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# Cyclic polyaniline nanostructures from aqueous/organic interfacial polymerization induced by polyacrylic acid

Siwei Liu, Kaizheng Zhu, Yi Zhang, Jiarui Xu*

*PCFM Lab, Materials Science Institute, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, PR China*

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**Abstract**

Cyclic nanostructural polyanilines have been synthesized by means of a simple modified aqueous/organic interfacial polymerization with the aid of polyacrylic acid, and yet only nanofiber nanostructural polyanilines were obtained by conventional interfacial polymerization in the presence of polyacrylic acid. These nanostructures were characterized using TEM, X-ray diffraction and UV−vis. The cyclic polyaniline nanostructures were formed by severe secondary overgrowth through the electrostatic interaction between aniline/oligoaniline and polyacrylic acid chains. The average diameter of the obtained cyclic-structure was *ca.* 400 nm and its conductivity was 1.06 S/cm.

*Keywords:* Cyclic polyaniline; Polyaniline nanostructure

## 1. Introduction

Polyaniline (PANi) has been investigated widely due to their unique electro-optical properties and market potential, good environmental stability, facility of synthesis (chemical or electrochemical oxidation of aniline) and inexpensive monomers, etc. [1−3]. In recent years, PANi nanostructures, including nano-wires, nano-rods, nano-tubes and so on, have attracted much more attention along with the development of nanotechnology. They can combine the advantages of organic conductors with low-dimensional systems and therefore create interesting physicochemical properties and potentially useful applications, thus such research would create new opportunities. To achieve PANi nanostructures, there are many different routes, including both chemical and electrochemical polymerization of the monomers by template, template-free or even physical methods such as electrospinning and mechanical stretching [4−7]. Among them, the aqueous/organic interfacial polymerization is a powerful method [8−12]. However, whatever synthetic routes have been used, the resultant PANi nanostructures are usually nano-rods, nano-wires, nano-tubes, or even helical shaped [8−19].

In this report, we describe a modified facile synthetic method to synthesize cyclic PANi nanostructures *via* a simple aqueous/organic interfacial polymerization process with the aid of polyacrylic acid (PAA, $M_n = 4.5 \times 10^4$, $M_w = 5.8 \times 10^4$, PDI = 1.3). The average diameter of the obtained cyclic PANi nanostructures is *ca.* 400 nm. Up to date, there are very little reports on the synthesis of such cyclic morphology of PANi nanostructures.

## 2. Experimental

The experiments were carried out by two different ways. Method-**I**: condensed hydrochloric acid (HCl, 3.0 mL), PAA (0.10 g) and ammonium persulfate (APS, 1.14 g) were dissolved in 100 mL of $H_2O$ in a 400 mL beaker, then petroleum ether (PE, 100 mL) was added to the surface of the water solution. Ten minutes later, distilled aniline (0.72 g) was added to the petroleum ether carefully. The reaction was then started at the interface of petroleum ether and water. Method-**II**: dichloromethane (DCM, 100 mL) was added to a 400 mL beaker, condensed HCl (3.0 mL), PAA (0.10 g) and ammonium

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* Corresponding author. Fax: +86 20 8411 1081.
*E-mail address:* xjr@mail.sysu.edu.cn (J. Xu).

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persulfate (1.14 g) were dissolved in 100 mL of $H_2O$, the mixture was then added to the surface of dichloromethane. Ten minutes later, aniline (0.72 g) was carefully added to the dichloromethane phase through a tubule. Both reactions were carried out under room temperature for 6 h, filtrated through Buchner funnel and washed with dimethyl formamide to remove organic compounds such as PAA and low molecular PANi, then washed with distilled water several times to remove inorganic compounds. The resultant products were dried in a vacuum oven under 80 °C for 24 h.

## 3. Results and discussion

The two similar synthetic routes produce completely different micro-morphologies of PANi. As shown in the transmission electron microscope (TEM, JEM-2010HR) photographs in Fig. 1, sheet-like shaped crystals were produced (PANi-**I**-1 and PANi-**I**-2) when water phase is in the lower layer of Method-**I**; however, rod-like nano-wires were obtained (PANi-**II**-1 and PANi-**II**-2) when water phase is in the upper layer of Method-**II**. It is very interesting to notice that the

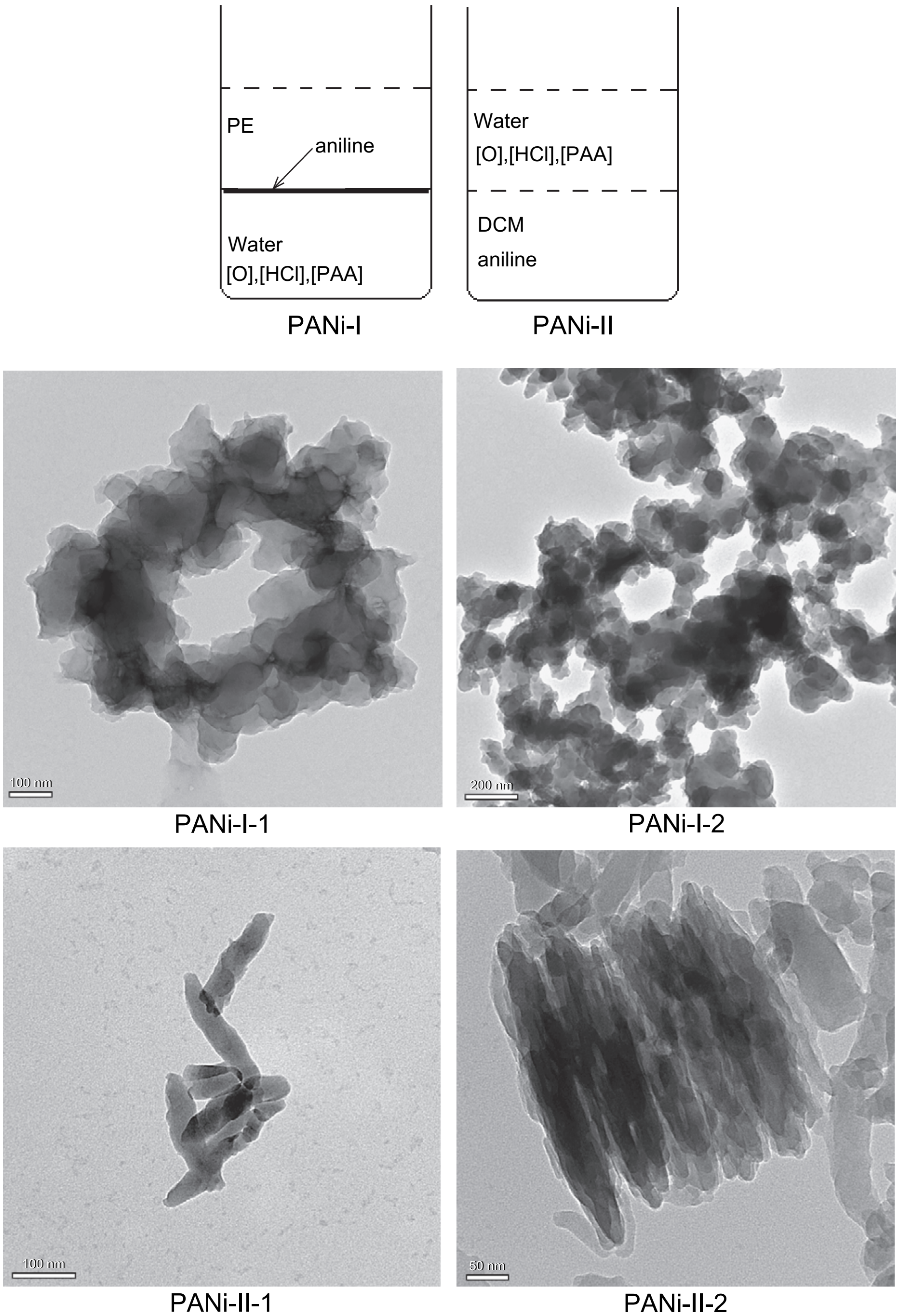

Fig. 1. TEM images of PANi nanostructures synthesized by interfacial polymerization induced by PAA.

PANi nanostructures produced from Method-**I** have aggregated cyclic nanostructures with average diameter about 400 nm. However, in Method-**II**, the generated rod-like PANi nanostructures can aggregate also, but to form more compact linear raft-like ones and not the cyclic shaped structures as observed for Method-**I**.

To understand the completely different aggregation morphologies of the PANi nanostructures obtained by the interfacial polymerization processes in the two similar conditions, we ascribe it to the interaction of the functional groups ($-NH_2$/NH and $-COOH$) between aniline/oligoaniline (growing PANi chains) and PAA chains throughout the polymerization process. When all the reaction reagents were added, the reaction started at the aqueous/organic interface only, with aniline being in the organic phase and the oxide reagent in aqueous phase. On the spot of the reaction at the interface, the $-COOH$ groups of PAA would induce aniline/oligoaniline to align with PAA chains' direction [20,21].

In Method-**I**, because aniline cannot dissolve in PE but can slightly dissolve in water, aniline will form a very thin film between PE and water phase when added to PE. It should be noticed that the density of aniline is very close to that of water; sufficient care is required when adding aniline to PE to form a thin film at the interface. The existence of the PE layer can make a steadier thin aniline layer than when the aniline layer is exposed to air directly. Along with the polymerization of aniline at the interface of aniline/water, the size of PANi particles grow larger and larger. Due to the gravity and hydrophilic nature [9], the generated PANi diffuse into water phase, leaving the interface available for further reaction [8,22]. Such reaction step will merely produce pure nanofiber structure [8–12]. However, because of slight solubility in water, aniline will diffuse slowly into water phase, especially in the acid aqueous. In aqueous solution, due to its hydrophobic property, aniline will form micro-sphere-like particles and attach to the growing PANi chains easily. These particles will grow continually on their surface when exposed to ammonium persulfate. This is the so-called secondary overgrowth. As a result, the morphology of PANi is flake crystal in part and amorphous in bulk. However, these growing particles are induced by PAA chains through electrostatic interaction along with the severe secondary overgrowth process. Therefore, the generated PANi flake crystals will aggregate cyclic nanostructures circling around PAA chains. Because the aggregation state is formed by the electrostatic interaction of $-NH_2$/$-NH$ and $-COOH$ groups, the PANi nanostructures are not very compact. This can be supported by its X-ray spectrum (Fig. 2), which is very similar to that of the PANi powder obtained by conventional approach without any extra inducement.

As to Method-**II**, aniline can be easily dissolved in DCM; it is impossible for aniline to diffuse into the water phase. At the DCM/water interface, the concentration of aniline in Method-**II** is always lower than in Method-**I**. Along with the polymerization, since the generated PANi is in its hydrophilic emeraldine salt form, it will diffuse away from the reactive interface into the water layer [9]. Further oxidative polymerization is forbidden as there is no more aniline monomer in the water phase and the severe secondary overgrowth should be avoided [22]. Therefore, the resulted PANi forms its own intrinsic nanofibrillar morphology [9,22], which will aggregate more and more compact nanostructures in the later stages through electrostatic interaction of itself because each single nanofiber formed in the initial stage is aligned. This can be explained by the X-ray spectrum that its crystallinity is higher than that of PANi obtained by Method-**I** (Fig. 2).

We also investigated the UV–vis spectra of these PANi products with different morphologies (Fig. 3). In order to retain their original nanostructures, these PANis were dispersed in water by ultrasound prior to measurement. The characteristic bands of PANi-**I** and PANi-**II** appear at about 340, 440,

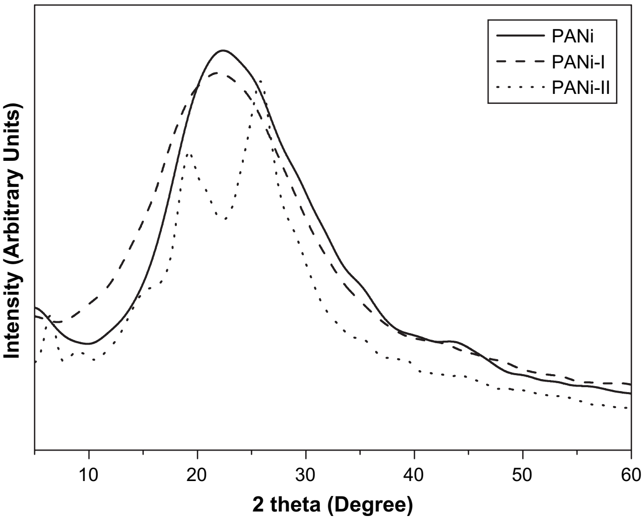

Fig. 2. XRD scattering patterns of PANi powder. PANi was obtained through conventional method, chemical oxidative polymerization in HCl solution by APS.

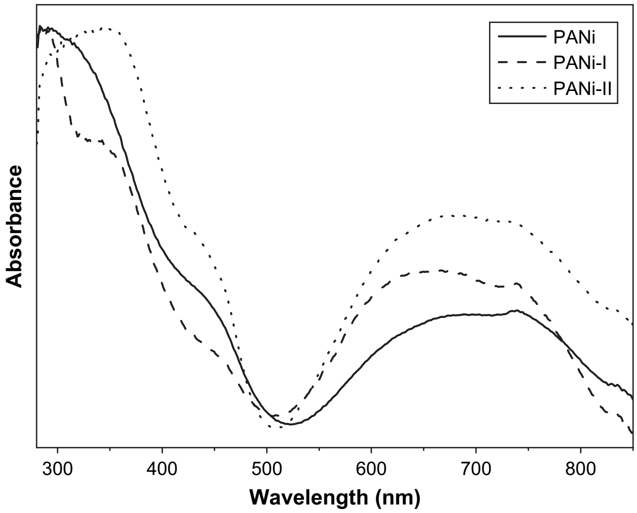

Fig. 3. UV–vis spectra of PANi, dispersed in water. PANi was obtained through conventional method, chemical oxidative polymerization in HCl solution by APS.

and 670 nm, which are attributed to π–π*, polaron–π* and π–polaron transitions, respectively [23]. Their spectra are slightly different in intensity of absorption. The more intensive absorption of PANi-**II** indicates that it has more compact and regular microstructure than that of PANi-**I**. In other words, the conjugated degree of PANi-**II** is greater than that of PANi-**I**. (The UV–vis spectra have been already normalized.)

The conductivity was determined by a standard four-probe technique. Both PANi-**I** and PANi-**II** were dissolved in *N*-methyl-2-pyrrolidone (NMP) and doped with *d*-camphor-10-sulfonic acid. The films were fabricated by coating the solution onto slide quartz glass, followed by the evaporation of the solvent under 80 °C. The conductivity of the film was estimated to be 1.06 S/cm for PANi-**I** and 1.34 S/cm for PANi-**II**. This was consistent with the difference in their microstructures. The compact raft-like nanostructure of PANi-**II** has slightly higher conductivity than that of PANi-**I**. We assume the microstructures have been destroyed by NMP before forming thin films. Similar result was observed from their UV–vis spectra in their NMP solution.

## 4. Conclusion

In summary, we have successfully synthesized cyclic nanostructural PANi *via* a simple modified aqueous/organic interfacial polymerization with the aid of PAA. The cyclic nanostructures are formed by severe secondary overgrowth through the electrostatic interaction between aniline/oligoaniline and PAA chains. The average diameter of the obtained cyclic-structures is *ca*. 400 nm. The results of XRD and UV–vis show that PANi-**II** has more conjugated structure than PANi-**I**.

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