

Effects of Ultrasonic Irradiation on the Morphology of Chemically Prepared Polyaniline Nanofibers

Yu Li, Yangyong Wang, Dan Wu, Xinli Jing

Department of Chemical Engineering, School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

Received 25 July 2008; accepted 26 December 2008

DOI 10.1002/app.29970

Published online 30 March 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Polyaniline (PANI) nanofibers were chemically prepared through ultrasonic irradiated polymerization with varying ultrasonic power, frequency, and reaction temperature. It was found that PANI nanofibers with smoother surfaces and uniform diameters can be achieved by increasing the ultrasonic power or the reaction temperature in the studied ranges; a higher reaction temperature was also beneficial for producing PANI nanofibers with larger aspect ratios. With the ultrasonic power set to 250 W, although the polymer prepared at higher frequencies showed higher purity as well as smoother surfa-

ces than those at lower frequencies, the one prepared at 50 kHz with uniform diameters of about 80 nm and lengths of about 700 nm performed best. With the ultrasonic power and frequency fixed and aniline polymerization carried out between 0 and 75°C, PANI nanofibers exhibiting larger aspect ratio and less agglomeration were obtained under a higher reaction temperature. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 868–875, 2009

Key words: polyaniline; nanofibers; ultrasonic irradiation; frequency; power

INTRODUCTION

Polyaniline (PANI) has been one of the extensively studied intrinsically conducting polymers in the last two decades due to its lower monomer cost, easy synthesis, good environmental stability, and unique doping–dedoping properties.^{1,2} PANI nanofibers, bearing both the features of conducting polymers and nanomaterials, are considered to perform better than their microsized irregular-shaped counterparts in application fields such as chemical sensors,³ separation membranes,⁴ storage devices,⁵ field emission devices,⁶ and so forth.

In addition to the earlier known hard-template method^{7,8} and electrochemical approach^{9,10} for preparation of PANI nanofibers, a number of novel chemical methods, including interfacial polymerization,^{11,12} rapid mixing polymerization,^{13,14} radiolytic polymerization,¹⁵ seeding polymerization,¹⁶ template-free or surfactant-free synthesis,¹⁷ and sonochemical synthesis^{18–20} have been reported in the last few years. The formation mechanisms of the nanofibers in chemical oxidative polymerization have also been discussed extensively.^{14,21–23}

Although great advantages of facileness, effectiveness, and ease of use have been demonstrated by these methods, one of the remarkable disadvantages

is the difficulty to scale up the synthesis of PANI nanofibers, especially from the technological point of view. For example, the yield of the interfacial polymerization is only 6–10 wt %, ²⁴ and the monomer concentration in the rapid mixing polymerization is too low to achieve a large quantity of PANI nanofibers in one batch. In our previous studies, we have pointed out that secondary growth as well as agglomeration of the polymerization products can be effectively suppressed by introducing ultrasonic irradiation into the chemical oxidative polymerization of aniline. PANI nanofibers can be easily obtained in the presence of ultrasonic irradiation either with secondary addition of monomers or with relatively higher monomer concentrations,^{18,19} which both lead to the possibility of scaled production of PANI nanofibers.

However, no further study concerning the influences of specific ultrasonic parameters on the morphology of the as-prepared PANI nanofibers was found. In this paper, PANI was synthesized by the sonochemical method, and effects of power and frequency of the ultrasonic source as well as the reaction temperature on the morphology of PANI nanofibers were investigated.

EXPERIMENTAL

Synthesis of PANI

All chemicals were of analytical grade from Xi'an Chemical Reagent Factory (Xi'an, China). Aniline

Correspondence to: X. Jing (xljing@mail.xjtu.edu.cn).

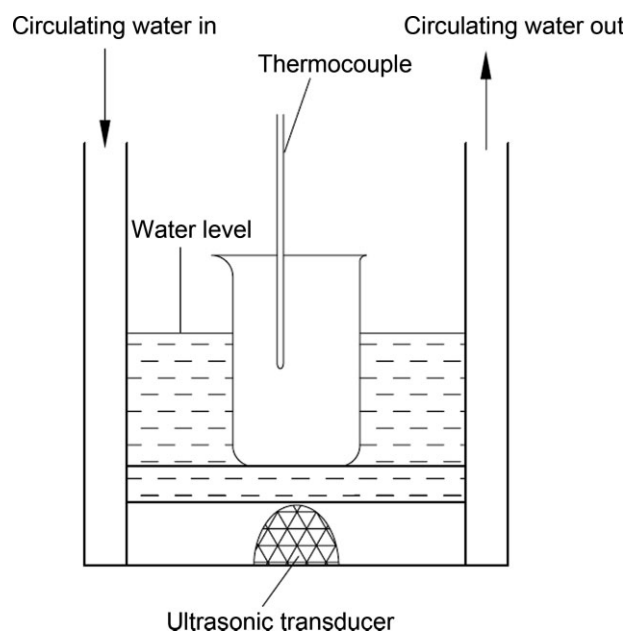


Figure 1 Schematic diagram of the main part of the custom-built ultrasonic wave reactor. Ultrasonic wave reactors with different transducers were used for adjusting the ultrasonic frequency and power.

was doubly distilled in the presence of zinc powder before use, and the others were used as received.

The ultrasonic irradiated chemical oxidative polymerization of aniline was carried out in a custom-built ultrasonic wave reactor (UWR), which consisted of an ultrasonic generator as well as the regulator and a cubic tank (20 cm × 20 cm × 20 cm) with a jacket connected to the circulating water to control the temperature inside the cubic tank (Fig. 1). In a typical procedure, 3.16 g (ca. 0.034 mol) aniline and 7.75 g (ca. 0.034 mol) ammonium peroxydisulfate (APS) were dissolved in 170 mL hydrochloric acid (1 mol/dm³), respectively. A 500-mL beaker containing the aniline hydrochlorate was fixed at the center of the cubic tank of the UWR and the water level height in the cubic tank was maintained at about 10 cm for all the processes to control the ultrasonic power dissipated to the reaction system. The APS hydrochloric solution was added dropwise into the aniline hydrochlorate at a constant rate and the addition was completed within 2 h. The power and frequency of the ultrasonic wave reactor, as well as the reaction temperature, were varied for different samples. Without specification, the polymerization temperature was kept at 20°C ± 2°C.

The temperature fluctuations during polymerization were also recorded to compare the ultrasonic irradiated process with the mechanical stirred polymerization and the rapid mixing polymerization. In those cases, 0.93 g (ca. 0.01 mol) aniline and 2.28 g (ca. 0.01 mol) APS were dissolved in 100 mL hydrochloric acid contained in a 500-mL beaker, respec-

tively. The ultrasonic irradiated polymerization was performed as described above with the ultrasonic power and frequency set as 100 W and 40 kHz, respectively. For the mechanical stirred polymerization (also referred to as traditional polymerization), aniline hydrochlorate was mechanically stirred at a speed of 370 rpm and the APS hydrochloric solution was simultaneously added dropwise at the same rate as that used in the sonochemical polymerization. The rapid mixing polymerization was carried out by pouring all the 100 mL APS hydrochloric solution into the aniline hydrochlorate for one synthesis. Temperature variation during the three processes was recorded according to the digital indication of the thermocouple inserted into the reaction medium.

The crude products were separated by vacuum filtering 3 h after completion of the addition of the APS hydrochloric solution for all the syntheses. The filter cake was washed with copious deionized water and acetone until the filtrate became colorless. Finally, the doped sample was dried in a vacuum (50°C) for 4 h and collected for characterization.

Characterization

Morphology examination of the samples was characterized with a JSM 6700F field emission scanning electron microscope (FE-SEM, JEOL, Japan) without gold sputtering. Typical SEM micrographs of the products were examined using the image editing software Adobe Photoshop 8.0; the approximate length and diameter of PANI nanofibers presented in the SEM micrograph were determined with the Measure Tool provided by the software according to the scale bar given in the SEM micrograph. The aspect ratio of the nanofiber is defined as the ratio of its length to its diameter. Average length, diameter, and aspect ratio of PANI nanofibers for one sample were determined by evaluating the sizes of nanofibers shown in its SEM micrographs.

Because the samples have their major morphology as nanofibers whereas some samples were nearly pure nanofibers, the yield of PANI nanofibers was approximately considered as the polymer yield, which was determined as described in our previously work.²⁰

RESULTS AND DISCUSSION

Ultrasonic power

It is well known that oscillatory pressure with repeating of lower and higher intensities can be induced by the propagation of ultrasound in a liquid,²⁵ resulting in the phenomenon of cavitation. Implosive collapse of cavitation microbubbles can

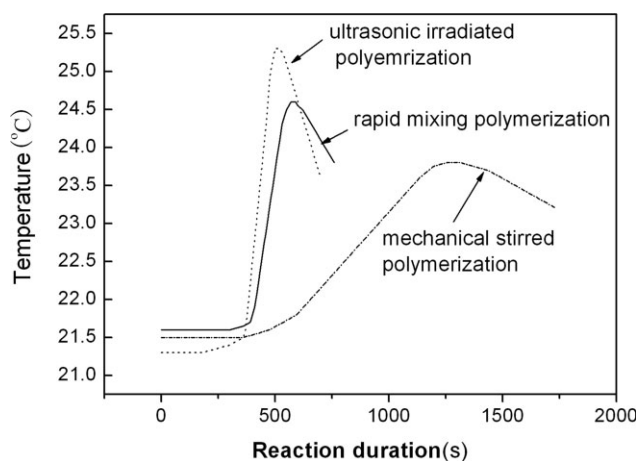


Figure 2 Temperature variation during the ultrasonic irradiated polymerization, rapid mixing polymerization, and traditional polymerization.

release larger amount of energy into small spatially resolved regions, which are usually referred as the “hot spots.” These localized “hot spots” can generate local peak temperatures as high as 5000 K and local pressures ca. 500 atm, respectively, a very rigorous environment.²⁶ With the same synthetic conditions explored (i.e., concentrations of monomer and oxidant, volume of reaction system, etc.), aniline polymerization performed with the ultrasonic irradiation gave the fastest temperature rise and the highest peak temperature (Fig. 2). Aniline polymerization with ultrasonic irradiation probably goes faster than that in the mechanically stirred or rapidly mixed reaction system. A higher polymerization rate was reported to be responsible for the fibrillar growth of the aniline polymerization products.²⁷ When aniline polymerization proceeds at a higher rate, larger amounts of reactants will be consumed to produce new nuclei of polymerization products or form new primary PANI nanofibers during a short period at the beginning of the polymerization; thus, less monomer will be left to participate in the further growth of those primary nanofibers. Symmetrical or asymmetrical collapse of these cavitation bubbles can create shock waves or microjets; the former ones subsequently cause microscopic turbulence or microstreaming of the surrounding media and the latter ones can bombard the particle surface close to them.²⁸ Because the PANI products are insoluble in the polymerization system and have the tendency to agglomerate to minimize their surface energy, larger-sized particles of polymerization products will present in the reaction system. These insoluble solid products will probably be disturbed or bombarded by the shock waves or microjets and have few opportunities to undergo further growth or agglomerate to larger size. That may be the reason it

is much easier to achieve PANI nanofibers through ultrasonic irradiated polymerization than with traditional polymerization.¹⁸

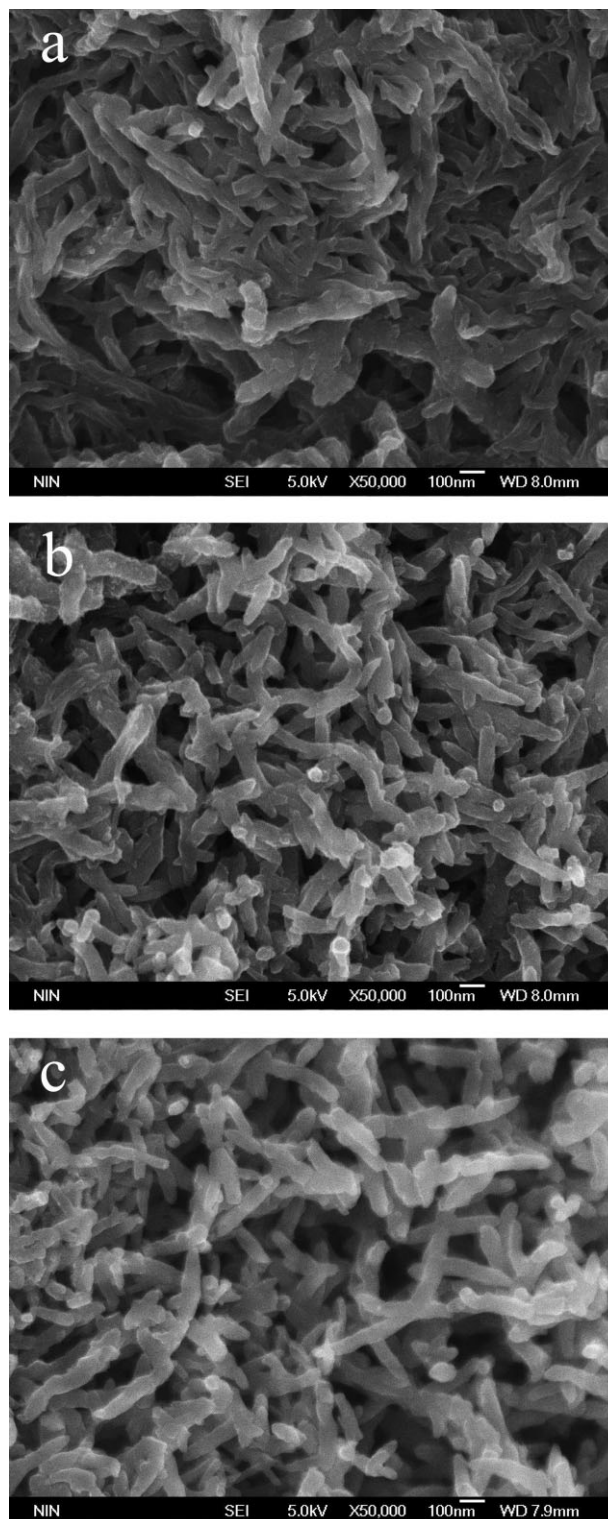


Figure 3 PANI prepared with ultrasonic power of (a): 100 W, (b): 200 W, and (c): 250 W, respectively. The ultrasonic frequency was kept at 40 kHz.

TABLE I
Morphology Characterizations of PANI Prepared with Different Ultrasonic Powers

Ultrasonic power (W)	Sample uniformity	Length of nanofibers (nm)	Diameter of nanofibers (nm)	Aspect ratio of nanofibers
100	Nanofibers and larger-sized irregular agglomeration (minority)	400–650	40–60	7–11
150	Nanofibers and smaller-sized irregular agglomerations (minority)	350–600	50–80	5–7
200	Nanofibers and thick, short nanorods with rough surfaces (minority)	400–600	45–75	6–8
250	Nearly pure nanofibers with smooth surfaces	350–500	55–70	5.5–7.5

With the ultrasonic frequency kept at 40 kHz, PANI nanofibers prepared with increased ultrasonic power exhibit enhanced uniformity and purity. As shown in Figure 3 and Table I, when the power of the ultrasonic reactor was increased from 100 to 250 W, PANI nanofibers with diameters and lengths in the ranges of 40–80 nm and 300–700 nm, respectively, were achieved in all cases, corroborating again the positive effect of ultrasonic irradiation on the formation of PANI nanofibers that we reported previously.^{18–20} SEM micrographs of PANI nanofibers obtained under ultrasonic power of 100 and 150 W showed nearly similar images [Fig. 3(a)], indicating that change of ultrasonic power in this range has negligible effects on the morphology of these nanofibers. With further increasing of the ultrasonic power to 200 and 250 W, the number of the PANI nanofiber agglomerations decreased and the uniformity of the nanofibers was enhanced. For example, much smoother surfaces and uniform diameters were exhibited by the product prepared with ultrasonic power of 250 W than those of others [Fig. 3(c); Table I].

These results show that ultrasonic irradiation with higher power is beneficial for producing PANI nanofibers with less agglomeration and higher uniformity. As in ultrasonic irradiation introduced with higher power, cavitation bubbles can collapse more violently. Shock waves and/or microjets are then produced with larger velocities and can attack or erode these insoluble PANI agglomerates much more vigorously, leading to a decreased number of agglomerations (Fig. 3) compared with those obtained under lower ultrasonic powers. Furthermore, higher ultrasonic power can accelerate the mass transfer in the reaction mixture effectively, and the polymerization products will have an increased opportunity to collide with each other,²⁹ resulting in their more uniform depositing or growth on the primarily formed nanofiber nuclei. It is possible that PANI nanofibers with smooth surfaces were obtained under higher ultrasonic power [Fig. 3(b,c)]. However, the average length of PANI nanofibers was slightly decreased as the ultrasonic power increased (Table I), probably due to enhanced attack

and erosion provided by the shock waves and/or microjets on the solid products under higher ultrasonic power. Therefore, the ultrasonic power should not be too high to obtain PANI nanofibers with larger aspect ratios; in our study, ultrasonic power around 200–250 W is appropriate for producing PANI nanofibers with higher purity and uniformity.

Ultrasonic frequency

Similarly, uniformity of the PANI nanofibers increased and the number of the agglomerations in the products decreased with the increased ultrasonic frequency when the ultrasonic power was kept at 250 W (Fig. 4). For instance, the products prepared at lower frequencies are mixtures of PANI nanofibers and their agglomerates, though in a small fraction. At lower ultrasonic frequencies (namely 20 and 30 kHz) explored here, the prepared PANI nanofibers showed no significant morphological differences [Fig. 4(a)]. These are similar to results of ultrasound-assisted crystallization, in which ultrasonic frequencies lower than 30 kHz were found to have no substantial effects on the morphology of crystals. The explanations may be that ultrasonic waves with longer wavelengths at lower frequencies may not interact adequately with species in the reaction medium.³⁰ When the ultrasonic frequency was increased, nearly pure PANI nanofibers were achieved at ultrasonic frequencies of 40, 50, and 100 kHz [Fig. 4(b–d)]. Further examination on the SEM images of PANI nanofibers indicates that samples produced at an ultrasonic frequency of 50 kHz show the smoothest surfaces and uniform morphology [Figs. 4(c) and 5]. In contrast, the one prepared at a frequency of 40 kHz is a mixture of nanofibers with diameters ranging from less than 30 nm to about 100 nm [Figs. 4(b) and 5(b)], and the one prepared at a frequency of 100 kHz, however, showed surfaces rougher than those prepared at lower frequencies [Fig. 4(d)].

It is evident that relatively higher ultrasonic frequency is also helpful for the preparation of high-quality PANI nanofibers, whereas extremely high frequency would lead to negative effects. At lower

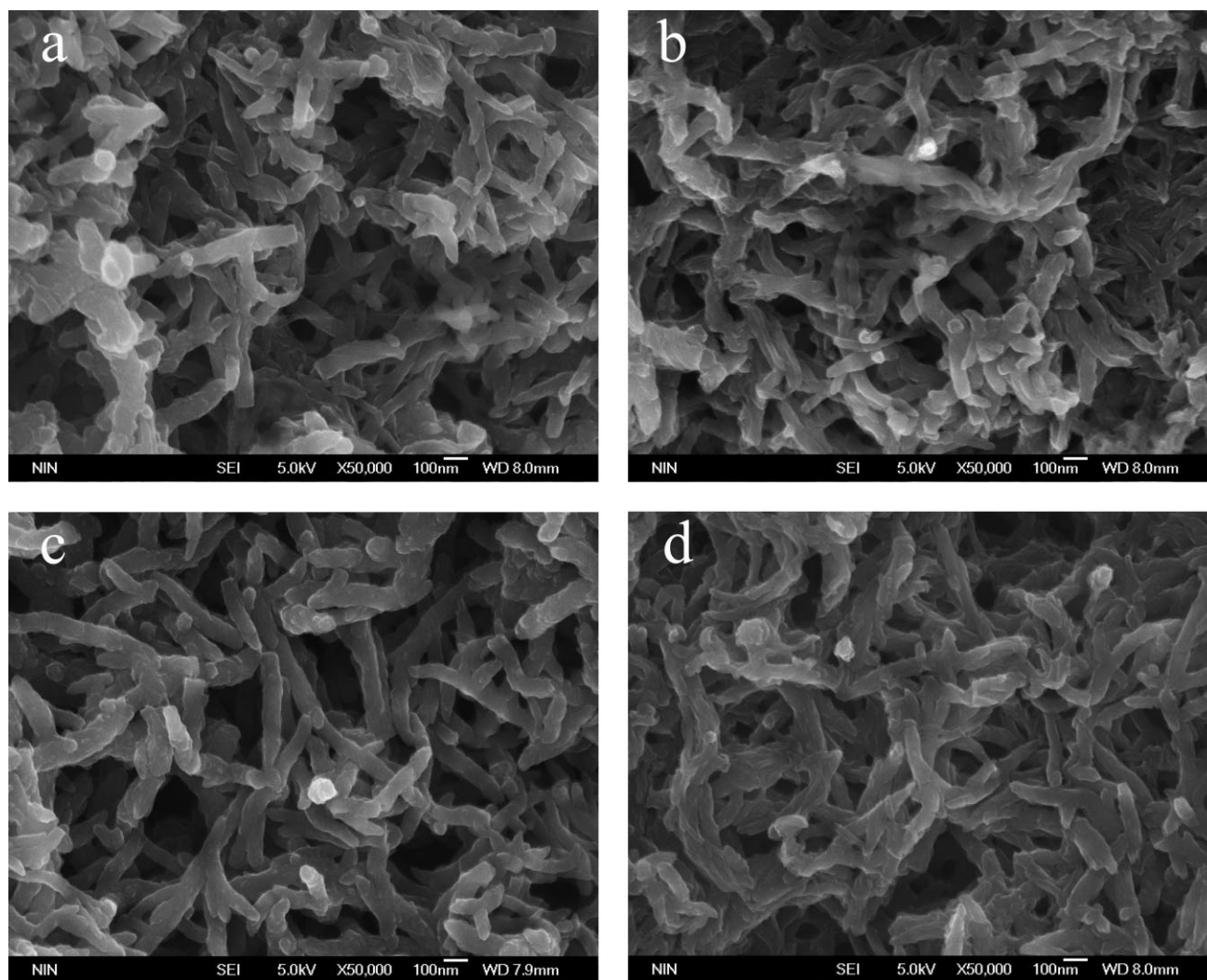


Figure 4 PANI prepared with ultrasonic frequency of (a): 20 kHz, (b): 40 kHz, (c): 50 kHz, and (d): 100 kHz, respectively. The ultrasonic power was kept at 250 W.

frequencies, the alternation of expansion and compression of the local liquids is slower, and longer periods are left for negative pressure. Cavitation bubbles would then collapse less frequently and the roles of shock waves and microjets may not be displayed adequately. The polymerization system under this condition is similar to that without exertion of ultrasonic irradiation; as a result, PANI prepared with an ultrasonic frequency of 20 kHz (or 30 kHz) is a mixture of PANI nanofibers and their agglomerates [Fig. 4(a)]. When ultrasonic irradiation with relatively higher frequency was applied to the polymerization, collapse of the bubbles was capable of producing shock waves or microjets that bombarded and eroded the insoluble PANI more frequently. In these cases, the secondary growth and agglomeration were effectively inhibited or suppressed and uniform PANI nanofibers were obtained [Fig. 4(b,c)]. However, with further increase of the ultrasonic frequency, the existing negative pressure

period became shorter and shorter, and the cavitation bubbles would not grow large enough before collapse. Collapse of these bubbles was less vigorous, resulting in weakened bombarding provided by microwaves and microjets on the insoluble polymers. Consequently, PANI nanofibers with rough surfaces were formed when the ultrasonic frequency was increased to 100 kHz [Fig. 4(d)].

Polymerization temperature

When the ultrasonic power and frequency were kept at 100 W and 40 kHz, respectively, effects of reaction temperature on the morphology of the as-prepared polymer were also examined. It is evident from Figure 6 that at lower temperatures (e.g., 0°C), mixtures of larger-sized irregular PANI and fibrous PANI products resulted [Fig. 6(a)], and the amount of the larger-sized irregular PANI particles decreased with increasing reaction temperatures. PANI

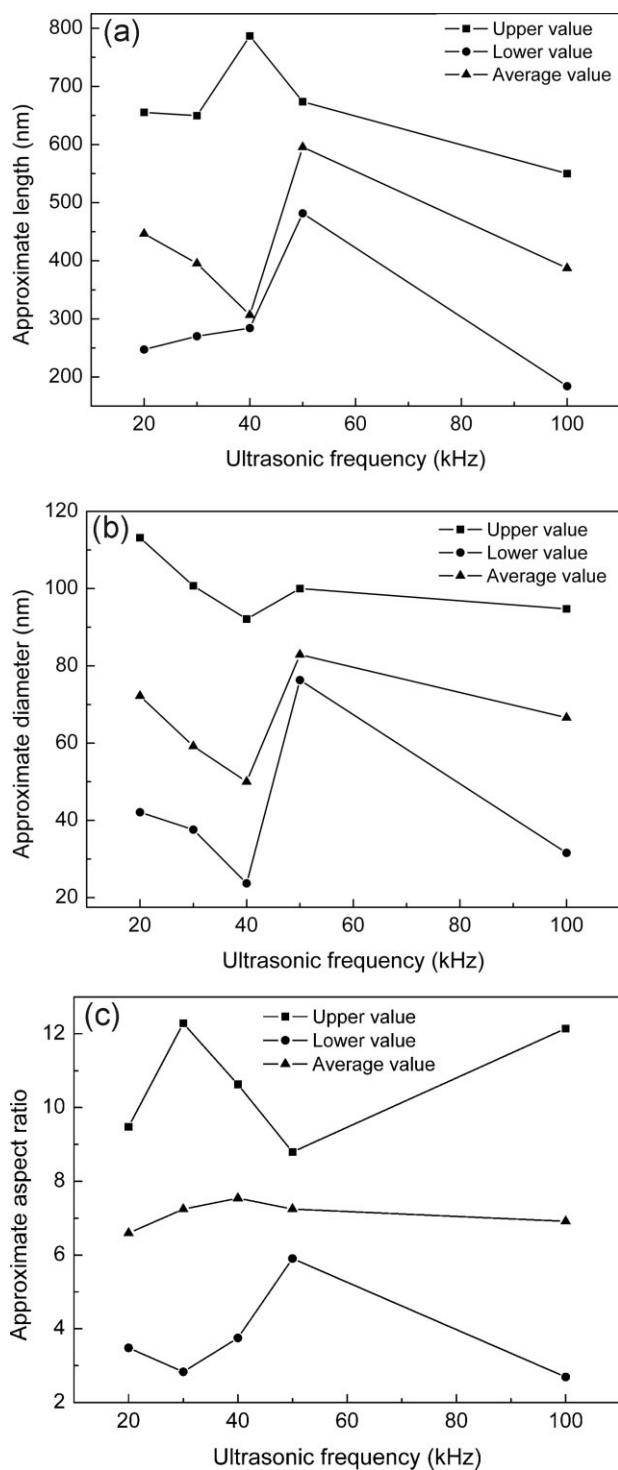


Figure 5 Approximate length (a), diameter (b), and aspect ratio (c) of PANI nanofibers prepared with different ultrasonic frequencies.

obtained at under 25°C showed morphology similar to the nanofibers shown in Figure 6(a), except that their average aspect ratio was slightly larger (Table II). With further increasing of the reaction temperature to 50 and 75°C, not only did the amount of the irregular PANI particles decrease drastically, but the

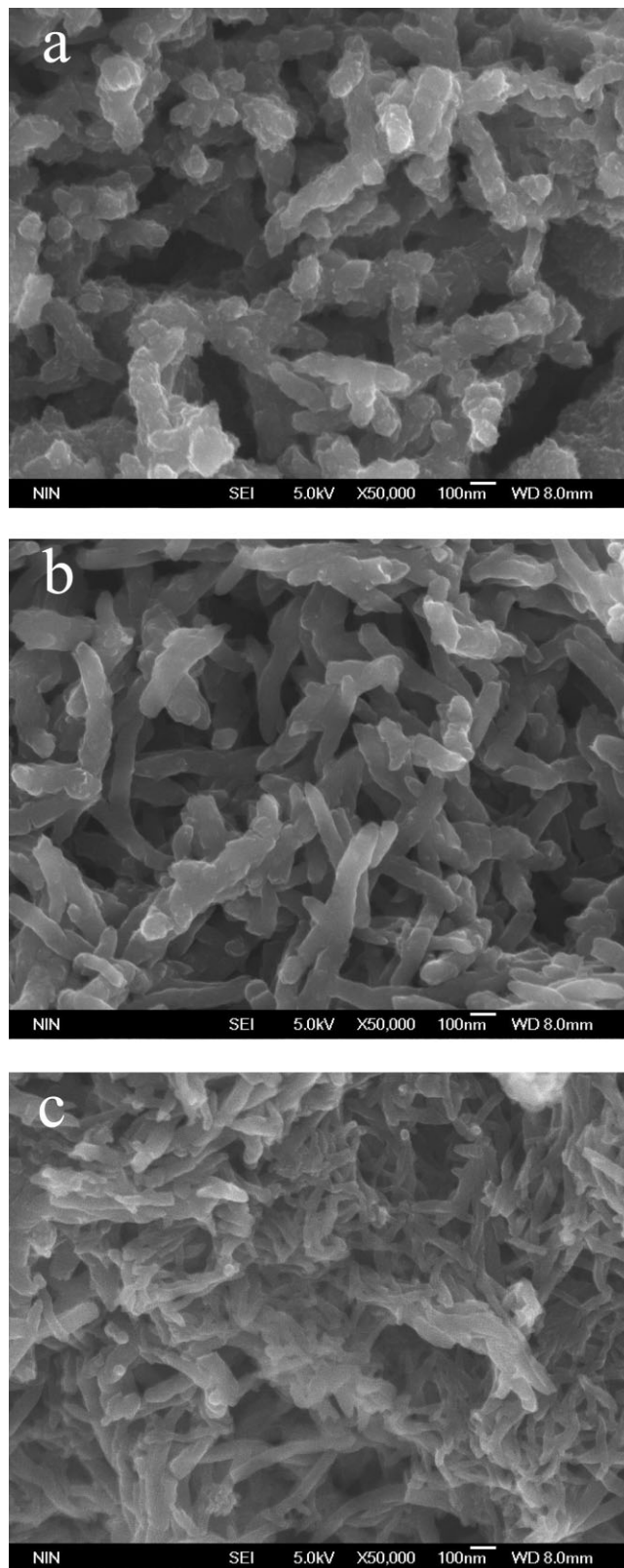


Figure 6 PANI prepared at reaction temperatures of (a): 0°C, (b): 50°C, and (c): 75°C, respectively. The ultrasonic power and frequency were kept at 100 W and 40 kHz, respectively.

TABLE II
Approximate Sizes of PANI Nanofibers Prepared Under Different Temperatures

Sizes of PANI nanofibers	0°C	25°C	50°C	75°C
Length (nm)	300–400	300–500	400–700	500–700
Diameter (nm)	100 ± 20	70 ± 10	80 ± 15	40 ± 10
Aspect ratio	4 ± 1	5 ± 1	7 ± 2	11 ± 2

quality of the PANI nanofibers was enhanced. It can also be said that smoother surfaces, more uniform diameters, and larger aspect ratios were demonstrated for the PANI nanofibers prepared under higher temperatures [Fig. 6(b,c); Table II]. For example, the average diameter and aspect ratio of the PANI nanofibers prepared at 75°C are in the range of 30–50 nm and ca. 11, respectively.

As far as the reaction temperature on the morphology of PANI is concerned, it is proposed that an increase of reaction temperature has two effects on facilitating the formation of PANI nanofibers. On one hand, under higher temperatures, reactants can collide more vigorously and thus produce more active sites than that at lower temperatures; larger amounts of the reactants will be consumed in producing new active sites and propagation of the polymer chains. As a result, few reactants were left to be incorporated into secondary growth of these polymerization products. It is easier for these newly formed polymers to preserve their intrinsic morphology (nanofibers)¹⁴ from secondary growth under higher reaction temperatures. Similar morphology transition of PANI, i.e., from spherical to coral-like cylindrical, with increasing of polymerization temperature was also reported by Stejskal et al.²⁷ in the study of PANI dispersions, in which morphology change of PANI was assigned to accelerated polymerization rate induced by higher polymerization temperatures. On the other hand, species movement and diffusion can be enhanced by increasing the reaction temperature; reactants, reaction intermediates, and polymer molecules then will probably transfer elsewhere rather than to stay or gather at a specific point in the reaction system. Except for the attraction force between these species due to their small size, PANI obtained under higher temperatures will form less agglomeration and disperse well in the system. It is no wonder that chemical polymerization of aniline under higher reaction temperatures yields uniform PANI nanofibers with larger aspect ratios [Fig. 6(b,c)]. If the reaction temperature is too low, both the polymerization rate and the diffusion rate are slow, and the negative effect on formation of PANI nanofibers was hardly balanced by the positive effect of ultrasonic irradiation,^{18–20} leading to formation of a mixture of larger-sized irregu-

lar particles and nanofibers [Fig. 6(a)]. Whereas APS will easily decompose under higher temperatures, the polymerization temperature should not be too high to ensure an acceptable yield of PANI. Therefore, a polymerization temperature around 50–75°C can be selected for the preparation of PANI nanofibers with ultrasonic irradiation.

Yield

When the ultrasonic power and frequency were 100 W and 40 kHz, respectively, polymerization of aniline performed at 20°C can produce PANI nanofibers with a yield of about 45 wt %; as the polymerization temperature increased to 75°C, the yield of PANI nanofibers was found to be close to 57.5 wt %. It should be noted that all the polymerizations were carried out with the monomer concentration of 0.1 mol/dm³, which was much higher than that used in the dilute polymerization.²² Thus it was demonstrated again that our method, i.e., preparing PANI nanofibers through ultrasonic irradiated polymerization, has the potential to produce PANI nanofibers on a large scale.

CONCLUSIONS

PANI was chemically synthesized by the sonochemical method, and effects of ultrasonic power, frequency, and reaction temperature on the morphology of the final products were examined. It was found that in the examined ranges, increase of ultrasonic power (up to 250 W) or the reaction temperature (up to 75°C) both have positive effects on the formation of PANI nanofibers with smoother surfaces and more uniform diameters. The length or aspect ratio of PANI nanofibers decreased as the ultrasonic power increased, whereas a higher polymerization temperature led to longer nanofibers with larger aspect ratios. In the case of ultrasonic frequency, though as a whole, the polymers prepared at higher frequencies showed higher purity; the one prepared at 50 kHz showed the highest uniformity and smoothest surfaces. PANI nanofibers prepared with ultrasonic irradiation were obtained with a higher yield than some reported methods, and the morphology of these nanofibers can be tuned by adjusting the ultrasonic parameters or the reaction temperature. It is possible, then, with rational combination of the reaction parameters, to prepare PANI nanofibers with higher purity and larger aspect ratio by the sonochemical method. However, the as-prepared nanofibers are randomly distributed in the final product, which may restrict some of their potential applications in which ordered arrays are demanded. Further work on mass

preparation of ordered PANI nanofibers is in progress in our group.

References

1. Wang, Y. Y.; Jing, X. L. *Polym Int* 2007, 56, 126.
2. Wang, Y. Y.; Jing, X. L. *Polym Adv Technol* 2005, 16, 344.
3. Virji, S.; Huang, J. X.; Kaner, R. B.; Weiller, B. H. *Nano Lett* 2004, 4, 491.
4. Kaner, R. B. *Synth Met* 2001, 125, 65.
5. Tseng, R. J.; Huang, J. X.; Ouyang, J.; Kaner, R. B.; Yang, Y. *Nano Lett* 2005, 5, 1077.
6. Wang, C. W.; Wang, Z.; Li, M. K.; Li, H. L. *Chem Phys Lett* 2001, 341, 431.
7. Wu, C.-G.; Bein, T. *Science* 1994, 264, 1757.
8. Martin, C. R. *Chem Mater* 1996, 8, 1739.
9. Okamoto, H.; Okamoto, M.; Kotaka, T. *Polymer* 1998, 39, 4359.
10. Liang, L.; Liu, J.; Windisch, C. F.; Exarhos, G. J.; Lin, Y. H. *Angew Chem Int Ed* 2002, 41, 3665.
11. Huang, J. X.; Kaner, R. B. *J Am Chem Soc* 2004, 126, 851.
12. He, Y. J. *Appl Surf Sci* 2006, 252, 2115.
13. Huang, J. X.; Kaner, R. B. *Angew Chem Int Ed* 2004, 43, 5817.
14. Huang, J. X.; Kaner, R. B. *Chem Commun* 2006, 367.
15. Pillalamarri, S. K.; Blum, F. D.; Tokuhira, A. T.; Story, J. G.; Bertino, M. F. *Chem Mater* 2005, 17, 227.
16. Zhang, X. Y.; Goux, W. J.; Manohar, S. K. *J Am Chem Soc* 2004, 126, 4502.
17. Li, G. C.; Pang, S. P.; Peng, H. R.; Wang, Z. B.; Cui, Z. L.; Zhang, Z. K. *J Polym Sci Part A: Polym Chem* 2005, 43, 4012.
18. Jing, X. L.; Wang, Y. Y.; Wu, D.; She, L.; Guo, Y. *J Polym Sci Part A: Polym Chem* 2006, 44, 1014.
19. Jing, X. L.; Wang, Y. Y.; Wu, D.; Qiang, J. P. *Ultrason Sonochem* 2007, 14, 75.
20. Wang, Y. Y.; Jing, X. L.; Kong, J. H. *Synth Met* 2007, 157, 269.
21. Chiou, N. R.; Epstein, A. J. *Synth Met* 2005, 153, 69.
22. Chiou, N. R.; Epstein, A. J. *Adv Mater* 2005, 17, 1679.
23. Wang, Y. Y.; Jing, X. L. *J Phys Chem B* 2008, 112, 1157.
24. Huang, J. X.; Virji, S.; Weiller, B. H.; Kaner, R. B. *J Am Chem Soc* 2003, 125, 314.
25. McCausland, L. J.; Cains, P. W.; Martin, P. D. *Chem Eng Prog* 2001, 97, 56.
26. Xia, H. S.; Wang, Q. *Chem Mater* 2002, 14, 2158.
27. Stejskal, J.; Spirkova, M.; Riede, A.; Helmstedt, M.; Mokreva, P.; Prokes, J. *Polymer* 1999, 40, 2487.
28. Hagenson, L. C.; Doraiswamy, L. K. *Chem Eng Sci* 1998, 53, 131.
29. Li, H.; Wang, J. K.; Bao, Y.; Guo, Z. C.; Zhang, M. Y. *J Cryst Growth* 2003, 247, 192.
30. de Castro, M. D. L.; Priego-Capote, F. *Ultrason Sonochem* 2007, 14, 717.