Bulk Heterojunction Photovoltaic Cells with Triphenylamine-Based Amorphous Polymer and Non-Halogenated Solvent Processing Provide Reproducible Performance

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The performance of bulk heterojunction (BHJ) organic photovoltaics (OPVs) based on an amorphous polymer, poly(3HTBT-TPA), and fabricated using either halogenated or non-halogenated solvents was investigated. All the BHJ OPVs exhibited almost the same power conversion efficiencies of around 2.2%, indicating that their performance is independent of the casting solvent. These experimental results indicate that the use of amorphous π-conjugated polymers in the fabrication of BHJ OPVs offers two advantages over the use of polycrystalline π-conjugated polymers: highly reproducible OPV performance and the possibility of an environmentally friendly process for fabricating OPVs.

Keywords: bulk heterojunction, amorphous, photovoltaic, non-halogenated solvent, triphenylamine

1. Introduction

Organic photovoltaics (OPVs) offer a new source of electrical energy, in particular because of their advantages such as low fabrication cost and ease of processing on flexible substrates [1]. The most successful example is OPVs of a soluble n-type fullerene blended with π-conjugated p-type polymers to form bulk heterojunction (BHJ) cells [2–5]. BHJ OPVs have been investigated extensively in the past decade, and power conversion efficiencies (PCEs) above 10% have been reported [6,7]. A major attraction of these devices, which are processed from solution, is that their active layer can be deposited over large areas in a single step using techniques such as inkjet printing, spin-coating, and spray-coating [8,9]. However, BHJ OPVs with the best performance were often obtained using halogenated solvents such as chloroform, chlorobenzene, and 1,2-dichlorobenzene (o-DCB), the toxicity of which has potential problems for high-volume manufacturing. Thus, alternatives to halogenated solvents have been sought [10]. Although some non-halogenated binary solvents have been successfully used to obtain BHJ OPVs with PCEs equivalent to the high PCEs of those fabricated using halogenated solvents [11–14], these binary solvents require a great deal of time to optimize the fabrication conditions.

In this study, we report that non-halogenated solvents consisting of a single component can be successfully used to fabricate BHJ OPVs based on an amorphous polymer, and then we demonstrate that BHJ films spin-coated from halogenated or non-halogenated solvents exhibited almost the same PCEs of around 2.2%. BHJ films fabricated using various solvents and annealed at different temperatures were studied in detail using UV–vis spectroscopy and atomic force microscopy (AFM).
2. Experimental section

2.1. Materials and methods

An amorphous polymer, poly(3HTBT-TPA), which consists of benzothiadiazole and triarylamine units, was prepared according to methods described in the literature [15]. The chemical structure of poly(3HTBT-TPA) is shown in Fig. 1. The number-average molecular weight ($M_n$), weight-average molecular weight ($M_w$), and polydispersity ($M_w/M_n$) were estimated to be 16,400, 21,900, and 1.3, respectively. The glass transition temperature of poly(3HTBT-TPA) was 85 °C.

Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS P VP Al 4083) was purchased from Heraeus. PC 70BM (purity 99%) was purchased from Solenne. UV–vis absorption spectra were recorded on a U-3010 spectrometer (HITACHI). The thicknesses of the films were measured using an automatic microfigure measuring instrument (Surfcorder ET200, Kosaka Laboratory Ltd.). As part of the structural characterization, the surface morphologies were studied using AFM (Nanocute, SII NanoTechnology Inc.).

2.2. Fabrication and characterization of OPVs

The OPVs were fabricated in the following configuration: ITO/PEDOT:PSS/BHJ layer/LiF/Al. Patterned indium tin oxide (ITO, conductivity: 10 $\Omega$/square) glass was precleaned in an ultrasonic bath of acetone and ethanol and then treated in an ultraviolet/ozone chamber. A thin layer (40 nm) of PEDOT:PSS was spin-coated at 3000 rpm and subsequently dried at 110 °C for 10 min on a hot plate under air. The substrates were transferred to a N$_2$ glove box and then dried again at 110 °C for 10 min on a hot plate. A solution of poly(3HTBT-TPA):PC$_{70}$BM (1:4, weight ratio) blend was subsequently spin-coated onto the PEDOT:PSS surface, forming a BHJ layer. This weight ratio of 1:4 is the optimum weight ratio for high performance, as reported in our previous paper [15]. The solvents used in this study were o-DCB, 1,2,4-trimethylbenzene (TMB), and 1,2-dimethylbenzene (o-xylene). The substrates with the active layers were dried in the N$_2$ glove box for 10 min at 110 °C for the films spin-coated from o-DCB, TMB, and o-xylene, and at 60 °C for the film spin-coated from o-xylene. Finally, LiF (1 nm) and Al (80 nm) were deposited on the active layer by conventional thermal evaporation at a chamber pressure lower than 5 × 10$^{-4}$ Pa, which provided devices with an active area of 2 × 2 mm$^2$. The current density–voltage ($J$–$V$) curves were measured using an ADCMT 6244 DC Voltage Current Source/Monitor under simulated AM 1.5G solar light irradiation at 100 mW cm$^{-2}$ (OTENTO-SUN III, Bunkoh-Keiki Co., Ltd.). The incident-photon-to-current conversion efficiency (IPCE) spectra were measured using an SM-250 system (Bunkoh-Keiki Co., Ltd.).

3. Results and discussion

3.1. Thin-film properties of poly(3HTBT-TPA):PC$_{70}$BM blends

The optical absorption spectra of poly(3HTBT-TPA):PC$_{70}$BM (1:4) films are shown in Fig. 2. The absorption spectra were normalized at 475 nm and exhibit nearly identical characteristics, indicating the independence of the optical absorption spectra from the casting solvent and thermal annealing temperature. AFM images of the poly(3HTBT-TPA):PC$_{70}$BM films show that the surfaces of the BHJ layers are very similar and flat, as shown in Fig. 3(a)–(d), and the root-mean-square (rms) surface roughnesses are found to be between 0.18 and 0.24 nm. The lack of absorption changes and
the homogeneous surfaces observed for all the poly(3HTBT-TPA):PC$_{70}$BM films fabricated under completely different conditions indicate that poly(3HTBT-TPA) and PC$_{70}$BM are homogenously intermixed and that the polymer exhibits low electronic coupling between neighboring polymer chains owing to the amorphous nature of poly(3HTBT-TPA).

3.2. Photovoltaic properties of poly(3HTBT-TPA):PC$_{70}$BM blends

Figure 4(a) shows the $J$–$V$ curves of OPVs based on films of poly(3HTBT-TPA):PC$_{70}$BM blends with thicknesses of about 100 nm fabricated using different organic solvents and thermal annealing temperatures. Their shapes (PCEs) are almost the same. Table 1 lists the average device characteristics, including the short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$), fill factor (FF), and PCE under illumination with AM 1.5G at 100 mW cm$^{-2}$. The OPV that was fabricated using a typical halogenated solvent, $o$-DCB (boiling point of 181 °C), and annealed at 110 °C for 10 min exhibited a $J_{sc}$ of 6.31 mA cm$^{-2}$, a $V_{oc}$ of 0.85 V, an FF of 0.40, and a PCE of 2.15%. Moreover, the OPV fabricated using a non-halogenated solvent, $o$-xylene, with the different boiling point (144 °C), and annealed at 110 °C for 10 min exhibited a PCE of 2.39%. The IPCE spectra in Fig. 4(b) also show almost the same shapes and values for all the BHJ OPVs fabricated under completely different conditions.

Generally, the BHJ OPV characteristics of typical $\pi$-conjugated polymers such as MDMO-PPV, P3HT, and PTB7 spin-coated from non-halogenated solvents were reportedly inferior to those of polymers from halogenated solvents [14,16,17]. For example, Park et al. reported that P3HT-based BHJ OPVs with PCEs of 1.53% and

![Fig. 3. AFM images (5 x 5 $\mu$m$^2$) of poly(3HTBT-TPA):PC$_{70}$BM (1:4) films fabricated by spin-coating with (a) o-DCB (annealed at 110 °C), (b) TMB (annealed at 110 °C), (c) o-xylene (annealed at 110 °C), and (d) o-xylene (annealed at 60 °C). The rms surface roughnesses were 0.18, 0.18, 0.18, and 0.24 nm, respectively.

![Fig. 4. (a) J–V curves and (b) IPCE curves of BHJ OPVs based on poly(3HTBT-TPA):PC$_{70}$BM (1:4) films fabricated by spin-coating from various organic solvents. Numbers in parentheses indicate temperatures used for 10-min annealing.](375)
3.92% were fabricated by spin-coating from the non-halogenated solvent 1,3,5-trimethylbenzene (mesitylene: MS) and the halogenated solvent o-DCB, respectively [14]. Although the PCEs of poly(3HTBT-TPA)-based OPVs fabricated using non-halogenated solvents were lower than those of P3HT-based OPVs fabricated using the typical halogenated solvent o-DCB [18,19], the use of amorphous polymers in BHJ OPVs offers two advantages over the use of polycrystalline polymers films: highly reproducible BHJ OPV performance and the possibility of an environmentally friendly process for fabricating BHJ OPVs.

4. Conclusion

We reported the performance of BHJ OPVs based on amorphous poly(3HTBT-TPA) films fabricated using o-DCB or the non-halogenated solvents TMB and o-xylene. All the BHJ OPVs exhibited almost the same PCEs (around 2.2%) and IPCEs, indicating that their performance was independent of the casting solvent. Although the PCEs of the poly(3HTBT-TPA)-based OPVs were lower than those of P3HT-based OPVs fabricated under optimized conditions, the use of an amorphous film in the fabrication of OPVs offers two advantages over the use of a polycrystalline film: highly reproducible BHJ OPV performance and the possibility of an environmentally friendly process for fabricating BHJ OPVs.

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