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Morphology and properties of poly(2-methoxy-5-(2'-ethyl-hexyloxy)p-phenylenevinylene) (MEH-PPV): *N,N'-*bis(1-ethylpropyl)-3,4:9,10-perylene bis(tetracarboxyl diimide) (EP-PTC) based solar cells

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ABSTRACT

The influence of two components blend ratio, solution concentration and thermal annealing on the morphology of poly(2-methoxy-5-(2'-ethyl-hexyloxy)-p-phenylenevinylene) (MEH-PPV): N,N'-bis(1-ethylpropyl)-3,4:9,10-perylene bis(tetracarboxyl diimide) (EP-PTC) blend films spin-cast from chloroform solutions has been studied using atomic force microscopy (AFM). The AFM images show that the dimension of the phase separation increases with the EP-PTC content and total solution concentration. When the annealing temperature increases from 90 to 150 \degree C, the EP-PTC crystal-like clusters grow rapidly. Solar cells based on MEH-PPV:EP-PTC blend films with different weight ratios were fabricated. The device with 1:3 weight ratio has a higher power conversion efficiency (PCE) of 0.072% compared with the devices with 1:1, 1:2 and 1:4 ratio, which increases by about 14 times over that of the device with 1:1 ratio that has a PCE of 0.005%. It is indicated that the optimum performance of the photovoltaic device is strongly related to the finer phase separation between MEH-PPV and EP-PTC on a submicron scale which enables an efficient dissociation of photogenerated excitons, and the pure EP-PTC phase can build up a percolating network with pathways large enough to enhance electron transport.

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1. Introduction

Thin-film organic photovoltaic devices (PVDs) have been extensively studied because of their motivation for developing inexpensive, efficient and renewable energy sources. In the last few years, increasing efforts have been made to develop PVDs based on mixture of organic molecules and conjugated polymers [\[1–5\].](#page--1-0) The main progress to improve the power conversion efficiency (PCE) of organic PVDs is to construct bulk heterojunction structural photoactive layer which consists of a blend of a donor (p-type) and an acceptor (n-type). The donor material can be conjugated polymer, such as poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV), poly(3-hexylthiophene) (P3HT), poly(2 methoxy-5-(2'-ethyl-hexyloxy)-p-phenylene-vinylene) (MEH-PPV), etc. and the acceptor material can be electron withdrawing molecule, such as fullerene (C_{60}) and its derivative [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM), perylene diimide (PDI) and its derivative N,N'-bis(1-ethylpropyl)-3,4:9,10-perylene bis(tetracarboxyl diimide) (EP-PTC), etc.

Recently, the PCE as high as 2.5–5.1% has been reported for polymer PVDs based on conjugated polymer and PCBM blend film [\[6–8\]](#page--1-0) which forms bulk heterojunction structure. The main characteristic of a bulk heterojunction is that the photoactive interface area between the donor and acceptor is large enough to enable a high efficient charge transfer and charge separation. The bulk heterojunction can form a bicontinuous and interpenetrating network between the donor and the acceptor, which is favorable for holes in the donor phase and electrons in the acceptor phase to transport to the opposite contact electrode. Thus, for bulk heterojunction devices, the morphology of the blend film is a crucial factor in acquiring high PCE. It has been established that both the processing conditions of the film formation such as the blend ratio between the two components, the solution concentration, etc. and the treatments afterwards such as thermal annealing, etc. can influence the morphology and phase separation of the blend film, and further the performance of the devices [\[9\]](#page--1-0).

Perylene diimide (PDI) has attracted much interest and been widely investigated because of its unique merits such as thermal stability, inexpensiveness, and especially its large molar absorption coefficient, good electron accepting property and ability to form crystals within the polymer matrix [\[10–12\].](#page--1-0) Recently, much work about polymer:PDI bulk heterojunction photovoltaic devices using PDIs as the acceptor has been accomplished [\[13,14\]](#page--1-0), but most of those work mainly refers to the effects of the material chemical structure on the photovoltaic performance. Moreover, the interplay among film processing conditions, post-treatments,

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morphology and photovoltaic performance for polymer/fullerene blends has been studied extensively [\[11,15,16\]](#page--1-0), however, for the conjugated polymer/PDI system, no much work has been reported.

In our previous work, we investigated the effect of annealing time on the photocurrent generation of solar cell based on MEH-PPV:EP-PTC blend film [\[17\]](#page--1-0). In this paper, we studied the influence of more factors including two components blend ratio, total solution concentration and thermal annealing temperature on the morphology of the MEH-PPV (Fig. 1a):EP-PTC (Fig. 1b) blend films more systematically by atomic force microscopy (AFM). It has been found that the scale of phase separation strongly depends on the blend ratio of MEH-PPV:EP-PTC and the total solution concentration. The crystal-like clusters grow rapidly as annealing temperature increases. Solar cells based on MEH-PPV:EP-PTC blend films

Fig. 1. Chemical structure of poly(2-methoxy-5-(2-ethyl-hexyloxy)-p-phenylene vinylene) (MEH-PPV) (a) and N,N-bis(1-ethylpropyl)-3,4:9,10-perylene bis(tetracarboxyl diimide) (EP-PTC) (b).

with different weight ratios (1:1, 1:2, 1:3 and 1:4) were fabricated. The device with 1:3 blend ratio has the highest PCE of 0.072% under the white light illumination with an intensity of 100 mW/cm², which is almost 14 times as high as that of the device with 1:1 blend ratio that has a PCE of 0.005%. The optimum performance of the photovoltaic device is related to the finer phase separation between MEH-PPV and EP-PTC on a submicron scale which enables an efficient dissociation of photogenerated excitons, and the pure EP-PTC phase can build up a percolating network with pathways large enough to enhance electron transport.

2. Experimental

MEH-PPV and EP-PTC were synthesized according to the litera-ture [\[18,19\].](#page--1-0) The M_w of the MEH-PPV is 653,200 g/mol and its polydispersity index is 3.3. The values of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of MEH-PPV are 5.05 and 2.80 eV, and for EP-PTC they are 5.95 and 3.66 eV, respectively. Because we mainly focus on the influence of the film processing conditions on the film morphology and the relationship between the morphology of MEH-PPV:EP-PTC blend film and the properties of the PVD based on this film, we used chloroform as the solvent (rather than chlorobenzene or o-dichlorobenzene, which are commonly used) due to the more obvious phase separation of the blend film from chloroform solution than from chlorobenzene or o-dichlorobenzene solution. The chloroform was distilled after dehydration using conventional method. The morphology of the blend films was investigated by the Nanoscope III AFM with the tapping mode (TM).

Fig. 2. AFM images of MEH-PPV:EP-PTC blend films with weight ratio of 1:1 (a), 1:2 (b), 1:3 (c), and 1:4 (d) spin-cast from chloroform solution. For 1:1 ratio, the film surface looks flat and shows no features, and increasing the content of EP-PTC it gives rise to obvious phase separation. Scan size is 5 μ m \times 5 μ m.

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