



## Polymer Communication

## Polyacrylamide-controlled growth of centimeter-scaled polyaniline fibers

Qunwei Tang, Jihuai Wu\*, Xiaoming Sun, Qinghua Li, Jianming Lin, Leqing Fan

The Key Laboratory for Functional Materials of Fujian Higher Education, Institute of Materials Physical Chemistry, Huaqiao University, Quanzhou 362021, China

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## ABSTRACT

In this communication, we first report a novel route to synthesize centimeter-scaled polyaniline (PANI) fiber in the presence of oligo-acrylamide (OAAm). The Fourier transform infrared and ultraviolet–visible spectra reveal that the fiber is copolymers of PANi and PAAm, and PANi is in high conductive emeraldine salt state. Acrylamide feed significantly affects the morphology of the fiber, the conductivity and yield of the fiber depend on hydrochloric acid and potassium peroxydisulfate concentration in the preparation process. Under optimized conditions, a hexagonal PANi/PAAm fiber with conductivity of  $3.7 \text{ S cm}^{-1}$  and length of 6 cm is obtained, which provides a facile method for preparing conductive long fiber. It is proposed that the oligo-acrylamide acted as in-situ seeds directs the fibriform morphology of the fiber.

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## 1. Introduction

Because of its easy preparation, high conductivity, good environmental stability, interesting redox properties, and excellent application in electronic and optical devices, polyaniline (PANI) has become one of the most important conducting polymers and been intensively studied in last two decades [1–3]. Recently, PANi nanostructures including particles, rods, wires, tubes, fibers, and films, have received intense interest because of their physical and chemical properties differing from their macro-sized counterparts, which it is possible used in polymeric conducting molecular wires [4], chemical sensors [5–8], biosensors [9], light-emitting and electronic devices [10,11].

The classical chemical synthesis of PANi uses aniline monomer, an oxidant, and a strong acid. The acid acts as a dopant to protonate PANi, which results in a conductive emeraldine salt, but anisotropic growth is often suppressed in such a system [12]. Recently, a variety of synthetic approaches, such as interfacial polymerization [6,13], seeding polymerization [14], rapidly mixed reaction [15], dilute polymerization [16,17], and template polymerization using porous materials [4,18] structural directing agents and oligomer [19–28], have been developed for the synthesis of PANi nanostructure. These synthetic methods are limited to the formation of the preferred PANi nanostructure or PANi derivate fibers due to their highly anisotropic growth character along *c* axis. However, the above methods are moderate intricacy and the preparation of PANi

derivate long fibers without templates still remains a challenge. Herein, we report a facile and high yield synthesis of centimeter-scaled PANi fibers by a low-temperature, environmentally benign, solution-phase approach in the presence of oligo-polyacrylamide (oligo-PAAm) as growth modifiers. The preparation conditions are investigated and the formation mechanism is proposed.

## 2. Experimental part

## 2.1. Materials

Aniline monomer (ANI) and acrylamide monomer (AAM) were distilled under reduced pressure prior to use, respectively. Potassium peroxydisulfate (KPS) as a radical initiator for the polymerization reaction of AAM to oligo-PAAm and the growth of ANI to PANi was purified by recrystallization from 66 wt.% ethanol/water solution. *N,N'*-Methylene bisacrylamide (NMBA) was used as a crosslinker for preparation of PAAm. Inorganic hydrochloric acid (HCl) was used as the dopant for conducting PANi fibers. The above materials were all purchased from Shanghai Chemical Reagents Co., China.

## 2.2. Growth of PANi fiber

Typical PANi fiber was prepared by the following route. ANI of 1 ml was dissolved in an AAM solution with 5 g AAM and 15 ml HCl (1.0 M). The mixed solution was vacuum-degassed for 30 min. NMBA of 0.01 g and KPS of 2.97 g was added to the above mixed solution. Under an ambient atmosphere and stirring, aqueous oxidative polymerization reaction carried out at 80 °C for 30 min

\* Corresponding author. Tel./fax: +86 595 22693999.  
E-mail address: [jhwu@hqu.edu.cn](mailto:jhwu@hqu.edu.cn) (J. Wu).

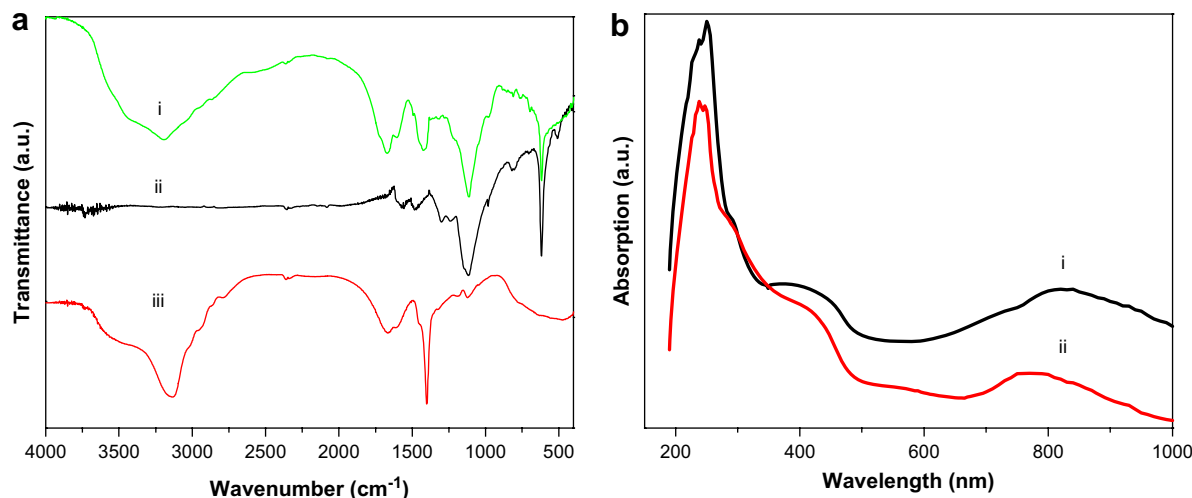


Fig. 1. (a) FTIR spectra of PANi/PAAm fiber (i), pure PANi (ii), and PAAm fiber (iii); (b) UV-vis spectra of PANi/PAAm fiber (i), and pure PANi (ii).

until all KPS dissolved and green jelly formed. The resultant colloid was immediately turned to an ice-cold vessel. After growth for 6 h, the fibroid products were separated, rinsed with acetic acid and vacuum dried.

### 2.3. Characterization

The morphology of PANi fiber was observed by a scanning electron microscopy (SEM) with a S-3500N, HITACHI, mounting the sample on metal stub, coated with gold. The sample was identified by Fourier transform infrared spectra (FTIR) with a Nicolet Impact 410 FTIR spectrophotometer using KBr pellets. The UV-vis spectra of PANi powder and PANi fiber were measured by dissolving the samples in distilled water and recording with a UV-3100 UV-vis spectrophotometer (Shimadzu Corporation, Japan). The chemical compositions of samples were identified by element analysis with a Vario EL III, Elementar Inc., Germany. The chemical compositions of the fiber was identified as about C:N:H = 9:2:10, which indicates that a molar ratio of PANi (C<sub>6</sub>H<sub>5</sub>N) to PAAm (C<sub>3</sub>H<sub>5</sub>NO) is 1:1 in the fiber. The conductivity of sample was determined by milling and pressing the sample in sheet (diameter: 13 mm, thickness: 1 mm) under 14 MPa with a Carver model C Press and measuring by using a standard four-probe method with a Keithley 196 System DMM digital multimeter. The resultant fibers show conductivity of 2–4 S cm<sup>-1</sup>, which imply the formation of PANi in the samples.

## 3. Results and discussion

### 3.1. Identification of the fiber

FTIR spectra of PANi, PAAm and the PANi/PAAm fiber are shown in Fig. 1a. It can be seen that the line (i) is the superposition of the lines (ii) and (iii), in other words, the fiber consisted of PANi and PAAm. The absorption peak at 617 cm<sup>-1</sup> is caused by the deformations of the benzene ring in PANi [28]. The band at 1114 cm<sup>-1</sup> is assigned to a vibration mode of the –NH<sup>+</sup>= structure due to the protonation of amine group in PANi [29]. The peaks at 1400 cm<sup>-1</sup> belongs to the C–N bond from PAAm, the peak at 1662 cm<sup>-1</sup> is a characteristic peak of carbonyl group in PAAm [30]. The absorption band at 3168 cm<sup>-1</sup> is attributed to the N–H bending in PAAm [31].

UV-vis spectra of PANi/PAAm fiber (i) and PANi powder (ii) synthesized in the same conditions are shown in Fig. 1b. The PANi/

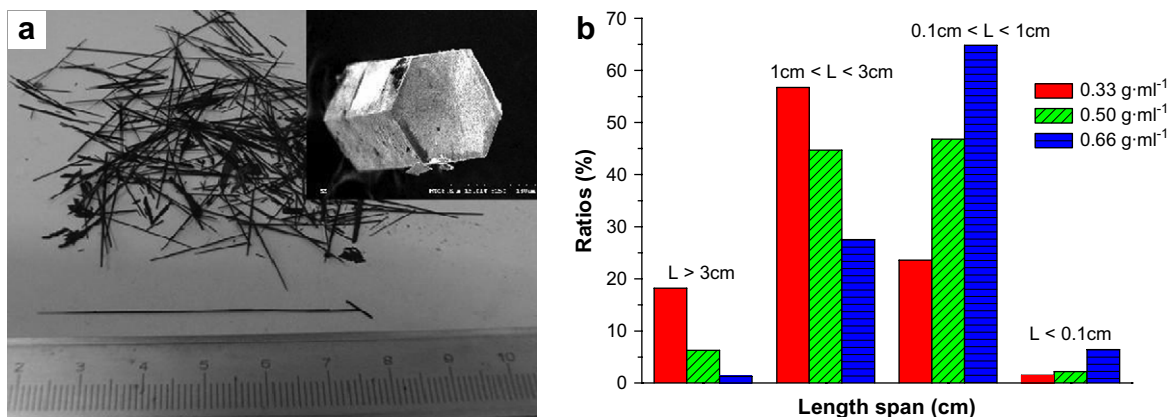
PAAm fiber solution presents an emerald green color and homogeneous system. Three absorption peaks, 251, 384, and 828 nm are observed in PANi/PAAm fiber. The 251 nm peak arises from  $\pi$ – $\pi^*$  electron transition within the benzenoid segments, while the absorption peaks at 384 and 828 nm originate from the charged cationic species known as polarons [32]. These peaks indicate that PANi reacts with doped HCl in PANi/PAAm fiber and exists in its conducting form, i.e. emeraldine salt, which is similar to that obtained by either chemical or electrochemical methods. Compared with pure PANi powders, the polaron transition absorption band at 778 nm is red shifted to 828 nm for PANi/PAAm fiber, which is due to the lower energy band transition for PANi/PAAm fiber than that for PANi powder, and indicates a longer  $\pi$  conjugation bond length in the centimeter-scaled PANi/PAAm fiber than in PANi powder. The longer  $\pi$  conjugation bond in the PANi/PAAm fiber is available to enhance the conductivity of PANi/PAAm fiber.

Because the polymerization conditions for ANI is similar to the conditions for AAm, considering the monomer/initiator ratio and reaction conditions in our experimental, it is suggested that a copolymerization between ANI and AAm monomers takes place to form PANi/PAAm copolymers. However, the mechanism of the copolymerization must be studied further. The chemical composition, conductivity and presented color of the resultant fiber further confirm the formation of PANi/PAAm.

### 3.2. The morphology and mechanism

As shown in Fig. 2a, in an optimized condition, the resultant PANi/PAAm fibers have a cross-section of hexagonal prism, diameters of 200–400  $\mu$ m, and length varying from millimeters to several centimeters, and the longest fiber is about 6 cm. The longest fiber grows in an AAm concentration of 0.33 g ml<sup>-1</sup>. With increasing of AAm concentration, the length and diameter of product decrease rapidly (Fig. 2b). Accordingly, we obtain a simple method to control the size (length and diameter) of PANi/PAAm fibers.

The morphology of PANi/PAAm fiber depends on reactant and medium. When no AAm monomer or AAm concentration lower than 0.25 g ml<sup>-1</sup> in the reaction system, spherical nanoparticles with diameters ranging from 100 to 300 nm are obtained (Fig. 3a). When the concentration of HCl is 2.0 M, the resulting PANi product is serrated lamella (Fig. 3b).



**Fig. 2.** (a) PANi/PAAm fibers prepared under optimized conditions; (b) the length span of the PANi/PAAm fibers prepared in AAm concentration of  $0.33 \text{ g ml}^{-1}$  (red column),  $0.50 \text{ g ml}^{-1}$  (green column) and  $0.66 \text{ g ml}^{-1}$  (blue column), respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

From the above, the AAm concentration is a key factor influencing the morphology of the fiber. It is well known that polymer can be used as template to fiber growth [33]. Under a higher AAm concentration, AAm monomers crosslink to form three-dimensional PAAm network [34,35], which cannot be used as a template to grow PANi fiber. Contrarily, under a lower AAm concentration, AAm monomers cannot crosslink effectively and only exist in small molecules, which PANi fiber also cannot grow. Under a suitable AAm concentration, the AAm monomers are bond to form one-dimensional PAAm chains, which act as the in-situ generated seeds in directing the fibriform morphology of the final product. This explanation is different from Zhang et al. [36,37] that PANi nanofibers prepared in chemical oxidative polymerization with an oxidant were resulted from the rod-like structure of oxidant ion clusters formed during the induction period.

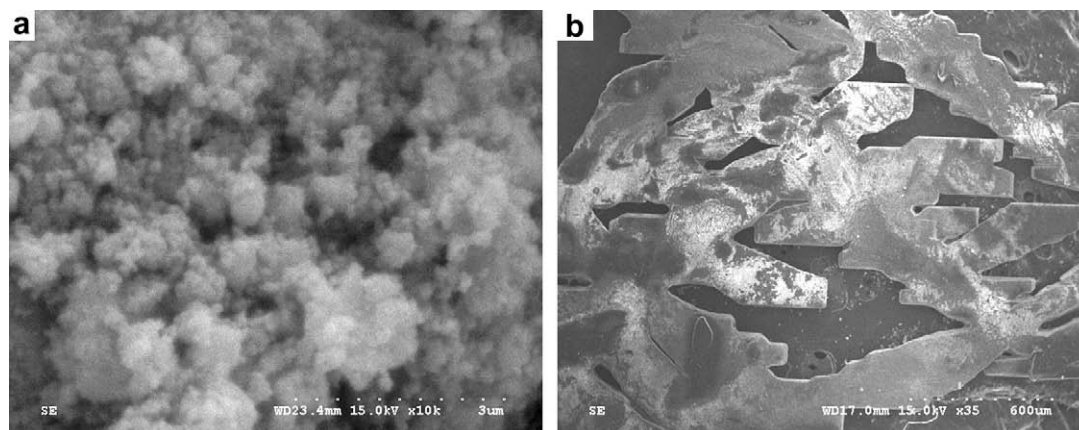
### 3.3. Conductivity and yield

Fig. 4a shows the dependence of conductivity and yield of PANi/PAAm fibers on KPS dosage (HCl concentration at 1.0 M). The conductivity of fiber increases with the increase of KPS dosage in the range of 0.6–1.0 ( $\text{mol}_{\text{KPS}}/\text{mol}_{\text{ANI}}$ ), beyond a molar ratio of 1.0, the conductivity decreases. KPS is an initiator for the polymerization of AAm and an oxidant for PANi. A smaller KPS dosage is not enough to construct PAAm chain, while high concentration of KPS will cause an overoxidation of PANi chains and the intense

polymerization of AAm (to form 3D PAAm, instead of 1D PAAm chain). Accordingly, to obtain the highest conductivity of the fiber, a molar ratio of KPS to ANI of 1 has been experimentally determined to be better.

KPS has a similar influence on the yield of PANi fiber as on the conductivity, but the maximum yield appears at the molar ratio of KPS to ANI at 1.2 (Fig. 4a). It is well known that the conductivity depends on the length of PANi fiber, and the yield depends on the quantity of PANi fiber. In the KPS dosage range from the molar ratio 1.0 to 1.2, the length of PANi fiber decrease and the quantity of the fiber increase due to the overoxidation for PANi chain and the formation of crosslinked PAAm by KPS. Once the KPS dosage exceeds the molar ratio of 1.2, both conductivity and yield of PANi fiber increase with the increase of KPS dosage.

Fig. 4b shows the dependence of conductivity and yield of PANi/PAAm fibers on HCl concentration (molar ratio for KPS to AAm at 1:1). The conductivity of PANi/PAAm comes from the protonated PANi, higher HCl concentration results in the more protonated PANi and higher conductivity. Therefore, the conductivity of the PANi/PAAm fibers increases from  $9.36 \times 10^{-4}$  to about  $3.7 \text{ S cm}^{-1}$  when the HCl concentration changes from 0.1 to 1.5 M (Fig. 4b). Similar phenomena were also found by Kang et al. [3]. On the other hand, the yield of PANi/PAAm fiber increases with the increase HCl concentration from 0.1 to 1.0 M. Beyond the concentration of 1.0 M, the yield decreases with the increase of HCl concentration. The oxidative polymerization mechanism of PANi has been investigated



**Fig. 3.** (a) PANi/PAAm prepared in a low AAm concentration ( $<0.25 \text{ g ml}^{-1}$ ); (b) PANi/PAAm prepared in higher AAm, NMBA or HCl dosages.

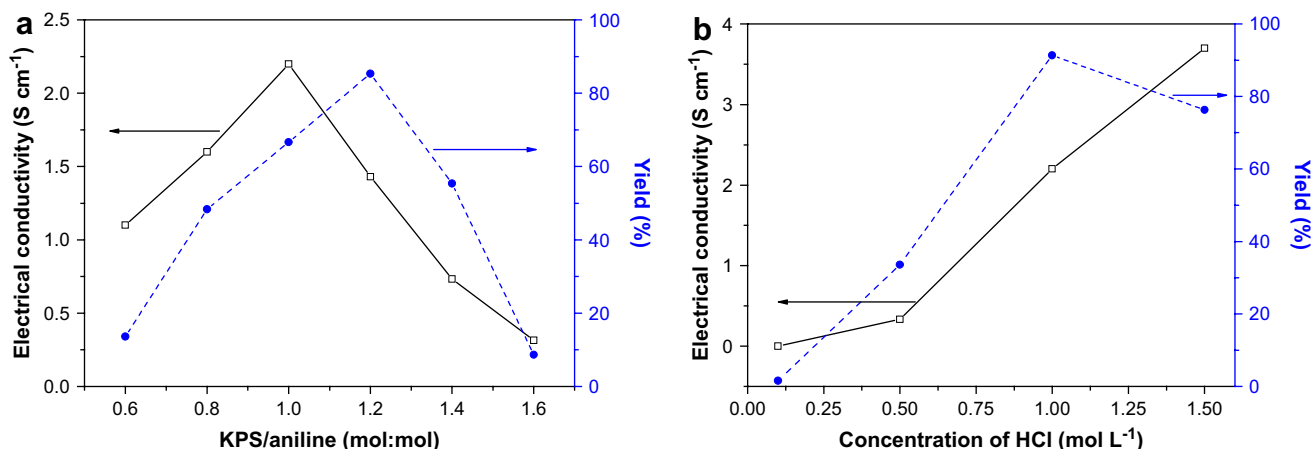


Fig. 4. Electrical conductivity and yield of PANi/PAAm fibers as a function of KPS dosage (a) and HCl concentration (b). Polymerization conditions:  $W_{AM}/W_{ANI} = 5.0$ ,  $W_{NMBA}/W_{AM} = 0.001$ ,  $V_{ANI}/V_{HCl(1.5M)} = 1:15$ , reacted at 80 °C for 30 min; and growth at 0 °C for 6 h.

widely. According to most authors [3], the formation of PANi fibers has an optimized pH condition. HCl concentration at 1.0 M has been experimentally determined by us to be better.

#### 4. Conclusion

In summary, a centimeter-scaled PANi fiber is synthesized by an aqueous oxidative polymerization of ANi monomers in the presence of oligo-AAm. The fibers are validated as PANi/PAAm copolymers and PANi exist in high conductive emeraldine salt state. The morphology, conductivity and yield of the copolymer can be devised by controlling the feed compositions and preparation conditions without templates. Under polymerization conditions:  $M_{AM}/W_{ANI}$  at 5.0,  $W_{NMBA}/W_{AM} = 0.001$ ,  $V_{ANI}/V_{HCl(1.5M)} = 1:15$ , reacted at 80 °C for 30 min; and growth at 0 °C for 6 h, a hexagonal PANi/PAAm fiber with conductivity of 3.7 S cm<sup>-1</sup> and length of 6 cm is obtained. It is suggested that the oligo-acrylamide acted as in-situ seeds directs the fibriform morphology of the fiber.

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