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Increased order and improved hole mobility in MEH-PPV thin films by removing shortest chains

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ABSTRACT

The effect of polydispersity on morphology and charge transport in MEH-PPV drop-cast films was investigated using grazing incidence X-ray diffraction and time-of-flight. Removing short chain segments promoted the capability of crystallization resulting in higher hole mobility and non-dispersive transport down to lower temperatures. The slope for the Poole–Frenkel relationship at 298 K was increased, and its change with temperature decreased, indicating reduced spatial inhomogeneity. Analysis using Bässler's Gaussian disorder model, found minimal impact on energy disorder and infinite temperature zero field mobility. A good fit for hopping site separation and spatial disorder was only possible for the lower polydispersity device, suggesting that the lower polydispersity films have less mesoscopic inhomogeneity.

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1. Introduction

Conjugated or semiconducting polymer thin films have been the focus of extensive investigations over the years due to their potential use in the active layer in light emitting and light collecting devices alone or bulk heterojunction structures [1]. Such thin films are also of considerable scientific interest due to mesoscopic, i.e., between the atomic/molecular scale (angstroms) of individual atoms and molecules, and the microscopic scale (micrometres and up) where the bulk properties dominate, structural inhomogeneity. As this regime (\sim 5 to \sim 100 nm) lies in a blind area for traditional optical techniques, i.e., less than the diffraction limit and greater than the Förster radius, it is only recently, with the advent of Atomic Force Microscopy (AFM) based techniques and higher power X-ray sources, that direct observations of this supermolecular organization have been reported [2–9]. In general, these studies showed that polymer films are composed of ordered, sometimes crystalline, domains formed by interacting polymer chains embedded in a disordered matrix formed by less or non-interacting polymer molecules [10].

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While mesoscopic inhomogeneity influences many macroscopic properties of the thin films, its importance to charge transport is one of the best studied. Monte Carlo simulations by Rakhmanova and Conwell [11] showed that the inclusion of spacial (structural) inhomogeneity into the Gaussian Disorder Model (GDM) [12] was necessary to fit the experimental data for thin films of MEH-PPV. Blom and Vissenberg [13], seeking to understand the experimentally observed relationship between mobility and electric field in PPV, showed that incorporating alternating regions of high and of low mobility into the GDM could extend the predicted Poole-Frenkel type behavior down to lower fields as observed experimentally. In their simulation, they found that while carriers moved rapidly through regions of high mobility, these areas also served as traps forcing long jumps across the regions of lower mobility. Currentsensing atomic force microscopy (CS-AFM) and Kelvin probe microscopy (KFM) measurements identify the crystalline or ordered domains as having relatively higher conductivity and the disordered phase in which they are embedded as having a relatively lower conductivity [14]. Inigo et al. [15] compared the mobility in MEH-PPV films in which 50% of the film was in ordered cylindrical domains oriented in the direction of charge transport embedded in an amorphous matrix with films whose ordered domain structure was destroyed by deposition under the influence of an external electric field. Their slightly non-intuitive result an order of magnitude increase in mobility by removing higher





conductivity ordered domains – was; however, in accord with the predictions of Blom and Vissenberg [13]. Further work by this group on spin coated films in which the large domains were broken up, showed that the film structure, and transport properties, is further complicated by the formation of a thin (\sim 5 nm) high electron density layer between the substrate and the bulk of the thin film which along with a preferential lateral extension of the polymer backbone in the spin plane results in mobility being highly anisotropic [16].

While it is clear from the above work and that of other researchers [17] that processing conditions can affect the nature of this mesoscopic structure or inhomogeneity, only recently have researchers started to consider the factors driving the formation of this domain structure and, in particular, the role of polydispersity (PDI, δ) [10,18]. Semenikhin et al. [10] have analyzed the driving force for film formation as the difference in the Gibbs free energies ($\Delta G = \Delta H - T \Delta S$) of the polymeric species in the solid state and in the solution. As the entropy (S) of the solid phase is lower than the liquid, there must be a gain in the enthalpy (H)upon the solid phase formation. As enthalpy (H) concerns favor crystalline domain formation while entropy (S) concerns favor disordered regions, the minimal free energy structure would be expected to have a heterogeneous grain structure. It is at this point that polydispersity enters the picture. The change in chemical potential (molar Gibbs energy, μ) for deposition of an *i*th fraction with a certain molecular weight (MW) due to entropy:

$$\Delta \mu_i = -R_{\text{gas}} T \ln \left(\frac{C_i}{C_{is}}\right) \tag{1}$$

where C_i (C_{is}) is the actual (saturated) concentration of the *i*th fraction. As the higher MW fractions have lower solubility, they will feature a higher deposition driving force and be deposited first and thus form the core of the polymer grains while lower MW fractions will deposit at later times filling in the areas between the grains. Furthermore, the ability of a fraction to form a crystalline phase increases the enthalpy gain upon deposition and thus the driving force. This viewpoint of low MW fragments forming the bulk of the amorphous matrix is supported by considerable experimental evidence. For example, non-regio-regular polymers are largely amorphous at low MW and become semi-crystalline only at sufficiently high values of MW [10,18-20]. Therefore, one concludes that the principal reason for the occurrence of mesoscopic inhomogeneity in films of electronically conducting and semiconducting polymers is spatial and temporal segregation during the deposition process of the polymer molecules according to their MW and their ability to form crystalline phases [10]. All this points at polydispersity, that is, the presence of fraction with different MW in the polymer sample, as the main source of the resulting inhomogeneity of the deposited polymer material.

The implication of this is that the greater the polydispersity of the starting materials the greater the inhomogeneity (domain structure) of the resulting polymer film. Conversely, the lower polydispersity, the more homogeneous is the deposited film. From the work of Inigo [15] and Blom [13], increased homogeneity should result in improved charge transport. The purpose of this Letter is to test this connection by comparing the mobility and calculated Bässler parameters for films formed from MEH-PPV powder containing short chains and the same powder after removal of the shortest chains.

The above argument assumes that the morphology of the polymer film is such that the deposition technique allows for the Gibbs free energy to be minimized, i.e., is in equilibrium. Films formed by drop-casting (followed by solvent or thermal annealing) should approach this condition while thin films formed through spin-casting are more likely to be trapped in higher energy, non-equilibrium morphologies.

2. Experimental procedure

2.1. Sample preparation

Commercial MEH-PPV powder (M_w = 369 K, δ = 6.26, as determined by gel permeation chromatography) was obtained from Aldrich Scientific and divided into two parts. The first part was used as received. In the following discussion it is denoted as the high polydispersity (HPDI) sample. The second part was first dissolved in toluene at 308 K for 24 h. The supernatant containing lower MW chains was discarded and the remaining lower solubility fraction (M_w = 462 K, δ = 4.7) was vacuum dried. In the following discussion it is denoted as the low polydispersity (LPDI) sample. Devices were prepared from the two powders by dissolving MEH-PPV in room temperature chlorobenzene at the concentration of 5 mg/cm³ and filtered using a 100 nm filter. The solutions were drop-casted onto cleaned indium tin oxide coated glass (ITO thickness = 77 nm, cleaned using organic solvents in the ultrasonic bath, followed by acetone and oxygen plasma). Films were then dried for 12 h at room temperature under a solvent-rich environment and the residual solvent removed under dynamic vacuum for another 12 h. Subsequently 100 nm thick gold electrodes were thermally evaporated by the shadow mask procedure to yield the active area of 4 mm² for time of flight (TOF) studies on the \sim 4 µm thick films. All processing was conducted under low-light conditions and samples were stored in a nitrogen environment to minimize contact with oxygen.

2.2. Film characterization

Film morphology was studied by means of Grazing Incidence Xray Diffraction (GIXD) at the powder X-ray diffraction end station of beamline 01C at the National Synchrotron Radiation Research Center (NSRRC). Two-dimensional (2D) GIXD patterns were recorded with a Mar345 imaging plate at a wavelength (λ) of 0.775 Å and sample-to-detector distance = 400 mm. For background subtraction, the WAXS pattern from the ITO glass substrate was measured. The scattering wavevector $q = 4\pi \sin (2\theta)/\lambda$ (with 2θ the scattering angle) was calibrated using silver behenate and silicon powder. The one-dimensional (1D) GIXD profile was collected in the out-plane depth (z) directions of the films from the 2D pattern.

Film thicknesses (*d*) were determined using a Veeco Dektak 150 Stylus Profiler and/or 3030 Surface Profile Measuring System.

2.3. Charge transport

Charge transport was measured by the time-of-flight method. After attaching leads, the devices were mounted in a vacuum cryostat at controlled temperature and kept under dynamic vacuum (1 mPa) for 12 h before measurements at this pressure. A 5 ns pulse (λ = 532 nm) from a frequency-doubled Nd:YAG laser was used for optical excitation. Photocurrent transients were measured by recording the voltage across a 5.74 k Ω resistor using a digital storage oscilloscope (Tektronix TDS 5104 1 GHz) and averaging over a few hundred pulses. The intersection of asymptotes to the plateau and the declining slope of the current transient in the log–log plots were used to determine the transit time (t_0). The mobility was then calculated using:

$$\mu = d/(E \times t_0) = d^2/(V \times t_0) \tag{2}$$

where d is the thickness of the sample and E is the applied electric field and V is the applied voltage. Temperature dependent mobility was measured at temperatures ranging from 225 to 325 K and applied voltages ranging from 20 to 110 V (Corresponding to electric

fields ranging from 50 kV/cm to 250 kV/cm for the d ~ 4 μ m thick films). The time resolution of the experiment was limited at short transit times by the RC time constant of the circuit at high temperature and dielectric breakdown at high fields, while the signal-to-noise ratio was the limiting factor for obtaining data at low temperatures and low applied electric fields. Full details of sample preparation and TOF instrumentation are available in our previous publications [15,21,22].

Note that the time (t_0) reflects the transit time of the front edge of the packet. Some authors use the time at which the photocurrent drops by a factor of two $(t_{1/2})$, corresponding to the time that the mean position of the drifting packet of charge carriers arrives at the counter electrode, to define the transient time used in their calculations of mobility [25]. We have chosen to use the first definition for consistency with our previous experimental based work. As the relative values of $t_{1/2}$ of the two films follow the same relationship as does t_0 , this should affect only the absolute values of mobility presented here and not the relative values or ratios.

2.4. Data analysis

While there are more complicated models, we chose to analyze our charge transport results using the Gaussian Disorder formalism of Bässler and coworkers [12] to allow our results to be directly compared with our previous works [22]. In GDM, a material is characterized by energy disorder (σ) and position disorder (Σ). The energy disorder (σ) describes the distribution of energy levels (DOS) associated with transport and the position disorder (Σ) describes the fluctuation in the distance and orientation of the Miller-Abrahams hopping sites associated with the hopping carriers. Physically, the smaller the value of Σ , the more homogeneous the structure on a sub-nanometer length scale. These two parameters are influenced by material morphology which depends not only on chemical structure but also on processing conditions such as temperature treatment and solvent. While the equations do not permit an analytical solution, based on the results of Monte Carlo simulation, the dependence of mobility on electric field and temperature in the ranges used in our devices can be approximated by:

$$\mu(E,T) = \mu_0 \exp\left(\frac{2\sigma}{3k_{\rm B}T}\right)^2 \exp\left(\left[\left(\frac{\sigma}{k_{\rm B}T}\right)^2 - \Omega^2\right]C\sqrt{E}\right) \tag{3}$$

where *T* is the absolute temperature, $k_{\rm B}$ is the Boltzmann constant, $\mu_0 = \mu(0, \infty)$ is the mobility at zero field and infinite absolute temperature, and *C* is an experimental constant that, according to the model, scales with the square root of intermolecular distance. Ω is defined as follows: if $\sum > 1.5$, $\Omega = \sum$, otherwise $\Omega = 1.5$. In practice, μ_0 , σ , \sum and *C* are determined by measuring mobility as a function of electric field and temperature. In general, $C \sim 3 \times 10^{-4} \, (\text{cm/V})^{1/2}$ [22,23].

3. Results and discussion

3.1. Film characterization

Figure 1 compares optical properties of the two films. In (a) the photo-luminescence (PL) spectra is displayed. As can be seen in the figure the curves are quite similar. The peak emission wavelength in both cases is at $\lambda = 609$ nm. In addition the Huang–Rhys factors are similar. The lack of a strong secondary peak at $\lambda \sim 640$ nm indicates that emission is predominately from intrachain rather than interchain, e.g., aggregate, species. This indicates that the polymers are well dissolved in the chlorobenzene solutions and have an extended rather than a collapsed coil formation (as seen when MEH-PPV is dissolved in room temperature toluene). Figure 1b compares



Figure 1. Optical properties of the two thin films of MEH-PPV dissolved in chlorobenzene. (a) Peak normalized photoluminescence (PL) spectra. In both cases the maximum PL occurs as 609 nm. Data was recorded in front face geometry. Excitation wavelength was 510 nm. (b) Photoluminescence excitation (PLE) spectra.

the PLE spectra for the two thin films. As in the case of PL, the two films exhibit similar optical properties.

Figure 2 presents 1D GIXD profiles for two polydispersity samples. According to amorphous state on spin- or drop-casting films of MEH-PPV in general, the HPDI sample displays an amorphous halo and no crystalline peaks in the GIXD profile. However, for the LPDI sample a small and broad peak emerges at $q \sim 0.29$ Å⁻¹



Figure 2. Grazing Incidence X-ray Diffraction data for the two films. The thick (magenta) lines are for the sample with greater polydispersity while the thin (black) lines are for the films formed from the sample having the shortest chains removed. A small peak is observed at $q = 0.29 \text{ A}^{-1}$ for the LPDI sample (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

corresponding to d-spacing of ~2.2 nm, in agreement with a bilayer spacing of MEH-PPV reported by Jeng et al. [24]. The grain size estimated by the Scherrer relation was ~8 nm. This finding indicates that removing short chain segments promotes the capability of crystallization to form smectic-like bi-layer order during the solvent evaporation and film formation.

The LPDI film ($d = 4.3 \pm 0.3 \mu$ m) was slightly thicker than the HPDI film ($d = 3.4 \pm 0.3 \mu$ m). In drop-cast films, unlike spin coated films, there is some variation in thickness as one move across the film. The error bar quoted here reflects this variation across the film. As the thesis of this Letter is that mobility is improved by reducing polydispersity, we have chosen to use, except where otherwise noted, the lower bound for the thickness of the LPDI film, i.e., 4 μ m, and an upper bound for the thickness of the HPDI film (4 μ m) in calculations.

3.2. Charge transport

Figure 3 presents the room temperature time-of-flight photocurrent transients for the two devices under an applied potential of V = 30 V. Comparing the transients in (a) it can be seen that the transit time is shorter for the LPDI then for the HPDI device. The actual transit times were determined from the kink in the log–log graph as discussed in the experimental section. The transit times for the two devices were $t_0 = 2.4$ ms and $t_0 = 1.4$ ms for the HPDI and LPDI devices respectively. The transient time of the LPDI is almost a factor of two shorter. Taking into account the different



Figure 3. Time-of-flight photocurrent transient at an applied potential of 30 V for the (a) δ = 6.3 and (b) δ = 4.7 devices at room temperature. (a) The top figures displays the data with a linear scale. (b) The bottom figure is the log(*i*)-log(*t*) plots. The transit time is denoted by to and the time to half intensity is denoted by $t_{1/2}$ in the figures. The residual current is the result of a direct current (DC) component that is not subtracted from the background. The photocurrent at the plateau region is ~1 μ A for the LPDI device and ~200 nA for the HPDI device.

thicknesses of the two films, this corresponds to $\mu_{\delta} = _{6.7}$ (E = 88 kV/ cm) = $1.6 \times 10^{-6} \text{ cm}^2/\text{Vs}$ and $\mu_{\delta} = _{4.3}$ (E = 70 kV/cm) = $4.4 \times 10^{-6} \text{ cm}^2/\text{Vs}$ for the HPDI and LPDI devices, respectively. Using $d = 4.0 \text{ }\mu\text{m}$ for the two films, one can calculate that $\mu_{\delta} = _{6.7} = 2.2 \times 10^{-6} \text{ cm}^2/\text{Vs}$ and $\mu_{\delta} = _{4.3} = 3.8 \times 10^{-6} \text{ cm}^2/\text{Vs}$, where the former is an upper bound on the mobility and the latter is a lower bound.

Figure 4 compares the electric field dependence of the room temperature mobilities of the two films using $d = 4.0 \,\mu\text{m}$. The lower bounds for the mobilities recorded for the device made with LPDI device are consistently a factor of two or more higher than the upper bounds for the HPDI device. This increased mobility is more pronounced at higher electric fields where the ratio rises to a factor of three. While the measured mobilities in general follow the Poole–Frenkel relationship,

$$\ln(\mu(E)/\mu_{E=0}) = SE^{1/2} \tag{4}$$

where *E* is an externally applied electric field, *S* is the slope of the field dependent mobility and $\mu_{\rm E=0}$ is the zero-field mobility), the slope is higher for the LPDI device than for the HPDI device. This indicates that the positional disorder present in the HPDI devices is larger than in the LPDI devices, and that the positional disorder seems to dominate charge transport characteristics [12]. Finally we note that while the mobilities follow the Poole–Frenkel relationship at high electric fields, at low electric fields the mobilities recorded for the HPDI device start to deviate from this relationship.

The field dependent mobility for different temperatures in HPDI and LPDI films was also measured at 10 K intervals from 225 to 325 K. Before considering these results, we would like to briefly comment on the temperature dependence of the shape of the photocurrent transients for the two devices. Under an applied electric field of 175 kV/cm, the transients of the LPDI devices at all temperatures were characterized by a clear plateau in the linear plots, suggesting non-dispersive transport across the full measurement range. In contrast, for the HPDI devices, the shape of the transient varied as a function of temperature (Figure 5). At room temperature there was a clear plateau. At the lowest temperature (225 K), the plateau has disappeared suggesting dispersive transport. At higher temperatures (325 K), a cusp appears in the transient. We note that such a cusp was seen, but not commented on, in previous work on MEH-PPV [15] for samples in which the formation of nanodomains had been suppressed by the application of an electric field. The origin of this cusp has been discussed in detail by Laquai et al. [26]. They argued that if carriers are injected into the sample at a level below the quasi-equilibrium level, there



Figure 4. Comparison of the electric field dependence of mobility at room temperature (T = 295 K) for the two devices. The solid black line indicates the ratio of the mobility of the lower polydispersity device with that of the higher polydispersity device. (The solid lines connecting points are for the convenience of the reader).



Figure 5. Representative Time-of-flight photocurrent transients for the HPDI device at 325, 295, 265 and 235 K under an applied electric field of 175 kV/cm. The main figure displays the data with a linear scale while the insets are $\log(i)-\log(t)$ plots from which transit times were obtained. At lower temperatures, the tail lengthens and the plateau (although clear in the log–log plot) disappears in the linear plot. At higher temperatures a cusp develops.

will be a finite 'heating time' in which the carriers are excited thermally to the equilibrium energy. Because the occupied density of states (ODOS) is higher at higher temperatures, more thermal energy is required to raise the ensemble of generated carriers to the transport level resulting in a cusp at higher temperatures. In any case, the key point is that not only is the mobility higher for the LPDI devices than for the HPDI devices, the reduction in polydispersity has lowered the transition temperature from nondispersive to dispersive transport.

The non-dispersive behaviour of the LPDI devices at low temperature is characteristic of MEH-PPV devices of high quality with low defect density and low structural disorder. In general, more dispersive transport is correlated with higher defect density or higher structural disorder. While we cannot rule out the former effect, i.e., that the defect density of shorter chains is higher than that for longer chains, the difference in slope of the mobility vs electrical field curves observed at room temperature suggest that structural disorder is the primary cause for dispersive transport in the HPDI devices.

For the sake of clarity, Figure 6 displays the field dependent mobility at 20 K intervals (See Supplementary material for data taken at 10 K intervals). While for the LPDI devices, we were able to determine the mobility for almost all combinations of temperature and electric field strengths used, for the HPDI sample, the curves became dispersive as the electric field and temperature were lowered. At any given temperature and electric field, the mobility is higher for the LPDI device than for the HPDI. Throughout the temperature range, the slopes are higher for the LPDI devices than that of HPDI devices and the mobilities higher. In addition, in the HPDI sample the slope changes gradually from low *T* to high *T*, while in the LPDI sample, the slope does not change that much. The latter is a good indication that the LPDI films are more homogeneous than the HPDI film.

The temperature dependent data, shown in Figure 6, allows for the calculation of the Bässler parameters [27]. The results of the calculations are shown in Table 1. Following the procedure of Ref. [23], the energy disorders and pre-factors for the two films were first calculated. The resulting energy disorders for the two films are the same within experimental error indicating that the removal of shorter chains has no significant effect on the distribution of energy levels within the thin film. Given the PL intensity results shown in Figure 1, this is not surprising as there appears to be little difference between the two films – either in peak position or Huang–Rhys factor – suggesting a similar DOS for both films.



Figure 6. Temperature dependence of electric field dependent mobility of the two devices. (a) Polydispersity = 6.3 and (b) polydispersity = 4.7.

Secondly, the pre-factor, μ_0 , for the two films was also similar. The difference between the two films comes in the calculation of the positional order (Σ) and the value of *C*. Considering first the LPDI film, there is very little positional disorder in the samples. The value of *C* is found to be $\sim 2 \pm 1 \times 10^{-4} (\text{cm/V})^{-1/2}$. In the Monte Carlo simulation from which Eq. (2) is derived, a value of $C = 2.9 \times 10^{-4} (\text{cm/V})^{-1/2}$ corresponds to an average hopping distance of 0.6 nm in the simulation [28]. The slightly lower value of *C* for this film suggests that the hopping sites are more closely spaced for this thin film. In contrast to the LPDI sample, the value for positional disorder obtained for the HPDI sample was \sim 7. However, it was not possible to obtain a reasonable value of *C*.

This suggests that while the Bässler GDM model successfully handles the case of the LPDI sample, it breaks down for the HPDI sample. As discussed by Rakhmanova and Conwell [11] as well as Blom and Vissenberg [13], the main limitation of the Bässler GDM model is its inability to handle correlated spacial disorder. This suggests that there is a difference in mesoscopic structure, i.e., correlated disorder, between the two films. In the HPDI film the amount of correlated disorder is too great for a model based on homogeneous non-correlated disorder to handle. The fact that the Bässler model works well in describing the LPDI film indicates that reducing the polydispersity of the MEH-PPV by removing shorter chains has reduced the correlated disorder (mesoscopic structure) sufficiently within the film for the Bässler GDM model to be applicable.

Unfortunately for many papers published on hole mobility in MEH-PPV, the polydispersity of the samples are not specified. In papers in which the Bässler GDM model has been successfully applied without modification (without including extensions to take into account correlated disorder), it seems that the polymer used had very low polydispersity, e.g., $\delta = 1.1$ in Ref. [16]. The above research suggests that polydispersity is a key parameter to specify when discussing charge transport in MEH-PPV.

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Bässler Parameters	for the	two	films.

PDI (δ)	M _w [kD]	<i>M</i> _n [kD]	μ [cm²/Vs] <i>T</i> = 295 K, <i>E</i> = 150 kV/cm	σ [meV]	Σ [-]	C [(cm/V) ^{-1/2}]	μ_0 [cm ² /Vs]
6.3 4.7	369 462	59 99	$\begin{array}{l} 4.1 \times 10^{-6} \\ 8.4 \times 10^{-6} \end{array}$	51 ± 5 55 ± 4	_ <1.5	$-2\pm1\times10^{-4}$	$\begin{array}{c} 2.8 \pm 1.1 \times 10^{-6} \\ 3.0 \pm 0.5 \times 10^{-6} \end{array}$

4. Conclusions

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In conclusion, prior work suggests that the principal reason for the occurrence of mesoscopic inhomogeneity in films of electronically conducting and semiconducting polymers is spatial and temporal segregation during the deposition process of the polymer molecules according to their MW and their ability to form crystalline or ordered phases. This suggests that polydispersity, in particular the presence of short chains in the sample, has a strong influence on structure and hence charge transport properties. In this work, we have shown that reducing MEH-PPV polydispersity through the removal of short chains promotes the capability of crystallization and results in increased hole mobility and non-dispersive transport at lower temperatures. While it was not possible to fit all parameters of the Bässler GDM model for untreated commercial MEH-PPV, by reducing polydispersity, it was possible to fit all parameters of the Bässler GDM model. This suggests that the removal of short chains results in reduced correlated disorder within the film.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2011.02.026.

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