Influence of the Molecular Weight of Poly(3-hexylthiophene) on the Performance of Bulk Heterojunction Solar Cells

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The efficiency of poly(3-hexylthiophene) (P3HT)/[6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) bulk heterojunction solar cells dramatically depends on the molecular weight of the donor polymer P3HT. Only for P3HTs with a number-average molecular weight (M_n) of >10 000 have high power conversion efficiencies of >2.5% been reached. This behavior is caused by distinctly reduced charge carrier (hole) mobility in the donor phase of the devices built from lower M_n P3HT samples. The reduced performance of such devices is related to a reduced intermolecular ordering (π-stacking) of the P3HT phase. These findings highlight the important role of the molecular weight in semicrystalline semiconducting polymers for the device performance and may help in the further development of novel, efficient, lower band gap donor polymers for photovoltaic applications.

Introduction

Low-cost photovoltaic (PV) cells which are light and flexible could open up many new applications for solar cells, from self-powered electronic newspapers to self-sufficient buildings. While the introduction of inorganic thin film solar cells has reduced material costs, production costs still remain high. Production typically also requires high-temperature steps, which makes production on polymer foil substrates impossible. Thin-film polymer solar cells have the potential to change all this. They can be produced from solutions at low temperatures, and recent advances have allowed significant increase in the light conversion efficiencies to a level which makes them economically interesting. Therefore, polymer photovoltaic offers great technological potential as a renewable, alternative source for electrical energy. This demand for inexpensive renewable energy sources was the driving force for new approaches in the production of low-cost photovoltaic devices, and, during the last few years, the development of polymeric solar cells has progressed rapidly.[1−4] Utilizing the nanoscopic interpenetrating network of the two constituents (donor/acceptor) in such a "bulk heterojunction" composite allows the construction of a large interfacial area and ensures a homogeneous, efficient charge generation throughout the sample. High power conversion efficiencies exceeding 3% under AM1.5 illumination and between 4 and 5% under white light illumination from a solar simulator have recently been reported for bulk heterojunction plastic solar cells (PSC).[5−7]

The limiting factor in these plastic solar cells is, of course, still the relatively low power efficiency which origins from the absence of properly absorbing and transporting organic semiconductors. At present, substituted poly(*p*-phenylene vinylene)s and polythiophenes are typically used in the construction of PSCs and solar cells from these polymers showed high internal and external quantum efficiencies.[8,9] However, the optical band gap of these conjugated polymers ($E_g = 2.0-2.2$ eV) does not allow efficient collection of the solar emission, which has the maximum photon flux around 1.8 eV. Until now, the performance of low band gap polymers ($E_g < 1.8$ eV) to expand the spectral region of bulk heterojunction solar cells has been unsatisfying. For none of these lower band gap polymers have high external quantum efficiencies (i.e., exceeding 50%) been demonstrated, and today, regioregular poly(3-alkylthiophene)s are still the most promising class of polymers.

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Table 1. Molecular Weight and Polydispersity of the Individual P3HT Fractions[a]

P3HT fraction	molecular weight M_n [g/mol]	polydispersity M_w/M_n (degree of polymerization DP)	mobility of pristine P3HT fractions (from TFT) [cm^2/Vs]	mobility of bulk heterojunction P3HT/PCBM composites (from OPV)[b] [cm^2/Vs]
pristine, not fractionated sample	11 300	1.9 (68)	not measured	$1-3 \times 10^{-3}$
fractionated with chloroform ($CHCl_3$)	19 000	1.35 (114)	2.6×10^{-3}	$1-3 \times 10^{-3}$
fractionated with dichloromethane (CH_2Cl_2)	13 800	1.48 (83)	1.3×10^{-3}	$0.8-1 \times 10^{-3}$
fractionated with hexane (C_6H_{14})	5600	1.18 (34)	1.6×10^{-5}	$1-3 \times 10^{-4}$
fractionated with ethyl acetate ($CH_3COOC_2H_5$)	2200	1.43 (13)	5.5×10^{-7}	$1-3 \times 10^{-4}$

[a] Mobility data from FET measurements are from ref 10. [b] The OPV mobility data have been calculated via simulation of *I*/*V* curves according to ref 20. Please note that the simulation gives the product of mobility times the carrier lifetime, the $\mu\tau$ product. To derive the mobility, a carrier lifetime of 1 μs was assumed for all fractions[21,22].

In this article we discuss the importance of a high molecular weight of the donor polymer for application in organic photovoltaic cells. A strong correlation between the molecular weight of a conjugated polymer and its photovoltaic performance is demonstrated. This correlation originated in the recently reported dependence of the charge carrier mobility on the molecular weight and was investigated in detail for P3HT.[10] It appears that the molecular weight of a polymer is as important as other well-known parameters influencing mobility, such as the chemical structure, the chain length, or the bulkiness of the side chains. This should hold at least for polymers with a tendency for aggregation (π-stacking). These findings bring in a new and important aspect for the development of novel photovoltaic polymers, and, especially, for low band gap polymers. Most of the low band gap polymers evaluated so far for OPV failed to meet the transport specifications. Materials and whole material classes which do not meet the performance expectations for photovoltaic applications in initial tests may have to be reevaluated under the aspect of their molecular weight.

Experimental Section

Devices were fabricated on glass/ITO substrates (MDT). After cleaning of the ITO the conducting polymer poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate) (PEDOT-PSS, Bayer AG) was spin-coated to a layer with a thickness of 80 nm. The active layer consisting of different fractions of poly(3-hexylthiophene) (P3HT) in a 1:1 (w/w) blend with the methanofullerene [6,6]-phenyl C61 butyric acid methyl ester (PCBM) was spin-coated from 1.8% xylene solutions at 800 rpm on 2-in. substrates, giving 8 devices with an active area of 4 mm^2 on each substrate. The metal electrode (Ca/Ag) was thermally deposited with a thickness exceeding 100 nm. Characterization of the devices was performed under white light illumination from a solar simulator at 25 °C. No corrections for the spectral mismatch were taken into account. The spectral photocurrent was measured by lock-in technique, using as reference a calibrated Si solar cell.

Regioregular poly(3-hexylthiophene) P3HT was prepared by the so-called Grignard metathesis procedure according to McCullough, which involves the Ni-mediated polycondensation of 2-bromo-3-hexylthiophene-5-magnesium bromide.[11] The raw polymer was fractionated by applying the so-called solvent extraction method.[12] Subsequent extraction steps with solvents of an increasing solubility for P3HT (ethyl acetate, hexane, dichloromethane, and chloroform) yielded four polymer fractions with a narrow molecular weight distribution (M_w/M_n: 1.2−1.5). The average molecular weights were measured with respect to narrowly distributed polystyrene PS standards using gel permeation chromatography GPC of the polymers dissolved in THF (Table 1). However, comparisons between the molecular weights measured by MALDI-TOF and GPC methods showed that GPC-based molecular weights are a factor of 1.2−2.3 times higher than MALDI values.[13] The ^1H NMR analysis of all P3HT fractions did not show significant structural differences of the samples, only the amount of endgroup-related signals increases gradually with decreasing molecular weight.

Results and Discussion

Absorption and Photocurrent Measurements. Figure 1A shows the solid-state absorption spectra of the various P3HT fractions blended into PCBM. We observe a strong dependence of the absorption spectra on the molecular weights of the polymer. In the following we will call the ethyl acetate and hexane fractions the low-molecular-weight fractions (molecular weight $M_n < 10\,000$ g/mol), and we will call the dichloromethane and chloroform fractions the high-molecular-weight fractions (molecular weight $M_n > 10\,000$ g/mol). Composites from the lowest weight molecular fraction and PCBM exhibit a featureless absorption spectrum which is an overlap of the absorption features from P3HT and from PCBM in the 350−450 nm region. For the composite with the next higher M_n P3HT fraction, the absorption maximum λ_{max} shifts toward 500 nm, and for the first time a small absorption shoulder around 600 nm is observed. With increasing molecular weight, the absorption maximum λ_{max} of the composites begins to broaden and the 600 nm features become more and more prominent. It is important to note

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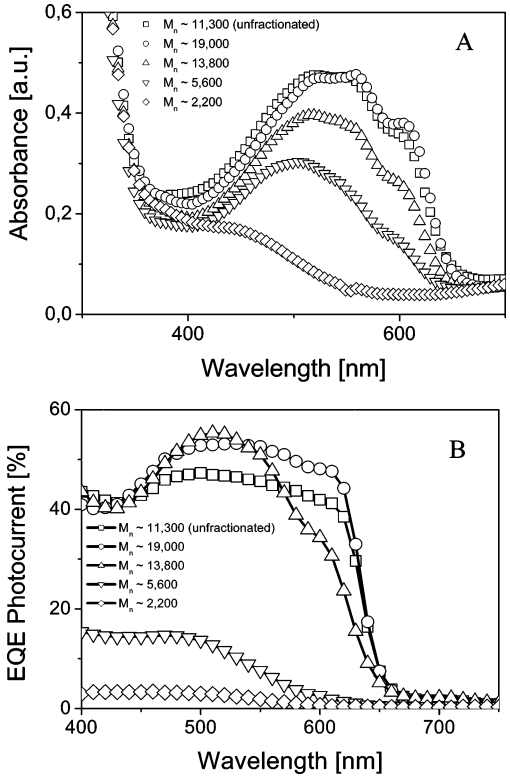

Figure 1. (A) Solid-state absorption spectra of bulk heterojunction composites consisting of different P3HT fractions blended into PCBM. Thin films were spin-cast to a film thickness of 100 nm. The fractions were prepared by subsequent extraction with ethyl acetate (◊, M_n ~2200 g/mol, polydispersity PD ~1.43), hexane (▽, M_n ~5.600 g/mol, PD ~1.18), dichloromethane (△, M_n ~13.800 g/mol, PD ~1.48), and chloroform (○, M_n ~19.000 g/mol, PD ~1.35). Open squares (□) reference a thin film P3HT/PCBM composite of the blend based on the as-synthesized P3HT before fractionation. (B) Photocurrent spectra (external quantum efficiency) of bulk heterojunction solar cells with different P3HT fractions blended into PCBM. Legend is identical to that of part A.

that thin films from pristine P3HT (i.e., without the addition of PCBM) exhibit qualitatively and quantitatively the same features and trends. The solid-state spectra of the pristine polymer fractions are shown elsewhere.[10] The thin-film absorption features of P3HT have been extensively studied in the past and are now well understood. Depending on the regioregularity of the P3HT, attractive interchain interaction in the solid state results in the formation of lamellar structures (crystallites), in which the rotation about the inter-ring single bond is highly restricted. As a result, the polymer backbone can be described as a "plate-like" rigid rod molecule with extended conjugation. The π-stacking of the planarized individual polymer chains leads to the well-structured and red-shifted absorption features of the P3HT layers. The formation of these lamellar structures or interchain aggregates causes phenomena like solvatochromism,[14] thermochromism,[15−17] and the well understood formation of interchain excited states.[18] In contrast, the solution UV−Vis spectra[10a] show only a very slight bathochromic shift of the long wavelength absorption maxima with increasing chain length.

For our investigations, it is sufficient to denote that the molecular weight has an influence on the solid-state morphology of P3HT similar to that of the degree of regioregularity of poly(alkylthiophene)s.[10] High molecular weights, as well as a high regioregularity, support the formation of lamellar structures which is a safe indication for higher mobility due to more extended crystalline regions.[18,19]

For the high-molecular-weight fractions, the spectral photocurrent of the P3HT/PCBM composites (Figure 1b) is in excellent agreement with the solid state absorption spectrum. Peak EQE values between 50 and 60% are observed. The photocurrent of the low-molecular-weight P3HTs is significantly reduced and its spectral shape differs from the corresponding absorption spectra. The EQE drops down to ~5% for the lowest molecular weight P3HT fraction. The antibatic photocurrent behavior together with low EQE are clear indications that charge separation is inefficient for the low-molecular-weight P3HT fractions.

For the other fractions, the spectral photocurrent density follows the trend of the thin film solid state absorption spectra. With increasing molecular weight the photocurrent maximum at 500 nm establishes (already for the hexane fraction) and begins to broaden for even higher molecular weights (dichloromethane and chloroform fraction) until it forms a plateaulike region between 400 and 600 nm. These aggregation-related features are observed only for molecular weights M_n higher than 10 000 (dichloromethane and chloroform fractions) with a low energy edge of the photocurrent at ~600 nm (dichloromethane fraction) and at ~650 nm for the highest molecular weight fraction (chloroform fraction). The symbatic photocurrent behavior of the high M_n fractions together with the high EQE demonstrates that charge separation is inefficient for the low-molecular-weight fractions.

Photovoltaic Results. For all fractions, solar cell devices were prepared by blending the P3HT with PCBM in equal weight ratios. The device performance for the individual fractions was statistically evaluated and is depicted as box plot diagrams in Figure 2A−D. A 10−20-fold efficiency increase (Figure 2B) is observed for the solar cells made of the high-molecular-weight fractions compared to those made of the lower molecular weight fractions. The photovoltaic performance of the various fractions is investigated and analyzed in more detail. Figure 2A, C, and D compare the open circuit voltage V_{OC}, the fill factor FF, and the short circuit current density J_{SC} for the different fractions. The low-molecular-weight fractions show a reduced performance in all of these parameters. V_{OC} and FF of the low-molecular-weight P3HT fractions are reduced by approximately 50% compared to the high-molecular-weight fractions. The difference in J_{SC} is even more dramatic. High-molecular-weight P3HT/PCBM-based solar cells have a 5−10-fold higher J_{SC}

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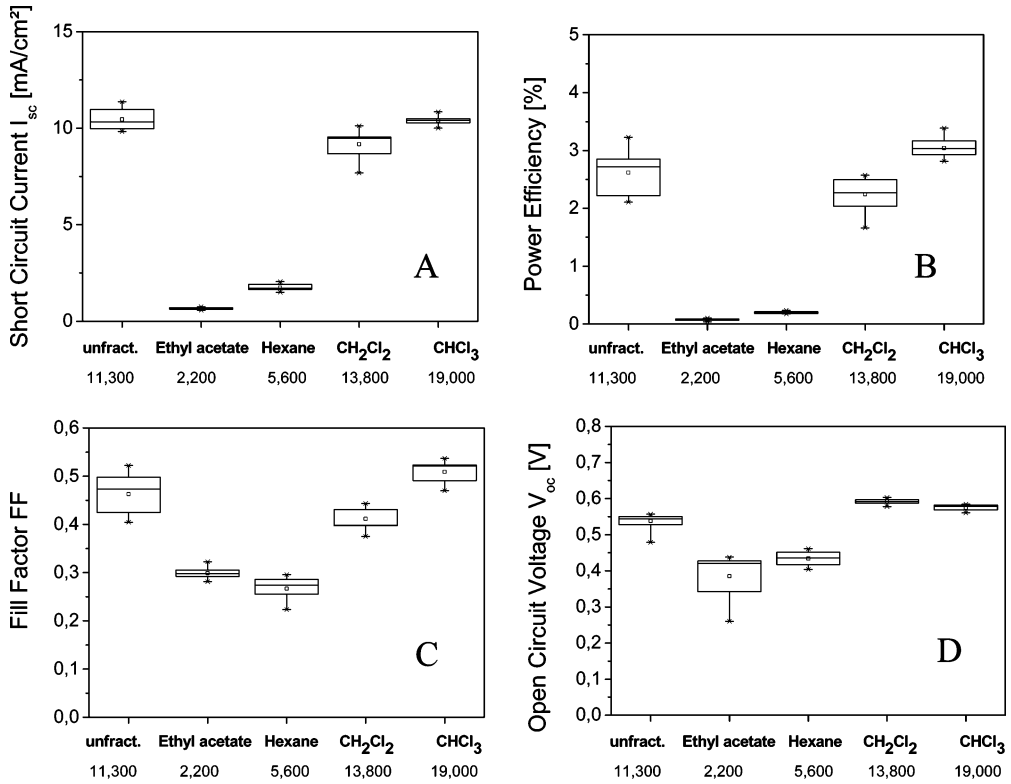

Figure 2. Performance analysis of bulk heterojunction solar cells made from various P3HT fractions with different molecular weights. More than 16 individual devices from 2 production cycles are compared. Data are presented in box plots. The horizontal lines in the box denote the 25th, 50th, and 75th percentile values. The error bars denote the 5th and 95th percentile values. The two symbols below and above the 5th/95th percentile error bar denote the highest and the lowest observed values, respectively. The height of the box is the measure for the tolerance. (A) Box plot diagram of the short circuit current density J_{SC}, (B) the power efficiency, (C) the fill factor FF, and (D) the open circuit voltage V_{OC} of the investigated devices.

than the low-molecular-weight P3HT-based solar cells. This reason for this dramatic change will be analyzed in more detail in the next section. A small but nonnegligible difference is also observed within the high-molecular-weight fractions. An increase in the photocurrent is observed for the chloroform fraction versus the dichloromethane fraction. This increase can be attributed to the more red-shifted photocurrent spectrum of the chloroform fraction (see Figure 1B).

Figure 3A and B show representative *J*/*V* curves for PSC devices made of different P3HT fractions in the dark and under illumination. The low-molecular-weight P3HT fraction-based composites lead to qualitatively and quantitatively different *J*/*V* characteristics compared to the devices made of the high-molecular-weight P3HTs. Most significantly, current densities are approximately one order of magnitude lower. A further peculiarity is the non-diode-like *J*/*V* characteristics for the low M_n hexane fraction. The diode behavior of illuminated and dark *J*/*V* curves is analyzed at the hand of the equivalent circuit shown in Figure 3C. Small variations of the diode parameters n and J_0 for the different molecular weight fractions are observed. However, these changes are too small to explain the performance difference of the various fractions. The serial and parallel resistivities are investigated separately. Interestingly, it is observed that the parallel resistivity R_P, i.e., the shunt, is nearly independent of the molecular weight of the polymer (Figure 3D). Diodes produced from low-molecular-weight fractions do not suffer from insufficient film quality (i.e., pinholes), their shunt is comparable to the one of high-molecular-weight diodes. Therefore, it can be ruled out that the observed V_{OC} reduction for low-molecular-weight fractions is caused by a reduced shunt. On the other hand, the serial resistivity R_S exhibits a clear correlation with the molecular weight. Please note that the serial resistivity reflects the bulk conductivity of the semiconductor, additional to feed line and contact resistivities. The bulk resistivity σ of the semiconductor is given by $\sigma = ne\mu$, with n as the carrier density, e as the elementary charge, and μ as the bulk mobility. Since the carrier density n is expected to be constant for the different molar masses, it is sound to correlate the observed changes in R_S to changes in the mobility. Photovoltaic composites with low-molecular-weight fractions have an overall reduced mobility.

A more detailed, quantitative insight of the composite's mobility is derived from analysis of the current density under illumination. The concept of a field dependent current was introduced recently to explain J_{SC} in bulk heterojunction solar cells.[20] This concept explains the field dependence of the photocurrent by the field dependence of the drift length, i.e., by $\mu\tau E$ product of the bulk heterojunction composite with the applied electrical field. Naturally, this field dependence is recognized most easily at the zero field regimes, i.e., around V_{OC}. It is therefore the "zero current" or open circuit regime which contains valuable information on the correlation between the $\mu\tau$ product of the semiconductor and the photocurrent. This type of analysis is now applied to verify the correlation between molecular weight and solar cell

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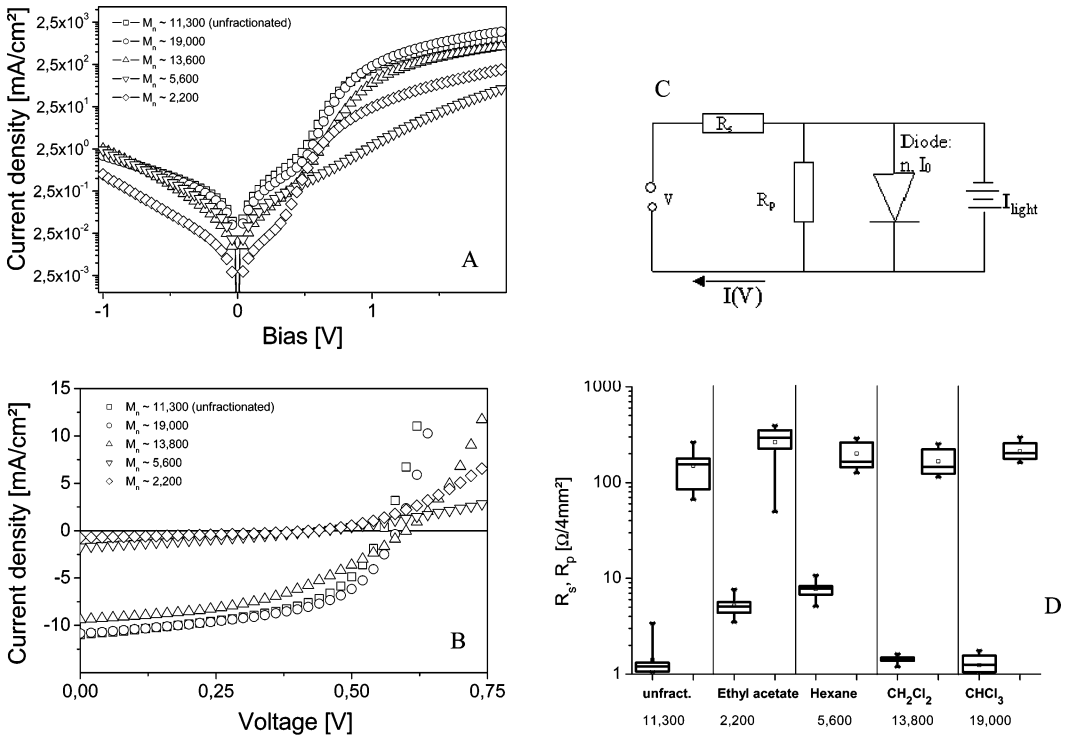

Figure 3. (A and B) Typical *J*/*V* curves of bulk heterojunction solar cells comprising P3HT fractions with different molar mass distributions in the dark in a semilog plot (A) and under light in a linear (B) plot. The fractions were prepared by subsequent extraction in ethyl acetate (◇), hexane (▽), dichloromethane (△), and chloroform (○). Squares (□) reference the P3HT/PCBM device from the as-synthesized P3HT blend before fractioning. Devices were prepared by spin-coating. (C) Equivalent circuit diagram of the macroscopic model for describing a solar cell with one diode. The total current for a given voltage V is the sum of the single currents through the diode, which is represented by the parameters n and I_0, the shunt resistance R_p, the light current I_{light}, and is limited by the series resistance R_s. The diode equation is given by

$$I - I_0 \times (e^{[e\times(V - I\times Rs)]/[nk_BT]}\text{-}1) - \frac{V - I \times Rs}{Rp} + I_{light} = 0$$

with I_{light} as

$$I_{light}(V) = \begin{cases} -|Isc| & \text{if } \mu \times \tau \times (-V + V_{bi})/L > L \\ |Isc| & \text{if } \mu \times \tau \times (V - V_{bi})/L > L \\ |Isc| \times \mu \times \tau \times (-V + V_{bi})/L^2 & \text{else} \end{cases}$$

(D) Box plot diagram of the serial (R_S, left side) and the parallel (R_P, right side) resistivity of the individual devices calculated from the equivalent circuit (part C).

performance analogue to that in ref 20. The results for the $\mu\tau$ product of the bulk heterojunction composite are converted to mobility data assuming a constant carrier lifetime of 1 μs[21,22] and are summarized in Table 1. A drop by approximately one order in magnitude (from $\sim 10^{-3}$ down to $\sim 10^{-4}$) is found for the mobility of the low-molecular-weight fraction composites. This is in qualitative agreement with the R_S analysis.

Mobility considerations so far were performed for composites. Please note that the composite mobility is a weighted average of the electron and hole mobility of the individual components. So far no information has been gained on the transport properties of the individual components. However, the hole mobility of the pristine P3HT fractions is known from thin film transistor (TFT) transport measurements[10] and is included in Table 1. The TFT mobility of the two high-molecular-weight fractions was found between 10^{-3} and 10^{-2} cm^2/Vs in good accordance with mobility data for the photovoltaic composites derived from *J*/*V* analysis ((2−3) $\times 10^{-3}$ cm^2/Vs). A significant difference is observed for both low-molecular-weight P3HT fractions. The pristine, lowest molecular weight P3HT fraction (ethyl acetate fraction) showed a TFT mobility of $\sim 10^{-6}$ cm^2/Vs while the corresponding bulk heterojunction PCBM/P3HT composite displayed a mobility of $\sim 10^{-4}$ cm^2/Vs. This difference only can be explained by assuming that the mobility of the PCBM/P3HT composite is dominated by electron carrier transport via PCBM. This is in good agreement with electron mobility data for pristine PCBM, which was reported in the order of 10^{-4} to 10^{-3} cm^2/Vs.[23]

The combination of *J*/*V*, mobility, and spectral photocurrent analysis draws a sound picture for the processes in bulk heterojunction composites from P3HT fractions with different molecular weight. Composites with the lowest molecular weight fractions are dominated by the transport properties of PCBM. The photocurrent is low due to the absence of efficient hole transport, the spectral photocurrent shows antibatic behavior. Small increase of the molecular weight (hexane fraction) results in slightly more balanced transport

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and is accompanied by an increase of the photocurrent. However, the absence of diode-like behavior (Figure 3A) and the still antibatic shape of the overall low EQE indicate that the transport properties of the composite are far from being optimized. Further increase of the molecular weight improves the transport properties of the composite and the photovoltaic performance. EQE values exceeding 50% are found for composites with molecular weight fractions with $M_n > 10\,000$ g/mol.

In conclusion, we have demonstrated that lowering the molecular weight of P3HTs dramatically decreases the performance of P3HT/PCBM bulk heterojunction solar cells. A pronounced decrease in the J_{SC} by a factor of 5−10 is accompanied by a reduction of the V_{OC} and FF by ∼50%. The well-established correlation between molecular weight and charge carrier mobility of regioregular P3HT is responsible for this dramatic performance decrease of devices with low-molecular-weight polymers. All experimental findings can be explained in terms of a reduced mobility respective to $\mu\tau$ product. The dependence of the mobility on the molecular weight is based on by the formation of polymer aggregates. The formation of these aggregates is monitored by the formation of low energy absorption and photocurrent features, which are only found for high-molecular-weight polymer fractions. An important outcome of this study is the finding that the presence of PCBM does not hinder the formation of these aggregates.

These findings highlight the important role of the molecular weight of semicrystalline semiconducting polymers in parallel to their molecular structure (e.g., their regioregularity). We emphasize the importance of these findings especially for the development of novel low band gap polymers. The full photovoltaic potential of such a polymer only can be recognized for sufficiently high-molecular-weight fractions. In contrast, most of the low band gap semiconducting polymers studied until now have been obtained with low molecular weights.

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