Nanostructures

Nanofiber Formation in the Chemical Polymerization of Aniline: A Mechanistic Study**

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Polyaniline is unique among conducting polymers because of its simple nonredox doping/dedoping chemistry based on acid/base reactions.[1,2] The conventional chemical oxidative polymerization of aniline is carried out in an aqueous solution in which aniline is dissolved in a strong acidic solution (for example, 1M HCl) at about 0°C and the polymerization is initiated by adding an oxidant (for example, ammonium peroxydisulfate) into the solution.[1] Polyaniline nanostructures, such as nanofibers/-wires/-rods/-tubes, can be made by introducing "structural directors" into the chemical polymerization bath. These structural directors include "soft templates" such as surfactants,[3] organic dopants,[4,5] or polyelectrolytes[6] that assist in the self-assembly of polyaniline nanostructures, and "hard templates" such as porous membranes[7] or zeolites[8] where the templated polymerization of aniline occurs in the 1-D nanochannels. Films containing polyaniline nanofibers can also be made by using electrospinning[9] or electrochemical methods to control the polymerization rate.[10–12] Nanostructures of polyaniline are of great current interest since they combine the properties of low-dimensional organic conductors with high surface area materials. This situation can lead to enhanced properties in applications such as chemical sensors.[13–16]

Recently we have developed a general chemical route to polyaniline nanofibers by using interfacial polymerization at an aqueous/organic interface.[15,17] The reactants—aniline, ammonium peroxydisulfate, and a doping acid such as HCl—are separated by the interface between an organic solvent containing aniline and an aqueous phase containing the oxidant plus the doping acid. The polyaniline product, polymerized at the interface, contains almost exclusively nanofibers with relatively uniform diameters. The nanofiber diameter is determined by the doping acid used in the polymerization.[17] This synthesis is very general and does not require any template, special dopant, or specific solvent. Careful analysis of polyaniline made in a conventional single-phase polymerization reaction by microscopy have shown the presence of a small amount of nanofibers.[17] This observation indicates that the formation of nanofibers is not necessarily determined by the interface but more likely by the nature of the oxidative polymerization of aniline. To more fully understand the formation mechanism of polyaniline nanofibers, several important questions need to be addressed. These include: 1) Why does interfacial polymerization produce "pure" nanofibers while conventional synthesis produces irregularly shaped particles? 2) Why can small amounts of nanofibers be found in polyaniline made by conventional synthesis? 3) Why does polyaniline form such extended, elongated fiberlike nanostructures? Herein we provide answers to these questions by reporting experimental results on the factors affecting the morphology of chemically polymerized polyaniline.

To address the first question we studied the morphological evolution of polyaniline during traditional chemical oxidative polymerization. A solution of the oxidant ammonium peroxydisulfate dissolved in 1M HCl was fed continuously into a solution of aniline dissolved in 1M HCl by using a syringe pump at a preset flow rate. This procedure is analogous to the "drop by drop" titration used in traditional synthesis (Figure 1) but with a precisely controlled feeding rate. The reaction vessel was kept in an ice bath at between −5 and 0°C. Small amounts of product for transmission electron microscopy (TEM) studies were periodically extracted from the reaction bath as soon as the green color of polyaniline was visible. At this point, the samples were immediately diluted with distilled water, cast onto TEM grids, and dried in air to quench the polymerization. Polyaniline nanofibers form at an early stage in the polymerization process (Figure 2a). These nanofibers have average diameters of 30–35 nm, which is consistent with those obtained using interfacial polymerization.[17] As more ammonium peroxydisulfate is fed into the reaction, the nanofibers become scaffolds for secondary growth of polyaniline (Figure 2b) and finally turn into

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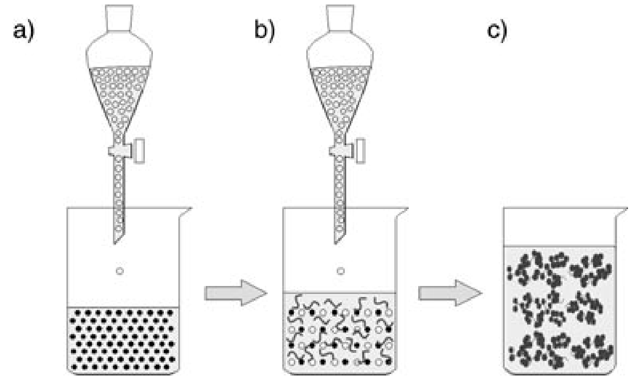

Figure 1. Schematic diagram illustrating the formation of polyaniline agglomerates during conventional chemical synthesis. a) The oxidant (open circles) dopant solution is added slowly to the aniline (solid circles) dopant solution. b) Polyaniline nanofibers form as soon as the polymerization begins. Since the nanofibers are exposed to aniline and oxidant, they are subject to secondary growth. c) Agglomerates of polyaniline particles plus a few nanofibers are found because of severe secondary growth.

irregularly shaped agglomerates containing nanofibers and particulates (Figure 2c). The whole process is illustrated schematically in Figure 1. Therefore, if secondary growth can be suppressed, the yield of nanofibers in the final product could be greatly increased.

Interfacial polymerization represents one effective method to suppress secondary growth (Figure 3).[17] Since the monomer aniline and the initiator ammonium peroxydisulfate are separated by the boundary between the aqueous and the organic phase, polymerization occurs only at this interface where all the components needed for polymerization come together.[14,15,17] Polyaniline then forms as nanofibers. Since these newly formed nanofibers are in the doped emeraldine salt form, they are hydrophilic and can rapidly move away from the interface and diffuse into the water layer (Figure 3b). In this way, as the nanofibers form they are continuously withdrawn from the reaction front, thus avoiding secondary growth and allowing new nanofibers to grow at this interface. This effect explains why nanofibers are obtained no matter which solvent is used as the organic phase in interfacial polymerization. Hence, the interface between the immiscible aqueous/organic layers does not contribute directly to the formation of nanofibers; it simply separates nanofiber formation from secondary growth.

With the knowledge that the key to synthesizing polyaniline nanofibers is preventing secondary growth, we have now designed a new, even simpler method to make pure polyaniline nanofibers (Figure 4). The idea is that if all the reactants can be consumed during the formation of nanofibers, secondary growth will be greatly suppressed since no reactants will be available for further reaction. To achieve this goal, the initiator solution (ammonium peroxydisulfate in 1M HCl) was added into the monomer solution (aniline in 1M HCl) all at once (Figure 4a), rather than slowly feeding it in by titration or syringe-pumping. Sufficient mixing can be achieved with a magnetic stirrer or shaker to evenly distribute the initiator and monomer molecules before polymerization (Figure 4b). As the polymerization begins, the initiator molecules induce the formation of nanofibers by rapidly polymerizing aniline monomers in their vicinity. Therefore, all the initiator molecules are consumed to form polyaniline nanofibers, thus suppressing the secondary growth of polyaniline. The product from a fast-mixing reaction in an ice bath is

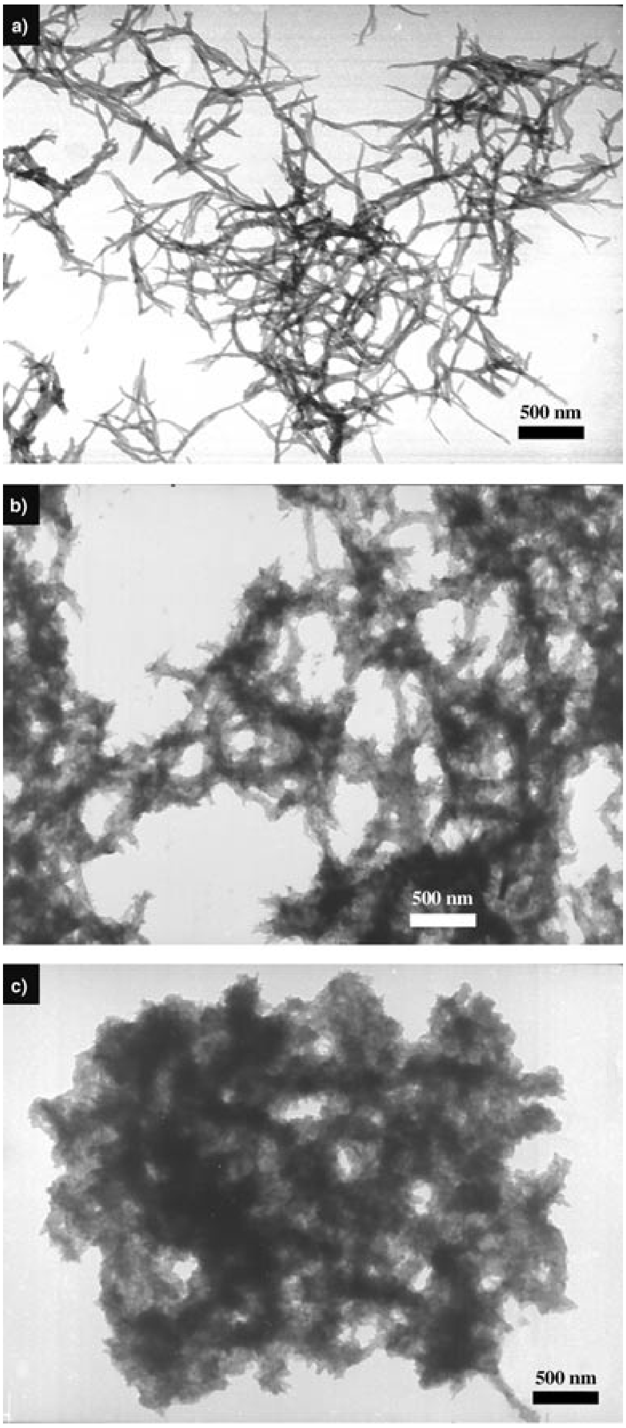

Figure 2. Typical TEM images showing the morphological evolution of polyaniline during chemical oxidative polymerization in 1 M HCl at about 0 °C. The samples were extracted: a) as soon as the green color of polyaniline became visible, b) after 25 minutes, and c) after 100 minutes.

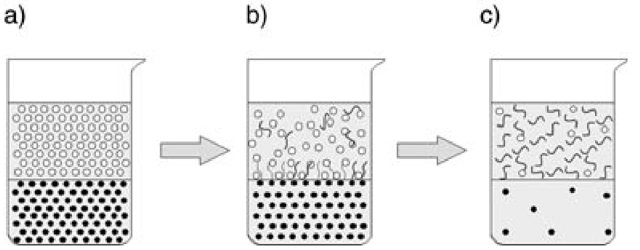

Figure 3. A schematic illustration of the synthesis of polyaniline nanofibers by using interfacial polymerization. a) An interface is set up between an organic phase containing dissolved aniline (solid circles) and an aqueous phase containing the oxidant (open circles). b) Polyaniline nanofibers form at the interface, where aniline meets the oxidant and diffuse into the water phase. Note that this carries the nanofibers away from the reactive interface so they are not subject to further secondary growth. c) As the polymerization proceeds, nanofibers accumulate in the aqueous phase.

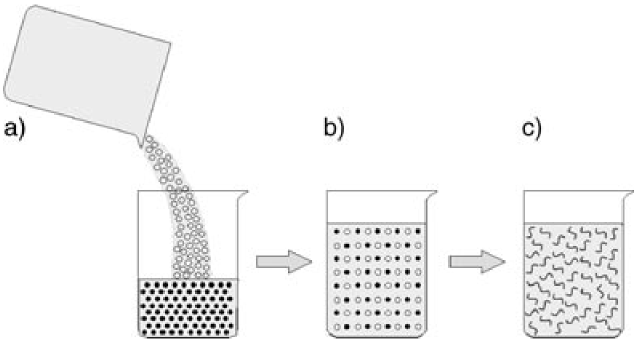

Figure 4. A schematic illustration of the synthesis of polyaniline nanofibers in a rapidly mixed reaction. a) The oxidant (open circles) dopant solution is quickly added into the aniline (solid circles) dopant solution and mixed. b) A homogenous solution is obtained where all the aniline and oxidant molecules are evenly distributed, thus leading to fast polymerization across the entire solution. c) Since all the reactants are consumed in the formation of nanofibers, secondary growth is suppressed.

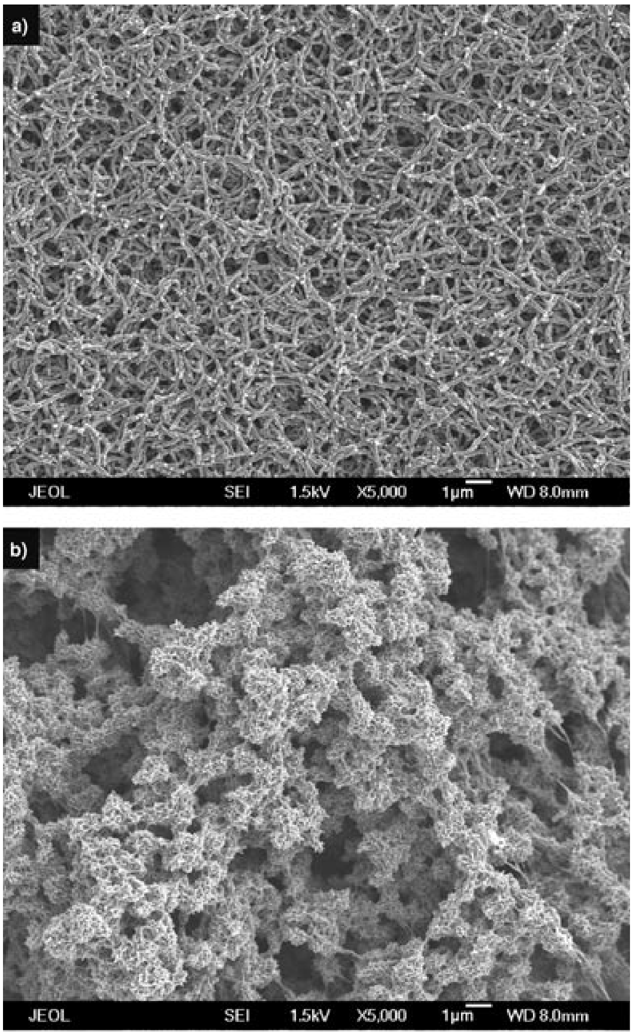

Figure 5. SEM images showing the morphology of polyaniline synthesized from a) a rapidly mixed reaction and b) a slowly mixed reaction. High-quality nanofibers are obtained in the rapidly mixed reaction, while irregular agglomerates form in the slowly mixed reactions.

almost exclusively polyaniline nanofibers of uniform sizes as observed using scanning electron microscopy (SEM; Figure 5a). The nanofibers formed are similar to those obtained by interfacial polymerization. In contrast, agglomerates of nanofibers and irregular particulates are produced by using traditional slow-mixing reactions (Figure 5b). Comparable results are obtained when monomer solution is fed into the initiator solution.

Reactions that are rapidly mixed using other doping acids, including sulfuric, camphorsulfonic, and perchloric acids also produce "pure" nanofibers with comparable shapes and sizes to those made by interfacial polymerization.[17] Fast-mixing reactions carried out at different temperatures, including in an ice bath (ca. 0°C), at room temperature (ca. 20°C), and at 100°C, all yield high-quality nanofibers. When the reactant concentrations are increased, the induction time of the reaction is reduced, but no apparent difference in the morphology of the product is observed. It is now clear that nanofibers of polyaniline form naturally during chemical oxidative polymerization in aqueous solutions. By suppressing the secondary growth of irregular particles, either through interfacial polymerization or rapid-mixing reactions, essentially pure polyaniline nanofibers can be obtained without the need for any templates or seeds.[18] Nanofibers appear to be a basic morphological unit for chemically polymerized polyaniline as they are for polyacetylene.[19]

The next question is why does polyaniline favor an elongated, well-extended 1-D nanofiber morphology in water? The successful rapid-mixing reaction route to making polyaniline nanofibers in water is also applicable to other solvents, which is difficult to do using interfacial polymerization. Figure 6 shows the morphology of polyaniline obtained through rapid-mixing reactions in water, ethanol, and isopropanol at room temperature. Well-defined, relatively long nanofibers are created in water (Figure 6a). The product formed in ethanol is a mixture of short nanofibrils with many irregular particles attached to them (Figure 6b). The reaction in isopropanol produces only agglomerates of 100–300-nm particulates with no discernable nano-

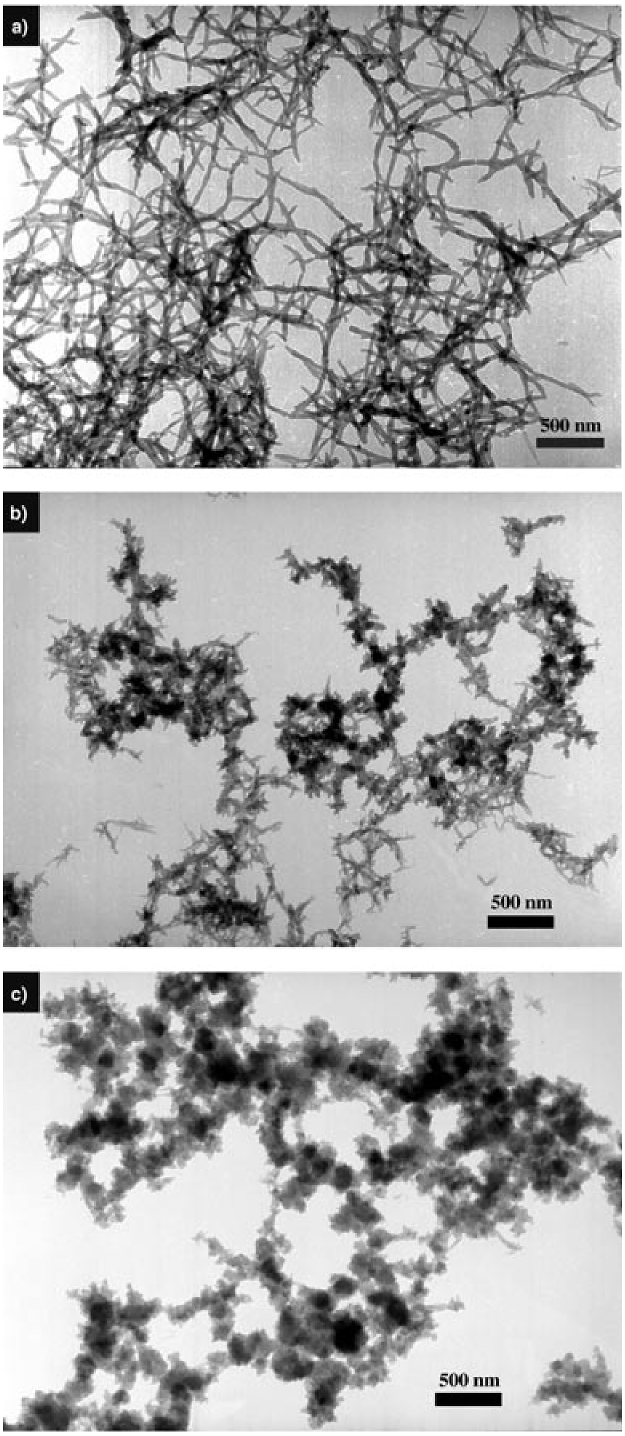

Figure 6. Typical TEM images showing the morphology of polyaniline obtained in different solvents through rapidly mixed reactions in a) water, b) ethanol, and c) isopropanol.

fibers. Note that since the as-prepared polyaniline is in its doped, hydrophilic emeraldine salt form, the affinity of the polyaniline salt for the solvent will decrease from water to ethanol to isopropanol as the polarity decreases. Therefore, it is not surprising that polyaniline favors more compact morphologies in ethanol and isopropanol, while in water elongated 1-D nanofibers form.

In summary, polyaniline preferentially forms as nanofibers in aqueous solution during chemical oxidative polymerization. The nanofibers produced in the early stage of polymerization during slow-feeding reactions are subject to secondary growth, which leads to the large agglomerates containing irregularly shaped particles and nanofibers. Pure nanofibers can be obtained by preventing the secondary growth. In interfacial polymerization secondary growth is suppressed when freshly formed nanofibers diffuse away from the reactive interface. Secondary growth is limited in rapid-mixing reactions by quickly consuming the reactants during the initial polymerization. Rapid-mixing reactions in less-polar solvents produce less-perfect nanofibers, which indicates that water is the best solvent for the synthesis of nanofibers. The rapid mixing reaction route is an even simpler method than interfacial polymerization to make polyaniline nanofibers, especially on a laboratory scale where sufficient mixing can be easily achieved by stirring or shaking before the polymerization starts. This mechanistic study may offer important insights into the synthesis of other conducting polymer nanostructures. It may also help to explain the variation in the properties of polyaniline made in different reactions, since the rate of addition of reactants affects the final morphology, thus resulting in different fractions of nanofibers in the final product.

Experimental Section

Synthesis and purification**:** All chemicals were of analytical grade and used as received. Reactions were generally carried out in 20-mL vials. Typically, an aqueous solution of aniline (3.2 mmol) in 1M doping acid (10 mL) and another solution of ammonium peroxydisulfate (0.8 mmol) in the same doping acid (10 mL) were prepared and mixed using a syringe pump. HCl was used as the dopant unless otherwise mentioned. The feeding rate of one solution into another was set at 5 mLh^{-1} so that it took 2 h to completely feed into the solution. Reactions were carried out at different temperatures: ca. 0 °C (using an ice bath), ca. 20 °C (at room temperature), and at ca. 100 °C (using boiling water). Sulfuric acid was used as the dopant for reactions at ca. 100 °C because of its thermal stability. Rapid-mixing reactions were performed by pouring the two solutions together and immediately stirring or shaking to ensure sufficient mixing before polymerization begins. Polymerization can be observed when the characteristic green color of polyaniline emeraldine salt became visible. More reactions were carried out by increasing or decreasing the reactant concentrations by 10 times; in all cases uniform nanofibers were observed. For reactions in ethanol and isopropanol, the monomer and ammonium peroxydisulfate solutions were prepared in the solvent. Solutions of 1M HCl in ethanol and isopropanol were prepared by diluting a concentrated aqueous solution of HCl (12.1M) with the corresponding alcohols. The products were purified by centrifugation using the reaction solvent until the suspension reached a neutral pH value.

Morphology**:** The morphologies of the product were examined by TEM (JEOL 100CX) and SEM (JEOL 6700). For the morphological evolution experiments (Figure 2), samples (0.1 mL) were extracted from the reaction at different times and diluted immediately in distilled water (0.5 to 2 mL). An appropriate amount of this suspension was then cast onto copper TEM grids (Formvar coated, 300 mesh, Ted-Pella Inc.). The grids were placed on filter paper to absorb any extra suspension and facilitate rapid drying, therefore quenching the polymerization. Other TEM samples were prepared by diluting the purified products and casting suspensions onto TEM grids. Samples for SEM experiments were made on conducting stages and observed without gold coatings.

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