Substituted Polyaniline Nanofibers Produced via Rapid Initiated Polymerization

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ABSTRACT: A bulk, template-free method to synthesize nanofibers of substituted polyanilines is presented. The morphology of the substituted polyanilines changes from agglomerates or micron-sized spheres to a nanofiber network when an initiator, such as *p*-phenylenediamine, is introduced into the conventional reagents used to synthesize these polymers. UV−vis spectroscopy and cyclic voltammetry reveal that the oxidation state and chemical composition of the substituted polyaniline nanofibers do not differ significantly from that of conventional polyaniline derivatives possessing an agglomerated morphology. Gel permeation chromatography indicates that the nanofibers formed possess an unusually low polydispersity compared to substituted polyanilines synthesized by other methods. Open-circuit potential measurements obtained during the synthesis of these polyaniline derivatives confirm that there is a significant increase in the reaction rate of the polymerization which is directly related to nanofiber formation. This synthetic method appears quite general as a wide variety of substituted aniline monomers have been polymerized into nanofibrillar polymers.

Introduction

In recent years, one-dimensional (1-D) nanostructures have attracted a great deal of attention due to the unique properties associated with these materials.[1] Many nanostructures of conducting polymers have been examined in the quest for combining the advantages of an inexpensive, processable organic conductor with low dimensionality. In particular, polyaniline nanofibers, due to their ease of synthesis and unique chemistry, have been intensively investigated. Many methods currently exist to synthesize polyaniline nanofibers including the use of soft templates such as surfactants or bulky dopant acids,[2] hard templates such as the growth of nanofibers inside zeolites,[3] biotemplated nanofiber formation,[4] nanowire seeding,[5] interfacial polymerization,[6] and a number of template-free methods that form nanofibers spontaneously in all-aqueous solutions.[7] These synthetic methods have facilitated a number of potential applications for polyaniline nanofibers including their use in chemical sensors,[8] molecular memory devices,[9] and capacitors.[10]

In contrast, 1-D nanostructures of substituted polyanilines have been far less studied. Although an extensive literature on conventional substituted polyanilines exists, studies on 1-dimensional *nanofibers* of these polymers have been rare.[11] This is likely due to the fact that many methods to synthesize polyaniline nanofibers only produce agglomerates or nanofibers of poor quality when applied to substituted polyanilines. Yet there remains a desire to develop a simple and general method to synthesize nanofibers of substituted polyanilines since these materials have the potential to improve upon several of the properties associated with nanofibers of the parent polymer. For example, substituted polyanilines are known to have a higher dispersibility in various solvents than that of the parent polymer,[11,12] and certain substituted polyanilines possess a higher resistance to microbial degradation.[13] Furthermore, the ability to selectively tailor chemical sensors makes these materials an attractive target as the active layer in these devices.

Recently, we have discovered that accelerating the rate of polymerization is a key parameter in producing nanofibers of a number of substituted polyanilines.[11a] This is achieved by introducing an aromatic additive such as *N*-phenyl-1,4-phenylenediamine (henceforth referred to as aniline dimer) or *p*-phenylenediamine into the reaction between monomer and oxidant. The introduction of these additives, which serve as initiators for the polymerization, changes the bulk morphology of the product from a granular, agglomerated structure to a network of interconnected 1-D nanofibers. In this report, we explore using initiators to create substituted polyaniline nanofibers from a wide range of substituted aniline monomers and provide new insights into the formation mechanism. This synthetic procedure is easily scalable and quite general and should facilitate the integration of these materials for applications such as chemical sensors.

Experimental Section

Synthesis and Purification. All chemicals were of analytical grade and used as received. In a typical procedure to prepare substituted polyaniline nanofibers, 3.2 mmol of a substituted aniline monomer (such as ethylaniline or anisidine) is dissolved in 10 mL of 1 M HCl in a 20 mL scintillation vial. Added to this solution is a solution of 5−10 mg of *p*-phenylenediamine (aniline diamine) or aniline dimer dissolved in a minimal amount of methanol. In a separate container, ammonium peroxydisulfate (0.18 g, 0.8 mmol) is dissolved in 10 mL of 1 M HCl. The two newly prepared solutions are then rapidly mixed and vigorously shaken for ∼15 s, after which time the product is left undisturbed for 1 day. The crude product is purified by dialysis against deionized water, using tubing with a 12 000−14 000 MW cutoff (Fisher Scientific). Dedoped polymers are obtained by dialysis using 0.1 M NH_4OH and then deionized water. Monomers that have been polymerized into polymer nanofibers include 2-ethylaniline, 3-ethylaniline, *o*-toluidine, *m*-toluidine, *o*-anisidine, 2-fluoroaniline, 3-fluoroaniline, 2-chloroaniline, 3-chloroaniline, *N*-methylaniline, *N*-ethylaniline, 2-propylaniline, 2-methylthioaniline, and 2,3-dimethylaniline (Supporting Information, Figure S1).

Microscopy. Samples for scanning electron microscopy (SEM) are prepared by drop-casting an aqueous dispersion (∼1 g/L) of the doped substituted polyaniline nanofibers onto a silicon wafer.

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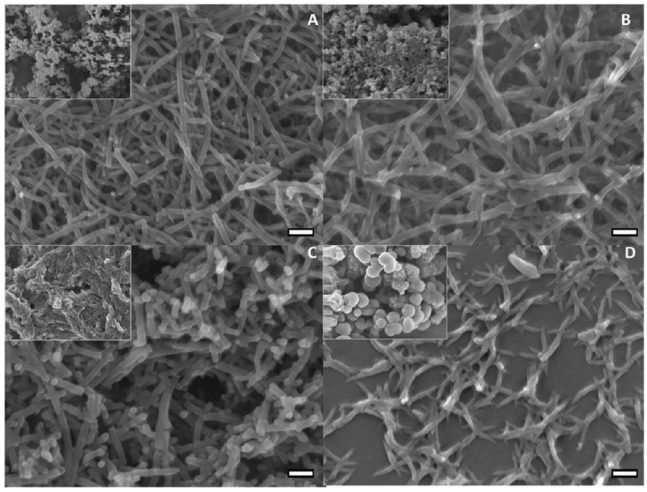

Figure 1. SEM images of (A) polychloroaniline, (B) polyethylaniline, (C) poly-*N*-ethylaniline, and (D) polyanisidine nanofibers synthesized through the addition of initiators that accelerate the rate of polymerization. The insets are SEM images showing the analogous control reactions performed in the absence of the initiator. Scale bars: 100 nm.

SEM images are taken with a JEOL JSM-6700-F field emission SEM microscope. Samples for transmission electron microscopy (TEM) are prepared on copper grids, and images are taken with a JEOL 100CX TEM.

UV−vis Spectroscopy. The absorption spectra of the substituted polyaniline nanofibers are obtained on an HP 8452 spectrometer by dissolving the dedoped polymers in *N*-methylpyrrolidone (NMP).

Molecular Weight. Molecular weight distributions of the nanofibers are obtained by gel permeation chromatography (GPC) using a Waters 2690 HPLC pump with a Waters 996 photodiode array (PDA) detector. The gel permeation chromatography column used was a Waters Styragel HR 5E, and the temperature of the column is held at 60 °C. HPLC grade NMP containing 0.01 M $LiBF_4$ is used as the eluent. A flow rate of 0.35 cm^3 min^{-1} is used for the eluent with an injection volume of 50 μL. Polystyrene (PS) standards with 10 narrowly distributed M_w values (Polymer Laboratories Easical PS-1 and PS-2) are used to calibrate the columns. Samples are prepared by dissolving 0.02 mass % of dedoped substituted polyaniline nanofibers in a $LiBF_4$/NMP solution, filtered with a 0.45 μm Teflon syringe filter, and then allowed to equilibrate overnight under ambient conditions.

Electrochemistry. To monitor the polymerization of the aniline derivatives, open-circuit potentials of the reaction solutions are measured as a function of time on a single-component two-electrode cell: Pt|reaction solution||reference electrode. A saturated calomel electrode (SCE) is used as the reference electrode. Cyclic voltammetry (CV) is performed in a standard three-electrode cell using SCE as the reference electrode. The platinum electrode is coated with the conducting polymer during the polymerization, and this coated electrode is 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.

Results and Discussion

Synthesis and Characterization. A wide variety of substituted polyaniline nanofibers have been synthesized to date from the corresponding substituted aniline monomers using our synthetic procedure. These polyaniline derivatives are comprised of an interconnected network of 1-D nanofibers similar in morphology to nanofibers of the parent polymer and other conducting polymers that have been reported previously.[14] There appears to be little limitation in synthesizing polymer nanofibers of the most commonly used substituted aniline monomers. However, we have found that, in general, the more sterically

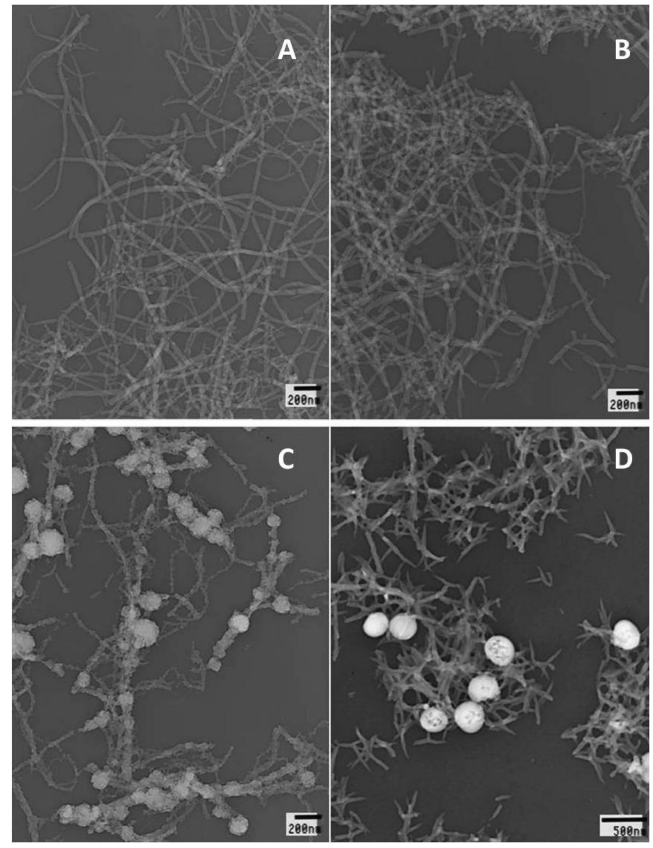

Figure 2. TEM images of (A) polychloroaniline, (B) polyethylaniline, (C) poly-*N*-ethylaniline, and (D) polyanisidine nanofibers.

hindered the monomer, the less likely it is to produce a nanofibrillar morphology. In this study, we focus on four different polyaniline derivatives that are representative of the range of derivatives that have been synthesized to date. These four examples consist of polymers containing either a strongly electron-donating substituent (polyanisidine) or an electron-accepting substituent (poly-2-chloroaniline) and aniline derivatives alkylated on either the aromatic ring (polyethylaniline) or on the nitrogen (poly-*N*-ethylaniline). A listing of the substituted polyaniline nanofibers synthesized to date is provided in the Experimental Section.

In a typical synthesis, an initiator such as *p*-phenylenediamine or aniline dimer is added into the conventional reagents used to synthesize substituted polyanilines. The presence of the initiator, which accelerates the rate of polymerization, is crucial to the formation of substituted polyaniline nanofibers. Only a minimal amount—typically ∼1−2 mol % with respect to the monomer concentration—of the additive is needed in order to catalyze the reaction and facilitate the morphological change. The selection of the appropriate initiator is also an important factor as differences in the morphology are occasionally observed when different initiators are used. This synthesis of substituted polyaniline nanofibers also appears to be much more sensitive to concentration effects than the synthesis of nanofibers of the parent polymer. Upon addition of the oxidant, ammonium peroxydisulfate, to the solution containing monomer and initiator, an immediate color change is observed from a clear solution to an intensely colored blue/violet solution, which is characteristic of the formation of the conducting polymer polyaniline in its pernigraniline oxidation state. The polymer typically precipitates out of solution after several minutes and is left to stand unagitated for 1 day, after which time the crude product can be easily purified by dialysis, filtration, or centrifugation. In contrast, reactions performed in the absence of an initiator

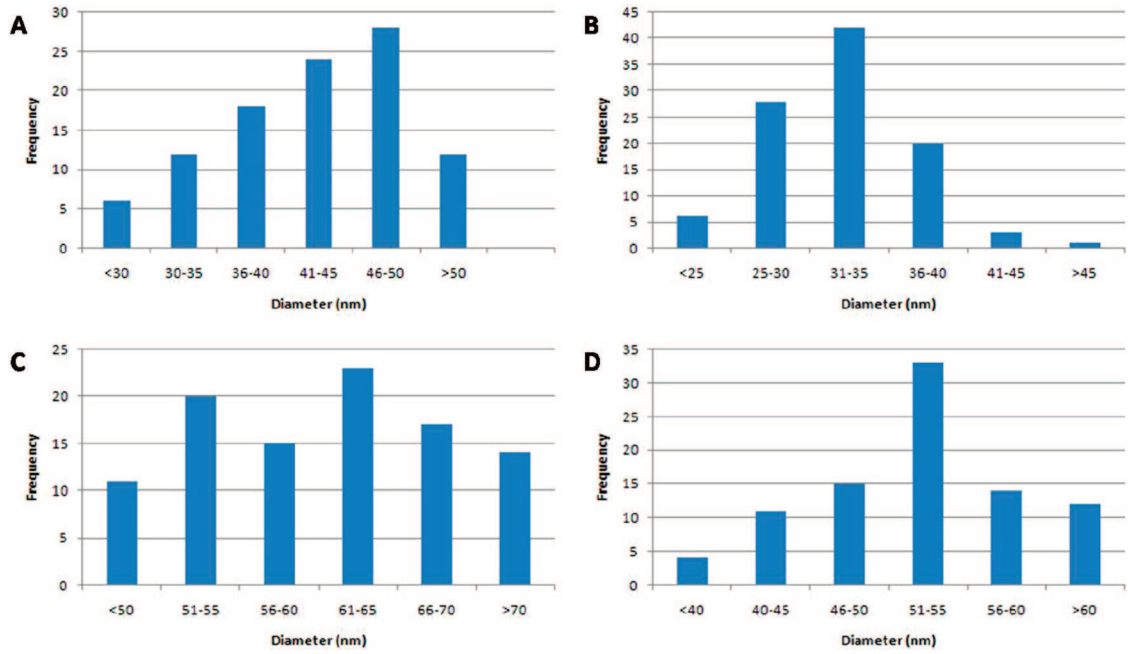

Figure 3. Histogram showing the diameter distributions of nanofibers of (A) polychloroaniline, (B) polyethylaniline, (C) poly-*N*-ethylaniline, and (D) polyanisidine.

Table 1. Weight-Average Molecular Weight (M_w), Number-Average Molecular Weight (M_n), and Polydispersity Index (PDI = M_w/M_n) of Select Substituted Polyaniline Nanofibers

polymer	M_w	M_n	PDI
polyethylaniline	7800	4200	1.7
poly-*N*-ethylaniline	5300	2900	1.8
polyanisidine	14400	6300	2.3
polychloroaniline	7100	2800	2.5

often take hours before a noticeable color change is observed and as much as 1 day before solid polymer precipitates are seen.

SEM images of the purified product reveal a distinct difference between reactions performed with an initiator present and the analogous control reactions performed in the absence of an initiator (Figure 1). For reactions performed without the initiator present, large, agglomerated particulates are typically observed reminiscent of "conventional" polyaniline. These particulates have been observed frequently in previous studies of polyaniline derivatives.[15] However, for reactions performed in the presence of an initiator, the purified product consists of a continuous network of interconnected 1-D nanofibers. TEM images (Figure 2) reveal that the nanofibers have an average diameter ranging from 30 to 60 nm with characteristic lengths on the order of several microns (Figure 3) depending on which monomer is being polymerized. Nanofibers are the dominant morphology observed under these synthetic conditions, although nanospheres are occasionally seen by SEM. These spheres can be eliminated by changing the acidic solution from HCl to $HClO_4$.

The UV−vis spectra of the purified dedoped polymer nanofibers reveal that the degree of oxidation is dependent on the monomer being polymerized. This is consistent with previous studies on substituted polyanilines which indicate that the stability of certain substituents on the polyaniline backbone decreases the window of stability of the emeraldine oxidation state.[16,17] For polyaniline, the excitonic transition of the dedoped emeraldine oxidation state occurs at ∼630 nm. This oxidation state corresponds to an equal number of oxidized and reduced aniline units along the polymer chain. Polyaniline that is more oxidized than the idealized emeraldine oxidation state often displays a shift in the excitonic transition to a lower wavelength.[18] The UV−vis spectra of polyanisidine and polyethylaniline nanofibers display a λ_{max} at the excitonic transition of ∼619 nm, which indicates that the polymers are slightly more oxidized than the idealized emeraldine oxidation state. However, for poly-*N*-ethylaniline or polychloroaniline, there is an even more significant excitonic shift to lower values. The excitonic transition occurs at approximately 608 and 579 nm for poly-*N*-ethylaniline and polychloroaniline, respectively, indicating that the conjugated polymers are more oxidized than the half-oxidized emeraldine oxidation state and, in the case of polychloroaniline, may be more accurately described as being closer to the pernigraniline oxidation state. This phenomenon is also observed in conventionally synthesized poly-*N*-ethylaniline and polychloroaniline and is attributed to torsional strain due to the bulkiness of the substituents and for polychloroaniline because of its lowered basicity.[16,17,19]

The molecular weight distributions of the substituted polyaniline nanofibers are determined by gel permeation chromatography (GPC) using NMP/$LiBF_4$ as the eluent. Traditional GPC analysis of polyaniline has focused on using NMP as an eluent which typically results in a bimodal distribution of molecular weights due to the fact that there is a high degree of aggregation of polyaniline in NMP.[20] Since molecular weight measurements are calibrated to a polystyrene standard with a nearly Gaussian distribution, highly accurate determination of molecular weight distribution of a sample with a bimodal distribution is difficult. The addition of lithium salts such as $LiBF_4$ into NMP reduces aggregation and provides a more Gaussian chromatographic peak which enables more accurate molecular weight determination.[20] In general, we observe that the molecular weight distribution of substituted polyaniline nanofibers are much lower than that of conventionally synthesized polyaniline.[21] Similar results are observed for the parent polymer (data not shown). This is not surprising since substituents on aniline are known to reduce the degree of polymerization, thereby reducing the molecular weight of the corresponding polymer. However, as compared to conventionally synthesized polyanilines, the substituted polyaniline nanofibers have a significantly lower polydispersity index (Table 1), which is typically ∼5−7 for conventionally synthesized material. The presence of the initiator

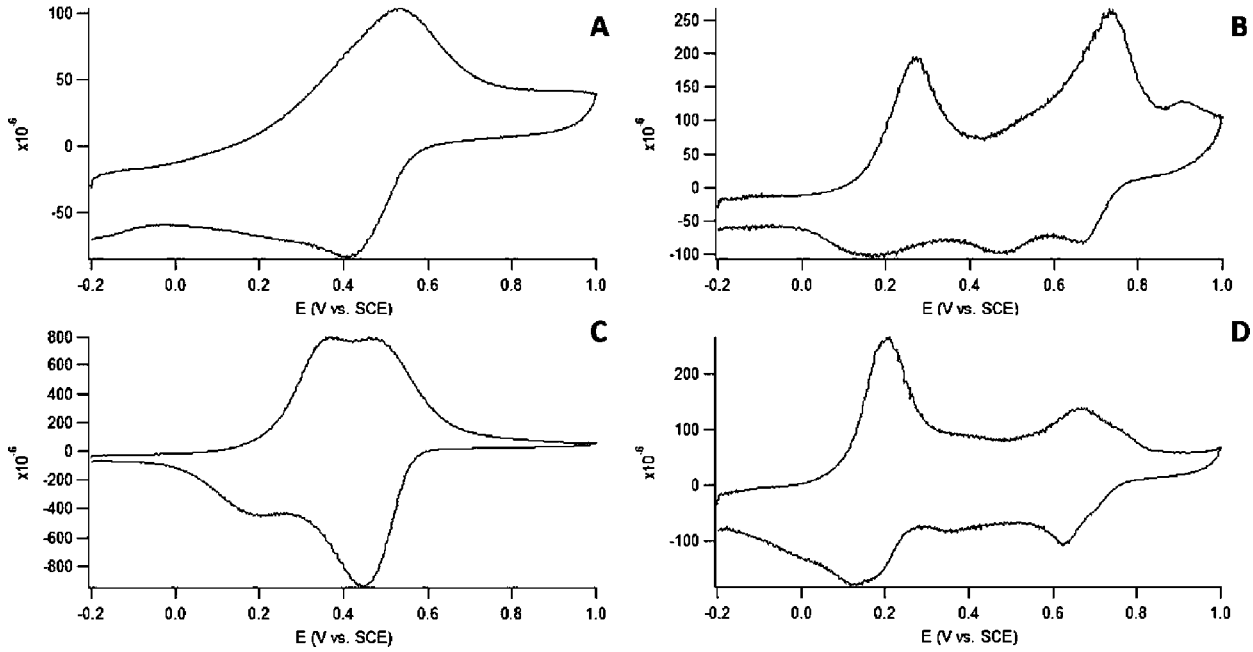

Figure 4. Cyclic voltammograms of (A) polychloroaniline, (B) polyethylaniline, (C) poly-*N*-ethylaniline, and (D) polyanisidine nanofibers at a sweep rate of 50 mV/s.

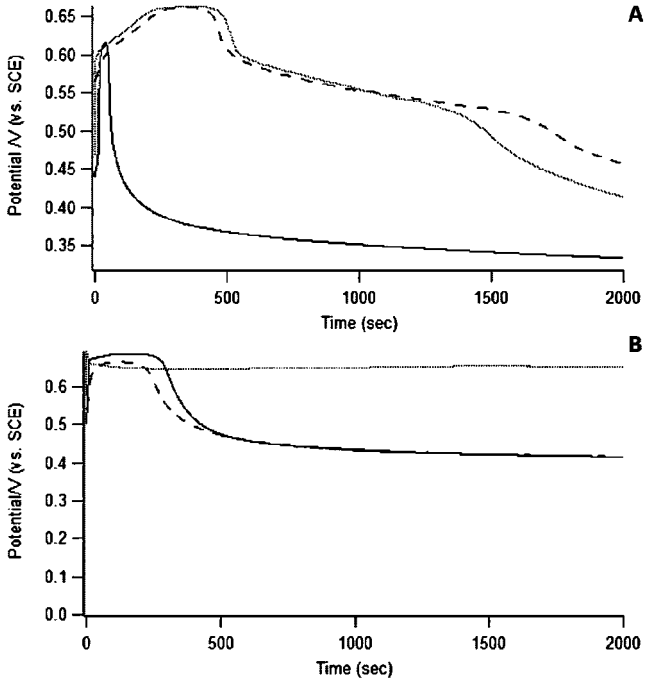

Figure 5. Open circuit potential monitored as a function of time of (A) polyanisidine and (B) polyethylaniline with no initiator (dotted line), with *p*-phenylenediamine as an initiator (dashed line), and with aniline dimer as an initiator (solid line).

may lower the PDI by serving as a growth center for polymer chains, thus allowing polymer growth throughout the solution to initiate simultaneously and to grow in similar environments. A lower PDI may actually help in nanofiber formation since it is known that a more uniform polymer distribution will assist in supramolecular, interchain packing of polymer chains.[22] This may explain the relatively uniform nanofiber networks of polyaniline derivatives shown in Figure 1.

The electrochemical response of substituted polyaniline nanofibers was investigated in order to determine the differences, if any, to conventionally synthesized polyaniline derivatives. Experiments were performed in aqueous 1.0 M HCl solutions, and the potential cycled from −0.2 to 0.9 V at a sweep rate of 50 mV/s. Figure 4 shows representative CVs of substituted polyaniline nanofibers. For polyanisidine, polyethylaniline, and poly-*N*-ethylaniline, two major pairs of redox peaks attributed to the quasi-reversible redox reactions associated with polyaniline are observed. The first pair of peaks corresponds to the radical-cation formation of the fully reduced leucoemeraldine oxidation state, while the second redox process corresponds to the fully oxidized pernigraniline oxidation state. For the case of polychloroaniline, only a single pair of redox peaks is observed due to the difficulty of obtaining the polymer in the emeraldine oxidation state at low acid concentration. This observation is well-known for polychloroanilines as well as for other halogenated polyanilines.[19] The observed CVs are consistent with those reported for conventionally substituted polyaniline derivatives, which indicates that the polymers synthesized with and without the additives are essentially the same. In other words, the presence of the initiator does not significantly alter the molecular structure of the polymer, and the expected polymer is formed from the polymerization of the monomer rather than homopolymerization of the initiator.[17,19,23]

Mechanism. We have previously shown that nanofibers of the parent polymer polyaniline[24] as well as polypyrrole[14] can reliably be produced by promoting conditions that favor homogeneous nucleation over heterogeneous nucleation. This is primarily obtained by accelerating the rate of polymerization which can be achieved through an increase in temperature or with the addition of an initiator. Increasing the rate of polymerization enhances the likelihood that polymer nuclei will evolve to create homogeneous nucleation sites because the opportunity to diffuse to heterogeneous nucleation sites becomes limited. Because the initiator molecules have a lower redox potential than that of the monomers,[25] they can serve as nucleation centers for the growing polymer chains. This limits diffusion of polymer nuclei to heterogeneous nucleation sites and reduces renucleation onto preexisting polymer chains often called secondary growth.[7a] Nanofibers of substituted polyanilines rarely form under the "rapidly mixed" conditions employed to synthesize nanofibers of the parent polymer because the reactions proceed much more

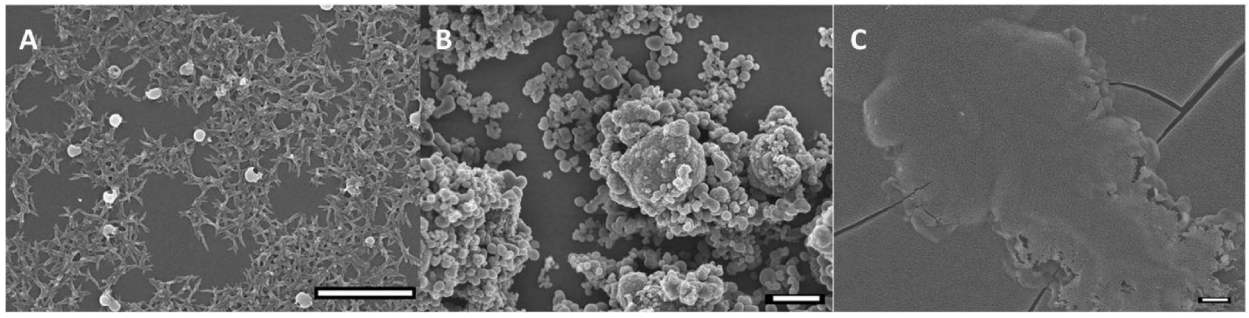

Figure 6. SEM images of polyanisidine produced in reactions performed with (A) aniline dimer and (B) *p*-phenylenediamine as the initiator in a 2% molar ratio and (C) with aniline dimer in a 25% molar ratio. Scale bar: 1 μm.

slowly compared to that of the parent polymer. The slower rate of polymerization allows polymer nuclei the opportunity to diffuse to heterogeneous nucleation sites, such as the container side walls, which leads to an agglomerated morphology. Polymerization on surfaces has been shown to proceed more rapidly than polymerization in the bulk for aniline,[26] and this is even more so for substituted anilines. Indeed, in conventional reactions to produce substituted polyanilines, a large amount of polymer deposition on the container side walls is observed. The morphology of films deposited on the side walls is generally granular in nature. However, with the aromatic initiator added to reactions that produce substituted polyaniline nanofibers, no deposition of the polymer is observed on the container side walls. The polymer thus forms exclusively in bulk solution and by avoiding secondary growth leads to a nanofibrillar morphology.

Open circuit potential (OCP) measurements are useful for monitoring the polymerization of aniline and its derivatives.[27] By monitoring the reaction by OCP with and without the presence of the initiator, the rate of oxidant consumption can be observed, and therefore the overall aniline polymerization rate can be determined. The OCP of polyaniline and its derivatives is typically characterized by three regions: a short induction period (t_1), the formation of the pernigraniline oxidation state (t_2), and finally a rapid decay in OCP characteristic of reduction of pernigraniline to the emeraldine oxidation state (t_3). The faster the reaction is, the shorter the $t_1 + t_2$ time.[27] This technique is thus a useful tool for determining in a semiquantitative manner the optimal reaction rate for nanofiber formation. Furthermore, OCP can potentially help elucidate the differences in morphology observed when different initiators are used.

When monitoring the polymerization of anisidine in the presence of an added initiator, we observe a significantly lower value for $t_1 + t_2$ as compared to the reaction performed without the initiator present (Figure 5A). This indicates a substantial increase in the rate of polymerization. This increase is visible to the naked eye as the characteristic color changes associated with aniline polymerization are observed immediately in the presence of the aniline dimer, as opposed to minutes without dimer. In the presence of aniline dimer, the $t_1 + t_2$ value is $\sim$1 min for the polymerization of anisidine; however, in the absence of the dimer, the $t_1 + t_2$ value is $\sim$9 min. Interestingly, when anisidine is polymerized in the presence of *p*-phenylenediamine, only an incremental increase in the rate of polymerization is observed. SEM images of the purified product reveal that only the reaction with aniline dimer added produces nanofibers, while the reaction with *p*-phenylenediamine produces only large, micron size agglomerates similar to those reactions performed without any initiator added (Figure 6).

Conversely, in observing the polymerization of 2-ethylaniline, we observe that reactions with *p*-phenylenediamine have a lower value of $t_1 + t_2$ as compared to reactions performed with aniline dimer—approximately 90 s lower (Figure 5B). The analogous reaction without aniline dimer or *p*-phenylenediamine proceeds so slowly that no change is observed after the initial unstable region ($\sim$15 s) for the entire duration of the experiment ($\sim$1 h). Left to react to completion, the morphology of the polymer consists of only large, micron size agglomerates. Comparing SEM images of the purified products reveal that reactions performed with *p*-phenylenediamine produce nanofibers that are far more uniform, defined, and less entangled than reactions performed with aniline dimer. Thus, the choice of initiator (*p*-phenylenediamine or aniline dimer) plays a crucial role in the synthesis of substituted polyaniline nanofibers, although it is not yet clear why certain initiators increase the reaction rate for certain monomers more than others. This phenomenon is currently under investigation.[28]

In general, we have observed that the additive/monomer combination which accelerates the rate of polymerization the most will be most successful at producing nanofibers of the highest quality. However, this view is somewhat tempered because if the rate of polymerization is too great (by addition of too much additive or with certain pairings of additive and monomer), the molecular weight will be too low to allow proper precipitation of the polymer. This typically leads to a product possessing a smooth morphology (Figure 6C). The addition of the correct initiator in the proper amount may thus be a generally effective method to produce 1-D nanofibers of conducting polymers by promoting homogeneous nucleation and thereby suppressing secondary growth.

Conclusions

Bulk quantities of substituted polyaniline nanofibers are readily synthesized by the addition of an initiator into the traditional synthesis between monomer and oxidant. This can be used to synthesize a wide range of substituted polyaniline nanofibers. Open-circuit potential measurements show that the additive/monomer combination which accelerates the polymerization rate the most often leads to high-quality nanofibers provided that the polymer precipitates from solution. Cyclic voltammetry and UV−vis studies show that the nanofibers produced are similar to conventionally synthesized polyaniline derivatives in chemical composition and oxidation state. Although the impact of the initiator on the molecular structure of the polyanilines is negligible, its impact on the assembly of the polymer chains is significant. This simple and general procedure to synthesize substituted polyaniline nanofibers should facilitate the further study of this promising class of materials in applications such as chemical sensors, molecular memory, and catalysis.

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Supporting Information Available: SEM images of substituted polyaniline nanofibers. This material is available free of charge via the Internet at http://pubs.acs.org.

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