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Richard P. Kingsborough[a]; David Waller[a]; Russell Gaudiana[a]; David Mühlbacher; Mauro Morana; Markus Scharber; Zhengguo Zhu[a]
[a] Konarka Technologies Inc., Lowell, MA

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Processible Cyclopentadithiophene Copolymers for Photovoltaic Applications

RICHARD P. KINGSBOROUGH[1], DAVID WALLER[1,*] RUSSELL GAUDIANA[1], DAVID MÜHLBACHER[2], MAURO MORANA[2], MARKUS SCHARBER[2] and ZHENGGUO ZHU[1]

[1]*Konarka Technologies Inc., Boott Mill South, Lowell, MA*
[2]*Konarka Austria, Linz, Austria*

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We designed and synthesized a series of conjugated polymers containing alternating 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene units and comonomers consisting of 2,2’-bithiophene, 3″,4″-dihexyl-α-pentathiophene, 3,4-ethylenedioxythiophene and 5,5′-bis(2-thienyl)-4,4′-dihexyl-2,2′-bithiazole. These polymers possess optical bandgaps in the range of 1.75 to 2.0 eV. The desirable absorption attributes of these materials make then excellent candidates for use in photovoltaic cells. Electrochemical studies indicate desirable HOMO-LUMO levels for use with fullerene derivatives as electron transporters. Field effect transistors made of these materials show hole mobilities in the range of 7.5×10^{-4} cm^2/Vs to 2.0×10^{-3} cm^2/Vs. Due to the combination of these characteristics, power conversion efficiencies up to 3.1% were achieved on devices made of bulk heterojunction composites of these materials with soluble fullerene derivatives.

Keywords: Photovoltaic, conjugated polymer, bulk heterojunction, processible, cyclopentadithiophene, bithiazole

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1 Introduction

With the discovery of a photoinduced electron transfer from a conjugated polymer to a C_{60}, conjugated polymers provide an alternative to crystalline silicon photovoltaic devices due to the advantage of solution processibility, leading to the low-cost fabrication of flexible, large-area, light-weight solar panels (1–3). The low cost aspect of polymer solar cells can therefore offset the lower power conversion efficiencies relative to traditional inorganic photovoltaics. The most common way conjugated polymers are incorporated into photovoltaic cells is in a bulk heterojunction active layer that homogeneously mixes the conjugated polymer and an electron-accepting fullerene derivative (i.e., [6,6]-phenyl-C_{61}-butyric acid methyl ester, PCBM) (2–16). Recent efforts have brought about device power conversion efficiencies approaching 5% in a blend of regioregular poly(3-hexylthiophene) (P3HT) and PCBM.2a (11,12). Other polymer systems have also shown promise. The attractiveness of conjugated polymers lies in the ability to tune their optical and electronic properties via a rational synthetic methodology (9,13–16).

Polyfluorenes and their copolymers have been extensively tested in photovoltaic devices (13–16). Most of these polymers have been low-bandgap materials based on alternating donor-acceptor (DA) units. These DA fluorene copolymers show moderate efficiencies in bulk heterojunction solar cells (13–16). Some of the issues limiting the overall photovoltaic efficiency are bandgap mismatches with the solar spectrum, low short circuit currents, and low fill factors. Charge carrier mobility plays a crucial role in determining the operating current and fill factor in the photovoltaic cell, and many of the polyfluorene copolymers that have been investigated have hole mobilities of $<10^{-3}$ cm^2 V^{-1} s^{-1} (16). Mobilities $>10^{-3}$ cm^2 V^{-1} s^{-1} are needed to prevent appreciable photocurrent loss in a thick active layer.

An excellent component for the synthesis of conjugated polymers has been 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene due to the forced planarity of the bithiophene moiety (17–21). Polymers initially made with this moiety were grown electrochemically, but lacking solubilizing side chains, their intrinsic insolubility made processing these polymer films quite difficult (19). The bridging carbon of the 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene can be easily functionalized with solubilizing alkyl substituents to promote increased polymer solubility. Turner, et al. (20) have recently reported the solution preparation of soluble homopolymers of hexyl-, octyl- and hexadecyl-disubstituted cyclopentadithiophenes. These were polymerized by a variety of methods resulting in moderate to high molecular weight, soluble homopolymers.

Previous experience incorporating these alkyl-substituted cyclopentadithiophenes into alternating donor-acceptor copolymers showed a number of spectroscopic

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*Address Correspondence to: David Waller, Konarka Technologies Inc., Boott Mill South, 3rd Floor, 116 John Street, Suite 12, Lowell, MA 01852. E-mail: dwaller@konarka.com

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and electronic differences when compared to the corresponding fluorene analogue (22). In particular, we find smaller HOMO values, higher hole mobilities, and a significant red-shift of the λ_{max} of the polymers both in solution and as cast films. This red-shift can allow the polymers to capture more of the solar spectrum, thereby increasing the efficiency of the bulk heterojunction solar cells. To this end, we have investigated a number of copolymers of cyclopentadithiophene using other donor monomers such as bithiophene, pentathiophene, ethylenedioxythiophene, and a bis(thienyl)bithiazole. A recent paper describes the bis(thienyl)bithiazole polymer (23).

2 Experimental

2.1 General Methods

All syntheses were performed under a dry argon atmosphere using standard Schlenk techniques. Anhydrous THF and toluene were purchased from Aldrich and distilled from sodium benzophenone ketal prior to use. All other reagents were purchased from Aldrich, Alfa, and Strem and used as received. Tert-butyl methyl ether (MTBE) was used in place of diethyl ether in all preparations for safety reasons. Compounds 4*H*-cyclopenta[2,1-*b*:3,4-b′]thiophene (**1**), (21) 5,5′-dibromo-2,2′-bithiophene (**4**),[24] 5,5′′′′-dibromo-3′′,4′′-dihexyl-α-pentathiophene (**5**), (25) 2,5-dibromo-3,4-ethylenedioxythiophene (**6**) (26) and 5,5′-bis(5-bromo-2-thienyl)-4,4′-dihexyl-2,2′-bithiazole (**7**) (27) were prepared and purified by literature methods. A sample of F8T2 was obtained from Dow Chemicals. NMR (^{1}H and ^{13}C) spectra were recorded on a Bruker 200 MHz, 250 MHz, or 500 MHz spectrometer. Chemical shifts were recorded in parts per million (ppm) using an internal TMS standard, and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). The molecular weights of polymers were determined using a Plgel 5 μm Mixed-B (600 × 7.5 mm) column and a diode array detector at 300 nm at a flow rate of 1.0 mL/min. Polymer molecular weights are reported relative to polystyrene standards purchased from Aldrich.

2.2 Optical and Electrochemical Characterizations

UV absorption spectra were recorded on a Perkin-Elmer Lambda 35 UV/Vis spectrometer. Solid state absorption spectra were obtained on thin films coated on quartz prepared by spin coating of the polymer solution in chlorobenzene. Electrochemical characteristics were determined by cyclic voltammetry (CV) experiments carried out on drop-cast polymer films at room temperature in a glovebox. The supporting electrolyte was tetrabutylammoniumhexafluorophosphate ($TBAPF_6$, electrochemical grade, Aldrich) in anhydrous acetonitrile (~0.1 M). The working electrode (WE) and the counter electrode (CE) were platinum foils. A silver wire coated with AgCl was used as the reference electrode (RE). After each measurement the RE was calibrated with ferrocene ($E^0 = 400$ mV vs. NHE) and the potential axis was corrected to NHE (using –4.75 eV for NHE) according to the difference of E^0 (ferrocene) and the measured $E^{1/2}$ (ferrocene). The onset for oxidation and reduction was determined by drawing two tangents for each peak and is assumed to be where the two lines intersect (28).

2.3 Polymer Solar Cell Fabrication and Analysis

Conductive indium tin oxide (ITO) coated glass was purchased from Merck. The ITO-glass substrate was cleaned by ultrasonification sequentially in acetone, isopropyl alcohol and deionized water. On top of the conductive side was coated a layer of PEDOT:PSS (Baytron PH from H.C. Starck, ~60 nm thick) applied by doctorblading. After being dried, this PEDOT:PSS film is covered by a layer of a blend of the polymers (**8**, or **9a–c**)/$PC_{61}BM$ or $PC_{71}BM$ (purchased from Nano-C) in a 1:3 w/w ratio by doctorblading method from *o*-dichlorobenzene solution. The active layer thickness was determined by AFM to be between 150 – 250 nm. As the cathode, a thin layer of LiF (c.a. 1 nm thick) and a film of Aluminum (c.a. 80 nm thick) were thermally evaporated. Device characterization was carried out under AM 1.5G irradiation (100 mW/cm^2) on an Oriel Xenon solar simulator with a spectral mismatch of 0.95 for the spectral range down to 1000 nm. I-V characteristics were recorded with a Keithley 2400. Active areas were in the range of 15 to 20 mm^2.

2.4 2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-4,4-bis(2′-ethylhexyl)cyclopenta[2,1-*b*:3,4-*b*′]thiophene

100 mL oven dried Schlenk flask was charged with 1.097 g (2.72 mmol) of 4*H*-4,4-bis(2′-ethylhexyl)cyclopenta[2,1-*b*:3,4-*b*′]dithiophene. The flask was evacuated and purged with argon three times. To this flask was then added 20 mL of dry, distilled THF. The resulting solution was cooled to −78°C and 4.35 mL (10.88 mmol, 4 equv.) of 2.5M BuLi was added drop wise. The reaction was stirred for 1 h at −78°C and then warmed to room temperature and stirred for an additional 3 h. The solution was cooled again to −78 °C and 2.77 mL (13.6 mmol, 5 equiv.) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added in one portion via syringe. The reaction was stirred at −78°C for 1 h and then allowed to warm to room temperature overnight. The solution was poured into water and extracted with 4 × 150 mL of MTBE. The organic layers were combined and washed with 2 × 150 mL of brine, dried with anhydrous $MgSO_4$, and filtered. The solvent was removed under vacuum to yield and orange oil, which was purified by column chromatography (5% EtOAc in hexanes) to yield a colorless, viscous oil, 1.34 g (2.05 mmol, 75%). ^{1}H-NMR

(250 MHz, $CDCl_3$): δ 7.45 (t, 2H), 1.86 (t, 4H), 1.36 (s, 24H), 1.04–0.80 (m, 18H), 0.74 (t, 6H), 0.60 (t, 6H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 161.4, 144.5, 132.3, 84.3, 53.1, 43.6, 35.5, 34.3, 28.6, 27.8, 25.2, 25.1, 23.2, 14.5, 11.0.

2.5 General Polymeriztion Method of Polymers 4p-7p

A 50 mL Schlenk flask was charged with 0.275 g (0.420 mmol) of 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-4,4-bis(2′-ethylhexyl)cyclopenta[2,1-*b*:3,4-*b*′] thiophene, 0.136 g (0.420 mmol) of 5,5′-dibromo-2,2′-bithiophene, (23) 3.8 mg Pd_2dba_3 (0.0042 mmol), 7.7 mg PPh_3 (0.0294 mmol), and 0.063 g (0.155 mmol) of Aliquat 336. The flask was evacuated and refilled with argon three times. The solids were dissolved in 20 mL of toluene and then 2 mL of 2M Na_2CO_3 was added via syringe. The reaction was then heated to 90°C with stirring for 48 h. Phenylboronic acid (0.027 g, 0.223 mmol) was dissolved in 1 mL of THF and added to the reaction mixture, and stirring was continued for 16 h at 95°C. The reaction mixture was diluted with toluene (50 mL) and the organic layer was separated and washed with warm water (3 × 50 mL). The solution was then treated with an aqueous solution of sodium diethyldithiocarbamate (7.5%, DDC, 10 mL) and heated at 80°C overnight. The aqueous layer was separated and discarded and the organic layer was washed with warm water (3 × 50 mL), concentrated, and the polymer precipitated into methanol (500 mL). The polymer was collected by filtration, washed with methanol (100 mL), acetone (100 mL) and again with methanol (100 mL). The polymer was then dried *in vacuo* overnight to yield a brick red solid polymer **4p** (0.207 g, 87%). ^1H NMR (200 MHz, $CDCl_3$): δ 7.15–7.05 (br, 6H), 1.95 (br, 4H), 1.17–0.92 (br, 16H), 0.88–0.62 (br, 14H).

Polymer 5. Brick red solid (0.327 g, 71%). ^1H-NMR (200 MHz, $CDCl_3$): δ 7.2–7.08 (br, 10H), 2.77 (br, 4H), 1.96 (br, 4H), 1.40 (br, 12H), 1.14–0.92 (br, 24H), 0.88–0.64 (br, 16H).

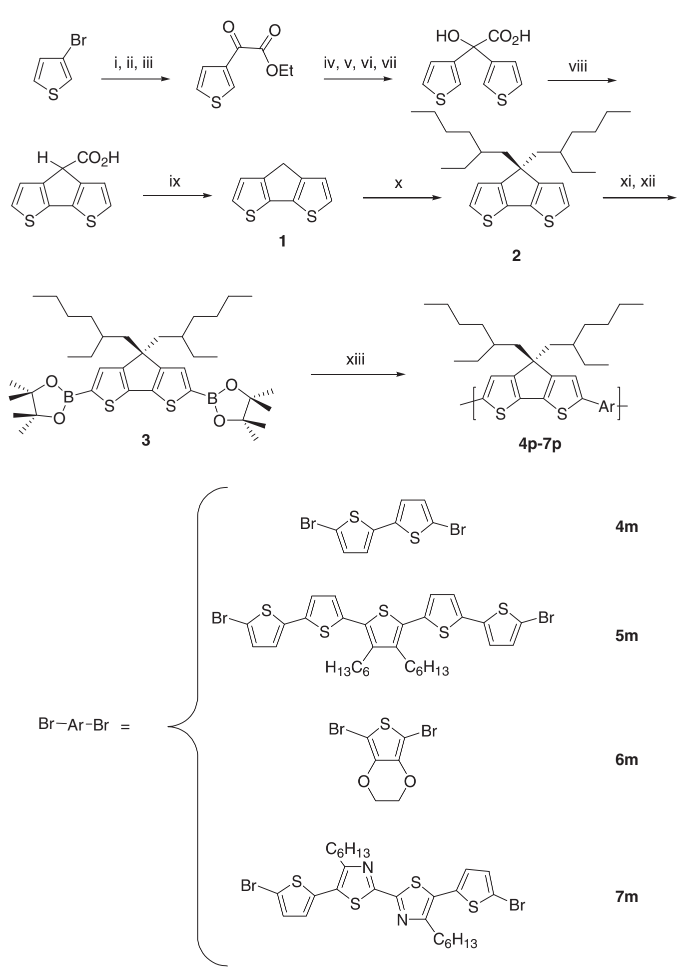
Polymer 6. Dark blue powder (0.084 g, 97%). ^1H-NMR (200 MHz, $CDCl_3$): δ 7.05 br (2H), 4.43 (br, 4H), 1.86 (br, 4H), 1.05–0.96 (br, 18H), 0.77 (t, 6H), 0.65 (t, 6H)

Polymer 7. Brown solid (0.195 mmol, 84%). ^1H-NMR (200 MHz, $CDCl_3$): δ 7.2–7.1 (br, 6H), 3.0 (m, 4H), 1.86 (m, 8H), 1.6 (br, 16H), 1.20–0.65 (br, 32H).

3 Results and Discussion

3.1 Synthesis

While the preferred synthetic route to the parent 4*H*-cyclopenta[2,1-*b*;3,4-*b*′]dithiophene is through the Wolf-Kishner reduction of the corresponding cyclopenta[2,1-*b*;3,4-*b*′]dithiophene-4-one (24) as described by Turner, et al., (20) we have found that the method of MacDowell (21) for the preparation of **1** (Scheme 1) to be a more facile route for large-scale synthesis. Alkylation of **1** with 2-ethylhexyl bromide, using previously reported methods for similar compounds, (20) gave 2 in high yield (22b). The bis(pinacol borate) monomer **3** was prepared by direct lithiation of **2** in THF, followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The dibromide monomers **4m-7m** were prepared according to published procedures (25–28).



Sch. 1. *Reagents and conditions*: i. ^{i}PrMgCl, LiCl, THF, rt, 2 h; ii. Diethyl oxalate, −78°C, 2 h; iii. 2M HCl, −20°C; iv. 3-bromothiophene, ^{i}PrMgCl, LiCl, THF, rt, 2 h; v. **A**, THF, −78°C, 1 h; vi. 2M HCl, 9°C; vii. KOH, EtOH, rt. 18 h; viii. $AlCl_3$, toluene, reflux, 1 h; ix. Cu, quinoline, 200°c, 4 h; x. KOH, KI, 2-ethylhexyl bromide, DMSO, 0°C to rt; xi. BuLi, THF, −78°C, 1 h, then rt, 3 h; xii. 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, −78°C, 1 h, then rt 18 h; xiii. Br-Ar-Br, Pd_2dba_3, PPh_3, 2M Na_2CO_3, toluene, 90°C, 2 d.

The polymerization of **3** with monomers **4m-7m** was carried out utilizing palladium(0)-catalyzed Suzuki coupling reactions utilizing equimolar amounts of the diboronic ester and dibromide monomers in hot toluene solutions using 2M Na_2CO_3 as the aqueous base, resulting in the formation of dark red to purple hazy solutions. To a certain extent, the polymers are soluble in chloroform, tetrahydrofuran,

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Table 1. Physical and optical properties of the copolymers

Polymer	M_n^a *(kDa)*	M_w/M_n	λ_{abs} *(nm)*^{b}	λ_{abs} *(nm)*^{c}	E_g *(eV)*^{c,d}
4	13.5	1.5	545	561	1.93
5	16.3	1.4	509	533	2.00
6	13.0	1.5	582, 624	590, 623	1.80
7	19.0	1.6	521	560, 600	1.75

[a]Number-average molecular weights determined by GPC using polystyrene standards in chlorobenzene; [b−c]Wavelength of the maximum of absorption of [b]$CHCl_3$ solution and [c]spin-coated film; [d]Optical band gap.

toluene and *o*-xylene and are more soluble in haloaromatic solvents such as chlorobenzene and *o*-dichlorobenzene. The molecular weights of polymers **4p-7p** are listed in Table 1. All of the polymers were characterized by GPC using chlorobenzene as a solvent and have similar number-average molecular weights (M_n) of between 13 kDa to 19 kDa (based on polystyrene standards). This narrow range is perhaps an indication that the polymerization reaction is solubility limited. Multiple polymerizations with these monomers resulted in similar M_n values. Changing the polymerization solvent to *o*-xylene had little effect on the molecular weight or the polydispersity. High quality films of **4p-7p** can be prepared by casting the polymer from chlorobenzene or *o*-dichlorobenzene solutions.

3.2 Optical and Electrochemical Properties

The absorption spectra of polymers 4p-7p were recorded in both solution and solid state and the solid state spectra are presented in Figure 1 with the data summarized in Table 1. Comparing the absorption spectra of polymer **4p** to the fluorene analog F8T2 reveals the influence of the cyclopentadithiophene unit. In the solution spectra, there is an 87 nm red shift in the λ_{max} as well as a 79 nm shift in the absorption edge. The 15 nm red shift between the solution and solid state spectra for polymer **4p**, as well as the broadening of the spectra are indicative of significant interchain aggregation in the solid state. All of the polymers **4p-7p** show this interchain aggregation in the solid state. There seems to be only a small influence of the comonomer upon the absorption properties of the polymers. The more electron-donating EDOT and bis(thienyl)bithiazole based polymers (polymers **6p** and **7p**) are significantly red-shifted with respect to the bithiophene and pentathiophene derivative **4p** and **5p**. Optical band gaps in the solid state were estimated from the absorption edges (Table 1) and ranged from 1.75 eV to 2.0 eV. Again, the more highly electron-rich polymers had the lowest band gaps.

The electrochemical properties of these polymers were investigated by cyclic voltammetry. HOMO and LUMO values were taken at the onset of oxidation and reduction, respectively (28). As expected, these polymers had smaller HOMO values than their fluorene counterparts. The bithiophene, pentathiophene and bis(thienyl)bithiazole copolymers **4p**, **5p** and **7p** all have HOMO values near 5.4 eV (Table 2). However, the electron-rich EDOT copolymer **6p** had a substantially smaller HOMO of 4.9 eV due to the highly electron-rich nature of the EDOT moiety. LUMO values were all fairly similar at around 3.3 eV, with the exception being polymer **5p** with a LUMO of 2.95 eV. The reason for this discrepancy is unclear at this time. Except

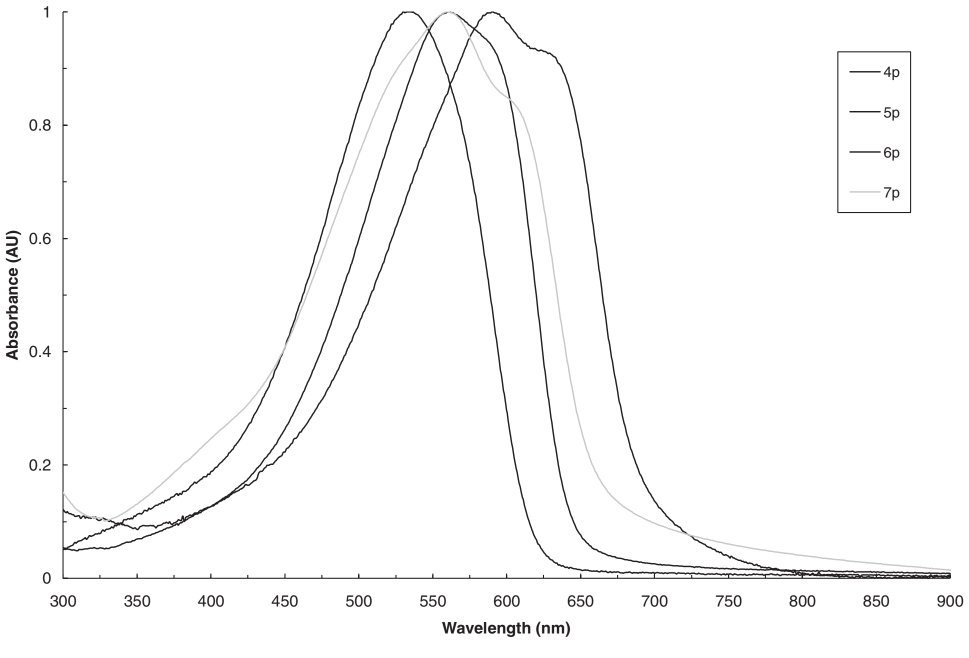

Fig. 1. Absorbance spectra of spin-coated polymer films on glass.

Table 2. Electrochemical properties of the copolymers

Polymer	E_{ox} $(V)^a$	E_{red} $(V)^a$	$HOMO$ $(eV)^b$	$LUMO$ $(eV)^b$	E_g $(eV)^c$	μ_h (cm^2/Vs)
4	0.70	−1.50	−5.45	−3.25	2.2	2×10^{-3}
5	0.63	−1.80	−5.38	−2.95	2.43	2×10^{-3}
6	0.14	−1.45	−4.89	−3.30	1.59	8×10^{-4}
7	0.65	−1.50	−5.40	−3.25	2.15	9×10^{-4}

[a] E_{ox} and E_{red} are the onset potential of oxidation and reduction, respectively, [b]Calculated from the empirical formula, $E_{(HOMO)}$ = -(E_{ox}+ 4.75) (eV), $E_{(LUMO)}$ = -(E_{red}+ 4.75) (eV), [c] $E_g = |E_{(HOMO)} - E_{(LUMO)}|$.

for polymer **6p**, the electrochemical bandgaps were in the range of 2.15 eV to 2.43 eV, indicative of mid-visible absorption. Only **6p** had a smaller bandgap (1.59eV); this is due to the easily oxidized nature of this polymer.

The hole mobilities of these polymers were measured using field effect transistors. Hole mobilities were relatively high, ranging from 7.5×10^{-4} cm²/Vs to 2.0×10^{-3} cm²/Vs. From studies on ZZ50 we have learned that there is a correlation between molecular weight and mobility. The correlation seemed to have a sharp onset at a specific molecular weight, followed by a weak increase of mobility if the molecular weight is increased beyond that critical molecular weight point. A similar behavior is expected for the class of polymers introduced here, and we would expect even higher mobilities for higher mol. weight polymers. Muellen et al showed in that the mobility of a low molecular weight bridged thiophene significantly increased upon high thermal treatment (some 250–300°C) (29). Such high T treatments have not been tried, though this might be a pathway to further increase the mobility of the lower molecular weight polymers studied here. The electrochemical and physical parameters of these polymers make them promising candidates for high-performance solar cells.

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3.3 Photovoltaic Properties

Conventional single-junction photovoltaic devices were prepared by blending the donor polymer **4p-7p** with soluble fullerene derivatives ($PC_{60}BM$ and $PC_{70}BM$). The photovoltaic characteristics are listed in Table 3. The I-V characteristics of devices with polymers **5p-7p** are shown in Figure 2. Interestingly, the F8T2 analog polymer **4p** gave no discernable cell efficiency while the polymer with the pentathiophene comonomer had a cell efficiency of 2.0%. The failure of polymer **4p** most likely was poor film quality leading to shunting (instead of morphology, optical or electronic defects). The best photovoltaic cell consisted of a blend of polymer **7p** and $PC_{70}BM$ and had an open-circuit voltage of 0.81 V with a current density of 8.2 mA/cm² and gave a power conversion efficiency of 3.1% under standard AM1.5 conditions. This efficiency value is respectable for these materials, however it is lower than what would be predicted based on the electro-optical parameters of the polymers (2b). The cause of this deficiency for all of these polymers is due to a low fill factor (<0.50). Preliminary AFM studies of a related cyclopentadithiophene copolymer and PCBM blends (22b) indicates a lack of continuity in the polymer phase, resulting in poor charge transport and a low fill factor. Control of the film morphology has been found to be one of the main factors in increasing the power conversion efficiency or organic solar cells (8b,30). Further optimization of these promising polymers will include increasing the molecular weights and modifying the side chains to promote a better bicontinuous phase separation.

Table 3. Photovoltaic characteristics of the copolymers

Polymer	V_{OC} (mV)	$J_{SC}(mA/cm^2)$	FF	$\eta(\%)^a$
4	<100	<0.2	<0.25	0
5	690	6	0.49	2.0
6	250	1.37	0.36	0.12
7	810	8.2	0.46	3.1

[a]Efficiencies have been measured on a AM1.5 solar simulator which was calibrated to have a mismatch factor of ~1 for polymers with an absorption close to P3HT. Efficiencies in Table 3 have not been corrected for the true AM1.5 values, and variations of up to 10% are possible.

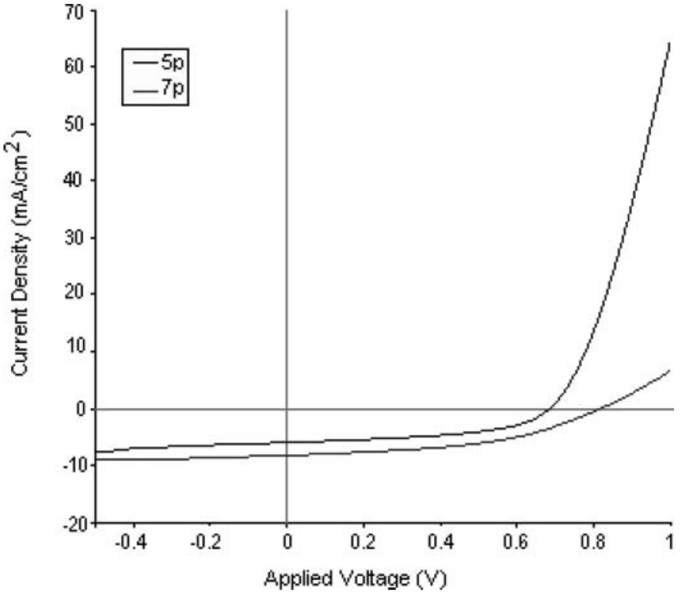

Fig. 2. I-V characteristics of organic PV cells prepared from polymers **5p** and **7p** and $PC_{70}BM$ (1:3 by weight) under AM 1.5 irradiation (100 mW/cm²).

4 Conclusions

Polymers containing the 4H-cyclopenta[2,1-b;3,4-b']dithiophene unit with various comonomers have been synthesized by Suzuki methodologies. The easily modified

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nature of the 4-carbon of the 4H-cyclopenta[2,1-b;3,4-b']dithiophene unit allows the attachment of solubilizing alkyl groups without introducing steric hinderance between the comonomers. The absorption spectra of these polymers covers a broad part of the visible spectrum and electrochemical studies show that polymers **4p, 5p,** and **7p** possess desirable HOMO-LUMO levels for photovoltaic applications. Relatively high mobility values were measured by field effect transistors. In photovoltaic cells, these desirable properties afforded devices with high power conversion efficiencies for polymers **5p** and **7p**. The high open circuit voltage, moderate short circuit currents but low fill factor of these two devices indicate possible optimization can still be done with these systems.

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