Annealing effects on the photovoltaic performance of all-conjugated poly(3-alkylthiophene) diblock copolymer-based bulk heterojunction solar cells†

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The effects of thermal and solvent vapor annealing on the photovoltaic performance of a new class of all-conjugated poly(3-butylthiophene)-b-poly(3-hexylthiophene) diblock copolymer/PC71BM bulk heterojunction (BHJ) solar cells were scrutinized and theoretically analyzed using the single diode model combined with experimental measurements. The meanings of physical parameters in the model were elucidated in the context of crystalline order and phase separation to gain fundamental insight into the mechanism of annealing effects on the device performance of a new class of all-conjugated diblock copolymer-based BHJ solar cells.

Introduction

The performance of polymer bulk heterojunction (BHJ) solar cells has been significantly improved over the past decade. Recently, considerable efforts have centered on understanding the photovoltaic mechanism that underpins these enhanced power conversion efficiencies (PCEs).1–6 One of the most widely studied polymer BHJ solar cells utilizes poly(3-hexylthiophene) (P3HT) as the electron donor and fullerene derivative (i.e., [6,6]-phenyl-C61-butyric acid ethyl ester (PCBM)) as the electron acceptor. Reproducible, high efficiency (PCE = 3–5%) can be readily achieved by performing various post treatments on these devices, including the application of thermal annealing7,8 and solvent vapor annealing,9,10 the use of solvent additives,11 etc. It has been widely recognized that annealing, including both thermal and solvent vapor annealing, are of critical importance in optimizing the film morphology of the P3HT:PCBM blend by facilitating the nanoscale phase separation of P3HT and PCBM (i.e., producing small-sized domains that are comparable to or less than the exciton diffusion length of conjugated polymers (~10 nm) and a large interface between P3HT and PCBM) for efficient exciton dissociation and charge generation, and yielding the molecular packing of P3HT chains within the photoactive layer to form percolation networks for efficient charge transport and collection without significant recombination loss.3,12

It is noteworthy that the solubility of poly(3-alkylthiophene) (P3AT) homopolymers is dictated by the length of alkyl side chains, which exerts a profound influence on the phase separation and interfacial interaction between P3ATs and PCBM during the annealing process.13 Recently, better optimized polymer BHJ nanostructures in a new class of all-conjugated poly(3-butylthiophene)-b-poly(3-hexylthiophene) diblock copolymer (P3BHT)-based devices were reported,14 where the solubility can be readily tuned by adjusting the molar ratio of P3BT to P3HT blocks, leading to markedly improved photovoltaic performance of P3BHT/[6,6]-phenyl-C71-butyric acid ethyl ester (PC71BM) solar cells. A comprehensive study on the effect of changes in the ratio of butyl to hexyl side chains in P3BHT on the blend film morphology and the resulting device performance was performed. The study revealed that the P3BHT diblock copolymer at the P3BT: P3HT = 2:1 molar ratio, denoted P3BHT21, which exhibited an improved performance over the P3HT/PC71BM solar cell prepared under the same conditions, was able to accomplish a better balance between the chain flexibility that rendered effective exciton dissociation and charge generation (i.e. forming fine phase separation on the 10-nm scale) and the crystallization of P3BHT21 chains that facilitated efficient charge transport and collection.14,15

Herein, using the single diode model,4 we scrutinized and theoretically analyzed the effects of thermal annealing and solvent vapor annealing on the photovoltaic performance of all-conjugated P3BHT21 diblock copolymers blended with PC71BM. The meanings of physical parameters yielded from the fitting of the electrically equivalent single diode model were elucidated in the context of phase separation and crystallization to gain fundamental insight into the possible photophysical
mechanisms responsible for the varied performances, which were further verified experimentally by the X-ray diffraction, UV-Vis absorption and AFM measurements.

**Experimental**

Photovoltaic devices with the configuration of ITO/poly(3,4-ethylendioxythiophene): poly(styrenesulfonate) (PEDOT:PSS)/P3BHT21:PC71BM/Ca/Al were fabricated at the P3BHT:PC71BM = 1:0.75 wt/wt (Fig. 1 and See Experimental in Supporting Information). The thickness of PEDOT:PSS, P3BHT21:PC71BM, Ca, and Al layers are approximately 40 nm, 200 nm, 50 nm, and 100 nm, respectively. Typically, the device area was 0.10 ± 0.01 cm². In the present study, a series of devices without annealing treatment (i.e., pristine sample), with thermal annealing at 140 °C for 20 min, and with CHCl3 vapor annealing for 12 h, respectively, were evaluated under a simulated AM 1.5 G irradiation (100 mW cm⁻², calibrated with Daystar Meter).

Fig. 2 shows the current-density-voltage (J–V) characteristics of devices. The photovoltaic performances were summarized in Table 1. A remarkable increase in J_sc and FF emerged upon thermal annealing (red circles), compared with the pristine device without annealing (black squares). The maximum PCE of 3.81% was obtained in the thermally annealed device with V_oc of 0.65 V, J_sc of 9.56 mA cm⁻² and FF of 61.7%. The higher FF suggested that thermal annealing promoted the blend film to achieve improved BHJ nanostructures with well-defined demixing of two components and extended percolation networks for each component.16,17 Quite intriguingly, compared the performance of solvent vapor annealed device (blue triangles) with pristine (black squares) and thermally annealed devices (red circles), a strong increase of J_sc from 8.29 mA cm⁻² to 10.9 mA cm⁻² with a decrease of V_oc from 0.63 V to 0.53 V after annealed with CHCl3 vapor for 12 h was observed. The highest J_sc obtained after solvent vapor annealing could be primarily related to an increased crystallinity of P3BHT21 in the blend film (Fig. 3a).

The XRD profiles of P3BHT21 in the blend films before and after thermal annealing exhibited a distinct single [100] peak at 2θ = 6.5°, corresponding to the d-spacing of 13.2 Å, which indicated that the P3BT and P3HT blocks co-crystallized into a lamellar packing with the interdigitation of butyl and hexyl side chains one another,18 adopting the edge-on orientation with the thienyl backbone aligned parallel to the substrate (inset in Fig. 3a).19 A slight peak shift from 2θ = 6.5° to 6.3° was observed in the blend film after CHCl3 vapor annealing, corresponding to a slightly increased d-spacing of 13.8 Å. This demonstrated that the molecular packing of P3BHT21 was not significantly affected by the thermal annealing, but the inter-chain distance of alkyl side chains along [100] axis could be enlarged by the solvent vapor annealing. Considering the thicknesses of all blend films were approximately 200 nm, the intensity of the [100] peak in Fig. 3a was nearly proportional to the size or the number of polymer crystals per unit volume in the blend films,20 and the highest crystallinity of P3BHT21 in the blend film with CHCl3 vapor treatment was responsible to the largest J_sc observed in the vapor-annealed devices (Table 1).21 Despite the increased J_sc, however, a decreased V_oc with the CHCl3 vapor treatment was seen and needed to be addressed.

To explore the origin of the reduced V_oc, the J–V characteristics of devices (Table 1) were fitted with the electrically equivalent single diode model (inset in Fig. 2), which consists of a diode (with reverse saturation current, I_D, and ideality factor, n) and photogenerated current, I_ph representing an ideal photovoltaic device. Considering no device can actually reach the ideal
Table 2 Summary of photovoltaic parameters of the single diode model extracted from the J–V characteristics of P3BHT21/PC71BM solar cells without annealing treatment, with thermal annealing at 140 °C for 20 min, and with chloroform vapor annealing for 12 h, respectively

<table>
<thead>
<tr>
<th>P3BHT21/PC71BM</th>
<th>J_L (mA cm⁻²)</th>
<th>J_D (mA cm⁻²)</th>
<th>n</th>
<th>r_s (Ω cm²)</th>
<th>r_sh (Ω cm²)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine sample</td>
<td>8.47</td>
<td>0.032</td>
<td>4.32</td>
<td>3.10</td>
<td>1.38 × 10⁴</td>
<td>2.83</td>
</tr>
<tr>
<td>Thermally annealed</td>
<td>9.91</td>
<td>0.021</td>
<td>4.06</td>
<td>1.49</td>
<td>1.41 × 10⁴</td>
<td>3.81</td>
</tr>
<tr>
<td>CHCl₃ vapor annealed</td>
<td>11.2</td>
<td>0.049</td>
<td>3.74</td>
<td>1.83</td>
<td>6.4 × 10⁴</td>
<td>3.25</td>
</tr>
</tbody>
</table>
electron and hole transports became unbalanced. Therefore, a higher degree of charge recombination occurred in the blend film (i.e., increased interfacial charge leakage), representing a large \( J_{sc} \) and thus decreased \( V_{oc} \).

To confirm the analysis as noted above, AFM measurements on the blend films were performed by examining the film morphology and structural order in the BHJ solar cells before and after annealing (Fig. 4). It is clearly evident that all blend films revealed nanoscale phase separation composed of grain-like P3BHT21 crystalline domains. Compared to the pristine sample (inset in Fig. 4a), the crystalline P3BHT21 domains were denser and the domain size became smaller after thermal annealing (i.e., a finer scale of phase separation; inset in Fig. 4b), which can be attributed to the higher ordered molecular packing of P3BHT21 chains. Quantitatively, the average size of P3BHT21 crystalline domains decreased from 12.8 nm without annealing to 10.9 nm with thermal annealing in the blend film, calculated from the full width at half-maximum (FWHM) of the diffraction peaks in Fig. 3a. Moreover, much more crystalline domains emerged in the CHCl3 vapor annealed blend film (inset in Fig. 4c), correlating very well with the increased XRD peak (Fig. 3a) and enhanced optical absorption observed (Fig. 3b). We note that no dewetting or defects were observed in the blend film after solvent annealing (Fig. 4c and Figure S1 in Supporting Information).

However, the crystalline domain size of P3BHT21 in the vapor-treated film appeared to grow larger (inset in Fig. 4c), from 12.8 nm without annealing to 18.8 nm with vapor annealing in the blend based on the FWHM calculations, which may result in poor phase separation (i.e., a large-scale demixing) and increased charge recombination (i.e., increased \( J_{sc} \); Table 2). As a result, it can be concluded that CHCl3 vapor greatly promotes the crystallization of P3BHT21 chains, leading to increased optical absorption (blue curve in Fig. 3b) with improved \( J_{sc} \), and, conversely, the increased P3BHT21 crystalline domain size would suppress the diffusion of PC71BM molecules in the blend film to form nanoscale phase separation with P3BHT21 crystalline domains, limit the formation of the PC71BM network, and perturb the balance of electron and hole transport (i.e., faster hole transport through the P3BHT21 phase due to the large-size crystalline P3BHT as compared to slower electron transport through the PC71BM phase due to constrained formation of percolation network), thereby resulting in increased reverse saturation current, \( J_{sc} \), and thus reduced \( V_{oc} \). The surface roughness of active layer (i.e., the active layer/cathode interface) may also be affected by different annealing treatments, resulting in a crucial influence on the PCE. The AFM height images of the P3BHT21/PC71BM blend films before and after annealing treatments are shown in Figure S1 (See Supporting Information).

It is clear that thermal annealing slightly smoothed the surface of P3BHT21/PC71BM blend film, while solvent annealing made the surface rougher. The rougher surface after solvent annealing may originate from the formation of enhanced ordering of polymer structures (i.e., enhanced crystallinity of P3BHT21). In conclusion, the effects of thermal annealing and solvent vapor annealing on the performance of P3BHT21/PC71BM BHJ solar cells were theoretically analyzed by the single diode model and experimentally explored by X-ray diffraction, UV-Vis absorption and AFM studies. Thermal annealing achieved a better balance between increased ordered packing of P3BHT21 chains and finer nanoscale phase separation in the P3BHT21/PC71BM blend film. In the case of CHCl3 vapor annealing, although the treatment further improved the crystallization of P3BHT21 chains as compared to thermal annealing, larger crystalline P3BHT21 domains suppressed the dispersion of PC71BM molecules in the blend film, resulting in unbalanced respective electron and hole transports and thus increased charge recombination. The present integrated study via experimental measurements and theoretical modeling may provide much physical insight into the mechanism responsible for charge generation and transport in the polymer BHJ solar cells. The single diode model demonstrated in this work can be implemented to guide the optimization of processing parameters for fabrication of high-efficiency photovoltaic devices.
Acknowledgements

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Notes and references

14 M. He, W. Han, J. Ge, Y. Yang, F. Qiu and Z. Lin, Energy Environ. Sci., 2011, DOI: 10.1039/c1ee01590e.