Polyaniline Nanofiber Synthesis by Co-Use of Ammonium Peroxydisulfate and Sodium Hypochlorite

Abdelaziz Rahy,[†] Mohamed Sakrout,[†] Sanjeev Manohar,[‡] Sung June Cho,[§] John Ferraris,[†] and D. J. Yang[*,†]

Department of Chemistry & the Alan G. MacDiarmid NanoTech Institute, The University of Texas at Dallas, Richardson, Texas 75080, Center for Green Chemistry, Department of Chemical Engineering, University of Massachusetts Lowell, Lowell, Massachusetts 01854, and Department of Applied Chemical Engineering, Chonnam National University, Kwang-Ju, Korea

Received December 24, 2007. Revised Manuscript Received January 30, 2008

The polymerization to polyaniline nanofibers was carried out in an aqueous system using aniline, 1 M HCl. and ammonium peroxydisulfate (APS) with additional use of sodium hypochlorite solution as a co-oxidant. The addition of sodium hypochlorite solution was made either before or after the addition of APS. This new method always produces polyaniline nanofibers with long length. Additional advantages of this new method are discussed. The effect of aniline concentration, hypochlorite concentration, different acid use, reaction temperature, and both aniline and hypochlorite purity on morphology and electrical property of the nanofibers synthesized by this new method was investigated.

1. Introduction

Conductive polymers, such as polyacetylene and polyaniline, have been the subject of numerous investigations in the past two decades.[1] Among the electrically conducting polymers, polyaniline (Pani) has attracted intense attention due to its environmental stability, ease of synthesis, exciting electrochemical, optical, and electrical properties.[2,3] Nanofibers of polyaniline have attracted even more interest because of their properties that make them possibly suitable for applications as sensors,[4–6] batteries,[7,8] molecular electronic devices, corrosion inhibitors[9,10] and separation membranes.[11,12] Polyaniline may be synthesized by either electrochemical or chemical oxidative techniques[13] and can be doped to a highly conducting state by protonic acids. In recent years, considerable efforts have been made to find specific synthesis conditions and methods for the synthesis of polyaniline nanofibers. There are several reports by the use of hard templates,[14] soft templates,[15] seeding,[16] interfacial polymerization,[17] and electrospinning.[18] Recently, David et al. synthesized nanofibers of semiconducting and metallic polyaniline nanofibers. Li et al.[21] reported the synthesis of polyaniline nanofibers by conducting the conventional polymerization reaction at an elevated temperature without mechanical agitation, and Jing et al. synthesized polyaniline nanofibers by dropwise addition of a solution of ammonium peroxydisulfate (APS, $(NH_4)_2S_2O_8$) into an aqueous aniline solution in the presence of the ultrasonic irradiation.[22]

As described above, synthesis of polyaniline nanofibers requires specific conditions. We report here that our new

---

[*] Corresponding author. Tel.: 1 972 883 6681. Fax: 1 972 883 2925. E-mail: djyang@utdallas.edu.

[†] The University of Texas at Dallas.

[‡] University of Massachusetts Lowell.

[§] Chonnam National University.

(1) Chandrasekhar, P. *Conducting Polymers, Fundamentals and Applications: A Practical Approach*; Kluwer Academic Publishers: Boston, 1999..

(2) (a) MacDiarmid, A. G. *Angew. Chem. Int. Ed.* **2001**, *40*, 2581. (b) MacDiarmid, A. G. *Synth. Met.* **1997**, *84*, 27.

(3) MacDiarmid, A. G. Chiang, J. C. Richter, A. F. Somasiri, N. L. D. Epstein, A. J.; Alacer, L., Ed. *Conducting Polymers*; D. Reidel Publications: Dordrecht, The Netherlands, 1987; pp 105–120.

(4) Janata, J.; Josowicz, M. *Nat. Mater.* **2003**, *2*, 19.

(5) Huang, J. X.; Virji, S.; Weiller, B. H.; Kaner, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 314–315.

(6) Virji, S.; Fowler, J. D.; Baker, C. O.; Huang, J.; Kaner, R. B.; Weiller, B. H. *Small* **2005**, *1* (N 6), 624–627.

(7) MacDiarmid, A. G.; Somasiri, N. L. D.; Mu, S. L.; Wu, W. Q.; Chiang, J. C.; Huang, W. S.; Halpern, M. J. *J. Electrochem. Soc.* **1984**, *131*, C328.

(8) MacDiarmid, A. G.; Yang, L. S.; Huang, W. S.; Humphery, B. D. *Synth. Met.,* **1987**, *18*, 393.

(9) Deberry, D. W. *J. Electrochem. Soc.* **1985**, *132*, 1022.

(10) Mengoli, G.; Musiani, M. M.; Pelli, B.; Vecchi, E. *J. Appl. Polym. Sci.* **1983**, *28*, 1125.

(11) Anderson, M. R.; Mattes, B. R.; Reiss, H.; Kaner, R. B. *Science* **1991**, *252*, 1412.

(12) Kaner, R. B. *Synth. Met.* **2001**, *125*, 65.

(13) Huang, W. S.; Humphrey, B. D.; G MacDiarmid, A. *J. Chem. Soc., Faraday Trans.* **1986**, *82*, 2385.

(14) (a) Martin, C. R. *Acc. Chem. Res.* **1995**, *28*, 61. (b) Martin, C. R. *Chem. Mater.* **1996**, *8*, 1739.

(15) Qiu, H.; Wan, M.; Matthews, B.; Dai, L. *Macromolecules* **2001**, *34*, 675.

(16) (a) Zhang, X.; Goux, W. J.; Manohar, S. K. *J. Am. Chem. Soc.* **2004**, *126*, 4502–4503. (b) Xing, S.; Zhao, C.; Jing, S.; Wang, Z. *Polymer* **2006**, *47*, 2305–2313.

(17) (a) Huang, J.; Kaner, R. B. *Angew. Chem., Int. Ed.* **2004**, *43*, 5817–5821. (b) Huang, J.; Kaner, R. B. *J. Am. Chem. Soc.* **2004**, *126*, 851. (c) Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 314. (d) Zhang, X.; King, R. C. Y.; Jose, A.; Manohar, S. K. *Synth. Met.* **2004**, *145*, 23–29.

(18) (a) Pinto, N. J.; T Johnson, A., Jr.; MacDiarmid, A. G.; Mueller, C. H.; Theofylaktos, N.; Robinson, D. C.; Miranda, F. A. *Appl. Phys. Lett.* **2003**, *83*, 4244. (b) Zhou, Y.; Freitag, M.; Hone, J.; Staii, C.; Johnson, A. T., Jr.; Pinto, N. J.; MacDiarmid, A. G. *Appl. Phys. Lett.* **2003**, *83*, 3800.

(19) Sarno, D. M.; Manohar, S. K.; MacDiarmid, A. G. *Synth. Met.* **2005**, *148*, 237–243.

(20) Chiou, N. R.; Epstein, A. J. *Synth. Met.,* **2005**, *153*, 69–72.

(21) Li, D.; Kaner, R. B. *J. Am. Chem. Soc.* **2006**, *128*, 968–975.

(22) Jing, X.; Wang, Y.; Wu, D.; Qiang, J. *Ultrasonic Sonochem.* **2006**, *14*, 75–80.

10.1021/cm703678m CCC: $40.75

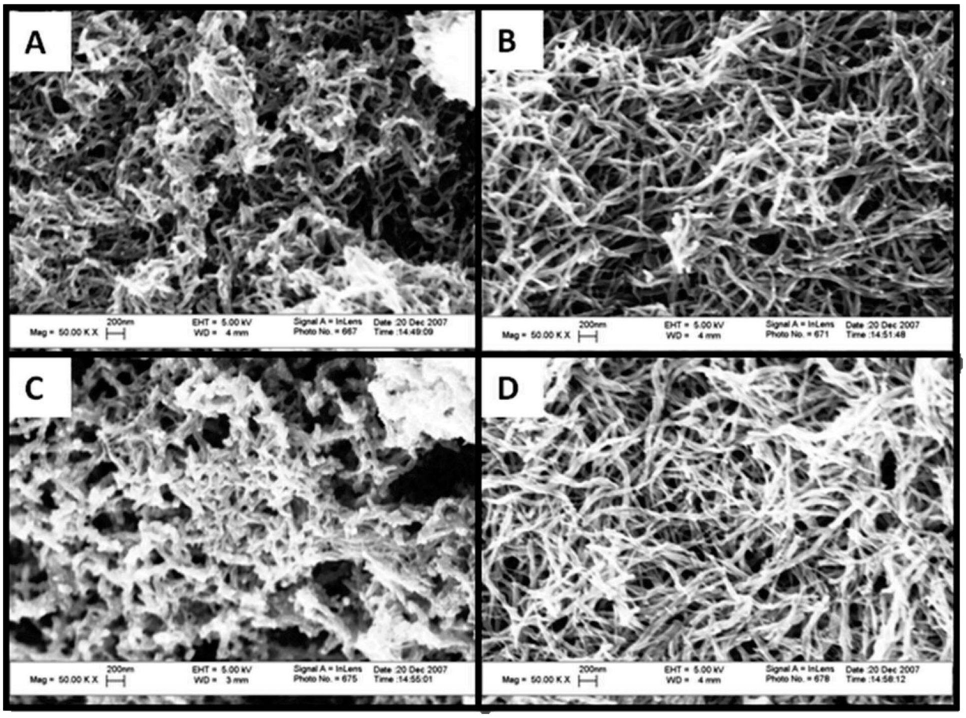

Figure 1. SEM of polyaniline obtained in different temperatures. (A) Control at room temperature. (B) Using NaOCl at room temperature. (C) Control in ice bath. (D) Using NaOCl in ice bath.

robust method, comprising the addition of sodium hypochlorite before of after APS addition, always produces nanofibers at wide ranges of aniline concentrations and that of temperature (0–30 °C). Polyaniline nanofibers produced by this new method are several micrometers in length with less than 40 nm diameter with narrower molecular weight distributions compared to the synthesis done with APS alone.

2. Experimental Section

2.1. Reagents. Aniline (Aldrich, ACROS) was either used as received or distilled and stored in a refrigerator prior to use. Ammonium peroxydisulfate (APS, ACROS), sodium hypochlorite 14% (VWR), and hydrochloric acid were used without further purification.

2.2. Synthesis of Polyaniline Nanofibers. In a typical synthesis, 1.9 mL of aniline was dissolved in 100 mL of 1 M hydrochloric acid while 5.7 g of ammonium peroxydisulfate (APS) was dissolved in 100 mL of 1 M hydrochloric acid. Twenty milliliters of APS solution was added quickly to the aniline mixture and mixed. This gives aniline to APS molar ratio of 1:1.25. The reaction vessel was maintained either at ice bath temperature (0 to 5 °C) or room temperature. Once the reaction starts, 2 mL of an aqueous sodium hypochlorite (5% by wt) solution was quickly added dropwise with agitation after which the stirring was stopped. The reaction vessel was then left standing without mixing for 25 min. The thick precipitated polymer was filtered, washed with 1 M HCl, DI water, and then acetone, followed by drying in an oven 80 °C overnight.

2.3. Instrumental Analysis and Measurements. *2.3.1. Electrical Conductivity Measurement.* The standard four-probe technique using a Keithley 2000 instrument was employed to measure the electrical conductivity of compressed pellets of each polyaniline sample.

2.3.2. UV–Visible Spectroscopy (UV–vis). All UV–vis absorbance spectra were measured on a Shimadzu UV–vis 1601PC spectrometer on solutions of 0.05 g of EB dissolved in 20 mL of NMP solvent. The emeraldine salt, initially green in color, changes to blue upon washing with 5% ammonium hydroxide, indicating that the polyaniline salt was deprotonated to the emeraldine base (EB) form.

2.3.3. Gel-Permeation Chromatography. A Perkin-Elmer series 200 GPC comprising an autosampler, pump, column oven, and refractive index detector, and NMP/$LiBF_4$ (0.8% $LiBF_4$) as the mobile phase was used. Two different columns were used, one for low and medium molecular weight polyaniline (column range 2–100 K), and the other for high molecular weight polyaniline (column range 10–1000 K). The instrument was calibrated using narrow molecular weight distribution polystyrene standards and the polyaniline number and weight average molecular weights and resulting PDIs are relative to these standards.

2.3.4. Electron Microscopy. The morphology of each sample was determined by using a Zeiss-LEO model 1530 variable-pressure field-effect scanning electron microscope and the dried sample for SEM was prepared by coating each sample on carbon conductive grid.

Results and Discussion

In order to find the optimal conditions for the synthesis of polyaniline nanofibers using our new method, we first investigated the influence of reaction temperature. When the reaction was carried out at ice bath temperatures, fibers approximately 39 nm in diameter and 2 μm in length were produced. However, when the reaction was conducted at room temperature, fibers of approximately the same diameter (37 nm) but only half the lengths (1 μm) were obtained, as shown in Figure 1. We also investigated the effect of aniline concentration on the morphology of the polymerization product, and found that as aniline concentration increases, the diameter of nanofibers also increases from (~35 nm with 0.1*M* aniline, ~39 nm with 0.2 M aniline to ~47 nm with 0.5 M aniline) as shown in Figure 2. Thus, a low concentration of aniline is favorable for the synthesis of small diameter

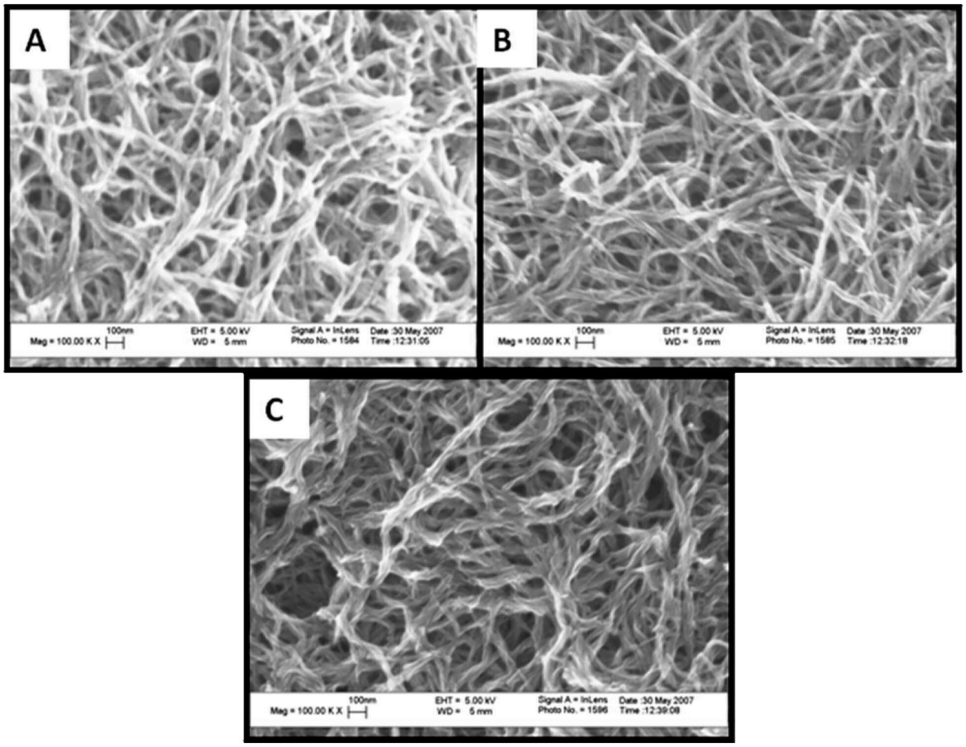

Figure 2. SEM of polyaniline fibers obtained in different concentrations of aniline: (A) 0.1 M, (B) 0.2 M, and (C) 0.5 nM.

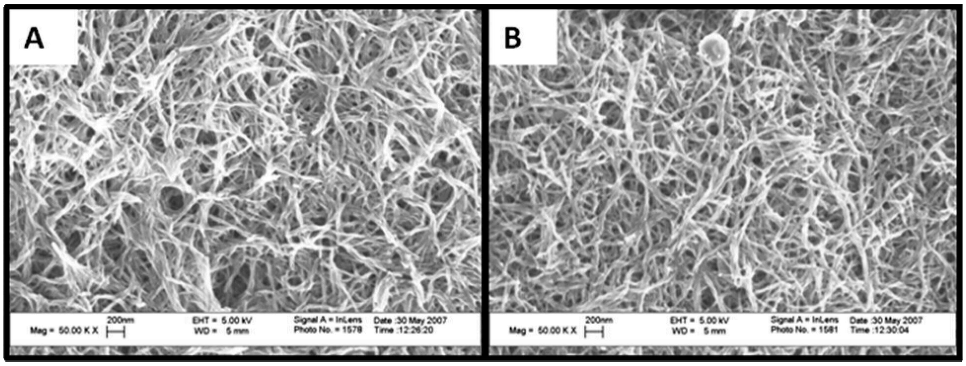

Figure 3. SEM of polyaniline synthesized using 0.1 M aniline (1 mL), 1 M HCl (100 mL), 5% sodium hypochlorite (2 mL), and 0.60 g APS: (A) adding APS dropwise, (B) adding APS all at once.

fibers and, furthermore, the diameter of the fibers could be directly controlled by the appropriate selection of aniline concentration. These results are consistent with a recent report of polyaniline nanofibers synthesis via the seeding method.[14] Figure 3 shows the SEMs of polyaniline samples obtained from both the rapid and dropwise addition of APS. We observe that in both cases, polyaniline nanofibers were obtained. This result shows that our synthesis method is very robust compared to the several different methods reported.[14–22] The concentration of HCl (0.01 and 0.1 M) was also important since at the lower acid concentration, no nanofibers were formed. The effect of sodium hypochlorite concentration was studied as shown in Figure 4. When the hypochlorite concentration was increased from 1, 5 to 10%, polyaniline nanofibers were obtained. But when 14% sodium hypochlorite was used, essentially no nanofibers were obtained (Figure 4d). From the results, we concluded that there is an optimum concentration range to synthesize nanofibers. In addition, when lower concentrations (1 and 5%), of sodium hypochlorite were used, longer length polyaniline nanofibers were obtained with 60% yield. APS use alone (control) gave 28% yield. The UV–vis absorption spectra of the polyaniline samples dissolved in NMP are shown in Figure 5. In all of these spectra, peaks were observed at 321 and 635 nm. The lower wavelength band is often assigned to $\pi-\pi^*$ transition in the benzenoid structure, whereas the longer wavelength band is assigned to the quinoid ring. The UV–vis absorption spectra of polyaniline fibers obtained are consistent with previously reported results.[23]

We also found that, as long as the polymerization was performed with couse of sodium hypochlorite with APS, the morphology of nanofibers maintains even when other acids such as H_2SO_4 and HNO_3 were used, as shown in Figure 6. Unlike the common synthesis using APS only, we found that our synthesis method always gave nanofibers whether or not

---

[23] Manohar, S. K.; MacDiarmid, A. G. *Synth. Met.* **1991**, *711*, 41–43.

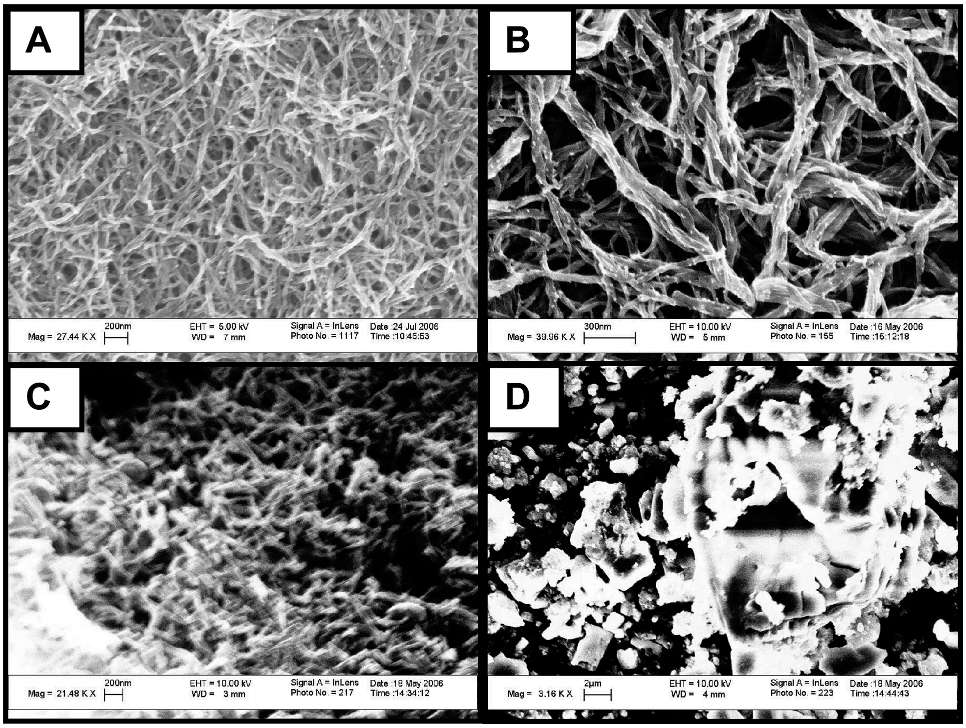

Figure 4. SEM picture of polyaniline obtained in 1 mL of HCl, 1 mL of aniline, 0.62 g of APS, and 2 mL of NaOCl: (A) 1% NaOCl, (B) 5% NaOCl, (C) 10% NaOCl, and (D) 14 %NaOCl.

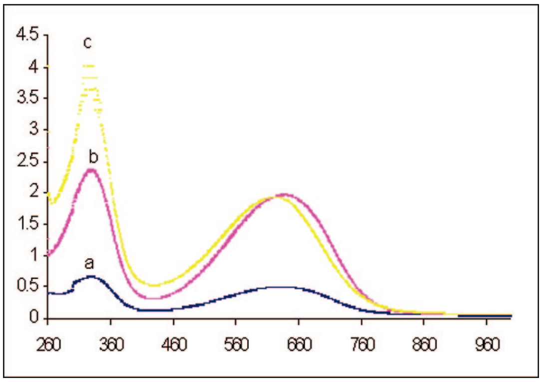

Figure 5. UV–vis spectra of polyaniline: (a) no bleach at room temperature, (b) no bleach in ice bath, (c) with bleach at room temperature.

aniline was purified as shown in Figure 7. Additionally, we found that both commercial bleach and reagent grade sodium hypochlorite gave essentially the same nanofibers quality as shown in Figure 8. Thus, we can conclude that the use of hypochlorite makes the synthesis of polyaniline nanofibers be a robust method.

J. Huang et al. reported that using relatively dilute aniline solutions (3.2 mmol) and APS (0.8 mmol), polyaniline nanofibers were obtained when the oxidant was added all at once, whereas only granular polyaniline particulates resulted when the oxidant was added dropwise.[17] The mechanism offered was that when the oxidant is added dropwise, a secondary growth process competes with fibril formation, which is normally favored when the oxidant is added all at once.

However, we observed that with the couse of sodium hypochlorite, addition method of APS had no influence on the formation of nanofibers. Although the mechanism governing the formation of polyaniline nanofibers by sodium hypochlorite use remains unclear at this point, we observed that the use of sodium hypochlorite preferably directs to the fibril polymerization as nanofibers. The sodium hypochlorite appears to facilitate the growth of nanofibers along the axes of the polymer chains. We suggest that the growth of nanofibers follows the classical theory of nucleation and growth [24–28] and that sodium hypochlorite reduces the formation of the number of nucleation sites on the surface of the nanofibers, therefore, allowing polyaniline to grow preferably into fibril direction to produce longer and thinner fibers. FTIR spectra not shown exhibited absorption peaks corresponding to the stretching of quinoid (1580 cm^{-1}) and benzenoid (1492 cm^{-1}) rings, as well as N−H stretching (3405 cm^{-1}), in agreement with previous literature characterization of polyaniline.[29] The elemental analyses of polyaniline prepared by the conventional method and the sodium hypochlorite-modified method described above are shown

---

(24) Bunker, B. C.; Rieke, P. C.; Tavasevich, B. J.; Cambell, A. A.; Gryxell, G. E.; Graff, G. L.; Song, L.; Liu, J.; Virden, J. W.; Mcvay, G. L. *Science* **1994**, *264*, 48.
(25) Sohnel, O. Garside, J. *Precipitation: Basic Principles and Industrial Applications*; Butterworth Heinemann: Oxford, U.K., 1992..
(26) Chiou, N. R.; Epstein, A. J. *Adv. Mater.* **2005**, *17*, 1679–1683.
(27) Johnson, D. F.; Craft, B. J.; Jaffe, S. M. *J. Nanopart. Res.* **2001**, *3*, 63.
(28) Liang, L.; Liu, J.; Windisch, C. F.; Exarhos, G. J.; Lin, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 3665.
(29) Hasik, M.; Drehinkiewicz, A.; Wenda, E.; Paluszkiewicz, C.; Quillard, S. *J. Mol. Struct.* **2001**, *596*, 89.
(30) McCall, R. P.; Ginder, J. M.; Roe, M. G.; Asturias, G. E.; Scherr, E. M.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1989**, *39*, 10174–10178.
(31) Zhang, Z.; Wei, Z.; Wan, M. *Macromolecules* **2002**, *35*, 5937–5942.
(32) Kahol, P. K.; Guan, H.; McCormick, B. J. *Phys. Rev.* **1991**, *44*, 44–10393.
(33) Lee, K.-S. Hino, T. and Kuramoto N. *Chem. Lett.* **2007**, *36* (No. 2).
(34) Madathil, R. *Synth. Met.* **2005**, *150*, 123–126.
(35) Zhang, X.; Kolla, H. S.; Wang, X.; Raja, K.; Manohar, S. K. *Adv. Funct. Mater.* **2006**, *16*, 1145–1152.

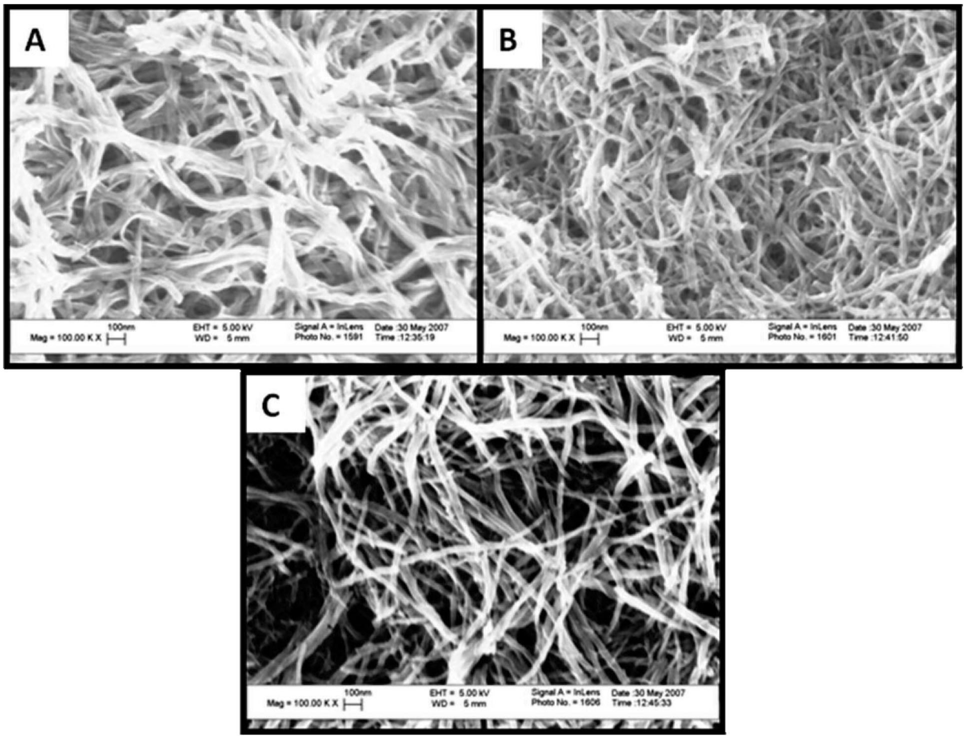

Figure 6. SEM images of polyaniline obtained in 1 mL of aniline, 0.60 g of APS, and 2 mL of NaOCl and 100 mL of acid: (A) 1 M HCl, (B) 1 M HNO_3, and (C) 1 M H_2SO_4.

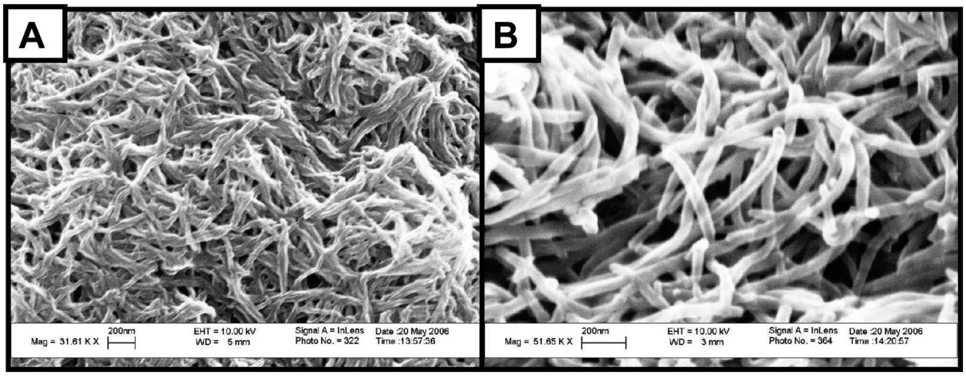

Figure 7. SEM of polyaniline nanofibers synthesized using (A) distilled aniline, (B) nondistilled aniline using NaOCl.

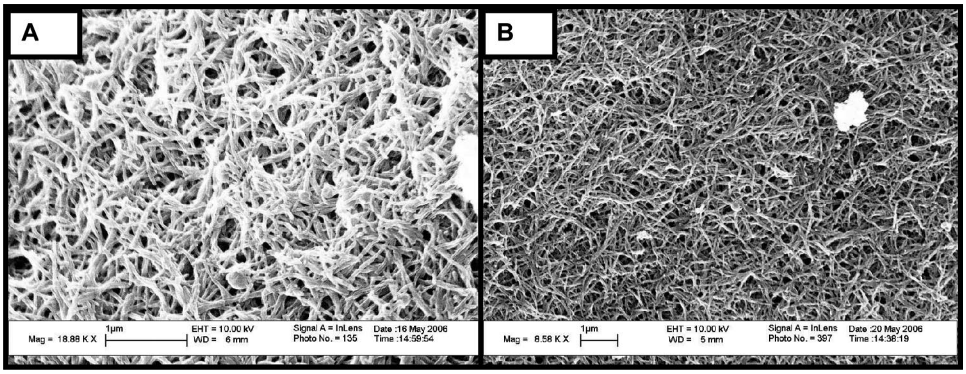

Figure 8. SEM images of polyaniline obtained 75 mL of 1 M HCl, 1 mL of aniline, 0.62 g of APS, (A) commercial bleach (5% NaOCl), and (B) 5% NaOCl from VWR.

in Table 2. The results indicate the presence of oxygen in polyaniline (12.07% vs 7.03% without hypochlorite use). The higher oxygen content in the sample synthesized using hypochlorite may be due to the partial oxidation of the polyaniline chains; a further investigation is in progress.

The bulk room-temperature conductivities of polyaniline nanofibers were obtained using the standard four-probe method. As shown in Table 1, the conductivity increased with the type of acid used, with HCl giving the highest conductivity among the samples. Many groups have also

Table 1. Synthesis Conditions vs Conductivity (S cm^{-1})

aniline (mL)	APS (g)	NaOCl (ml)	acid	conductivity[a] (S cm^{-1})
1	0.62	2	HCl	24.4
1	0.62	2	HNO_3	3.42
1	0.62	2	H_2SO_4	6.48
2	0.62	2	HCl	18.65
5	0.62	2	HCl	22.81

[a] Conventional method: 1 × 10^{-2} (S cm^{-1}).

Table 2. Elemental Analysis of Polyaniline

reaction conditions	%C	%H	%N	%Cl	%O
conventional only APS	60.87	5.20	11.57	14.31	7.03
APS and NaOCl	57.06	5.28	11.37	14.45	12.07

reported that among different dopant acids such as HCl, H_2SO_4, and H_3PO_4, HCl dopant gave the highest conductivity as we observed.[31–34] They elaborated a few reasons why HCl dopant gives the highest conductivity. It could be due to size of ion[31] and solvation effect of Cl^- with absorbed water that leads to increased conductivity.[32,33] The bulk conductivity trend seems to suggest that the pK_a of the acid plays an important role in determining the amount of doping sites or doping level along the polymer's backbone, as the HCl (with lowest pK_a of −9.0) and HNO_3 (with highest pK_a of −1.5) exhibited the highest and lowest bulk conductivity, respectively.[33] Another explanation was due to the characteristics of dopant anions such as their electron affinity and size as well as their orientation with respect to polyaniline chains that can cause variation in conductivities.[34] We found that the conductivity increases when the concentration of aniline was decreases in our synthesis. Additionally, we found that crystallinity of nanofibers synthesized by our new method is higher than that synthesized by the conventional method using APS alone (Figure 9). This high crystallinity should contribute to have high conductivity.[30] The GPC data show a M_w of 42 206 with M_w/M_n ratio of 2.3 for the Emeraldine base synthesized at room temperature from the conventional method while a value of M_w of 9995 with a M_w/M_n ratio of 1.2 for the Emeraldine base synthesized from our new method was obtained. Although polymer produced by our new method has lower molecular weights, our new method gives nanofibers with much narrower molecular weight distributions. We extended our new synthesis method to the preparation of poly-*N*-methylaniline (PNMA). PNMA is an interesting conductive polymer since it is known as a derivative of polyaniline to have better solubility and processability.[35] Figure 10 shows that the co-use of hypochlorite gave longer PNMA nanofibers whereas no use of hypochlorite produced the irregularly shaped agglomerates. Thus, the morphology difference in the case of PNMA was even more pronounced than observed in polyaniline synthesis. We plan to do kinetic studies of both polyaniline and PNMA polymerizations possibly to elucidate the mechanism of selective fibril formation observed in our new synthesis method.

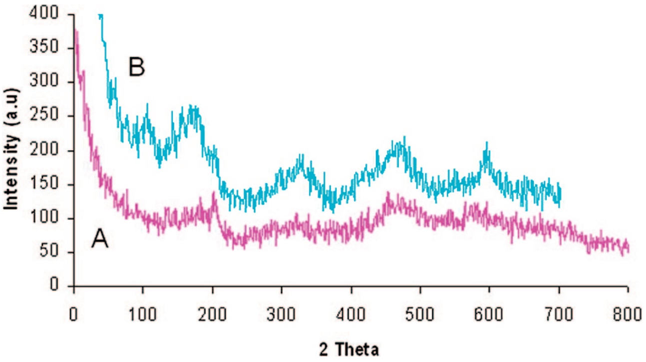

Figure 9. X-ray diffraction patterns of PANI samples synthesized using (A) APS only at room temperature and (B) APS and bleach at room temperature.

4. Conclusion

The additional use of sodium hypochlorite with APS in aniline polymerization produced longer length (2 μm) and thinner (39 nm in diameter) polyaniline nanofibers compared to fibers produced using APS alone. Our results also indicate that the diameter of the polyaniline nanofibers can be controlled by changing the concentration of aniline with lower concentrations producing fibers with thinner diameters. The additional use of hypochlorite added the synthesis of polyaniline nanofibers to be robust by reducing its sensitivity to variations of temperature (0–30 °C), aniline concentration (0.1–0.5 M), of acid kind, the purity of aniline and hypochlorite compared to the methods reported. This new synthesis method preferably directs the fibril directional growth to nanofibers along the axes of the polymer chains. We observed this one directional preferred nanofibers growth in both polyaniline and poly-*N*-methylaniline synthesis with the couse of hypochlorite. The morphological differences in nanofibers obtained with and without hypochlorite use is more pronounced in the case of PNMA synthesis. Addition-

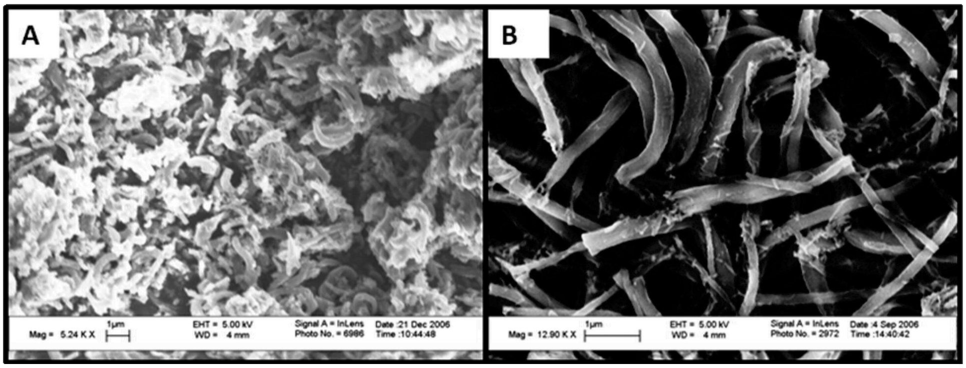

Figure 10. SEM of N-methyl-polyaniline obtained using (A) only APS at room temperature, (B) APS and NaOCl at room temperature.

ally, we found that the new synthesis method affords nanofibers having a narrow molecular weight distribution with good electrical conductivity as high as 24.4 S/cm.

Further kinetic studies to elucidate the mechanism of selective fibril polymerization observed using hypochlorite with APS as well as studies on the applications of the polyaniline and poly-*N*-methylaniline nanofibers synthesized by the new method are in progress.

Acknowledgment. We gratefully acknowledge the people at the UTD's Alan G. MacDiarmid Laboratory for Technical Innovation, and we also acknowledge the valuable discussions and suggestions about this work with our late colleague and friend, Dr. A. G. MacDiarmid, before he passed away and AFOSR for financial support.

CM703678M