

# Enhancing Power Conversion Efficiency of P3HT/PCBM Polymer Solar Cells

Nidal H. Abu-Zahra, Mahmoud Algazzar

**Abstract**—In this research, n-dodecylthiol was added to P3HT/PC70BM polymer solar cells to improve the crystallinity of P3HT and enhance the phase separation of P3HT/PC70BM. The improved crystallinity of P3HT:PC70BM doped with 0-5% by volume of n-dodecylthiol resulted in improving the power conversion efficiency of polymer solar cells by 33%. In addition, thermal annealing of the P3HT/PC70MB/n-dodecylthiol compound showed further improvement in crystallinity with n-dodecylthiol concentration up to 2%. The highest power conversion efficiency of 3.21% was achieved with polymer crystallites size L of 11.2nm, after annealing at 150°C for 30 minutes under a vacuum atmosphere. The smaller crystallite size suggests a shorter path of the charge carriers between P3HT backbones, which could be beneficial to getting a higher short circuit current in the devices made with the additive.

**Keywords**—n-dodecylthiol, Congugated PSC, P3HT/PCBM, Polymer Solar Cells.

## I. INTRODUCTION

**B**ULK-heterojunction (BHJ) based organic solar cells with composites made of a conjugated polymer and fullerene derivative active layer, possess substantial potential for renewable energy resources due to their low-cost, light-weight and flexible large-area applications [1]-[5]. Blends of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) are widely used as an active layer and have a power conversion efficiency (PCE) of up to 5% due to their thermal stability [6] and high electron mobility [7], [8]. They can also be fabricated on a large area substrate using a roll-to-roll (R2R) solution process because of their high solubility in organic solvents [9], [10]. During the past few years, researchers have been focusing their efforts on the processing and development of solar cells based on conjugated polymers. The most important step towards processing efficient polymer solar cells (PSCs) is the development of bulk-heterojunction, in which the photoactive layer consisting of blends of electron-donating material and electron-accepting material forms nanomaterial with a relatively large donor/accepter interface [11].

Using bulk-heterojunction structure, several research groups independently reported new records of efficiencies for polymer solar cells, approaching the efficiency barrier of 5%

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under AM1.5 (AM = air mass) irradiation [12], [13]. So far, one of the most effective PSC systems is the blend of regioregular poly(3-hexylthiophene) (rrP3HT) with fullerene derivative [6,6]-phenyl-C61-butyric acid methyl ester (C61-PCBM). Many researchers have demonstrated that an optimum morphology of P3HT/PCBM film in PSCs is crucial for high efficiency performance [14], [15]. The optimum morphology contains two major factors: the first factor is the molecular ordering within the donor or acceptor phase, which affects photon absorption and carrier mobility. The second is the scale of phase separation between the donor and acceptor, which has a direct influence on exciton dissociation and charge transport and/or collection [16]-[17].

Since the first report on additives used to improve the performance of polymer solar cell devices by Bazan et al. [18], many researchers have focused their attention on this subject. Sariciftci et al. [19] fabricated polymer solar cells with additives that showed red-shifted absorption, an increased optical absorption coefficient, and improved charge carrier mobility and carrier equilibrium mobility. Alan Heeger et al. [20] focused their efforts on investigating the mechanism of the modified morphology via the introduction of a small concentration of additives. They attributed the modified morphology to the selective solubility and difference in boiling points between the host solvent and additives, where the additives prevent isolated fullerene molecules from being dissolved throughout polymer phases and leave more space for P3HT to undergo a crystallization process during the film-forming process. However, the provided mechanism is limited to the role that the additive plays in the film-forming process and it gives no clear explanation of how the scale of phase segregation is tuned by the additive. Gang et al. [21] reviewed the effect of thermal annealing and solvent annealing on the performance of P3HT:PC60BM. Recently; Jiangang Liu et al. [22] studied the role of dynamic measurements in bulk-heterojunction solar cells for five different polymer/fullerene polymer solar cells. Results show that it is possible to actively control BHJ film morphology, e.g., crystallinity, during the film forming process.

In this work, the role of n-dodecylthiol additive is revealed by investigating the crystallization process of P3HT and the J-V characteristics of P3HT/PC70BM blends. The effect of adding n-dodecylthiol to P3HT/PC70BM on the performance of PSCs was comparatively studied by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and Solar simulation. Kinetics analysis of cold crystallinity for P3HT/PC70BM PSCs was performed using Avrami model.

## II. EXPERIMENTAL WORK

A series of P3HT/PC70BM PSCs with different n-dodecylthiol contents were prepared and analyzed under the same operating conditions. Regioregular P3HT Rieke ‘E’ was purchased from Rieke Metals, Inc., and used as received. PC70BM was purchased from SES Research Inc. Poly (3,4-ethylenedioxythiophene) poly (styrenesulfonate) (PEDOT:PSS) 1.3 wt% dispersion in H<sub>2</sub>O, conductive grade was purchased from Sigma-Aldrich. ITO coated glass slides (25 x 75 x 1.1mm, 10 Ohm/sq, and ITO thickness 20-100nm) were purchased from nanocos.com.

All samples had a glass/ITO/PEDOT:PSS/P3HT:PC70BM:n-dodecylthiol/Al structure, as shown in Fig. 1. The glass ITO substrate was cleaned in an ultrasonic bath with acetone and isopropanol, and then rinsed in deionized water before drying in an oven at 110°C for 30min. A 30-50nm thick PEDOT:PSS layer was spin-coated on the ITO glass and dried at 110-160°C for 30min using a Laurell Spin Coater (WS-400 BZ 6 NPP/LITE) at 1000rpm. A 150nm-200nm thick active layer (P3HT/PC70BM:n-dodecylthiol blends) was then deposited by spin-coating in a glove box under a nitrogen atmosphere at 1000rpm. The spin-coated solution was prepared as the following: Regioregular P3HT was blended with PC70BM at a ratio of 1:1 (w/w) and then dissolved in a chlorobenzene (CB) solvent to make 10mg/ml solution, n-dodecylthiol (0-5%) was added to the solution and was stirred for 12h prior to use. Finally, the samples were transferred into an evaporator where a 100nm thick Al layer (electrode) was deposited by evaporation. The active surface area of a typical device is 0.25cm<sup>2</sup>. Some samples were annealed at 150°C for 30min inside a vacuum furnace immediately after Al electrode deposition.

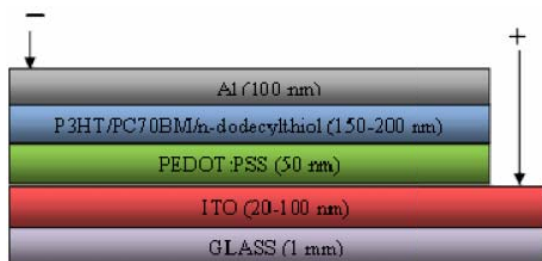


Fig. 1 Schematic diagram of the synthesized polymer solar cell

## III. RESULTS AND DISCUSSION

The structural properties of the films were studied by X-ray diffraction (XRD) using Cu K- $\alpha$  source under 40kV and 40mA tube current. The X-ray spectrum was recorded from 4° to 7° with a rate of 0.2°/minute using automatic slits. The improvement of P3HT self-organization ability with the addition of n-dodecylthiol was reflected in the XRD results shown in Figs. 2 and 3. All P3HT:PC70BM:n-dodecylthiol films showed an intense diffraction peak at  $2\theta = 5.4^\circ$ , corresponding to the ordered structure of P3HT main chains. This indicates that some of the P3HT chains escaped from the amorphous region and then rearranged as single molecules in

the solution. Also, it is evident in Fig. 2 that there is a small increase in the peaks of the polymer with 0-5% n-dodecylthiol before annealing. The intensity of the peaks at  $2\theta = 5.4^\circ$  shows that increasing the crystallinity of the films is directly proportional to the addition of n-dodecylthiol.

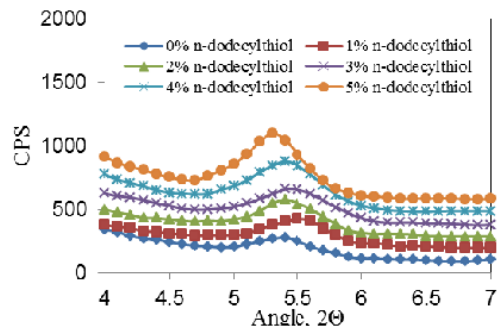


Fig. 2 XRD spectra before thermal annealing

Fig. 3 shows XRD spectra for PSC samples which were annealed for 30 minutes at 150°C in vacuum. Annealing temperature and time were selected in line with previous research work [6] showing that P3HT:PC70BM exhibited optimum electrical properties after annealing at 150°C. Annealing shows an increase in the peak intensity with increasing the amount of n-dodecylthiol, which increases crystallinity of P3HT due to the enhanced self-organization ability in the presence of n-dodecylthiol. However, diffraction peaks caused by PC70BM were barely noticeable in the XRD spectra of P3HT:PC70BM films, both with and without n-dodecylthiol. Therefore, it is safe to assume that the addition of n-dodecylthiol only affects the crystallization of P3HT with little or no influence on the crystallization of PC70BM. Previous research [23] showed that PCBM is not a crystalline material. The highest crystallinity among the heat treated samples occurred with 2% n-dodecylthiol concentration. Increasing n-dodecylthiol content above 2% led to a decline in crystallinity due to uncontrolled phase separation, interruption in P3HT crystallization, and/or agglomeration and insufficient dissolving of particles.

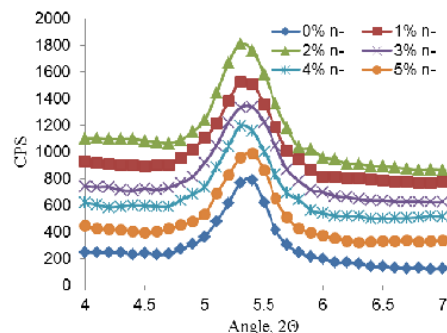


Fig. 3 XRD spectra after thermal annealing

The crystallite size ( $L$ ) was calculated using Scherrer's equation [24], as the following:  $L$  (nm) =  $0.9 \lambda / (\Delta 2\theta \cdot \cos\theta)$

where  $\lambda = \text{Cu K-}\alpha$  wave length = 0.154 nm,  $\Delta 2\theta$  is the full width half maximum of the peak,  $\theta$  is half the angle at peak. The higher XRD peaks indicate that more P3HT crystallites have been formed; i.e. higher crystallinity. However, these crystallites are higher in numbers but shorter in size as depicted in Fig. 4. Crystallite size calculations for annealed samples show that 2% n-dodecylthiol samples exhibit the smallest crystallite size of 11.19 nm. A smaller crystallite size suggests a shorter path of the charge carriers between P3HT backbones, which is beneficial for getting a higher short circuit current ( $J_{sc}$ ) of the devices.

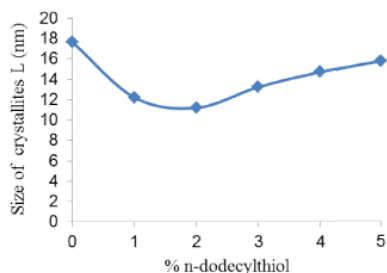


Fig. 4 Effect of % n-dodecylthiol on crystallite size (L)

To further investigate the effect of n-dodecylthiol on the crystallinity of P3HT:PC70BM, differential scanning calorimetry (DSC) measurements were obtained using TA instruments Q2000 at a heating rate of 5°C/min and a sample weight of 5-10 mg. The crystallinity ratio ( $X_c$ ) of P3HT in a blend of P3HT:PC70BM:0-5 vol.% n-dodecylthiol was calculated using DSC melting peak as the following [25]: % Crystallinity ( $X_c$ ) =  $100 \cdot \Delta H / (\Delta H_u \cdot W_i)$  where  $\Delta H$  is the melting enthalpy (in J/g of sample) of semicrystalline polymer in a blend,  $\Delta H_u$  is the melting enthalpy of the theoretical 100% crystal (e.g.,  $\Delta H_u, \text{P3HT} = 99 \text{ J/g}$ ) and  $W_i$  is the weight fraction of component  $i$ . Percent crystallinity calculations show an increase in crystallinity by adding n-dodecylthiol to P3HT:PC70BM polymer blends before annealing, as shown in Fig. 5. However, after annealing, crystallinity starts to decline when the content of n-dodecylthiol is higher than 2%. This is possibly due to the agglomeration and polymer entanglement with excess amounts of n-dodecylthiol during the annealing process, or due to uncontrolled phase separation and interruption in P3HT crystallization. Studies of agglomeration using DLS showed an increase of agglomeration of P3HT:PC70BM by adding n-dodecylthiol above 2%.

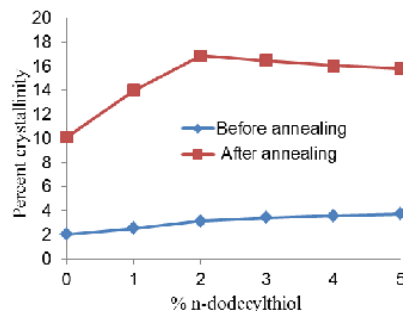


Fig. 5 Effect of % n-dodecylthiol on crystallite size (L) after annealing at 150°C for 30 minutes

External quantum efficiency (EQE) is defined as the ratio of the number of charge carriers collected by the solar cell to the number of photons shining on the solar cell from outside sources. Fig. 6 shows that EQE increases by increasing the percentage of n-dodecylthiol in P3HT:PC70BM between 0% and 5%. Un-annealed devices with 5% n-dodecylthiol exhibit the highest EQE value of 70.4% compared to 60.1% for the device without n-dodecylthiol additives. The EQE value corresponds to a wavelength ranging from 450 to 570 nm. The improvement of EQE is attributed to increased hole and electron polaron mobilities. Results from EQE are compatible with the results obtained from UV-vis absorption, which indicates that the higher the percentage of n-dodecylthiol, the more absorption and EQE obtained from the cell, i.e. higher electron mobility and better J-V characteristics.

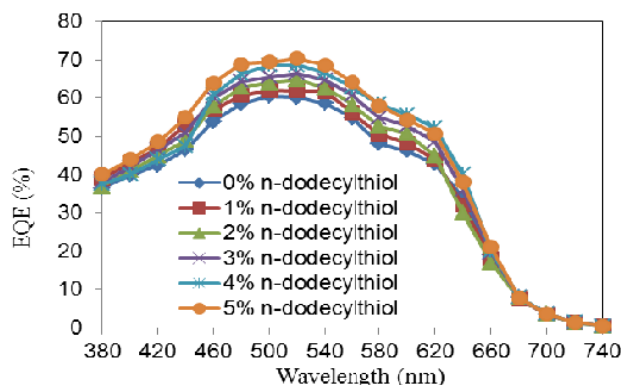


Fig. 6 EQE of synthesized polymer solar cell without annealing

Current density–voltage (J–V) analysis of the fabricated photovoltaic devices was performed using a solar simulator (Newport, 94021A) at one sun (AM 1.5G, 100 mW/cm<sup>2</sup>) supplied by a Keithley 2420 source meter equipped with a calibrated Si-reference cell (Oriel, P/N 91150V). Quantum Efficiency was measured using Newport 200. Fig. 7 shows the power conversion efficiency (PCE) curves for P3HT:PC70BM PSCs under white light illumination (100 mW/cm<sup>2</sup>). The samples were annealed at 150°C for different annealing times (0, 10, 20, 30 and 40 minutes). PSC devices without heat treatment (0-min) show a lower PCE between 1% and 1.5%. However, after heat-treatment, PCE values increased by

increasing the annealing temperature up to 150°C, and as a result, the photovoltaic cells prepared with heat treatment at 150°C and 30 minutes showed the best device performance ( $J_{sc} = 8.59 \text{ mA/cm}^2$ ,  $V_{oc} = 0.64 \text{ V}$ ,  $FF = 0.58$ , and  $PCE = 3.21\%$ ).

The cell performance started to deteriorate at temperatures higher than 150°C, and the Al electrode reflection was not as strong as with lower temperatures. This is attributed to partial melting of the polymer composite under the Al electrode. This was confirmed with the visibility of some cracks on the Al electrode and a change in the color of the polymer from purple to brown. Therefore, it is evident that there is an optimum annealing temperature and time combination to achieve optimum electrical and physical properties of the photoactive cells.

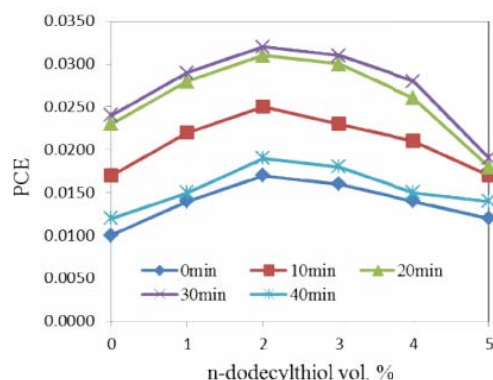


Fig. 7 PCE curves for cells annealed at 150°C for 10-40 minutes

J-V characteristics for PSC samples prepared with 0-5% n-dodecylthiol concentrations under optimum thermal annealing conditions (150°C and 30 minutes) are summarized in Table I.

TABLE I  
J-V CHARACTERISTICS AFTER ANNEALING AT 150 °C FOR 30 MINUTES

% n	$V_{oc}$	$J_{sc}$	FF	PCE
0	0.66	6.15	0.59	2.41%
1	0.66	7.36	0.59	2.88%
2	0.64	8.60	0.58	3.21%
3	0.64	8.44	0.57	3.08%
4	0.63	7.54	0.58	2.77%
5	0.62	5.18	0.58	1.87%

The J-V relationship for the prepared devices is shown in Fig 8. Open circuit voltage ( $V_{oc}$ ) and short-circuit current density ( $J_{sc}$ ) are measured at the intersections of the J-V curves with the x-axis and the y-axis; respectively.

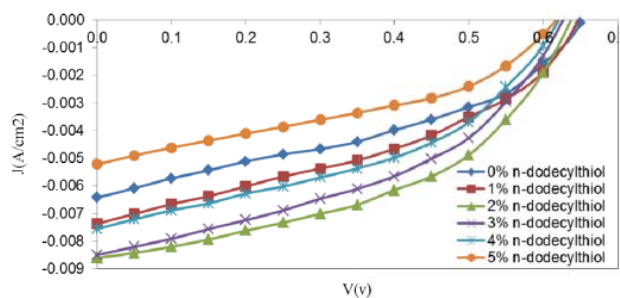


Fig. 8 J-V characteristics under AM 1.5G illumination after annealing

The effect of n-dodecylthiol content on the open circuit voltage ( $V_{oc}$ ) and the short-circuit current density ( $J_{sc}$ ) is shown in Fig. 9. It is well known that open circuit voltage ( $V_{oc}$ ) of polymer solar cells depends on the difference in energy levels between the HOMO of the donor and the LUMO of the acceptor. The addition of n-dodecylthiol results in decreasing the value of  $V_{oc}$  for the polymer solar cell device since n-dodecylthiol increases the active layer P3HT conjugation length. As a result, it decreases the HOMO energy level of P3HT.

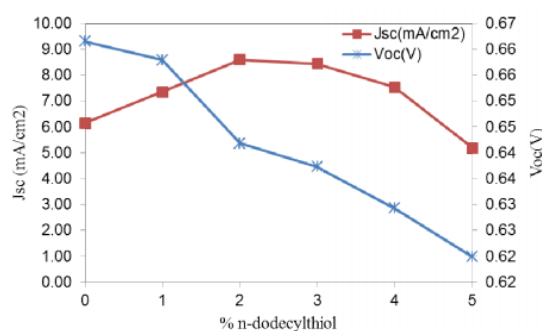


Fig. 9  $J_{sc}$  and  $V_{oc}$  under AM 1.5G illumination after annealing

Unlike  $V_{oc}$ , the short-circuit current density ( $J_{sc}$ ) has a different response to adding n-dodecylthiol. The short circuit current increases by adding n-dodecylthiol up to 2%. This can be attributed to a smaller crystallite size; i.e. better electron mobility and higher crystallinity. After that, the value of  $J_{sc}$  starts to decrease by increasing n-dodecylthiol. Adding more than 2% n-dodecylthiol can contaminate the  $J_{sc}$  and affect phase separation which is not suited for the exciton dissociation, i.e. resulting in a reduction in  $J_{sc}$  and final power conversion.

The power conversion efficiencies ( $PCE = V_{oc} * J_{sc} * FF / \text{Total incident power density}$ ) was measured for solar cells prepared with and without thermal annealing, as shown in Fig. 10. The results show that the maximum efficiency obtained was 1.65% (2 volume % n-dodecylthiol) for the samples prepared without annealing. The efficiency values were almost doubled after annealing at 150°C for 30min. At volume fractions of n-dodecylthiol up to 2%, PCE increased by adding n-dodecylthiol, which is a sign of lowering the number of recombine charges before reaching the electrode. At higher



concentrations of n-dodecylthiol (> 2%), the efficiency starts to fall, which is a direct sign of recombining charges and less charge phase separation.

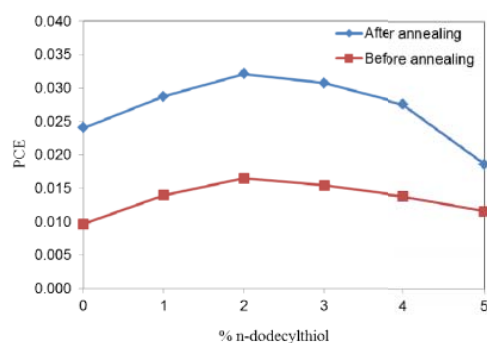


Fig. 10 PCE before and after annealing at 150°C for 30min

The optimum balance between exciton dissociation and charge transport and/or collection at the electrodes was obtained at 2% n-dodecylthiol, resulting in a PCE maximum value of 3.2%, which was almost a 33.3% increase compared with devices without any n-dodecylthiol in the photoactive layer. P3HT/PC70BM/n-dodecylthiol has a 3.21% PCE compared to 2.57% for P3HT/PC60BM/n-dodecylthiol, which shows an enhancement of PCE by 25%. This phenomenon is consistent with the dynamical Monte Carlo modeling of organic solar cells. The maximum efficiency was 3.2% at 2% n-dodecylthiol, associated with the samples prepared and heat treated at 150°C for 30min.

#### IV. CONCLUSION

In this work, n-dodecylthiol (0-5% vol.) was added to P3HT/PC70BM polymer solution to improve the crystallinity of P3HT and enhance the P3HT/PC70BM phase separation. EQE analysis showed enhancement of self-organization ability, which led to improved P3HT crystallinity and intensified phase separation of P3HT/PC70BM in polymer films. EQE increased due to enhanced hole and electron polaron mobilities with n-dodecylthiol. Higher P3HT crystallinity reduces the amount of PCBM dissolved in the amorphous regions of P3HT, thus promoting the aggregation of PC70BM, which contributes to PC70BM/P3HT phase separation. Adding 2% n-dodecylthiol to the active layer resulted in forming the smallest polymer crystallites size  $L$ , which was nearly 11.2nm after annealing at 150°C for 30min in a vacuum atmosphere. The smaller crystallite size suggests a shorter path of the charge carriers between P3HT backbones, which increased the short circuit current ( $J_{sc}$ ) and increased the open circuit voltage ( $V_{oc}$ ) in the solar cells. The increase in phase separation balancing for exciton dissociation and charge transport and/or collection resulted in a 33% increase in solar cell efficiency when the volume fraction of n-dodecylthiol is 2%. The enhancement of cell performance after thermal annealing deteriorated at temperatures higher than 150°C.

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