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The Impact of Aggregation on the p-Doping Kinetics of Poly(3-hexylthiophene)

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Abstract

The morphological effects of regioregular poly(3-hexylthiophene) (P3HT) on its p-doping kinetics with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ) in solution are studied using optical absorption spectroscopy and stopped-flow technique. Two morphological forms, solubilized (s-P3HT) and nanowhiskers (nw-P3HT), are investigated. Both P3HT solubilized and aggregated solutions show similar characteristic near-IR absorption bands for integer charge transfer products with F₄-TCNQ. Kinetic analysis on p-doping of s-P3HT with F₄-TCNQ indicates that the doping reaction proceeds with a single reaction mechanism that is first order in s-P3HT. The doping kinetics of P3HT aggregate solution shows two distinctive reaction mechanisms. The slow mechanism has a reaction rate constant similar to that of solubilized P3HT solution, so it likely results from s-P3HT components that are present in the aggregate solution. The fast one is assigned to the nw-P3HT component, probably due to more efficient charge delocalization in the aggregated P3HT nanostructures. Additionally, the kinetic trends of the p-doping reactions are better fitted with the consideration of a Gaussian-like distribution of reactivities from P3HT, matching the complexity of polymeric systems originating from molecular weight and morphology variations. This study highlights the importance of considering different morphological forms of conjugated polymers on their charge-transfer reaction kinetics. The knowledge gained here should be fundamentally and practically important for future chemical doping applications in organic electronic device fabrications.

Graphical abstract

P3HT nanowhiskers are p-doped by F₄-TCNQ faster than solubilized P3HT chains in toluene because of their highly ordered molecular packing.

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Electronic Supplementary Information (ESI) available: Additional figure as discussed in text are presented.

Introduction

Chemical doping has been demonstrated as an efficient way to improve the performances of organic electronic materials and devices.^{1–3} Chemical dopants can be introduced into host materials through a variety of ways including vapor co-deposition, solution mixing, surface doping, and sequential doping.^{1, 3–8} Among them, solution-based doping methods are particularly appealing as they can be readily integrated into less expensive and scalable solution processing steps for organic electronic devices.

In solution, the added dopant molecules, being either electron donors (n-dopant) or electron acceptors (p-dopant), undergo charge transfer reactions with the host materials. In the case of p-doping, the LUMO of the p-dopant molecule needs to be lower than the HOMO of the host molecules to enable the charge transfer. Recently, many efforts have been devoted to developing effective and easy-to-handle dopant molecules with suitable HOMO/LUMO levels for organic electronic materials.^{1, 2, 7, 9–13} Understanding the doping mechanism between dopant and host molecules is crucial for utilizing the doping process in a more efficient and controllable manner. The doping of poly(3-hexylthiophene) (P3HT) by 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ) is one of the most extensively studied p-doping systems in both solution and thin film forms.^{14–23} Pingel et al. showed that although most F₄-TCNQ molecules have integer charge transfer with P3HT, only a small fraction (5%) of the charge transfer will lead to the formation of free charge carriers.¹⁵ Optical absorption spectroscopy measurements demonstrated that after reacting with F₄-TCNQ, P3HT would form bipolaron or polaron in solution and thin film, respectively.²⁴

It is well known that conjugated polymers can have different properties resulting from their various molecular conformations and aggregation forms, with P3HT being a classic example.^{25–28} It is reasonable to expect the P3HT/F₄-TCNQ doping reaction can be profoundly influenced by the morphology of P3HT. A new crystalline phase in F₄-TCNQ doped P3HT thin film was confirmed by Duong et al. as a result of F₄-TCNQ being incorporated into the ordered domains of P3HT.¹⁸ Gao et al. compared the p-doping of regiorandom and regioregular P3HT with F₄-TCNQ and proposed that regioregular P3HT will undergo a more efficient charge-transfer due to its stronger ability to delocalize charge carriers in its aggregated form.^{19, 20} Their later studies showed that in toluene, fully solubilized regioregular P3HT chains tend to form J-type aggregates; while H-type aggregates are expected in anisole. Furthermore, the doping efficiency with J-type P3HT nanofibers is substantially higher than that of H-type due to their differences in polymer

chain packing.²¹ In P3HT solution, the most basic morphological forms of P3HT in solution are its fully solubilized form (s-P3HT) and its aggregated nanowhisker form (nw-P3HT) which could be either H-type or J-type depending on the experimental conditions.²⁹ However, there has not been a report on a direct comparison of doping mechanisms between these two forms of the same polymer.

Besides the doping mechanism and doping efficiency of P3HT/F₄-TCNQ, its doping reaction kinetics is a crucial aspect that has unfortunately drawn little attention so far. Investigating the doping reaction kinetics can elucidate the reaction mechanism. Moreover, understanding the doping process and being able to predict the doping reaction rate are of practical importance for gaining greater control of the doping process. The doping products of P3HT and F₄-TCNQ have characteristic absorption bands in the near IR region that do not overlap with the absorption of either reactants, making optical absorption spectroscopy a suitable technique to monitor the reaction progress. Optical absorption spectroscopy, usually in the UV-vis-NIR range, is a versatile method to study reaction kinetics in solution at the time scale of seconds and longer. For rapid reactions taking place at the sub-second range, stopped-flow technique is often used to trace the reaction with millisecond time resolution.

Herein we investigate the influences of two different P3HT morphological forms, s-P3HT and nw-P3HT, on their p-doping reaction kinetics and mechanisms with F₄-TCNQ. The experiments are carried out with the same batch of polymer and the same solvent to eliminate the possibility of property variations induced by different molecular weights, polydispersities, and solvent-sample interactions. The reaction temperature is maintained at 23.0 °C because room temperature is most relevant for practical applications. The optical spectra of aggregated P3HT solution are decomposed to separate the s-P3HT and nw-P3HT components within it. Our kinetic studies on the p-doping of s-P3HT solution indicates a single reaction mechanism. The doping reaction of the P3HT aggregated solution appears to takes place with two simultaneous reaction mechanisms whose reaction rate constants are orders of magnitude different. The rate constant of the slow mechanism is comparable with that of the s-P3HT, suggesting that the fast and slow mechanisms observed for aggregated P3HT solution probably represent the nw-P3HT and s-P3HT components, respectively. Moreover, nw-P3HT demonstrates substantial higher doping susceptibility for producing F₄-TCNQ anions per P3HT monomer. These solution doping kinetics studies will significantly enhance our fundamental understanding of the charge-transfer process for conjugated polymer and provide the critical reaction-rate information to achieve controllable chemical doping in practical applications.

Experimental

Poly(3-hexylthiophene-2, 5-diyl) (P3HT) ($M_n = 70.5$ kDa, PDI=1.7, head-to-tail regioregularity > 98%) and 99.8% anhydrous toluene assay were purchased from Sigma-Aldrich. 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ) (98.0 %, purified by sublimation) was purchased from TCI America. The s-P3HT solution is prepared by heating a dilute solution of P3HT in toluene (6–40 µg/mL) to 90 °C for 10 min and then cooled down to room temperature (23 °C) within 5 min. The s-P3HT solution is used immediately after cooling to room temperature for doping reaction or optical measurements.

The nw-P3HT solution is prepared by heating a 2 mg mL⁻¹ solution of P3HT in toluene to 90 °C for 10 min and then cooled to room temperature at a rate of ~ 1 °C/min overnight and stored in dark. The resulting nw-P3HT solutions are diluted at room temperature in toluene for further studies. All solutions are prepared and handled under nitrogen atmosphere to minimize oxygen exposure.

UV-vis absorption spectra and stopped-flow kinetics are recorded on a Cary-60 spectrometer equipped with a SFA-20 rapid kinetics accessory (TgK Scientific) at 23.0 °C. All p-doping reactions are carried out at 23.0 °C maintained by a Quantum Northwest TC1 temperature controller. Each stopped flow experiment is repeated at least 8 times and the averaged trace is used. The spectra and kinetic trend lines are fitted with the Curve Fitting Toolbox in Matlab 2016a.

Results

Ordered P3HT nanostructures such as nanowhiskers can be formed by slowly cooling down regioregular P3HT solution in marginal solvents.^{29–31} During the cooling and aging process, s-P3HT gradually packs into nw-P3HT while the solution color turns from bright orange into dark purple. Upon heating, the nw-P3HT converts back to s-P3HT and the solution color returns to bright orange. The black solid line in Figure 1(a) displays the UV-vis absorption spectra of a 30 µg/mL P3HT aggregated solution. The 2.02 eV (614 nm) and 2.19 eV (567 nm) peaks are the characteristic 0-0 and 0-1 transitions for π - π stacked P3HT.^{32–34} The same aggregated solution is converted to a s-P3HT solution by heating at 90 °C for 10 min; its spectra taken immediately after cooling down to room temperature is shown as the red solid line in Figure 1(a). The 2.76 eV (450 nm) peak is the typical absorption peak for s-P3HT in solution.

The aggregated P3HT solution is actually a mixture of s-P3HT and nw-P3HT. By decomposing the spectra of the aggregated P3HT solution, the amount of s-P3HT and nw-P3HT components in it can be resolved. The following formula is used for the decomposition:

$$A_{mixture} = A_{s-P3HT} + A_{nw-P3HT} = C_{s-P3HT} A_{s-P3HT}^0 + A_{0-0} + A_{0-1} + A_{0-2} + A_{0-3}$$

A_{s-P3HT}^0 is retrieved directly from the spectra of P3HT solubilized solution (all s-P3HT content) in Figure 1(a), and C_{s-P3HT} is the scaling factor for the s-P3HT spectra. $A_{nw-P3HT}$ is fitted using 4 Gaussian peaks representing the 0-0, 0-1, 0-2, and 0-3 vibronic transitions of nw-P3HT.^{33–35} In order to achieve the best fit of the overall spectra, an ad-hoc vibronic model that allows non-uniform widths for the fitted peaks is used here. One fitting example is shown in Figure 1(b). The vibronic peaks are centered at 2.02 eV, 2.19 eV, 2.35 eV, and 2.51 eV. The total concentration [s-P3HT]⁰ is acquired from the corresponding heated s-P3HT solution, and [s-P3HT] in the aggregated solution is calculated from C_{s-P3HT} after the fitting. A quality fitting assures that the nw-P3HT component is isolated correctly from the s-P3HT component in the overall spectra. The concentration of nw-P3HT can be reliably obtained using [nw-P3HT] = [s-P3HT]⁰ - [s-P3HT]. Additionally, the ratio of 0-0/0-1 peaks

from the fitting result indicates that the nanowhiskers in this aggregated solution are J-type aggregates,³³ consistent with the previously reported results by Gao et al.²¹

When p-doping a 30 µg/mL s-P3HT solution with 5.3 wt% F₄-TCNQ, it takes around 10 h to have any discernable absorption peaks of doping products centered at 1.61 eV (768 nm) and 1.46 eV (850 nm), as shown in Figure 2(a). These two peaks are the characteristic absorbance peaks of F₄-TCNQ anion resulting from integer charge transfer,^{15, 36} while the elevated broad baseline between 1.8 eV and 1.1 eV is attributed to P3HT polaron and bipolaron.^{15, 24, 37} In Figure 2(a), the 5.3 wt% doping ratio equals to a molar ratio of 1:33 between F₄-TCNQ and P3HT monomer. If assuming the limiting reactant F₄-TCNQ is totally consumed in the doping reaction, the combined extinction coefficient (ϵ) for both doping products (F₄-TCNQ⁻ and P3HT polaron) at 1.61 eV is $3.1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The p-doping of s-P3HT appears to enhance the aggregation peaks, which has been focused in a separate study.³⁸ The p-doping of a 30 µg/mL P3HT aggregated solution by F₄-TCNQ also yields F₄-TCNQ anion and P3HT polaron, as evidenced by the emergence of identical absorbance bands in the NIR range shown in Figure 2(b). An interesting finding here is that the p-doping reaction of the aggregated solution is dramatically faster than that of s-P3HT. Under the same concentration conditions, the p-doping of the aggregated solution yields more doping products in 1 min than s-P3HT does in 20 h based on the absorption at 1.61 eV.

Stopped-flow optical absorption spectroscopy is used to investigate the reaction kinetics between P3HT and F₄-TCNQ, especially for the fast reaction in the doped P3HT aggregated solution. The 1.61 eV absorbance peak is monitored as it represents the simultaneous formation of both p-doping products, P3HT⁺ and F₄-TCNQ⁻. By keeping the F₄-TCNQ in large excess (125 µg/mL), P3HT concentrations are varied as the limiting reactant in the pseudo-single-reactant reaction.

The 1.61 eV absorbance trend lines from four pseudo-single-reactant reactions of s-P3HT/F₄-TCNQ are shown in Figure 3(a). The single exponential fits ($Abs = A_f(1 - e^{-k_1(t-t_0)})$) for the bulk part of the trend lines are displayed as the red lines in Figure 3(a). The fitting parameters, amplitude A_f and pseudo-first-order rate constant k_1 , are listed in Table 1. The fitted amplitude A_f is the expected Abs(1.61 eV) at $t = \infty$, which represents the total doping products that will be formed under this mechanism. At the initial stage of the reaction, there appears to be an induction period which is corrected by t_0 . In general, the fit curves match the experimental trend lines, indicating that the doping reaction is first order in s-P3HT. The pseudo-first order rate constants k_1 have similar values for these 4 different s-P3HT concentrations ($k_1 = 1.40 \pm 0.13 \times 10^{-2} \text{ s}^{-1}$), further confirming that there is only one reaction mechanism when s-P3HT is the limiting reactant.

The trend lines for the aggregated P3HT solution with excess F₄-TCNQ are fitted with a double exponential equation ($Abs = A_1(1 - e^{-k_1 t}) - A_2(1 - e^{-k_2 t})$), and the fit curves are shown in Figure 3(b). The fitting parameters are listed in Table 1. In general, both k_1 and k_2 maintain their values at different total P3HT concentrations: $k_1 = 3.00 \pm 0.82 \times 10^{-2} \text{ s}^{-1}$, $k_2 = 29.2 \pm 11.1 \text{ s}^{-1}$. The double exponential fitting indicates that there are probably two simultaneous reaction mechanisms contributing to the formation of P3HT⁺ and F₄-TCNQ⁻ in solution, and both mechanisms are first order in P3HT. One probable explanation is that

there are two distinctive P3HT morphological forms that react with F₄-TCNQ simultaneously at different rates. The k_1 values from the double exponential fitting is comparable to the k_1 values of s-P3HT doping, suggesting that the s-P3HT components in the aggregated solution undergo doping reaction in a similar manner as in the s-P3HT solution. On the other hand, the k_2 values from the double exponential fittings are about three orders of magnitude larger than k_1 , and are likely contributed from the nw-P3HT components in the aggregated solution. Gao et al. compared the p-doping reactions of regioregular and regiorandom P3HT with F₄-TCNQ and reported more efficient charge transfer for regioregular P3HT due to the delocalized hole charges in the ordered aggregates of regioregular P3HT.¹⁹ In this work, only regioregular P3HT is used to study the impacts of polymer chain packing on their p-doping reaction kinetics. For s-P3HT, the solubilized polymer chains could be relatively difficult to p-dope and the integer charge transfer will not readily take place. nw-P3HT could get p-doped quicker because the P3HT molecules are already in aggregated forms, which may have a lower oxidation potential as indicated by X-ray photoelectron spectroscopy (XPS/UPS) and cyclic voltammetry measurements.^{19, 39–41} So it is possible that aggregated P3HT forms are essential for it to get p-doped by F₄-TCNQ in toluene. It should be noted that k_2 values obtained here indicate a reaction half-life to be around 23 ms. Our spectrometer's 12.5 ms time resolution may not completely resolve the details of the initial reaction stage, which could partially explain the large uncertainty obtained for the k_2 in aggregated solutions. Nevertheless, our conclusion about the orders of magnitude faster reaction rate constant of nw-P3HT component compared to s-P3HT component should still be valid.

The plots of the fitted amplitudes A vs. the concentrations of the specific P3HT components (limiting reactant) are shown in Figure 4. The expected concentration of doping product [F₄-TCNQ⁻] that directly derived from the fitted amplitudes is also listed as the y-axis on the right side. The expected doping products formed in the k_1 and k_2 mechanisms match linearly with the s-P3HT and nw-P3HT components in aggregated solution, further confirming our assignments of k_1 and k_2 to these two P3HT components in solution. The different slopes of these linear trends indicate that the stoichiometries of reacting with F₄-TCNQ per P3HT monomer vary among different morphological forms. In the p-doping reaction of P3HT, typically a small segment of the whole conjugated polymer chain is involved in the initial charge-transfer process with the dopant molecule,⁴² and the reacting segment is normally composed of several repeating monomer units. The reacting stoichiometric ratios can be derived from the slopes in Figure 4 when assuming that for the reactions shown in Figure 3, the limiting reactant P3HT is totally consumed when F₄-TCNQ is in large excess. For example, in Figure 4, the P3HT solubilized solution (the black solid line) has a slope of $3.76 \times 10^3 \text{ M}^{-1}$ (for 1 cm optical pathway), which indicates that on average each F₄-TCNQ dopant molecule will react with 8.3 monomer units in the P3HT solubilized solution. For nw-P3HT and s-P3HT components in aggregated solution, the stoichiometric ratio are 4.1 and 11.0, respectively. The 4.1 ratio of nw-P3HT matches the value of 4 obtained by Pingel et al. in their thin film F₄-TCNQ/P3HT studies,²³ consistent with the solid characteristic of P3HT nanowhiskers here. Another study by Pingel et al. concluded that about 30% of F₄-TCNQ molecules do not have charge transfer reaction with P3HT,¹⁵ which is contradictory to our assumption of 100% doping efficiency of F₄-TCNQ for obtaining the combined

extinction coefficient (ϵ) for both doping products (F_4 -TCNQ⁻ and P3HT polaron) at 1.61 eV in Figure 2(a). If taking into account of the possible ~70% doping efficiency of F_4 -TCNQ when P3HT is in excess, then all the reacting stoichiometric ratios derived from Figure 4 should be increased by a factor of 1.43. However, not all P3HT monomers can have effective charge transfer either when F_4 -TCNQ is in large excess. Many causes including chain bending or kinks, misfolded chains, or local defects could also leave some monomers in a “non-reactive” state. So our stoichiometric ratio estimations may still be qualitatively suitable. More importantly, the almost 3 times difference between the stoichiometric ratios of nw-P3HT and s-P3HT components should be valid, which highlights the impacts of different morphological forms of conjugated polymer on the doping process. In addition, the overall ratio for the aggregated solution is 6.8, meaning that besides reacting faster with F_4 -TCNQ, the aggregated solution is also able to produce more doping products per monomer than the solubilized solution.

Another factor needs to be considered is the molecular weight and molecular weight distribution for polymer samples. Even for samples with the same M_n , the one with a larger polydispersity index (PDI) has a broader distribution of polymer chain lengths. The aggregation process of nanowhiskers in toluene could be accompanied by fractionation, which means that on average the nanowhiskers may have higher molecular weights than the remaining solubilized chains in solution. Polymer chain length differences may lead to variations in their chances of reacting with dopant molecules. Therefore it is possible that there are some low molecular weight s-P3HT molecules in solution that do not react with F_4 -TCNQ easily. Wang et al. reported that each F_4 -TCNQ anion would bleach 4.9 P3HT monomer units in solution doping, and their ratios do not change with the molecular weight of P3HT sample.²⁴ However, their methods mainly probe the chemically active portions of P3HT. Our methods here include all the P3HT initially present in solution, so the doping reaction stoichiometric ratios from s-P3HT, particularly the s-P3HT component in the aggregated solution, could appear larger than the theoretical value by including some amount of “non-reactive” monomers due to polydispersity effects.

Two typical ways of obtaining the reaction order for a reactant are the pseudo-single-reactant method and the initial rate method. However, there are experimental difficulties in implementing either of them to resolve the reaction order of F_4 -TCNQ in this study. To carry out a pseudo-single-reactant reaction with P3HT in large excess, the concentration of P3HT needs to be at least 500 $\mu\text{g/mL}$. Because P3HT is marginally soluble in toluene, it is impossible to maintain P3HT in fully solubilized form at such a high concentration at room temperature. Although P3HT aggregated solutions are relatively stable at high concentrations, the miniature sized tubings and optical cells in the stopped flow apparatus could be easily clogged by high concentrations of P3HT nanowhiskers. So the kinetic data obtained with high concentrations of aggregated P3HT will have large systematic errors and may not provide reliable results. As for the initial rate method, the presence of an induction period makes it difficult to extract the true initial reaction rates in the doping reaction of low concentration s-P3HT. In the case of doping of P3HT aggregated solution, the reaction is too fast for our instrument to resolve the initial rate reliably. Assuming the reaction order of F_4 -TCNQ in the p-doping reaction is also 1, the p-doping reaction rate constants obtained from the stopped flow studies for s-P3HT in solubilized solution, s-P3HT in aggregated solution,

and nw-P3HT in aggregated solution would be $30.9 \pm 2.8 \text{ M}^{-1}\text{s}^{-1}$, $66.2 \pm 18.1 \text{ M}^{-1}\text{s}^{-1}$, and $6.46 \pm 2.46 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, respectively.

The p-doping reaction pathways of s-P3HT and nw-P3HT are proposed in Figure 5. For s-P3HT, once it charge transfers (C.T.) with F₄-TCNQ, the resulting ion pair may remain bound until they are separated by external perturbations. Either of the steps can be the rate-determining step (R.D.S.), as illustrated in pathway (a). The doping reaction of nw-P3HT with F₄-TCNQ may have two similar steps of C.T. and charge separation, as shown in pathway (b). If both pathway (a) and (b) have the same R.D.S., be it the C.T. or charge separation step, and assuming that the pre-exponential factor is the same for the R.D.S., then the ~2000 times difference in the reaction rate constants indicates that the activation energy of the R.D.S. for the nw-P3HT pathway (b) is about 18 kJ/mol less than that of s-P3HT pathway (a). This is probably due to either the ordered molecular packing of nw-P3HT that promote the initial hole injection in this first step, or the quick delocalization of injected hole into the π - π aggregated motifs of nw-P3HT via enhanced intrachain interactions to finish the p-doping process.¹⁹⁻²¹ There is an equilibrium between s-P3HT and nw-P3HT in solution, their conversions are slow considering that the aggregation process of P3HT in solution typically takes hours to days to accomplish in the dilute concentrations used here. It is possible that s-P3HT first aggregates into nw-P3HT, then the newly formed nw-P3HT will be immediately p-doped by F₄-TCNQ to finish the charge transfer process, as illustrated in pathway (c) with the initial aggregation step as the R.D.S. One thing to note is that s-P3HT gets p-doped about twice as fast in aggregated solution vs. in solubilized solution, evidenced by the obtained rate constants. Possible reasons include (1) the presence of nw-P3HT facilitates the initial C.T. of s-P3HT; and (2) nw-P3HT induces the aggregation of s-P3HT, followed by fast C.T., similar to pathway (c).

Although the fit curves shown in Figure 3 generally follow the trend lines of doping products, there are still some noticeable deviations from the experimental data, particularly for the aggregated solution doping results. Here we attempt to fit the reaction trend lines with a consideration of reactivity variations. A Gaussian-like distribution function is employed to simulate the variations of rate constants in the fitting function. The modified pseudo-single-reactant reaction fitting functions are listed below:

$$Abs = \sum (A'_1 e^{-\left(\frac{\Delta_1}{\sigma}\right)^2} (1 - e^{-e^{(\ln k_1 + \Delta_1)(t-t_0)}}))$$

$$Abs = \sum (A'_1 e^{-\left(\frac{\Delta_1}{\sigma}\right)^2} (1 - e^{-e^{(\ln k_1 + \Delta_1)t}}) + \sum (A'_2 e^{-\left(\frac{\Delta_2}{\sigma}\right)^2} (1 - e^{-e^{(\ln k_2 + \Delta_2)t}}))$$

One Gaussian-like fitting result of the aggregated solution sample is shown in Figure 6 and the simple double exponential fit is also displayed for comparison. The fitting plots for all reaction trend lines are displayed in supporting information and the fitting parameters are listed in Table 2. The rate constant is varied in the form of $\ln k_1$ which directly relates to the activation energy variations in the system, the main source of reactivity non-uniformity. The width σ is kept at 1.3 sec^{-1} , which means that the standard deviation of rate constants is 2.24 times from the centered value. The Gaussian-like distribution is simplified into segments for easier calculation, and its histogram is illustrated in the inset of Figure 6. This Gaussian-like

fitting method provides better fits for aggregated P3HT solutions, with $R^2 > 0.996$ for all samples. The Gaussian exponential fit results have similar values to the simple double exponential fits, confirming that adding a distribution does not fundamentally alter the fit. In theory, most polymer samples are a mixture of polymer chains with different chain lengths, conjugation lengths, and even head-to-tail regioregularities for the case of P3HT used here.^{19, 21, 27, 43, 44} All these factors could alter the properties of polymer chains or their aggregates, so it could be a very crude approximation to express the reactivities of a polymer sample with just a single value. The residual plot in Figure 6 shows that the Gaussian-like method provides a better fit particularly in the late stage of the reaction when the slow s-P3HT mechanism takes over, which is not observed for s-P3HT in solubilized solution. In addition, Table 1 shows that the k_f for s-P3HT is about 2 times larger in the aggregated solution than in the solubilized solution. It is likely that the p-doping of s-P3HT can be facilitated by the presence of neutral and charged nw-P3HT, either via the induced aggregation in pathway (c) or promotion of C.T. through charge delocation into nw-P3HT in pathway (a). In both pathways, the heterogeneities of nw-P3HT, including different intrachain or interchain coupling, and molecular packing or backbone bending defects occurring naturally or induced by chemical doping, could lead to different degrees of reactivity enhancements for p-doping of s-P3HT. Although the simple exponential fits can provide qualitative results using single reaction rate constant values, an accurate description of the reaction progress may require a consideration of reactivity distributions originated from heterogeneities of polymer chain, reacting segments, or polymer aggregates.

Conclusion

This study provides the first comprehensive kinetic study on the p-doping reactions between P3HT and p-dopant F₄-TCNQ in solution. Our initial results show that P3HT aggregated solution will get p-doped substantially faster than s-P3HT solution. Kinetic analysis demonstrates that there is likely a single reaction mechanism for the p-doping of s-P3HT. The P3HT aggregated solution show two distinctive p-doping reaction mechanisms whose reaction rate constants are orders of magnitude different. The slow one is assigned to the s-P3HT component while the fast one is assigned to the nw-P3HT component. This reactivity difference is probably due to different P3HT morphologies that lead to variations in charge-transfer and hole-delocalization rates. The doping reaction appears to be first order in P3HT. The nw-P3HT component also shows lower stoichiometric numbers in the p-doping reaction in comparison to the s-P3HT component, indicating that P3HT aggregates have a superior doping efficiency in terms of both reaction rate and monomer consumption. Finally, a Gaussian-like distribution of reactivity is introduced to improve the fitting quality, which is consistent with the property variations of polymer materials resulting from many factors including molecular weight and different packing geometries. The results here emphasize the impacts of conjugated polymer morphology on its doping reaction kinetics, which needs to be taken into consideration when integrating chemical doping into the field of organic electronic materials. For example, during the last period of the drying process in solution-based fabrication methods, the concentration of conjugated polymer increases dramatically and could form various aggregates. Although this last drying step is very brief, dopant molecules nearby may charge transfer with the aggregates in a much faster rate and

potentially accomplish the doping process in the last moment. Hopefully the knowledge gained here could help to reach greater control of the chemical doping process including dopant spatial distributions by manipulating the aggregation arrangements of the host organic materials.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(a) UV-Vis absorption spectra of a 30 $\mu\text{g/mL}$ P3HT aggregated solution in toluene and the spectra of the same solution after heating P3HT. (b) Decomposition of the spectra of the aggregated P3HT solution into s-P3HT and nw-P3HT components. The absorption of nw-P3HT component can be further deconvoluted into 4 vibronic transitions.

Figure 2.

Time-lapse UV-Vis absorption spectra of (a) a P3HT solubilized solution and (b) a P3HT aggregated solution recorded at different times after p-doping with 5.3 wt% F₄-TCNQ. The concentrations of P3HT in both solutions are 30 $\mu\text{g/mL}$.

Figure 3.

The 1.61 eV absorbance of p-doping products versus time for various (a) P3HT solubilized and (b) P3HT aggregated solutions mixed with excess amount of F₄-TCNQ. The initial concentrations of P3HT are marked in the image, and the initial concentration of F₄-TCNQ is 125 μg/mL. The red lines in (a) are the single exponential fit curves ($Abs = A_1(1 - e^{-k_1(t-t_0)})$). The red lines in (b) are the double exponential fit curves ($Abs = A_1(1 - e^{-k_1t}) - A_2(1 - e^{-k_2t})$).

Figure 4.

The amount of doping product obtained from the fitted amplitudes (A_1 and A_2 in Table 1) vs. the concentrations of corresponding P3HT components/solutions. The molar concentration of P3HT is shown in the form of the P3HT monomer unit. The right-side y-axis shows the amount of doping product in the form of reacted F_4 -TCNQ. The slopes of the linearly fitted lines show the reaction stoichiometries of F_4 -TCNQ per P3HT monomer.

Figure 5.
 Possible reaction pathways for charge-transfer reaction between P3HT and F₄-TCNQ.

Figure 6.

Examples of two fit methods for the 1.61 eV absorbance of p-doping products versus time: (a) s-P3HT and (b) aggregated P3HT solution mixed with excess amount of F₄-TCNQ. The green lines are the fit curves with a Gaussian-like distribution of each rate constant. The red lines are the simple exponential fit curves. Residuals from both methods are plotted in the bottom for comparison. Inset shows the histograms of the Gaussian-like distributions of reaction rate constants.

Table 1

The single and double exponential fitting parameters for the 1.61 eV absorbance fit curves of p-doping reactions shown in Figure 3. The molar concentration of P3HT is shown in the form of the P3HT monomer unit.

[s-P3HT] ($\times 10^{-5}$ M)	[mw-P3HT] ($\times 10^{-5}$ M)	A_1	$\ln k_1$ (sec $^{-1}$)	A_2	$\ln k_2$ (sec $^{-1}$)	R^2
5.30		0.194	-4.39			0.999
7.11		0.254	-4.28			0.999
8.98		0.342	-4.24			0.999
10.36		0.398	-4.17			0.999
1.48	0.49	0.042	-3.97	0.060	3.63	0.987
3.13	1.75	0.091	-3.54	0.143	3.67	0.981
5.45	3.22	0.152	-3.35	0.239	3.16	0.975
7.23	4.10	0.202	-3.30	0.313	2.79	0.970

The fitting parameters for the 1.61 eV absorbance trend lines of p-doping reactions shown in Figure 3 when there is a Gaussian-like distribution for each rate constant. The molar concentration of P3HT is shown in the form of the P3HT monomer unit.

Table 2

[s-P3HT] ($\times 10^{-5}$ M)	[nw-P3HT] ($\times 10^{-5}$ M)	A_1	$\ln k_1$ (sec $^{-1}$)	A_2	$\ln k_2$ (sec $^{-1}$)	R^2
5.30		0.220	-4.52			0.998
7.11		0.285	-4.39			0.996
8.98		0.383	-4.35			0.996
10.36		0.440	-4.23			0.997
1.48	0.49	0.051	-3.89	0.055	3.96	0.998
3.13	1.75	0.109	-3.32	0.129	4.28	0.998
5.45	3.22	0.183	-3.07	0.212	4.07	0.997
7.23	4.10	0.246	-3.01	0.276	3.88	0.996