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Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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To cite this article: Hayoung Kim, Youngjun Jeong & Youngu Lee (2013) Synthesis and Characterization of Polymers Based on Benzimidazole Segments for Polymer Solar Cells, Molecular Crystals and Liquid Crystals, 581:1, 25-30

To link to this article: http://dx.doi.org/10.1080/15421406.2013.808141

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Mol. Cryst. Liq. Cryst., Vol. 581: pp. 25–30, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.808141

Synthesis and Characterization of Polymers Based on Benzimidazole Segments for Polymer Solar Cells

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A series of polymers based on electron-deficient benzimidazole segments and electron-rich benzodithiophene segments for polymer solar cells was designed and synthesized. The polymer solar cell devices with benzimidazole based polymers achieved power conversion efficiency (PCE) close to 1%. This work implies that polymers based on benzimidazole segment can achieve high PCE through structural modification of the polymers.

Keywords Benzimidazole derivatives; benzodithiophene derivatives; donor-acceptor type of copolymer; polymer solar cell

Introduction

Polymer solar cells (PSCs) have attracted considerable attention because of their advantage of light weight, flexibility, and low costs of materials [1]. The bulk heterojunction structure for PSCs is composed of a phase-separated blend of electron-donor units such as p-type conjugated polymers and electron-acceptor units such as n-type fullerene materials. The polymer solar cells based on P3HT and $PC_{61}BM$ showed power conversion efficiency (PCE) up to 5% [2]. However, it is necessary to develop new types of electron-donor polymers to achieve high power conversion efficiency in device performance. The electron-donor polymers need to possess several characteristics such as harvesting photons in a wide range of spectrum, efficient exciton dissociation, high hole mobility, suitable HOMO and LUMO energy levels, and good miscibility with the electron-acceptor materials. To obtain these characteristics for electron-donor polymers, various donor-acceptor types of copolymers which contain electron-rich and electron-deficient segments alternatively have been synthesized [3]. For example, electron-deficient benzothiadiazole has been used as the acceptor segment to afford copolymers with various electron-rich segments [4]. One of drawbacks of benzothiadiazole is the synthetic difficulty in modifying chemical structures for tuning the optoelectronic properties of the molecules. Various benzimidazole derivatives have been used as electron injecting and transporting materials in organic light-emitting diodes (OLEDs) because of their high electron accepting and transporting properties. In

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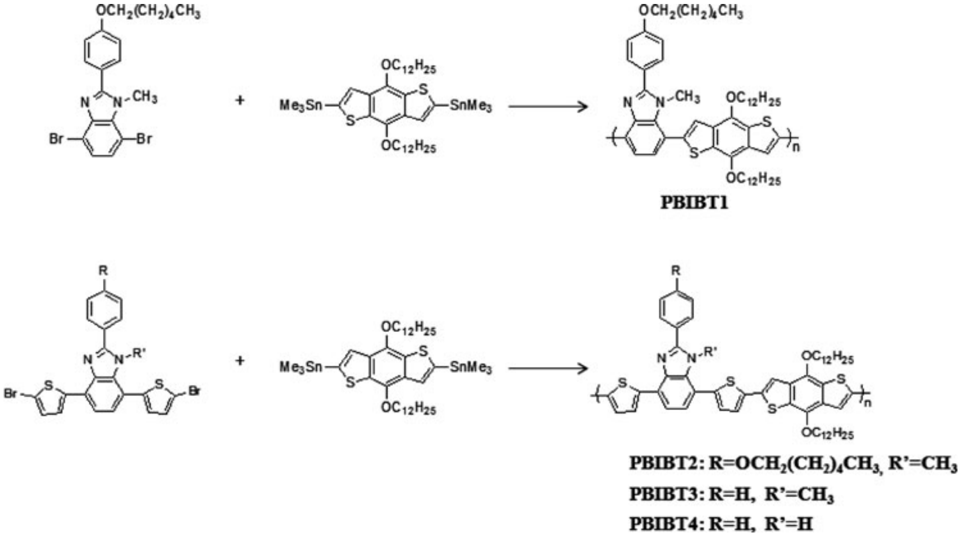
addition, the optoelectronic properties of the benzimidazole segments can be easily tuned by introducing various functional groups [5,6]

In this paper, we describe the synthesis and characterization of a series of copolymers with benzodithiophene segments as donor units and benzimidazole segments as acceptor units for polymer solar cells. The optical and electrochemical properties of the synthesized polymers were characterized by UV/Vis spectroscopy and cyclic voltammetry measurements. It was found that the synthesized polymers exhibited low bandgaps and suitable HOMO and LUMO energy levels for photovoltaic applications. The bulk heterojuction solar cell devices with the polymers achieve power conversion efficiency close to 1%. This study will provide more opportunities for development of a new class of materials for polymer solar cells which can achieve high PCEs.

Results and Discussion

Synthesis of Polymers

Electron-deficient benzimidazole segments were synthesized by acid catalyzed cyclization reaction of 3,4-Dibromo-benzene-1,2-diamine. The benzimidazole monomers were copolymerized with benzodithiophene monomers using the Stille polycondensation reaction. The general synthetic routes toward the polymer are outlined in Scheme 1. Four polymers (PBIBT1 ~ PBIBT4) with the structural variation were synthesized. Table 1 summarizes gel permeation chromatography (GPC) results of the polymers including number-average molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity (PDI) of polymers. The polymers have M_n of 6,012 ~ 10,148 and M_w of 9,313 ~ 15,865 with PDI of 1.43 ~ 1.84. PBIBT1 and PBIBT2 are readily soluble in organic solvents such as chloroform, tetrahydrofuran, and dichlorobenzene because they possess a hexyloxy side



Scheme 1. Synthesis of PBIBT polymers by the Stille polycondensation reaction.

Table 1. Gel permeation chromatography (GPC) results of PBIBT polymers

Polymer	weight-average molecular weight (M_w)	number-average molecular weight (M_n)	polydispersity (PDI)
PBIBT1	14562	10148	1.43
PBIBT2	10529	7113	1.48
PBIBT3	9313	6012	1.50
PBIBT4	15865	8599	1.84

chain on benzimidazole segment. However, PBIBT3 and PBIBT4 exhibit limited solubility in dichlorobenzene due to the lack of alkyl side chain on the benzimidazole segment.

Optical and Electrochemical Properties of Polymers

The UV/Vis absorption spectra of PBIBT1 ∼ PBIBT4 in solution and films are shown in Fig. 1. The polymer solution was prepared in chloroform and the thin film was prepared by spin-coating dichlorobenzene solution of polymers on a glass substrate. Optical properties of the polymers are summarized in Table 2. In the absorption spectra of solution, the polymers showed strong absorption peak around 400 nm presumably due to a delocalized excitonic π-π^* transition in the polymer backbones [7]. The maximum absorption bands of the polymers are observed around 500 nm, which is assigned to the intramolecular charge transfer (ICT) between the benzimidazole and benzodithiophene segments. PBIBT1 exhibits a maximum absorption wavelength at 429 nm and an onset absorption wavelength at 497 nm, corresponding to an optical bandgap of 2.49 eV. Compared to PBIBT1, it was found that UV/Vis absorption spectra of PBIBT2 and PBIBT3 polymers are red-shifted by 10 nm because a thiophene bridge between benzodithiophene and benzimidazole segments extends a conjugation length. In addition, PBIBT4 exhibited red-shifted maximum absorption wavelength and onset absorption wavelength by 30 nm, resulting in optical bandgap of 2.32 eV. This result clearly indicates that the intramolecular charge transfer in PBIBT4 with a hydrogen atom on the benzimidazole segment is stronger than other polymers with a methyl substituent because the hydrogen atom on the benzimidazole segment in PBIBT4

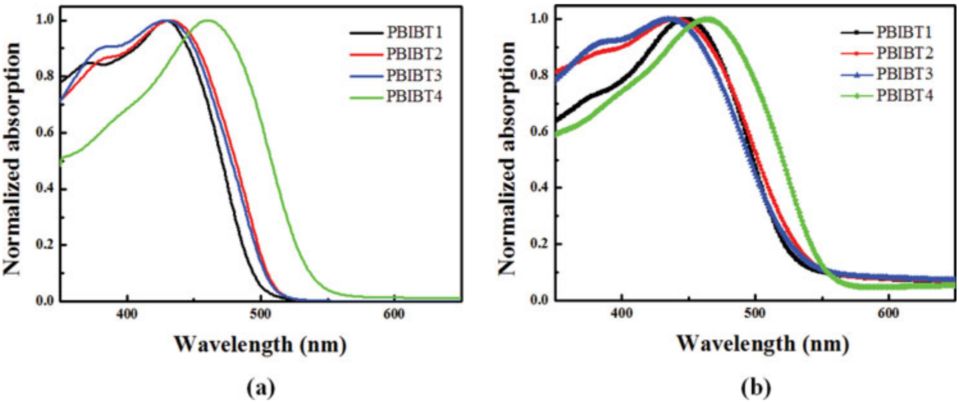


Figure 1. UV/Vis absorption spectra of PBIBT polymers in solution (a) and solid film on a glass (b).

Table 2. Optical properties of PBIBT polymers in chloroform solution and film on a glass

Polymer	λ_{abs} in $CHCl_3$ (nm)	λ_{onset} in $CHCl_3$ (nm)	E_g^{opt} (eV)	λ_{abs} in films (nm)	λ_{onset} in films (nm)	E_g^{opt} (eV)
PBIBT1	429	497	2.49	447	526	2.36
PBIBT2	432	510	2.43	440	540	2.29
PBIBT3	429	508	2.44	435	533	2.32
PBIBT4	460	534	2.32	464	552	2.24

can enhance electron-accepting property of the benzimidazole segment. The absorption spectra in film states were similar to their corresponding absorption spectra in solution. The absorption spectra in film showed longer maximum absorption peak and onset wavelength. The red-shift absorption wavelength in film states was ascribed to intermolecular interaction in solid state of polymer [8].

Cyclic voltammetry (CV) measurement was used to investigate electrochemical properties of the polymers such as the energy levels of HOMO and LUMO as well as electrochemical bandgaps. Electrochemical properties of the polymers are summarized in Table 3. The oxidation onsets of PBIBT1 ~ PBIBT4 are 1.72, 1.40, 1.65, and 1.60 V, corresponding to HOMO energy levels of −6.05, −5.75, −6.0, and −5.95 eV, respectively. It is well known that an open circuit voltage (V_{oc}) in a polymer solar cell is determined by the energy gap between a HOMO level of electron-donor polymer and a LUMO level of electron-acceptor PCBM. Therefore, it is expected that open circuit voltage (V_{oc}) values for solar cell devices based on these polymers may be enhanced due to the low-lying HOMO energy values compared to conventional P3HT polymer (−5.1 eV of HOMO energy value). The LUMO energy levels of PBIBT1 ~ PBIBT4 are estimated to be around −3.60 eV. The reduction onsets of the polymers are −0.75, −0.90, −0.73, and −0.73 V, resulting in LUMO energy levels of −3.60, −3.45, −3.62, and −3.62 eV, respectively. The electrochemical bandgap values of the polymers calculated from CV are 2.45, 2.30, 2.38, 2.33 eV, indicating that these values are in good agreement with the optical bandgap values. These results clearly demonstrate that the electrochemical properties of the polymers can be tuned by changing the molecular structure of the polymers.

Photovoltaic Properties of Polymers

In order to investigate photovoltaic performance of the polymers as electron donors, the bulk heterojunction polymer solar cell devices were fabricated with a structure of glass/ITO/PEDOT:PSS/polymer:$PC_{70}BM$/LiF:Al. Figure 2 shows the current density-voltage

Table 3. Electrochemical potentials and energy levels of PBIBT polymers

Polymer	E_{red}^{onset} (V)	E_{LUMO} (eV)	E_{ox}^{onset} (V)	E_{HOMO} (eV)	E_g (eV)
PBIBT1	−0.75	−.3.60	1.72	−6.05	2.45
PBIBT2	−0.90	−3.45	1.4	−5.75	2.30
PBIBT3	−0.73	−3.62	1.65	−6.0	2.38
PBIBT4	−0.73	−3.62	1.60	−5.95	2.33

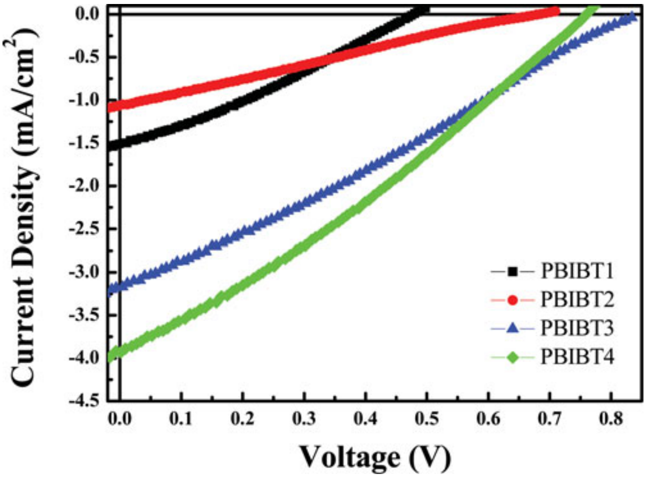


Figure 2. Current density-voltage (J-V) characteristics of polymer:PC$_{70}$BM (1:4) solar cell under AM 1.5 condition.

(J-V) characteristics of bulk heterojunction polymer solar cells with the polymers under AM 1.5G illumination (100 mWcm^{-2}). Representative characteristics of the polymer solar cells such as open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF), and power conversion efficiency (PCE) are summarized in Table 4. It was observed that increasing w/w ratios of PC$_{70}$BM from 1:1 to 1:4 in the solar cell devices with all the polymers enhance the Jsc and FF, resulting in the improved PCE values. For instance, PCE values of solar cell devices with PBIBT3 increase from 0.05% to 0.74% when w/w ratios of PC$_{70}$BM from 1:1 to 1:4. It was also found that PBIBT4 exhibits the best solar cell with V_{oc} of 0.74 V, J_{sc} of 4.03 mAcm^{-2}, and FF of 30.25%, resulting in PCE of 0.9%. However, PBIBT1 and PBIBT2 exhibited PCEs of 0.21 and 0.18%, respectively, presumably due to low J_{sc} values. The lower PCE values of PBIBT1 and PBIBT2 might be caused by larger steric hindrance

Table 4. Photovoltaic properties of the solar cell devices with PBIBT polymers

Polymer	Polymer:PC$_{70}$BM (w:w)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
PBIBT1	1:1	0.46	0.17	27.62	0.02
	1:2	0.49	1.25	24.48	0.15
	1:4	0.48	1.51	29.48	0.21
PBIBT2	1:1	0.65	0.24	22.56	0.04
	1:2	0.61	0.53	22.01	0.07
	1:4	0.68	1.06	24.68	0.18
PBIBT3	1:1	0.68	0.36	20.59	0.05
	1:2	0.82	2.02	23.80	0.40
	1:4	0.78	3.18	29.53	0.74
PBIBT4	1:1	0.79	1.91	25.32	0.38
	1:2	0.74	3.12	28.45	0.66
	1:4	0.74	4.03	30.25	0.90

of long alkyl side chain of the polymers. The long hexyloxy side chain on benzimidazole segments can hinder π-π interaction between the polymer backbones, resulting in decrease of charge carrier mobility in the polymers [9]. Moreover, the long side chain of the acceptor unit can interrupt intramolecular charge transfer between the donor unit and the acceptor unit of polymer [10]. The solar cell devices based on PBIBT4 exhibited a higher J_{sc} by 0.85 mAcm^{-2} than corresponding PBIBT3 based solar cell device. Accordingly, the solar cell efficiency was improved from 0.74% of PBIBT3 to 0.9% of PBIBT4. These results clearly indicate that the hydrogen and phenyl substituents in PBIBT4 play a key role in enhancing light harvesting property and efficient interpenetrating network for achieving high PCE values.

Conclusion

We synthesized a series of copolymers with benzodithiophene segments and benzimidazole segments using the Stille polycondensation reaction. The optical and electrochemical properties of the synthesized polymers were characterized by UV/Vis spectroscopy and CV measurements. It was found that the polymers containing benzimidazole and benzodithiophene segments exhibit low bandgaps and suitable HOMO and LUMO energy levels for photovoltaic applications. The solar cell devices with the polymers exhibited about 1% power conversion efficiency. This study implies that polymers containing electron-deficient benzimidazole segments can achieve high PCE through structural modification of the polymers.

Acknowledgments

This work was supported by the DGIST R&D Program of Ministry of Education, Science, and Technology of Korea (13-BD-0403). This research was also supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (NRF-2012R1A1A1040811).

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