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Block copolymer compatibilized polymer: fullerene blend morphology and properties

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ABSTRACT

Recent studies have shown the role of block copolymer as compatibilizer in tuning the phase separated morphology of the active layer so as to improve the overall photovoltaic efficiency of organic photovoltaic (OPV) devices. Here, we substantiate this observation by investigating the role of a rod-coil block copolymer poly-(3-hexylthiophene)-b-polystyrene (P3HT-b-PS) as compatibilizer in influencing the blend morphology and device performance of several polymer:fullerene blend systems. Fullerene derivatives *N-(3-methoxypropyl)-2-(carboxyethyl)-5-(4-cyanophenyl) fulleropyrrolidine* (NCPF) and *N-(3-methoxypropyl)-2-(carboxyethyl)-5-(5, 5-difluorobenzo-dioxole) fulleropyrrolidine* (FFNCPF) were synthesized using Prato reaction, while P3HT-b-PS copolymer was synthesized using the combination of Grignard metathesis, ATRP, and click chemistry. The addition of P3HT-b-PS in P3HT:PCBM blend led to the formation of more homogenous structure compared to the pure P3HT:PCBM blend. Also, a reduction in domain size was observed in P3HT: FFNCPF system upon P3HT-b-PS addition which can be attributed to the compatibilization effect of BCP. Incorporation of P3HT-b-PS block copolymer was found to effectively alter the thin film nanostructure of polymer/fullerene derivative blends and polymer crystalline structure. Maximum enhancement in power conversion efficiency (PCE) of compatabilized P3HT:PCBM blend system was noticed followed by P3HT:FFNCPF and P3HT:NCPF. The moderate improvement in photovoltaic properties can be correlated with face-on orientation of P3HT crystallites and the segregation of the fullerene domains at the bulk heterojunction (BHJ) cathode interface which facilitates the efficient charge collection as respective electrodes.

1. Introduction

Organic solar cells based on polymer/fullerene bulk heterojunction (BHJ) morphologies constitute an emerging approach to a low cost, solution processable, and highly scalable renewable energy avenue. Yet, one of the major challenges limiting the broad applicability of these solar cells is their lower device efficiencies relative to their inorganic counterparts. In this regard, several studies have shown that organic photovoltaic (OPV) device performance can be optimized by tuning donor/acceptor blend morphology [1–4]. The active layer of polymer/fullerene solar cells (BHJ layer) consist of interpenetrating network of electron donor polymer (e.g. poly(3-hexylthiophene), P3HT) and electron acceptor fullerene derivatives (e.g. 6,6-phenyl C61-butyric acid methyl ester, PCBM). Typically, the phase domain size of BHJ components should be within the range of exciton diffusion length of 10–20 nm for efficient exciton diffusion and charge dissociation as well as improved device efficiencies. The phase separation of the blend films is typically influenced by thermodynamics and kinetic effects, leading to poly-dispersed domain sizes on the order of nanometers to tens of nanometers or greater.

Previously, a number of methods have been studied to tune the BHJ morphology including thermal annealing [4,5], solvent vapor annealing [6,7], external electric fields [8], and use of processing additives [9–12]. However, these approaches have shortcomings. Especially, the approach based on use of processing additive can provide only short term morphological stability because upon aging the volatile additives evaporate and the interfacial area reduces. The reduction in interfacial area results in deactivation of generated excitons and suppression of the charge separated moieties. More recently, the addition of non-volatile compatibilizers to provide

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long term morphological stability of blends has been studied. In this context, inclusion of processing aids such as block copolymer additives has been considered to control the evolution of the thin film nanostructure during processing. Block copolymers (BCPs) are considered as promising candidates to control nanoscale morphology due to their ability to phase separate into periodic domain structures in the range of 5 nm–100 nm [13,14], which is comparable to the exciton diffusion length. Indeed, by rationally selecting the block ratio, molecular weight, and interactions of each block of the BCP with the constituents of the host matrix, many studies [15–17] have demonstrated that significant control can be exercised on domain sizes and morphologies of polymer blend systems.

Generally, BCPs act by mitigating the interfacial energy barrier between blend components and thereby suppresses the particle aggregation, giving rise to improved interpenetrating network, controlled domain size, and long term morphological stability [18,19]. Yang and coworkers [20] have synthesized a rod-coil diblock copolymer with P3HT as one block and C_{60} chromophores as the other block and showed that performance can be significantly improved by adding diblock copolymer into P3HT:PCBM blend. It has also been reported that controllable domain sizes can be achieved via adding P3HT-PEO into P3HT:PCBM blends [21]. They noticed that donor/acceptor domain sizes decreased with the increasing amount of copolymer compatibilizer addition upon thermal treatment. Sun et al. [22] demonstrated that incorporation of the P3HT-b-PS in P3HT:PCBM blend induced desirable interpenetrating nano-morphology and favorable vertical distribution of P3HT and PCBM in blend due to enthalpic contribution from the interactions between PS and PCBM. To date, BCP compatibilizing effect has been exhaustively demonstrated only on P3HT:PCBM model system therefore there is knowledge gap in generalizing the effect of BCP addition on other polymer/fullerene blend systems. To address that, we made an attempt to investigate the BCP compatibilizing effect on different polymer/fullerene blend systems and compared the observations to the conventional P3HT:PCBM model system.

In this work, we report the synthesis and characterization of novel fullerene derivative (FFNCPF), P3HT-b-PS BCP and the role of P3HT-b-PS BCP addition on the morphology of different polymer:fullerene blend systems and on the corresponding device performance. The synthesized fullerene derivative *N-(3-methoxypropyl)-2-(carboxyethyl) -5-(5,5-difluorobenzo-dioxole) fulleropyrrolidine* (FFNCPF) was characterized for its optical, thermal, and electronic properties. AFM and GIWAXS were used to characterize the morphology of P3HT-b-PS block copolymer compatabilized blend systems and results were compared with pure blend system. The addition of BCP to blend was found to effectively alter the thin film nanostructure and polymer crystalline structure. In the ternary blend of polymer:fullerene/BCP, a more homogeneous structure of blend components was noticed and a more favorable domain size was achieved. GIWAXS results show that there was an enhancement in polymer order and degree of crystallinity within P3HT phase in P3HT:NCPF and P3HT:FFNCPF systems while face-on orientation of P3HT π-π stacking was found to be increased in P3HT:PCBM system upon BCP addition. Furthermore, XPS results show evidence of change in surface compositions of P3HT/PCBM system upon BCP addition. The moderate improvement in device performance of BCP compatibilized P3HT:PCBM blend can be largely attributed to the increased population of face-on oriented P3HT crystallites and the favorable distribution of blend components, while a marginal improvement in device performance of BCP compatibilized P3HT:NCPF and P3HT:FFNCPF blend systems can be a result of a reduction in domain size.

2. Experimental section

2.1. Materials

3-methoxypropylamine, ethyl bromoacetate, triethylamine, benzene, DMF, and toluene were purchased from Alfa Aesar. 2,2-difluoro-5-formylbenzodioxole, C60 (99.5%), sodium azide, copper bromide, *N*, *N*, *N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) dichloro [1,3-bis(diphenylphosphino)propane]nickel,tert-butylmagnesiumchloride, ethynylmagnesium chloride, and 1, 2-dichlorobenzene (ODCB, anhydrous, 99%) were purchased from Sigma-Aldrich and used as received. Poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Al 4083) was purchased from Clevios. P3HT (average molecular weight between 50 and 70 kg/mol) was obtained from Rieke Metals and PCBM was obtained from NanoC and used as received. For column chromatography, silica gel (particle size 70-230 mesh) was purchased from Alfa Aesar. Hexane, THF, chloroform, and methanol were purchased from Fisher Scientific.

2.2. Instrumentation

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 spectrometer for ^{1}H NMR (400 MHz) and for ^{13}C NMR (100 MHz). Chemical shifts are given in parts per million (d) relative to tetramethylsilane (TMS). For ^{1}H NMR and ^{13}C NMR spectra, peaks are calibrated to 7.26 ppm and 77.16 ppm, respectively. The UV–visible absorption spectra (both in solution and films) were recorded using a HP 8453 spectrometer, and the Fourier-transform infrared (FTIR) spectra were obtained with a Perkin Elmer FTIR 100 Plus spectrometer.

2.3. Synthesis of N-(3-methoxypropyl)-2-(carboxyethyl)-5-(5,5-difluorobenzodioxole) fulleropyrrolidine (FFNCPF)

A mixture of ethyl N-3-methoxypropylglycinate [23] (0.035 g, 0.2 mmol), fullerene (C_{60}) (0.070 g, 0.1 mmol), and 2,2-difluoro-5-formylbenzodioxole (0.093 g, 0.5 mmol) was dissolved in toluene. The mixture was refluxed for 6 h at 110 °C. The reaction progress was monitored by thin layer chromatography (TLC). After completion of reaction, the reaction mixture was allowed to cool to room temperature and the solvent was vacuum-evaporated. The crude mixture was purified by column chromatography using toluene as eluent. A purple color band of unreacted C_{60} eluted initially from the column, followed by the elution of the desired brown color band of product. Solvent was removed from brown color product using rotary evaporator, and the desired product was collected and further dried in vacuum oven for 6 h to yield a brown solid powder.Yield: 48%, Rf value (0.28 in toluene). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.58 (broad peak, 2H), 7.08 (s, 1H), 6.47 (s, 1H), 5.77 (s, 1H), 4.38–4.47 (m, 2H), 3.77 (d, 2H), 3.48 (s, 3H), 3.27 (d, 1H), 3.05 (s, 1H), 2.19 (broad peak, 2H), 1.34 (t, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 171.11, 155.69, 153.28, 153.23, 150.67, 147.51, 147.38, 146.49, 146.43, 146.41, 146.39, 146.33, 146.23, 146.19, 146.16, 146.03, 146.0, 145.63, 145.58, 145.51, 145.48, 145.39, 145.37, 145.32, 145.30, 145.18, 145.16, 143.66, 143.21, 143.11, 143.05, 142.79, 142.66, 142.62, 142.22, 142.20, 142.18, 142.14, 142.11, 142.06, 142.03, 141.98, 141.82, 141.77, 141.71, 141.66, 140.18, 140.17, 139.69, 139.67, 137.58, 136.35, 136.06, 136.02, 133.91, 75.47, 73.27, 70.66, 70.04, 61.32, 58.74, 44.38, 28.32, 14.43.). FT-IR (cm^{-1}): 2925, 2855, 2189, 1733 (-COO stretch), 1619, 1492 (C60 stretch), 1235, 1150. UV–Vis (Toluene): 314 nm, 328 nm, 432 nm. Detail synthesis and characterization of another fullerene derivative (NCPF) can be found elsewhere [27].