

# A Simple Approach to Control the Growth of Polyaniline Nanofibers<sup>†</sup>

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## Abstract

Polyaniline nanofibers are synthesized via controlled chemical oxidative polymerization. The interconnected, branched network-like nanostructures are demonstrated through scanning electron microscopy (SEM). Using different synthetic conditions as well as different dopant acids we can control the diameters of polyaniline nanofibers ranging from 30nm to 80nm. UV/vis spectra of polyaniline nanofibers are consistent with nonfibrous polyaniline powders prepared by the conventional chemical synthesis. The nanofibrous morphology has no significant change when redoped/dedoped multiple times by the acid/base solutions. The formation mechanism of the nanofibers is discussed.

**Keywords:** Polyaniline; Nanofiber; Nanostructure; Chemical polymerization; Dilute polymerization

## 1. Introduction

Polyaniline is prepared via either chemical [1-3] or electrochemical [3] oxidative polymerization in the presence of proton acids. The conventional chemical polymerization only produces nonfibrous or irregular shaped morphologies [8,9]. In the past several years, a variety of chemical methods were reported that yield polyaniline nanofibers, such as use of hard templates [4,5], soft templates [6], electrospinning [7], interfacial polymerization [8], and seeding polymerization [9]. Recently, we discovered that polyaniline nanofibers can be directly synthesized in dilute chemical polymerization without aid of specific templates or techniques. The method we report here is very simple, economic, and scalable to produce polyaniline nanofibers.

## 2. Experimental

### 2.1. Reagents

Aniline (Aldrich) was distilled under vacuum before use. Ammonium peroxydisulfate (APS; 99.99%, Aldrich), deionized water (OSU Chemical Store) and dopant acids

were used directly as received without further purification.

### 2.2. Synthesis of polyaniline nanofibers

A small amount of aniline/1M dopant acid solution was carefully transferred to the solution of ammonium peroxydisulfate (APS;  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ )/1M dopant acid solution with little or no disturbance (unstirred polymerization). The dark-green precipitate was collected after 24 hours, and then purified via dialysis with deionized water (Dialysis Tubing, MWCO 12k-14k). 8mM, 16mM, 64mM and 128mM of initial concentrations of aniline based on the total volume of reaction mixture were used to study the formation of polyaniline nanofibers. Syntheses were carried out at different temperatures, e.g., 24°C (room temperature) and 0–5 °C (ice bath). The molar ratio of aniline to APS was kept at 2. Three different acids, such as hydrochloric acid (HCl), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA), methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ) were used. Stirred polymerization was carried out on the magnetic stirring plate with a magnetic stirring bar.

### 2.3. Characterization

Samples sputtered with a thin layer of Au/Pd were used for scanning electron microscopy (SEM, Philips XL-30 ESEM) studies. UV/vis absorption was studied using a

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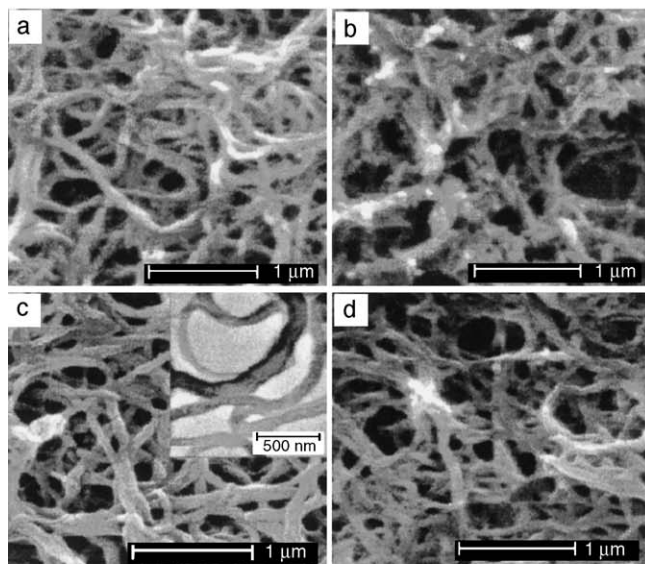


Fig. 1. Scanning electron micrograph (SEM) of polyaniline nanofibers obtained in different dopant acids at [aniline] = 8mM and 24 °C without mechanical stirring (a) AMPSA (b) HCl (c) CH<sub>3</sub>SO<sub>3</sub>H (d) CH<sub>3</sub>SO<sub>3</sub>H at 0–5 °C (scale bar = 1 μm; scale bar of the inset image = 500nm).

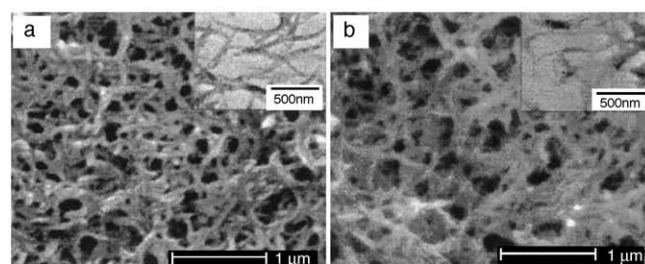


Fig. 3. Scanning electron micrograph (SEM) of polyaniline/ CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> nanofibers synthesized in different concentration of aniline with a molar ratio of [aniline]/[APS] = 2 and at 24 °C without mechanical stirring (a) [aniline] = 64mM (b) [aniline] = 128mM. (scale bar = 1 μm; scale bar of the inset images = 500nm)

UV/VIS/NIR Spectrometer (PERKIN ELMER Lambda 19) employing the polyaniline dispersion in deionized water.

### 3. Results and discussion

Figure 1 shows SEM images of polyaniline synthesized in different dopant acids. The morphology of polyaniline obtained shows an interconnected, branched network-like nanofibrous structure with the nanofiber diameters varying in the range of 30nm to 80nm. There are no significant differences on the branched interconnected network structures of polyaniline nanofibers when syntheses are carried out in 1M methanesulfonic acid at 24°C (Fig. 1c) and 0°C (Fig. 1d), respectively. However, a smaller average diameter is observed at lower temperature in dilute polymerization. Unstirred and stirred polymerizations result in very similar nanostructured morphology as shown in

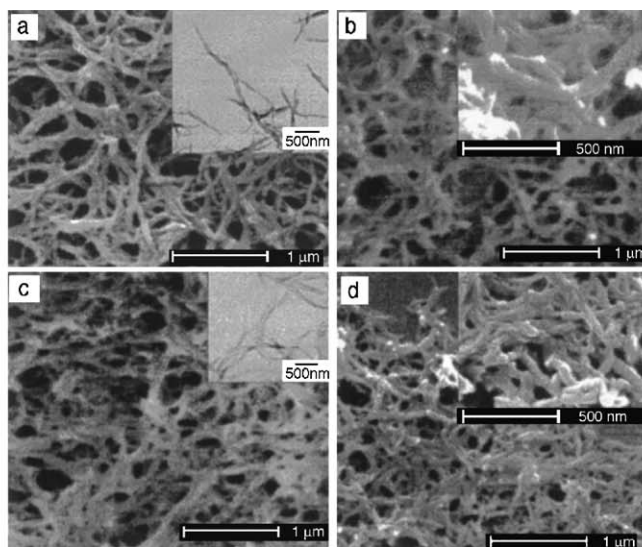


Fig. 2. Scanning electron micrograph (SEM) of polyaniline/ CH<sub>3</sub>SO<sub>3</sub><sup>-</sup> nanofibers obtained with a molar ratio of aniline to APS of 2 at room temperature, 24 °C, without mechanical stirring (a) [aniline] = 16mM, (b) [aniline] = 128mM, and with mechanical stirring (c) [aniline] = 16mM, (d) [aniline] = 128mM (scale bar= 1 μm; scale bar of the inset image = 500nm)

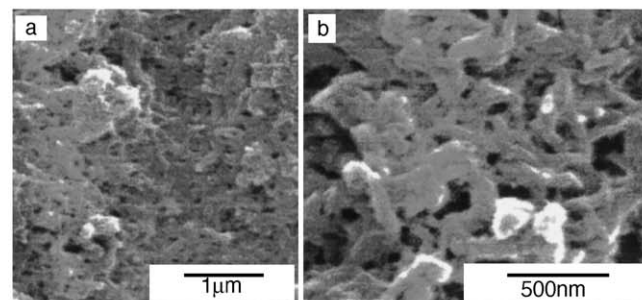


Fig. 4. Scanning electron micrograph (SEM) of polyaniline powder obtained in the conventional polymerization [2]. (a) x20,000 magnification, scale bar = 1 μm and (b) x50,000 magnification, scale bar = 500nm.

SEM images of Figure 2. However, closer examination shows a clear “stirring” effect for dilute polymerization. For the same synthetic conditions, stirred solution yields shorter fibers with smaller diameters as shown in Figures 2a and 2c. We note that samples polymerized at higher concentration (e.g., [aniline] = 128mM) do not dramatically change fiber diameters or lengths with stirring as shown in Figures 2b and 2d.

Different concentrations of aniline monomer with a constant molar ratio to APS oxidant (quoted with respect to the total volume of mixture) are used to study the formation of nanofibers, e.g., 8mM (Fig. 1c), 16mM (Fig. 2a), 64mM (Fig. 3a), and 128mM (Fig. 2b and 3b). This contrasts to the conventional polymerization in which the relatively high concentration of aniline of ~400mM (Fig. 4) is used [2]. The lower concentration of aniline/APS has a higher likelihood to form less branched polyaniline nanofibers with larger diameters (Fig. 1c). Additionally, a few of nonfibrous particulates are found in all samples. The quantities of the

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