

Controlling the Field-Effect Mobility of Regioregular Polythiophene by Changing the Molecular Weight**

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Semiconducting conjugated polymers are being developed for light-emitting diodes,^[1,2] photovoltaic cells,^[3,4] and thin-film transistors^[5-7] because they can readily be deposited from solution onto almost any substrate. Clearly, it is important to maximize the charge carrier mobilities for all of these applications, especially for transistors and photovoltaic cells. Most conjugated polymers have hole mobilities in the range of 10^{-7} – 10^{-5} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. The electron mobility is usually even lower because of traps with energies slightly below the lowest unoccupied molecular orbital (LUMO) level of the polymer. Poly(9,9'-dioctylfluorene-co-2,2'-bithiophene) (F8T2) has a higher hole mobility (as high as 10^{-2} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) because of its liquid crystalline character.^[8,9] Regioregular poly(3-hexylthiophene) (RR P3HT) has an even higher mobility (with quoted values as high as 10^{-1} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)^[10-12] because the regular arrangement of its side chains allows efficient π -stacking of the conjugated backbones.^[11] Despite the achievements that have been made towards improving the mobility of conjugated polymers, much is still not known about how charge moves through the films and how the chain packing can be optimized to obtain even higher mobilities.

Reported values for the mobilities in RR P3HT vary by orders of magnitude.^[10-12] We now show a clear correlation between the field-effect mobility of RR P3HT and its molecular weight (MW) with mobility values increasing from 1.7×10^{-6} to 9.4×10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ as the MW is increased from 3.2 to 36.5 kD. These variations in MW are also accompanied by significant changes in film morphology. These observations probably explain why the mobility values obtained in different labs vary so widely and suggest that optimizing the MW of conjugated polymers could lead to significant improvements in device performance.

Our studies were performed both on batches of RR P3HT that were synthesized in our laboratory by a modified McCullough route^[13-15] and also with a commercial sample purchased from Aldrich, which was said to be prepared through

the Rieke route.^[16] MW control in our samples prepared by the modified McCullough route was achieved by adjusting the polymerization time. Since the commercial sample had a large polydispersity, we separated it into several low polydispersity fractions with different MWs through a series of Soxhlet extractions with solvents of increasing solvency (hexane, dichloromethane, and chloroform).^[17] The MWs were measured by both matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) and gel permeation chromatography (GPC). The values measured by GPC tended to be slightly lower than those obtained by MALDI-MS as a result of the differences in hydrodynamic volumes between the polystyrene samples used as calibration standards and the stiffer RR P3HT chains.^[18] We report the GPC values here since MALDI-MS analysis was not performed on all samples, and these values are more commonly reported in the literature. The MALDI-MS data provided useful additional structural information indicating that most of the polymer chains are terminated with one hydrogen atom and one bromine atom. Since bromine atoms could affect the mobility of the polymer, we also made some polymers without bromine end groups by the modified McCullough route, using 5-methylthienylzinc chloride as a chain-termination reagent during the polymerization. In this report, we refer to the bromine-terminated polymers made by the modified McCullough route as Group A, the commercial Rieke route polymers as Group B, and the methylthiophene-terminated polymers as Group C. Table 1 lists the MWs and polydispersities of all the samples in each group.

Table 1. List of polymer samples used in study. Molecular weight (M_n) and polydispersity (PDI) measured by GPC. Regioregularity (RR) was calculated from NMR spectra.

Sample	M_n [kD]	PDI	RR
A1	4.0	1.1	>99%
A2	9.0	1.2	>99%
A3	11.6	1.2	>99%
A4	33.8	1.5	>98%
B1 (hexane fraction)	4.6	1.3	–
B2 (CH_2Cl_2 fraction)	13.4	1.8	>95%
B3 (CHCl_3 fraction)	29.8	1.9	>98%
B4 (CHCl_3 fraction)	36.5	1.7	–
C1	3.2	1.4	>98%
C2	16.2	1.2	>98%
C3	31.1	1.4	>98%

The field-effect mobilities of RR P3HT were measured using a bottom-contact thin-film field-effect transistor (FET) geometry (Fig. 1) similar to that used in previous work.^[10] A 230 nm thick silicon oxide gate dielectric (capacitance = 18 nF cm^{-2}) was thermally grown on a highly doped n-type $\langle 100 \rangle$ silicon wafer. Source and drain electrodes were fabricated using conventional lift-off photolithography and electron-beam evaporation of 5 nm of titanium and 40 nm of gold. The transistors had channel widths of 2 or 40 μm and a channel length of 5 μm . The silicon oxide surface was modi-

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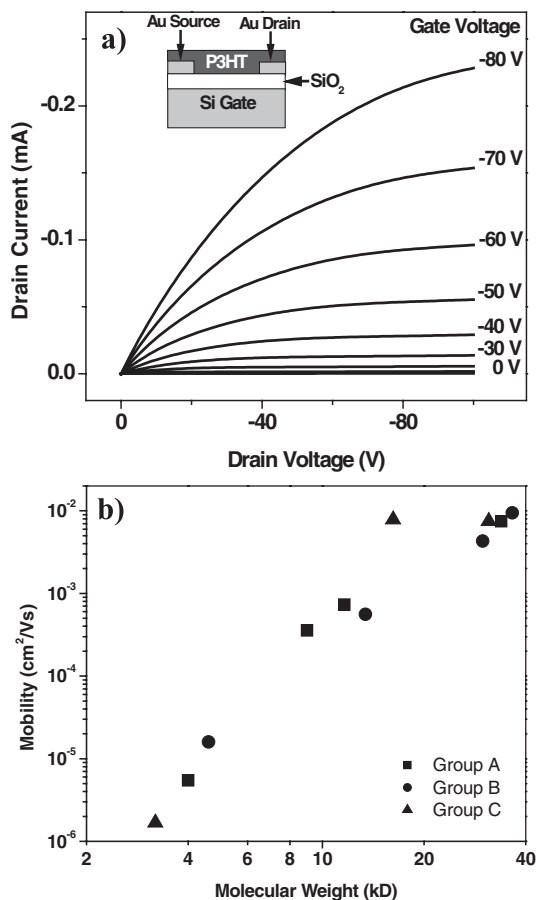


Fig. 1. a) Current–voltage curves of a 10 μm long by 40 μm wide transistor with a molecular weight of 33.8 kD. The inset shows a diagram of the device structure. b) Plot of field-effect mobility versus the number average molecular weight. Group A is represented as squares, Group B is represented by circles, and Group C is represented by triangles.

fied with hexamethyldisilazane (HMDS) by spin-coating a 20 % HMDS/80 % propylene glycol monomethyl ether acetate (PGMEA) solution at 5000 rpm, and the P3HT films were then spin cast from 0.5 wt.-% solutions of polymer in chloroform at 2500 rpm in a nitrogen-filled glove box. Figure 1a shows typical current–voltage curves of a transistor prepared using P3HT with MW = 33.8 kD at several gate voltages. The on/off ratios observed in this study using various polymers typically varied from 10^3 to 10^5 and were not correlated to MW. The high value of the on/off ratio indicates that the samples did not have significant levels of unintentional dopants.

The average field-effect mobility of each transistor was calculated in the saturation regime ($V_{\text{ds}} = -95$ V) by plotting the square root of the drain current versus gate voltage and fitting the data to the equation^[19]

$$I_{\text{ds}}^{0.5} = \left(\frac{W\mu C_{\text{ox}}}{2L} \right)^{0.5} (V_{\text{g}} - V_{\text{t}}) \quad (1)$$

Contact resistance was neglected because previous work has shown that the potential drop at the interface is small,^[20] and the measured mobility did not increase with increasing

channel length as would be expected for a contact-resistance-limited device.^[21] The field-effect mobility values reported in this report are the average values measured from six transistors. Figure 1b plots the mobility versus MW for all three groups of polymers. It shows that the mobility steadily increases with MW from a value of $1.7 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 3.2 kD to $9.4 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 36.5 kD. Factors that must be considered in explaining this large dependence of mobility on MW include charge trapping by end groups, the density of chemical defects, the regioregularity of the chains, variations in the energy levels due to polydispersity, the morphology of the films, and the distance that charge carriers can travel before they have to hop from one chain to another.

If the end groups of the polymer chains were limiting the mobility by trapping charge, we would expect the mobility of the polymers with a bromine end group, which is a strong electron acceptor, to be different than the mobility of the polymers with methylthiophene end groups. In fact, the mobility of all three groups of polymers has essentially the same dependence on the MW. Consequently, we conclude that trapping by the end groups is not likely to be the main factor that determines the mobility.

Previous work has shown that the regioregularity of P3HT has a large impact on the way the chains pack on each other, and that this, in turn, has a significant effect on the charge carrier mobility.^[22] To see if the lower MW samples had a lower mobility due to a reduced regioregularity, we measured the regioregularity of each sample by comparing the ^1H NMR signal intensities at 7.05, 7.03, 7.00, and 6.98 ppm.^[23] As shown in Table 1, all but one of the samples measured had a regioregularity greater than 98 %. Since the regioregularity of all of the samples is very high, it is unlikely that the large observed variations in mobility are solely the result of small variations in regioregularity.

One must also consider the possibility that the lower molecular weight chains might have a higher concentration of chemical defects. For the polymers in Group B, one might suspect that the lower MW samples have more defects, since they are made up of the chains whose polymerization was terminated first. This would not be expected, however, for the polymers in Group A, since their MW was varied by adjusting the polymerization time, or for the samples of Group C, since their MW was varied by adjusting the methylthiophene to monomer ratio. Since the polymers made by the three different synthetic routes showed the same trend for mobility versus MW, it is not likely that the mobility was limited by chemical defects.

Others have suggested that polymer films with higher polydispersity have lower mobility, since longer chains are statistically more likely to have a region with longer conjugation length that can act as a trap site due to its reduced bandgap.^[24] Table 1 shows that there is no correlation between polydispersity and mobility for the samples we studied. Thus it seems unlikely that the mobility trend in RR P3HT can be explained by traps that arise from polydispersity.

The nature of the chain packing is clearly an important factor on the mobility of a polymer film. Others have observed

morphological differences in drop-cast films of polythiophenes of varying MW.^[17,25] The morphology of our films was determined using X-ray diffraction (XRD) and atomic force microscopy (AFM). It must be kept in mind that most of the current in an organic FET is carried within approximately 5 nm of the interface with the gate dielectric.^[26] Our XRD measurements reveal the type of crystalline order that prevails throughout the film, while the AFM measurements provide an image of the top surface. We present this data because it probably indicates the type of structure that exists at the bottom interface. We cannot, however, rule out the possibility that interactions with the substrate lead to a different structure at the bottom interface. AFM images (Fig. 2) show a rod-like structure for a 3.2 kD film and an isotropic nodule structure for a 31 kD film. Images of other low and high molecular weight films showed similar morphologies. The images suggest that the lower molecular weight samples are more crystalline. This notion is further supported by the X-ray diffraction measurements in Figure 3, which show that a 3.2 kD film has a more intense $\langle 100 \rangle$ diffraction peak than a 33.8 kD film. It is not surprising that the lower MW polymer chains are more able to pack into crystals. It is interesting, however, that the

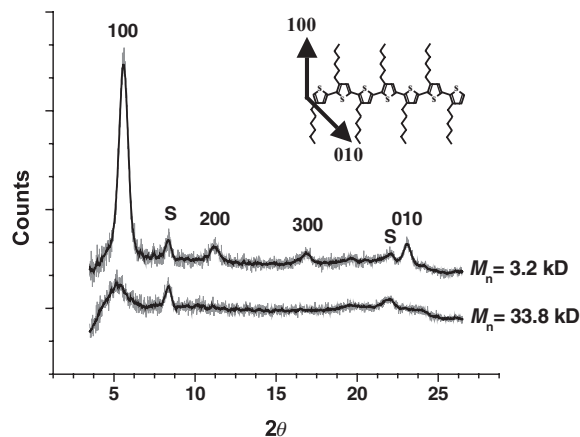


Fig. 3. X-ray diffraction (XRD) analysis shows a more intense $\langle 100 \rangle$ peak (alkyl chain spacing) for the 3.2 kD film compared to the 33.8 kD film, confirming a higher degree of crystallinity in the low MW films. The $\langle 010 \rangle$ peaks (π -stack direction) of 3.2 kD and 33.8 kD samples were small and showed no evidence for a change in preferential orientation. The peaks labeled S are not from the polymer film; they are from either the substrate or the sample mount.

samples with a higher degree of crystallinity have significantly lower mobility. The AFM data clearly suggest that the rod-

like crystals of the low MW films have more defined grain boundaries than the isotropic nodules of the high MW films. Others have shown that grain boundaries limit the mobility in transistors made by polycrystalline small organic molecules such as sexithiophene and octithiophene.^[27] We hypothesize that RR P3HT films with higher MW might have higher mobility because the regions of crystalline order are less well defined, and possibly because the longer chains connect the ordered regions to provide a pathway for charge transport between crystalline domains.

Recent studies have shown that charge carriers and excitons in RR P3HT delocalize over several neighboring chains.^[28,29] The π -stacking that causes this delocalization occurs when several chains are locally aligned, allowing the chains to have a strong wavefunction overlap. The delocalization over several chains makes it easier for the charge carriers to bypass single chain defects that would stop the carrier on an isolated chain. It is likely then that mobility could increase with MW because charge carriers can travel farther along longer chains before they have to hop to another chain, and because longer chains give charge carriers more opportunities for hopping to neighboring chains. This net reduction

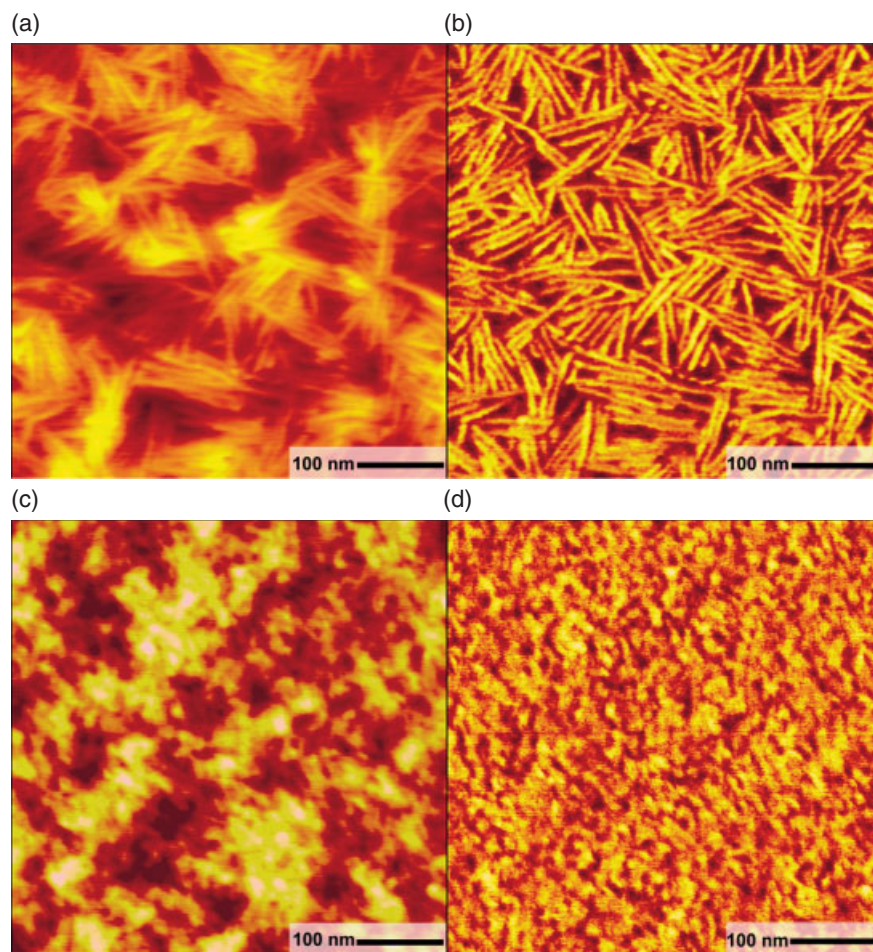


Fig. 2. Tapping mode atomic force microscope (AFM) images of a 3.2 kD polymer film [a) topography and b) phase] with root-mean-square (rms) roughness of 6.6 Å and a 31.1 kD polymer film [c) topography and d) phase] with rms roughness of 5.8 Å.

in hopping events could result in an increased mobility. Further experiments will be required to determine the exact nature of chain packing and charge transport.

We conclude that the MW of RR P3HT has a substantial effect on the way that the chains pack on each other, and that this, in turn, causes the mobility to vary by at least four orders of magnitude. Our data does not show that disordered films are intrinsically better than highly crystalline films. It does show that factors other than crystallinity can have a strong effect on mobility, and that these other factors must be considered when optimizing polymer devices. It is possible that some of the variations in mobility observed in previous studies were at least in part due to variations in MW instead of some of the variables that were reported. As attempts are made to make FETs with higher mobilities and photovoltaic cells with higher energy conversion efficiency, it will clearly be important to optimize the MW of the polymers. We have not yet found a MW at which the mobility saturates or declines. We therefore speculate that higher mobilities could be obtained if longer chains could be synthesized without introducing defects.

Experimental

Regioregular poly(3-hexylthiophenes) of Group A were synthesized by a modified McCullough route [14,15]. The molecular weight of the samples was varied by adjusting the polymerization time (5 min, 11 min, 17 min, and 12 h, respectively). The polymerization was terminated by quenching with methanol. After precipitation from methanol, the polymer was purified by continuous extraction with methanol and then chloroform under nitrogen atmosphere. Polymers of Group B were prepared by performing continuous extraction of a sample from Aldrich with increasingly better solvents (hexane, dichloromethane, and chloroform). Polymers of Group C were synthesized similarly to the modified McCullough route, except that the polymerization system was a mixture of the monomer and a 5-methylthienylzinc chloride in a ratio of $n:1$. The methylthienylzinc chloride can statistically incorporate into the chain ends of the polymer and terminate the chain growing. The ratio $n:1$ was adjusted to give variety of molecular weights and degrees of polymerization. After polymerization, the polymer batches of each group were purified by precipitation in methanol and continuous washing of the precipitate with methanol for 24 h under nitrogen atmosphere. The regioregularity of our samples were estimated with ^1H NMR by comparing the signal intensity of 7.05, 7.03, 7.00, and 6.98 ppm that arise from the aromatic region of the spectrum [23].

Films for structural characterization were deposited on silicon oxide/silicon substrates identical to those the devices were made on but lacking the gold source/drain electrodes. A Digital Instruments Multimode Atomic Force Microscope (AFM) operating in tapping mode with a silicon cantilever was used to characterize the surface morphology of the samples. A Phillips Expert X-ray diffractometer (XRD) was used to characterize the crystallinity of the sample. The 3.2 kD film had a thickness of 30 nm and the 33.8 kD film had a thickness of 60 nm. The XRD data was smoothed using a nearest neighbor smoothing routine and the background was removed from the data by fitting the background to a power law and subtracting the fit from the data.

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Luminescent Nanoring Structures on Silicon

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In recent years, nanoparticles (NPs) have found numerous applications in a wide variety of fields. Here, we report on a unique self-organization process of cadmium sulfide (CdS) NPs, resulting in the formation of well-defined, luminescent nanometer-sized ring structures (luminescent nanorings) on a

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