

Molecular-weight-dependent mobilities in regioregular poly(3-hexyl-thiophene) diodes

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We have investigated the transport properties in the direction perpendicular to the substrate of regioregular poly(3-hexyl-thiophene) of different molecular weights (MW) in a diode geometry. In these devices, which exhibit space-charge-limited behavior, we find that the mobility values at room temperature increase from $1.33 \times 10^{-5} \text{ cm}^2/\text{V s}$ to $3.30 \times 10^{-4} \text{ cm}^2/\text{V s}$ as the MW is increased from 2.9 to 31.1 kg/mol. The mobility is found to be field independent for high MW films, but field dependent for the low MW films. The current–voltage characteristics of the diodes are also studied as a function of temperature from 160 K to 300 K. The activation energy for carrier transport, extracted from the Arrhenius plot, is found to decrease gradually from 143 meV to 126 meV as the MW is increased. © 2005 American Institute of Physics. [DOI: 10.1063/1.1891301]

Semiconducting regioregular poly(3-hexyl-thiophene) (RR-P3HT) is used extensively in polymer thin-film transistors and photovoltaic cells because of its highly-ordered packing in films that results in high carrier mobilities. It has been used to make field effect transistors with a mobility of up to $0.1 \text{ cm}^2/\text{V s}$ (Refs. 1–3) and photovoltaic cells with a reported energy conversion efficiency as high as 3.5%.^{4–6} While much work has been done in characterizing its field effect mobilities in thin-film transistor geometry, where the current travels in the plane of the film (parallel to the substrate), little has been reported on its transport properties in the direction perpendicular to the substrate.^{7–9}

Previously we have demonstrated that the field effect mobility of RR-P3HT increases from $1.7 \times 10^{-6} \text{ cm}^2/\text{V s}$ to $9.4 \times 10^{-3} \text{ cm}^2/\text{V s}$ in field effect transistors (FET) as the molecular weight (MW) is increased from 3.2 to 31.1 kg/mol.¹⁰ The MW was found to affect the way chains pack on each other and thus cause the variation in the observed mobility. We found that low MW chains crystallize in the form of nanorods, as observed with x-ray diffraction (XRD) and atomic force microscopy (AFM), and hypothesized that these films have lower mobility due to less connected pathways for transport. In this letter, we extend the investigation of MW dependence of RR-P3HT mobility to the direction perpendicular to the substrate. The mobility is measured in the hole-only devices in the space charge limited current (SCLC) regime. Fitting SCLC current–voltage curves has been successfully used to determine the mobility of semiconducting organic materials used in organic light emitting diodes and photovoltaic cells.^{11–14}

RR-P3HT end-capped with methylthiophene moieties was synthesized and characterized as described previously.¹⁰ The number average molecular weights and polydispersity index (PDI) of the various samples are shown in Table I. The regioregularity (RR) of the polymers used here is above 96%. Diodes of the structure indium tin-oxide (ITO)/poly(3,4 -ethylenedioxythiophene) :poly(4 -styrenesulfonate) (PEDOT:PSS)/RR-P3HT/aluminum were fabricated. The

different molecular weight polymers were dissolved in tetrahydrofuran (THF) and spin cast on top of the PEDOT-coated ITO substrate. Aluminum electrodes were evaporated through a shadow mask, defining active areas of $0.05\text{--}0.08 \text{ cm}^2$. All the fabrication and testing steps were done under a nitrogen atmosphere. For the temperature dependent measurements, the devices were taken into air briefly and then loaded into a vacuum probe station equipped with a Joule-Thompson refrigerating stage (MMR Technologies). The film thickness was determined by AFM.

In our devices, ITO/PEDOT is the anode, while aluminum is the cathode. PEDOT has a work function of about 5.2 eV (Ref. 15) and serves as an Ohmic contact for hole injection into the highest occupied molecular orbitals (HOMO) of RR-P3HT at 5 eV.¹⁶ The work function of aluminum is 4.2 eV, which is largely mismatched with the lowest unoccupied molecular orbitals (LUMO) of the polymer (2.9 eV) and prevents injection of electrons into the device. When sufficient voltage is applied to this hole-only device, the transport of holes through the polymer film is limited by the space charge that accumulates and the SCLC is described by

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_h \frac{V^2}{L^3}, \quad (1)$$

where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer, μ_h is the hole mobility, V is the voltage drop across the device, and L is the P3HT thickness. Equation (1) holds if the mobility is field independent. But for most conjugated polymers, which are intrinsically disordered, it has been found that the carrier mobility goes as $\mu_h = \mu_{h0} e^{\gamma \sqrt{E}}$, where E is the electric field, μ_{h0} the zero-field mobility, and γ the field dependence prefactor, and that the SCLC can be described by¹⁷

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_{h0} e^{0.89 \gamma \sqrt{E}} \frac{V^2}{L^3}. \quad (2)$$

In our current–voltage (J – V) analysis, the voltage drop due to contact resistance and series resistance (V_r) across the

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TABLE I. Number average molecular weight (MW), polydispersity (PDI), and regioregularity (RR) of samples used in this study. Included also are the measured hole mobility (μ_h) at room temperature and activation energy Δ of the samples in diodes. The electric-field coefficient γ is included for the low MW film.

Sample	MW (kg/mol)	PDI	RR	μ_h (cm ² /V s)	Δ (meV)	γ (m/V) ^{1/2}
Low MW	2.89	1.33	>96%	$1.33 \pm 0.41 \times 10^{-5a}$	143 ± 1.7	$2.4 \pm 0.4 \times 10^{-4}$
Medium MW	9.72	1.66	>97%	$1.13 \pm 0.37 \times 10^{-4}$	131 ± 3.3	...
High MW	31.1	1.40	>98%	$3.30 \pm 0.73 \times 10^{-4}$	126 ± 6.8	...

^aZero field mobility using field-dependent mobility model.

electrodes is subtracted from experimental data. This resistance was measured in a reference device without the polymer layer and was found to be about 22–30 Ω . The built-in voltage (V_{bi}) due to the difference in work function of PEDOT and aluminum is further subtracted from experimental values.¹⁸ The V_{bi} was deduced from the best fit of the $J^{0.5}$ versus V_{app} plot at voltages above 1.5 V to Eq. (1) for films with field-independent mobility, and to Eq. (2) for films with field-dependent mobility. We find that V_{bi} varies between 0.9–1.2 V and annealing at 95 °C for 1 h after device fabrication is essential to achieve the final V_{bi} . The dielectric

constant, ϵ_r , is assumed to be 3 in our analysis, which is a typical value for a conjugated polymer.

Figure 1 shows the $J^{0.5}$ versus V plots for RR-P3HT diodes of varying MW and thickness. The thickness was varied to confirm that the current is space charge limited. A straight line going through the origin of $J^{0.5}$ versus V curves, in both high MW [Fig. 1(a)] and medium MW films [Fig. 1(b)], signifies that the mobility is field independent at fields up to 2×10^5 V/cm. The field-independent mobilities calculated from Eq. (1) are 3.3×10^{-4} cm²/V s and 1.1×10^{-4} cm²/V s for the high MW (Refs. 7 and 8) and medium MW films, respectively. For the low MW film [Fig. 1(c)], Eq. (1), shown as a solid line, does not fit the experimental data. Equation (2), shown as a dashed line, fits the data better. This indicates that the low MW film exhibits field-dependent mobility. The zero-field mobility, μ_{h0} , and the field dependence prefactor, γ , of the low MW films are found to be 1.3×10^{-5} cm²/V s, and 2.4×10^{-4} (m/V)^{1/2}, respectively. These fitting values are summarized in Table I.

The J – V characteristics of the diodes were studied as a function of temperature from 160 K to 300 K in order to determine the activation energy of the charge carrier transport. The carrier mobility, μ_h in Eq. (1) and μ_{h0} in Eq. (2), varies with temperature according to

$$\mu_h, \mu_{h0} = \mu^* e^{-\Delta/kT}, \quad (3)$$

where μ^* is the mobility prefactor, Δ the activation energy, and k the Boltzmann constant. The $J^{0.5}$ versus V curves for the high MW and medium MW films were well described by Eq. (1) throughout the investigated temperature range. We obtained from the Arrhenius plots of μ_h versus T^{-1} , shown in Fig. 2(a), activation energies of 126 meV and 131 meV for the high MW and medium MW films, respectively. If the low MW film is analyzed similarly with Eq. (1), the resulting Arrhenius plot is in disagreement with the trend of the other two higher MW films. However if Eq. (2) is used, the contribution of the temperature activation and field assistance can be decoupled. By plotting the zero-field mobility, μ_{h0} , as the temperature is varied, an activation energy of 143 meV is obtained, which follows the trend with the higher MW films. The temperature dependence of the electric-field coefficient γ is analyzed with the empirical relation,^{13,19}

$$\gamma = \left(\frac{1}{kT} - \frac{1}{kT_0} \right) B \quad (4)$$

with B and T_0 the fitting constants. Figure 2(b) shows the plot of γ versus T^{-1} , and we find $B = 1.7 \pm 0.1 \times 10^{-5}$ eV (m/V)^{1/2} and $T_0 = 452 \pm 38$ K.

As the MW of RR-P3HT increases, the hole mobility in the diodes also increases. These results coupled with our

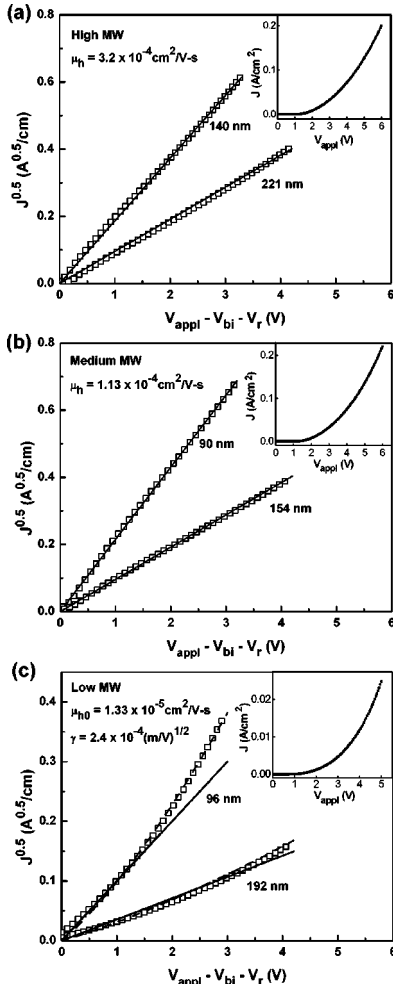


FIG. 1. $J^{0.5}$ vs V plots for (a) high MW film (31.1 kg/mol), (b) medium MW film (9.72 kg/mol), and (c) low MW film (2.89 kg/mol) at room temperature. The thickness of the films is indicated in the plots. The solid lines are fits to the data points using Eq. (1). The dashed lines are fits using Eq. (2). The inset in each figure shows the J vs V_{app} plot of the thicker film device before any correction for the voltage.

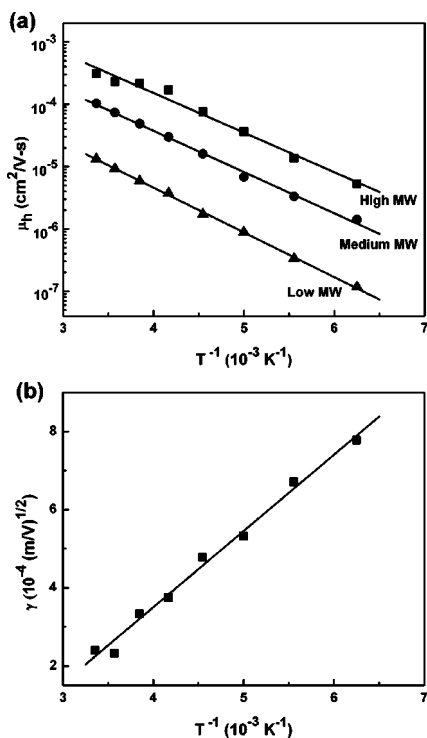


FIG. 2. (a) Arrhenius plots of μ_h vs T^{-1} of the different MW films. Square: High MW film (31.1 kg/mol), circle: medium MW film (9.72 kg/mol), triangle: low MW film (2.89 kg/mol). (b) The temperature dependence of γ in the low MW film.

earlier results on the field effect mobilities strongly suggest that higher MW RR-P3HT is better for charge transport.¹⁰ Although previous work used chloroform as the solvent, we have also found that transistors made with RR-P3HT spun from THF exhibit a similar three orders of magnitude increase in mobility with MW. AFM and XRD studies of the THF-spun films both show nanorod morphology for the crystalline low MW films with a significant hopping barrier stemming from grain boundaries, and less well-defined crystalline regions for the high MW films. Our previous hypothesis of charge transport in low MW films being hindered at grain boundaries¹⁰ may well apply here for charge transport in the direction perpendicular to the substrate. The dependence of the SCLC diode mobility in the direction perpendicular to the substrate on the MW is found to be not as strong as the MW-dependent FET mobility in the plane of the film, with only one order of magnitude difference in the former. According to Tanase *et al.*, the difference in mobility values measured in isotropic conjugated polymers between the diode and transistor geometries can be explained by the increase in carrier density in the film. We expect that the anisotropy in RR-P3HT chain orientation^{20,21} should also contribute to the differences in the transistor and diode mobilities.

The mobilities in medium and high MW films are both found to be field independent, whereas the low MW diodes show apparent field-dependent mobility. We rule out the possibility of injection problems in the low MW film devices based on cyclic voltammetry measurement showing the HOMO of the low MW film is similar to that of the higher MW films, and the fact that the data fits well to the SCLC

model for diodes of varying thickness. Our high MW film results corroborate previous time-of-flight (TOF) experimental results on RR-P3HT, which shows that there is either small or negligible field dependence.^{7,8} The different behaviors in high and low MW films point to the need for a model that can explain transport in these semicrystalline films.

In conclusion, we have shown that RR-P3HT exhibits space charge limited transport in sandwich diodes for different MW. The hole mobility is found to increase with MW and this can be correlated with the film morphology. The mobilities of the higher MW films are found to be field independent, while the low MW film exhibits field-dependent mobility. The semicrystalline films of RR-P3HT show significantly lower activation energies compared to other conjugated polymers; this finding is consistent with RR-P3HT exhibiting one of the highest mobilities among the conjugated polymers.

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