

Poly(3-hexylthiophene) monolayer nanowhiskers†

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We report poly(3-hexylthiophene) (P3HT) nanowhiskers of monolayer thickness which self-assemble in a dilute solution. These nanowhiskers are tens of micrometers in length, ~30 nm in width, but only 1.6 nm in thickness, corresponding to the height of P3HT in the side-chain direction. The field-effect mobility of these nanowhiskers reached $1.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Regioregular poly(3-hexylthiophene) (P3HT) is a promising semiconducting polymer for use in field-effect transistors (FETs) and solar cells. Its chemical stability, solution processability and high charge carrier mobility are attractive properties.^{1–3} For these applications, control of the morphology and, in particular, the crystalline structure of P3HT is crucial for optimizing its charge transport properties and hence device performance.⁴ As a typical π -conjugated polymer, P3HT contains a rigid conjugated backbone modified with soft alkyl side chains, and its crystallization behavior has stimulated significant interest.⁵ Because of the backbone rigidity and the immiscibility of the main chains and the side chains, P3HT molecules tend to self-assemble into fibrillar nanostructures, such as nanowhiskers⁶ and nanofibers,⁷ with stacked main chains in layers and side chains between the layers. On substrates these nanostructures usually exhibit an edge-on orientation, *i.e.* the side chains are perpendicular to the substrate, and the rigid backbones are parallel to the substrate and perpendicular to the long axis of the nanostructures.^{6–8} P3HT nanowhiskers or nanofibers can be obtained by the

“whisker method” which involves cooling the P3HT solution in a marginal solvent,^{6,8–12} by adding a poor solvent into the P3HT solution^{13,14} and spin-coating the P3HT solution under a high solvent vapor pressure.^{15,16} P3HT nanowhiskers generally exhibit lengths greater than $10 \mu\text{m}$ ^{6,8,17} and heights of 3–6 nm,^{6,8,16} corresponding to 2–4 molecular layers. The width increases as a function of molecular weight before reaching a maximum of 15–20 nm, determined by transmission electron microscopy (TEM), as the polymer chains change from being fully extended to folding in the direction of the side chains when the molecular weight is above a critical value.¹¹ The maximum width of the nanowhiskers measured by atomic force microscopy is about 30 nm,⁸ which is much larger than the TEM values, and likely due to the exaggeration effect of the AFM tip.² The molecular weight dependence of the width is also observed in P3HT nanofibers, with a maximum width of ~30 nm, as determined by AFM.⁷ The field-effect mobilities of these nanostructures measured in the film, network and isolated single fiber states are around $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^{10,11,17,18} which is consistent with the calculated result of the inter-chain mobility of P3HT.¹⁹ On the other hand, ultrathin films of monolayer P3HT molecules have been obtained by dip-coating²⁰ and liquid-crystal hybridization,²¹ however, the field-effect mobility in these monolayer materials is much lower than in the thicker films because the P3HT molecules are poorly ordered. In the present work, we report a new morphological structure of P3HT grown in a good solvent at low concentration over an extended period of time.

After a chloroform solution of P3HT was maintained in a sealed vessel in darkness at $20 \pm 2 \text{ }^\circ\text{C}$ for a week, it remained transparent but its color changed from yellow to red, with new absorption bands emerging in the 550–625 nm region of the UV-vis spectrum (ESI†), which suggests the formation of ordered structures in the solution.^{8,13} A clean Si wafer was dipped into this solution for 1 min and then immediately into chloroform for 1 min, and the surface was examined by AFM (Fig. 1a). A network of nanowhiskers with contact, overlap and bifurcation is clearly observed. Most of the nanowhiskers are longer than

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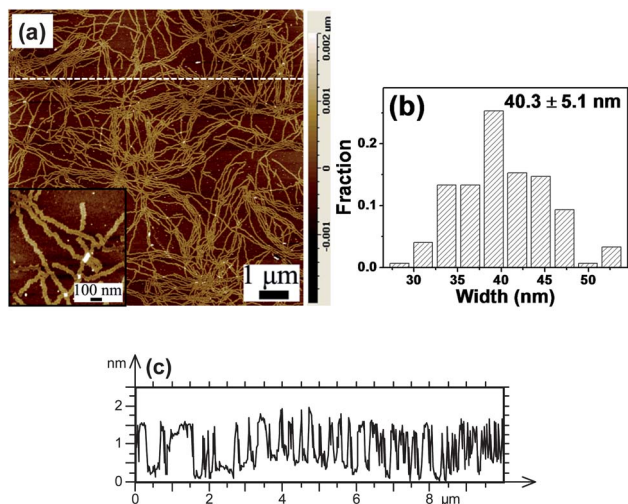


Fig. 1 (a) Topography image of the P3HT monolayer nanowhiskers on Si wafer (inset is an enlarged view), and (b) AFM width distribution and (c) typical cross-section profile of (a) at the position marked by the white dashed line.

10 μm . The average width (Fig. 1b) is about 40 nm, much larger than the reported maximum width of the P3HT nanostructures measured by AFM.^{7,8} More strikingly, the heights of these nanowhiskers are all ~ 1.6 nm (Fig. 1c), which matches the P3HT crystal plane spacing in the direction of the side chains, or the height of a P3HT molecule in the direction of the side chains.^{5,22} Fig. 2a shows the TEM image and the selected area electron diffraction (SAED) pattern of the nanowhiskers on copper grids. The appearance of (020) diffraction confirms long-range ordering with an edge-on orientation of the P3HT molecules and an inter-chain π - π stacking distance of 0.38 nm (ESI[†]) between the adjacent thienyl backbones. The average width is ~ 29 nm (Fig. 2b), again much greater than the reported maximum width measured by TEM (15–20 nm). In the grazing incidence X-ray diffraction (GIXRD) patterns (Fig. 2c), the (100) peak at $2\theta = 5.4^\circ$, characteristic of the chain layered structure,²³ is absent. These results indicate that the nanowhiskers are of monolayer thickness in the direction of the side chains, with long-range ordering in the direction of the π - π stacking and along the thienyl main chains.

In Fig. 2d, the UV-vis absorption spectrum of the P3HT monolayer nanowhiskers is compared with that of normal nanowhiskers prepared from the same P3HT sample following a literature procedure¹³ (ESI[†]). The heights of the latter are 3–6 nm and the width by AFM is ~ 30 nm (ESI[†]), consistent with the literature values,⁸ and (100) diffraction is clearly observed by GIXRD (Fig. 2c). The absorption bands of the nanowhiskers at 558 and 605 nm are attributed to the π - π^* transitions caused by the increased conjugation length due to the stacking of P3HT backbones and inter-chain interactions, respectively.^{14,24,25} For the P3HT monolayer nanowhiskers, however, the first band occurs at 565 nm, which is red-shifted compared to that of the normal nanowhiskers, indicating a longer conjugation length than in the latter.¹³ The relative intensity of the 605 nm band is also higher, implying a higher degree of crystallinity.^{14,24} This result further supports the above conclusion that the nanostructure we

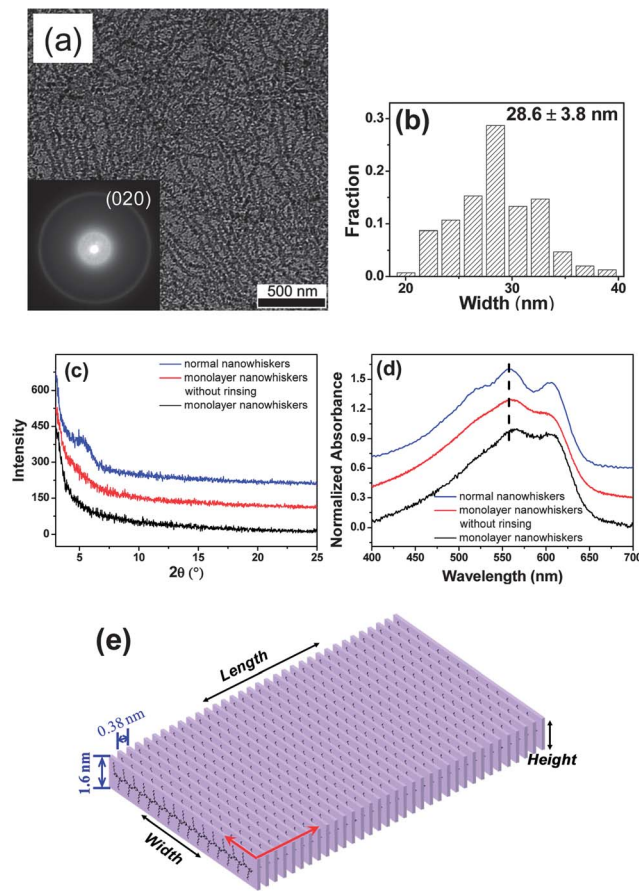


Fig. 2 (a) TEM image and SAED pattern of the P3HT monolayer nanowhiskers formed in chloroform, and (b) width distribution measured by TEM. (c) Out-of-plane GIXRD patterns and (d) UV-vis spectra of the P3HT samples prepared under different conditions. (e) Schematic illustration of the structure of the monolayer nanowhiskers, with the two directions with long-range ordering indicated by the red arrows.

prepared is a highly ordered crystalline material, and in these P3HT monolayer nanowhiskers the P3HT chains are more extended than in normal nanowhiskers. Fig. 2e is a schematic illustration of the monolayer nanowhisker structure.

We turn our focus to the width of the P3HT monolayer nanowhiskers. The number average molecular weight (M_n) of the P3HT sample used in these experiments is 16 000, which is well above the reported critical value of chain folding in nanowhiskers.¹¹ Yet as mentioned above, both the AFM and TEM results are much larger than the reported maximum widths. Furthermore, the monolayer height value has excluded the possibility of chain folding in the side chain direction,^{5,11} and the UV-vis absorption spectrum suggests a higher crystallinity than in normal nanowhiskers, where chain folding occurs. Therefore, we can deduce that in these nanowhiskers the chains are extended without folding. The average contour length of the P3HT molecules can be calculated as $L_n = I_0 M_n / (M_0 B)$, where I_0 and M_0 are the length and molecular weight of the thiophene repeat unit. B is a correction coefficient, which is about 2.^{7,11,26} The value of L_n obtained for the P3HT used in this study is about 18 nm, which is much smaller than the width of the nanowhiskers determined by TEM, which is ~ 29 nm (Fig. 2b). This indicates that the high-molecular-weight

fraction was selected and the low-molecular-weight fraction remained in solution during the formation of the P3HT monolayer nanowhiskers.⁸

To explore the origin of the P3HT monolayer nanowhiskers, several control experiments were carried out. A Si wafer was pulled out of the aged P3HT solution and dried directly without rinsing with chloroform. A large number of similar nanowhiskers of 1.6 nm height are observed by AFM, although they are slightly obscured by the overlaid disordered phase, formed from the drying of the residual solution on the wafer (ESI†). The out-of-plane GIXRD pattern shows no (100) diffraction (Fig. 2c), and the UV-vis spectrum (Fig. 2d) indicates a lower degree of order than in the rinsed sample (where only monolayer nanowhiskers are present), which confirms that the additional portion is more disordered. This disordered phase is also seen in the TEM image (Fig. 2a). No nanowhiskers were observed when a freshly prepared P3HT solution was used, and after 1 day some monolayer nanowhiskers were found in the solution, which were shorter than the ones observed after 1 week (ESI†). These results clearly indicate that the monolayer nanowhiskers are formed and grow in the chloroform solution over several days rather than in the drying/rinsing process. We offer the following explanation. In the chloroform solution, the high-molecular-weight fraction is slightly oversaturated and starts to crystallize, whereas the low-molecular-weight fraction is more soluble and stays in solution. The oversaturation is small; in fact, we observed no nanocrystal formation in a similar solution maintained at a slightly higher temperature of 28 ± 2 °C for a week and more. Under such mild conditions and a small oversaturation, the crystallization process is very slow, which results in the more thermodynamically stable extended-chain crystals. Because the hexyl side chains are much more soluble and the van der Waals interactions between them are much weaker compared to the thienyl main chains, crystal growth in the side chain direction is so unfavorable that it cannot proceed, resulting in monolayer nanowhiskers. On the other hand, the addition of a small amount of hexane, a poor solvent for P3HT, to the chloroform solution produced the normal thicker nanowhiskers (ESI†).

Top-contact devices were fabricated to measure the field-effect mobility of networks of the P3HT monolayer nanowhiskers, and the representative transfer and output characteristics of the devices are shown in Fig. 3a and b. The average field-effect mobility obtained is $0.91 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and the maximum value is $1.3 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is very close to the reported values for other P3HT nanofibers,^{10,11,17,18} and 2–3 orders of magnitude greater than that of P3HT monolayers

fabricated by dip-coating.²⁰ It has been reported that bridging between nanofibers does not reduce charge transport inside the web,²⁷ which is consistent with the corresponding calculated results.¹⁸ Our investigation provides experimental results for the charge transport properties of monolayer P3HT molecules along the π - π direction (inter-chain).

In summary, we have discovered a new morphology of P3HT, nanowhiskers of monolayer thickness, with a much greater width than the literature values. These nanowhiskers exhibit long-range ordering in two directions and single molecule thickness in the third direction, and may be considered as two-dimensional extended-chain crystals. Two factors are critical for the formation of this novel structure: the π -conjugation provides not only chain rigidity to suppress folding in the chain direction, but also a directional attractive interaction of sufficient strength normal to the molecule plane for the crystal to grow in this direction. Then the side chains of suitable length solubilize the semi-rigid molecule, and their interactions with the solvent prevent crystal growth in the side chain direction. These monolayer nanowhiskers of P3HT in a network state, of single molecule thickness, exhibit a high field-effect mobility. This work provides new insight into the self-assembly behavior of semi-rigid conjugated polymers, and affords new building blocks for optoelectronic devices. Further investigation of the molecular weight effects and the growth kinetics of the nanowhiskers is underway.

Notes and references

- 1 H. Sirringhaus, N. Tessler and R. H. Friend, *Science*, 1998, **280**, 1741–1744.
- 2 A. Salleo, R. J. Kline, D. M. DeLongchamp and M. L. Chabinyc, *Adv. Mater.*, 2010, **22**, 3812–3838.
- 3 Y. Sun, J. G. Liu, Y. H. Geng and Y. C. Han, *Chin. J. Appl. Chem.*, 2012, **29**, 1399–1405.
- 4 R. J. Kline, M. D. McGehee and M. F. Toney, *Nat. Mater.*, 2006, **5**, 222–228.
- 5 M. Brinkmann, *J. Polym. Sci., Part B: Polym. Phys.*, 2011, **49**, 1218–1233.
- 6 K. J. Ihn, J. Moulton and P. Smith, *J. Polym. Sci., Part B: Polym. Phys.*, 1993, **31**, 735–742.
- 7 R. Zhang, B. Li, M. C. Iovu, M. Jeffries-EL, G. Sauve, J. Cooper, S. J. Jia, S. Tristram-Nagle, D. M. Smilgies, D. N. Lambeth, R. D. McCullough and T. Kowalewski, *J. Am. Chem. Soc.*, 2006, **128**, 3480–3481.
- 8 S. Samitsu, T. Shimomura, S. Heike, T. Hashizume and K. Ito, *Macromolecules*, 2008, **41**, 8000–8010.
- 9 S. Berson, R. De Bettignies, S. Bailly and S. Guillerez, *Adv. Funct. Mater.*, 2007, **17**, 1377–1384.
- 10 S. Samitsu, T. Shimomura, S. Heike, T. Hashizume and K. Ito, *Macromolecules*, 2010, **43**, 7891–7894.
- 11 J. H. Liu, M. Arif, J. H. Zou, S. I. Khondaker and L. Zhai, *Macromolecules*, 2009, **42**, 9390–9393.
- 12 E. T. Niles, J. D. Roehling, H. Yamagata, A. J. Wise, F. C. Spano, A. J. Moule and J. K. Grey, *J. Phys. Chem. Lett.*, 2012, **3**, 259–263.
- 13 L. G. Li, G. H. Lu and X. N. Yang, *J. Mater. Chem.*, 2008, **18**, 1984–1990.

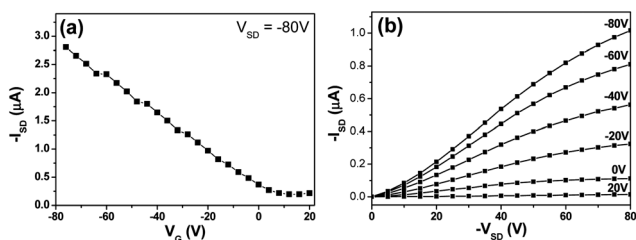


Fig. 3 Typical transfer (a) and output (b) characteristics of a top-contact device fabricated from a network of the P3HT monolayer nanowhiskers.

- 14 N. Kiriya, E. Jahne, H. J. Adler, M. Schneider, A. Kiriya, G. Gorodyska, S. Minko, D. Jehnichen, P. Simon, A. A. Fokin and M. Stamm, *Nano Lett.*, 2003, **3**, 707–712.
- 15 D. H. Kim, Y. D. Park, Y. Jang, S. Kim and K. Cho, *Macromol. Rapid Commun.*, 2005, **26**, 834–839.
- 16 D. H. Kim, Y. Jang, Y. D. Park and K. Cho, *J. Phys. Chem. B*, 2006, **110**, 15763–15768.
- 17 F. S. Kim, G. Ren and S. A. Jenekhe, *Chem. Mater.*, 2011, **23**, 682–732.
- 18 T. Shimomura, T. Takahashi, Y. Ichimura, S. Nakagawa, K. Noguchi, S. Heike and T. Hashizume, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 115314.
- 19 Y. K. Lan, C. H. Yang and H. C. Yang, *Polym. Int.*, 2010, **59**, 16–21.
- 20 H. G. O. Sandberg, G. L. Frey, M. N. Shkunov, H. Sirringhaus, R. H. Friend, M. M. Nielsen and C. Kumpf, *Langmuir*, 2002, **18**, 10176–10182.
- 21 S. Nagano, S. Kodama and T. Seki, *Langmuir*, 2008, **24**, 10498–10504.
- 22 R. D. McCullough, S. Tristramnagle, S. P. Williams, R. D. Lowe and M. Jayaraman, *J. Am. Chem. Soc.*, 1993, **115**, 4910–4911.
- 23 S. Y. Sun, T. Salim, L. H. Wong, Y. L. Foo, F. Boey and Y. M. Lam, *J. Mater. Chem.*, 2011, **21**, 377–386.
- 24 P. J. Brown, D. S. Thomas, A. Kohler, J. S. Wilson, J. S. Kim, C. M. Ramsdale, H. Sirringhaus and R. H. Friend, *Phys. Rev. B: Condens. Matter*, 2003, **67**, 064203.
- 25 J. Clark, C. Silva, R. H. Friend and F. C. Spano, *Phys. Rev. Lett.*, 2007, **98**, 206406.
- 26 J. S. Liu, R. S. Loewe and R. D. McCullough, *Macromolecules*, 1999, **32**, 5777–5785.
- 27 J. C. Bolsee, W. D. Oosterbaan, L. Lutsen, D. Vanderzande and J. Manca, *Adv. Funct. Mater.*, 2012, **23**, 862–869.