# Ordering of Poly(3-hexylthiophene) in Solution and on Substrates Induced by Concentrated Sulfuric Acid

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S *Supporting Information*

ABSTRACT: The ordering of poly(3-hexylthiophene) (P3HT) molecules in dilute P3HT/chloroform solutions was accelerated by adding small amounts of concentrated H_2SO_4. The concentrated H_2SO_4 stimulates the nucleation of crystals, which controls the overall rate of P3HT crystallization. Dispersed nuclei spur P3HT solution crystallization, and adsorbed nuclei induce P3HT crystallization on substrates. By AFM, the morphology of P3HT nanowhiskers prepared in solution differ from those prepared on substrates, and nanowhisker structure and growth kinetics was further investigated using Raman spectroscopy and UV−vis adsorption spectroscopy. All P3HT nanowhiskers are well-ordered.
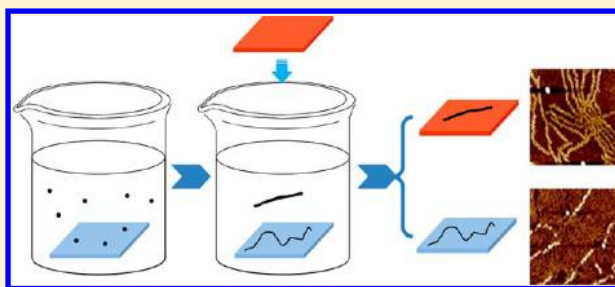
INTRODUCTION

Compared to their inorganic counterparts, conjugated polymers are lighter, cheaper, and solution processable, features offering potential advantage in large-area flexible organic optoelectronic devices. And, unlike the three-dimensional charge transport in inorganic semiconductors, charge transport in conjugated polymers, which relies on π-orbital overlap among adjacent chains, is anisotropic.[1−3] Polymers never crystallize perfectly, leaving coexisting ordered and disordered domains;[4,5] charge transport in the disordered regions is by hopping, a mechanism that limits the charge mobility.[1,6] Therefore, to achieve desirable charge mobility in semicrystalline polymer films, conjugated polymer films must be assembled with a high degree of intrachain order. Recently, one-dimensional conjugated polymer nanostructures displaying high order and unique optoelectronic properties have been widely investigated, and in some cases, employed in optoelectronic devices.[7−12] Poly(3-hexylthiophene) (P3HT) is one of the most promising conjugated polymer candidates for semiconductor applications such as organic field-effect transistors (OFETs), organic solar cells (OSCs), and other optoelectronic devices.[13−16] This material offers high charge mobility, chemical stability, and solvent processability.[13,16] Because of $\pi-\pi$ interactions between their rigid thienyl backbones, dissolved P3HT molecules tend to self-assemble into one-dimensional nanostructures like nanofibers and nanowhiskers when solution solubility is reduced by temperature, addition of nonsolvent, or evaporation.[17−22] Compared to other morphologies, these one-dimensional P3HT nanostructures effectively improve the performance of OFETs[23,24] and OSCs.[25,26]

One-dimensional P3HT nanostructures have been produced by various solution-based procedures. Examples include prolonged evaporation of solvent from films made by dip-coating,[27] adding nonsolvent to a stable P3HT solution,[25] lowering the temperature of a P3HT solution prepared with a marginal solvent,[19] spin-coating P3HT films under high pressure solvent vapor,[28,29] exposing a P3HT solution to ultrasound,[30] and adding dopant to a P3HT solution.[1,23] It is particular interesting that a dopant can induce the ordering of P3HT molecules. Janssen et al. found that regio-irregular poly(3-alkylthiophene), which usually does not form ordered structures, adopts a high degree of order in films made from solution by adding oxidant.[1] And Cho et al. promoted the formation of P3HT nanocrystals from solution using $HAuCl_4$, a procedure that improves the field-effect mobility of P3HT films by 2 orders of magnitude.[23] The oxidant heavily dopes the dissolved P3HT molecules and causes their structural transformation, as manifested in ∼700−1100 nm bands in the UV−vis absorption spectra attributed to polaron transition.[1,23,31] Although there are extensive reports in the literature on P3HT aggregation from solution, the field of crystallization of conjugated polymers is largely virgin, and the mechanism is not well understood.[32,33]

Recently, we reported that in a dilute chloroform solution, P3HT can self-assemble into extended-chain nanowhiskers of monolayer thickness.[34] These nanowhiskers are ∼30 nm in width, much larger than reported maximum widths for normal P3HT nanowhiskers, and only 1.6 nm in thickness, corresponding to single molecular layer of P3HT in the side-chain direction, formed via a slow crystallization process in the solution over a long period of about 1 week.[34] In the present paper, we describe how P3HT molecules in dilute chloroform
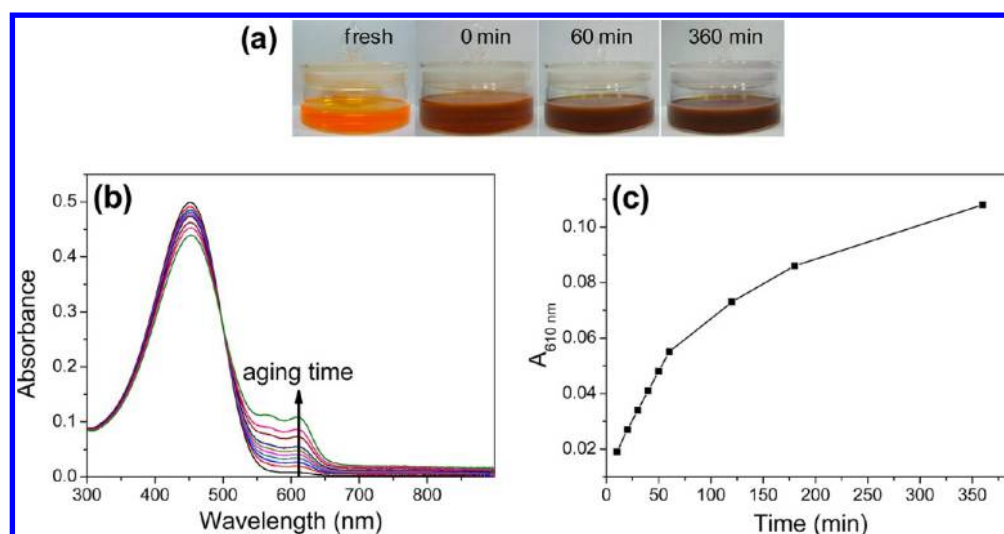
Figure 1. (a) Evolving appearance of P3HT/chloroform solutions as prepared and after adding concentrated H_2SO_4. (b) Corresponding P3HT UV−vis absorption solution spectra. (c) Absorbance at 610 nm plotted against time.
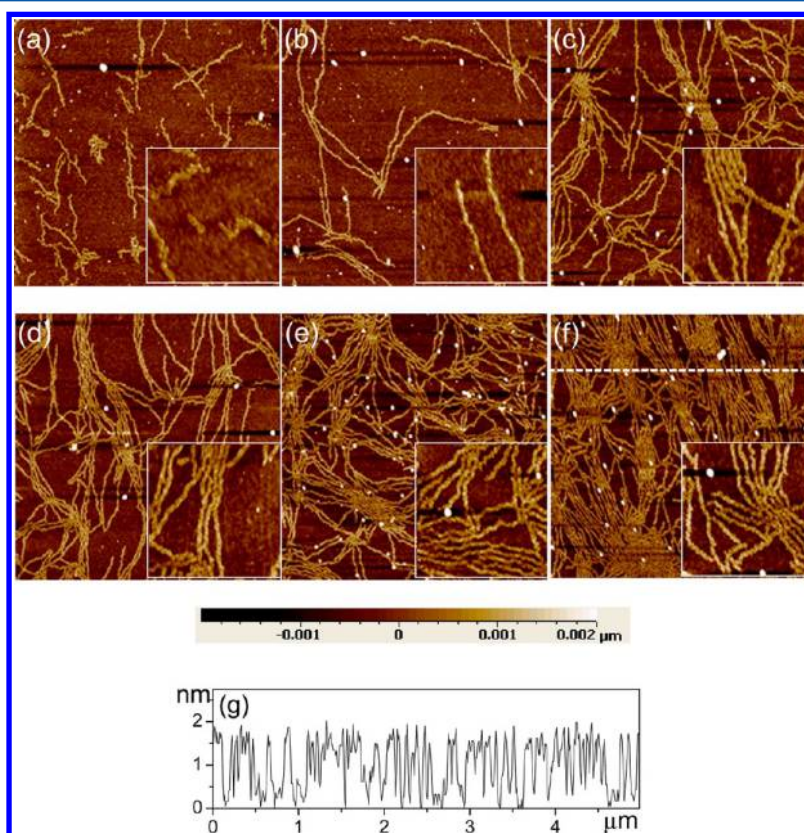

Figure 2. AFM topography images (5 μm × 5 μm) of P3HT nanowhiskers deposited on silicon substrates at aging times of (a) 0 min, (b) 10 min, (c) 30 min, (d) 1 h, (e) 3 h, and (f) 6 h. The insets are enlarged views (1 μm × 1 μm). A common scale bar is given below the set of images and (g) is a cross section of (f) along the dashed line.

solutions form the same quantity of similar structures in just a few minutes by simply adding a small amount of concentrated H_2SO_4 to the chloroform. The acceleration is also observed on silicon substrates with SiO_2 surface layers.

■ EXPERIMENTAL SECTION

Regioregular P3HT (M_w = 32000, PDI = 1.9, 98% H-T) was purchased from Rieke Metals Inc. and used without further purification. Chloroform (A. R.) and concentrated sulfuric acid

(98 wt %, A. R.) were purchased from Beijing Chemical Works and used as received. Silicon and quartz substrates were cleaned in boiling piranha solution (H_2SO_4/H_2O_2 = 70:30 v/v), rinsed with adequate ultrapure water, and dried with nitrogen. (*Caution*! Piranha solution is aggressive and explosive. Never mix piranha waste with solvents. Check the safety precautions before using it.) The P3HT was dissolved in chloroform at 0.1 mg/mL by reflux with stirring before cooling to room temperature (22 °C). A trace of concentrated H_2SO_4 was

introduced onto the wall of a separate flask and then the P3HT/chloroform solution was poured into the flask, stirred for 10 min, and stored in darkness. To investigate changes to the P3HT molecules, into the P3HT solution aged for different times silicon substrates were dipped for 1 min to collect the P3HT nanowhiskers grown in the solution, and these substrates were then transferred to chloroform for a 1 min rinse. Another series of silicon substrates was placed into the P3HT solution right after preparation to allow crystal growth on the substrates, removed at different aging times, and then immediately immersed in chloroform for 1 min.

UV−vis spectra of P3HT in the chloroform solutions and in the nanowhiskers on quartz substrates were acquired on a TU-1901 spectrometer (Beijing Purkinje General Instrument Co. Ltd.) and a Lambda 750 spectrometer (Perkin-Elmer, Wellesley, MA), respectively. AFM images for the same samples were obtained using an Agilent Technologies 5500 scanning probe microscope in tapping mode with Si tips (radii <10 nm) at the resonance frequency of 250−300 kHz. Raman spectra were recorded in the backscattering geometry on a LabRam HR 800 (Horiba Jobin Yvon) coupled with a Olympus BX 41 microscope; the confocal hole and the silt width were both fixed at 200 μm. The excitation wavelength was 633 nm (He−Ne laser, 1.8 mW at the sample), and the laser was focused on the sample with a 100× objective lens (0.90 NA). Raman signals were dispersed with a 600 lines/mm grating and collected by a charge-coupled device (CCD). The spectrometer was calibrated with the 520.7 cm^{-1} band of a Si standard. Each reported spectrum is an average of three acquisitions, each of 10 s exposure.

■ RESULTS AND DISCUSSION

The color of a pristine 0.1 mg/mL P3HT/chloroform solution is yellow, but after a trace of concentrated H_2SO_4 was added and the solution was stirred for 10 min, the color turned from yellow to light red, and then with extended aging, dark red (Figure 1a). Similar color changes were observed for a same solution without the addition of H_2SO_4, which occurred much slower, over a period of about 1 week.[34] The corresponding UV−vis adsorption spectra reveal an evolution of P3HT molecular structure (Figure 1b). For the pristine solution, P3HT is molecularly dissolved. After H_2SO_4 is added, low energy absorption bands (~610 nm) appear and their intensity slowly grows, consistent with an increase in conjugation length as P3HT orders.[19,25] The absorbance at 610 nm is given as a function of aging time in Figure 1c, and the figure's rise demonstrates the slow aggregation/crystallization of previously dissolved P3HT. Because the solution concentration was low and only trace of H_2SO_4 was added, the amount of P3HT crystals formed as indicated by the relative absorbance at 610 nm was small.

The nature of the dissolved/dispersed P3HT at different aging times was investigated by dipping clean silicon substrates into the mixture for 1 min and then washing these substrates for 1 min in chloroform to remove still-dissolved P3HT.[34] The deposited material was examined by AFM. Nanowhiskers were observed on all substrates, with the length and density of these objects increasing with time, as shown in Figure 2a−f. AFM cross sections, as demonstrated in Figure 2g, indicate a nanowhisker height ~1.6 nm, a value matching the width of P3HT molecules in the direction of side chains.[34] Figure 3 plots a downward trend in nanowhisker width with aging time, the initial width of ~35 nm transformed to a long time width of
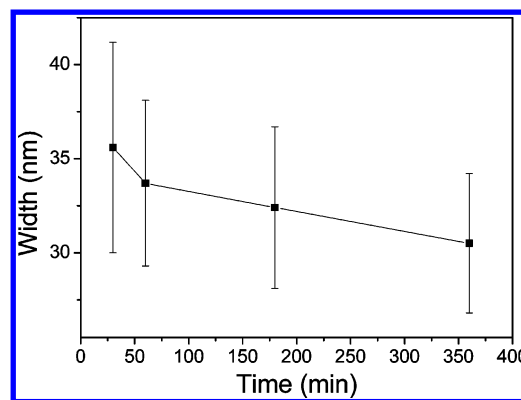

Figure 3. Width vs aging time for P3HT monolayer nanowhiskers grown in solution (error bars depict standard deviations).

~30 nm. We previously reported that nanowhiskers made without H_2SO_4 have widths ~40 nm, a higher value suggesting the incorporation of only higher molecular weight P3HT.[34] By comparison, we conclude that H_2SO_4 causes nanowhisker incorporation of lower molecular weight P3HT. Figure 2a shows coexistence of two nanowhisker populations, with widths of ~35 and ~29 nm, respectively. Only the former are formed in solution and described here; the latter will be the focus of the next section.

Another series of silicon substrates were dipped into the P3HT/chloroform/H_2SO_4 mixture immediately upon the acid addition and then removed at various aging times. After washing with chloroform, their surfaces were scanned by AFM. As shown in Figure 4a−f, the nanowhiskers on these substrates are much different from those already described. Now, the nanowhiskers have a curly appearance, and they are interconnected, preventing the determination of their lengths. The new nanowhiskers obviously grew on the substrate surfaces. For early aging, roughly 1−30 min, nanowhisker height remains ~1.6 nm, the same as for solution-grown nanowhiskers. Beyond this time, the nanowhisker height grows, suggesting the appearance of multilayers, characterized in Figure 4d−f by linear domains with heights so large as to appear white. The AFM cross-section of Figure 4g reveals heights sometimes in excess of 3 nm. Once again, width decreases with aging time, from ~29 nm at the start to ~22 nm at 3 h, a trend plotted in Figure 5. At still greater time (Figure 4f), the nanowhiskers pack too closely for their width to be measured. Polymers in solution can adsorb onto solid surfaces[35,36] with their crystallization perturbed.[37] Here, adsorption extends to lower molecular weight P3HT, leading to lower width as smaller polymers are incorporated; the P3HT chains approaching the crystal growth front are restricted in mobility by their interactions with the substrate, moving much less freely than in solution, resulting in less than optimum packing and more curly nanowhiskers with lower degree of order.

To understand the impact of H_2SO_4 on nanowhisker growth, 1 mL of more diluted 0.1 M H_2SO_4 in H_2O was added to a P3HT/chloroform solution, which was stirred for 10 min, and then placed in darkness. No nanowhiskers were found after 12 h, identifying oxidation by H_2SO_4 rather than acidity as the source of enhanced P3HT ordering. To verify this point, $FeCl_3$, an oxidating agent, was employed instead of concentrated H_2SO_4, and similar enhancement in P3HT ordering was observed. Previous studies clearly showed that oxidation can
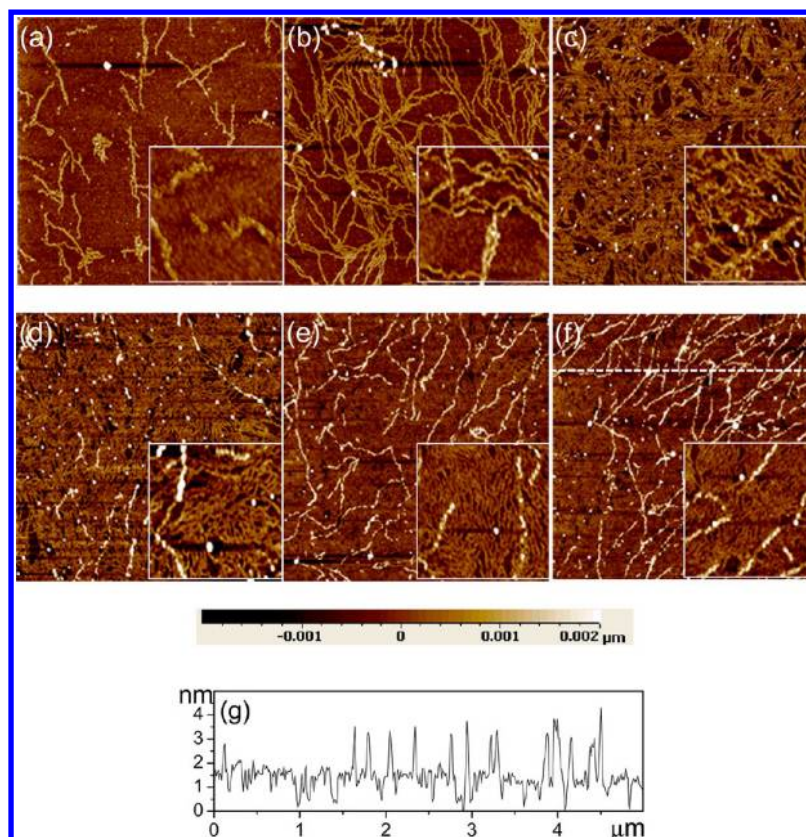
Figure 4. AFM topography images (5 μm × 5 μm) of P3HT nanowhiskers grown on immersed silicon substrates at aging times of (a) 0 min, (b) 10 min, (c) 30 min, (d) 1 h, (e) 3 h, and (f) 6 h [(a) is the same as Figure 2a]. The insets are enlarged views (1 μm × 1 μm). A common scale bar is given below the set of images and (g) is a cross section of (f) along the dashed line.
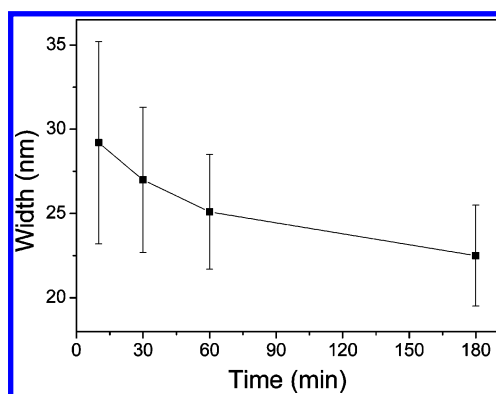

Figure 5. Width vs aging time for P3HT monolayer nanowhiskers grown on substrates immersed in solution (error bars depict standard deviations).

dramatically impact the aggregation of P3ATs and proposed that oxidation transforms the P3HT thienyl backbone from a benzoid to a quinoid structure, increasing the double bond character of the bridges between thienyl rings; This transformation would stiffen the thienyl backbone, strengthening interactions between adjacent chains.[1,23] This idea nicely explains why H_2SO_4 improves P3HT ordering. However, in these pioneering works P3HT oxidation was extensive, as evidenced by the significant polaron transition bands at wavelengths above 700 nm associated with doping and structural transformation,[1,23] yet in the present study these bands are not seen in the UV−vis spectra of Figure 1b, which means the level of P3HT oxidation is small.

Another explanation is needed. The growth of polymer crystals proceeds through steps of nucleation and growth.[37,38] Nucleation for P3HT is known to be slow, and so usually low temperature, large oversaturation, or self-seeding is needed to start crystallization.[32,39] For this reason, crystallization from chloroform of P3HT at 0.1 mg/mL is sluggish, a week or more required at 20 ± 2 °C, for abundant nanowhiskers to form.[34] We speculate that adding a little H_2SO_4 leads to slight P3HT oxidation, the ensuing small change in P3HT properties causing a vastly increased rate of nucleation. Some of the nuclei remain in solution and others can adsorb to substrate, leading to two types of crystallization, solution and surface.

Figure 6a shows that the Raman bands of P3HT ordered on a silicon substrate are narrow and distinct. The band of highest intensity is attributed to symmetric C=C stretching of the thiophene ring. For spin-coated P3HT films and P3HT monolayer nanowhiskers formed in solution spontaneously, this band is located at ∼1445 and ∼1440 cm^{-1}, respectively.[40] For the P3HT nanowhiskers formed in solution and on substrates in this study, the band shifts to 1441 and 1442 cm^{-1}, respectively. The frequencies of the symmetric C=C stretching band manifest the conjugation length of the P3HT molecules, with lower frequency revealing longer conjugation length.[41] Therefore, the P3HT in both new sets of nanowhiskers have longer conjugation length than established in spin-coated films but not as long as that found in spontaneously formed P3HT nanowhiskers. This is consistent with the narrower widths (Figures 3 and 5) of these nanowhiskers as compared to that of the spontaneously formed P3HT nanowhiskers.[34] Going further, the broad Raman Si band at 900−1040 cm^{-1} offers a
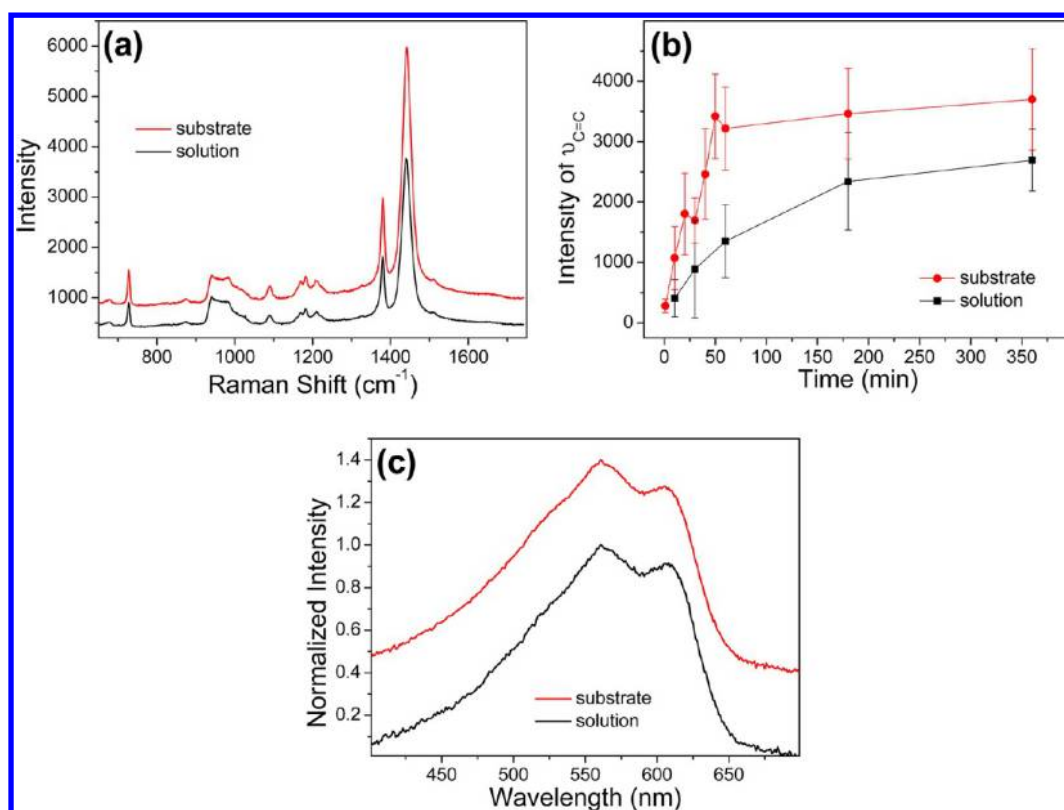
Figure 6. (a) Raman spectra of P3HT nanowhiskers formed in solution and on substrates at an aging time of 360 min; (b) intensity of C=C symmetric stretching at ~1440 cm^{-1} vs aging time (error bars represent standard deviations); (c) UV−vis spectra of P3HT nanowhiskers on quartz substrates.

internal intensity standard for the C=C stretching band, allowing quantifications of this band for different samples. Larger intensity demonstrates greater order (i.e., higher crystal content), and Figure 6b shows the expected trend with aging time. The crystal contents reported by the Raman intensity (Figure 6b) and UV absorbance (Figure 1b) as functions of aging time were fitted to the Avrami equation, and the Avrami indices thus obtained were ~0.8−0.9 (Supporting Information), values characteristic of one-dimensional crystal growth with predetermined nuclei[38,42] both in solution and on substrates. This trend is consistent with the observation that the crystals are induced by the trace of quickly depleted H_2SO_4 and that the crystals have monolayer thickness. The trace amount of H_2SO_4 is depleted quickly as compared to the entire crystallization process; thus the nuclei are predetermined. The nanowhiskers formed are only monolayer in thickness and one chain length in width; therefore, their growth can only be along the length direction of the nanowhiskers, i.e., one-dimensional.

The UV−vis absorption spectra of the two new nanowhiskers are depicted in Figure 6c. Peaks at 530, 562, and 607 nm reportedly manifest intrachain $\pi-\pi^*$ transition, conjugation due to stacking of P3HT backbones, and interchain $\pi-\pi$ interactions, respectively.[43,44] The band at 530 nm is barely discerned because of the strength of higher wavelength bands and the 562 nm band is red-shifted from its typical 558 nm position.[25] Thus, attention focuses on the intensity of the 607 nm band, which correlates to the degree of interchain order.[43,44] For the two nanowhiskers, the relative intensity of this band is much greater than observed for spin-coated films,[45] again implying better order. In addition, the nanowhiskers formed on substrate exhibited a slightly lower relative intensity

of the 607 nm band and a higher C=C stretching frequency compared to those formed in solution, trends consistent with a lower degree of order as reflected in a more curly appearance.

Preparing nanowhiskers by adding H_2SO_4 to P3HT/chloroform solutions has a drawback. Although the nanowhiskers have reproducible appearance as formed both in solution and on substrate, the yield of nanowhiskers is somewhat irreproducible. We presume the cause is immiscibility between H_2SO_4 and chloroform, which makes the solution composition hard to control. This issue continues to be studied.

■ CONCLUSIONS

Introducing a small amount of concentrated H_2SO_4 into dilute P3HT in chloroform solutions can accelerate the ordering of P3HT, both in the bulk solution and on immersed silicon substrates. The ordered P3HT adopts one-dimensional structures, i.e., nanowhiskers. The impact of H_2SO_4 addition can be explained through the slight oxidation of P3HT, which subsequently nucleates the growth of the nanowhiskers. The nuclei can remain in solution or deposit on an immersed substrate, providing two environments for nanowhisker growth. The height of P3HT nanowhiskers formed in solution is ~1.6 nm, which matches the height of monolayer P3HT molecules in the direction of alkyl side chains. The majority of P3HT nanowhiskers formed on silicon substrates are also ~1.6 nm in height, but some are thicker and also narrower. Our findings provide a new and quick approach to obtain highly ordered structures of P3HT, one amenable to development of P3HT-based optoelectronic devices with improved performance. These findings also direct further fundamental investigations

of conjugated polymer crystallization, some pursued by the authors presently.

ASSOCIATED CONTENT

ⓈSupporting Information

Avrami plots for data in Figure 1c and Figure 6b. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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