

Effect of Ethanol on Chemically Synthesized Polyaniline Nanothread

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ABSTRACT: The nanothread of polyaniline (PANI) using ammonium persulphate ((NH₄)₂S₂O₈) as an oxidant was prepared. The solution is composed of 0.4 mol dm⁻³ aniline, 1.0 mol dm⁻³ hydrochloric acid, and different proportions ethanol. The resulting products were characterized using infrared spectroscopy, UV-vis spectra, transmission electron microscope, thermogravimetric analysis techniques, and X-ray diffraction. The experimental results show that the content of ethanol has effects on the morphology of PANI, but

the effects on the conductivity are not very obvious. When the volume ratio of ethanol to aniline is 1:2, the more uniform and regular PANI nanothread can be prepared. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1848–1853, 2006

Key words: polyaniline; nanothread; ethanol; transmission electron microscope; thermogravimetric analysis; X-ray diffraction

INTRODUCTION

Polyaniline (PANI), a representative conducting polymer, has attracted extensive attention in recent two decades because of its prospective applications in various hi-tech aspects, including biosensors,^{1,2} electrochromic displays,³ electrocatalysis,^{4,5} anticorrosive coatings,^{6,7} rechargeable batteries, etc.^{8–10} Owing to the special physical and chemical properties of PANI, as well as its unique conduction mechanism, of all conducting polymers, PANI was considered as one of the most promising candidates within the potential application fields of microsensors, microactuators, and so on.¹¹ Recently, many researchers have focused on its nanostructures deriving mainly from its promising applications in molecular electronics, energy conversion, storage, etc.¹² PANI can be easily synthesized by both the chemical and electrochemical methods. Although considerable efforts are currently being devoted to electrochemical method studies on conducting polymers, the chemical method is also of great importance, since it is a very feasible route for the mass production of PANI.^{13,14}

PANI nanoparticles can be obtained in the presence of some chemicals. For instance, PANI doped with *p*-toluene sulfonic acid (*p*-TSA) was synthesized by *in situ* chemical polymerization method using ammo-

niun persulphate as an oxidizing agent¹⁵; microtubes of PANI using ammonium persulphate as an oxidant in the presence of *b*-naphthalenesulfonic acid (*b*-NSA) as a dopant were prepared with a self-assembly process¹⁶; conducting polymer fibers (diameter 950~2100 nm) of PANI doped with *D,L*-camphorsulfonic acid (CSA) as a blend in polyethylene oxide were fabricated^{17,18}; composite films of PANI nanostructures blended with water-soluble poly(vinyl alcohol) (PVA) as a matrix were reported¹⁹; Huang et al.²⁰ reported the preparation of PANI nanofiber under ambient conditions using aqueous/organic interfacial polymerization.

In this work, we reported the simple preparation of PANI nanothread with chemical method in the presence of ethanol. Ethanol not only is cheaper than *p*-TSA, *b*-NSA, CSA, and PVA, but also is hardly harmful to environment. The properties of PANI nanothread were characterized using Fourier transform-infrared (FTIR) spectra, UV-vis spectra, transmission electron microscope (TEM), thermogravimetric analysis (TGA), and X-ray diffraction (XRD).

EXPERIMENTAL

Aniline (Merck) was purified into colorless by distillation under reduced pressure prior to use. Other chemicals are reagent grade and were used as received without further pretreatment. All of the aqueous solutions were prepared with double distilled water.

The nanothread of PANI were prepared in the solution containing 0.4 mol dm⁻³ aniline, 1.0 mol dm⁻³ hydrochloric acid (HCl), and different proportions of

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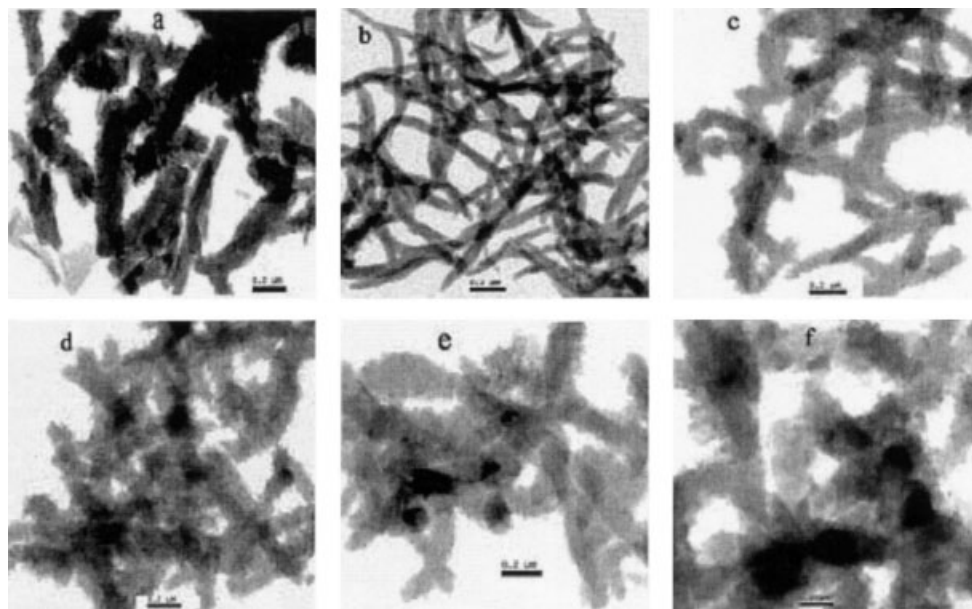


Figure 1 Effect of different proportions of ethanol on the morphology of PANI. The volume ratios of ethanol to aniline: (a) 0; (b) 1:2; (c) 1:1; (d) 2:1; (e) 4:1; (f) 6:1.

ethanol. The chemical polymerization of aniline was carried out at ambient temperature, $\sim 20^{\circ}\text{C}$, and the ammonium persulfate of same molar ratio as aniline was added into the solution in the rate of about $0.4564 \text{ g min}^{-1}$ while the solution was stirred. At the end of reactions, the resulting products were filtered, washed successively with 1.0 mol dm^{-3} HCl until filtrate was colorless, and the resulting products were dried at 78°C for 48 h.

The morphologies of PANI were observed using a TEM (Holland Philips, model Tecnai-12). The PANI samples were characterized by UV-vis spectroscopy using Shimadzu UV-2550 spectrophotometer in the wavelength range of 200–900 nm. The FT-IR spectra of PANI were obtained from a FT-IR spectrometer (Bruker, model Tensor 27) in the wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$ with 4 cm^{-1} resolutions. Pressed pellets were prepared of the powder samples ground with KBr for this purpose. TG was performed using a SDT Q600 instrument (USA) at a heating rate of $10^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere, from 80 to 800°C , so as to study the thermal stability and obtain the decomposition temperature of PANI synthesized. Conductivity measurements of the resulting products were made using conventional four-probe technique on pressed pellets of the powder samples prepared at ambient temperature. Wide-angle X-ray diffraction patterns for the powder samples were taken on a M03XHF²² diffractometer (Mac Science, Japan), using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$), which was used to obtain the degree of crystallinity.

RESULTS AND DISCUSSION

The morphology of the PANI

Figures 1(a)–1(f) show the morphologies of PANI prepared in the solution containing 0.4 mol dm^{-3} aniline, 1.0 mol dm^{-3} hydrochloric acid, and different proportions of ethanol. It is seen from Figure 1(a) that the diameters of PANI prepared without ethanol are $\geq 100 \text{ nm}$. When appropriate proportion of ethanol was added to the solution, the PANI presents more regular and uniform thread-shaped morphology. Figure 1(b) shows that when the volume ratio of ethanol to aniline is 1:2, the PANI nanofibers with diameters about 50 nm were obtained. However, with increasing ethanol content, the PANI nanofibers become more and more indistinct. When the volume ratio of ethanol to aniline is 4:1, the PANI with diameters over 100 nm formed (see Fig. 1(e)), and when the volume ratio of ethanol to aniline is 6:1, the nanofiber morphology has almost disappeared (see Fig. 1(f)).

The afore-mentioned facts indicate that the content of ethanol affected the morphology of PANI. In the absence of ethanol, the newborn state of PANI tended to aggregate together and formed the larger club-shaped structure during the polymerization. When the appropriate proportion of ethanol was added to the solution, there may be existed strong intermolecular H-bonding between the PANI and ethanol molecules, and such interaction made the PANI particles be wrapped by ethanol molecules,²¹ which prevented PANI from aggregating together during the polymerization and tended to form the thread-shaped struc-

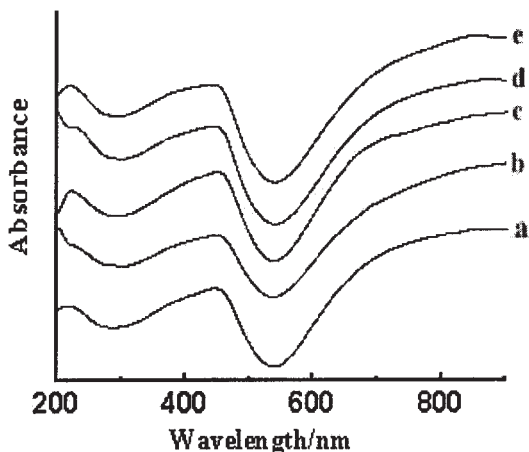


Figure 2 Effect of different proportions ethanol on the UV-vis spectra of PANI. The volume ratios of ethanol to aniline: (a) 0; (b) 1:2; (c) 1:1; (d) 2:1; (e) 6:1.

ture, with a relative smaller size. However, with further increase of ethanol content, the aggregation of PANI encapsulated by ethanol molecules probably occurred, which is similar to the aggregation of micelles, and the PANI size also increased. So, too much ethanol is disadvantageous to obtain the more uniform and regular PANI nanofibers.

UV-vis spectra of PANI

Figure 2 shows the UV-vis absorption spectra of the PANI prepared in the solution containing 0.4 mol dm⁻³ aniline, 1.0 mol dm⁻³ hydrochloric acid, and different proportions of ethanol. It is seen from Figure 2(a) that there are three obvious absorption peaks, and the peak about $\pi-\pi^*$ transition of the benzenoid ring cannot be seen clearly. The peak at 446 nm was assigned to the localized polaron band, which is characteristic of the protonated PANI, and the peak at 853 nm with extended tail was attributed to polaron band transition of PANI backbone, which indicates that the afore-mentioned PANI is in the doped state. The results are consistent with those in literatures.^{22,23} The PANI synthesized with ethanol has three similar absorption peaks with that of the PANI without ethanol. It is interesting to note that by increasing the ethanol/aniline volume ratio, the polaron band exhibits a bathochromic shift and appears at the higher wavelength when compared with that of PANI without ethanol (curve a). It is seen from Table I that the red shift of the peaks are more obvious when the volume ratio of ethanol to aniline is 1:1, which indicates that the polarons in PANI prepared under this condition are more delocalized than other ratios.²⁴ The optimum might occur owing to an optimum in the effective conjugation length, with increase of the volume ratio of ethanol/aniline. However, with the further increase

of ethanol/aniline volume ratio, the red shifts of polaron band begin to decrease, and when the volume ratio of ethanol to aniline is 6:1, the polaron bands of PANI come back to that of the PANI without ethanol. This may be due to the decrease in effective conjugation length as the ratio further increases. Owing to the addition of large amounts of ethanol, the PANI may become less compatible with excessive ethanol and the segments increase of PANI tend to decrease the contact with the ethanol by coiling the chains.²⁴ From the comparison of these UV-vis absorption spectra, it is deduced that excessive ethanol has negative effects on the synthesis of PANI nanofibers, which is also consistent with the results of TEM.

FTIR spectra of PANI

Figure 3 shows the FTIR spectra of PANI prepared in the solution containing 0.4 mol dm⁻³ aniline, 1.0 mol dm⁻³ hydrochloric acid, and different proportions of ethanol. As shown in Figure 3(a), the band approximately at 1556 cm⁻¹ in the PANI sample is attributed to the C=C bonds stretching vibrations of the quinoid units. The band at 1479 cm⁻¹ corresponded to the stretching of the benzenoid ring. The peak observed at 1292 cm⁻¹ was related to C-N stretching vibration of the benzenoid ring. The in-plane C-H bending motion of the quinoid units appeared at 1110 cm⁻¹.^{25,26} It was reported that the band fell in the range 800–860 cm⁻¹ was identified with the out-of-plane bending of C-H bond in the 1,4-disubstituted ring, which has been used as a key to identify the type of substituted benzene. As for the PANI prepared, the mode was observed as a single band at 796 cm⁻¹, which is close to the spectrum range reported in the literature.²⁷ In addition, the bands located at 3416 and 3122 cm⁻¹ may be due to the N-H bond stretching, which are not shown here. When PANI was synthesized in the solution containing different proportions of ethanol (curve (b–e) in Fig. 3), these bands are similar to that of afore-mentioned PANI except for a few shifts in the wavenumbers. By comparing curves (b–e) with curve (a) in Figure 3, it is observed that the absorption peaks of PANI prepared with ethanol shifted to higher wavenumbers. When the volume ratio of ethanol to

TABLE I
Shift of Wavelength of Absorption Peak Due to the Addition of Ethanol

Volume ratios of ethanol to aniline	Shift of wavelengths of absorption peaks (nm)		
0	219	446	853
1:2	221	451	856
1:1	224	454	861
2:1	223	443	859
6:1	223	445	853

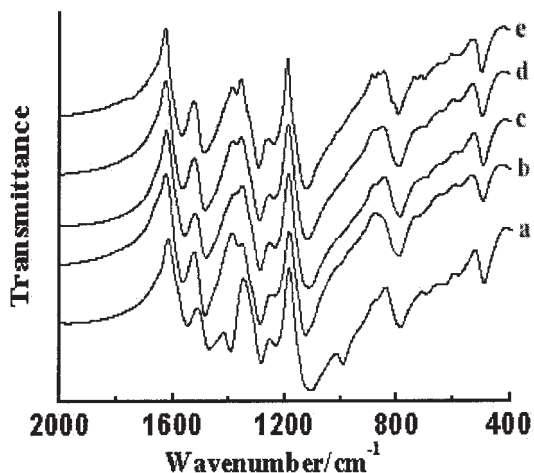


Figure 3 Effect of different proportions of ethanol on the FTIR of PANI. The volume ratios of ethanol to aniline: (a) 0; (b) 1:2; (c) 1:1; (d) 2:1; (e) 6:1.

aniline is 1:2, the peaks shifted from 1556 and 1479 cm^{-1} to 1572 and 1494 cm^{-1} and the absorption bands at 1292 and 1110 cm^{-1} shifted to 1295 and 1136 cm^{-1} , respectively; other peaks did hardly shift. It was reported that the blue shifts were probably due to the fact that the very small size and relatively heavy surface tension of the nanometer material units resulted in the distortion in the inner of particles,²⁸ and the distortion made the average bond length shorter and resulted in higher vibration frequencies of bonds. In addition, according to the literature reported,²⁹ the quantum size of the nanometer material made energy levels wide, which also induced the blue shifts of FTIR spectra. From the results of TEM, it is known that the diameter of fibers shown in Figure 3(b) is smaller than that in Figures 3(a) and 3(c)–3(e), and so the higher

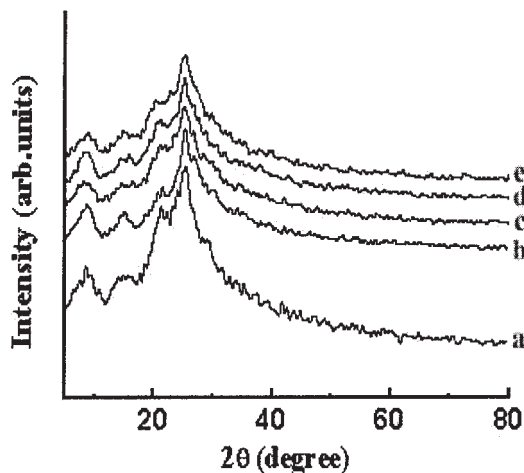


Figure 4 XRD patterns of PANI prepared with and without ethanol. The volume ratios of ethanol to aniline: (a) 0; (b) 1:2; (c) 1:1; (d) 2:1; (e) 6:1.

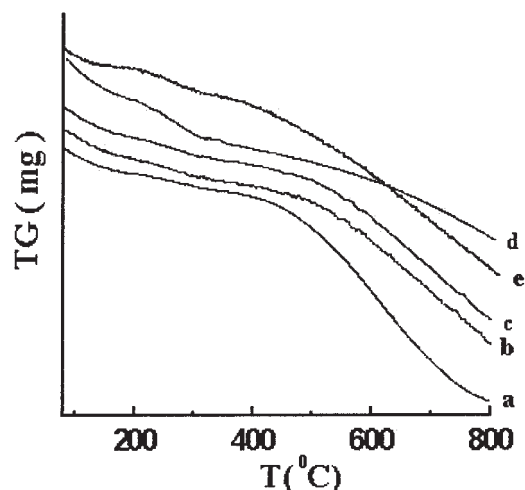


Figure 5 TGA curves of PANI prepared without and with ethanol. The volume ratios of ethanol to aniline: (a) 0; (b) 1:2; (c) 1:1; (d) 2:1; (e) 6:1.

wavenumbers in Figure 3(b) may be due to the effects of the small size and the afore-mentioned quantum size.

X-ray diffraction spectra

Figure 4 shows the XRD patterns of the PANI prepared in the solution containing 0.4 mol dm^{-3} aniline, 1.0 mol dm^{-3} hydrochloric acid, and different proportions of ethanol. The XRD profiles of the PANI with ethanol are similar to that of the PANI without ethanol, which indicates that all samples are almost isomorphous. The presence of peaks between 10° and 40° 2θ -values in the samples reveals the local crystalline nature of the PANI.^{30–33} The peak of $2\theta \approx 8.7^\circ$ was assigned as the scattering along the orientation parallel to the PANI chain,³⁴ and the bands at $\sim 2\theta$ -values of 14.9° and 21.3° demonstrated a partially amorphous nature.³⁵ It is concluded from this similar profiles that the PANI synthesized is the local crystalline nature, and the content of ethanol has no significant effects on the degree of crystallinity. It has been known that PANI of high crystallinity has a higher conductivity than amorphous one.³⁶ As expected from the X-ray profiles, the effect of ethanol content on the conductivity of all samples synthesized is not very distinct. In addition, the experimental results also show that difference of the conductivity among different samples is small, and the values of conductivity are about $2\sim 10 \text{ S cm}^{-1}$.

Thermogravimetric analysis

Figure 5 shows the TGA curves of PANI synthesized in the solution containing 0.4 mol dm^{-3} aniline, 1.0 mol dm^{-3} hydrochloric acid, and different propor-

tions of ethanol, and the temperature range taken between 80 and 800°C. From the thermograms, we can clearly see that the weight losses of PANI samples prepared in different temperature ranges. In general, the thermal behavior of the PANI prepared without ethanol shows a three-step weight-loss process. The first stage weight loss from 80 to 150°C is about 10.69%, which was attributed to the loss of water entrapped in the PANI and low-molecular-weight oligomers.^{37,38} The second stage weight loss is 20.54% from 200 to 350°C, which is probably related to the elimination of acid dopant (HCl) from the polymer structure.^{39–41} The third weight loss observed starting at about 400°C corresponds to the thermal decomposition of PANI backbone chains.^{42–43} As for the PANI prepared with ethanol, the weight losses of the same temperature ranges as the PANI without ethanol become smaller, and the thermal decomposition temperature of PANI backbone chains is larger than that of PANI without ethanol, which implies the thermally stable of PANI prepared with ethanol increases, gradual weight loss over the wide temperature range also indicates the good thermal stability of the PANI main chain. It is probably due to the strong interaction between molecules of PANI and ethanol, which enhanced the strength of PANI chains and resulted in the stabilization of the PANI prepared with ethanol. The phenomenon is consistent with the FTIR spectra. With the further increase of ethanol, the weight loss of PANI in the same temperature ranges also increased and the thermal decomposition temperature of PANI backbone chains became lower. This may be due to the presence of excessive ethanol induced the PANI backbone with lots of defect sites, and so the thermal stability decreased.¹⁵ The relationship between ethanol content and the thermal stability remains under further detailed investigations.

CONCLUSIONS

In summary, the method of chemical synthesis of the PANI nanothread in the presence of ethanol was introduced. The TEM results indicate that the content of ethanol affected the morphology of PANI, and when the volume ratio of ethanol to aniline is 1:2, the more regular and uniform thread-shaped morphology PANI can be obtained in the solution containing 0.4 mol dm⁻³ aniline, 1.0 mol dm⁻³ hydrochloric acid, and ethanol. The UV-vis spectra and FTIR spectra show that there existed interaction between PANI and ethanol molecules. With the addition of ethanol, the absorption peaks of UV-vis spectra shifted to the higher wavelength, but excessive ethanol induced the decrease of the polaron band red shifts. In FTIR spectra, due to the effects of the small size and quantum size, the absorption peaks shifted to the higher wavenumbers. The TGA results show an improvement of

the thermal stability for PANI nanothreads with appropriate content of ethanol when compared with that of PANI without ethanol.

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