

Conducting Polyaniline Nanofiber Networks Prepared by the Doping Induction of Camphor Sulfonic Acid

Chang He, Yiwei Tan, Yongfang Li

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received 27 December 2001; accepted 8 May 2002

ABSTRACT: Branched nanofibers of conducting polyaniline (PANI) buried in the crystals of camphor sulfonic acid (CSA) were prepared from an *m*-cresol solution of PANI and excessive CSA. After the excessive CSA was dissolved through ultrasonication in deionized water, networks of PANI nanofibers with spherical nodes, nanoparticles, leaf-vein-shaped nanofibers, and so forth were obtained accord-

ing to the strength of the ultrasonic treatment. The X-ray diffraction patterns of the CSA-doped PANI showed high crystallinity. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1537–1540, 2003

Key words: fibers; networks; morphology

INTRODUCTION

In recent years, nanoscale devices have been attracting considerable attention because of the demands for ultra-large-scale integration technology. Conducting nanowires are among the key elements in fabricating and connecting the devices. Therefore, nanowires have been studied intensively, particularly those associated with carbon nanotubes^{1–4} and conducting polymers.⁵ Among conducting polymers, polyaniline (PANI) has attracted great interest because of its easy preparation, good stability, and structural versatility.^{6,7}

Conducting PANI prepared by routine methods usually shows a granular morphology or fibers entangled together. The fibrous morphology of electropolymerized PANI has been reported in the literature. Chen and Lee⁶ reported the fibrous network morphology of PANI electropolymerized in a tetrafluoroboric acid (HBF₄) aqueous solution. A similar fibrous morphology of electrochemically polymerized PANI was also observed by Desilvestro and Scheifele⁷ and Bedekar and coworkers.^{8,9} Recently, Österholm et al.¹⁰ obtained conducting PANI fibers by emulsion polymerization. Norris et al.¹¹ prepared conducting PANI nanofibers with electric spraying technology. However, the PANI fibers were tangled up in the powder or films. Arrayed nanofibers or nanotubes of PANI were obtained by a template method. PANI nanowires were synthesized by Wu and Bein,¹² who used mesoporous zeolites as templates. Martin¹³ made great

progress in the template synthesis of conducting polymer microwires and nanowires. However, for pure nanostructures to be obtained, the template had to be removed by a postprocess procedure.

In this study, a novel conducting PANI nanofiber network with spherical nodes was prepared by the doping induction of camphor sulfonic acid (CSA). The diameters of the nanofibers were 70–80 nm. The formation mechanism and crystal structure of the nanofibers were investigated.

EXPERIMENTAL

Synthesis

Aniline (analytically pure; Beijing Chemicals, Inc.) was distilled under reduced pressure before use. CSA (98%; Aldrich, Milwaukee, WI), ammonium persulfate (chemically pure; Beijing Yili Chemicals, Inc.), *m*-cresol (chemically pure; Beijing Chemicals), and other solvents were used as received. Emeraldine-base PANI was prepared with Chaing and MacDiarmid's method.¹⁴ Aniline (2 mL, 0.022 mol) dissolved in 120 mL of a 1 mol/L HCl solution and then cooled to 0–5°C in an ice–water bath. Forty milliliters of a 0.5 mol/L NH₄S₂O₄ and 1 mol/L HCl solution was added to the aniline solution dropwise in 1 h with magnetic stirring at 0–5°C; stirring was continued for 7 h for the reaction. The precipitate produced in the reaction was removed by filtration, washed repeatedly with 1 mol/L HCl, and dried under a dynamic vacuum for 48 h. The PANI powder so obtained was in an HCl-doped state (PANI–HCl). For the emeraldine-base PANI, the PANI–HCl powder was put in 0.1 mol/L ammonia water and stirred for 3 h at room temperature. The deposits were filtered, washed with deionized water until the water was neutral, and dried *in*

Correspondence to: Y. Li (liyf@infoc3.icas.ac.cn).

Contract grant sponsors: Chinese Academy of Sciences; Ministry of Science and Technology of China (through the Key Project on Basic Research).

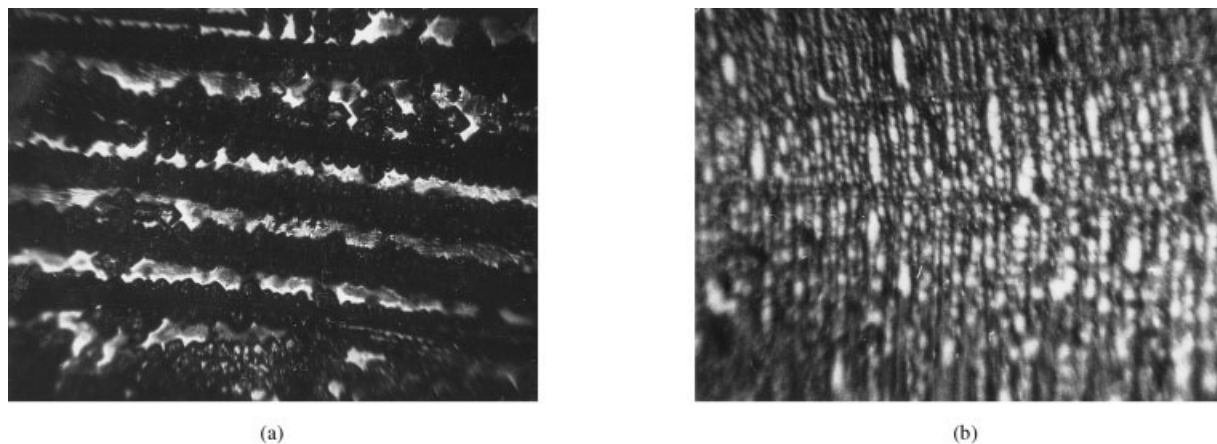


Figure 1 Optical microscopy photographs of (a) a (PANI)CSA film ($\times 150$) and (b) a PANI(CSA) fiber network ($\times 150$).

vacuo for 48 h; in this way, the emeraldine PANI was obtained.

The PANI nanofiber network was prepared as follows. Emeraldine PANI powder (0.091 g, 0.001 mol) and 3.949 g (0.017 mol) of CSA were dissolved in 100 mL of *m*-cresol; an ultrasonic treatment for 1 h and magnetic stirring at room temperature for 24 h followed. The solution was dropped on a glass plate, the solvent was removed gradually by the irradiation of an IR lamp, and a film of PANI in CSA [(PANI)CSA] was obtained. The (PANI)CSA film was separated from the glass plate by the glass plate with the film being dipped into deionized water. For the conducting PANI nanofiber to be separated from (PANI)CSA, a sample of (PANI)CSA was put into deionized water and ultrasonically treated for hours to dissolve the excessive CSA and obtain a nanofiber suspension solution. The sample so obtained was denoted PANI(CSA).

Structural characterization

An optical microscope (Olympus BH-2) was used to observe the morphology of the film on the glass plate. Transmission electron microscopy (TEM) observations were undertaken with a JEOL-JEM-100 CX II electron microscope operated at 100 kV. The specimen preparation for the TEM observations was performed by the drop-casting of two drops of a freshly prepared suspension containing PANI(CSA) nanofibers onto a standard carbon-supported (200–300-Å) 300-mesh copper grid and by slow and natural drying in air. X-ray diffraction (XRD) measurements were performed at room temperature with Cu $K\alpha$ X-rays ($\alpha = 1.5418 \text{ \AA}$) with a D/Max-2400. Data were recorded from 3 to 45° in steps of 0.02° . The samples were prepared by PANI(CSA) being dropped in *m*-cresol on a glass plate and dried with an IR lamp. In the same way, a sample of pure CSA in an *m*-cresol solution was obtained. Ultraviolet–visible absorption spectra were taken with a Shimadzu 3010 spectrometer in a wavelength range of 300–900 nm with a 1-cm quartz cell.

The spectrum of dedoped PANI was measured with a solution of emeraldine PANI in *N*-methylpyrrolidone (NMP) with NMP as a reference, and the spectrum of doped PANI was measured with a solution of PANI and CSA in *m*-cresol with *m*-cresol as a reference.

RESULTS AND DISCUSSION

Morphology

Figure 1(a) shows a photograph of a (PANI)CSA film taken with a 15×10 optical microscope. A very interesting regular morphology can be observed in the photograph. The square crystal of CSA partially overlaps and makes a set of parallel strips. Green doped PANI fibers with regular branches are located in the middle lines of the strips. This morphology can be considered PANI fibers in CSA crystals. The results are reasonable because fully doped PANI with CSA is PANI(CSA)_{0.5} (i.e., two aniline units are doped by one CSA molecule);¹⁵ the amount of CSA in this case is much more than needed for doping PANI. Observations from reflectance microscopy (the photograph is not given here) indicate that the surface of the film is very smooth and that the conducting PANI chains are enveloped by the CSA crystal. So that the PANI chain structure could be observed more clearly, a sample film with its glass substrate was dipped in deionized water for 24 h to dissolve excessive CSA from the film. Then, the remaining PANI(CSA) chain was observed with optical transmission microscopy, as shown in Figure 1(b). The PANI(CSA) chains show the structure of a regular network with some holes. Obviously, the macroscopic regular structure was induced by the crystallization process of CSA.

The microstructure of PANI(CSA) induced by the crystallization process of CSA was investigated with TEM. Figure 2 shows the TEM photographs of the PANI(CSA) samples. Figure 2(a–d), taken from different places in the sample, displays different morphologies, which indicate that the sample is not uniform.

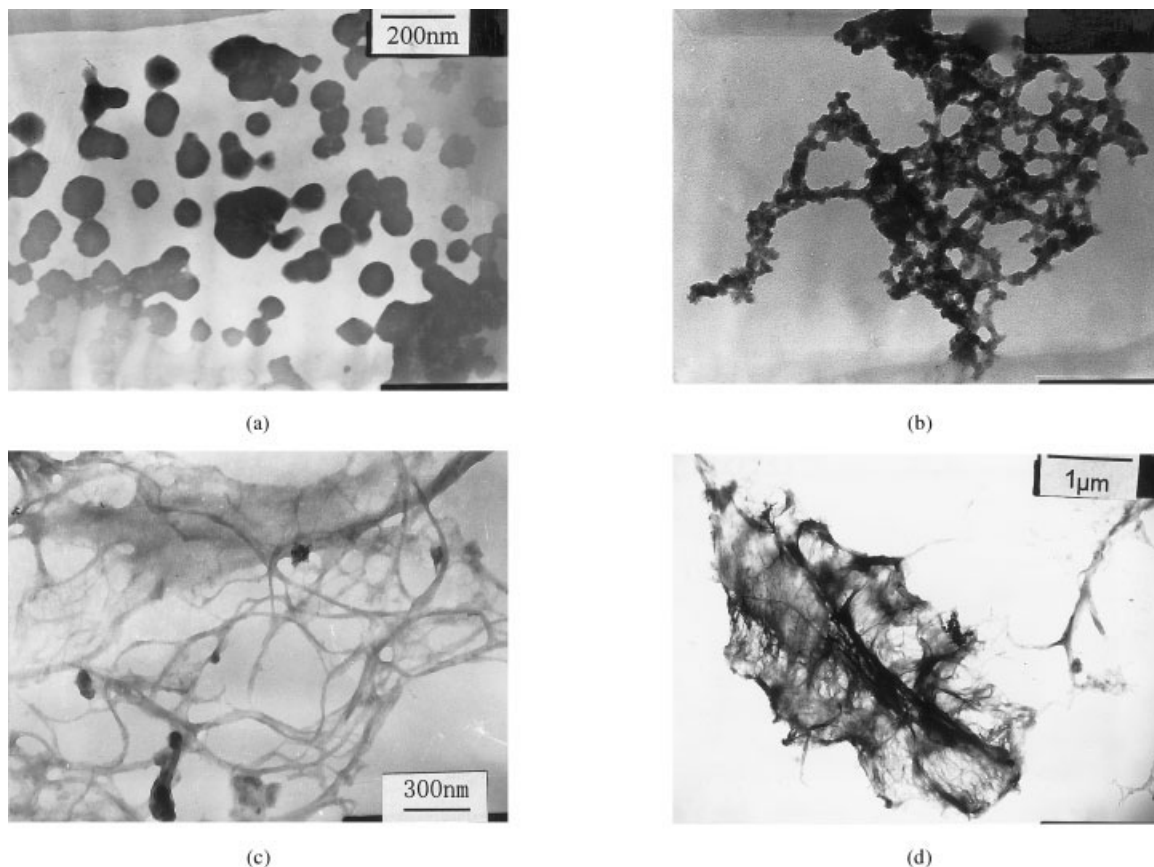


Figure 2 TEM photographs of the different morphologies of PANI(CSA): (a) nanoparticles, (b) networks of nanofibers with spherical nodes, (c) extended nanofibers, and (d) nanofiber networks with the leaf-vein structure.

The morphology of Figure 2(a) is separated polymer balls 70–80 nm in size; this means that the polymer chain is rolled up. Figure 2(b) is very interesting, showing a three-dimensional network with spherical nodes. Figure 2(c) shows spread fibers of PANI(CSA) chains. Figure 2(d) displays a morphology similar to a leaf vein composed of a main chain and many branched fibers of the polymer. The different morphologies may be related to the rate of the crystallization of CSA relative to the aggregation of PANI(CSA). That is, if the crystalline growth rate of CSA is much slower than the aggregation rate of PANI(CSA), colloidal particles of PANI(CSA) [Fig. 2(a)] form. On the contrary, if the crystalline growth rate of CSA is much faster than the aggregation rate of PANI(CSA), PANI(CSA) is forced to grow between the crystal of CSA, and then fibrous structures with different morphologies can be obtained [Fig. 2(c,d)]. The most interesting possibility is that, if these two speeds are comparable, three-dimensional networks with spherical nodes are produced [Fig. 2(b)]. Therefore, if we can control the crystalline growth rate of CSA or the aggregation rate of PANI(CSA), various morphologies of PANI(CSA) can be obtained.

Absorption spectrum and XRD analysis

Figure 3 shows the absorption spectra of an emeraldine PANI solution and a solution of PANI and ex-

cessive CSA. There are two absorption peaks for the PANI solution at 325 and 630 nm [Fig. 3(a)], and this agrees with the undoped PANI.¹⁶ The absorption peaks in Figure 3(b) are at 400 and 900 nm, respectively, values characteristic of doped PANI.¹⁶ The results indicate that PANI in a high-concentration CSA solution is in its doped state.

The XRD pattern of (PANI)CSA exhibits sharp peaks, as shown in Figure 4(b). Because of the exist-

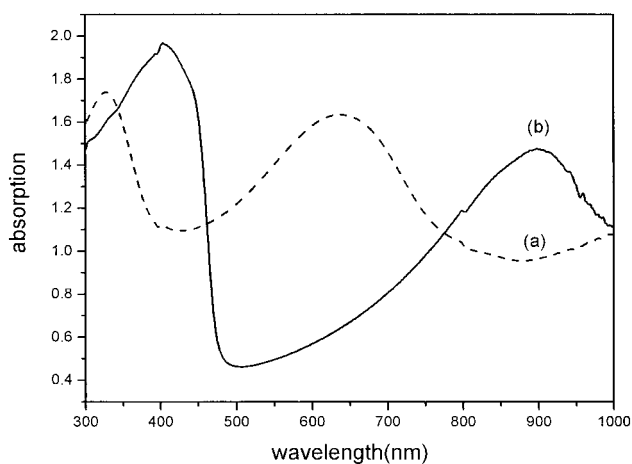


Figure 3 Absorption spectra of (a) an emeraldine PANI solution and (b) a PANI–CSA solution.

tence of a large amount of CSA crystals in the (PANI)CSA sample, the XRD pattern of pure CSA crystal was also measured and put in the figure [cf. Fig. 4(a)]. Obviously, the peaks at $2\theta = 11.24, 13.68, 18.66,$ and 19.32° in the XRD pattern of (PANI)CSA belong to CSA, but their strength has changed a lot because of the complex of PANI in CSA. The new peaks in Figure 4(b), at $2\theta = 15.22, 21.18,$ and 27.4° ($d = 5.82, 4.19,$ and 3.26 \AA , respectively), belong to the crystal structure of PANI.^{17,18} The sharpness of the PANI peaks indicate that the PANI chains in the (PANI)CSA sample are in a more ordered structure.

Formation mechanism of the PANI nanofibers

The formation of PANI nanofibers induced by CSA can be analyzed as follows. In an *m*-cresol solution of PANI and CSA, there exist large amounts of electrostatic interactions and hydrogen-bonding interactions, such as the interactions between the PANI amine and the sulfonate anion of deprotonated CSA, the hydrogen-bonding interaction between the carbonyl oxygen of CSA and the PANI ring, and the phenyl-phenyl interaction (see Fig. 5).¹⁹ The molecular interactions make the crystalline growth rate of CSA or the aggregation rate of PANI(CSA) correlated, so different morphologies of PANI(CSA) could be obtained, as mentioned previously.

CONCLUSIONS

Because of the overlap of the conjugated π bond in PANI, PANI chains tend to aggregate together. The existence of CSA dopants weakens the interaction between PANI chains, which induces the better solubility of PANI(CSA) in an *m*-cresol solution.¹⁵ This effect also results in PANI chain extension.²⁰ When there is a large amount of excessive CSA in the solution, the PANI chains are separated by CSA molecules. During

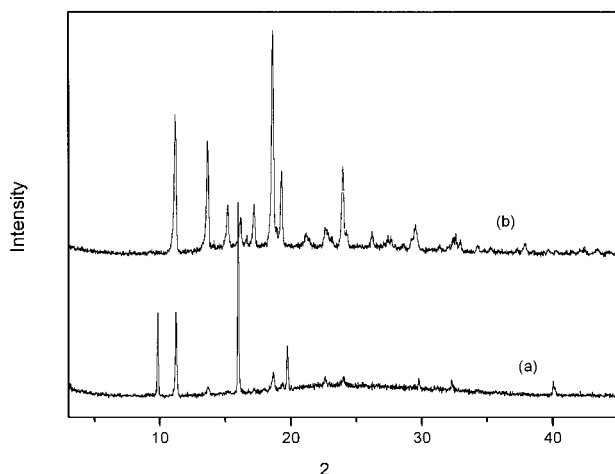


Figure 4 XRD patterns of (a) CSA and (b) (PANI)CSA.

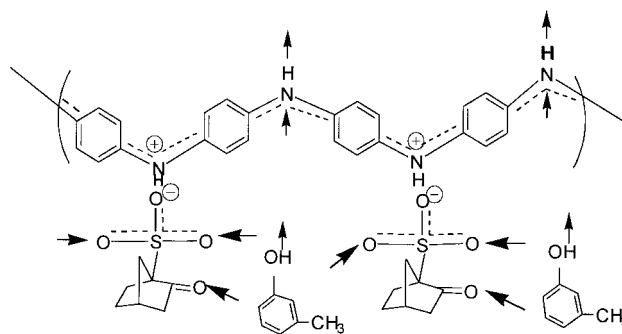


Figure 5 Electrostatic interactions and hydrogen-bonding interactions in PANI(CSA).

the preparation process, through the removal of the *m*-cresol solvent from the solution under IR irradiation, excessive CSA crystallizes, forming a template for the aggregation of PANI chains. Then, the PANI chains aggregate into nanofibers, and a more ordered PANI structure is formed in the CSA crystal template.

References

- Morpurgo, A. F.; Kong, J.; Marcus, C. M.; Dai, H. *Science* 1999, 286, 263.
- Kasumov, A. Y.; Deblock, R.; Kociak, M.; Reulet, B.; Bouchiat, H.; Khodos, I. I.; Gorbatov, Y. B.; Volkov, V. T.; Journet, C.; Burghard, M. *Science* 1999, 284, 1508.
- Journet, C.; Maser, W. K.; Bernier, P.; Loiseau, A.; de La Chapelle, M. L.; Lefrant, S.; Deniard, P.; Lee, R.; Fischer, J. E. *Nature* 1997, 388, 756.
- Thess, A.; Lee, R.; Nikolaev, P.; Dai, H.; Petit, P.; Robert, J.; Xu, C.; Lee, Y. H.; Kim, S. G.; Rinzler, A. G.; Colbert, D. T.; Scuseria, G. E.; Tománek, D.; Fischer, J. E.; Smalley, R. E. *Science* 1996, 273, 483.
- Kosonen, H.; Ruokolainen, J.; Knaapila, M.; Torkkeli, M.; Jokela, K.; Serimaa, R.; Brinke, G.; Bras, W.; Monkman, A. P.; Ikkala, O. *Macromolecules* 2000, 33, 8671.
- Chen, S. A.; Lee, T. S. *J Polym Sci Part C: Polym Lett* 1987, 25, 455.
- Desilvestro, J.; Scheifele, W. *J Mater Chem* 1993, 3, 263.
- Bedekar, A. G.; Patil, S. F.; Patil, R. C.; Agashe, C. *Polym J* 1995, 27, 319.
- Okamoto, H.; Okamoto, M.; Kotaka, T. *Polymer* 1998, 39, 4359.
- Österholm, J.-E.; Cao, Y.; Klavetter, F.; Smith, P. *Polymer* 1994, 35, 2902.
- Norris, I. D.; Shaker, M. M.; Ko, F. K.; MacDiarmid, A. G. *Synth Met* 2000, 114, 109.
- Wu, C.-G.; Bein, T. *Science* 1994, 264, 1757.
- Martin, C. R. *Chem Mater* 1996, 8, 1739.
- Chaing, J.-C.; MacDiarmid, A. G. *Synth Met* 1986, 13, 193.
- Cao, Y.; Smith, P.; Heeger, A. J. *Synth Met* 1992, 48, 91.
- Wan, M. X.; Li, Y. F. In *Organic Solids*; Zhu, D. B.; Wang, F. S., Eds.; Shanghai Science and Technology: Shanghai, 1999; Chapter 5.
- Pouget, J. P.; Jozefowicz, M. E.; Epstein, A. J.; Tang, X.; MacDiarmid, A. G. *Macromolecules* 1991, 24, 779.
- Pouget, J. P.; Oblakowski, Z.; Nogami, Y.; Albouy, P. A.; Laridjani, M.; Oh, E. J.; Min, Y.; MacDiarmid, A. G.; Tsukamoto, J.; Ishiguro, T.; Epstein, A. J. *Synth Met* 1994, 65, 131.
- Ikkala, O. T.; Pietilä, L.-O.; Ahjopalo, L.; Österholm, H.; Passiniemi, P. J. *J Chem Phys* 1995, 103, 9855.
- MacDiarmid, A. G.; Epstein, A. J. *Synth Met* 1994, 65, 103.