J|A|C|S
COMMUNICATIONS

Nanostructure Dependence of Field-Effect Mobility in Regioregular Poly(3-hexylthiophene) Thin Film Field Effect Transistors

Rui Zhang,[†] Bo Li,[‡] Mihaela C. Iovu,[†] Malika Jeffries-EL,[†] Geneviève Sauvé,[†] Jessica Cooper,[†]
Shijun Jia,[†] Stephanie Tristram-Nagle,[§] Detlef M. Smilgies,[⊥] David N. Lambeth,[‡]
Richard D. McCullough,[†] and Tomasz Kowalewski*,[†]

Department of Chemistry, Department of Electrical and Computer Engineering, and Department of Physics, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, and Cornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, New York 14853

Received August 16, 2005; E-mail: tomek@andrew.cmu.edu

One of the outstanding challenges in the field of organic semiconductors, in particular those of macromolecular nature, is the establishment of the relationship between their structure and transport properties. One of the potential advantages of polymer semiconductors in comparison with low-molecular weight systems is the possibility to achieve particularly extensive charge delocalization (and thus fast transport pathways) along the conjugated polymer backbone.[1] This advantage became particularly clear with the development of regioregular poly(3-hexylthiophenes) (RR-P3HTs), which, owing to their regioregularity, have a high tendency to self-assemble into highly ordered, partially crystalline structures which facilitate high conjugation and result in dramatic improvement of field effect mobility.[2a,b] Results of more recent work indicate that mobility of these materials can be further improved by the increase of their molecular weight[2c−e] and through the choice of deposition methods[2f] favoring formation of ordered structures (e.g., nanofibrils/nanowires).[2g]

Herein we go one step further, by demonstrating that the careful choice of processing conditions of RR-P3HTs with narrow polydispersities can lead to the formation of very well-defined nanofibrillar morphologies in which the width of the nanofibrils corresponds very closely to the weight average contour length of polymer chains. Moreover, we show that the charge carrier mobility in field effect transistors (FETs) fabricated from these well-ordered polymers increases exponentially with the nanofibril width. The significance of this remarkable correlation is then discussed in context of recent theoretical work focused on the role of reorganization energies in conductive heterocyclic oligomers.[2h]

Narrow molecular weight distribution RR-P3HTs with number average molecular weights ranging from 2 to 13 kDa were synthesized as described elsewhere.[3a,b] Number average molecular weights were determined using high-resolution NMR end group analysis and converted to weight average molecular weights (M_w) using polydispersity indices (PDIs) obtained from gel permeation chromatography (GPC) (cf. Supporting Information [SI]). Ultrathin films were prepared by drop casting from 1 mg/mL RR-P3HT solutions in toluene onto highly doped *n*-type silicon wafers covered with a 200-nm thick layer of thermally grown oxide and patterned with Au source and drain FET electrodes (for more details on FET fabrication and testing cf. SI). Surface morphology of polymer films comprising FET channels was visualized with tapping mode atomic force microscopy (TMAFM, see Figure 1). In all cases, phase contrast TMAFM images revealed the presence of densely packed, elongated features of highly uniform widths, which will be referred to as nanofibrils. As shown in Figure 2a (red symbols), the width of nanofibrils, w_{AFM}, (determined by Fourier analysis of AFM images) initially increased linearly with M_w and then leveled off. This dependence turned out to be particularly revealing when plotted as a function of weight average contour length L_w of RR-P3HT (see top abscissa axis in Figure 2a). This close, direct relationship between w_{AFM} and L_w is highly suggestive of a structure composed of one-molecule-wide, stacked sheets of RR-P3HT, with polymer backbones aligned perpendicular to the nanofibril axis. Such structure is consistent with (although not fully proven by) grazing incidence X-ray diffraction (GIXRD) studies (cf. SI), which revealed the presence of familiar[2b] layered, π-stacked structures, with the π-stacking plane perpendicular (in-plane diffractogram) and periodic layering parallel (out-of-plane diffractogram) to the film surface.

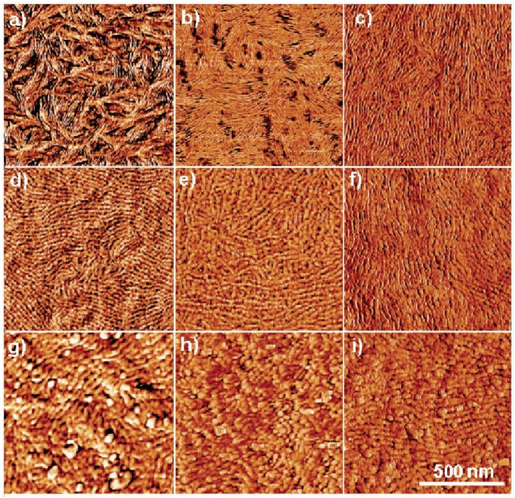

Figure 1. Tapping mode AFM images (phase contrast, 1 μm × 1 μm) of thin films of RR-P3HTs of various molecular weights in FET devices prepared by drop casting from toluene. Corrected weight average molecular weights in (a−i) were respectively equal to: 2.4, 4.8, 5.1, 7.0, 7.5, 11.8, 15.7, 17.3, and 18.4 kDa. (For higher-resolution version of AFM images, cf. SI).

Since AFM observations are limited only to the surface, the bulk nanoscale morphology of the RR-P3HT films was further studied with the aid of grazing incidence small-angle X-ray scattering (GISAXS),[5a,b] utilizing the Cornell High Energy Synchrotron Source (CHESS, cf. SI). GISAXS scattering patterns (Figure 2b) revealed the presence of periodicity which corresponded very well to one measured in TMAFM images (Figure 2d). The hump in the GISAXS scattering patterns observed at a variety of X-ray beam

---

[†] Department of Chemistry, Carnegie Mellon University.
[‡] Department of Electrical and Computer Engineering, Carnegie Mellon University.
[§] Department of Physics, Carnegie Mellon University.
[⊥] Cornell High Energy Synchrotron Source (CHESS), Cornell University.

10.1021/ja055192i CCC: $33.50

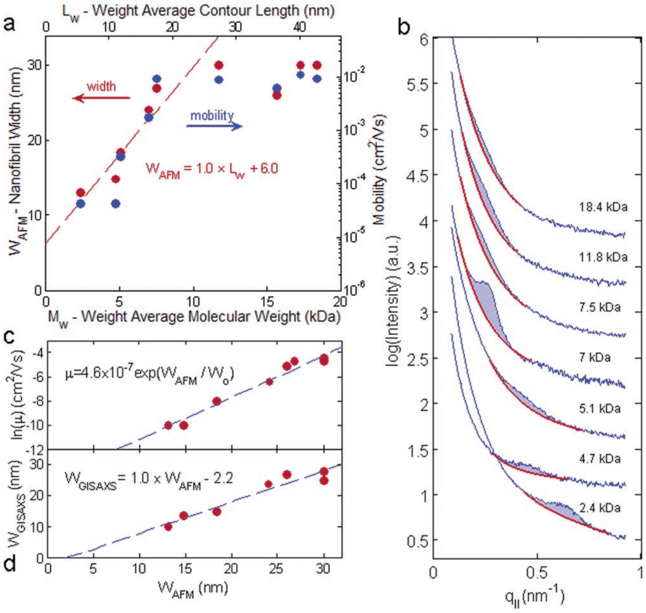

Figure 2. (a) Dependence of nanofibril width (w_{AFM}, red) and charge carrier mobility (μ, blue) on weight average molecular weight (M_w, bottom axis) and weight average contour length (L_w, top axis) of RR-P3HT. (b) GISAXS scattering profiles for thin films of RR-P3HTs with various molecular weights. (c) Data and exponential fit (dash) of μ vs w_{AFM}. (d) Linear correlation between GISAXS periodicities and nanofibril widths (w_{GISAXS} vs w_{AFM}).

incident angles (cf. SI), i.e., at different X-ray penetration depths, indicates that the observed periodicities extended across the entire thin films.[6a,b]

Most interestingly, as shown in Figure 2a (blue symbols) the logarithm of charge carrier mobility μ obtained from the analysis of $I-V$ characteristics of FET devices can be mapped directly against the periodicities revealed by AFM/GISAXS observations. This mapping points to an exponential dependence of the form $\mu = \mu_o \exp(w_{AFM}/w_o)$, with $\mu_o = 4.6 \times 10^{-7}$ cm^2/Vs and $w_o \approx 3$ nm (Figure 2c). Since, as shown above, the nanofibril widths w_{AFM} tend to directly reflect the contour length of polymer molecules, the observed exponential dependence of μ vs w_{AFM} appears to directly point to the prominent role of extended, conjugated states in the charge transport in semiconducting polymers.[7]

Whereas answering the question about the origin of this remarkable dependence extends beyond the scope of this communication, it is worth pointing to some parallels with the results of a recent theoretical study focused on thermally activated hopping transport in heterocyclic conjugated oligomers.[2h] In that study, Hutchinson et al. pointed out the analogies between the charge transport in conjugated oligomers and other charge transfer reactions. In particular, they noted that the primary contribution to the hopping energy barrier may originate from the reorganization energy, which represents the energetic consequence of the "sluggishness" of molecular backbones at the time scales characteristic for charge transfer. Results of their theoretical calculations demonstrated the marked decrease of reorganization energy with the length of the conjugated backbone, which translated to an approximately exponential increase of charge-transfer rate with oligomer length, in agreement with experimental results published by other authors.[4a,8] The results of our work raise an interesting question, whether reorganization energy effects are still important for polymers such as those studied here.[2h,4b−d] One other factor that should be considered in explaining the observed exponential dependence of mobility on nanofibril width is the possibility of the change of the nature of grain boundaries between adjacent nanofibrils (e.g. due to the increase of polydispersity with molecular weight). The latter effect could be also responsible for the observed leveling off of nanofibril width at higher molecular weights, which otherwise could imply some conformational change such as chain folding.

In summary, a distinct correlation between FET mobility, molecular weight, and nanostructure of RR-P3HT thin films has been established in this study. The revealed dependencies may prove particularly useful in optimization of the performance of devices based on regioregular polythiophenes and, perhaps, other heterocyclic conjugated systems, and may provide a well-directed stimulus for further studies of electrical transport mechanisms in conjugated polymer systems.

Acknowledgment. This work was supported by an AFOSR MURI (Contract No. F49620-02-1-0359), NIOSH-CDC (Contract No. 200-2002-00528), and NSF (CHE-0415369) (R.M.C). Jason Wolf is gratefully acknowledged for the XRD characterization. CHESS is a national user facility supported by NSF/NIH-NIGMS Award DMR-0225180.

Supporting Information Available: Experimental conditions and detailed characterization results. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685−688.
(2) (a) Bao, Z.; Dodabalapur, A.; Lovinger, A. J. *Appl. Phys. Lett.* **1996**, *69*, 4108−4110. (b) McCullough, R. D.; Tristram-Nagle, S.; Williams, S. P.; Lowe, R. D.; Jayaraman, M. *J. Am. Chem. Soc.* **1993**, *115*, 4910−4911. (c) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J. S.; Frechet, J. M. J. *Adv. Mater.* **2003**, *15*, 1519−1522. (d) Zen, A.; Pflaum, J.; Hirschmann, S.; Zhuang, W.; Jaiser, F.; Asawapirom, U.; Rabe, J. P.; Scherf, U.; Neher, D. *Adv. Funct. Mater.* **2004**, *14*, 757−764. (e) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J. S.; Frechet, J. M. J.; Toney, M. F. *Macromolecules* **2005**, *38*, 3312−3319. (f) Wang, G. M.; Swensen, J.; Moses, D.; Heeger, A. J. *J. Appl. Phys.* **2003**, *93*, 6137−6141. (g) For more references, cf. SI. (h) Hutchison, G. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2005**, *127*, 2339−2350.
(3) (a) Loewe, R. S.; Ewbank, P. C.; Liu, J. S.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324−4333. (b) Loewe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250−253.
(4) (a) A qualitatively similar prediction was made by Baughman and Shacklette who considered the influence of conjugation length on conductivity, cf. Baughman, R. A.; Schacklette, L. W. *Phys. Rev. B* **1989**, *39*, 5872−5886. (b) According to Hutchison et al.,[2h] while for all-trans oligoenes the reorganization energy effect leveled off for molecules the length of which exceeded several double bonds (the length self-localized polarons), no leveling off was observed in calculations for heterocyclic conjugated systems, such as oligothiophenes. (c) Izumi, T.; Kobashi, S.; Takimiya, K.; Aso, Y.; Otsubo, T. *J. Am. Chem. Soc.* **2003**, *125*, 5286−5287. (d) Sirringhaus, H. *Adv. Mater.* **2005**, *17*, 2411−2425.
(5) (a) Tang, C. B.; Tracz, A.; Kruk, M.; Zhang, R.; Smilgies, D. M.; Matyjaszewski, K.; Kowalewski, T. *J. Am. Chem. Soc.* **2005**, *127*, 6918−6919. (b) Smilgies, D.-M.; Busch, P.; Papadakis, C. M.; Posselt, D. *Synchrotron Radiat. News* **2002**, *15*, 35−42.
(6) (a) Broadening of the feature in the GISAXS pattern with the increase of the incident angle points to some decrease of the degree of nanofibrillar ordering with the increase of distance from the surface, *cf.* SI. (b) Importantly, the periodicity was not observed in the samples cast from chloroform, pointing to the potential variability of the degree of nanofibrillar order under the influence of kinetic factors and/or solvent properties, *cf.* SI.
(7) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741−1744.
(8) Nagamatsu, S.; Kaneto, K.; Azumi, R.; Matsumoto, M.; Yoshida, Y.; Yase, K. *J. Phys. Chem. B* **2005**, *109*, 9374−9378.

JA055192I