*Graphical Abstract

Monitoring the Dynamics of Miscible P3HT:PCBM Blends: A Quasi Elastic Neutron Scattering Study of Organic Photovoltaic Active Layers

Thusitha Etampawala¹, Dilru Ratnaweera¹, Brian Morgan¹, Souleymane Diallo², Eugene Mamontov³, Mark Dadmun^{1,4}

¹ The University of Tennessee, Department of Chemistry, Knoxville, TN 37996

² Quantum Condensed Material Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

³ Chemical & Engineering Material Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

⁴ Chemical Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

ABSTRACT:

This work addresses the detail molecular dynamic behavior of miscible blends of Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) and their pure counterparts by quasi-elastic neutron scattering measurements (QENS). The study provides the measure of pico-to-nano time scales of relaxation processes. A single relaxation process was observed in pure P3HT and PCBM while two relaxation processes: one fast and one slow were observed in the blends. The fast process was attributed to the dynamics of P3HT while the slow process was correlated to the dynamics of PCBM. The results show that the relaxation process is a balance between two opposing effects: increase mobility due to thermal activation of P3HT molecules and decrease mobility due to the presence of PCBM which is correlated to the percent crystallinity of P3HT and local packing density of PCBM in the amorphous phase. The threshold for the domination of thermally activated relaxation is between 5 and 9 vol.% of PCBM loading. Two distinct spatial dependences of the relaxation processes in which the cross over length scale depends neither on temperature nor composition were observed for all the samples. They were attributed to the collective motions of the hexyl side chains and the rotational motions of the C-C single bonds of the side chains. These results provide an understanding of the effects of PCBM loading and temperature on dynamics of the polymer-fullerene blends which provides a tool to optimize the efficiency of charge carrier and exciton

transport within the organic photovoltaic (OPV) active layer to improve the high performance of organic solar cells.

Introduction

The molecular dynamics of electron donor and acceptor materials used in organic electronic and opto-electronic devices such as organic photovoltaics and field effect transistors play a key role in applications that require controlled exciton and charge transport across the interfaces. While high production cost of inorganic material limits the fabrication of highly efficient photovoltaics, low band gap polymers and PCBM blends have gained considerable attention over the last decade as a cost-effective material to convert solar energy to electricity [1-5]. Even though power conversion efficiencies of organic photovoltaics (OPV) are limited primarily due to the relatively large binding energy of excitons and limited exciton diffusion length within the OPV active layer, the efficiency of OPVs can be enhanced by controlling the morphology and dynamics of the charge carriers in the matrix. Pioneering work in the OPV field has revealed that device performance is greatly enhanced by controlling the active layer morphology, especially by post-deposition thermal and solvent annealing of the active layer and the use of chemical additives [3-12]. However, one critical issue that remains is the excitons and electron-hole pairs will recombine or become trapped in the matrix as space charges. The space charges inhibit the flow of new carriers, leading to a decrease in device performance. Optimization of the dynamics of the electron acceptor and donors and the coupling of their motions to charge transport are areas that require further study and could be used to improve the performance of conjugated polymer:fullerene active layers. Thus, an understanding of the molecular dynamics of bulk heterojunction materials is needed, as this information will introduce a unique approach to better tune the performance of the final devices.

The current study probes the spatial dependence of the molecular dynamics of the polymer and fullerene on the time scale of pico-to-nano second in blends of poly(3-hexyl thiophene) (P3HT) and

[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) as a function of temperature. In particular, this study will clarify the role of the presence of PCBM on the P3HT motion in the miscible state, whether it is reinforcing (i.e. slows dynamics) or plasticizing (i.e. speeds up dynamics), which will aid in understanding the role of dynamic-assisted transport of excitons, electrons and holes in P3HT:PCBM blends. In contrast to our study, using QENS Paternó et al. [13] recently probed the dynamics of P3HT:PCBM blends consisting of 50 wt.% PCBM that are cast from different solvents; chloroform, chlorobenzene and ortho-dichlorobenzene. These experiments qualitatively observe the frustration of polymer dynamics in the presence of PCBM, but do not observe an appreciable difference in the frustration as a function of the solvent choice. In another study, Gulbinas et al. [14] examined the correlation between the dynamics of the donor and the acceptor to that of the dynamics of charge transport of as-spun and annealed P3HT:PCBM films using ultrafast time-resolved optical probing. They found that the sub nanosecond initial carrier drift rates increased to nanosecond time scales after annealing the blends. Their Monte Carlo simulation studies have further shown that an increase in carrier separation rate reduces the probability of charge recombination and thus enhanced the yield of free charge carrier generation.

In contrast to other techniques that measure molecular dynamics, QENS provides a method to probe the spatial dependence of molecular motions such as rotation, segmental relaxation and diffusion, where a variation in Q (momentum transfer vector) can be equated to a change in the magnification of a microscope. Consequently, the same dynamic process can be observed over a variety of spatial scales or a single dynamic process that only occurs at a given length scale can be selectively probed. These QENS results mainly monitor the dynamic information of the P3HT hexyl side chains as P3HT holds thirteen hydrogen atoms on the side chain and just one hydrogen atom on the thiophene backbone. This is also true in the PCBM blends, as the PCBM has a very small

incoherent cross sectional contribution that exclusively comes from the butyric acid methyl ester group of PCBM.

The molecular structure of the P3HT and PCBM are presented in Figures 1a and b respectively. Pristine P3HT and PCBM are both semi-crystalline. Recent small angle neutron scattering studies indicate that P3HT and PCBM blends below *ca.* 20 wt.% PCBM are composed of a two phase complex interpenetrated network of nano-scale crystalline and amorphous P3HT domains in which PCBM molecules are exclusively confined to the amorphous regions of the matrix [7]. Increasing the PCBM loading above ~20 wt.% results in the phase separation of PCBM into a separate phase forming a three phase structure that consists of pure crystalline P3HT domains, PCBM rich phase and a miscible phase of amorphous P3HT and PCBM [7, 15].

Figure 1. Molecular structures of (a) poly(3-hexylthiophene) (P3HT) and (b) [6,6]-phenyl-C61-butyric acid methyl ester (PCBM).

It is difficult to observe a sharp glass transition temperature, T_g for semicrystalline polymeric materials such as P3HT as suggested by many studies in which T_g of P3HT was found in the range of -14 °C to 24 °C [16-18]. Moreover, Kim et al. [19] showed that the T_g of P3HT elevates from -14 °C to 51 °C with increases PCBM loading from 0 wt.% to 75 wt.%. Even though an elevated T_g is observed,

the melting point and the crystallization temperature decreased from 225 °C to 205 °C and 190 °C to 160 °C respectively with the addition of 12.5 wt.% PCBM.

Recently, Yazawa et al. [20] have distinguished three relaxation processes as a function of temperature for polythiophenes decorated with butyl side chains using NMR spin-lattice relaxation. Below T_g of the polymer, a slow β -relaxation, which is an Arrhenius-type thermally activated process [21] dominates. At $T_g < T < 1.2T_g$, both the β -relaxation and α -relaxation processes, which are modeled by stretched exponential functions, occur simultaneously. Finally, at $T > 1.2T_g$, the α -relaxation process dominates. Further, they recognize that twist-like motions began in the thiophene units at about 300 K to 340 K. At temperatures greater than the twist glass transition temperature, most of the poly(3-alkylthiophenes) become plastic crystals in which twist-like motions can be observed even in the crystalline states.

Particularly in this study we elucidate the pico-to-nano second molecular relaxation processes in miscible P3HT:PCBM blends as a function of PCBM loading and contrast this to the dynamics of their pure counterparts at 313 K and 428 K by quasi-elastic neutron scattering. A single relaxation process is observed in the neat components while two processes, one fast and one slow, are identified in the blends. The results clearly show that the PCBM loading and temperature provides unique tools to precisely tune the local dynamics of the components in an OPV active layer, which in turn may provide additional insight that can be used to impact the mobility of excitons and charge carriers.

Experimental

Blend Preparation. Hydrogenated regioregular poly(3-hexylthiophene) [P3HT, $M_n = 25$ kg/mol] and [6,6]-phenyl-C61-butyric acid methyl ester [PCBM, >99.5%] were purchased from Sigma-Aldrich. Both compounds were used without further purification. Four QENS samples were prepared, neat P3HT, neat PCBM, 5:95 wt.% PCBM:P3HT and 10:90 wt.% PCBM:P3HT, by deposition from dichloromethane solutions. The solution was deposited onto glass slides and allowed

to dry at room temperature followed by in a vacuum oven for overnight. The resulting films were used without further modification for the quasi elastic neutron scattering measurements.

QENS Experiment. The QENS measurements were completed on the BASIS instrument at the Spallation Neutron Source at the Oak Ridge National Laboratory. All the measurements were performed in the standard operation regime with 3.5 μeV (overall Q) energy resolution. The films were loaded into rectangular aluminum sample holders and sealed. The backscattering spectra of each sample were collected in situ at 100 K, 313 K and 428 K at Q values ranging from 0.3 $\text{\AA}^{-1}$ to 1.55 $\text{\AA}^{-1}$. The corresponding spectra collected at 100 K where all relevant motions freeze on the instrument time scale were used as the instrument resolution function, which is dominated by the elastic scattering of the sample. The slightly higher broadening visible on the positive energy transfer side of all the quasi elastic peaks is caused by the specific design of the analyzer and it is not related to the samples [22]. The sample thickness of 0.12 ± 0.02 mm was used to provide transmissions higher than 90% so that multiple scattering effects are negligible. The acquired data were corrected for detector efficiency and sample container before converting the time of flight spectra to energy transfer, $I(Q, \omega)$ vs. ΔE , representation.

Data Analysis. The QENS spectra were analyzed using DAVE [23] (Data Analysis and Visualization Environment) software developed at the National Institute of Standards and Technology (NIST). The dynamic range of $\pm 100 \mu\text{eV}$, where the instrument background is known to be linear, was selected for the data analysis. In general, the measurable quantity that provides dynamic information of the samples in QENS experiment is the dynamic scattering function, $S(Q, \omega)$ where Q is the magnitude of the momentum transfer and ω is the frequency of the transferred energy. As shown in Equation 1, the experimentally observed intensity, $I_{\text{exp}}(Q, \omega)$, as a function of energy transfer can be considered as the

dynamic scattering function convoluted with the instrumental resolution function and a linear background term.

$$I_{exp}(Q, \omega) = S(Q, \omega) \otimes R(Q, \omega) + Bkg \quad (1)$$

In general, the resolution function, $R(Q, \omega)$, is the quasi-elastic spectrum of the sample obtained when only purely elastic scattering events take place. In this study, we used the QENS spectrum of the same sample obtained at 100 K where all the dynamic processes except elastic events are frozen, as the $R(Q, \omega)$. The background term accounts the dynamic processes that are faster than the instrument resolution. As shown in Equation 2, the $S(Q, \omega)$ term of the data obtained in the BASIS instrument is generally modeled as the sum of two different contributions [24]: elastic and quasi-elastic components. It should be noted that the inelastic structure factor, $S_{IN}(Q, \omega)$, is inaccessible due to the accessible energy window of the BASIS instrument..

$$S(Q, \omega) = DWF \{ A_0(Q) \delta(\omega) + (1 - A_0(Q)) S_{QE}(Q, \omega) \} \quad (2)$$

In Equation 2, DWF is the Debye–Waller factor, $A_0(Q)$ is the elastic incoherent structure factor that describes the fraction of the scattering that is elastic, $\delta(\omega)$ is the delta function that accounts for the elastic peak at $\omega = 0$ and $S_{QE}(Q, \omega)$ is the quasi-elastic scattering. The $S_{QE}(Q, \omega)$ term in Equation 2 appears as a broadening of the elastic peak around $\omega = 0$, and provides information about the diffusive and relaxation processes in the sample.

The Fourier transform of the intermediate scattering function, $FT[S(Q, t)]$, is also known as the dynamic scattering function, $S(Q, \omega)$. $FT[S(Q, t)]$ reflects the pair and auto correlation functions of nuclei in the sample. Sub-linear dependence of relaxation times is observed in our experiment, which is generally explained as anomalous relaxation process. This is attributed to the presence of a distribution of relaxation processes and/or gradients in the dynamics of the sample due to relaxation of components in different environments. This heterogeneity can be modeled by the phenomenological Kohlrausch-Williams-Watts (KWW) equation [24] where $S(Q, t)$ is described in Equation 3.

$$S(\omega, t) = A(\omega) \exp \left[- \left(\frac{t}{\tau_{KWW}(\omega, T)} \right)^{\beta} \right] \quad (3)$$

where $A(\omega)$ is the prefactor, τ_{KWW} is the characteristic KWW relaxation time and β is the stretching exponent that can take any value between 0 and 1.

Since the P3HT and PCBM are semi-crystalline materials, the dynamic scattering functions were modeled using one KWW function to account for the relaxation processes of each amorphous component. We assume that the dynamics of the crystalline domains are out of the energy resolution of the BASIS instrument. In P3HT:PCBM mixtures below *ca.* 20 vol.% PCBM loading, it is known that PCBM molecules readily mix and distribute homogeneously in the amorphous P3HT domains [7, 25, 26]. Thus, the blends require the use of two KWW functions; one for P3HT and the other for PCBM. For the sake of simplicity, two KWW functions were combined linearly as shown in Equation 4 to account for the dynamics of both components in the blends.

$$S(\omega, t) = A_1(\omega) \exp \left[- \left(\frac{t}{\tau_{KWW-1}(\omega, T)} \right)^{\beta_1} \right] + A_2(\omega) \exp \left[- \left(\frac{t}{\tau_{KWW-2}(\omega, T)} \right)^{\beta_2} \right] \quad (4)$$

In Equation 4, the subscripts 1 and 2 represent the relaxation of each component. Moreover, in this equation $A_1(\omega)$ and $A_2(\omega)$ encapsulate the relative spectral weights of each relaxation process, and is set by area under the curve. At the beginning of the fitting process, we set the spectral weights to the relative ratio of total incoherent cross sectional contributions of P3HT and PCBM as determined from their molecular formula. However, the quality of fits was improved by fitting all three parameters: $A_i(\omega)$, KWW relaxation time and β . We will discuss the meaning and the interpretation of each parameter in the results and discussion section.

Results and Discussion

The dynamics of pure P3HT, pure PCBM and their blends at 5 and 10 wt.% PCBM loadings were determined as a function of temperature, where the motion of P3HT and PCBM side chains fall within the time scale of the neutron backscattering instrument (BASIS) at ORNL. The QENS experiments were completed at 313 K and 428 K as they are above the glass transition temperature of the pure P3HT and they represent important temperatures in the operation and processing of P3HT:PCBM photovoltaic devices. 313 K is slightly above room temperature and therefore mimics typical operating temperature of a solar cell, while 428 K approximates the temperature at which P3HT:PCBM active layers are annealed after deposition. A comparison of the dynamic structure factor, $S(Q,\omega)$, of the four samples studied as a function of energy transfer, ΔE , at two momentum transfer windows, $0.3 \text{ \AA}^{-1}$ and $1.55 \text{ \AA}^{-1}$, and the two temperatures are presented in Figure 2. All of these QENS spectra consist of a sharp peak centered at $\Delta E = 0$ and an expansive tail around $\Delta E = 0$. The width of the quasi-elastic peak correlates to the motion of the hydrogen atoms within the sample. For all momentum transfer windows, the pure P3HT has the broadest peak, while the pure PCBM sample has the narrowest peak, indicating that the motions of the P3HT are the fastest, while those of PCBM are the slowest. Moreover, the presence of PCBM in the P3HT samples decreases the width of the quasi elastic peak, yet the spectral shapes of the blend samples are similar to those of the pure P3HT. This confirms that the behavior of all blends is dominated by the dynamics of P3HT rather than the dynamics of PCBM. Further, the decrease of the peak width in the presence of PCBM is indicative of the slowing down of the polymer dynamics associated with the presence of the PCBM.

Figure 2. QENS spectra of pure P3HT, pure PCBM and their blends obtained at 313 K (a & b) and 428 K (c & d) at $Q = 0.3 \text{ \AA}^{-1}$ and $Q = 1.55 \text{ \AA}^{-1}$ respectively. Scattering intensities have been normalized to the maximum intensity. The y-axes are in log scale and x-axes are in linear scale. Symbols represent the experimental data and solid lines that coincide with the data represent the best fits to the models described in the text. A representative resolution function is shown in black dotted line. Note that the x-axis is truncated to $\pm 100 \text{ \mu eV}$ for clarity.

The impact of increased temperature on the local dynamics in P3HT:PCBM blends is not obvious. For instance, it is known that [27-29] annealing at high temperatures ($\sim 150 \text{ }^{\circ}\text{C}$) increases the crystallinity of the P3HT, where the fullerene molecules are excluded from the newly formed crystalline domains. Consequently, the packing density of PCBM in the remaining amorphous P3HT domains increases, leading to a possible enhancement of the steric hindrance of the motion of amorphous hexyl chains. At the same time, one would expect that the local motions of the P3HT side chains would become faster at elevated temperatures. Therefore, at high temperatures, it is expected that two opposite effects govern the relaxation processes of the P3HT: increased temperature promotes

faster dynamics and steric hindrance imposed by increasing the number density of PCBM molecules reduces the dynamics. Consequently, it is difficult to predict the changes in the quasi elastic peaks of the P3HT:PCBM blends with an increase in temperature.

Characterization of the Dynamic Processes. One can classify at least seven primary inter-conformational motions for pure P3HT in terms of the hydrogens that exist in different environments: the motions of the methyl group and of the five methylene groups on the hexyl side chains, along with the hydrogen attached to poly(thiophene) backbone. Given this complexity, some approximations must be made to simplify and interpret the QENS results. A recent solid state NMR study [8, 20, 30] of P3HT:PCBM blends has shown that the correlation time of the twisting motions of the poly(thiophene) backbone are on the time scale of nano-seconds which is out of the energy resolution of our measurements. Thus, the backbone motions of the poly(thiophene) are excluded from the analysis of the dynamics of the system in this experiment. For further simplicity, we assume that all hydrogens in the hexyl side chain relax on the same correlation time scale. However, one can expect a distribution of associated times for the localized motions and possibly a gradient of the dynamics due to variation in the local environment of the different hydrogens.

Such a distribution of different time scales of dynamics in polymers are modeled well by the phenomenological Kohlrausch-Williams-Watts (KWW) equation as described in the experimental section. In general, the relaxation times of both small molecules and polymeric systems show a strong temperature and q dependence. However, the stretched exponent, β , shows very little dependence on either temperature or momentum transfer vector for most polymeric systems [31-33]. Two approaches were attempted to analyze the data using the KWW equation, one where β_{KWW} is fitted, and the other where β_{KWW} is set to a constant value. When allowed to vary while fitting the data to the KWW equation, a good fit is only found when β_{KWW} approaches 0.5 ± 0.02 . In the second approach, the data was fitted to the KWW equation by fixing beta to 0.2, 0.5 or 0.8. These values were chosen as the

value of β is related to the heterogeneity of the motions in the system. When $\beta = 1$, all nuclei move in a simple manner and an exponential decay is observed rather than a stretched exponential decay. Values of $\beta_{\text{KWW}} < 1$ indicate an increase in the heterogeneity of the motion of the system, where $0.4 < \beta_{\text{KWW}} < 0.6$ is typical for macromolecules. A good fit of the data to the KWW equation was only obtained when β_{KWW} is set to 0.5. Thus, we fit all of the data to the KWW equation with $\beta_{\text{KWW}} = 0.5$, which are then interpreted to gain insight into the molecular dynamic processes of the blends of P3HT:PCBM and their pure counterparts.

Determination of P3HT Crystallinity from QENS Data: As discussed in the data analysis section, the dynamics of the pure P3HT or PCBM samples were modeled using a single KWW function while the blends require the use of two KWW functions; one for P3HT and the other for PCBM. A representative data of a blend with the contribution of each function is presented in Figure 3. The KWW 1 accounts the dynamics of P3HT while KWW 2 accounts the dynamics of PCBM. The area under the curve of each KWW function accounts for the relative contributions of each different component in the blends to the overall scattering curve. The relative contributions to the coherent and incoherent scattering of the components in the samples as determined from the component scattering cross sections are given in Table 1. In both blends, the incoherent scattering of P3HT clearly dominates and slightly decreases with increasing the PCBM loading, which is consistent with a decrease in the width of the quasi-elastic peak with increasing PCBM loading.

Figure 3. Representative data (90:10 wt.% P3HT:PCBM at 313 K) and the functions used to model the data as explained in the text. The symbols correspond to the experimental data while solid lines correspond to the functions. Note that x-axis is truncated to $\pm 40 \mu\text{eV}$ for clarity.

Table 1. Contributions to the incoherent and coherent scattering from P3HT and PCBM in each sample

Sample	Inc. Scat. from P3HT (%)	Coh. Scat. from P3HT (%)	Inc. Scat. from PCBM (%)	Coh. Scat. from PCBM (%)
100% P3HT	93.27	6.73	0.00	0.00
100% PCBM	0.00	0.00	72.20	27.80
95%P3HT+5%PCBM	92.13	6.65	0.88	0.34
90%P3HT+10%PCBM	90.89	6.56	1.84	0.71

Inspection of these results shows that the relative area under the KWW fits are not consistent with the ratios of the theoretical values calculated for the blends using the relative incoherent cross section of the components. This is not surprising because the relative expected contributions will only be observed if the samples are 100% amorphous. The presence of crystalline domains in pure P3HT and P3HT:PCBM blends decreases the incoherent scattering contribution to the broadening of QENS profiles. Therefore, the differences between the theoretically expected and observed ratios are

attributed to the presence of P3HT crystalline domains. Furthermore, the growth of P3HT crystalline domains (i.e. decrease in amorphous P3HT) with increasing temperature decreases the contributions of P3HT to the broadening of the quasi-elastic peak.

Table 2. Expected and observed relative contribution of each component in the blends to the total scattering.

Sample	Expected [*]	Observed	
		313 K	428 K
95%P3HT+5%PCBM	99.05 : 0.95	81.28 : 18.72	78.92 : 21.08
90%P3HT+10%PCBM	98.02 : 1.98	78.76 : 21.24	76.97 : 23.04

^{*} It is assumed that the blends are 100% amorphous to calculate the expected values.

The crystalline domains mainly have vibrational motions, which are not within the QENS energy resolution. Consequently, the growth of crystalline domains decreases the contributions to its line broadening of QENS spectra. This means that one can estimate the percent P3HT crystallinity, a characteristic that is difficult to accurately determine by other techniques in the blends by determining the relative area under the curves of KWW fits with respect to the estimated contributions determined by the theoretical incoherent cross sections. The results of this analysis are presented in Table 3, which shows that the blends exhibit *ca.* 20% crystallinity and it is interesting to note that these values follow trends observed by many other studies: the percent crystallinity increases with increasing PCBM loading and annealing temperature of the blends [2, 11, 26, 27, 29, 34, 35].

Table 3. Percent P3HT crystallinity of the blends calculated from the observed relative contribution of each component in the blends to the total scattering.

Sample	Observed % Crystallinity	
	313K	428K
95%P3HT+5%PCBM	17.9±0.3	20.3±0.2

90%P3HT+10%PCBM	19.6 ± 0.4	21.5 ± 0.6
-----------------	----------------	----------------

Impact of the Presence of PCBM on the Dynamics of P3HT: The spatial dependence of the two relaxation times obtained from the analysis of the QENS data using the KWW equation for all samples at 313 K and 428 K are presented in Figure 4. The main figures show the spatial dependence of the relaxation time of the fast process while the corresponding insets show the relaxation times of the slow process. The relaxation times vary in the range of *ca.* 10 ps to *ca.* 500 ps for the fast processes and *ca.* 30 ps to *ca.* 800 ps for the slow processes. The time scales of the fast processes in the blends are similar to the time scale of the motions of pure P3HT, while the slow processes are the same order of magnitude as the relaxation times of pure PCBM. The relaxation times of fast process of the blends are slightly higher than those of the relaxation times of the pure P3HT indicating a decrease in the dynamics of the hexyl side chains with inclusion of PCBM into the amorphous P3HT. Interestingly, with increasing temperature the relaxation times of the fast process decrease. This can be attributed to the balance between two opposing effects: increase mobility due to thermal activation of P3HT motions and decrease mobility due to an increase in effective PCBM loading in the amorphous P3HT due to the P3HT crystallization. In contrast, the fast process of PCBM shows little change at low temperature, while more variation in the PCBM motion is observed at the high temperature and large length scales (i.e. low momentum transfer vectors). The marginally different relaxation times, particularly at high Q (i.e. at small length scales) indicate that common relaxation processes occur in all systems on these length scales. We attribute these dynamics to the C-C rotational motions of the side chains of both PCBM and P3HT, which will be discussed in detail later in this discussion.

Figure 4. Composition dependence of relaxation time of the fast process and slow process (inset) obtained from KWW fits of neat P3HT, neat PCBM and the blends of P3HT/PCBM at (a) 313 K and (b) 428 K.

The relaxation times of P3HT at a given composition as a function of temperature are presented in Figure 5, which provides the information required to correlate the variation in the dynamics of P3HT to the PCBM loadings and temperature. At 10 wt.% PCBM loading, the relaxation times of the P3HT side chains at 313 K are slightly higher than that of the 5wt.% loaded sample. The enhancement of PCBM loading imposes steric hindrance by the bulky PCBM molecules to the motion of the amorphous hexyl chains on P3HT molecules. Consequently, the dynamics of P3HT are dominated by PCBM loading rather than the thermal effects. However, at 5wt.% PCBM loading, the relaxation times decrease slightly with increasing temperature from 313 K to 428 K. In contrast, at 10 wt.% PCBM loading, the relaxation times of P3HT decrease significantly with respect to the relaxation times of the 313K samples for all momentum transfer vectors. These results show that the dynamics of the P3HT hexyl side chains at 5 wt.% PCBM loading are a delicate balance between thermal effects which enhance the dynamics with increasing temperature and the effects of PCBM loading which decreases side chain dynamics due to the steric hindrance. Moreover, at higher temperature, the steric hindrance is further aggravated due to an increase in effective PCBM loading in the amorphous P3HT because the P3HT crystallinity increases. Table 3 shows that increasing the temperature from 313 K to 428 K

increases the crystallinity by $\sim 2\%$. These values of P3HT crystallinity allow us to estimate the increase in the volume fraction of PCBM in the amorphous phase for each sample. This calculation shows that the local packing density of PCBM in the amorphous phase is 4.52 vol.% in the 5 wt.% (3.7 vol%) PCBM sample at 313 K and 4.64 vol.% in this sample at 428 K and is 9.42 vol.% in the 10 wt.% (7.5 vol%) PCBM sample at 313 K and 9.61 vol.% in this sample at 428 K. Note that the 5 wt.% and 10 wt.% PCBM loadings are equivalent to the 3.71 vol.% and 7.54 vol.% respectively assuming the densities of PCBM and P3HT are 1.5 g cm^{-3} and 1.1 g cm^{-3} respectively. Thus, it is clear that there exists a threshold loading of PCBM in the amorphous phase below which the presence of the PCBM dominates the dynamics of the P3HT side chains, but above this amount thermal effects dominate the hexyl motions, where this threshold is between 5 and 9 vol.% PCBM.

Figure 5. The spatial dependence of the relaxation time of P3HT at 313 K and 428 K of (a) 5 wt% PCBM loading and (b) 10 wt% PCBM loading.

Spatial Dependence of P3HT Dynamics: In order to evaluate the spatial dependence of the dynamic processes present in these systems, the spatial variations of the relaxation times are presented in Figure 6. In this representation, the existence of two dynamic regimes is apparent. The crossover between these regimes is located between $Q = 0.9 \text{ \AA}^{-1}$ and $1.1 \text{ \AA}^{-1}$, i.e. $\sim 6 \text{ \AA}$. Interestingly, the crossover length

scale depends neither on temperature nor composition. The dynamics of the length scale above ~ 6 Å may be attributed to the collective motions (i.e. random diffusion as a whole) of the side chains which show near Q^{-2} time dependence as shown in Table 4. However, when the side groups attach to larger groups such as the P3HT backbone, their freedom of motion is restricted and hence the time dependence deviates from Q^{-2} dependence. The dynamic processes below ~ 6 Å are attributed to local motions of individual segments, such as the crankshaft rotational motion of the side chains. The crankshaft motions have been observed as relaxation processes in certain polymers where, these rotors can be methylene, ethylene, or aromatic groups, as well as some complex substructures [36, 37].

Figure 6. Spatial dependence of the KWW relaxation times obtained from the fits for the fast and slow processes. The solid lines represent the q range that we used to calculate the n . The corresponding n values are given in Table 4.

Our analysis, as expected, indicates that the dynamics of the PCBM increases with increasing temperature, regardless of the P3HT content. However, in the presence of P3HT, the dynamics of PCBM decrease relative to those of pure PCBM. This is exemplified at 428K, where Figure 4-b shows an increase in the PCBM relaxation times with PCBM loading. The slower dynamics of PCBM in the presence of P3HT is attributed to the steric hindrance imposed by P3HT to the motions of the phenyl

butyric acid methyl ester side chains. With increasing PCBM content from 5wt.% to 10wt.%, the PCBM dynamics further decreases due to an increase in the number density of the PCBM molecules in the amorphous P3HT phase. It has been shown that the distribution of PCBM in P3HT with comparatively low loadings especially well below the miscible limit (*ca.* 20 wt.% PCBM) is homogeneous and distributed only in the amorphous phase of P3HT [7]. Consequently, almost all the PCBM feels the same environment and undergo similar relaxation processes. However, as shown in the inset of Figure 4-b, an increase in the **PCBM** relaxation times with increasing PCBM loading is observed at 428K. This is attributed to the steric hindrance introduced by increasing PCBM loading in the P3HT amorphous phase.

Table 4. The spatial dependence of the KWW relaxation times at 313 K and 428 K for the fast and slow processes.

Sample	313 K		428 K	
	Fast Process	Slow Process	Fast Process	Slow Process
100% P3HT	2.20	NA	2.28	NA
100% PCBM	NA	2.01	NA	2.02
95% P3HT	2.27	2.02	2.36	2.03
90% P3HT	2.34	2.02	2.41	2.04

Conclusions

The detail molecular dynamic information of a miscible organic photovoltaic active layer blend: P3HT and PCBM were provided by careful analysis of quasi elastic neutron scattering profiles. A single relaxation process was observed in pure components while two relaxation processes: one fast and one slow were used to explain the dynamics of the blends. The fast process was attributed to the dynamics of P3HT while the slow process was correlated to the dynamics of PCBM. The QENS

analysis demonstrated that the presence of the PCBM slows down the dynamics of P3HT side chains. The variations in the dynamics of P3HT to the PCBM loadings and temperatures were correlated to the percent crystallinity of P3HT and the local packing density of PCBM in the amorphous phase. Further we found that the PCBM loading between 5 and 9 vol.% is a threshold that determines the thermally activated dynamics of these blends. Below this limit steric hindrance of PCBM controls the relaxation of hexyl side chains. The spatial dependence of the relaxation processes clearly exhibits two distinct relaxation time scales in which the cross over length scales depends neither on composition nor temperature. One relaxation time scale was attributed to the collective motions of the hexyl side chains while the other one is due to the rotational motions of the C-C single bonds of the side chains.

The results presented here suggest that the relative percentage of PCBM and P3HT in the OPV active layer and the temperature is critical to tune the dynamics of electron donor and acceptor molecules which will ultimately determine the device performance. Thus, regulating the dynamics of OPV active layer components can be as important as modification of morphologies in determining the efficiency of the BHJ devices.

Acknowledgement

The authors wish to acknowledge the Sustainable Energy Education Research Center and the Joint Institute for Neutron Sciences at the University of Tennessee, as well as the National Science Foundation (DMR-1005987) for support of this project. MDD also acknowledges the support of the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering. The quasi-elastic neutron scattering measurements conducted using the BASIS at ORNL's Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy.

References

1. He ZC, Zhong CM, Su SJ, Xu M, Wu HB, and Cao Y. *Nature Photonics* 2012;6(9):591-595.
2. Po R, Maggini M, and Camaioni N. *Journal of Physical Chemistry C* 2010;114(2):695-706.
3. Ma WL, Yang CY, Gong X, Lee K, and Heeger AJ. *Advanced Functional Materials* 2005;15(10):1617-1622.
4. Chen HP, Hu S, Zang HD, Hu B, and Dadmun M. *Advanced Functional Materials* 2013;23(13):1701-1710.
5. Chen HP, Peet J, Hu S, Azoulay J, Bazan G, and Dadmun M. *Advanced Functional Materials* 2014;24(1):140-150.
6. Ameri T, Khoram P, Min J, and Brabec CJ. *Advanced Materials* 2013;25(31):4245-4266.
7. Yin W and Dadmun M. *ACS Nano* 2011;5(6):4756-4768.
8. Martini F, Borsacchi S, Spera S, Carbonera C, Cominetti A, and Geppi M. *Journal of Physical Chemistry C* 2013;117(1):131-139.
9. Chirvase D, Parisi J, Hummelen JC, and Dyakonov V. *Nanotechnology* 2004;15(9):1317-1323.
10. Li G, Shrotriya V, Yao Y, and Yang Y. *Journal of Applied Physics* 2005;98(4).
11. Vanlaeke P, Swinnen A, Haeldermans I, Vanhoyland G, Aernouts T, Cheyns D, Deibel C, D'Haen J, Heremans P, Poortmans J, and Manca JV. *Solar Energy Materials and Solar Cells* 2006;90(14):2150-2158.
12. Chen DA, Nakahara A, Wei DG, Nordlund D, and Russell TP. *Nano Letters* 2011;11(2):561-567.
13. Paterno G, Cacialli F, and Garcia-Sakai V. *Chemical Physics* 2013;427:142-146.
14. Abramavicius V, Vithanage DA, Devizis A, Infahsaeng Y, Bruno A, Foster S, Keivanidis PE, Abramavicius D, Nelson J, Yartsev A, Sundstrom V, and Gulbinas V. *Physical Chemistry Chemical Physics* 2014;16(6):2686-2692.

15. Watts B, Belcher WJ, Thomsen L, Ade H, and Dastoor PC. *Macromolecules* 2009;42(21):8392-8397.
16. Kuila BK and Nandi AK. *Macromolecules* 2004;37(23):8577-8584.
17. Zhao Y, Yuan GX, Roche P, and Leclerc M. *Polymer* 1995;36(11):2211-2214.
18. Hugger S, Thomann R, Heinzl T, and Thurn-Albrecht T. *Colloid and Polymer Science* 2004;282(8):932-938.
19. Kim JY and Frisbie D. *Journal of Physical Chemistry C* 2008;112(45):17726-17736.
20. Yazawa K, Inoue Y, Yamamoto T, and Asakawa N. *Physical Review B* 2006;74(9).
21. Johari GP and Goldstein M. *Journal of Chemical Physics* 1970;53(6):2372-&.
22. Mamontov E and Herwig KW. *Review of Scientific Instruments* 2011;82(8):085109.
23. Azuah RT, Kneller LR, Qiu YM, Tregenna-Piggott PLW, Brown CM, Copley JRD, and Dimeo RM. *Journal of Research of the National Institute of Standards and Technology* 2009;114(6):341-358.
24. Bée M. *Quasielastic Neutron Scattering*, illustrated ed.: Adam Hilger, 1988.
25. Chen HP, Hegde R, Browning J, and Dadmun MD. *Physical Chemistry Chemical Physics* 2012;14(16):5635-5641.
26. Collins BA, Gann E, Guignard L, He X, McNeill CR, and Ade H. *Journal of Physical Chemistry Letters* 2010;1(21):3160-3166.
27. Campoy-Quiles M, Ferenczi T, Agostinelli T, Etchegoin PG, Kim Y, Anthopoulos TD, Stavrinou PN, Bradley DDC, and Nelson J. *Nature Materials* 2008;7(2):158-164.
28. van der Hofstad TGJ, Di Nuzzo D, van den Berg M, Janssen RAJ, and Meskers SCJ. *Advanced Energy Materials* 2012;2(9):1095-1099.

29. Agostinelli T, Lilliu S, Labram JG, Campoy-Quiles M, Hampton M, Pires E, Rawle J, Bikondoa O, Bradley DDC, Anthopoulos TD, Nelson J, and Macdonald JE. *Advanced Functional Materials* 2011;21(9):1701-1708.
30. Yazawa K, Inoue Y, Shimizu T, Tansho M, and Asakawa N. *Journal of Physical Chemistry B* 2010;114(3):1241-1248.
31. Sakai VG, Maranas JK, Peral I, and Copley JRD. *Macromolecules* 2008;41(10):3701-3710.
32. Gerstl C, Schneider GJ, Fuxman A, Zamponi M, Frick B, Seydel T, Koza M, Genix AC, Allgaier J, Richter D, Colmenero J, and Arbe A. *Macromolecules* 2012;45(10):4394-4405.
33. Cendoya I, Alegria A, Alberdi JM, Colmenero J, Grimm H, Richter D, and Frick B. *Macromolecules* 1999;32(12):4065-4078.
34. Fukushima T, Kimura H, Shimahara Y, and Kaji H. *Applied Physics Letters* 2011;99(22).
35. Verploegen E, Mondal R, Bettinger CJ, Sok S, Toney MF, and Bao ZA. *Advanced Functional Materials* 2010;20(20):3519-3529.
36. Moro GJ. *Journal of Physical Chemistry* 1996;100(40):16419-16422.
37. David L, Girard C, Dolmazon R, Albrand M, and Etienne S. *Macromolecules* 1996;29(26):8343-8348.