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# Study on Nanofibers of Polyaniline via Interfacial Polymerization

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*Uniform polyaniline nanofibers were prepared by interfacial polymerization. The nanofibers had a diameter of 80 nm and a length of about 1 μm. The effect of centrifugal force on the morphology of the nanofibers is discussed. In situ UV-Vis spectra indicated that the interfacial polymerization process was similar to the solution polymerization process. An "expanded-partly doped" stage of interfacial polymerization was observed for the first time in the in situ UV-Vis spectra.*

**Keywords** poyaniline, conducting polymer, nanofibers, interfacial polymerization, UV-Vis spectra

## Introduction

Since intrinsic conducting polymers (ICPs) were rediscovered in the early 1980s, a great amount of research has been carried out in the field of potential applications including lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings, and sensors (1). Polyaniline (PANI) is unique among conducting polymers because of its simple nonredox doping/dedoping chemistry based on acid/base reactions (2). In recent years, PANI with one-dimensional (1-D) nanostructures (nanowires/-rods/-tubes) has attracted much research interest since the material possesses the advantages of both low-dimensional systems and organic conductors.

In general, 1-D PANI nanostructures have been synthesized chemically or electrochemically through "hard" or "soft" templates synthesis. As reported, hard templates involve zeolite channels (3), track-etched polymer membranes (4) and anodized alumina membrane (5); whereas, soft templates include surfactants (6), micelles (7), liquid crystals (8) and thiolated cyclodextrins (9), all of which have been employed to induce the growth of the 1-D nanostructures of PANI. Physical methods, including electrospinning (10) and mechanical stretching (11) have also been used to prepare PANI nanofibers. Recently, some new methods have been developed to synthesize 1-D PANI. Among them,

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an interfacial polymerization method can produce nanofibers of PANI with a diameter of ~50 nm at the interfaces of two immiscible liquids (12). This method does not depend on any specific template or dopant. A "nanofiber seeding" technique (13) has been developed to prepare PANI nanofibers, in which a very small amount of organic, inorganic or biological nanofibers were used as seeds in the conventional chemical oxidative polymerization of aniline, resulting in bulk quantities of PANI nanofibers. In addition, Wang et al. (14) has obtained the PANI nanofibers accompanied with aggregated gold nanoparticles by conventional polymerization of aniline using the chloraurate acid ($HAuCl_4$) as the oxidant.

The interfacial polymerization process is based on the well-known chemical oxidative polymerization of aniline in the strongly acidic environment, with ammonium peroxydisulfate as the oxidant. Instead of using the traditional homogeneous aqueous solution of aniline, acid and oxidant, however, the interfacial polymerization is performed in an immiscible organic/aqueous biphasic system, to separate the byproducts according to their solubility in the organic and aqueous phases (15).

In this report, PANI nanofibers were synthesized via interfacial polymerization. The morphologies of the nanofibers were observed using SEM and TEM. The influence of physical conditions on the morphology and related properties of PANI nanofibers are discussed. The polymerization process was recorded by means of *in situ* UV-Vis spectra, by which the "long tail" phenomenon was observed. It is possibly assigned to an expanded molecular conformation of the PANI. The concept of "expanded-partly doped" stage is proposed to explain the long tail phenomenon.

## Experimental

### *Materials*

Aniline, ammonium peroxydisulfate (APS), chloroform, benzene, xylene, acetone, and hydrochloric acid (37%) were purchased from Sinopharm Group Chemical Reagent (Shanghai). Aniline was distilled under reduced pressure, and other reagents were used as received without further treatment. Water was deionized prior to use by a Millipore apparatus (Direct-Q).

### *Preparation and Purification*

The typical interfacial reaction was performed in a 50 ml glass cuvette at room temperature (Figure 1). Ammonium peroxydisulfate (APS) (2 mmol) was dissolved in 25 ml of a 1.0 mol/l solution of hydrochloric acid in a 50 ml cuvette. A solution of aniline (8 mmol) in chloroform (25 ml) was added gently along the sides of the cuvette using a syringe. The aniline/chloroform solution forms the lower organic layer and the APS solution forms the upper aqueous layer. The parallel synthesis was carried out at a low temperature, 0–5°C.

To remove excess acid and byproducts from the polymerization, the as-prepared PANI was purified by removing the organic phase, and the aqueous phase was centrifuged, resulting in a dark green precipitate. The precipitate was washed with acetone and distilled water several times. The doped PANI in the form of powder was obtained after drying in a dynamic vacuum.

### *Characterization*

The morphology of the nanofibers obtained above was observed using transmission electron microscopy (Hitachi-800 TEM) and scanning electron microscopy

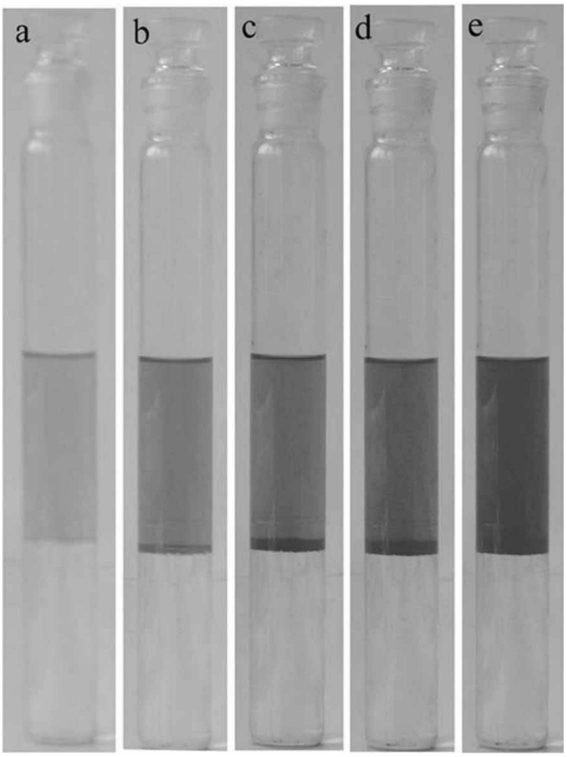


**Figure 1.** The formation of PANI nanofibers via the interfacial polymerization: the top phase (aqueous phase) is APS/aq. 1.0 M HCl, and the bottom layer is aniline dissolved in the chloroform. From a to e, the reaction times are 10, 60, 90, 140, and 200 sec, respectively. The dark doped PANI is produced in the aqueous phase.

(JSM-5600LV SEM). Fourier-transform infrared analyses were recorded on Nexus-670 FTIR spectrophotometer (Nicolet Instruments, USA). The doped PANI powder was pressed into pellets at 30 MPa for 2 min, and the conductivity of the compressed pellets was measured by a standard four-probe technique under 45% RH. The contact angle with water for the compressed pellet of PANI-HCl obtained via interfacial polymerization was measured on a contact angle system (OCA30, Dataphysics).

The UV-visible spectra of the PANI as aqueous dispersions were recorded on a PE Lambda35 spectrometer. To monitor the polymerization process more easily *in situ*, a solution of aniline in benzene was used as the top organic phase and acidic APS solution was used as the bottom aqueous phase. The height of the sample cell was adjusted to ensure UV or visible radiation was just below the interface because the PANI would diffuse into the aqueous phase. In this reaction, the aniline to APS molar ratio was kept at 4 to 1. The *in situ* UV-Vis spectra were recorded from 200–1100 nm with the scanning speed of 900 nm/min. Similarly, the UV-Vis spectra of a conventional solution polymerization were recorded by adding the acidic APS solution into the acidic aniline solution all at once. The aniline to APS molar ratio was kept at 2 to 1.

## Results and Discussion

Interfacial polymerization was carried out in an aqueous/organic biphasic system (Figure 1) with the aniline/chloroform solution as bottom phase and APS solution forming the top phase. During the very early stages of the reaction, a gradual darkening can be observed at the interface followed by thin streams of dark blue-green material, diffusing gradually into the aqueous phase. With further reaction, the aqueous phase becomes dark, and the entire aqueous phase is filled homogeneously with dark green PANI after 2 h, as shown in Figure 1. On the other hand, the organic phase appears red-orange, likely due to the formation of aniline oligomers. The aqueous phase is then collected, and the by-products removed. The average diameter of the nanofibers obtained above was ~80 nm, which will be discussed later in detail.

The hydrophobic monomer aniline is soluble in chloroform, and its oligomer can be dissolved in the organic phase. However, why is the polymer, PANI, suspended in the aqueous phase? To explain it, we measured the hydrophilicity of PANI. Figure 2 shows a photograph of a water drop on a PANI-HCl pellet. The PANI doped by HCl exhibits hydrophilic behavior since the contact angle with water is 56°. Therefore, the doped PANI diffuses into the aqueous phase once the polymer is produced at the interface. In another experiment, in which xylene was used as the organic phase at the top, the PANI produced via the interfacial polymerization diffuses into aqueous phase at the bottom.

Figures 3(a) and (b) show typical scanning electron microscopy images of the PANI nanofibers produced via interfacial polymerization using hydrochloric acid as a dopant and chloroform as an organic solvent, at room temperature and 0–5°C respectively. The diameters of the nanofibers are ~80 nm, and their lengths are from 200 nm to several micrometers. It was found that the synthesis of nanofibers appears to be insensitive to polymerization temperature; in the range between room temperature and near 0°C, the nanofibers exhibit similar morphology.

The traditional oxidative chemical polymerization is known to produce granular PANI, while interfacial polymerization yields nanofibers. The reason for the formation of nanofibers during interfacial polymerization is not clear. A possible explanation is as

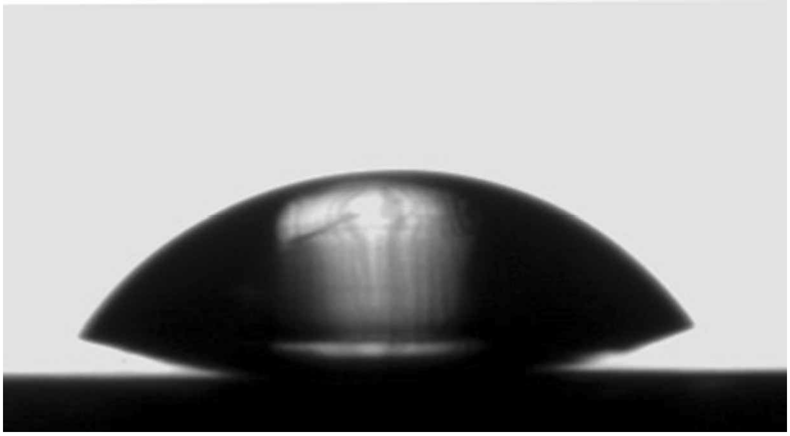


**Figure 2.** Photograph of a water drop on the compressed pellet of PANI-HCl nanofibers exhibiting the hydrophilic behavior.

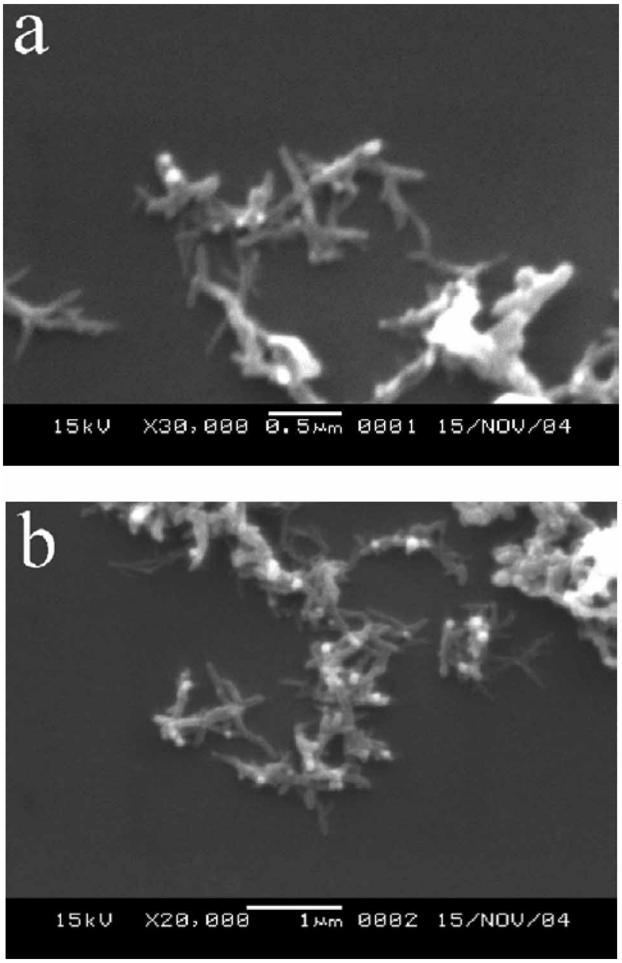


**Figure 3.** SEM images of PANI nanofibers produced via interfacial polymerization in a water/chloroform system at different polymerization temperature: (a) room temperature, (b) 0–5°C.

follows: in the conventional chemical polymerization process a small quantity of PANI nanofibers also forms at an early stage (16). As more oxidant is fed into the reaction, the reactive nanofibers were surrounded by abundant monomer and oxidant. The free radical reaction proceeds and finally turns them into irregularly shaped granular PANI. If the further reaction can be suppressed after the nanofibers appear at the early stage, bulk quantities of PANI nanofibers could be produced. In the interfacial polymerization, the monomer and the oxidant separate at the interface, so only at the interface there coexist all the components (monomer, oxidant and dopant) needed for the polymerization reaction. So the radical reaction occurs at the interface and results in PANI nanofibers. Since the newly formed PANI are doped by the dopant acid and rapidly diffuse into the aqueous phase, they thus avoid being surrounded by the abundant monomer. This may be the mechanism for the nanofibers formation in the interfacial polymerization.

To discuss the effect of an outside force on the morphology of the nanofibers, we designed an experiment in which the polymerization process is performed under centrifugal force. The aqueous phase including APS at the bottom and an organic phase including benzene and aniline were carefully transferred to the centrifuge tube. The reaction was performed at different centrifuging speed. Figure 4 shows TEM images of PANI prepared via the interfacial polymerization at the different centrifugal force. As shown, the morphology of the products can be strongly affected by the centrifugal effect.

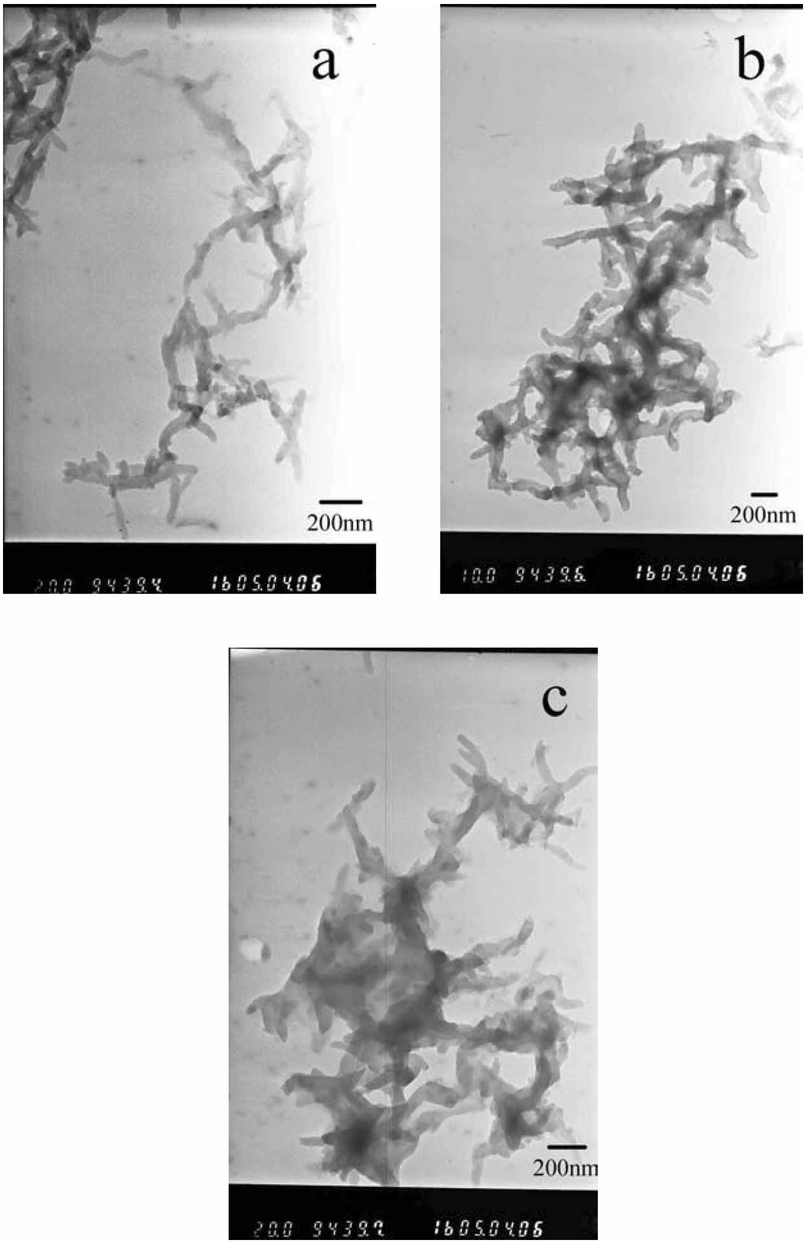


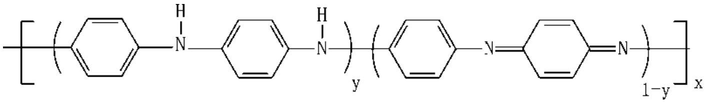
**Figure 4.** TEM images of PANI nanofibers at the different centrifuged speed: (a) 1000 rpm, (b) 2000 rpm, and (c) 4000 rpm (scale bar = 200 nm).

The TEM image at low centrifuge speed (1000 rpm), as shown in Figure 4a, exhibits clear nanofibers with diameters of 80–90 nm, similar to the SEM images in Figure 3. However, for the same system reacting at higher centrifuge speeds (2000 rpm (Figure 4b) and 4000 rpm (Figure 4c)), some of the products appear as irregular flakes. With increasing the centrifuge speed, the products include more irregular flakes. The possible reason for the difference is as follows: Once the nanofiber appears at the interface between the aqueous and organic phase, the centrifugal effect forces the newly formed nanofibers to be compressed. The higher centrifugal force used, the more portions of the irregular flakes were produced.

The electrical conductivity of a pressed pellet of PANI nanofibers made with 1.0 M HCl was about 0.35 S/cm. This is comparable to the conductivity reported for PANI using interfacial polymerization (15).

A comparison of FTIR spectra of PANI-HCl obtained by interfacial polymerization and conventional chemical polymerization is shown in Figure 5. FTIR of the two PANI give similar spectra, indicating a similar backbone polymer structure. The characteristic peaks at 1567 and 1483 $cm^{-1}$ can be assigned to the stretching vibration of the quinoid ring and benzenoid ring, respectively. The bands at 1298 and 1240 $cm^{-1}$ correspond to C-H stretching vibrations with aromatic conjugation. The result indicates that the backbone structure of the PANI-HCl nanofibers obtained in this work is identical to that of the granular PANI-HCl synthesized by the conventional method (17).

As a background, a brief introductory summary of the doping of the PANI is necessary to understand the intrinsic and doped structures. The form of PANI has the generalized composition, represented by the index $y$ (reduced = unity) and $1 - y$ (oxidized = unity) as indicated in the chemical structure:



where $x$ is the polymerization degree. The completely reduced form of PANI, leucoemeraldine (LB), is obtained when $(1 - y) = 0$. The oxidized form $(1-y) = 1$ is called

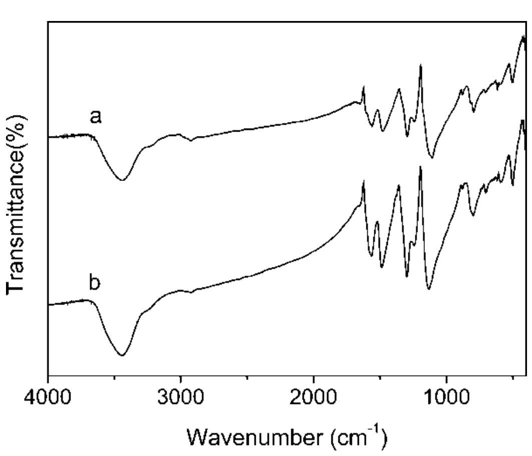


**Figure 5.** FTIR spectra of PANI-HCl obtained via different methods: (a) conventional chemical polymerization, (b) interfacial polymerization.

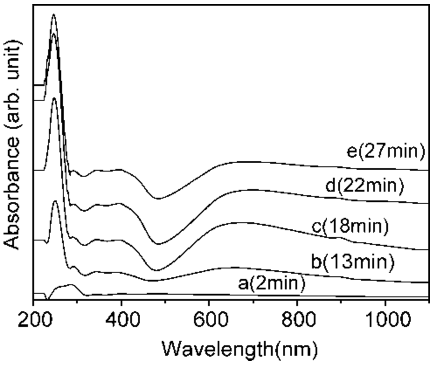


**Figure 6.** Time-dependent UV-Vis spectra of the formation of PANI in the interfacial polymerization.

pernigraniline (PB), while $(1-y)=0.5$ corresponded to the emeraldine base (EB) (18). The imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts, the degree of protonation depending on the pH of the aqueous dopant acid.

Time dependent UV-Vis spectra of the interfacial polymerization in a sample cell are shown in Figure 6. The bottom curve is the first scan taken at 2 min after formation of the interface. Curve b of Figure 6 has peaks around 325 and 620 nm, indicating the newly formed PANI is in EB state. The spectra then show that the intrinsic state gradually transforms into the doped PANI with peaks around 390 and a board band commencing at 700 nm (curve e of Figure 6). In the interfacial polymerization, the radical reaction occurs at the interface and results in the intrinsic state PANI nanofibers. Then, the freshly formed PANI are doped by the dopant acid and rapidly diffuse into the aqueous phase. *In situ* UV-Vis spectra of a rapidly mixed reaction were also recorded, for comparison to the interfacial polymerization. Figure 7 records the changes of the UV-Vis spectra for the conventional solution polymerization with the reaction time. The reaction system possesses a similar trend in UV-Vis spectrum to the interfacial polymerization. For both reaction systems, the intrinsic PANI is produced at the early stage of the reaction, and then it converts to the doped PANI.

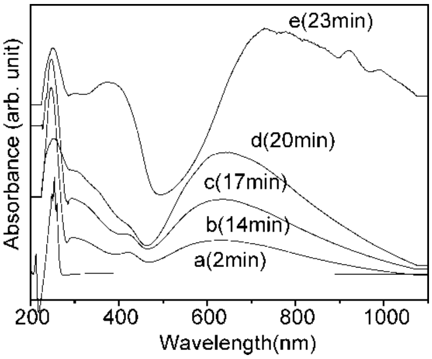


**Figure 7.** Time-dependent UV-Vis spectra of the PANI in a rapidly mixed reaction. The selected reactions (min) are shown at the spectra.

In general, for the charged PANI chains, electrostatic repulsion makes the chain a more open, expanded coil-like structure. MacDiarmid found in his work, that the conformation change was accompanied by a significant change in the polymer's electronic spectrum (19). It is considered that any factors that inhibit electrostatic repulsion on a macromolecular chain will lead to more tightly coil structures. With the doping process, the combination of the negative ions with the imine nitrogen atoms of the PANI chain tends to form ion pairs, and release the repulsion, resulting in a compact coil conformation of the chain. In the interfacial polymerization, the monomer and the initiator are separated by the boundary between the aqueous and the organic phases; polymerization occurs only at this interface. Since there is very limited dopant acid at the interface compared to the conventional polymerization, the macromolecular chains are partly doped. In this stage, it is reasonable to believe that the conformation of the chain is partly an expanded coil structure. Maybe it is the rigid and expanded chain structure of the PANI that serves as a template-like substance and leads to the 1-D nanofibers at the early stage. For some controlled conditions, the "expanded-partly doped" stage of interfacial polymerization was observed in our laboratory. As shown in Figure 6, the characteristic peak of intrinsic PANI appears at 630 nm at an early period of the polymerization, it then converts to a broad absorption band commencing at 700 nm (curve e of Figure 6). This long tail phenomenon is consistent with delocalization of electrons in the polaron band promoted by a "straightening-out" of the polymer chain as its coil-like structure becomes more expanded with concomitant reduction in $\pi$-defects caused by ring twisting (19).

## Conclusions

We studied the influence of centrifugal force and reaction temperature on the morphology of PANI nanofibers synthesized by the interfacial polymerization method. The formation of nanofibers appears to be insensitive to polymerization temperature, while a centrifugal force in the period of polymerization has an obvious influence on the morphology of the nanofibers. To study the forming mechanism of nanofibers, a UV-Vis spectrometer was employed to trace the synthetic process. The results show that the newly formed nanofibers are intrinsic polyaniline, and then nanofibers are doped by the acid. The molecular conformation of the newly formed polyaniline at the interface may be an expanded coil structure. It is possible that the rigid and expanded coil conformation served as a molecules template to form the 1-D nanofibers.

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