

# The effect of polymerization rate on the formation of polyaniline nanofibers

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## ABSTRACT

This study reports the synthesis of polyaniline (PANI) nanofibers with an average diameter of 30~50 nm using HCl as a dopant. Experiments controlled the polymerization rate in terms of temperature and oxidant concentration. Transmission electron microscopy (TEM) reveals the formation mechanism of PANI nanofibers. The polymers formed nanofibers in the early stages of polymerization for all polymerization states. However, as the reaction continued, these primary nanofibers exhibited different formation behaviors. In the cases of low polymerization rates, the primary nanofibers continued growing and then turned into agglomerates with irregular shapes. In contrast, aggregation can be effectively prevented under a high polymerization rate, thus preserving PANI nanofibers in the final product. These results imply that PANI nanofiber formation may be an intrinsic characteristic of polymerization, and the growth mechanism can be described as follows: (1) intrinsic PANI nanofiber formation in the initial reaction stages, and (2) secondary growth of the initially formed nanofibers. Evidence shows that the secondary growth behavior of PANI nanofibers is greatly dominated by the reaction rate.

**Keywords:** polyaniline, nanofiber

## 1 INTRODUCTION

PANI nanofibers have been considerably interested because of their one-dimensional structure and metal-like properties. Several previous studies [1-5] have reported different approaches to obtain PANI nanotubes or nanofibers. These approaches include the use of templates or surfactants [1], electrospinning [2], coagulating media [3], radiolytic synthesis [4], and the template-free method [5].

However, aggregation is a common problem in the production and use of many chemical products in synthetic processes, especially in the surfactant-free chemical reactions. Aggregation makes it especially difficult to determine the intrinsic properties and applications of nanostructured materials [6]. A previous study suggests that three competing possible options exist in the PANI nanofiber polymerization process following the formation

of the primary PANI nanofibers. These three options are (1) the continuing formation of primary PANI nanofibers, (2) the growth of primary nanofibers into thicker fibers with uneven surfaces, and (3) the growth and aggregation of thicker fibers into irregular particles [7]. The continual occurrence of steps (2) and (3) in the conventional procedure produces irregular PANI particles. Therefore, the fibrous morphology of PANI might be preserved if the growth and aggregation of primary nanofibers can be effectively prevented during the polymerization process.

The polymerization rate is a critical factor in inhibiting the occurrence of the second and third step of PANI nanofiber growth [8]. Therefore, this study investigates the effect of the polymerization rate on the formation of PANI nanofibers in terms of temperature and oxidant levels. Nanofiber morphology is shown to be highly dependent on the polymerization rate, and high polymerization rates can effectively prevent aggregation

## 2 EXPERIMENTAL

### 2.1 Polymerization

Reactions were generally conducted in a 20-mL vial. An aqueous solution of aniline in 1M doping acid (5 mL) was prepared, and another solution of oxidants (ammonium peroxydisulfate) was mixed with same doping acid (5 mL). The solutions were then poured rapidly into a glass vial, shaken vigorously for 30 sec, and put in an ultrasonic water bath (Branson 1210, USA) at different temperatures for 2 hrs. The resulted PANI samples were isolated by gravity filtration and washed by deionized water. Finally, the products were dried in an oven for 1 day.

### 2.2 Characterization

Product morphologies were examined by transmission electron microscopy (TEM, JEOL JEM-2010) and field emission scanning electron microscopy (FESEM, JEOL JSM-7401F). For the TEM morphological evolution experiments, PANI samples were extracted from the reaction solutions at different stages and immediately diluted in distilled water. An appropriate amount of this suspension was then cast onto formvar-coated copper TEM grids. Specifically, the grids were placed on a filter paper to

absorb excess suspension and facilitate rapid drying, thus suppressing the extension of the polymerization process described elsewhere [8]. Ultraviolet–visible (UV–vis) spectra were recorded from a dilute dispersion of PANI in deionized water with a UV/Vis spectrophotometer (Perkin Elmer, Lambda 650).

### 3 RESULTS AND DISCUSSION

#### 3.1 Polyaniline nanofiber growth mechanism

This report studies the growth mechanisms of PANI nanofibers by observing their morphology evolution from the initial to final stages of the polymerization process. In the early stages of the polymerization process, samples were extracted from the reaction solution as soon as a green color became visible. Fig.1 shows the formation mechanism of PANI nanofibers obtained in different polymerization rates. Fig.1(a-c) show that the PANI nanofibers always formed in the early stages of polymerization, regardless of which synthesis condition was used. These results imply that the formation of PANI nanofibers is intrinsic to the initial stages of aniline polymerization.

However, with prolonged reaction, these primary nanofibers exhibit very different formation behaviors, as shown in Fig. 1(d-f). In the case of low polymerization rates, with low oxidant level or low reaction temperature, the primary nanofibers continued to grow and then gradually turned to agglomerates with irregular shapes [Fig. 1(e-f)]. In contrast, the aggregation can be effectively prevented by using high polymerization rate, with high oxidant level and high reaction temperature. This approach preserves PANI nanofibers in the final product [Fig. 1(d)]. These results imply that PANI nanofiber formation may be an intrinsic characteristic of polymerization, and the growth mechanism can be described as follows: (1) intrinsic PANI nanofiber formation in the initial reaction stages, and (2) secondary growth of the initially formed nanofibers. Evidence shows that the secondary growth behavior of PANI nanofibers is greatly dominated by the reaction rate

#### 3.2 The effect of polymerization rates on PANI nanofiber morphology

To verify the effects of the polymerization rate on polymer morphology, a series of polyaniline nanofibers were synthesized under different reaction conditions. Figure 2 (a-c) shows the typical morphologies of PANI nanofibers oxidized at different [ANI]/[APS] ratios, varying from 0.8:1 to 6.4:1. All the PANI samples have a nanofibrous morphology and measure 30~50 nm in diameter. However, when the [ANI]/[APS] ratio increased from 0.8:1 to 6.4:1, the nanofiber aggregation occurred during the polymerization process and became more pronounced with the decrease of oxidant as shown in Fig. 2 (a-c). Variations in the polymerization rate are thought to be responsible for

the different morphologies of the synthesized PANI. For example, when APS was used as the oxidant, the formation of new embryonic nuclei with a higher oxidant content (e.g. [ANI]/[APS] = 0.8:1) is faster than that with a lower oxidant content (e.g. [ANI]/[APS] = 6.4:1). A high polymerization rate rapidly consumes monomers, suppressing the secondary growth of polyaniline and preventing aggregation during the polymerization process [8].

The effects of polymerization temperature on the formation of PANI nanofibers were also studied based on a fixed [ANI]/[APS] ratio of 0.8:1. When the reaction was conducted with a low monomer concentration (0.05 M) at 0 °C, irregular agglomerates formed. In contrast, almost no granular particulates appeared in the product prepared at 60°C, as shown in Fig. 3(a) and (b). Li et al. [6] reported that polyaniline nucleation behavior is highly dependent on the polymerization rate, which is determined by the reaction temperature. They claimed that if the reaction temperature of PANI is low (e.g. 0 °C), new polyaniline molecules will precipitate on the preformed particles due to favorable heterogeneous nucleation conditions. On the other hand, as new polyaniline molecules form rapidly at higher temperature (e.g. 60 °C), it is more likely that the aniline monomers evolved to create initial nuclei instead of precipitation on the preformed particles to nucleate. Thus, more polyaniline molecules would be produced by homogeneous nucleation at higher temperature. Recently, Jing et al. [7] also revealed that primary nanofibers will grow into thick fibers with uneven surfaces, and finally grow and agglomerate into irregular particles under a conventional synthesis approach.

Based on the results above, Fig. 4 illustrates the formation of PANI nanofibers. In the early stages of polymerization, aniline monomers intrinsically induce the formation of nanofibers. However, as the reaction continues, these primary nanofibers exhibit different formation behaviors. At low polymerization rates (low amounts of oxidant or low reaction temperatures), secondary growth occurs in the polymerization process, turning nanofibers into agglomerates with irregular shapes. On the other hand, high polymerization rates can effectively prevent agglomerate formation, thus preserving PANI nanofibers in the final product.

#### 3.3 PANI characterization

Fig. 5 shows the UV–Vis absorption spectra of HCl-doped and dedoped PANI nanofibers dispersions in deionized water. The spectrum for the HCl-doped PANI nanofibers shows three characteristic absorption bands at wavelengths of 320–360, 400–420 and 600–700 nm, respectively. The first absorption band arises from  $\pi$ - $\pi^*$  electron transition within the benzenoid segments. The second and third absorption bands are related to the acid-

doped state and polaron formation, respectively [9], which are both attributed to the presence of the emeraldine salt form of PANI. When the nanofibers are dedoped by immersion in 1M  $\text{NH}_4\text{OH}$  for 1 day, two strong absorption bands appear at 318 nm and 604 nm. These bands are attributed to the formation of an emeraldine base [10].

#### 4 CONCLUSION

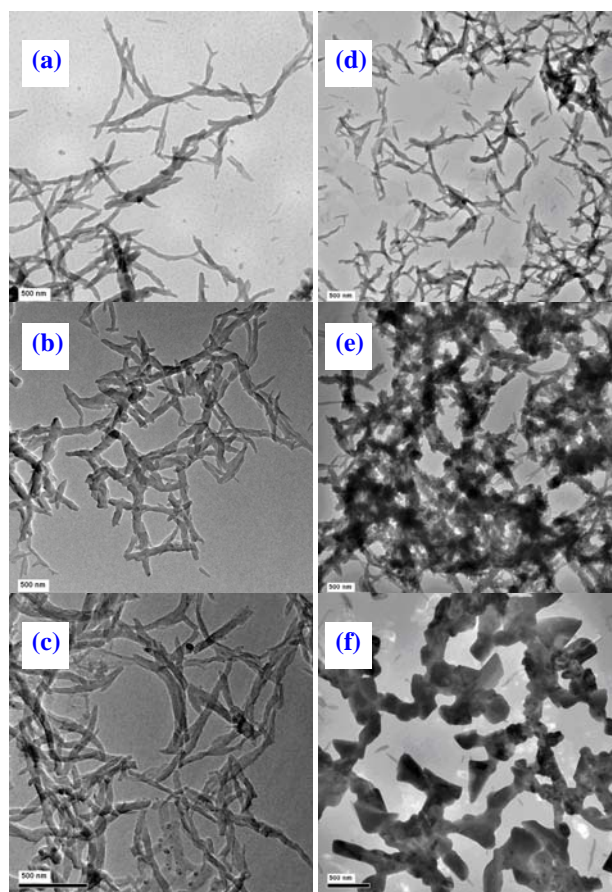
This study reports the synthesis of PANI nanofibers doped with HCl, and systematically investigates the effects of the polymerization rate on the formation of PANI nanofibers. The growth mechanism can be described as follows: (1) intrinsic nanofiber formation in the initial stages of the polymerization process, and (2) secondary growth of the primary nanofibers. Specifically, the likelihood of the secondary growth of PANI nanofibers depends greatly on the reaction rate. Higher reaction temperatures (e.g. 60 °C) and higher levels of oxidant (e.g.  $[\text{An}]/[\text{APS}] = 0.8:1$ ) are favorable to the formation of PANI nanostructures because they inhibit the occurrence of this secondary growth.

#### ACKNOWLEDGE

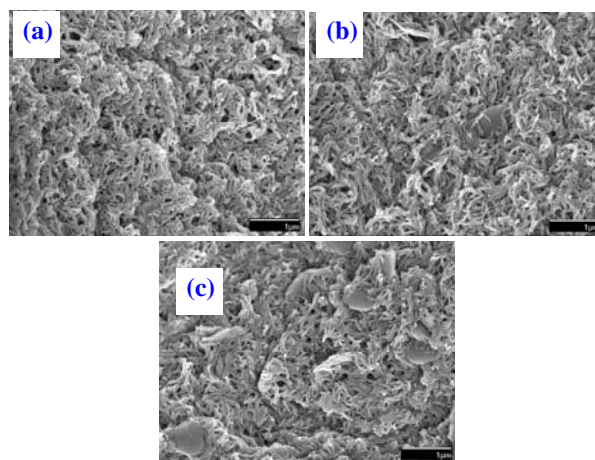
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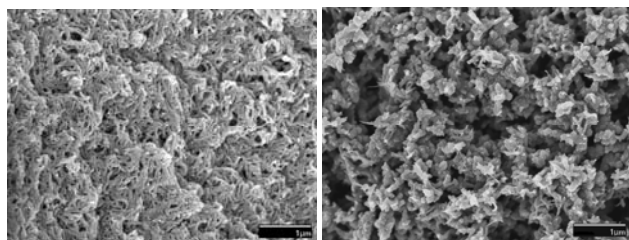
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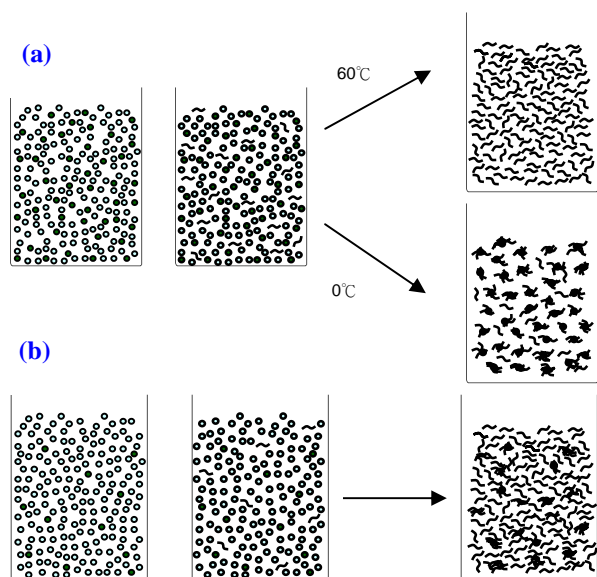
**Figure 1** Typical TEM images showing the morphological evolution of polyaniline during chemical oxidative polymerization in 1M HCl at different temperatures and  $[\text{ANI}]/[\text{APS}]$  ratios: (a,d)  $[\text{ANI}]/[\text{APS}] = 0.8:1$  at 60°C, (b,e)  $[\text{ANI}]/[\text{APS}] = 0.8:1$  at 0°C, and (c,f)  $[\text{ANI}]/[\text{APS}] = 6.4:1$  at 60°C. The samples were extracted either as soon as the green color of polyaniline became visible (a,b,c) or after a specific period of 120 minutes (d,e,f).



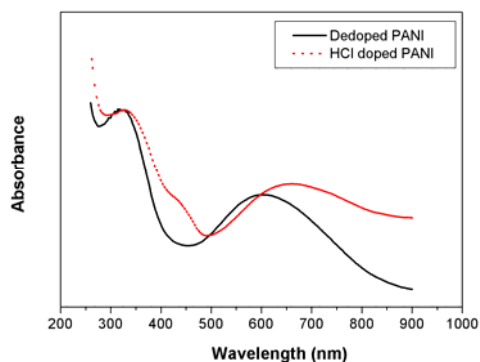
**Figure 2** SEM images of PANI nanofibers obtained at 60°C with different  $[\text{ANI}]/[\text{oxidant}]$  mole ratios: (a) 0.8:1 (b) 3.2:1, and (c) 6.4:1.



**Figure 3** SEM images of HCl-doped PANI nanofibers oxidized with a [ANI]/[APS] ratio of 0.8:1 at different temperatures and aniline concentrations: (a) oxidized at 60°C and (b) oxidized at 0°C



**Figure 4** Schematic illustrations of polyaniline nanofiber formation in different reaction conditions. (a) PANI nanofibers oxidized at 60°C and 0°C with [ANI]/[APS] ratios of 0.8:1 (b) PANI nanofibers oxidized at 60°C with [ANI]/[APS] ratios of 6.4:1



**Figure 5** UV-Vis spectra of PANI