# Kinetics and Mechanism of Poly(3-hexylthiophene) Crystallization in Solution under Shear Flow

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**ABSTRACT:** The morphology of poly (3-hexylthiophene) (P3HT) in its liquid phase and its manipulation via flow-induced solution crystallization and its crystallization kinetics was studied to determine its mechanism. Shear flow-induced ordering of semiconducting P3HT, which generates more perfect crystal structures than quiescent methods, is elucidated using in situ rheo-SANS and rheo-SALS measurements, and an Avrami analysis is performed. Characteristic lengths of P3HT crystals were measured as a function of time, and 3-D networks of percolated P3HT fibril crystals were determined by measuring the apparent fractal, ~2.6, by fitting the rheo-SANS data with a power law function. Additionally, UV–vis and DSC results revealed a process of P3HT crystal perfection determined by following the evolution of absorption peak characteristics of pi–pi stacking at 600 nm and the melting peaks as they shifted and narrowed with respect to increasing shear time. The Avrami exponent, m, reached a maximum value of 2 indicating homogeneous nucleation of P3HT macromolecules that allowed one-dimensional fibril crystal growth and was limited by contact time between the P3HT molecules rather than the diffusion of P3HT chains and this is attributed to the highly directional pi–pi stacking attractions of electron pi in the thiophene rings.

# ■ INTRODUCTION

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Poly (3-hexylthiophene) (P3HT) has been used commonly as an electron donor material for plastic solar cells (PSCs) with easy synthesis, good processability from solution, high carrier mobility, and high compatibility with available acceptor materials and solvents.<sup>1,2</sup> Controlling the order and disorder phases of P3HT is essential in controlling the charge transport within this semiconducting polymer for solar cell applications.<sup>3,4</sup> The conjugated structure of P3HT with rich electron pi systems and hexyl side chains significantly affects P3HT crystallization. Various P3HT crystal growth methods have been developed using different polymer molecular weights, solvent systems, casting techniques, and posttreatments, such as thermal annealing.<sup>4–13</sup>

Additionally, in plastic solar cells, the morphology of the active layer (a mixture of the donor and the acceptor), related to the crystal structures and the crystallinity of P3HT, plays a vital role in improving the charge carrier mobility. The low dielectric constant of the semiconducting polymer means electron—hole pairs are tightly bound together, so high energy

is needed for separating them at the interfaces of the donor and acceptor materials. Moreover, the short exciton diffusion length, ~10 nm, is a challenge as well.<sup>1,14–17</sup> Thus, to improve charge transport, defect-free and single crystals of P3HT were made.<sup>6,18,19</sup> However, very large needlelike crystals that were several hundreds of micrometers long and thick were made. These crystal dimensions are problematic for incorporating single crystals into PSC devices because the optimized active layer thickness for the PSC devices is ~200 nm.<sup>20</sup>

A simple method using flow-induced solution crystallization<sup>21</sup> was employed to improve both the quality and the quantity of the P3HT crystals. Using shear flow, defects can be

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removed, and micrometer-long P3HT single crystals of ~20 nm thickness and several nanometers high P3HT fibril crystals can be made as revealed in our recent study.<sup>21</sup> The P3HT fibril crystals created by shear flow can be assembled easily into the solar cell devices. We report that shear flow creates 3-D networks of micrometer-long P3HT fibrils, which can create transporting channels that promote and improve the charge carrier mobility.<sup>21</sup> Also, the formation of interconnected domains (amorphous and crystalline phases) due to the presence of micrometer-long crystals enhances the carrier mobility significantly.<sup>3</sup> Thus, the solar cell performance is expected to increase as a result of using this morphological control method. However, the kinetics and mechanism of crystal formation of P3HT macromolecules under shear flow are not clear and are the intent of this study.

Dynamic formation and interaction of polymer molecules under flow have been extensively investigated.<sup>21-27</sup> Also, structural formation and growth have been studied using scattering techniques such as small-angle neutron scattering (SANS), small-angle light scattering (SALS), and small-angle X-ray scattering (SAXS).<sup>28–39</sup> Herein, in situ rheological SANS (referred to as rheo-SANS) and in situ rheological SALS (referred to as rheo-SALS) measurements were used to investigate P3HT crystallization under shear flow. The fibrillar crystals were probed, beginning with the solution state and continuing through crystal nucleation, growth, and percolation, using time-resolved rheo-SANS. Micrometer-characteristic lengths of P3HT crystals were investigated using rheo-SALS measurements as well. The crystallization of P3HT was fully investigated in the liquid phase instead of thin films as reported recently.<sup>2</sup>

Furthermore, an Avrami analysis<sup>40</sup> has been used to investigate the kinetics and crystal formation mechanism of polymers. Isothermal crystallization of P3HT in the melt state enabled the kinetics of P3HT crystallization to be studied by differential scanning calorimetry (DSC).<sup>41</sup> It is simple to measure the P3HT crystallinity formed at different time periods under the crystal growth conditions. The measured melting enthalpy and the infinite crystal size melting enthalpy of P3HT samples were used to determine the P3HT crystallinity fractions. However, the crystallization mechanism of P3HT varies and depends on the crystallization method.<sup>42-45</sup> The kinetics of P3HT crystallization in shearinduced solution crystallization may be complex and has a different mechanism. In this study, the DSC cannot be used easily to quantify the crystallinity of P3HT in the liquid state. To overcome this difficulty, ultraviolet-visible (UV-vis) measurements of the interchain interaction (pi-pi stacking) absorption (~600 nm) were employed in which the crystalline fractions are proportional to the absorption magnitude at 600 nm. Herein, for the first time, the kinetics of P3HT crystallization under shear flow was studied comprehensively. It is revealed in this paper that the temperature and shear rates are considerable factors affecting the P3HT crystallization kinetics and mechanism. The measured Avrami exponent reaches a maximum value of 2 presenting a homogeneous nucleation mode and one-dimensional crystal growth, and it is limited by the contact time between the P3HT macromolecules.

## EXPERIMENTAL SECTION

P3HT,  $M_w \sim 50$  kDa and ~95% regioregularity, was purchased from BASF and was used without purification. A solution of 20 mg/mL of

P3HT in 2-ethylnapthalene (2-EN) (Sigma-Aldrich) was prepared by heating at 80 °C for 3 h to dissolve completely. In situ rheo-SANS measurements were carried out at the nSoft beamline at the Center for Neutron Research at NIST (the US National Institute of Standards and Technology). The P3HT in the 2-EN solution was sheared at 100 s<sup>-1</sup> using a bob and cup geometry with a 0.5 mm gap (Anton Paar, USA). The data were collected every 1 h for each shearing condition. The SANS reduction software was used to analyze the data. The rheo-SALS measurements were conducted using 50 mm diameter quartz parallel plates with a 0.5 mm gap (DHR, TA instruments, USA). The light wavelength used for the rheo-SALS measurements is 635 nm. The main UV-vis absorption peak of the P3HT crystals is at 500-600 nm. Very small absorption is determined at 635 nm from our UV-vis measurements (see the UV-vis data in the Results and Discussion section). In this study, the protocols and parameters were selected based on our previous report.<sup>21</sup> In particular, a  $M_{\rm w}$  of 50 kDa and a concentration of 20 mg/mL were used because these are the most common molecular weight and concentration that have been used in our laboratory to make the polymer-based solar cells. Additionally, a strain control rheometer (ARES-G2, TA instruments), with a 50 mm cone and plate geometry, was also used to prepare samples for ultraviolet-visible spectroscopy (UV-vis, UV-3600 UV-VIS-NIR spectrophotometer), atomic force microscopy (AFM, Veeco Dimension 3100 V), transmission electron microscopy (TEM, JEOL JEM-2010F high-resolution TEM), and differential scanning calorimetry (DSC, Discovery Series, TA instruments) by shearing at various shear rates for different time periods. In this study, all the samples used for DSC measurements were prepared in the same manner. The DSC data are used only as supporting information to understand the effect of different shear methods. To avoid the precipitating effect, in situ rheo-SANS, rheo-SALS, and UV-vis measurements were used to investigate the kinetics and mechanism of P3HT crystal formation in the solution state.

Samples for AFM characterization were prepared by spin coating the sheared solutions on silicon wafers at 5000 rpm for 5 min. The TEM samples were prepared by drop casting onto ultrathin carbon support grids from diluted solutions. The AFM and TEM data are used only as supporting information to visualize the P3HT crystals. To avoid the thin film processing effect, in situ rheo-SANS, rheo-SALS, and UV-vis measurements were employed. The after shear (sheared) solutions were rapidly precipitated in methanol and then filtered, dried, and left for 1 week in a vacuum oven at room temperature for complete drying. Then, these P3HT samples were collected for DSC characterization in a temperature range from -85 to 300 °C at a temperature ramp rate of 10 °C/min under a nitrogen gas atmosphere. The solutions of different sheared P3HT samples were immediately collected and used for UV-vis characterization using a thin film glass sample holder as illustrated in this report. It is noted that room temperature (RT) used in this study is ca. 20 °C. Specific temperatures used for different measurements are denoted in the Results and Discussion section.

## RESULTS AND DISCUSSION

In Situ Observation of P3HT Structural Evolution. In our previous study,<sup>21</sup> we showed that the collision between individual P3HT chains under a shear rate of  $100 \text{ s}^{-1}$  is dominated by Brownian motion rather than shear flow. At the beginning of shearing, Brownian motion and the interactions between P3HT bring P3HT chains together and initiate nucleation. As the crystals grow in size, their motion rapidly becomes dominated by shear flow because the Peclet number, the ratio of convective to diffusive motion of P3HT crystals, is very small.<sup>21</sup> Thus, fibril-like P3HT crystals are expected to become aligned along the flow direction at which point the tie molecules and defects are hypothesized to be removed under the shearing force. This process plays a particularly important



**Figure 1.** Data show the formation of P3HT crystals in 20 mg/mL solutions under in situ SANS conditions. (a) Scattering intensity evolution during shear and results obtained by power law fitting presenting a P3HT fibril structure formed and developed to create 3-D networks percolated by P3HT crystalline fibrils. Inset is the 3-D AFM image of the P3HT fibril network; (b) apparent fractal (slopes obtained from power law fitting) improvement corresponding to the viscosity increase under studied time periods; (c) 2-D neutron scattering patterns of P3HT solution collected over different time periods; (d) integrated scattering intensity along and perpendicular to the flow directions from 2-D neutron scattering patterns indicating anisotropic scattering development of P3HT crystals under shear flow (crystalline fibrils aligned along the flow direction); and (e) cartoon of the rheo-SANS cell setup.

role in forming larger and more perfect P3HT crystals because the pi-pi stacking of the thiophene rings is highly regular.

To study the dynamics of P3HT crystal formation under constant shear, rheo-SANS measurements were used to characterize its structural developments with the results shown in Figure 1a–d. The rheo-SANS geometry, Couette cell with a sample volume of approximately 4.5 mL, is illustrated in Figure 1e. The path length of the radial neutron beam is 1 mm. The flow direction is perpendicular to the neutron beam.

As shown in Figure 1a, the circular-averaged scattering intensity of the 20 mg/mL (P3HT/2-EN) solutions develops over a 39 h period under a constant shear rate of 100 s<sup>-1</sup> at 21 °C. The development of the scattering intensity is a result of shear-induced crystallization. The neutron scattering length density (SLD) contrast between the hydrogenated P3HT (0.74  $\times$  10<sup>-6</sup> Å<sup>-2</sup>) and 2-EN (1.33  $\times$  10<sup>-6</sup> Å<sup>-2</sup>) is only

moderate, which is the reason for the very little coherent scattering in the early stage of shearing. However, once the P3HT molecules are crystalized, the contrast is enhanced by the densification of nanoscopic fibrils and the formation of larger networks by aggregation. Therefore, such a structural development can be obtained in the SANS spectra despite the lack of significant contrast. Upon a closer examination of the SANS data shown in Figure 1a, we also found a distinct transition in the scattering patterns between the initial and later stages under continual shear. In the first 6 h, the SANS data are noisy, and there is no significant difference between the data taken at different times within the early stage. It is difficult to claim that there is really a peak there. The absolute intensity is very small, indicating that the initial aggregates are very small.

However, as the shearing persists, the scattering patterns transition into a power law function whose power law increases over time. This indicates that at some point between 6 and 10 h, the P3HT crystals form larger fractal networks of P3HT crystals. The dimension of the fractal network obtained from the power law fitting, along with the viscosity of the fluid, is plotted as a function of shearing time as shown in Figure 1b. The increase in apparent fractal from 1.3 to 2.6 suggests that the fibril-like objects gradually aggregate into networks of higher dimensions toward the final stage of the experiment. In addition, the nonlinear increase in viscosity also mimics the trend of apparent fractal changes over time. In particular, there is a sharp increase in the viscosity at around 20 h as the apparent fractal increases beyond 1.7. This result may arise due to percolation of the P3HT fibrils.<sup>21</sup> The inset 3-D AFM image, shown in Figure 1a, reveals a 3-D fibril network structure that agrees with an apparent fractal value of 2.6 indicating the 3-D network formation as acquired from the power law fitting.

To further verify that the changes in the scattering pattern are caused by the fibril-like P3HT crystals being induced by shear flow, anisotropy in the 2-D SANS patterns was investigated at different shear times, as shown in Figure 1c,d. The pattern becomes increasingly anisotropic, where the intensity is concentrated around an azimuth angle ( $\phi$ ) of 90 and 270°, which is orthogonal to the flow direction. This result indicates that the long axis of the fibrils is somewhat aligned along the direction of flow, resulting in more enhanced scattering intensity in the q direction perpendicular to the flow direction. Such anisotropy is more apparent when the scattering pattern is divided into four equal sectors, two of which are centered at the flow direction ( $\phi = 0, 180^{\circ}$ ) and the other two at the orthogonal angle. The 2-D SANS data collected after 5.9, 25.9, and 38.9 h of shear were integrated and plotted in the manner shown in Figure 1c, along with their respective circularly averaged counterparts. The stronger scattering intensity in the later stages of shearing is accompanied by increased azimuthal anisotropy, both of which are absent in the beginning of the time-resolved SANS experiments. Therefore, the rheology and structure response in rheo-SANS are a result of the formation and alignment of the P3HT fibrils by shear flow.

Further investigating the structural development of P3HT under the effect of shear flow, micrometer length P3HT crystals were observed using shear flow combined with SALS measurements. The rheo-SALS setup is illustrated in Figure 2a,b. The lower geometry is the Peltier plate, temperature controllable,  $\sim 21$  °C in these experiments in which a special



**Figure 2.** Digital images of a rheo-SALS setup with laser light and a camera capturing the light scattering of 20 mg/mL P3HT in 2-EN solutions: (a) before shear and (b) after shear for 24 h at 10 s<sup>-1</sup>; 2-D light scattering patterns of different P3HT solutions: (c) 10 mg/mL at 100 s<sup>-1</sup>, (d) 20 mg/mL at 10 s<sup>-1</sup>, (e) 20 mg/mL at 100 s<sup>-1</sup>, and (f) 30 mg/mL at 100 s<sup>-1</sup>. Inset arrow (e and f) is the flow direction.

pinhole is designed to set a 635 nm laser source indicated by a bright light spot, as shown in Figure 2a.

The upper geometry is a quartz plate that allows the laser to pass through and reach the camera system (located above the quartz plate) to capture all structural scattering from the sheared P3HT solution. The measured rheo-SALS data are given in Figure 2 indicating that the structural formation of P3HT crystals is sensitively dependent on shear rate and shear time. The digital image of before shear of P3HT solution of 20 mg/mL, shown in Figure 2a, presents a bright and uniform orange color. However, the digital picture of the 24 h 10 s<sup>-1</sup> sheared 20 mg/mL of P3HT sample, see Figure 2b, has a gradient color change from the edge of the quartz plate (dark brown color) to the center (bright orange color). This difference in color is attributed to the varied shear rate that is not homogeneous in parallel plate geometry. In particular, the shear rate decreases from the edge of the quartz plate (high shear rate) to the center (low shear rate) in which the shear rate approaches zero at the center of the plate. The sample color changes after shear corroborates the shear rate-dependent structural evolution of P3HT determined by 2-D light scattering patterns over different time periods (see Figure 2d,e). There is a slight increase in the light scattering intensity from 20 mg/mL of P3HT in 2-EN solution after shear for 20 h at 10 s<sup>-1</sup> as shown in Figure 2d. In contrast, the scattering results measured from the 20 mg/mL of sample after being sheared at a higher shear rate, 100 s<sup>-1</sup>, indicate much more P3HT crystal formation, as evidenced by the much stronger light scattering intensity after 20 h under shear in comparison to the sample sheared at 10  $s^{-1}$  (see Figure 2d,e).

Additionally, the P3HT structural development by shear flow is concentration-dependent,<sup>21</sup> which is corroborated by the rheo-SALS data shown in Figure 2c–f. The results shown in Figure 2c indicate no significant changes in the light scattering intensity of the 10 mg/mL of P3HT solution after 20 h shear at 100 s<sup>-1</sup>. The scattering is much less than that of the 20 and 30 mg/mL samples. For the 30 mg/mL solution, the P3HT structural formation was observed at an earlier time in comparison to the 20 mg/mL solution, after approximately 3 h shearing at 100 s<sup>-1</sup>, as shown in Figure 2f. However, the light scattering data of the 20 mg/mL solution indicate that there is a transition at a longer shear period, from 5 to 7 h (see Figure 2e). Moreover, there is an apparent decreasing trend in scattering intensity of the 30 mg/mL sample after 7 h under shear. This is from a thicker solution. When the P3HT crystallinity increases, the absorption peak at 600 nm of the pi-pi stacking increases. It is noted that the rheo-SALS measurements used a 635 nm laser. There could be a small absorption fraction of the light. Therefore, that drop of the light scattering intensity is attributed to the aggregation of P3HT crystal formation that decreased the transmitted light. In this study, the kinetics of the structural formation of P3HT are described by the measured data of rheo-SANS and rheo-SALS, which clearly corroborate the results revealed by AFM and TEM measurements.<sup>21</sup>

**Pi–Pi Stacking, UV–vis Absorption, and P3HT Crystallinity.** Herein, to thoroughly understand the kinetics and mechanism of P3HT crystallization under shear flow, an Avrami analysis<sup>40</sup> was performed, which describes the changes in crystallinity as a function of time. The Avrami equation is:

$$1 - \mathcal{O}_{c}(t) = 1 - \exp(-kt^{m}) \tag{1}$$

in which  $(1 - \emptyset_c(t))$  is the volume fraction of P3HT crystallites formed after shear at time *t* (second), k is the overall rate constant of the structural formation, and *m* is the Avrami exponent indicating nucleation mode, crystal formation type, and mechanism.<sup>40,41</sup>

Commonly, DSC is applied to measure the crystallinity of solid samples, but not those in the liquid phase. For this reason, another approach to quantitatively ascertain the P3HT crystalline fractions had to be employed. As described here, the UV-vis absorption measurements were used in this study in which the absorption peaks at 600 nm of the interchain interactions (pi-pi stacking) is proportional to the P3HT crystallinity.<sup>46</sup> Herein, a solution of 20 mg/mL P3HT in 2-EN was used to investigate the crystallization kinetics. Since the material absorbs quite strongly at this wavelength, it was not possible to employ a similar technique to rheo-SALS. Therefore, a new design of a UV-vis sample holder for the liquid phase was made as shown in Figure 3a. A very thin film layer of sheared P3HT solution could be loaded and held



**Figure 3.** Bottom insets show different P3HT gels formed on the lower geometry after shear at denoted shear rates. The top insets are pictures that show the nonuniform color that appeared after shear at a low shear rate,  $5 \text{ s}^{-1}$ . (a) A UV–vis thin film liquid sample holder with a 100  $\mu$ m gap (1: glass slices and 2: sheared P3HT solution); digital pictures of P3HT solutions after shear under ambient temperature (b) for 50 h at 5 s<sup>-1</sup>, (c) for 15 h at 100 s<sup>-1</sup>, and (d) for 50 h at 100 s<sup>-1</sup>. The insets in b and c are zoomed in three times.

between the two glass slides. The liquid surface tension between the two glass slides and the investigated P3HT solution holds the solution and prevents it from running out of the sample holder. A single layer of transparent tape,  $\sim 100 \ \mu m$  thickness, was used to create a sample gap as illustrated in a cartoon in Figure 3a. The UV–vis absorption of P3HT solutions under various shear rates, with respect to time and temperature, was measured. The P3HT absorption peaks at ca. 600 nm from the interchain interactions and the pi–pi stacking order were measured and analyzed.

The pictures given in Figure 3b-d are examples of different P3HT solutions loaded in the UV-vis sample holder from various samples after shear for 50 h at 5 s<sup>-1</sup>, 15 h at 100 s<sup>-1</sup>, and 50 h at 100 s<sup>-1</sup>, respectively. One can distinguish the color differences of these selected sheared solutions. The P3HT solution after 50 h shear at 100 s<sup>-1</sup> has a very uniform dark orange color, as shown in Figure 3d. In contrast, a bright orange color was observed in the solutions under a shorter shear period (15 h at 100 s<sup>-1</sup>) and at a low shear rate (50 h at 5 s<sup>-1</sup>), as shown in Figure 3b,c, respectively. These differences indicate less structural formation in comparison to the 50 hsheared P3HT sample at 100 s<sup>-1</sup> and corroborate the rheo-SANS and rheo-SALS data. Additionally, the inset pictures in the bottom-left corner present P3HT solutions after shear on a 50 mm diameter plate, the lower geometry in which the P3HT solution after 50 h shear at 100 s<sup>-1</sup> indicates a stronger gel formation with a distinct shape compared with the other two samples (see Figure 3b-d, the sheared P3HT solution on the geometry, the insets at lower left corners). The tight gel forms a small shape on the lower geometry (see the yellow arrow) as illustrated in Figure 3d, attributed to the strong and more rigid percolation of P3HT crystals in comparison to the other two (see Figure 3b,c). This argument is corroborated by the UVvis absorption results discussed below. Interestingly, a close inspection of the two samples after shear for 50 h at 5  $s^{-1}$  and 15 h at 100 s<sup>-1</sup> (see the two zoomed in pictures, top-left corner in Figure 3b,c) reveals clumps of P3HT crystals with nonuniform color after shear at a low shear rate of 5 s<sup>-1</sup>. In contrast, the sample after shear at a higher shear rate,  $100 \text{ s}^{-1}$ (regardless of time), reveals very smooth and uniform color. In terms of kinetics and mechanism of P3HT structural evolution under shear-induced solution crystallization, these observed differences are unexplainable.

To elucidate these differences, additional investigation of the sheared P3HT solutions by UV-vis measurements was carried out and the data were collected. The results shown in Figure 4 and Figure S1 (Supporting Information) show the UV-vis absorption data of different sheared P3HT samples, with respect to shear rate, time, and temperature. In particular, the increase in magnitude of absorption peaks at ca. 600 nm of sheared P3HT solutions indicates that the P3HT order is improved in the interchain, pi-pi stacking directions. The P3HT crystals grow along the pi-pi stacking direction; thus, micrometer-long crystals were made,<sup>21</sup> as illustrated by a cartoon shown in Figure 4h. In this manner, the polymer chains are aligned along the fibril-width axis. All samples were investigated at ambient temperature, except for the one presented in Figure 4f studied at 30 °C, which is close to the dissolution temperature of P3HT in 2-EN. It was found that the dissolution temperature of P3HT in 2-EN, ca. 40  $^{\circ}$ C, is a driving force for P3HT crystallization under shear flow.<sup>47</sup>

The UV-vis results given in Figure 4g show the absorption of the stored and unsheared P3HT solution with respect to



(a)

550

(d)

30

200

100

0

300

200

100

0

500

Absorption (cm<sup>-1</sup>)

500

Absorption (cm<sup>-1</sup>)

5s<sup>-1</sup>at RT 94h 50h 24h 22h 21h

20h 12h

700 500

(e)

550 600 6 Wavelength (nm)

– 9h – 7h

650

150 s<sup>-1</sup>

- 0h - 7h - 11h

18h

22h 28h

46h

50h

700 500

650

600

550 600 Wavelength (n

Wavelength (nm)

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(f)

550



100S<sup>-1</sup> at 30 °C

24h 22h 17h

12h 9h

7h

0h

650

700

500

600

Wavelength (nm)

(g)

550

Figure 4. UV-vis absorption data from P3HT solutions probed using different time periods, shear rates, and temperature conditions to determine the crystallinity of P3HT fibrils formed in the solution state. The absorption coefficient magnitude at ca. 600 nm, presented in the order of interchain interactions, is proportional to the crystallinity. Sheared P3HT samples under ambient/room temperature (RT), (a) 5 s<sup>-1</sup>; (b) RT, 50 s<sup>-1</sup>; (c) RT, 100 s<sup>-1</sup>; (d) RT, 150 s<sup>-1</sup>; (e) RT, 200 s<sup>-1</sup>; (f) 30 °C, 100 s<sup>-1</sup>; (g) RT, storage, and (h) cartoon of growing P3HT crystals along the pi-pi stacking direction.

700 500

200s<sup>-1</sup>at RT

0h 5h 5.5h 9h 15h

20h

40h

50h

. 650



Figure 5. (a) UV-vis absorption coefficient at 600 nm versus time of the P3HT order structure indicating the highly aligned pi-pi stacking formation under shear flow, with respect to shear rate, time, and temperature; (b) Avrami analysis, see equation (1), of studied samples presenting P3HT crystallinity fractions (proportional to the UV-vis absorption at 600 nm) plotted as a function of time (s); (c) Avrami exponent, m, determined from the slopes of linear fitting from Avrami analysis shown in (b), plotted as a function of shear rate  $(s^{-1})$ , and the standard deviation obtained by determined nucleation time windows as shown in Figure S1 (Supporting Information).

time. It has been determined that there are some small aggregations of P3HT crystals after storage (zero shear rate applied) of 20 mg/mL P3HT solution for 24 h as evidenced by digital TEM images.<sup>47</sup> The P3HT crystallinity was not much

Storage

1h
4h
7h
9h
12h
15h
17h
20h
24h

50h 94h

700

600 65 Wavelength (nm)

650

improved after 24 h storage under ambient conditions since the aggregation of nuclei and small P3HT crystals stops the growing sites of P3HT crystals. These results are corroborated by the unchanged viscosity of stored P3HT solutions.<sup>21</sup> Evidently, the UV–vis absorption of the P3HT solution slightly increases even after 94 h storage in which no significant differences are observed (see Figure 4g). Also, the absorption peak evolution at 600 nm is not apparently detectable.

In contrast, the sheared P3HT samples indicate significant development of the UV-vis absorption spectrum under various conditions with respect to shear rate, time, and temperature as shown in Figure 4a-f. The UV-vis absorption increases in the order from samples sheared at 5 to 100 s<sup>-1</sup> (see Figure 4a-c). Then the UV-vis absorption decreases in solutions sheared at higher shear rates, in the order from 150 to 200 s<sup>-1</sup> (at room temperature) as shown in Figure 4d,e, while the UV-vis absorption of samples sheared at  $100 \text{ s}^{-1}$ , 30 °C, has the lowest absorption coefficient magnitude in comparison to the other sheared samples (see Figure 4f). Overall, the samples sheared under ambient conditions at 100  $s^{-1}$  have the strongest absorption peaks of pi-pi stacking. We anticipate that shear influences the P3HT conformation and mediates the crystal formation and growth. At a certain shear rate, the shear force may result in a proper P3HT conformation promoting the pi-pi stacking of P3HT thiophene rings.<sup>21</sup> Therefore, an optimal shear rate exists. The absorption peaks at 600 nm for the P3HT samples were obtained and plotted appropriately with shear time as shown in Figure 5a. The sample after shear for 50 h  $(1.8 \times 10^5 \text{ s})$  at 100  $s^{-1}$  has the highest absorption value of ca. 143 cm<sup>-1</sup>. This value is the maximum number obtained for the samples that were considered and is used as a reference number to quantitatively determine the P3HT crystallinity. This is because the DSC results given in Figure S2a,d, and Table S1 (Supporting Information), indicate that the sample after shear for 50 h at 100 s<sup>-1</sup> has the highest melting enthalpy of fusion of ~25 (J/ g).

Additionally, the measured DSC data (heat flow versus temperature) of the P3HT samples are also shown in Figure S2 (Supporting Information). The melting temperatures of these samples are mostly identical, except for the one sheared at 30 °C, which has a higher melting temperature  $(T_m)$  of about 235 °C. The melting temperatures and crystallinity of the investigated P3HT samples obtained are shown in Table S1. The higher melting temperature of P3HT sheared at 30 °C is observed due to the crystallization employed near the dissolving temperature of P3HT in 2-EN, which is ca. 40 °C. Thus, perhaps, more perfect lamellar P3HT fibrils were achieved. The TEM images of these samples are collected and shown in Figure S3, Supporting Information. A careful examination of the P3HT fibrils from the TEM images indicate that similar P3HT fibrils, approximately 22 nm, are formed as shown in Figure S3 and Table S2. Also, a narrow melting peak is attributed to more perfect crystal formation. The areas under the heat of fusion of P3HT samples, Figure S2a, are measured and presented in Table S1 (Supporting Information). The given results of a decreasing trend of P3HT crystal formation under shear flow at various conditions are reasonably consistent with the measured UV-vis absorption data. Moreover, the DSC melting temperature results, Figure S2a,c,d (Supporting Information), apparently present broad and shallow melting peaks from 190 °C to around 235 °C, spanning a temperature window of nearly 45 °C. The melting

behaviors likely depend on the nature of the P3HT crystals in which small and defective (less perfect) P3HT crystal formed are attributed to the broad melting peaks. However, on shearing for longer time periods, these broad peaks no longer exist (see Figure S2c,d), which is thought to correspond to the formation of a more uniform and more perfect crystal structure.<sup>47</sup> Thus, there is a crystal perfection process during shear, as evidenced by the melting peaks of samples after 50 h at 5 s<sup>-1</sup> and after 90 h at 5 s<sup>-1</sup>, as shown in Figure S2c and supported in Figure S2d, Supporting Information. Remarkably, a distinctly sharp melting peak was observed in samples after 50 h shear at 100 s<sup>-1</sup> (ambient conditions). The DSC results in Figure S2d reveal that there are small and/or less perfect P3HT crystal portions after 50 h shear at 100 s<sup>-1</sup> under 30 °C, as evidenced by a secondary melting peak spanning nearly 37 °C, from 190 to 227 °C. In this study, all the DSC results were collected from the first heating scans of the sheared samples. The following cycles (second and third) are almost identical (see Supporting Information, Figure S4 and Table S3). The P3HT crystallinity and the melting temperatures of all the studied samples (after removing all the thermal history by the first heating) are almost identical. The measured melting enthalpy is ~16 (J/g), and the melting temperature is ~220 °C.

Avrami Analysis, Kinetics, and Mechanism of P3HT Crystallization. Herein, to elucidate the above uncertainties and arguments, the kinetics and the mechanism of P3HT crystallization from solution using the above processing protocols are determined. The UV-vis absorption peaks at 600 nm with respect to shear time, plotted as shown in Figure 5a, were investigated. As mentioned in previous paragraphs, the infinite crystalline P3HT has an absorption coefficient of 142 cm<sup>-1</sup> at 600 nm (see Figure 4). This maximum absorption magnitude is used as a reference number to proportionally quantify the crystallinity fractions of the samples. The number of P3HT molecules displaying pi-pi stacking is proportional to the absorption coefficient at 600 nm and so is proportional to the degree of P3HT crystallinity. The absorption coefficient for the sample sheared at 100 s<sup>-1</sup> reached a maximum value after 50 h shear. This is thought to be an almost all crystalline material. An Avrami analysis<sup>40,48</sup> for the sheared samples was conducted.

The eq 1 was employed to determine the Avrami power law by dividing the absorbance at 600 nm by 142 cm<sup>-1</sup> to find  $\mathcal{O}_{c}(t)$ . The initial absorption of the studied samples is close to 0 (during the first hours, the absorption magnitudes are about 0), even after a certain shear time period, called the induction time or nucleation time as illustrated in Figure 5a. The nucleation time is determined by the time when the absorption starts at 600 nm indicating the formation of P3HT crystals. The given UV-vis absorption results shown in Figure S1, Supporting Information, indicate the nucleation time windows of P3HT solutions under shear at different shear rates and temperatures. Hence, the time presented in the x-axis (Figure 5b) is determined by subtracting the appropriate nucleation time and is plotted as a function of P3HT crystallinity. The Avrami exponent (m) was determined from the slopes of  $Ln(-ln(1 - \emptyset_c))$  versus Ln(t). The Avrami power parameter (m) is around 2 for the sample sheared at a high shear rate, 100  $s^{-1}$  (see Figure 5b,c). The maximum value that the power law exponent can have for one-dimensional crystals is 2, and it is revealed that this number does not increase above 2 (see Figure 5c). However, it is known that if there is no shear (0)

shear rate), then *m* is  $\sim$  0, since there is no crystallization (see Figure 4g), and a spectrum of power laws is expected as the shear rate increases to the ultimate value of 2. In this study, the UV-vis absorption value of the sheared sample for 50 h at 100 s<sup>-1</sup> was set as a reference, assuming 100% P3HT crystallinity. Then, the m value was 1.9. However, if this sheared sample had only, for example, 60 or 70% P3HT crystallinity, the m value was from 1.7 to 1.8, still within the error bar (see Figure 5c). We anticipate that the trend of relative P3HT crystallinity increasing with the shearing time is the major factor affecting m values regardless of the UV-vis absorption value of 100% P3HT crystallinity. Herein, the crystals are one-dimensional strands, thus suggesting that crystallization occurs through homogeneous nucleation and is limited by the contact time between the individual macromolecules in solution and the growing crystal (rather than diffusion of the macromolecules to the crystal). Also, it is indicated that the P3HT crystals formed by solution shear follow 1-D crystal growth with the formation of crystal by contact<sup>40</sup> in which the micrometer-long P3HT crystals were made by introducing pi-pi stacking faces, which are favorable for crystal growth as depicted by a cartoon in Figure 4h. The results obtained from Avrami analysis corroborates the data measured by rheo-SANS/rheo-SALS and TEM, suggesting that longer and more perfect P3HT crystals are formed after shear.

# CONCLUSIONS

In this study, the evolution of P3HT crystals in solution, from nucleation to crystal growth under shear flow, was investigated in situ through rheo-SANS and rheo-SALS. The formation of P3HT crystal fibrils and 3-D network crystals from nanoscale to micrometers was successfully measured and determined. The increase in apparent fractal magnitude, from  $\sim$ 1.3 to  $\sim$ 2.6, indicates that a fibril-like structure formed and then developed to create 3-D networks of percolated P3HT crystals. This percolation can significantly contribute to the enhancement of charge carrier mobility by creating more charge transporting channels. By varying the shear protocols (with respect to time, concentration, shear rate, and temperature), the morphology of P3HT in its solution state can be controlled in a simple manner to potentially improve the plastic solar cell performance.

Importantly, this is the first time that the kinetics and mechanism of P3HT crystallization in the liquid phase under shear flow were comprehensively investigated and determined by (UV-vis) measuring the P3HT interchain interactions through the absorption peak magnitudes at 600 nm of the sheared P3HT solutions. The P3HT crystal fractions of the studied samples are reasonably measured by quantifying the characteristics of the pi-pi stacking absorption peak. The increases in P3HT crystalline fractions with time of shearing were used in Avrami analysis to understand the crystallization kinetics and mechanism. Herein, the fibril-like formation of P3HT crystals corroborates our hypothesis that micrometerlong P3HT crystals form by shear flow. The P3HT crystals are formed and limited by the contact time between the P3HT macromolecules in which the pi-pi stacking is strongly directionally affecting the crystal growth. Additionally, the measured UV-vis and DSC data indicate that there is a crystal perfection process related to the shear time. The results in this paper clarify the uncertainties of P3HT crystallization in the liquid state while being sheared.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c00717.

UV-vis absorption data and nucleation time of P3HT samples under shear flow, DSC data of sheared P3HT samples, and TEM images of P3HT fibril crystals (PDF)

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#### Notes

The authors declare no competing financial interest.

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