

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Correlation between morphology and device performance of pBTTT:PC₇₁BM solar cells





Wenluan Zhang ^{a,*}, Hao Shen ^b, Brett W. Guralnick ^b, Brian J. Kirby ^c, Ngoc A. Nguyen ^a, Roddel Remy ^a, Charles F. Majkrzak ^c, Michael E. Mackay ^{a,b,*}

^a Department of Materials Science & Engineering, University of Delaware, Newark, DE 19716, USA

^b Department of Chemical & Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA

^c National Institute of Standards and Technology Center for Neutron Scattering, Gaithersburg, MD 20899, USA

ARTICLE INFO

Article history: Received 14 May 2016 Received in revised form 16 June 2016 Accepted 17 June 2016 Available online 1 July 2016 MSC:

00–01 99–00

Keywords: Polymer:fullerene solar cells Co-crystal Neutron scattering Fullerene agglomerate Exciton recombination

ABSTRACT

Phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) could intercalate between the side-chains of poly(2,5-bis (3-tetradecylthiophen-2-yl)thiono[3,2-*b*]thiophene (pBTTT) creating a stable co-crystal structure, so optimal solar cell performance was obtained at high PC₇₁BM concentrations promoting phase separated electron conductive pathways. Neutron reflectivity, with the application of magnetic contrast variation, was used to investigate the concentration profile of PC₇₁BM within the active layer. And this profile was found to be homogeneous through the film thickness. Small angle neutron scattering was utilized to find there is amorphous PC₇₁BM even at 50 wt% of fullerene while previously it was believed that all fullerene was consumed to form co-crystals when its concentration is below 75 wt%. These fullerene molecules evolve into approximately 15 nm sized agglomerates to improve the electron transport when their concentration is above 75 wt%. Thermal annealing gives these agglomerates mobility to form micrometer sized crystals causing a decrease of device performance. These findings can therefore correlate the morphology, especially in terms of fullerene agglomerates, vertical concentration profile and percolating structure they formed, with the device performance and provide valuable guidance for optimal morphology design of polymer: fullerene solar cells.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Polymer:fullerene solar cells have attracted substantial interest in scientific and industrial research because of their potential for low cost and fast roll-to-roll production on a flexible light weight substrate [1,2]. The light absorbing material is typically a mix of conjugated polymer acting as the electron donor and a fullerene derivative, which is the electron acceptor. They are blended together to form a phase separated interpenetrating structure at the nanometer scale creating the so called bulk-heterojunction (BHJ) solar cells [3]. Strongly Coulomb-bound electron-hole pairs (excitons) are generated when light excites the polymer because of its low dielectric constant [4,5]. The exciton diffusion length is only 5– 10 nm, so it is required that they be created near the interface of the polymer and fullerene-rich domains to facilitate energetically favorable charge separation [6]. In order to warrant the charge transport, a certain degree of phase separation between donor and

* Corresponding authors. E-mail addresses: jasonzwl@udel.edu (W. Zhang), mem@udel.edu (M.E. Mackay).

http://dx.doi.org/10.1016/j.solmat.2016.06.042 0927-0248/© 2016 Elsevier B.V. All rights reserved. acceptor domains is also needed to form continuous pathway throughout the active layer. Such dual requirements suggest an optimum morphology for the active layer consisting of long interpenetrating domains of order 5–10 nm in dimension [7,8].

Therefore, much effort has been made to obtain efficient devices by controlling the morphology of the active layer through the use of various solvents, solvent additives and inclusion of inorganic materials in addition to post processing procedures such as thermal and solvent vapor annealing [1,9–12]. A wealth of knowledge on the correlation between morphology and device performance has been obtained based on a number of structural characterization techniques, including small angle and soft X-ray scattering [13,14], various electron microscopies [15,16] and atomic force microscopy [8].

Previous neutron reflectivity and small angle neutron scattering measurements on 1:1 wt ratio poly(3-hexylthiophene): [6,6]phenyl-C₆₁-butyric acid methyl ester, P3HT: PCBM, have shown a nonuniform vertical distribution of phase segregated PCBM in the P3HT matrix after film deposition. Relatively higher concentrations of PCBM were found near both the substrate and air interface than the active layer's bulk region, which is not a preferred structure, since PCBM is desired to be near the air interface and the subsequently deposited aluminum electrode can collect the electrons. By applying thermal annealing, the PCBM concentration near the air interface increases and PCBM agglomerates grow into a larger size, creating percolating structure and better electron transport pathways resulting in improved device performance [17–19]. Therefore, relative high amount of fullerene near the cathode is proved to benefit the electron transport. Hence, it is necessary to study whether this phenomenon could be found in many systems optimized for best device performance with a polymer: fullerene blend close to 1:4 by weight, such as poly(2-methoxy-5-(3',7'-dimethyloxy)-*p*-phylene vinylene) (MDMO-PPV: PC₆₁BM) [20] and poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno [3,2-*b*]thiophene: phenyl-C₇₁-butyric acid methyl ester (pBTTT: PC₇₁BM) [21].

It is discovered that in the pBTTT:PC₇₁BM system, PC₇₁BM can intercalate between the side chains to form a thermodynamically stable bimolecular structure because the side chains of pBTTT are further apart than they are in P3HT. A bimolecular crystal, i.e. cocrystal, of pBTTT and PC₇₁BM is formed when these two chemical species are in this ordered arrangement [22]. As a result of this intimate mixing, exciton harvesting is much better in pBTTT: PC₇₁BM [21] in contrast to the P3HT: PCBM system [17]. Since the formation of the co-crystal consumes a large amount of PC₇₁BM, a high ratio of fullerene relative to the polymer must be used in the active layer to form continuous conductive pathways to the electrodes through phase separation. Indeed, the optimum device performance was obtained at 75-80% PC71BM weight fraction. Due to the large amount of fullerene required, the limited solvent solubility and the large band gap energy of pBTTT, this system is not expected to perform as well as other polymer systems.

In this study, we rationalize the correlation between the pBTTT: PC₇₁BM's morphology and device performance through an analysis of the fullerene intercalation, vertical distribution of fullerene molecules, optical properties of the active layers, and the shape and size of PC₇₁BM aggregates that form electron conductive pathways. Magnetic contrast neutron reflectivity (MCNR), small angle neutron scattering (SANS) and other complimentary characterization methods were applied to obtain insight of the active layer's morphology for a system that promotes a co-crystal while simultaneously requires a phase separated structure.

2. Materials and methods

For device fabrication, an ITO (indium tin oxide) coated one inch square (1 in. square $= 6.45 \text{ cm}^2$) glass slide (sheet resistance of 8–12 Ω/\Box , Delta technologies, LTD) was cleaned by ultrasonic treatment in acetone and isoproponal sequentially for 15 min each. This was followed by spin coating a ~33 nm thick layer of Poly(3,4-ethylenedioxythio-phene): poly(styrenesulfonate) (PED-OT: PSS, H. C. Starck, Al 4083) which was then transferred to an oven and annealed for 20 min at ~130 °C. After this, the slide was transferred to a nitrogen-filled glove box (≤ 0.1 ppm of O_2 and H_2O to fabricate a device. The solutions required for spin coating the active layer were prepared by dissolving pBTTT-C₁₄ (Luminescence Technology Corp.) and PC71BM (Nano-C) in di-ortho-chlorobenzene in a nitrogen glove box. A wide PC₇₁BM loading range was used from 0 wt% to 91.7 wt% at a total polymer and nanoparticle concentration of 24 mg/ml. All materials were used as received. The solution preparation method was used as reported before [23]. In order to have complete dissolution, the solution was stirred for 9 h at 90 °C. Before spin coating onto the PEDOT substrate, it was cooled to 60 °C. The solution was then spin coated at 600 rpm = 1 hertz for 60 s, after filtering through a 0.2 µm Teflon filter, to obtain an approximately 90 nm thick layer. A hotplate set at 180 °C was used to anneal the films for 10 min to obtain a high degree of polycrystallinity. This temperature is above the glass transition temperature of pBTTT ($T_g \sim 50$ °C) [24]. Lithium flouride (0.8 nm thickness) and aluminum (80 nm thickness) were sequentially thermal evaporated in a deposition chamber at a vacuum of 2×10^{-6} mbar. The device area was approximately 0.1 cm². The current-voltage curves were measured with a Keithley 2400 source meter, under illumination of 100 mW/ cm² from 150 W solar simulator with AM1.5G filters.

For grazing incidence X-ray diffraction (GIXRD) measurements, the samples were prepared on silicon wafers instead of ITO glass. A Rigaku Ultimate IV multipurpose XRD system was used to perform all the X-ray scattering measurements which used a 1.54 Å wavelength Copper K α source with a 0.5° fixed incident angle in the 2θ mode. The UV–vis absorption spectra were measured on a Shimadzu UV-3600 spectrometer in transmission mode. All the samples were coated on soda-lime glass with a PEDOT:PSS layer, whose absorption was subtracted as a background signal. Photoluminescence measurement were performed on a Horiba Jobin Yvon Fluoromax-4 spectrofluorometer with an incident wavelength of 512 nm using identical samples to the UV–vis absorption measurements.

All neutron experiments were performed at the NIST Center for Neutron Research (NCNR). For neutron reflectivity, magnetic substrates with a permalloy and gold layer deposited on 2 in. (1in.=2.54 cm) diameter sapphire disks were prepared at NIST. Permalloy (thickness ~115 Å, 81% nickel, 19% iron) and gold (thickness ~170 Å) were deposited on the sapphire substrate sequentially in the same chamber by using a sputtering system. For neutron reflectivity, a rough film surface makes it difficult to collect high quality data during the limited available beam-time. So a higher spin coating speed was used to make a smoother film. In previous work done by Kiel et al., a very similar P3HT/PCBM concentration profile was obtained for samples spin coated at 2500 rpm and 800 rpm [18], which gives us confidence to use a higher spin coating speed to make a flatter film surface without completely changing the PC₇₁BM concentration profile. So a spin speed of 1500 rpm was used to have a uniform thin film to run the magnetic contrast neutron reflectivity (MCNR) test. The film thickness was ~30 nm. The NG-1 reflectometer was used for data collection with an incident neutron wavelength of 4.75 Å which had a spread of 1.5% or less. In order to increase the signal to noise (S/N) ratio within the limited beam-time a smaller q-range was used to collect data. Fitting of the data was performed by using ga_refl program [25].

A one inch diameter (100) silicon wafer was used as the substrate for small angle neutron scattering and a PEDOT:PSS and active layer were spin coated on it as described above. For SANS measurements, the film roughness is not as critical as it is for the reflectivity measurements. In order to mimic the active layer in actual devices, a spin coating speed of 600 rpm was used to make an active layer having a 90 nm thickness. Since the silicon substrate is essentially transparent to neutrons, a stack of 12 wafers was used as one sample to increase the scattering signal [26]. The NG3 30 m SANS instrument was used for the neutron scattering experiment. Three detector distances and two neutron wavelengths were used: distances of 1.33 m and 4 m were used with a wavelength of 6 Å and 13.2 m with a wavelength of 8.4 Å. Data were obtained over the scattering vector (q) range of $0.008 \le q \le 0.3 \text{ Å}^{-1}$, where $q = (4\pi/\lambda)\sin(\theta/2)$, and a total scattering count of $\sim 10^6$ was used to increase the S/N ratio. Empty cell scattering and background scattering were performed for data conversion to absolute scattering intensity versus scattering vector. Data reduction and SANS analysis was performed using NCNR SANS packages SANS Reduction v 5.20 and SANS Analysis v 7.1 [27]. The incoherent scattering background was obtained by

plotting $q^4 I(q)$ versus q^4 at large q [28]. The slope of this function is the sum of the incoherent scattering and a thermal scattering contribution both of which can be easily subtracted from the total scattering intensity. The magnitude of the background for all samples was small and around 0.7–1.8 cm⁻¹.

2.1. Disclaimer

Certain commercial equipment, instruments, materials, suppliers, or software, are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

3. Results and discussion

3.1. Grazing Incidence X-ray diffraction

Grazing incidence X-ray diffraction was used to determine the *d*-spacing, i.e. lamellar stacking spacing, for pure pBTTT polymer and pBTTT:PC71BM blends and to examine the ordering of the structure. A series of peaks corresponding to the *d*-spacing (h00) are shown in Fig. 1. For as cast samples, the *d*-spacing of pure pBTTT is about 21.2 Å. By increasing the PC₇₁BM weight fraction, an expansion in the lamellar stacking direction was seen until at a concentration of 50 wt% where it remained constant at 29.4 Å. This expansion is caused by PC71BM intercalation between the side chains of pBTTT as seen before [22,23]. It should be noted more PC₇₁BM improves the ordering of the co-crystal. However, when the fullerene concentration is above 75 wt%, less polymer is available to form this co-crystal structure resulting in a weaker signal. After thermal annealing, the (100) peak shifted to a lower q value for all the samples below 75 wt% PC71BM, which suggests a little larger distance between the polymer backbone [29,30].

3.2. Optical microscopy

Phase separation at micrometer length in annealed samples

was observed through optical microscopy for PC71BM weight fractions above 50% as shown in Fig. 2. Phase separation was only present for annealed samples while as cast samples showed none so they are not displayed here. Micrometer sized PC₇₁BM crystal are observed when the weight fraction is above 50% and the colored edges are due to light interference effects from changes in the film thickness. The size and substrate surface coverage of these crystal increased with higher PC71BM weight fraction. Similar phenomenon in other polymer:fullerene blends has been observed previously by several groups [31–34]. Obviously thermal annealing gave PC₇₁BM the mobility to form these large structures when the co-crystal could no longer incorporate more nanoparticles. Here we do a rough calculation assuming an average pBTTT molecular weight of 60 kDa based on the manufacturer's specifications. The repeat unit of pBTTT has a molecular weight of 0.695 kDa, so the degree of polymerization is N=86, PC71BM has a molecular weight of 1031 Da. So for a PC₇₁BM 50 wt% mixture, there are 58 PC₇₁BM molecules per pBTTT molecule which has 86 repeat units. A 60 wt% mixture will have 87 PC71BM molecules per pBTTT molecule, which is very close to the number of pBTTT repeat units. Based on this simple estimate, this implies the co-crystal fully formed at a concentration of approximately 60 wt%, which is consistent with the GIXRD data shown in Fig. 1 since above this concentration the excess fullerene form agglomerates. However, the Fig. 2(c) clearly shows fullerene agglomerates which are not supposed to be there because all the fullerene could have been mixed in the polymer matrix based on the calculations above. This suggests that us that not all PC71BM may participate in forming cocrystals with pBTTT, and the amorphous fullerene forms agglomerations upon thermal annealing.

3.3. Magnetic contrast neutron reflectivity

Kiel et al. demonstrated that the nanoparticle concentration profile played an important role in the performance of P3HT: PCBM solar cells and determined this by using phase sensitive neutron reflectivity (PSNR) [18,35]. Air and D₂O were used as two reference layers to get multiple neutron contrast conditions to yield a unique concentration profile from reflectivity data. Analysis with neutron reflectivity gives the fullerene concentration profile



Fig. 1. GIXRD pattern of pure pBTTT and pBTTT:PC₇₁BM blend thin Film at various fullerene weight fraction: (a) as cast and (b) annealed at 180 °C for 10 min. For pure pBTTT, (100) and (200) diffraction peaks can be used to calculate the *d*-spacing between the polymer backbone. Blending with PC₇₁BM lowered the diffraction intensity, so only one peak was observed which shifted to lower *q*.



Fig. 2. Optical microscope of the annealed samples with various PC₇₁BM Weight fraction. Large surface density of star-shaped micrometer sized PC₇₁BM crystal was seen with its higher loading.

throughout the whole active layer with quantitative accuracy [36,37]. In this study, we used state-of-the-art neutron reflectivity methods, with the application of magnetic contrast variation, to investigate the concentration profile of fullerene in the active layers in order to understand the morphological difference from 50 to 83.3 wt% PC71BM concentration and how it related to devices performance. There are two advantages in using magnetic contrast neutron reflectivity (MCNR): (i) it is simple to obtain multiple neutron contrast data from a reference layer by tuning the polarization of neutron beam [38-41], and (ii) MCNR avoids the use of D₂O as a contrast agent which dissolves the PEDOT:PSS layer if PSNR was used. However, there is also limitation to this technique. High quality data is difficult to be obtained from annealed samples due to the roughness induced by phase separation of PC71BM at micrometer length scale requiring much longer beam-time to increase the S/N ratio. Fig. 3 shows the MCNR data from as cast samples and the extracted nuclear scattering length density (SLD) profile ($\rho(z)$), which is a function of PC₇₁BM volume faction profile $(\phi_{PC_{7},BM}(z))$ within the active layer. We have

$$\rho(z) = \phi_{\rm PC_{71}BM}(z)\rho_{\rm PC_{71}BM} + \left(1 - \phi_{\rm PC_{71}BM}(z)\right)\rho_{\rm pBTTT}, \tag{1}$$

where $\rho_{\rm pBTTT}$ (=0.546 \times $10^{-6}\,{\rm \AA}^{-2})$ is the scattering length density of pure pBTTT and $\rho_{\rm PG_{71}BM}~(=3.91 \times 10^{-6}~{\rm \AA}^{-2})$ is the scattering length density of pure $PC_{71}BM$, which were determined by specular neutron reflectivity (shown in the supporting materials) [42-44]. Since the polarized neutron beam has two spin states (spin "up" and spin "down"), it interacts with the permalloy (iron-nickel) layer to have a large magnetic scattering length density difference. Reflectivity of the spin "up" state is about an order of magnitude larger than the value for the spin "down" state. This allows one the ability to overcome the ambiguity from a single reflectivity data by simultaneously fitting these two reflectivity curves. The fitting approach was based on a slab model, in which $\rho(z)$ is divided into a certain number of slabs each having a uniform thickness and constant SLD value [38]. Gaussian interfacial roughness was also added between slabs, and a certain number of steps can be chosen to smooth the overall profile [45]. Since the substrate's thickness and SLD is known beforehand, it is possible to make a set of constraints so only the PEDOT and active layer parameters like thickness and SLD profile are changed. The PEDOT's SLD was set at $1.64 \times 10^{-6} \text{ \AA}^{-2}$ based upon our previous results [18]. The active layer region is defined by putting a dividing line at the middle of



Fig. 3. Magnetic contrast neutron reflectivity from three PC₇₁ BM weight fraction as cast pBTTT:PC₇₁BM films are shown in (a), (b) and (c). Black line is simultaneous fitting curve. Homogeneous nuclear SLD profiles are gained in (d) from PEDOT to air side. A 95% confidence interval was used when the raw reflectivity data were averaged.

the interfacial (Gaussian) roughness region at the PEDOT and air interface. The quality of fitting was very good judged by the small χ^2 values, between 1 and 3($\chi^2 = 1$ is an indicative of perfect fit) [46].

As shown in Fig. 4 (a), the volume fraction profile of the PC₇₁BM within the active layer ($\phi_{PC_71BM}(z)$) converted from the SLD profile with Eq. (1). By integrating under the PC₇₁BM vol% profile curve in Fig. 4(a), we can obtain the average value of the PC₇₁BM volume fraction throughout the active layer. Comparing the PC₇₁BM vol% from fitting the reflectivity data to the expected value from the

initial mixture finds a good result, the difference between them is within 7% as shown in Fig. 4(b). This check of mass balance provides confidence in the accuracy of the fits to MCNR data.

In P3HT:PCBM organic solar cells, the PCBM nanoparticles were found to aggregate at both the substrate and near the air interface due to a balance of convective flow and enthalpic and entropic forces [18,47,48]. However, this phenomenon is not seen in the pBTTT:PC₇₁BM blend. From all these samples, a fairly homogeneous PC₇₁BM concentration profile is formed throughout the active layer with a decreasing concentration at both the substrate



Fig. 4. Normalized PC₇₁BM concentration profile is shown in (a), the higher concentration profile accompanied with higher PC₇₁BM weight fraction. In (b), integration under PC₇₁BM vol% profile curve in (a) was used to compare with PC₇₁BM vol% from Initial mixture to check the validity of fitting.



Fig. 5. The absorption spectra, normalized by active layer thickness, of the as cast and annealed samples are shown in (a) and (b). Photoluminescence from the same samples are shown in (c) and (d) respectively.

and air interfaces. It suggests that the formation of those cocrystals trapped most of the fullerene molecules in the active layers' bulk region. Although the desired accumulation of fullerene near air side is not seen in this system, the large amount of fullerene, in 75 and 83.3 wt% samples, should be still able to form a percolating structure to improve the transport of electrons to the cathode. It also should be noted that the data sets fit perfectly well to a uniform layer, but in principle we can not rule out inhomogeneity in general (for example a very thin increased SLD layer at the surface).

3.4. Optical properties

The results in Fig. 5(a),(b) depict the ultraviolet-visible absorption spectra of the as cast and annealed samples coated on glass slices. The absorption coefficient maximum from the as-cast pure polymer centered around 530 nm and decreases as PC71BM is added. Compared with PC₆₁BM, PC₇₁BM has lower structural symmetry allowing energy transitions which could improve light absorption also creating excitons [49]. However, this also induces exciton recombination in the fullerene phase when free charges not created. Therefore, photoluminescence (PL) data is plotted in logarithm scale in Fig. 5(c) and (d) to understand the degree of exciton recombination within these samples [17,50]. PL quenching from both graphs was observed when fullerene was blended with polymer due to fine mixing of the donor and acceptor materials forming a co-crystal, which is consistent with previous findings from the McGehee group [23], indicating exciton separation is highly efficient with the presence of a co-crystal structure. The signature peaks at 770 nm and 820 nm clearly point to the presence of pure PC₇₁BM, which suggests the excitons recombination also occurs in the pure fullerene phase. The PL intensity slightly increases in the annealed samples due to the growth of star

shaped $PC_{71}BM$ crystals observed in Fig. 2. This is expected since these large fullerene crystals at the length scale of micron meters (shown in Fig. 2) is much larger than the exciton diffusion length (~10 nm), resulting in a higher degree of exciton recombination and PL intensity.

3.5. Device performance

The corresponding device performance parameters as a function of PC₇₁BM weight fraction are shown in Fig. 6. The maximum power conversion efficiency obtained at a PC71BM concentration of 75% weight fraction for both the as cast and annealed samples is driven by the optimal short current density. Since the light absorption decreases due to less polymer in the blend, the higher current suggests more efficient exciton harvesting to compensate the negative effect from the insufficient exciton generation. However, the lower fill factor for higher PC₇₁BM loading samples implies that the charge collection at the electrode interface is poor despite a higher current density [51]. As discussed above, the increased amount of pure fullerene not forming a co-crystal at high PC71BM concentration, also absorbs light and induces exciton recombination, which leads to the reduction of the open-circuit voltage (V_{0C}) [52]. For annealed samples at higher fullerene loading, exciton recombination causes a drastic loss in V_{0C} due to the formation of large PC71BM crystals.

3.6. Small Angle Neutron Scattering

By using SANS, morphological information on the length scale of 2 ~ 80 nm was obtained. Absolute intensity, I(q), versus wave vector (q) as a function of PC₇₁BM weight fraction and thermal annealing are presented in Fig. 7a and b. As shown in Fig. 7(b), for annealed samples having 75 and 83.3 wt% PC₇₁BM, the scattering



Fig. 6. Power conversion efficiency (PCE) as a function of $PC_{71}BM$ weight fraction of as cast and annealed samples. The improvement of PCE is mainly from the higher J_{sc} . Rough interface and exciton recombination in fullerene crystal also affect the fill factor and V_{oc} . A 95% confidence interval was used when the collected data were averaged.

curves follow a power-law of the form $I(q) \sim q^{-4}$ at small q, which arises from the surface roughness of the films caused by phase separation of fullerene at micrometer length scale as shown in Fig. 2. A diffraction peak of (100) at $q = 0.21 \text{ \AA}^{-1}$ was observed after thermal annealing for the 50 wt% sample, which is caused by PC71BM intercalation and consistent with the X-ray diffraction patterns seen in Fig. 1. A much broader peak at the same position is also shown in as cast sample of 50 wt% suggesting a lower crystallinity of the co-crystal. For as cast samples, the scattering curves from 75 and 83.3 wt% fullerene concentration indicate polydisperse sphere behavior [53]. Modeling the PC₇₁BM agglomerates as polydisperse spheres (having a Schulz distribution) with a hard sphere interaction and surrounded by a matrix of pBTTT and solubilized PC71BM allowed some general conclusions to be made. The fitting results were obtained and listed in Table 1, which are PC71BM agglomerate diameter, PC71BM agglomerate vol% and PC₇₁BM vol% trapped in pBTTT matrix [17,19,54,55]. About 15 nm diameter size agglomerate formed in the matrix. The total volume fraction of PC71BM was used to confirm the validity of fitting. The total PC₇₁BM vol% from fitting are 72% and 81%, which are in good agreement with PC71BM vol% from initial mixture 71% and 80% respectively. By having the PC71BM agglomerate vol%, we can also estimate the distance, *H*, between these agglomerates by assuming random packing, $H/D = (1/\phi)^{1/3} - 1$, where *D* is the agglomerate mean diameter, and ϕ is the volume fraction of PC₇₁BM agglomerate [17,56]. The distance H decreases slightly from 10.4 nm to 8.6 nm simply because of the increased PC₇₁BM wt%. Thus, the electron transport could be improved by having shorter distance between fullerene agglomerates.

Kratky plots $(q^2I(q)vsq)$ are shown in Fig. 7(c) and (d) by plotting $q^2I(q)$ as a function of scattering vector q, which allows one to find, $q^2I(q) = 2\phi V(\Delta \rho)^2 / (R_g)^2$ in the high q limit $(q > 5R_g^{-1})$. Here, ϕ is the volume fraction of scattering centers, V is the volume of a single scattering center, $(\Delta \rho)^2$ is the square of the difference in the scattering length density between solvent and scatterer, i.e. contrast, and R_g is the radius of gyration of the scatterer. The curve should asymptotically reach a plateau (constant value) for an ideal Gaussian coil. However, the peak displayed in the low *q* regime is an indicative of particle-like feature caused by PC71BM agglomerates in this case [56,57]. For as cast 83.3 wt% sample, more $PC_{71}BM$ molecules are kinetically trapped in less amount of pBTTT matrix compared with as cast 75 wt% sample. This results in lower contrast, $(\Delta \rho)^2$, between polymer matrix and PC₇₁BM, thus, lower curve maximum. It should be noted that the *d*-spacing $(d = 2\pi/q)$ value converted from the peak position cannot be directly associated with the size of the particles or the distance between them. It simply points out the featured length scale of the studied structure. So in this case, for as cast samples, 75 and 83.3 wt% fullerene molecules form a structure at length scale of about 37 nm ($q \approx 0.017 \text{ rm}\text{\AA}^{-1}$). For annealed samples, 75 and 83.3 wt% samples show no peak in obtained q range and their curves go upward at ultra low q regime. Since the curve in Kratky plot has to reach origin point ($q^2 I(q) = 0$ when q = 0), so a peak has to be formed at ultra low q regime suggesting a structural feature at much larger length scale. This agrees with the micrometer sized fullerene crystals as demonstrated in Fig. 2. For 50 wt% samples, as cast sample shows a broad hump in the range of 0.04–0.08 $Å^{-1}$. a length scale of about 1.6-7.8 nm suggesting the existence of amorphous or small PC71BM agglomerates. The annealed sample's curve maximum is at $q \approx 0.03 \text{ Å}^{-1}$ indicating a length scale of about 21 nm, which suggests the formation of fullerene agglomerates causing higher degree of phase separation after thermal annealing. In previous Section 3.2, the existence of PC₇₁BM not forming co-crystal below 60 wt% is merely a speculation based on the optical microscopy images. Here, by analyzing the SANS data, a more affirmative answer has been given. Therefore, based on the above analysis, a schematic graph was drawn to summarize the morphological changes caused by different fullerene weight fractions and thermal annealing, as shown in Fig. 8. For as cast 50 wt%



Fig. 7. Small angle neutron scattering for as cast and annealed samples are shown in (a) and (b). The solid curves in (a) are from polydisperse sphere (Schulz distribution) model fitting to give the $PC_{71}BM$ agglomerate size and volume fraction within the active layer. The solid line in (b) is a power law fit indicating the scattering originating from rough surface. The arrow points to the (100) diffraction peak which indicates the *d*-spacing of the co-crystal. Kratky plots are shown in (c) and (d) to display the particle-like characteristic of the samples' morphology. A 95% confidence interval was used when the raw scattering data were averaged.

Table 1

Polydisperse spheres (with Schulz distribution) fitting results and distance between agglomerates of high concentration $PC_{71}BM$ as cast samples. $PC_{71}BM$ vol% in total was used to check the validity of fitting. A 95% confidence interval was used when the fitting procedures were performed.

	75 wt%	83.3 wt%
$PC_{71}BM$ agglomerate radius (nm) $PC_{71}BM$ agglomerate vol% $PC_{71}BM$ vol% in pBTTT matrix $PC_{71}BM$ vol% in total (from initial mixture) Distance between agglomerates (nm)	$7.9 \pm 0.5 \\ 22 \pm 3 \\ 50 \pm 4 \\ 72 \\ 10.4 \pm 1.3$	$\begin{array}{c} 7.1 \pm 0.9 \\ 24 \pm 2 \\ 57 \pm 3 \\ 80 \\ 8.6 \pm 2.3 \end{array}$

samples, some PC₇₁BM molecules mix into pBTTT and form not fully intercalated co-crystals, the others are amorphous or in the form of small agglomerates. After thermal annealing, these amorphous or small agglomerates grow into larger size causing higher degree of phase separation. For as cast 75–83 wt% samples, about 15 nm fullerene agglomerates and fully intercalated cocrystals improve excitons harvesting and electron transport to increase the device performance. However, after thermal annealing, micrometer sized fullerene crystals cause rough interface between the active layer and cathode resulting in low efficiency. From the MCNR results, for as cast samples, PC₇₁BM concentration profile on the vertical direction of active layers is basically homogenous. However, it is not for certain that the thermal annealing would not affect this homogenous PC₇₁BM distribution along the vertical direction. Further study is required to answer this question.

4. Conclusion

The correlation between morphology and device performance of pBTTT:PC₇₁BM solar cells was studied in this article. Co-crystals of polymer and fullerene are formed by PC₇₁BM molecules intercalating between polymer side chains improving the excitons dissociation. The weight fraction fullerene molecules for a fully intercalated co-crystal was calculated yielding a value of 60 wt% PC₇₁BM. Kinetically trapped fullerene not forming co-crystal was observed even below 60 wt% giving a more precise picture of the morphology for pBTTT:PC₇₁BM system. By having large amount of PC₇₁BM agglomerates, electron transport was improved. Thus, as cast 75 wt% PC₇₁BM sample delivers the optimal efficiency by



Fig. 8. Morphology schematic for as cast and thermal annealed samples with various PC71BM weight fraction.

having excellent excitons harvesting and efficient electron transport at the same time. However, this improved electron transport costs the price of less amount of polymer resulting in much less light absorbed in the system. So a more balanced polymer:fullerene ratio with improved charge transport will be the focus of future research. Both magnetic contrast neutron reflectivity and small angle neutron scattering are proved to be very helpful in analyzing this complex system. In the future, these advanced characterization techniques can bring more exciting discoveries in the field of organic electronics.

Acknowledgements

We acknowledge the support from the US Department of Energy, Materials Sciences Division, under Award No. DE-FG02-05ER46211. The help from Frank Heinrich at the NIST Center for Nanoscale Science and Technology in preparing the permalloy coated sapphire is also greatly appreciated.

References

- [1] C.J. Brabec, N.S. Sariciftci, J.C. Hummelen, Plastic solar cells, Adv. Funct. Mater. 11 (1) (2001) 15–26 $\scriptstyle \langle.$
- [2] G. Dennler, M.C. Scharber, C.J. Brabec, Polymer-fullerene bulk-heterojunction solar cells, Adv. Mater. 21 (13) (2009) 1323–1338, http://dx.doi.org/10.1002/ adma.200801283.
- C. Deibel, V. Dyakonov, Polymer-fullerene bulk heterojunction solar cells, Rep. Progress. Phys. 73 (9) (2010) 096401, http://dx.doi.org/10.1088/0034-4885/73/ 9/096401.
- [4] T.M. Clarke, J.R. Durrant, Charge photogeneration in organic solar cells, Chem. Rev. 110 (11) (2010) 6736–6767, http://dx.doi.org/10.1021/cr900271s.
- [5] B.C. Thompson, J.M. Frechet, Polymer-fullerene composite solar cells, Angew. Chem. Int. Ed. 47 (1) (2008) 58–77, http://dx.doi.org/10.1002/anie.200702506.

- [6] J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, A.B. Holmes, Efficient photodiodes from interpenetrating polymer networks, Nature 376 (6540) (1995) 498–500, http://dx.doi.org/10.1038/376498a0.
- [7] M.T. Dang, L. Hirsch, G. Wantz, J.D. Wuest, Controlling the morphology and performance of bulk heterojunctions in solar cells. lessons learned from the benchmark poly(3-hexylthiophene) [6,6]-phenyl-C₆₁-butyric acid methyl ester system, Chem. Rev. 113 (5) (2013) 3734–3765, http://dx.doi.org/10.1021/ cr300005u.
- [8] Y. Huang, E.J. Kramer, A.J. Heeger, G.C. Bazan, Bulk heterojunction solar cells morphology and performance relationships, Chem. Rev. 114 (14) (2014) 7006–7043, http://dx.doi.org/10.1021/cr400353v.
- [9] W.L. Ma, C.Y. Yang, X. Gong, K. Lee, A.J. Heeger, Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology, Adv. Funct. Mater. 15 (10) (2005) 1617–1622, http://dx.doi.org/ 10.1002/adfm.200500211.
- [10] J. Weickert, R.B. Dunbar, H.C. Hesse, W. Wiedemann, L. Schmidt-Mende, Nanostructured organic and hybrid solar cells, Adv. Mater. 23 (16) (2011) 1810–1828, http://dx.doi.org/10.1002/adma.201003991.
- [11] G. Li, Y. Yao, H. Yang, V. Shrotriya, G. Yang, Y. Yang, Solvent annealing effect in polymer solar cells based on poly(3-hexylthiophene) and methanofullerenes, Adv. Funct. Mater. 17 (10) (2007) 1636–1644, http://dx.doi.org/10.1002/ adfm.200600624.
- [12] H. Hoppe, N.S. Sariciftci, Organic solar cells: an overview, J. Mater. Res. 19 (7) (2004) 1924–1945, http://dx.doi.org/10.1557/JMR.2004.0252.
- [13] H.C. Liao, C.S. Tsao, T.H. Lin, C.M. Chuang, C.Y. Chen, U.S. Jeng, C.H. Su, Y.F. Chen, W.F. Su, Quantitative nanoorganized structural evolution for a high efficiency bulk heterojunction polymer solar cell, J. Am. Chem. Soc. 133 (33) (2011) 13064–13073, http://dx.doi.org/10.1021/ja202977r.
- [14] H. Ade, A.P. Hitchcock, NEXAFS microscopy and resonant scattering composition and orientation probed in real and reciprocal space, Polymer 49 (3) (2008) 643–675, http://dx.doi.org/10.1016/j.polymer.2007.10.030.
- [15] D.R. Kozub, K. Vakhshouri, L.M. Orme, C. Wang, A. Hexemer, E.D. Gomez, Polymer crystallization of partially miscible polythiophene/fullerene mixtures controls morphology, Macromolecules 44 (14) (2011) 5722–5726, http://dx. doi.org/10.1021/ma200855r.
- [16] B. Xue, B. Vaughan, C.-H. Poh, K.B. Burke, L. Thomsen, A. Stapleton, X. Zhou, G. W. Bryant, W. Belcher, P.C. Dastoor, Vertical stratification and interfacial structure in P3HT: PCBM organic solar cells, J. Phys. Chem. C. 114 (37) (2010) 15797–15805, http://dx.doi.org/10.1021/jp104695j.
- [17] J.W. Kiel, A.P.R. Eberle, M.E. Mackay, Nanoparticle agglomeration in polymerbased solar cells, Phys. Rev. Lett. 105 (16) (2010) 168701, http://dx.doi.org/ 10.1103/PhysRevLett.105.168701.
- [18] J.W. Kiel, B.J. Kirby, C.F. Majkrzak, B.B. Maranville, M.E. Mackay, Nanoparticle

concentration profile in polymer-based solar cells, Soft Matter 6 (3) (2010) 641–646, http://dx.doi.org/10.1039/B920979D.

- [19] H. Shen, W. Zhang, M.E. Mackay, Dual length morphological model for bulkheterojunction, polymer-based solar cells, J. Polym. Sci. Part B: Polym. Phys. 52 (5) (2014) 387–396, http://dx.doi.org/10.1002/polb.23426.
- [20] T. Martens, J. D'aen, T. Munters, Z. Beelen, L. Goris, J. Manca, M. D'Olieslaeger, D. Vanderzande, L. De Schepper, R. Andriessen, Disclosure of the nanostructure of MDMO-PPV PCBM bulk hetero-junction organic solar cells by a combination of SPM and TEM, Synth. Met. 138 (1–2) (2003) 243–247, http: //dx.doi.org/10.1016/S0379–6779(02)01311–5.
- [21] J.E. Parmer, A.C. Mayer, B.E. Hardin, S.R. Scully, M.D. McGehee, M. Heeney, I. McCulloch, Organic bulk heterojunction solar cells using poly(2,5-bis(3tetradecyllthiophen-2-yl)thieno[3,2,-b]thiophene, Appl. Phys. Lett. 92 (11) (2008) 113309, http://dx.doi.org/10.1063/1.2899996.
- [22] A.C. Mayer, M.F. Toney, S.R. Scully, J. Rivnay, C.J. Brabec, M. Scharber, M. Koppe, M. Heeney, I. McCulloch, M.D. McGehee, Bimolecular crystals of fullerenes in conjugated polymers and the implications of molecular mixing for solar cells, Adv. Funct. Mater. 19 (8) (2009) 1173–1179, http://dx.doi.org/10.1002/ adfm.200801684.
- [23] N.C. Cates, R. Gysel, Z. Beiley, C.E. Miller, M.F. Toney, M. Heeney, I. McCulloch, M.D. McGehee, Tuning the properties of polymer bulk heterojunction solar cells by adjusting fullerene size to control intercalation, Nano Lett. 9 (12) (2009) 4153–4157, http://dx.doi.org/10.1021/nl9023808.
- [24] N.C. Miller, R. Gysel, C.E. Miller, E. Verploegen, Z. Beiley, M. Heeney, I. McCulloch, Z. Bao, M.F. Toney, M.D. McGehee, The phase behavior of a polymer-fullerene bulk heterojunction system that contains bimolecular crystals, J. Polym. Sci. Part B: Polym. Phys. 49 (7) (2011) 499–503, http://dx.doi. org/10.1002/polb.22214.
- [25] P.A. Kienzle, M. Doucet, D.J. McGillivray, K.V. O'Donovan, N. F. Berk, C. F. Majkrzak, (http://www.ncnr.nist.gov/reflpak)(accessed 12.05.05) (2000).
- [26] D. Chen, A. Nakahara, D. Wei, D. Nordlund, T.P. Russell, P3HT/PCBM bulk heterojunction organic photovoltaics correlating efficiency and morphology, Nano Lett. 11 (2) (2011) 561–567, http://dx.doi.org/10.1021/nl103482n.
- [27] S. Kline, Reduction and analysis of SANS and USANS data using IGOR Pro, J. Appl. Crystallogr. 39 (6) (2006) 895–900, http://dx.doi.org/10.1107/ S0021889806035059.
- [28] T.P. Russell, H. Ito, G.D. Wignall, Neutron and X-ray scattering studies on semicrystalline polymer blends, Macromolecules 21 (6) (1988) 1703–1709, http://dx.doi.org/10.1021/ma00184a029.
- [29] M.L. Chabinyc, M.F. Toney, R.J. Kline, I. McCulloch, M. Heeney, X-ray scattering study of thin films of poly(2,5-bis(3-alkylthiophen-2-yl)thieno[3,2-b]thiophene, J. Am. Chem. Soc. 129 (11) (2007) 3226–3237, http://dx.doi.org/ 10.1021/ja0670714.
- [30] Y. Jung, R.J. Kline, D.A. Fischer, E.K. Lin, M. Heeney, I. McCulloch, D. M. DeLongchamp, The effect of interfacial roughness on the thin film morphology and charge transport of high-performance polythiophenes, Adv. Funct. Mater. 18 (5) (2008) 742–750, http://dx.doi.org/10.1002/ adfm 200701089
- [31] L. Chang, H. Lademann, J.-B. Bonekamp, K. Meerholz, A. Moule, Effect of trace solvent on the morphology of P3HT PCBM bulk heterojunction solar cells, Adv. Funct. Mater. 21 (10) (2011) 1779–1787, http://dx.doi.org/10.1002/ adfm.201002372.
- [32] M. Campoy-Quiles, T. Ferenczi, T. Agostinelli, P.G. Etchegoin, Y. Kim, T. D. Anthopoulos, P.N. Stavrinou, D.D.C. Bradley, J. Nelson, Morphology evolution via self-organization and lateral and vertical diffusion in polymer fullerene solar cell blends, Nat. Mater. 7 (2) (2008) 158–164, http://dx.doi.org/10.1038/nmat2102.
- [33] T.J. Savenije, J.E. Kroeze, X. Yang, J. Loos, The effect of thermal treatment on the morphology and charge carrier dynamics in a polythiophene-fullerene bulk heterojunction, Adv. Funct. Mater. 15 (8) (2005) 1260–1266, http://dx.doi.org/ 10.1002/adfm.200400559.
- [34] T. Wang, A.J. Pearson, A.D.F. Dunbar, P.A. Staniec, D.C. Watters, H. Yi, A.J. Ryan, R.A.L. Jones, A. Iraqi, D.G. Lidzey, Correlating structure with function in thermally annealed PCDTBT PC₇₀BM photovoltaic blends, Adv. Funct. Mater. 22 (7) (2012) 1399–1408, http://dx.doi.org/10.1002/adfm.201102510.
- [35] J.W. Kiel, M.E. Mackay, B.J. Kirby, B.B. Maranville, C.F. Majkrzak, Phase-sensitive neutron reflectometry measurements applied in the study of photovoltaic films, J. Chem. Phys. 133 (7) (2010) 074902, http://dx.doi.org/10.1063/ 1.3471583.
- [36] S. van Bavel, S. Veenstra, J. Loos, On the importance of morphology control in polymer solar cells, Macromol. Rapid Commun. 31 (21) (2010) 1835–1845, http://dx.doi.org/10.1002/marc.201000080.
- [37] S. van Bavel, E. Sourty, G.d. With, J. Loos, Three-dimensional nanoscale organization of bulk heterojunction polymer solar cells, Nano Lett. 9 (2) (2009) 507–513, http://dx.doi.org/10.1021/nl8014022.
- [38] C.F. Majkrzak, N.F. Berk, U.A. Perez-Salas, Phase-sensitive neutron

reflectometry, Langmuir 19 (19) (2003) 7796–7810, http://dx.doi.org/10.1021/ la0341254.

- [39] S.A. Holt, A.P. Le Brun, C.F. Majkrzak, F. Heinrich, M. Losche, J.H. Lakey, An ionchannel-containing model membrane structural determination by magnetic contrast neutron reflectometry, Soft Matter 5 (13) (2009) 2576–2586, http: //dx.doi.org/10.1039/B822411K.
- [40] B.J. Kirby, P.A. Kienzle, B.B. Maranville, N.F. Berk, J. Krycka, F. Heinrich, C. F. Majkrzak, Phase-sensitive specular neutron reflectometry for imaging the nanometer scale composition depth profile of thin-film materials, Curr. Opin. Colloid Interface Sci. 17 (1) (2012) 44–53, http://dx.doi.org/10.1016/j. cocis.2011.11.001.
- [41] B.W. Guralnick, B.J. Kirby, C.F. Majkrzak, M.E. Mackay, Morphological characterization of plastic solar cells using polarized neutron reflectivity, Appl. Phys. Lett. 102 (8) (2013) 083305, http://dx.doi.org/10.1063/1.4793423.
- [42] S.W. An, P.N. Thirtle, R.K. Thomas, F.L. Baines, N.C. Billingham, S.P. Armes, J. Penfold, Structure of a diblock copolymer adsorbed at the hydrophobic solid/ aqueous interface effects of charge density on a weak polyelectrolyte brush, Macromolecules 32 (8) (1999) 2731–2738, http://dx.doi.org/10.1021/ ma981146+.
- [43] R.S. Krishnan, M.E. Mackay, C.J. Hawker, B. Van Horn, Influence of molecular architecture on the dewetting of thin polystyrene films, Langmuir 21 (13) (2005) 5770–5776, http://dx.doi.org/10.1021/la0474060.
- [44] R.S. Krishnan, M.E. Mackay, P.M. Duxbury, C.J. Hawker, S. Asokan, M.S. Wong, R. Goyette, P. Thiyagarajan, Improved polymer thin-film wetting behavior through nanoparticle segregation to interfaces, J. Phys.: Condens. Matter 19 (35) (2007) 356003, http://dx.doi.org/10.1088/0953–8984/19/35/356003.
- [45] C. Thompson, G. Palasantzas, Y.P. Feng, S.K. Sinha, J. Krim, X-ray-reflectivity study of the growth kinetics of vapor-deposited silver films, Phys. Rev. B 49 (7) (1994) 4902, http://dx.doi.org/10.1103/PhysRevB.49.4902.
- [46] A. Nelson, Co-refinement of multiple-contrast neutron/X-ray reflectivity data using motofit, J. Appl. Crystallogr. 39 (2) (2006) 273–276, http://dx.doi.org/ 10.1107/S0021889806005073.
- [47] R.S. Krishnan, M.E. Mackay, P.M. Duxbury, A. Pastor, C.J. Hawker, B. Van Horn, S. Asokan, M.S. Wong, Self-assembled multilayers of nanocomponents, Nano Lett. 7 (2) (2007) 484–489, http://dx.doi.org/10.1021/nl062866u.
- [48] E.S. McGarrity, A.L. Frischknecht, M.E. Mackay, Phase behavior of polymer/ nanoparticle blends near a substrate, J. Chem. Phys. 128 (15) (2008) 154904, http://dx.doi.org/10.1063/1.2899329.
- [49] M.M. Wienk, J.M. Kroon, W.J.H. Verhees, J. Knol, J.C. Hummelen, P.A. van Hal, R. A.J. Janssen, Efficient Methano[70]fullerene/MDMO-PPV bulk heterojunction photovoltaic cells, Angew. Chem. Int. Ed. 42 (29) (2003) 3371–3375, http://dx. doi.org/10.1002/anie.200351647.
- [50] J.T. Bloking, T. Giovenzana, A.T. Higgs, A.J. Ponec, E.T. Hoke, K. Vandewal, S. Ko, Z. Bao, A. Sellinger, M.D. McGehee, Comparing the device physics and morphology of polymer solar cells employing fullerenes and non-fullerene acceptors, Adv. Energy Mater. 4 (12) (2014) 1301426, http://dx.doi.org/10.1002/ aenm.201301426.
- [51] L. Wu, H. Zang, Y.-C. Hsiao, X. Zhang, B. Hu, Origin of the fill factor loss in bulkheterojunction organic solar cells, Appl. Phys. Lett. 104 (15) (2014) 153903, http://dx.doi.org/10.1063/1.4871582.
- [52] A. Maurano, R. Hamilton, C.G. Shuttle, A.M. Ballantyne, J. Nelson, B. O'regan, W. Zhang, I. McCulloch, H. Azimi, M. Morana, C.J. Brabec, J.R. Durrant, Recombination dynamics as a key determinant of open circuit voltage in organic bulk a comparison of four different donor polymersheterojunction solar cells, Adv. Mater. 22 (44) (2010) 4987–4992, http://dx.doi.org/10.1002/ adma.201002360.
- [53] M.V. Avdeev, A.A. Khokhryakov, T.V. Tropin, G.V. Andrievsky, V.K. Klochkov, L. I. Derevyanchenko, L. Rosta, V.M. Garamus, V.B. Priezzhev, M.V. Korobov, V. L. Aksenov, Structural features of molecular-colloidal solutions of C₆₀ fullerenes in water by small-angle neutron scattering, Langmuir 20 (11) (2004) 4363–4368, http://dx.doi.org/10.1021/la0361969.
- [54] H. Shen, N.E. Valadez-Perez, B. Guralnick, Y. Liu, M.E. Mackay, Performance enhancement of polymer-based solar cells by induced phase-separation with silica particles, J. Mater. Chem. C 2 (47) (2014) 10087–10100, http://dx.doi.org/ 10.1039/C4TC01947D.
- [55] H.P. Chen, Y.C. Hsiao, B. Hu, M. Dadmun, Tuning the morphology and performance of low bandgap polymer fullerene heterojunctions via solvent annealing in selective solvents, Adv. Funct. Mater. 24 (32) (2014) 5129–5136, http://dx.doi.org/10.1002/adfm.201400552.
- [56] M.E. Mackay, T.T. Dao, A. Tuteja, D.L. Ho, B. Van Horn, H.-C. Kim, C.J. Hawker, Nanoscale effects leading to non-einstein-like decrease in viscosity, Nat. Mater. 2 (11) (2003) 762–766, http://dx.doi.org/10.1038/nmat999.
- [57] A. Tuteja, M.E. Mackay, C.J. Hawker, B. Van Horn, Effect of ideal, organic nanoparticles on the flow properties of linear polymers non-einstein-like behavior, Macromolecules 38 (19) (2005) 8000–8011, http://dx.doi.org/10.1021/ ma050974h.