Toward an Understanding of the Formation of Conducting Polymer Nanofibers

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ne-dimensional (1-D) nanostructures-structures that have a diameter between 1 and 100 nm and possess high aspect ratios-have received a great deal of attention in recent years due to their promise for improving upon applications that currently use their bulk counterparts.^{1,2} For this goal to be realized, simple synthetic procedures that can reliably produce 1-D nanostructures are required. For inorganic materials such as ZnO or GaN, exquisite control of 1-D nanoscale morphology has been demonstrated by a variety of methods.^{1,2} However, achieving this same level of control for organic polymers has been much more difficult. For this reason, it is highly desirable to develop a simple procedure to synthesize 1-D nanostructures of organic polymers that can be applied to a wide range of materials.

Many 1-D polymer nanostructures have been investigated³ and among them, 1-D conducting polymer nanostructures are particularly attractive target materials because of the potential advantages of combining inexpensive organic conductors with low dimensionality.⁴⁻⁶ The synthesis of 1-D conducting polymer nanostructures has generally followed one of several different routes. The first, using insoluble hard templates such as zeolites, produces 1-D nanostructures by confining the growth of the polymer chains within a nanoscale area.^{7,8} The use of soluble soft templates, such as surfactants or bulky dopant acids, is a second approach to synthesize 1-D nanostructures of conducting polymers.^{9–15} In this case, the external agents have been suggested to selfassemble into micelles that can orchestrate

ABSTRACT Introducing small amounts of additives into polymerization reactions to produce conducting polymers can have a profound impact on the resulting polymer morphology. When an oligomer such as aniline dimer is added to the polymerization of aniline, the nanofibers produced are longer and less entangled than those typically observed. The addition of aniline dimer can even induce nanofiber formation under synthetic conditions that generally do not favor a nanofibrillar morphology. This finding can be extended to both the synthesis of polythiophene and polypyrrole nanofibers. The traditional oxidative polymerization of thiophene or pyrrole only produces agglomerated particles. However, when minute amounts of thiophene or pyrrole oligomers are added to the reaction, the resulting polymers possess a nanofibrillar morphology. These results reveal important insights into a semirigid rod nucleation phenomenon that has hitherto been little explored. When polyaniline nucleates homogeneously, surface energy requirements necessitate the formation of ordered nuclei which leads to the directional polymerization of aniline. This ultimately leads to the one-dimensional nanofibrillar morphology observed in the final product. The synthetic procedures developed here are simple, scalable, and do not require any templates or other additives that are not inherent to the polymer.

KEYWORDS: conducting polymers · 1-D nanostructures · polyaniline · polypyrrole · polythiophene

the growth of 1-D nanostructures. Methods that exploit the pre-existing nanoscale morphology of an additive such as nanowire seeding^{16,17} or the use of biotemplates¹⁸ have also been reported recently.

1-D conducting polymer nanostructures can also be synthesized without any hard or soft templates. Thus far, this procedure has mainly been limited to polyaniline nanofibers. This templateless process exploits the fact that the nanofibrillar morphology appears intrinsic to polyaniline when the polymer is formed in an aqueous media.⁴ This includes interfacial polymerization in which the monomer and oxidant are separated in an immiscible organicaqueous biphasic system and as the reaction proceeds, hydrophilic polyaniline nanofibers move into the aqueous layer.^{19,20} Other "templateless" techniques that produce nanofibers include dilute

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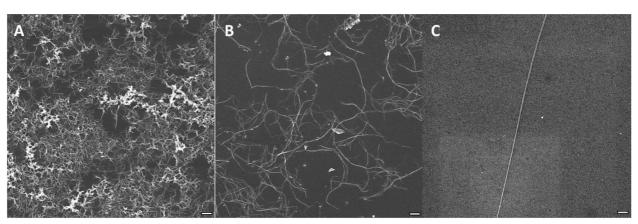


Figure 1. SEM images of (A) polyaniline nanofibers synthesized without the addition of any additives, (B) with *p*-phenylenediamine as an additive, and (C) an isolated polyaniline nanowire obtained from a diluted dispersion of polyaniline nanofibers synthesized with an initiator. Scale bar: 1 µm.

polymerization of aniline,^{21,22} rapid mixing of monomer and oxidant,²³ and sonochemical²⁴ and radiolytic assisted syntheses.²⁵ Although these syntheses are straightforward, their simplicity belies a complex formation mechanism.

A great deal of research has been devoted to elucidating how polyaniline nanofibers form.^{26–32} Much of our work has focused on relating the mode of nucleation to controlling the morphology of polyaniline.²⁶ For example, when aniline is polymerized under conditions that promote homogeneous nucleation, nanofibers of polyaniline are predominantly formed. However, an agglomerated morphology is observed when aniline is polymerized under heterogeneous nucleation conditions. Although much progress has been made at understanding the intrinsic nature of polyaniline nanofiber formation, many questions remain. For example, why is the nanofibrillar morphology intrinsic to polyaniline and not to other conducting polymers such as polythiophene or polypyrrole?

Here we present experiments designed to probe the formation of polyaniline nanofibers in order to develop a clearer mechanistic understanding. In particular, the role of aniline oligomers and other structurally similar additives are investigated in the polymerization of aniline. During the course of our studies, we have discovered that the addition of these additives into the polymerization of aniline can have a profound impact on the morphology of the observed product. For example, when minute amounts of aniline dimer are added into the reaction to synthesize polyaniline nanofibers, the resulting morphology contains 1-D nanostructures that are longer and less entangled than what is typically observed.

The insights learned from studying the mechanism of polyaniline nanofiber formation has facilitated the development of a simple procedure to synthesize nanofibers of other conducting polymers such as polythiophene and polypyrrole. This process only requires monomer, oligomer, oxidant, and solvent. As a result, polypyrrole and polythiophene nanofibers can now be synthesized without the aid of any external templates or other additives that are not inherent to the polymer. The remarkable similarities of the nanofiber syntheses for these different conducting polymers point to an underlying mechanism of formation. In fact, we believe this to be a general procedure potentially applicable to any semirigid rod polymer.

RESULTS AND DISCUSSION

Aniline oligomers appear crucial to the formation of polyaniline³³ and substituted polyaniline nanofibers;³⁴ however, little work has been done to clarify their role. For example, the addition of a catalytic amount of aniline dimer in the electrochemical polymerization of aniline not only increases the polymerization rate, but also produces thin films of polyaniline possessing a nanofibrillar morphology.³³ We first sought to understand the role of oligomers in the chemical formation of polyaniline nanofibers by introducing a catalytic amount of aniline dimer and other structurally related additives into a rapidly mixed reaction of aniline. The 1-D polyaniline nanostructures produced are less entangled and appear longer than nanofibers formed without the addition of aniline dimer (Figure 1A). This change in morphology is also seen when *p*-phenylenediamine is used as the additive. When synthesized in a 1 M HCl solution, the 1-D nanostructures have an average diameter of \sim 50 nm and range in length from $2-30 \ \mu m$ (Figure 1B,C).

Open-circuit potential (OCP) measurements indicate a substantial increase in the polymerization rate when a small amount of aniline dimer is added to the polymerization of aniline (Figure 2). In the presence of aniline dimer, the $t_1 + t_2$ time is significantly reduced, indicating a much faster polymerization.³⁵ The increased polymerization rate leads to a change in morphology from an entangled mat of 1-D nanofibers without dimer added, to longer and less entangled 1-D nanowires with dimer. Previously we have suggested

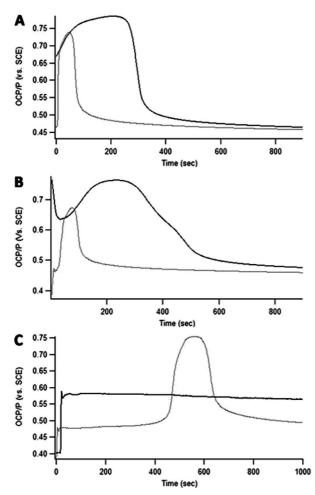


Figure 2. Open circuit potential (OCP) monitored *versus* a standard calomel electrode (SCE) as a function of time of polyaniline synthesized at 25 °C in (A) an aqueous 1 M solution of acid (HCl), (B) a 5 M solution of LiCl and (C) an isopropyl alcohol solution. The dotted line represents reactions performed with an initiator present, while the solid line represents reactions without an initiator.

that the morphology of polyaniline can be related to its mode of nucleation during polymerization.²⁶ This concept is intimately related to the rate of polymerization. When aniline is polymerized under conditions that favor homogeneous nucleation, the bulk morphology is nanofibrillar in nature. This is achieved if the polymerization rate is sufficiently fast and there is little mechanical agitation during polymerization.²⁶ However, when aniline is polymerized under conditions that favor heterogeneous nucleation, the bulk morphology is granular in nature. For a rapidly mixed polymerization to produce polyaniline nanofibers without the use of promoters, polymer chains can nucleate from the surface of other preexisting precipitated polymers (secondary growth) which we believe leads to the entangled nanofibrous mat of polyaniline that is typically observed (Figure 1A). However, with the addition of promoters such as aniline dimer, secondary growth is further suppressed. This is because the additives have a lower oxidation potential³⁸ than aniline and as a result they will serve as growth centers for polymerization in solution. By intentionally adding small quantities of dimer, the polymerization is initiated simultaneously throughout the solution, that is, homogeneous nucleation. This limits the possibility of secondary growth from preexisting polyaniline particles. Furthermore, if polymer growth continues at a faster rate than polymer nucleation, longer and less entangled 1-D nanostructures of polyaniline are expected. Indeed, this is what is observed (Figure 1B,C). Many of the same effects are seen when *p*-phenylenediamine is used as the additive instead of aniline dimer. Like aniline dimer,

p-phenylenediamine has a lower redox potential than aniline and has been shown to accelerate the electropolymerization rate of polyaniline.³⁹ In our study, when *p*-phenylenediamine is used as an additive for the chemical polymerization of aniline, an accelerated polymerization rate results in improvements to the nanofibers formed. The ratio of monomer to additive—approximately 40:1—is important for obtaining the observed morphology as too high a ratio results in nanofibers that are indistinguishable from those formed without any additive, while too low a ratio results in a smooth filmlike morphology.

Although the nanofibrillar morphology of polyaniline appears to be intrinsic under certain conditions, the addition of a catalytic amount of promoter into the polymerization of aniline can induce nanofiber formation under conditions that typically do not favor this morphology. For example, when the polymerization of aniline is carried out in an aqueous solution of acid and the oxidant is rapidly mixed with the monomer solution, the nanofibrillar morphology appears intrinsic to polyaniline.⁴ However, when the identical synthesis is carried out in a 5 M solution of salt such as NaCl or

LiCl, only agglomerated structures are observed. This has been attributed to adverse salt/counterion interactions, which prevent the organization of aniline oligomers into structures that may dictate nanofibrillar growth.²⁷ However, when a small amount of aniline dimer is added to this synthesis, the bulk morphology changes from granular particulates to a mat of 1-D nanofibers (Figure 3). The polyaniline nanofibers produced under these conditions appear identical to nanofibers produced by the rapidly mixed procedure.²³

A similar observation is seen when the polymerization of aniline is carried out in nonaqueous solvents such as isopropyl alcohol or acetonitrile. Under these conditions, only granular particulates are observed. This result has been attributed to the hydrophilic nature of polyaniline. In aqueous solvents, polyaniline favors an extended-like network, and, since organic solvents have a lower polarity than water, the polymer chains will form a more compact, granular morphology.²³ However, when a catalytic amount of a promoter such as aniline dimer is

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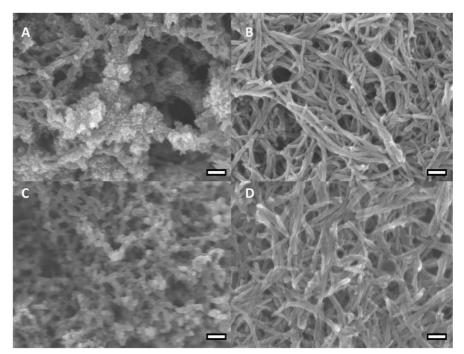
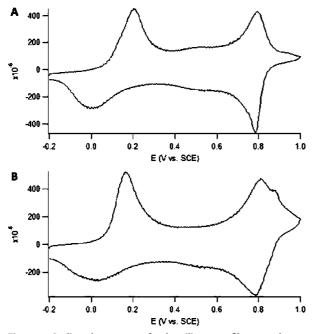
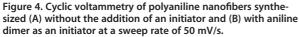


Figure 3. SEM images of (A) polyaniline synthesized in a 5 M LiCl solution, (B) polyaniline synthesized in a 5 M LiCl solution with the addition of aniline dimer, (C) polyaniline synthesized in an isopropyl alcohol solution, and (D) polyaniline synthesized in an isopropyl alcohol solution with the addition of aniline dimer. Scale bar: 200 nm.

added into the synthesis of polyaniline in organic solvents, a change in bulk morphology from granular particulates to a mat consisting of 1-D nanofibers is again observed (Figure 3). These polyaniline nanofibers appear indistinguishable from nanofibers formed by other methods. Note that only a very small amount of aniline dimer is required to change the *entire* morphology of reactions performed in organic solvents or in a 5 M salt solution





from agglomerated particulates to the nanofibers seen in Figure 3.

These results highlight the importance of oligomers in the formation of polyaniline nanofibers, since the nanofibrillar morphology can now be induced under conditions that are typically not conducive to nanofiber formation. An important factor appears to be the greatly accelerated polymerization rate. According to classical nucleation theory (CNT), homogeneous nucleation is achieved in aqueous solutions by creating sufficiently high levels of supersaturation.⁴⁰ As the level of supersaturation increases, both the activation energy and the critical nucleus size decreases. Eventually, as the degree of supersaturation continues to increase, the activation energy becomes so low that spontaneous and rapid nucleation can occur.41,42 Once the nucleus of the stable phase

reaches a critical size, growth can occur if the surroundings of the nuclei are favorable (sufficiently supersaturated). For the synthesis of polyaniline with the addition of aniline dimers and or other comparable additives, the polymerization rate is greatly accelerated, and supersaturation is guickly achieved. As a result, homogeneous nucleation (which leads to nanofibrillar morphology) dominates and diffusion of nuclei to heterogeneous nucleation sites is limited. This is evident in examining the container side walls. For the synthesis of polyaniline without the addition of a promoter, a thin coating of polyaniline covers the container side walls and any other surface that the reaction is exposed to. However, for the synthesis of polyaniline nanofibers with the addition of a promoter, no polyaniline deposition is observed on the container walls.

This concept may explain why nanofiber formation is intrinsic under certain conditions, but not for others. During polymerization of aniline in organic solvents, we have noticed a significantly depressed polymerization rate. This retardation is clearly visible to the naked eye as reactions in organic solvents typically take several extra minutes to produce the characteristic colors associated with polyaniline formation. A similar effect is observed for reactions performed in 5 M salt solutions *versus* those with no added salt. When monitored by OCP, the $t_1 + t_2$ times of reactions in either organic solvents or in 5 M salt solutions take significantly longer than the same reactions performed with the addition of aniline dimer (Figure 2B). For reactions in organic solvents, the polymerization rate is so slow that formation of the pernigraniline oxidation state is not even observed during the time frame of the experiment shown in Figure 2C. Since the reaction rate is significantly slower in these systems, supersaturation is not achieved. As a result, heterogeneous nucleation, which leads to an agglomerated morphology, dominates.

Cyclic voltammetry (CV) of the polyaniline nanofibers synthesized with the addition of an initiator reveals that the polymer exhibits similar redox properties to that of polyaniline nanofibers synthesized by other methods (Figure 4).43 UV-vis of these dedoped polyaniline nanofibers reveal two peaks centered at \sim 320 and \sim 619 nm, which are characteristic of polyaniline in its dedoped emeraldine oxidation state.⁴⁴ GPC, using NMP/LiBF₄ as an eluent, reveals that the molecular weight distribution and polydispersity index (PDI) of the polyaniline synthesized is lower than what is typically observed under these conditions without the addition of aniline dimer (Supporting Information, Table 1).⁴⁵ These results show that polyaniline synthesized with a small amount of initiator present has little effect on the redox properties or oxidation state of the polymer; however, its effect on the molecular weight and the morphology of polyaniline is quite dramatic. Interestingly, the addition of aniline oligomers also appears to play a central role in the formation of chiral polyaniline nanofibers.46

A fibrillar crystallization mechanism has been proposed to explain the fibrillar morphology observed for other polymers,⁴⁷ such as polyoxymethylene, and the formation of polyaniline nanofibers via homogeneous nucleation may involve a comparable mechanism. Macromolecular nucleation during polymerization can follow any number of nucleation pathways.⁴⁷ One of these pathways (Figure 5) is intermolecular oligomer nucleation in which oligomers form semiordered regions that dictate polymer growth. The major complication of oligomer nucleation lies in the initial formation of a sufficient oligomer concentration to cause nucleation.

This problem is overcome in our study by the addition of initiators that rapidly create high oligomer concentrations. The formation of semiordered oligomer nuclei is favored under homogeneous nucleation conditions because of the surface energy minimization afforded by the organization of oligomers to a critical size.48 However, under heterogeneous nucleation, the surface energy minimization provided by the foreign surface from which the polymer nucleates negates the need for oligo-

mer organization. Therefore, because of the anisotropic nature and growth of the polymer, it is not surprising that we observe 1-D nanostructures of polyaniline under homogeneous nucleation conditions.

Figure 5. Schematic representation of an in-

termolecular oligomer nucleus showing or-

dered regions of oligomers surrounded by a

must be reached first in order for nucleation

supersaturated solution of reactant mol-

ecules. A critical oligomer concentration

to occur and growth to commence.

We believe this concept explains why the nanofibrillar morphology is intrinsic to polyaniline and not other conducting polymers such as polypyrrole or polythiophene. The simplest synthesis of polyaniline nanofibers involves the oxidative polymerization of aniline in an aqueous solution of acid with ammonium peroxydisulfate.²³ Under these conditions, the polymerization rate is sufficiently rapid so that supersaturation and homogeneous nucleation is achieved. However, for the traditional oxidative polymerization of thiophene or pyrrole, the polymerization rate is significantly slower than for aniline. For this reason, supersaturation is not achieved and heterogeneous nucleation dominates. As

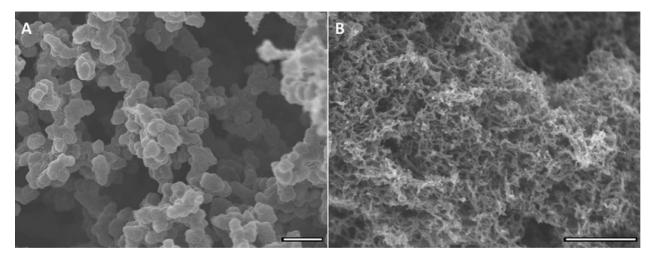


Figure 6. SEM images of polypyrrole synthesized (A) without the addition of bipyrrole and (B) with the addition of bipyrrole. Scale bar: 1 μ m.

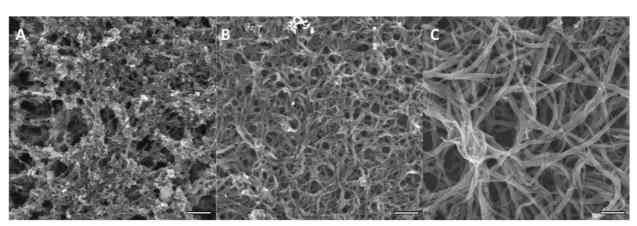


Figure 7. SEM images of polythiophene synthesized (A) without the addition of oligomers, (B) with the addition of terthiophene as an initiator, and (C) with sexithiophene as an initiator. Scale bar: 1 μ m.

a result, only agglomerated structures are observed and the nanofibrillar morphology does not appear "intrinsic" to polypyrrole or polythiophene.

With this in mind, we sought to use our hypothesis as a basis to develop reaction conditions in which the formation of polythiophene and polypyrrole nanofibers would be "intrinsic," that is, syntheses of polypyrrole and polythiophene nanofibers with no external additives besides oxidant. Recently, we reported that when a solution of pyrrole in methanol is reacted with a solution of oxidant in water, a thin black film of polypyrrole that coats the container side walls is observed after several hours.⁴⁹ The morphology of this film consists of micrometer-sized spherical particles (Figure 6A) that are not readily dispersible in any solvent. However, upon addition of bipyrrole to the starting material, the polymerization produces polymer precipitates in several seconds with no polypyrrole films coating the container walls.⁴⁹ This resulting polymer is highly dispersible in water and possesses a morphology consisting of 1-D nanofibers with an average diameter of 20 nm (Figure 6B). The formation of polypyrrole nanofibers under these conditions appears consistent with the model of nanofiber formation that we have proposed for polyaniline. Because formation of bipyrrole is the rate determining step in the synthesis of polypyrrole, intentionally introducing small amounts of it into the polymerization of pyrrole will accelerate the polymerization rate. This in turn provides the proper growth conditions for formation of polypyrrole nanofibers as can be seen in Figure 6B.

A similar phenomenon is observed for the synthesis of polythiophene. When a solution of thiophene and $FeCl_3$ are rapidly mixed, the formation of polymer precipitates typically takes several hours. This results in the expected granular morphology as shown in Figure 7A. However, when a catalytic amount of terthiophene is predissolved with the solution of thiophene monomer and the oxidant solution is added, we observe polymer precipitates in several seconds rather than hours. SEM images of the resulting purified product reveal that the morphology has changed from granular particulates to a mat of 1-D nanofibers with an average diameter of 50 nm and lengths that can extend up to several micrometers. Only a very small amount of

terthiophene—typically 2–3 mol%—is required to change the entire morphology of the product from agglomerates to a mat of nanofibers as seen in the representative SEM in Figure 7B.

The addition of different oligomers to the polymerization of thiophene also has an effect on its morphology. For example, when sexithiophene is added to the polymerization of thiophene, the resulting nanofibers possess an average diameter of 90 nm and are less entangled and longer than nanofibers produced with terthiophene as the additive (Figure 7C). The change in morphology appears comparable to the changes observed for the polymerization of aniline with and without the addition of oligomers. This appears consistent with the model of nanofiber formation we have proposed because as the length of the oligomer introduced increases, a larger more ordered nuclei may form. As a result, larger diameter nanofibers are observed. The overall processes that govern the diameter of conducting polymer nanofibers are still poorly understood; however, studies are currently underway to further elucidate this effect in polythiophene and other conducting polymers.

CONCLUSIONS

In this study, we have shown that adding small amounts of an additive such as *p*-aniline dimer or *p*-phenylenediamine to the polymerization of aniline can have a profound impact on the morphology of the resulting polymer. These additives can not only produce nanofibers that are longer and less entangled than those typically observed, but can also induce nanofiber formation under conditions that typically do not favor such a morphology. Experimental parameters such as ionic strength and solvent polarity appear to be only secondary factors affecting the morphology of polyaniline. The additives accelerate the polymerization rate

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of aniline which necessitates the formation of ordered nuclei which directs nanofibrillar growth. The proposed mechanism appears consistent with many of the different synthetic approaches used to synthesize polyaniline nanofibers without structural directing agents. We should caution that while the polymerization rate is an important factor in obtaining the nanofibrillar morphology, it is certainly not the only one as parameters such as reagent concentration⁵² and oxidation potential⁵³ are also important.

This idea also appears to explain why the nanofiber morphology is intrinsic to polyaniline and not other conducting polymers. By understanding this fundamental question, we have now successfully designed syntheses that can produce both polypyrrole and polythiophene nanofibers. The only "magic" ingredient required for nanofibrillar growth is the addition of oligomers to the oxidative polymerization of the corresponding monomer. Nanofibers of other conducting polymers besides polyaniline can now be synthesized without the aid of external structural directing agents that are not inherent to the polymer. Because the additives are naturally incorporated into the polymer backbone, no special purification steps are required to obtain pure conducting polymer nanofibers. We believe this to be a general concept that may be applicable to a wide variety of semirigid rod, precipitation polymerizations.

METHODS

Synthesis and Characterization. All monomers used were distilled prior to use. All other reagents were used as received. In a typical initiator assisted polymerization of aniline, an initiator such as *p*-phenylenediamine (2 mg, 0.02 mmol) is predissolved in a minimal amount of methanol and mixed with a solution of aniline (75 mg, 0.8 mmol) in 10 mL of 1 M HCI. A fresh solution of ammonium peroxydisulfate (45 mg, 0.2 mmol) in 10 mL of 1 M HCI is rapidly mixed with the solution containing the monomer and additive. The reaction is vigorously shaken for ~10 s and then left unagitated for 1 day. The crude product is purified by dialysis against deionized water until a neutral solution is obtained.

For the synthesis of polythiophene nanofibers, a solution of thiophene (42 mg, 0.5 mmol) and terthiophene (2 mg, 0.01 mmol) dissolved in 3 mL of o-dichlorobenzene is rapidly mixed with a solution of FeCl₃ (100 mg, 0.62 mmol) in 3 mL of acetoni-trile. The reaction is vigorously mixed for 10 s and left undisturbed for 1 day after which time the crude product is centrifuged and washed with copious amounts of acetonitrile.

Polypyrrole nanofibers are synthesized using a similar procedure to that described.⁴⁹ In brief, pyrrole (50 mg, 0.75 mmol) and bipyrrole (2 mg, 0.015 mmol) are dissolved in 10 mL of methanol and this solution is then rapidly mixed with a fresh solution of FeCl₃ (120 mg, 0.75 mmol) in 10 mL of water. The reaction is shaken for 10 s and left to stand for 1 day after which time the crude product is purified by centrifugation and washed with copious amounts of water.

Microscopy. Samples for scanning electron microscopy (SEM) are prepared by drop-casting a \sim 1 g/L dispersion of the conducting polymer onto a silicon wafer. SEM images are taken with a JEOL JSM-6700-F field emission SEM microscope. Samples for electron microscopy (TEM) are prepared on copper grids and images taken with a JEOL 100CX TEM.

UV—**Visible**. The absorption spectrums of the dedoped conducting polymers are taken after dissolving the polymer in *N*-methylpyrrolidone (NMP) on an HP 8452 spectrometer.

Gel Permeation Chromatography (GPC). Molecular weight distributions of the nanofibers are obtained by GPC using a Waters 2690 HPLC pump with a photodiode array (PDA) detector. The size exclusion chromatography (SEC) columns are Styragel HR 4E and 5E. The temperature of the column is held at 60 °C. HPLC grade NMP containing 0.01 M LiBF₄ is used as the eluent.⁵⁰ A flow rate of 0.35 cm³ min⁻¹ is used for the eluent with an injection volume of 50 µL. Polystyrene (PS) standards with 10 narrowly distributed M_w values were used to calibrate the columns. Samples were prepared by dissolving 0.02 mass % of dedoped substituted polyaniline nanofibers in a LiBF₄/NMP solution, filtered with a syringe filter, and then allowed to equilibrate overnight under ambient conditions.

Electrochemistry. To monitor the polymerization of aniline, open-circuit potentials of the reaction solutions were measured as a function of time on a single-component two-electrode cell: Pt|reaction solution||reference electrode.⁵¹ A saturated calomel

electrode (SCE) was used as the reference electrode. Cyclic voltammetry (CV) was performed in a standard three electrode cell using SCE as the reference electrode. The platinum electrode was coated with the conducting polymer during the polymerization, and this coated electrode was immersed in 1.0 M HCl. CVs are measured from -0.20 to 0.90 V at a sweep rate of 50 mV/s using a Princeton Applied Research 263A potentiostat.

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Supporting Information Available: Histogram showing the diameter distribution of conducting polymer nanofibers. This material is available free of charge via the Internet at http://pubs.acs.org.

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