Polymer Bulletin 60, 1–6 (2008)
DOI 10.1007/s00289-007-0828-z

Polymer Bulletin

Controlled Synthesis of Linear Polyaniline Tubes and Dendritic Polyaniline Fibers with Stearic Acid

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Received: 2 May 2007 / Revised version: 13 June 2007 / Accepted: 17 August 2007

Summary

One dimensional linear polyaniline (PANI) tubes (with cavity about 2-3 nm) and three dimensional dendritic PANI fibers (with different length) have been synthesized by chemical oxidation polymerization of aniline doped with stearic acid at room temperature. The shape of the as-prepared PANI could be easily tuned from line to dendriform and to network simply by controlling the concentrations of aniline and stearic acid. Scanning electron microscopy and transmission electron microscopy were applied to investigate the various kinds of morphologies. UV-vis absorption spectra and Raman spectra suggested these as-prepared PANI were in conductive emeraldine state and the various kinds of structures could affect their property.

Introduction

One dimensional (1D) micro- and nanostructured intrinsically conducting polymers (ICPs), such as fibers and tubes have recently attracted many attentions because of their unique properties and promising applications in materials science and micro/nanodevices [1]. Among intrinsically conducting polymers (ICPs), PANI is unique due to its good environmental stability, easy of synthesis, and adjustable electrical properties [2]. Low-dimensional nanostructured PANI, such as nanoparticles, nanofibers and nanotubes, nanosheets and nanobelts, have received considerable attention owing to their huge potential applications, especially in polymeric conducting molecular wires [3], light-emitting and electronic devices [4], chemical sensors [5], and biosensors [6].

In general, PANI nanofibers and nanotubes have been synthesized by chemical or electrochemical oxidation polymerization of the aniline monomer with the aid of either “hard” templates or “soft” template. Porous materials such as zeolite [7], anodized alumina [8] and track-etched polymeric membranes [9], have been used as “hard” templates to fabricate PANI nanofibers and nanotubes. PANI nanofibers and nanotubes also have been synthesized by using “soft” template such as liquid crystalline phases [10], micelles [11], and reverse microemulsion [12]. Following the extensive interests in linear low dimensional nanomaterials, dendritic nanomaterials have attracted another increasing attention due to their unusual structure and superior performances [13, 14]. One of the promising properties is their extremely low threshold value on forming network, which is rather important in condensed matter physics and materials science. Wan et al. synthesized sub-micrometer-sized junctions and dendrites of PANI via a self-assembly process [15]. Li et al. synthesized three dimensional (3D) dendritic PANI nanofibers by chemical oxidation polymerization of aniline in a C_{16}TMA surfactant gel at low temperature [16]. We have also succeeded in controlled synthesis of 3D dendritic and network PANI fibers with diameters from 30-400 nm by using salicylic acid as template and dopant at room temperature [17]. Although many methods have been used to synthesize 1D linear or 3D dendritic PANI fibers, there are no reports deals with controlling the morphologies of PANI from line to dendriform at the same time so far. Herein, we report a simple way for controlled synthesis of PANI from linear tubes to dendritic fibers and to networks via using stearic acid (SA) as "soft" template and dopant. Without using a "hard" template, linear tubes and dendritic fibers of PANI are chemically synthesized by polymerization in the presence of ammonium persulfate (APS) as the oxidant. It is found the formation mechanism of tubes and fibers are self-assembly, and SA acts in both doping and template function at the same time. When the concentration ratio of aniline to SA is adjusted properly, the morphologies of PANI can be tuned from linear tubes to dendritic fibers and to network structure.

Experimental

Chemicals

Aniline (Beijing Chem.Co.) was distilled under reduced pressure before using. Ammonium persulfate (A.R., Beijing 3rd Chemical Reagents Factory), Stearic Acid (SA) and other reagents were purchased from Beijing Chem.Co and were used as received.

Characterization

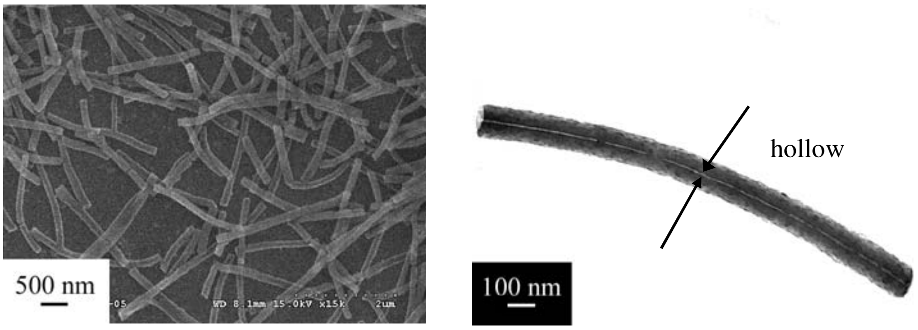
Morphologies of the as-prepared PANI were investigated with a Hitachi S-4300 field emission scanning electron microscope (SEM) and a JEOL JEM-100CX transmission electron microscope (TEM). PANI was dissolved in *m*-cresol by ultrasonication and their UV-Vis spectra were measured on a 1601UVPC UV-Visible (Shimadzu) spectrophotometer. Raman spectra were recorded by a LabRam I (Dilor) with 632.8 nm laser as the excitation wavelength. To measure the electrical conductivity of the as-prepared PANI tubes and fibers, they were compressed into pellets and measured by a standard four-probe method, using a Keithley 196 System DMM digital Multimeter.

Polymerization

0.284 g SA was dispersed in 80 ml water and 10 ml ethanol mixture solution. After stirred for 4 hours, 0.093 g aniline was added in above emulsion. Kept stirring for another 30 minutes, then stopped. 10 ml APS (1 mol/L) was added, shaking for several minutes with hand, the reaction was left for another 24 hours. During the polymerization process, a color change to dark green was observed. The resulting PANI precipitate was washed with water and ethanol for several times.

Results and Discussion

Figure 1a is a typical SEM image of PANI tubes with diameters about 200 nm that was synthesized in the reaction conditions: 0.2 mol/L aniline and 0.04 mol/L SA. It is found that more than 90% (volume fraction) of PANI tubes is about 180-220 nm diameters, and the length ranges from sub-micrometer to several micrometers. A typical TEM image (Figure 1b) shows the as-prepared PANI is interestingly internal hollow. A linear cavity with diameter about 2-3 nm is clearly found along the PANI tube center. One possible mechanism for the formation of the nanotubes is that rod-shape micelles of SA might be formed due to the hydrophobic and hydrophilic groups of SA, and the micelles act as templates in forming tubes. Due to the hydrophilic of the APS oxidant, aniline polymerization only takes place at the micelle/water interface [18]. As the polymerization proceeds, the polymerized PANI would become tubes by elongation [19]. The internal cavity thus is formed via the ordered arrangement of the hydrophobic long carbon chain of SA.

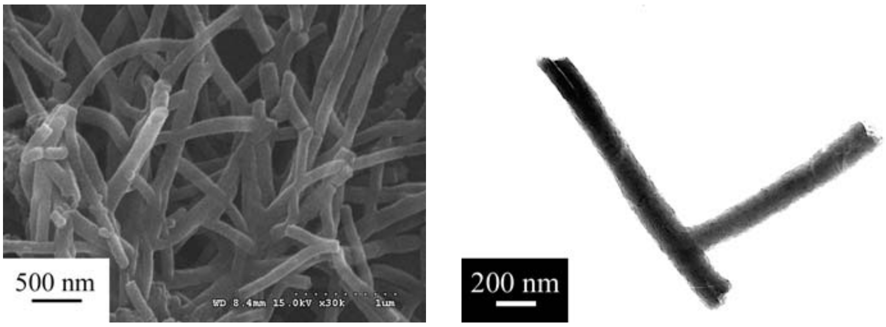


(a) (b)

Figure 1. Morphologies of PANI linear tubes synthesized with condition: 0.04mol/L SA, 0.2mol/L aniline: (a) SEM image; (b) TEM image.

The morphology of PANI could be easily controlled through adjusting the concentration ratio of aniline to SA. As figure 2a shows, dendritic PANI fibers is prepared when the concentration of SA is changed to 0.02 mol/L SA. From the typical SEM images of dendritic PANI fibers (Figure 2a), it is found the diameters of the branches are about 160-200 nm, and the lengths can be several micrometers and even longer. It is clear that these PANI fibers are inter-connected to form 3D dendritic and network structure, rather than isolated fiber. The typical TEM image (Figure 2b) of dendritic PANI shows the branches of the dendritic PANI fibers are solid instead of hollow. Similarly, the morphology of PANI changes when the concentration of SA is further decreased to 0.001 mol/L. As figure 3 shown, the diameters of the dendritic fibers decrease to about 80-120 nm, and the lengths decreased to submicrometers, short dendritic PANI rods become the dominant morphology. Some PANI nanoparticles can be also observed. The morphologies of the dendritic PANI fibers may indicate that when the concentration ratio is properly, aniline/SA can self-assemble to a special super-structure, like “gel”. Subsequent oxidation polymerization of aniline is confined in the “gel” like super-structure. This results in dendritic fibers. In addition, the super-structure of the aniline/SA is affected by the concentration of

SA. The aniline/SA with high SA concentration can effectively self-assemble into a sponge phase, which results a continuous 3D network of interconnected and branched fibers (Figure2). As the concentration of SA decreases, short-branched rod and some aggregated particles are obtained because of the lack of an effective self-assembly (Figure3).



(a) (b)

Figure 2. Morphologies of PANI dendritic fibers synthesized with condition: 0.02mol/L SA, 0.2mol/L aniline: (a) SEM image; (b) TEM image.

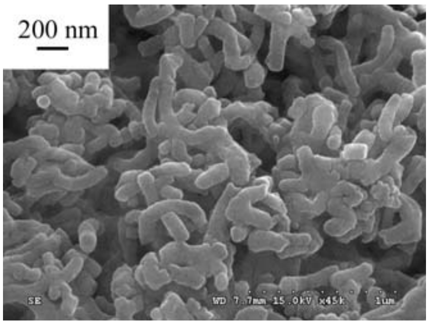


Figure 3. Morphology (SEM image) of PANI dendritic fibers synthesized with condition: 0.001mol/L SA, 0.1mol/L An.

Figure 4 is the UV-vis absorption spectra of the three typical samples. In the UV-vis absorption spectra, two peaks are observed around 319 and 422 nm, which can be assigned to the π-π* transition and the polaron band transition of the PANI backbone, respectively [20]. The results suggest that the as-prepared PANI is in a doped state. The typical absorption peak of acid-doped PANI, the p-polaron transition around 422 nm, is broader and shifts to a higher wavelength with the increasing of SA concentration. This result indicates that the doping level is higher, and the as-prepared PANI is more delocalized [21].

The doping level is changed as the changing of SA concentration, which is also conformed by Raman spectra. As shown in Figure 5, typical characteristic bands of the as-prepared PANI chains are observed in Raman spectra of both the tubes and dendritic fibers. C-C deformation bands of the benzenoid ring at 1638, 1602, and 1562 cm^{-1} are characteristic of semiquinone rings. The peak at about 1503 cm^{-1} corresponds to the N-H bending deformation band of the protonated amine. The band at 1337 cm^{-1} corresponds to the C-N·+ stretching mode of the delocalized polaron charge carriers, and the strong intensity of this band suggests that these entities are present in high concentration. The band at 1257 cm^{-1} can be assigned to the C-N stretching mode of the polaron units. The benzene C-H bending deformation band at 1171 cm^{-1} is characteristic of the semiquinone structure [22, 23]. The bands at 824 and 419 cm^{-1} are related to the C-H deformation, the band at 607 cm^{-1} attributed to the benzenoid ring deformation, and the band at 512 cm^{-1} ascribed to the C-N-C torsion are also observed [24]. These results indicate that the polymer chain of both tubes and dendritic fibers are in good agreement with previous spectroscopic characterizations of PANI [25]. However, significant differences in Raman spectra between tubes and dendritic fibers are also discovered. For instance, the band at 512 cm^{-1} assigned as the C-N-C torsion was very weak in the tubes, but strong in the shorter dendritic rods. The characteristic band of the semiquinone structure at 1171 cm^{-1} is also stronger than that of in the tubes. A broad overlapping feature in the rang of 1540 to 1660 cm^{-1} with a peak at 1597 cm^{-1} may result from the amalgamation of the peaks at 1638, 1602, and 1562 cm^{-1}. These results suggest that as the reaction concentration of SA increases, the doped level become higher. This is accordant to the results from UV-Vis spectra.

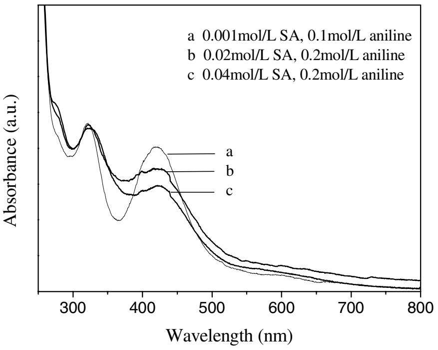


Figure 4. UV-visible spectra of three typical types of PANI synthesized with different conditions: (a) 0.001mol/L SA, 0.1mol/L aniline; (b) 0.02mol/L SA, 0.2mol/L aniline; (c) 0.04mol/L SA, 0.2mol/L aniline.

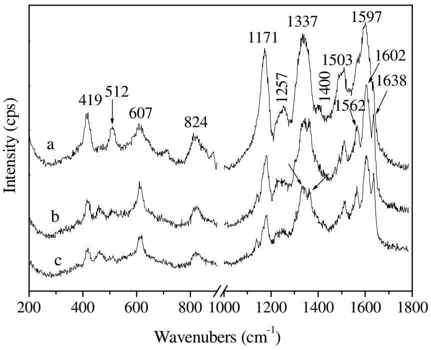


Figure 5. Raman spectra of three typical types of PANI with different conditions: (a) 0.001mol/L SA, 0.1mol/L aniline; (b) 0.02mol/L SA, 0.2mol/L aniline; (c) 0.04mol/L SA, 0.2mol/L aniline.

The information of the molecular vibration might be the reason that the conductivity of the as-prepared PANI is much different. The conductivity of nanotubes, the 160-200 nm dendritic fibers and the shorter dendritic fibers is about 1.3 $\times 10^{-4}$ $S{\cdot}cm^{-1}$, 5.2×10^{-3} $S{\cdot}cm^{-1}$and 3.7 $\times10^{-3}$ $S{\cdot}cm^{-1}$, respectively. Raman spectra indicate that the state of the as-prepared PANI fibers is emeraldine rather than solely the leucoemeraldine or pernigraniline form. However, the conductivity of the as-prepared PANI is not high. This might be because SA is a weak acid and its long c-c chains might be affect the conductivity of PANI during the synthesis process.

Conclusion

In conclusion, we report a simple and tunable method to synthesize PANI linear tubes and dendritic fibers by using SA as template and dopant via self-assembly process. The tubes have uniformly about 200 nm in diameter and submicrometer to micrometer in length. The dendritic PANI fibers are interconnected to form 3D network structures. It is found that the morphologies and sizes of the PANI fibers strongly depend on the concentration ratio of aniline to SA. Based on the results from UV-Vis and Raman spectra, the doped levels of the three typical samples are different due to the different reaction condition.

Acknowledgements. This work was supported by the Science Developing Foundation of Tianjin Education Committee (No. 20060514), Tianjin University of Science and Technology (No. 20070415) and Tianjin Municipal Science and Technology Commission (No. 06YFJMJC14900).

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