, P3 demonstrated the highest $J_{sc}$ of 5.19 mA cm$^{-2}$ and PCE of 0.86% among these polymers. It is important for polymer donor and PC$_{61}$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$_{61}$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 angle 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 three-component copolymers P3 exhibited the highest energy conversion efficiency of 0.86% in these polymer:PC$_{61}$BM photovoltaic devices.

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