

Photovoltaic Properties of Poly[(9,9-dioctylfluorenyl-2,7-vinylene)-*co*-{2-(3'-dimethyldodecylsilylphenyl)-1,4-phenylenevinylene}] for Electro-Active Devices

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Received May 10, 2006; Revised August 1, 2006

Abstract: New, thermally robust, arylenevinylene conjugated polymers, including poly(9,9-dioctylfluorenyl-2,7-vinylene) [poly(FV)] and poly[2-(3'-dimethyldodecylsilylphenyl)-1,4-phenylenevinylene] [poly(*m*-SiPhPV)], were synthesized and used for the fabrication of efficient photovoltaic cells. Bulk heterojunction photovoltaic cells fabricated by blending one of the polymers, [poly(FV)], [poly(*m*-SiPhPV)], and poly(FV-*co*-*m*-SiPhPV), with the fullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) were found to have a power conversion efficiency of up to 0.038%.

Keywords : organic photovoltaic cell, PCBM, PPV, PFV.

Introduction

The limited supplies of today's main energy sources such as oil, coal, and uranium will focus to replace most of the currently used power plants with renewable energy sources. Organic photovoltaic cells have advantages over the inorganic thin film photovoltaic cells such as reduced materials cost, possibility to make in large area cells, light-weight, and low temperature solution process. Recent advances in organic photovoltaic cells have allowed significant increase in the power conversion efficiency, which makes them economically interesting. Therefore, organic photovoltaic cells offer great technological potential as a renewable and alternative source for electrical energy. Organic photovoltaic cells are divided as bilayer heterojunction¹ and bulk heterojunction photovoltaic² cells by photoinduced electron trans-

fer from optically excited conjugated polymers to the C₆₀ derivatives. The essence of the bulk heterojunction photovoltaic cell is to intimately mix the donor and acceptor components in a bulk volume so that each donor-acceptor interface will be within a distance less than the exciton diffusion length of each absorbing site. Due to the interface being dispersed throughout the bulk, no loss due to too small exciton diffusion lengths is expected, because ideally all excitons will be dissociated within their lifetime. In this conception, the charges are also separated within the different phases. Hence, recombination is reduced to a large extent and the photocurrent often follows the light intensity linearly or slightly sublinearly. Therefore, the bulk heterojunction photovoltaic cells are much more sensitive to the nanoscale morphology in the blend.

Since the report of polymer light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene) (PPV) by Friend's group,³ π -conjugated polymers have attracted much attention

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because of their applications in flexible and wearable displays,^{4,5} organic thin film transistors^{6,7} and photovoltaic cells.^{8,9} Poly(9,9-dialkylfluorene)s (PFs)¹⁰ and PPVs¹¹ are considered to be the most promising light-emitting materials because of the many advantages such as chemical and thermal stability, high photoluminescence (PL) quantum efficiency, and ease of property tuning by copolymerization with various comonomers. These materials are also used for the photovoltaic applications because of their high quantum yield values, which is necessary for good photovoltaic properties. Recently, we synthesized poly(9,9-dioctylfluorenyl-2,7-vinylene) [poly(FV)] and its copolymers with MEH-PPV segments and highly luminescent poly(*m*-SiPhPV) derivatives using with the Gilch polymerization method.¹²⁻¹⁴ The structure of poly(FV) has the advantages of both PF and PPV, because the poly(FV) backbone is consisting of both fluorene and vinylene repeating units.

In this present article, we report the bulk heterojunction photovoltaic properties of high luminescent and high quantum yield poly(FV), poly(FV-*co-m*-SiPhPV), and poly(*m*-SiPhPV) polymers with PCBM. Different process parameters such as active layer thickness and ratio of donor to acceptor ratio on the performance are also studied.

Experimental

Materials. 2,7-Bis(chloromethyl)-9,9-di-*n*-octylfluorene, 1,4-bis(bromomethyl)-2-(3-dimethyldodecylsilylphenyl)benzene and the polymers were prepared according to the reported procedures.¹²⁻¹⁴ Soluble fullerene derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) was synthesized using the procedure published earlier.¹⁵

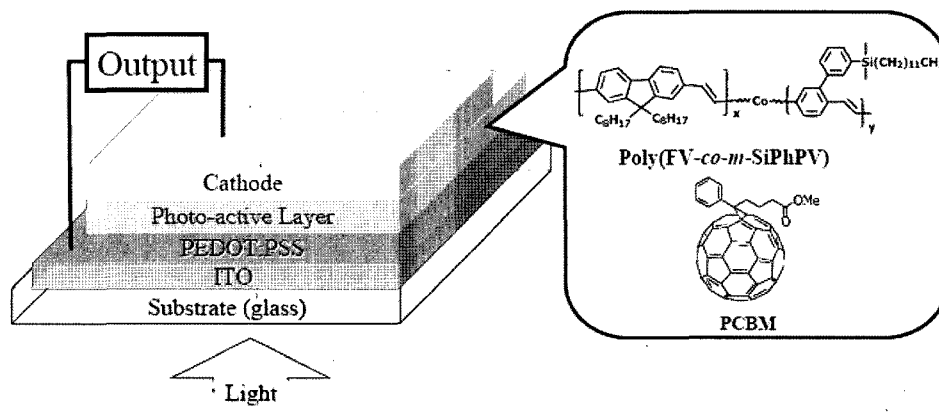
Bulk Heterojunction Photovoltaic Cell Fabrication. Bulk heterojunction photovoltaic cells were fabricated by spin-coating a 40 nm thick layers of PEDOT:PSS (Baytron PVP AI 4083) on the patterned ITO substrate, followed by baking on a hot plate at 120 °C for 10 min. The photoactive layer of the polymer was spin coated from 1.5-2.0 wt%

blend solutions prepared in chlorobenzene after filtering through 0.45 μm PP syringe filters. The thickness of the photoactive layer and the ratio of donor to acceptor materials were varied. The device structure was completed by depositing LiF (1 nm)/Al (200 nm) cathode as a top electrode under the pressure less than 3.0×10^{-6} torr in the vacuum evaporator attached with glove box onto the polymer active layer. The overlap of the two electrodes defined the active area of the cell and is 4 mm². The photovoltaic cells were characterized in the dark and under the illumination of simulated photovoltaic light at 100 mW/cm² (AM1.5) using Oriol 300 W solar simulator. The light energy was adjusted using Radiant Power/Energy Meter (model 70260, thermal type). Electric data were recorded using a Keithley 236 source-measure unit. The photocurrent action spectra were carried out by illuminating the bulk heterojunction photovoltaic cells with a 300 W Xenon lamp, dispersed by Dongwoo-opton (South Korea) DM150i single-grating monochromator. The thickness of the films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ±1 nm. All fabrication steps and characterization measurements were performed in an ambient environment without a protective atmosphere.

Results and Discussion

Scheme I represents the molecular structures of poly(FV-*co-m*-SiPhPV) and PCBM and the configuration of the bulk heterojunction photovoltaic cells fabricated in this study. The insertion of long-chain dimethyldodecylsilylphenyl groups as side chains on the PPV backbone yields unique properties, including good flexibility, solubility, and adhesion to the ITO-coated glass substrate, and improved the device performance.¹² High molecular weight poly(FV), composed of fluorene and vinylene repeating units, was synthesized using the Gilch polymerization method.^{13,14} Because of the vinylene units in its backbone, poly(FV) exhibits amorphous morphology and less excimer formation than poly(9,9-dialkyl-

Scheme I



fluorene) (PF) derivatives. The weight average molecular weights (M_w) and polydispersities were found to be in the range of $8.7\text{--}32.6 \times 10^4$ and 2.3–5.4, respectively. The copolymer compositions were calculated by comparing the area under the peaks at 0.28 ppm (from dimethyl groups on silicon atoms in poly(*m*-SiPhPV) segments) and 2.0 ppm (from methylene protons in octyl groups in the poly(FV) segments).

The thermal stability of photoactive materials is important for the long-term operating stability of photovoltaic cells. Most of the PF- and PPV-based polymers have relatively low glass transition and degradation temperatures. The glass transition temperature of poly(FV), poly(*m*-SiPhPV), and poly(FV-*co-m*-SiPhPV) were found to be in the range 154–180 °C, which is higher than those of PFs and PPVs.^{16,17} The TGA thermograms of poly(FV), poly(*m*-SiPhPV), and poly(FV-*co-m*-SiPhPV) demonstrate their high thermal stability up to 389 °C with respect to 5% weight loss.

Figure 1 shows the absorption and emission spectra of poly(FV), poly(*m*-SiPhPV), and poly(FV-*co-m*-SiPhPV) thin

films on quartz substrates. The emission spectra of 1:1 wt. ratio of poly(FV-*co-m*-SiPhPV) (35:65) and PCBM is also included in Figure 1(b). The absorption maxima of poly(FV) and poly(*m*-SiPhPV) are relatively sharp at 409 and 433 nm, respectively. It was found that regardless of the composition of the poly(FV-*co-m*-SiPhPV) copolymers, their absorption maxima was around 419 nm due to the $\pi\text{--}\pi^*$ transition of the conjugated polymer backbone.

The emission spectrum of poly(FV) has two peaks at 468 and 500 nm with a shoulder peak at 528 nm. As the poly(*m*-SiPhPV) content in poly(FV-*co-m*-SiPhPV) is increased, the emission peak is red-shifted toward 518 nm, and the emission spectrum becomes almost identical to that of poly(*m*-SiPhPV). However, the PL spectrum of the mixture of poly(FV-*co-m*-SiPhPV) and PCBM is almost quenched. The required transfer of charges can be realized at the interface between two materials, if one material has a higher LUMO and the other has lower HOMO energy levels. Since the LUMO level of PCBM 3.7 eV is lower than that of poly(FV-*co-m*-SiPhPV) (35:65) at 2.76 eV, we predict that the quenching of PL intensity of the blend film is due to the efficient photoinduced electron transfer reaction.

HOMO and energy levels of poly(FV), poly(*m*-SiPhPV), and poly(FV-*co-m*-SiPhPV) were measured using cyclic voltammetry. The HOMO binding energies of the polymers with respect to the ferrocene/ferrocenium (4.8 eV) standard were found to be about 5.26 eV for poly(FV), 5.18 eV for poly(*m*-SiPhPV) and 5.10–5.18 eV for poly(FV-*co-m*-SiPhPV) copolymers with various comonomer compositions. The band gaps obtained from the onsets of their absorption spectra were found to be in the range of 2.38–2.63 eV. The LUMO energy levels were calculated from the values of the band gaps and HOMO energies. The band gaps of the copolymer fall in between the band gaps of the two homopolymers.

The poly(FV-*co-m*-SiPhPV) copolymers with varying monomer feed ratio along with homopolymers of poly(FV) and poly(*m*-SiPhPV) were evaluated for their photovoltaic characteristics using PCBM as an electron acceptor and the results are summarized in Table I. Proper choice of the cathode is one of the important parameters in photovoltaic cells, because the ohmic contact between the metal used in cathode and the photoactive layer will affect the power conversion efficiency (PCE). In this paper, we chosen LiF/Al cathode instead of a pristine Al cathode for all of the photovoltaic cells in order to guarantee a good ohmic contact between the metal and the organic layer.^{18–20} The ratio of donor to acceptor is another important parameter to be studied, since the proper interpenetrating network formed between these two materials has strong influence on performance of the photovoltaic cells.²⁰ To study this effect, we have chosen poly(FV-*co-m*-SiPhPV) (49:51) copolymer as the electron donor, because it has the same composition of poly(FV) and poly(*m*-SiPhPV) units along the polymer backbone. Bulk heterojunction photovoltaic cells were fab-

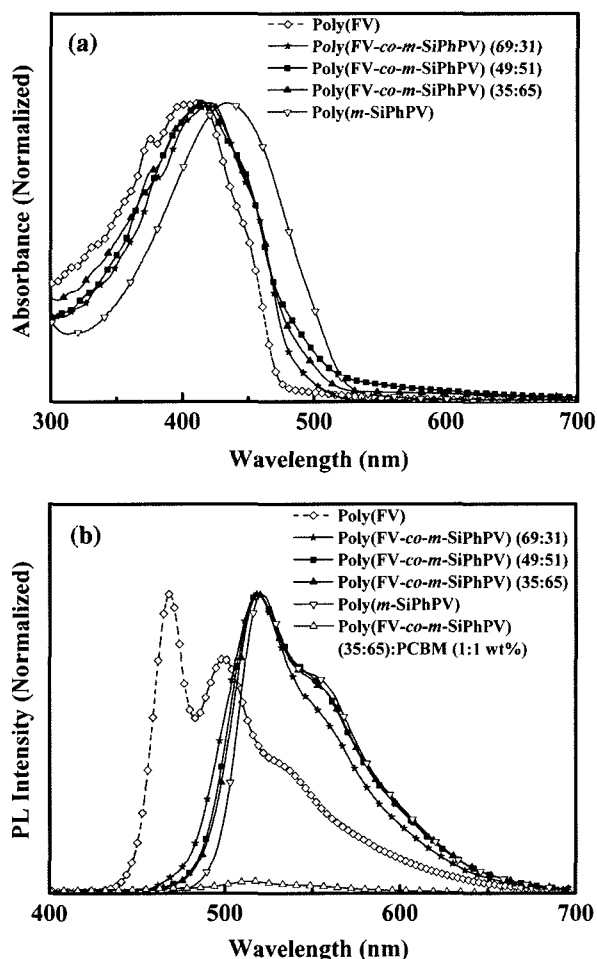


Figure 1. UV-vis absorption (a) and PL spectra (b) of poly(FV), poly(*m*-SiPhPV), poly(FV-*co-m*-SiPhPV), and poly(FV-*co-m*-SiPhPV) (35:65):PCBM (1:1 wt%) in the solid state.

Table I. Bulk Heterojunction Photovoltaic Cell Performances of Poly(FV), Poly(FV-co-m-SiPhPV), and Poly(m-SiPhPV)

Polymer	Polymer:PCBM	Photo-Active Layer Thickness (nm)	I_{sc}^a (mA/cm ²)	V_{oc}^b (V)	FF ^c	PCE ^d (%)
Poly(FV)	1:4	75	0.227	0.538	0.29	0.035
		90	0.128	0.733	0.28	0.026
		135	0.090	0.761	0.31	0.021
Poly(FV-co-m-SiPhPV) (69:31)	1:4	75	0.129	0.680	0.30	0.026
		90	0.095	0.725	0.29	0.020
		120	0.076	0.776	0.32	0.019
Poly(FV-co-m-SiPhPV) (49:51)	1:1	95	0.060	0.750	0.27	0.012
	1:4	70	0.217	0.632	0.28	0.038
		95	0.122	0.726	0.29	0.026
Poly(FV-co-m-SiPhPV) (35:65)	1:4	165	0.071	0.698	0.30	0.015
		70	0.140	0.500	0.30	0.021
		100	0.084	0.675	0.28	0.016
Poly(m-SiPhPV)	1:4	175	0.053	0.660	0.29	0.010
		75	0.136	0.600	0.33	0.027
		100	0.094	0.793	0.31	0.023
		160	0.093	0.824	0.31	0.024

^a I_{sc} : Short circuit current. ^b V_{oc} : Open circuit voltage. ^cFF: Fill factor. ^dPCE: Power conversion efficiency.

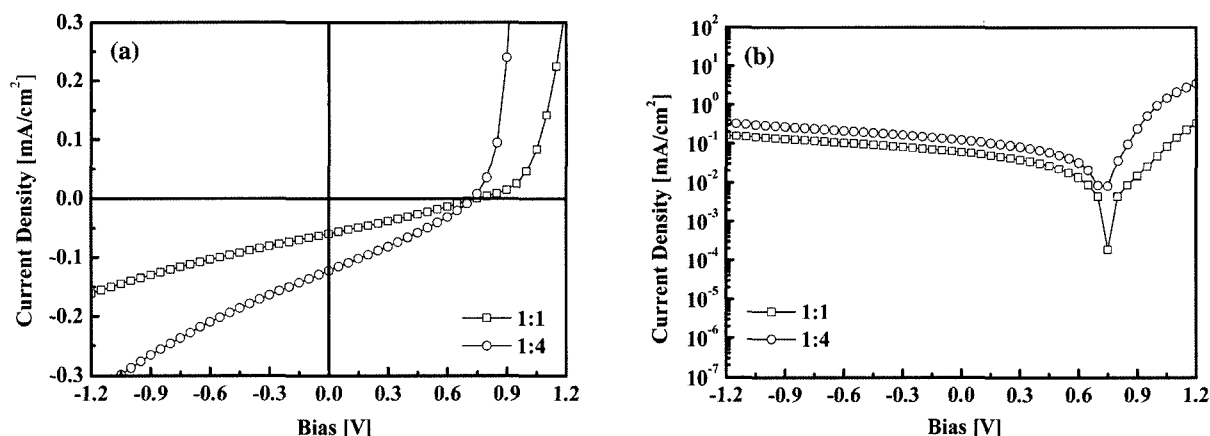


Figure 2. Liner (a) and semi-logarithmic (b) plot of the current density-voltage characteristics for poly(FV-co-m-SiPhPV) (49:51) :PCBM devices (1:1 and 1:4 wt%) with 95 nm active layer thickness under illumination (AM1.5, 100 mW/cm²).

ricated using 1:1 and 1:4 ratio of donor to acceptor materials at a fixed photoactive layer thickness of 95 nm with the bilayer cathode of LiF (1 nm)/Al (200 nm). Current density versus voltage (J-V) plots for these devices are presented in Figure 2. The open-circuit voltage (V_{oc}) of both the devices are almost identical, but the higher short-circuit current (I_{sc}) and the fill factor (FF) were observed for the device prepared with 1:4 ratio (Table I and Figure 2), which are the indication of the improved mobility of the charges inside the bulk heterojunction photovoltaic cell.²⁰ The combined

increase of these properties leads to the increase in the PCE of the 1:4 device to 0.026% than 0.012% for the 1:1 device. The AFM images of the active films of these devices are presented in Figure 3. The r.m.s. roughness of 1:1 and 1:4 ratio films is 2.4 and 3.4 nm, respectively. Both films show different texture. The texture and the roughness of 1:4 ratio film suggest the good contact present between the active layer materials and metal cathode.²¹ This contact might improve the I_{sc} of the device made with 1:4 ratio and showed higher PCE than the device made with 1:1 ratio of

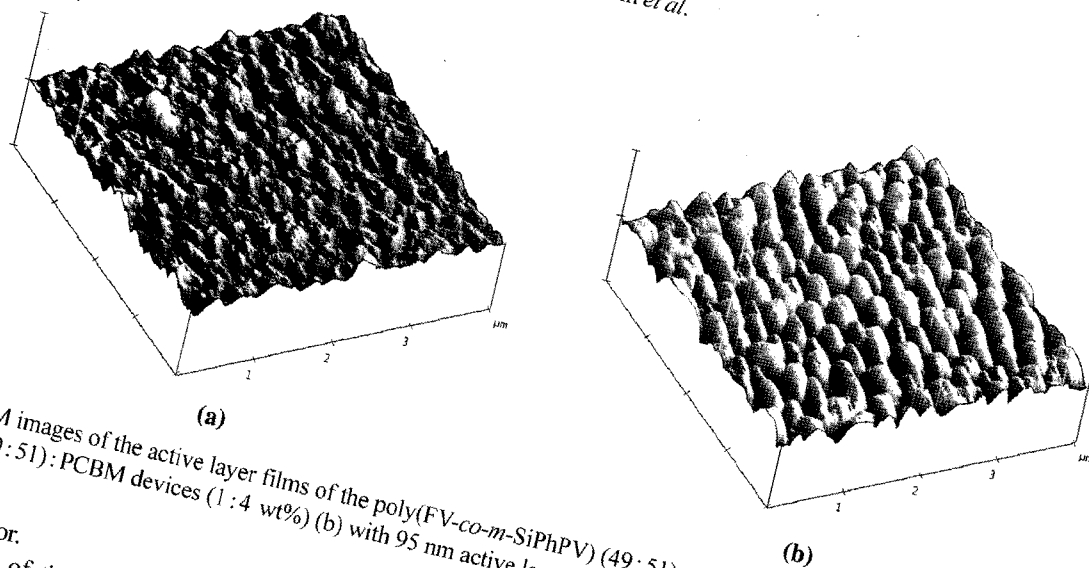


Figure 3. AFM images of the active layer films of the poly(FV-co-*m*-SiPhPV) (49:51):PCBM devices (1:4 wt%) (a) and poly(FV-co-*m*-SiPhPV) (49:51):PCBM devices (1:1 wt%) (b) with 95 nm active layer thickness.

donor to acceptor.

The thickness of the photoactive layer will also play a major role in the PCE of a bulk heterojunction photovoltaic cells, because the absorption of light, exciton dissociation and mobility of the charges depends on the thickness of the photoactive layer.²² Hence, we fabricated the bulk heterojunction photovoltaic cells with varying photoactive layer thickness from 70 to 175 nm using 1:4 ratio of the donor polymer and PCBM. Figure 4 shows the linear (a) and semi-logarithmic (b) plot of the J-V characteristics for poly(FV-co-*m*-SiPhPV) (49:51):PCBM (1:4 wt. ratio) cells with varying active layer thickness in the dark and under illumination (AM1.5, 100 mW/cm²). As the thickness of the photoactive layer decreased, the PCE of the photovoltaic cells increased and the V_{oc} was decreased. The decrease in V_{oc} may be due the pinholes and microcracks presents in the thin photoactive layer, which reduces the shunt resistance. This decreased shunt resistances were recognized from J-V curves in the dark. The shunt resistances will reduce as the slopes of J-V curves at 0 voltage increase. For good photovoltaic characteristics, the shunt resistance should be high.²³

As presented in Table I, the photovoltaic cells prepared with around 70 nm thick active layer have shown higher PCE with different donor materials. The photovoltaic cells prepared with poly(FV-co-*m*-SiPhPV) (49:51) has given the highest PCE of 0.038%, whereas the photovoltaic cells made with poly(FV) and poly(*m*-SiPhPV) were shown the PCE of 0.035 and 0.027%, respectively. We found that the copolymer system had better bulk heterojunction photovoltaic characteristics than the two homopolymers. The fill factors of all the cells are in the range of 0.27-0.33. Overall, the I_{sc} and PCE did not show any clear variation with the variation of copolymer ratio and the values are also too low. It means at the polymer didn't play enough role as a donor, since absorbance spectra of the polymer films cover the blue

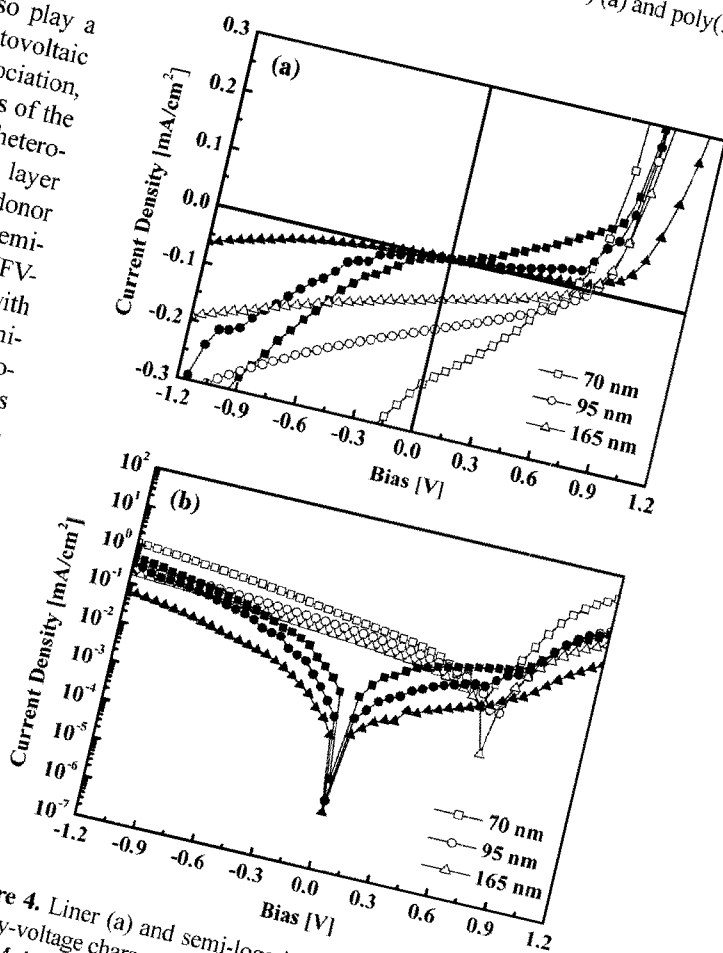


Figure 4. Linear (a) and semi-logarithmic (b) plot of the current density-voltage characteristics for poly(FV-co-*m*-SiPhPV) (49:51):PCBM devices (1:4 wt. ratio) with varying active layer thickness in the dark (full symbols) and under illumination with 100 mW/cm² (open symbols).

range of the visible light.

Results of the incident photon to current conversion effi-

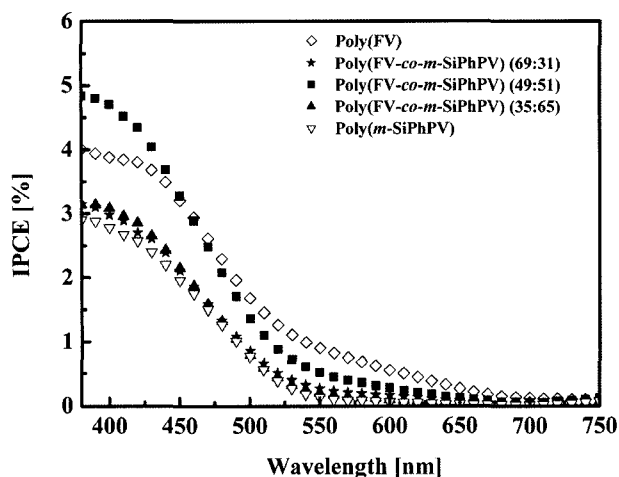


Figure 5. Incident photon to current conversion efficiency (IPCE) versus wavelength plots for polymer:PCBM(1:4 wt. ratio) devices with 70-75 nm photo-active layer thickness.

ciency (IPCE) measurements for the devices with about 70 nm thick active layers are shown in Figure 5. The ratio of the integrated IPCE spectra nearly corresponds to the ratio of the respective I_{SC} of the photovoltaic cells. Maximum of 4.8% of IPCE is observed in the case of poly(FV-co-m-SiPhPV) (49:51) bulk heterojunction photovoltaic cell at a wavelength of 385 nm.

Conclusions

Novel copolymers composed of fluorenylvinylene and phenylenevinylene repeating units were found to have high molecular weights and exhibit good solubility in common organic solvents. Due to the high glass transition temperatures, these polymers are promising materials for photovoltaic applications. Bulk heterojunction photovoltaic cells were fabricated using these new polymers as donor materials. Effect of electron donor to acceptor ratio and thickness of photoactive layer on the PCE was studied. The bulk heterojunction photovoltaic cells prepared with 70 nm thick photoactive layer and 1:4 donor to acceptor ratio have given the highest PCE. The device prepared poly(FV-co-m-SiPhPV) (49:51) has given the maximum PCE of 0.038%.

Acknowledgements. This research was supported by the University IT Research Center (ITRC) Project of the Ministry of Information and Communication (J. W. Lee) and the National Research Laboratory (NRL) program of KOSEF (S. H. Jin).

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