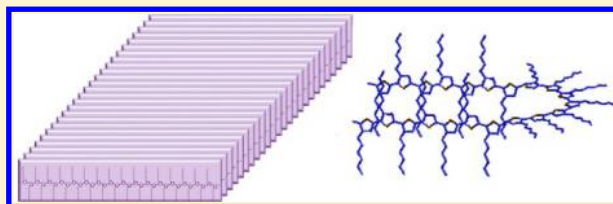


Chain Folding in Poly(3-hexylthiophene) Crystals

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ABSTRACT: Poly(3-hexylthiophene) (P3HT) is a typical conjugated polymer with rather rigid backbone due to π -conjugation of the thiophene rings. In this work, we grew nanowhiskers of monolayer thickness from P3HTs of different molecular weights, and found that the nanowhisker widths were all ~ 16 nm as measured by transmission electron microscopy, independent of the molecular weight and much smaller than the contour lengths of the P3HT chains, indicating the presence of chain folding in the nanowhiskers. Because of the geometry constrain, the chains must fold out of the conjugation plane. An out-of-plane folding model was established based on theoretical calculation results, and its energy was found to be lower than that of the in-plane folding. These results provide new insight into polythiophene crystallization behavior and suggest that conjugated polymers are more flexible than previously perceived.



INTRODUCTION

Poly(3-alkylthiophene)s (P3ATs) are typical conjugated polymers with potential application in flexible organic electronics and optoelectronics, such as organic field effect transistors and photovoltaic cells, because of their stability, solution processability and charge transport ability.^{1,2} Poly(3-hexylthiophene) (P3HT) is the most prominent one in the P3AT family with extraordinary optoelectronic properties.^{3–5} Because of their rigid π -conjugated backbones and immiscibility between the thienyl main chains and the alkyl side chains, P3HT molecules tend to self-assemble into one-dimensional nanostructures with the polymer backbone normal to the length direction, such as nanowhiskers and nanofibrils,^{6–9} which afford intrinsic one-dimensional carrier transport path and lead to high field-effect mobilities.⁶ Therefore, crystallization behavior of P3ATs, which is key to the formation and morphology control of these highly ordered one-dimensional crystalline structures, has stimulated great interest.

An important question in the P3AT crystallization is whether and how the polymer chain undergoes folding, which is assumed to be hindered by the relatively rigid conjugated backbone.⁶ So far few reports focused on chain folding of conjugated polymers, probably because effective approach to this important issue is lacking. Ihn and co-workers⁸ first reported P3AT nanowhiskers obtained from poor solvents, which were of ~ 15 nm width and with a thickness corresponding to two to three P3AT chain layers, and noted that chain folding should be considered because the chain contour length was considerably greater than the whisker width. By using scanning tunneling microscopy (STM), U-turn type chain folding in P3AT molecules adsorbed with face-on orientation on highly oriented pyrolytic graphite (HOPG) was directly visualized, which consisted of 7–10 thiophene rings in continuous all-*cis* conformation in the π -conjugation plane.^{10–12} On the basis of the observation that

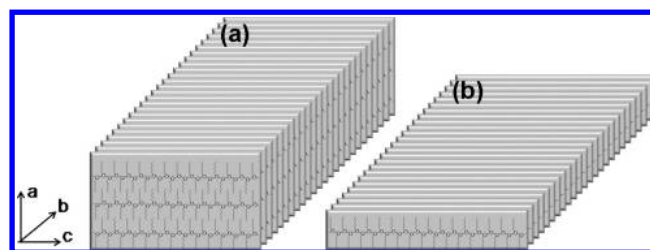


Figure 1. Schematic illustration of the molecular arrangement in (a) a normal P3HT nanowhisker and (b) a P3HT monolayer nanowhisker.

the width of P3HT nanowhiskers corresponded to the extended chain length up to a critical value (~ 10 kDa), and remained constant at about 15 nm for higher molecular weights,^{9,13} Zhai and co-workers¹³ concluded that the P3HT chains folded at molecular weights higher than the critical value, and proposed a folded-chain P3HT crystal model with the backbones folding in the direction of the side chains (i.e., the *a* direction) within the π -conjugation plane,^{13,14} the same folding conformation as that observed by STM.^{10–12} These elegant works convincingly demonstrate the presence of chain folding in P3HT crystals. However, the only established folding structure in P3HT crystals so far has been the folding in the side chain direction as directly observed by STM.

Recently we discovered a new type of P3HT nanowhiskers grown from dilute chloroform solution.¹⁵ Unlike the normal P3HT nanowhiskers reported in the literature, that typically consist of two to three molecular layers and are 3–6 nm or greater in thickness, this new structure consists of a monolayer

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Table 1. Molecular Parameters and Nanowhisker Widths for P3HTs of Different Molecular Weights

M_n^a (kDa)	PDI ^a	corrected M_n^b (kDa)	contour length ^c (nm)	average nanowhisker width (nm)	
				TEM ^d	AFM ^e
14.3	1.24	7.2	20.3	15.4 ± 1.9	28.5 ± 3.3
20.3	1.96	10.2	28.8	18.4 ± 2.9	32.3 ± 3.5
34.3	1.24	17.2	48.7	16.4 ± 2.1	30.8 ± 3.2
36.0	1.72	18.0	51.1	16.2 ± 2.4	33.2 ± 4.7

^a M_n and polydispersity index (PDI) determined by GPC. ^bCorrected M_n calculated from M_n^a using a scaling factor of 2.0.^{9,13,19} ^cCalculated from corrected M_n . ^dAverage width determined by TEM. ^eAverage width determined by AFM.

of π -stacked P3HT chains and is only ~ 1.6 nm thick.¹⁵ Figure 1 schematically illustrates the molecular arrangements in the two kinds of P3HT nanowhiskers. We then found that the growth of these monolayer nanowhiskers can be accelerated by a trace

amount of concentrated H_2SO_4 in the solution that stimulates the nucleation.¹⁶ In the present study, we investigate the effects of P3HT molecular weight on the width of the monolayer nanowhiskers thus grown, and show that the thienyl backbones can fold in the direction normal to the π -conjugation plane, providing evidence that the conjugated polymers are more flexible than previously perceived.

EXPERIMENTAL SECTION

Materials. Regioregular poly(3-hexylthiophene) (P3HT) ($M_n = 20300$) was purchased from Rieke Metals Inc. and used without further purification. Other regioregular P3HT of different molecular weights (M_n of 14300, 34300, and 36000 respectively) were synthesized via the GRIM method by adjusting the polymerization time as reported in literature. H-T regioregularity was all $>94\%$ as measured by comparing the ratio of signals at 2.8 and 2.6 ppm in nuclear magnetic resonance (NMR). Chloroform and sulfuric acid was purchased from Beijing Chemical Reagents Company and used as received. Water was purified with a PGeneral GWA-UN4 unit (18.2 M Ω -cm).

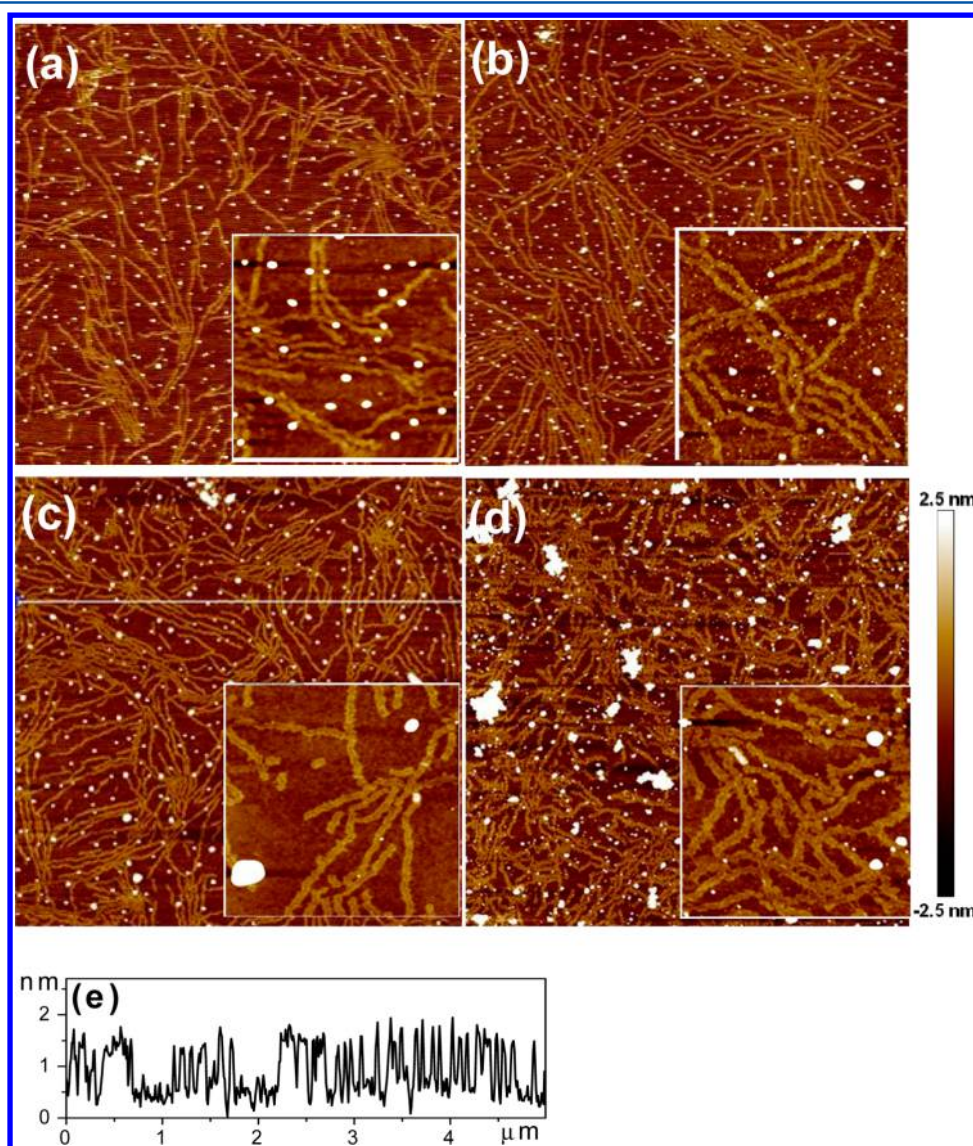


Figure 2. AFM topography images ($5 \mu\text{m} \times 5 \mu\text{m}$) of nanowhiskers collected on silicon substrates produced from P3HTs with M_n of (a) 14.3, (b) 20.3, (c) 34.3, and (d) 36.0 kDa. The insets are enlarged views ($1 \mu\text{m} \times 1 \mu\text{m}$). A color scale bar is given on the right of part d. (e) Cross section of part c along the white solid line.

Substrate Preparation. Silicon wafers and quartz slides were cleaned in a boiling piranha (Caution!) solution ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 = 30:70$ v/v), rinsed with adequate ultrapure water and dried with a stream of nitrogen.

Sample Preparation. The P3HT was dissolved in refluxing chloroform (0.1 mg/mL) with stirring before cooling to room temperature (20 °C). A trace of concentrated sulfuric acid was introduced, and the solution was stirred for 10 min and stored in darkness. To collect the P3HT nanowhiskers, silicon substrates were dipped into the P3HT solution for 1 min, and then removed and transferred to chloroform for 1 min rinse.

Characterization. ^1H NMR spectra were recorded on a Bruker Ascend 400 spectrometer using CDCl_3 as a solvent with tetramethylsilane as the internal reference. The number-average molecular weight (M_n) and polydispersity index (PDI) were determined by PL-GPC 220 equipped with a refractive-index detector, using polystyrene as standard and 1,2,4-trichlorobenzene as an eluent at 150 °C. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) pattern were obtained on a JEOL-2100F electron microscope operating at 200 kV. Atomic force microscopy (AFM) images were acquired on a Bruker Nanoscope IIIA scanning probe microscope in tapping mode with Si tips (radii <10 nm) at the resonance frequency of 250–300 kHz.

RESULTS AND DISCUSSION

Four regioregular P3HT samples with M_n of 14.3, 20.3, 34.3, and 36.0 kDa, respectively were used to prepare the monolayer nanowhiskers (Table 1). Figure 2 shows atomic force microscopy (AFM) height images of the nanowhiskers grown from the four samples of different molecular weights. All nanowhiskers were of several micrometers long and entangled with each other to form networks. The heights of these nanowhiskers were all about 1.6 nm (Figure 2e), which corresponds to the height of a P3HT molecule in the side chain direction. The orientation of the P3HT molecules in these monolayer nanowhiskers, as we previously determined,¹⁵ is schematically illustrated in Figure 1b.

Next we measured the width of these nanowhiskers by TEM. Figure 3 presents TEM images of the P3HT nanowhiskers of four different molecular weights, with a selective area electron diffraction (SAED) pattern confirming the ordered structure in the nanowhiskers. Table 1 lists the average widths of the nanowhiskers measured by TEM in comparison with the contour lengths for all four samples. The average widths of the nanowhiskers were approximately the same, ~16 nm, for all the P3HTs studied. This whisker width value is lower than the chain contour length of the 14.3 kDa sample, the shortest one, and much smaller than the contour lengths of the other three, indicating the presence of chain folding in the nanowhiskers, at least for the higher molecular weight samples. The independence of the whisker width on the molecular weight was also confirmed by AFM observation, although due to the tip effect¹⁷ the widths thus measured were ~15 nm greater than the corresponding widths measured by TEM (Figure 2 and Table 1). Chain-folding is common in the crystals of flexible polymers.¹⁸ Because of the polydispersity in polymer chain length, the folding of polymer chains reduces the defects of crystals resulting from chain length discrepancy.¹⁴ Since the P3HT samples used in this study are not monodisperse, presence of chain-folding of the P3HT backbones is reasonable. Also it should be pointed out that since oxidation stiffens the thienyl backbone,²⁰ the chain-folding observed is not caused by the trace sulfuric acid added to promote nanowhisker growth.

The trend we observed is consistent with that reported by Zhai and co-workers,¹³ that P3HT forms folded-chain crystals

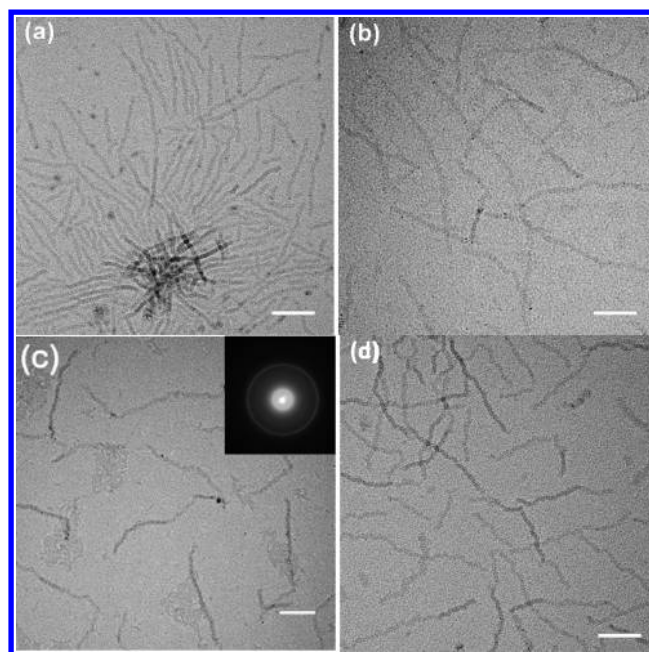


Figure 3. TEM images of nanowhiskers grown from P3HTs with M_n of (a) 14.3, (b) 20.3, (c) 34.3, and (d) 36.0 kDa. Scale bar: 200 nm. Inset in part c is the SAED pattern of the nanowhiskers.

at a M_n greater than a critical value of ~10 kDa, but with two distinct differences. First, the folded-chain whisker width we observed was about 2 nm greater than the limit value¹³ in literature. This probably is because our whiskers were grown from a good solvent, where the polymer chains may be more swollen and extended and the nanowhiskers grew slower. For flexible polymers, although extended-chain crystals are more stable than the ones with folded chains, it was found that the latter grow much faster, because the addition of shorter straight stretches is kinetically favored with a lower entropic barrier.²¹ In fact, in our previous study, without using concentrated H_2SO_4 to promote the crystallization, monolayer whiskers with much greater width (~30 nm as measured by TEM) were obtained under the same conditions as the present study but over a much slower process.¹⁵ These results show the similarity in crystallization behavior between the supposedly rigid polythiophenes and typical flexible polymers. In addition, this points to an effective approach to increase nanowhisker width, which is important for performance of devices based on these nanofibrils because the charge carrier mobility has been shown to correlate exponentially with the nanofibril width.⁹

Second and more importantly, the thickness of the typical nanowhiskers reported in the literature normally correspond to two to three P3HT chain layers (Figure 1a), and the P3HT backbone thus can fold in the side chain direction (a direction, see Figure 5a), joining thiophene stems in two different layers,¹³ whereas the nanowhiskers in this study consist of only one P3HT layer (Figure 1b), so the backbone folding can only occur within this layer, i.e. the P3HT chains must fold in the b direction normal to the π -conjugation plane (see Figure 5b).

In order to validate the out-of-plane folding structure and gain insight into the molecular conformation of the fold, a theoretical calculation was performed using the PM6 method in the Gaussian 2009 program package, which is a semiempirical method developed recently and a general purpose model of good quality for large conjugated organic systems.²² A model consisting of P3HT chains, each containing 35 thiophene units

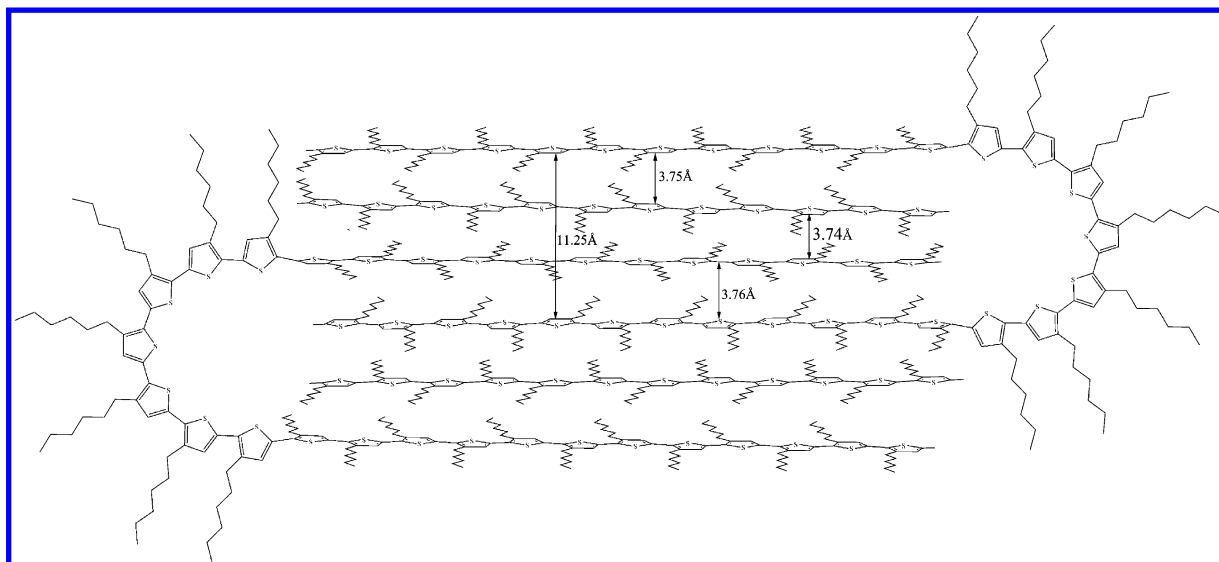


Figure 4. Schematic illustration of chain folding of P3HT in monolayer nanowiskers.

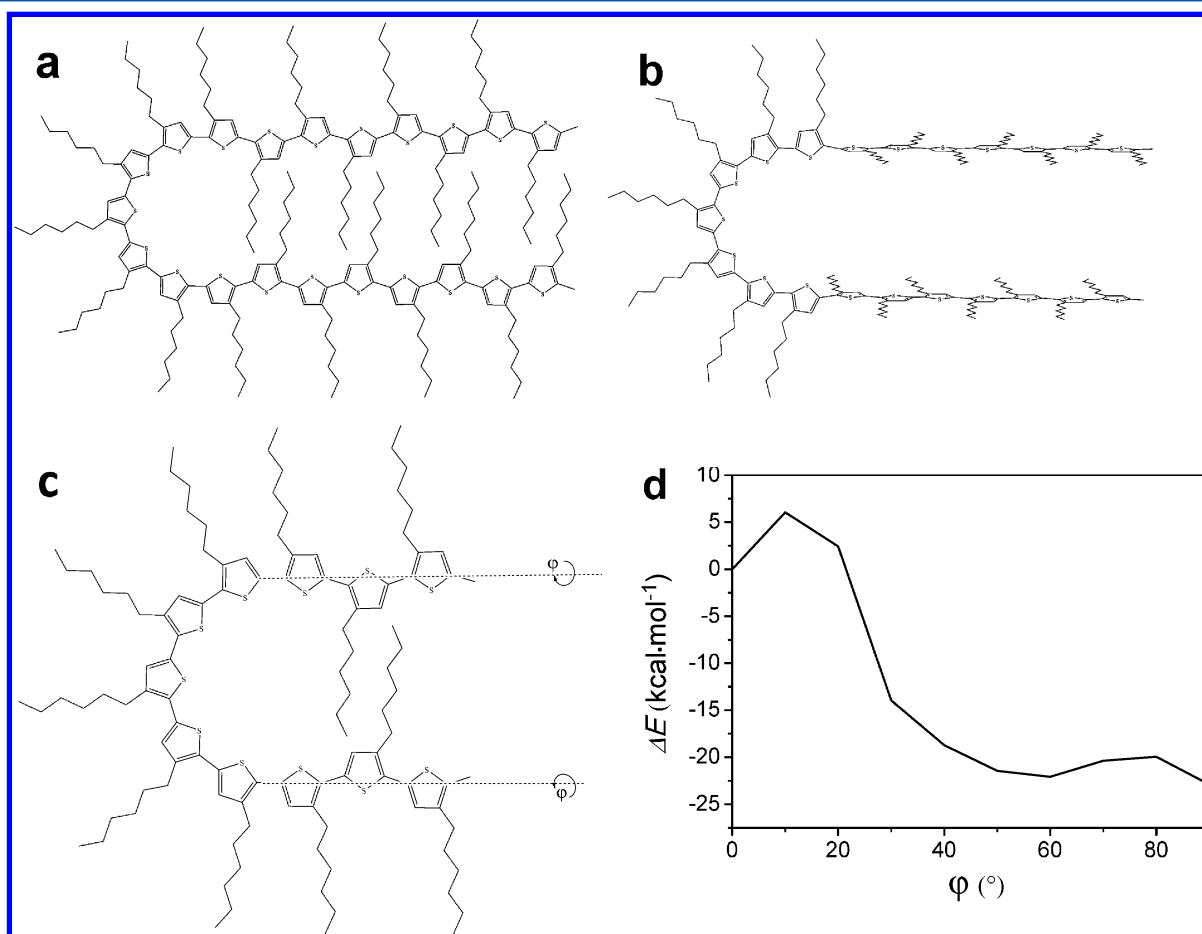


Figure 5. Schematic illustration of (a) the in-plane folding model, and (b) the out-of-plane folding model. (c) Rotation of the two stems of an in-plane fold, each containing seven thiophene units in all-*trans* conformation, and (d) calculated energy profile for the rotation in 10° steps.

with an out-of-plane fold in the middle, was optimized, and the minimum energy conformation obtained is shown in Figure 4. According to the calculation result, two face-to-face stacking thiophene chains with a distance of 1.125 nm is connected by an intramolecular hairpin fold composed of seven thiophene units in an all-*cis* conformation within a plane that is orthogonal

to the π -conjugation plane of the stems in the crystalline structure. Our model is a nested multilevel structure of such fold. The distance between each layer is about 0.375 nm, which is in excellent agreement with the experimental π - π stacking distance in P3HT crystals as determined by SAED, 0.38 nm.¹⁵

By comparing our out-of-plane fold model with the widely accepted in-plane fold model¹⁰ for P3HT crystals, illustrated in Figure 5, it can be seen that the conformation of the fold section is almost the same, both containing seven thiophene units in an all-*cis* conformation within a same plane, but the fold is joined to the all-*trans* thiophene trains in the crystalline section with different dihedral angles, around 0° for the in-plane fold and ~90° for the out-of-plane fold, respectively. In order to compare these two models, we used the HF/6-31G (d) method to calculate the energy difference between them. We started from a P3HT chain with 21 thiophene units and an in-plane fold structure, rotated the two all-*trans* thiophene trains (each containing seven units) 1.125 nm apart and connected to the fold by the σ bonds in steps of 10°, and calculated the energy of the conformations (Figure 5c,d). The result shows that the energy of the out-of-plane conformation is significantly lower than that of the in-plane one. Similar trend was obtained when the spacing between the two all-*trans* thiophene trains was set to 1.65 nm, corresponding to that in the in-plane fold in normal P3HT nanowhiskers. This may be attributed to lower repulsion among the hexyl side chains in the two all-*trans* thiophene trains in the out-of-plane fold model. Therefore, out-of-plane folding is reasonable and probable in terms of energy consideration. Furthermore, the energy profile in Figure 5d suggests that similar out-of-plane folding with a dihedral angle other than 90° is also possible in crystals thicker than monolayer.

CONCLUSION

In summary, we have investigated the formation of monolayer nanowhiskers from P3HTs of different molecular weights, and based on the experimental observation that the widths of these nanowhiskers were independent of the molecular weight and much smaller than the contour lengths of the P3HT chains, in conjunction with theoretical calculation results, we conclude that out-of-plane folding of the polythiophene backbones is energetically probable and is present in these nanowhiskers. The discovery of the out-of-plane folding conformation helps the understanding of crystallization behavior of polythiophenes, and suggests that contrary to the perceived rigidity of polythiophenes, these polymers are indeed quite flexible.

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Notes

The authors declare no competing financial interest.

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