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Controlled Synthesis of Dendritic Polyaniline Fibers with Diameters from Nanosize to Submicrometersize

Xiao Cong WANG[1,2]*, Shu Jiang DING[2], Jing CAO[1], Fa Lun WU[1],
Chen ZHOU[1], Zhen Zhong YANG[2]*

[1]College of Science, Tianjin University of Science and Technology, Tianjin 300022
[2]State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080

Abstract: Dendritic polyaniline nanofibers and submicrometer-sized fibers have been synthesized by chemical oxidative polymerization of aniline (An) doped with salicylic acid (SA). The diameters of the fibers could be controlled easily from 30 to 400 nm by varying the concentration of aniline and salicylic acid at room temperature. Scanning electron microscopy (SEM) and typical transmission electron microscopy (TEM) were applied to investigate their morphologies. Fourier transform infrared (FTIR) spectrum indicated that the state of the dendritic polyaniline fibers is emerialdine rather than solely the leucoemeraldine or permigraniline forms. The dendritic polyaniline fibers have potential applications as chemical sensors or actuators and neuron devices.

Keywords: Dendritic, polyaniline, synthesis, nanofiber.

Synthesis of dendritic nanomaterials is an increasingly active area[1, 2]. Dendritic nanomaterials not only have unusual structure but also posses potential application in many fields (such as nanoscale devices, photovoltaic behavior, chemical sensing)[1-5]. Many dendritic (or branched) materials have been synthesized in recent years. Zhao *et al.* reported a novel solution method for synthesis of metal dendritic nanocrystals[2]. Wang *et al.* described an approach to the growth of branched and hyperbranched nanowire structures in which the branch composition and diameter could be controlled using a multistep nanocluster-catalyzed vapor-liquid-solid (VLS) process[3]. Dick *et al.* have synthesized branched “nanotrees” by the similar method[4]. Hao *et al.* reported the synthesis of branched gold nanocrystals *via* a wet-chemical route[5]. On the other hand, nanostructures of conducting polymers have attracted intensive interest because of their novel physical properties and potential applications such as chemical sensors, polymeric conducting molecular wires. Among the known conducting polymers, polyaniline is unique due to its protonation-adjustable conductivity. Recently considerable efforts have been made on the synthesis of polyaniline

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* E-mail: wangxiaobc@yeah.net

nanofibers or nanotubes[6-8]. However, the synthesis of dendritic polyaniline nanofibers has rarely been reported. Wan *et al.* synthesized sub-micrometer-sized junctions and dendrites of polyaniline *via* a self-assembly process[9]. Li *et al.* synthesized polyaniline nanofibers by chemical oxidative polymerization of aniline in a C_{16}TMA surfactant gel at low temperature[10]. Here we describe a very simple method to synthesize dendritic polyaniline fibers with controlled diameters from nano-sized to submicrometer-sized at room temperature. The diameters of the nanofibers could be controlled from 30 to 400 nm by varying the concentration of aniline (An) and salicylic acid (SA).

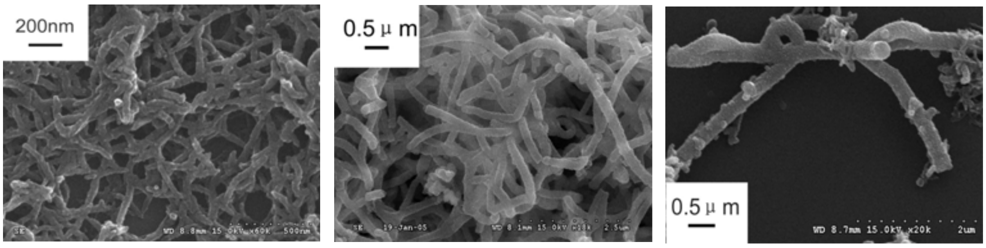
The typical precedure to prepare dendritic polyailine fibers is as follows: 0.0268 g SA was dissolved in 19 mL water and stirred for 30 minutes. 0.182 g An was added in the solution and stirred for another 30 minutes. Then, 1 mL APS (1 mol/L) was added, shaking for several minutes, the reaction was continued for 24 hours. During the polymerization process, the color changed to dark green. As **Table 1** shows, the diameters of dendritic polyaniline could be controlled easily by varying the concentration of An and SA.

Dendritic polyaniline nanofibers with diameters between 30 nm and 60 nm were synthesized using 0.01 mol/L aniline (An) and 0.001 mol/L SA (**Figure1a**). It is found that the dendritic polyaniline nanofibers with diameters 30-60 nm were > 90% (volume fraction). As **Table 1**and **Figure 1b** show, the diameters of the fibers increased to about 200 nm when the reactants' concentration increased 10 times. When the concentration of An is 0.2 mol/L, the diameters of nanofibers increase to about 400 nm, but the yield was only 30 – 40 %.

Table 1 Effect of Reaction conditions on the diameters of polyaniline, molecular weight and conductivity

Concentration of SA (mol/L)	Concentration of An (mol/L)	Diameters (nm)	Molecular Weight (Mw g • mol^{-1})	Conductivity (S • cm^{-1})
0.001	0.01	30 – 60	81600	2.1×10^{-2}
0.005	0.05	100 – 150	102200	4.4×10^{-2}
0.01	0.1	200 – 250	97640	4.3×10^{-2}
0.02	0.2	300 – 400	68330	3.3×10^{-2}

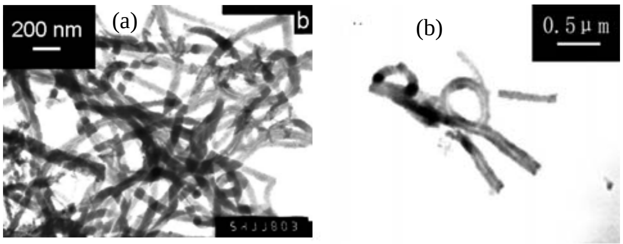
Figure 1 SEM images of dendritic polyaniline synthesized with different conditions:



(a) (b) (c)

(a) 0.001mol/L SA, 0.01mol/L An, APS/An = 1:1. (b) 0.01mol/L SA, 0.1mol/L An, APS/An = 1:1. (c) 0.01mol/L SA, 0.2mol/L An, APS/An = 1:1.

Figure 2 TEM images of dendritic polyaniline nanofibers



(a) with dimamerter about 120 nm
(b) a typical isolated dendritic polyaniline nanofiber.

Figure 3 FTIR spectrum of dendritic polyaniline nanofibers

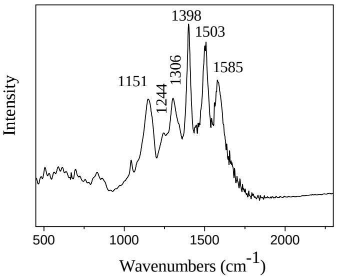


Figure 1c is a typical dendritic polyaniline fiber with diameter more than 300 nm, some polyaniline nanoparticles and smaller dendritic polyaniline could be also found. From these typical SEM images of dendritic polyaniline nanofibers with different diameters from 30 to 400 nm, and the length could be several micrometers. It is clear that most of these polyaniline nanofibers are solid and inter-connected to form dendritic or network structure, rather than isolated nanofibers. **Figure 2a** showed the typical TEM images of dendritic polyaniline nanofibers with dimamerter about 120 nm and showed few of them are hollow. A typical isolated polyaniline nanofibers in **Figure 2b** further revealed that the polyaniline nanofibers formed a dendritic structure.

One possible mechanism for the nanofiber formation is that micelles composed of aniline-SA might be formed in the reaction solution due to the hydrophobic and hydrophilic groups of An and SA. As known, surfactants can form micelles in water system which should act as templates for synthesizing polymers and the aqueous core is a microreactor for preparation polymer nanofiber. SA was not only the dopant but also acted as a kind of weak surfactant, the preparation process was simplified without using other surfactants. As the polymerization proceeds, the polymerized Polyaniline-SA would become tubes by elongation [11]. The TEM (**Figure 2**) showed that few of branches are hollow. On the basis of morphologies of polyaniline, it can be inferred that the aniline-SA can self-assemble to a special superstructure, and become a weak surfactant gel. Subsequent oxidative polymerization of aniline is confined in the weak surfactant gel.

Figure 3 is a FTIR spectrum of dendritic polyaniline. The characterictic peaks at 1398 and 1585 cm^{-1} assigned to the C-C stretching vibration of the quinoid and benzenoid rings[10,12]. The bands at 1151, 1306, and 1503 cm^{-1} corresponding to the C-H bending vibration, the C-N stretching of the cation radical and the N-H stretching mode, respectively[12, 13]. The bands of polyaniline at about 514 cm^{-1} ascribed to the C-N-C torsion [14]. The band at 1244 cm^{-1} related to the protonated C-N group and the band at 1297 cm^{-1} corresponded to the C-N stretching mode of the leucoemeraldine component [9,15]. All the information indicated that the dendritic polyaniline nanofibers were emeraldine rather than solely the leucoemeraldine or permigraniline forms. This structure is favoured to the conductivity of the dendritic polyaniline fibers.

In conclusion, dendritic polyaniline fibers with diameters from nanosize to submicrometersize were synthesized through *in-situ* polymerization in the presence of ammonium persulfate as the oxidant. The diameters of dendritic polyaniline nanofibers could be controlled easily by changing the synthetic conditions. These polyaniline fibers are interconnected to form dendritic or network structures. The dendritic polyaniline fibers have potential applications as chemical sensors or actuators, gas-separation membranes and neuron devices.

Experimental

Aniline (An, Beijing Chem.Co.) was distilled under reduced pressure before using. Ammonium persulfate ($(NH_4)_2S_2O_8$, APS, A.R.,Beijing 3rd Chemical Reagents Factory). Salycylic acid (SA) and other reagents were purchased from Beijing Chem.Co. Hitachi S-4300 field emission scanning electron microscope (SEM) and JEOL JEM-100CX transmission electron microscope (TEM) were used for investigation morphologies of the dendritic polyaniline. BRUKER EQUINOX 55 FT-IR was used for recording the infrared spectras. Keithley 196 System DMM digital multimeter was used for measurement the electrical conductivity of dendritic polyaniline fibers. The viscometer was used for measurement the molecular weights by dissolving the polyaniline in 98 wt % sulfuric acid.

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