

A general synthetic route to nanofibers of polyaniline derivatives

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Nanofibrous mats of a wide variety of polyaniline derivatives can be synthesized without the need for templates or functional dopants by simply introducing an initiator into the reaction mixture of a rapidly mixed reaction between monomer and oxidant.

Since their discovery, conducting polymers have shown great promise in a variety of applications such as light emitting diodes, chemical sensors, anti-corrosion coatings, batteries, and capacitors.¹ Among the family of conducting polymers, polyaniline has been one of the most widely studied due to its stability and simple, reversible acid–base doping–dedoping chemistry. In recent years, one-dimensional (1-D) nanostructures of polyaniline have attracted growing attention due to the potential advantages of having an organic conductor exhibit low-dimensionality. Such materials are potentially useful for applications that depend on ultra-small, high surface area features such as chemical sensors.²

A variety of chemical methods have been employed to synthesize 1-D nanostructures of polyaniline such as rods, wires, tubes, and fibers. Examples include template directed synthesis,³ the addition of surfactants,⁴ micelles⁵ or seeds,⁶ interfacial polymerization,^{7,8} and rapidly mixed polymerization.⁹ We have recently demonstrated that nanofibers appear to be the intrinsic morphology of polyaniline and that structural directing agents such as templates and surfactants are unnecessary for nanofiber formation.¹⁰ Furthermore, by not stirring the reaction mixture after the synthesis has begun, high-quality nanofibrous mats can be produced regardless of whether or not the monomer and oxidant solutions are added slowly or rapidly.¹¹ However, despite the variety of synthetic methods reported, nanostructures of polyaniline derivatives have been synthesized with only limited success. Compared to the parent polymer, polyaniline derivatives can exhibit enhanced properties such as improved dispersability in organic solvents such as methanol,^{12,13} have higher resistance against microbial and chemical degradation,^{14,15} and be an attractive alternative to charge dissipators for e-beam lithography.¹⁶ Here, we demonstrate a simple, scalable procedure for producing nanofibrous mats out of a wide variety of polyaniline derivatives by introducing an initiator into the reaction mixture of a rapidly mixed reaction between a solution of monomer and oxidant.

In a typical reaction, 1–2 milligrams of an initiator such as *p*-phenylenediamine (a dimer of aniline) or 1,4-benzenediamine is predissolved in a minimal amount of methanol and mixed with a solution of the monomer derivative (100–120 milligrams) in 1 M

acid. This solution is rapidly mixed with a solution of oxidant, ammonium peroxydisulfate (50 mg), in 1 M acid. Upon addition of the oxidant, the characteristic color changes associated with the formation of the polyaniline derivatives are observed within several seconds, an observation consistent with previous studies using oligomers to synthesize chiral polyaniline nanofibers.¹⁷ The reaction mixture is then left unagitated for 1 day, after which time the crude product is collected and purified by dialysis against deionized water. The purified product is characterized *via* UV-Vis spectroscopy, which indicates that the polyaniline derivatives exist in the emeraldine oxidation state. Fig. 1 shows the UV-Vis spectra of a representative polyaniline derivative, polyanisidine in its doped and dedoped state. For each polyaniline derivative synthesized, the ratio of the relative intensity of the 320 nm and 610 nm peaks for the dedoped material varies slightly, which may be due to slight deviations from the idealized half-benzenoid/half-quinoid units characteristic of polyaniline in the emeraldine oxidation state.¹⁸ SEM images of polyaniline derivatives reveal a striking contrast between reactions synthesized with an initiator (Fig. 2 B, D, F) and without an initiator (Fig. 2 A, C, E). For reactions performed in the absence of an initiator, irregularly shaped agglomerates or micron sized spheres are predominantly formed. However, upon introduction of the initiator into the reaction mixture, a dramatic change is seen in the morphology of the product from irregularly shaped agglomerates to nanofibers with length as long as several microns and diameters ranging from 25–120 nm, depending upon synthetic conditions such as the monomer being polymerized or the acid used during synthesis. For instance, when polymerized in the presence of HCl, *m*-toluidine gives an average nanofiber diameter of 25 nm while in perchloric acid, the average diameter is roughly 75 nm.

Recently, we have shown that nanofibers appear to be the intrinsic morphology of polyaniline.¹⁰ However, we have also observed that nanofibers do not form for polyaniline derivatives

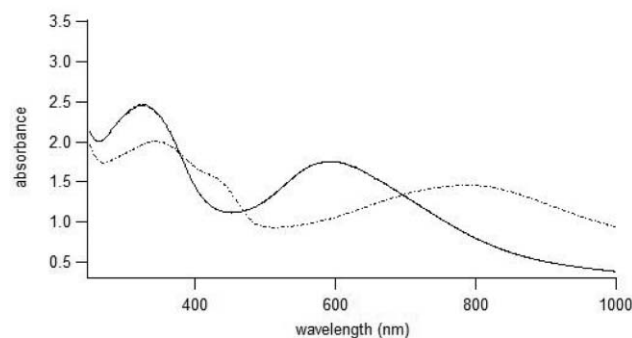


Fig. 1 UV-Vis spectra of dedoped (solid line) and doped (dotted line) polyanisidine in water.

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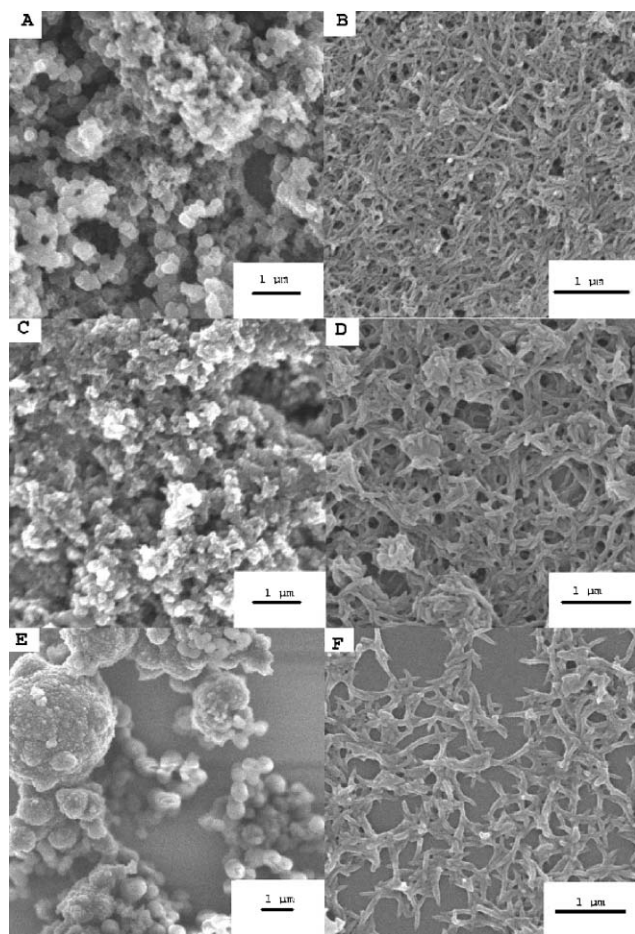


Fig. 2 SEM images showing the distinct morphology of poly-2-ethylaniiline (A,B), poly-*o*-toluidine (C,D), and poly-*o*-anisidine (E,F) synthesized with (right column) and without (left column) an initiator.

under the same synthetic conditions. This may be due to the slower reaction rate of substituted polyaniline because of both steric and electronic effects.¹⁹ As a case study, *o*-toluidine was analyzed during the early stages of polymerization and no fibrous structures were observed at any point. Only spherical agglomerates were seen, which suggests that nucleation and growth of polyaniline derivatives is identical in all directions. Therefore, in order to form nanofibers of polyaniline derivatives, anisotropic growth of the nucleation sites must be induced.

Wei *et al.*^{20,21} noted that by adding aromatic additives such as *p*-phenylenediamine or 1,4-benzenediamine to an electrochemical synthesis of polyaniline, the rate of polymerization is greatly enhanced. When introduced into our rapidly mixed reaction scheme,⁹ the polyaniline derivatives precipitate out of solution in just a few seconds as opposed to minutes or hours without the initiators. We believe that the dramatic change in morphology can be attributed in large part to the rate enhancement caused by the introduction of the initiator. The initiators may bias formation of nanofibers by accelerating growth of the nanofibers along the axes of the polymer chains. Furthermore, since the initiators have a much lower oxidation potential than the monomers,²² they will serve as nucleation sites for growing polymer chains.

We have recently shown that homogenous nucleation is crucial to the formation of polyaniline nanofibers.¹¹ In the presence of an

initiator, the formation of reactive nuclei is much faster, and as a result it is more likely that they will undergo homogenous nucleation leading to nanofibers rather than heterogeneous nucleation leading to agglomerated structures. Furthermore, when the reaction mixture with the initiator is vigorously shaken during polymerization, we observe an increase in agglomerated structures possibly due to an increase in heterogeneous nucleation of the embryonic nuclei. For the majority of the polyaniline derivatives synthesized, the same morphology is obtained using either the aniline dimer or benzenediamine as the initiator. However, we have noticed that in some instances a nanofibrous mat that is smoother and more continuous is produced when the benzenediamine is used and in other instances when the dimer is used. For instance, when the dimer is used to initiate growth of polyanisidine, more high-quality nanofibers are obtained than when benzenediamine is used. However, for the synthesis of polyethylaniline, this effect is reversed. The precise reason for this effect is unclear and is currently under investigation.

Nanofibrous mats of polyaniline derivatives display many potentially useful properties. Preliminary tests on the derivatives indicate that most undergo flash welding when exposed to a camera flash at close proximity, which may be useful in melt-blending polymer-polymer nanocomposites.²³ Stable aqueous colloids of derivatives such as polyanisidine in its doped state can be prepared in concentrations as high as 2.5 g L⁻¹—over 200 times more concentrated than that reported for the parent polymer.²⁴ Furthermore, polyanisidine nanofibers can be easily redispersed into solution after they are dried, which is often difficult to achieve with polyaniline.

In summary, a general chemical route to nanofibrous mats of a wide variety of polyaniline derivatives such as alkyl, methoxy, fluoro, and thiomethyl substituted polyanilines have been synthesized for the first time by simply adding an initiator into the reaction mixture. The initiators accelerate the rate of the reactions and promote homogenous nucleation, which lead to nanofibrous morphology consistent with previous studies. Enhanced processability parameters have been shown with polyanisidine which displays exceptionally high dispersability in various solvents. We expect that these materials will prove useful in applications requiring high quality films such as chemical sensing or anti-corrosion coatings. Because of the versatility of this method in producing nanostructures of a wide range of polyaniline derivatives we anticipate that nanostructures of other conducting polymers could be synthesized in a similar fashion.

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Notes and references

- 1 A. G. MacDiarmid, *Angew. Chem., Int. Ed.*, 2001, **40**, 2581–2590.
- 2 S. Virji, J. Huang, R. B. Kaner and B. H. Weiller, *Nano Lett.*, 2004, **4**, 491–496.
- 3 C. G. Wu and T. Bein, *Science*, 1994, **264**, 1757–1759.
- 4 J. C. Michaelson and A. J. McEvoy, *J. Chem. Soc., Chem. Commun.*, 1994, **1**, 79–80.
- 5 Y. S. Yang and M. X. Wan, *J. Mater. Chem.*, 2002, **18**, 917–921.
- 6 X. Zhang, W. J. Goux and S. K. Manohar, *J. Am. Chem. Soc.*, 2004, **126**, 4502–4503.
- 7 J. Huang, S. Virji, B. H. Weiller and R. B. Kaner, *J. Am. Chem. Soc.*, 2003, **125**, 314–315.
- 8 J. Huang and R. B. Kaner, *J. Am. Chem. Soc.*, 2004, **126**, 851–855.

- 9 J. Huang and R. B. Kaner, *Angew. Chem., Int. Ed.*, 2004, **43**, 5817–5821.
- 10 J. Huang and R. B. Kaner, *Chem. Commun.*, 2006, 367–376.
- 11 D. Li and R. B. Kaner, *J. Am. Chem. Soc.*, 2006, **128**, 968–975.
- 12 A. Gruger, A. Novak, A. Regis and J. Colomban, *J. Mol. Struct.*, 1994, **328**, 153–167.
- 13 S. M. Yang and J. H. Chiang, *Synth. Met.*, 1991, **41**, 761–764.
- 14 A. H. Kwon, J. A. Conklin, M. Makhinson and R. B. Kaner, *Synth. Met.*, 1997, **84**, 95–96.
- 15 A. Cihaner and A. M. Onal, *Eur. Polym. J.*, 2001, **37**, 1767–1772.
- 16 M. Angelopoulos, J. M. Shaw, R. D. Kaplan and S. Perreault, *J. Vac. Sci. Technol. B*, 1989, **7**(6), 1519.
- 17 L. Wenguang and H. L. Wang, *J. Am. Chem. Soc.*, 2004, **126**, 2278–2279.
- 18 J. E. Albuquerque, L. H. C. Mattoso, D. T. Balogh, R. M. Faria, J. G. Masters and A. G. MacDiarmid, *Synth. Met.*, 2000, **113**, 19–22.
- 19 L. H. C. Mattoso, S. K. Manohar, A. G. MacDiarmid and A. J. Epstein, *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 1227–1234.
- 20 Y. Wei, Y. Sun, G. W. Jang and X. Tang, *J. Polym. Sci., Part C: Polym. Lett.*, 1990, **28**, 81.
- 21 Y. Wei, G. W. Jang, C. C. Chan, K. F. Hsueh, R. Hariharan, S. A. Patel and C. K. Whitecar, *J. Phys. Chem.*, 1990, **94**, 7716–7721.
- 22 G. D'Aprano, M. Lecler and G. Zotti, *Synth. Met.*, 1996, **82**, 59–61.
- 23 J. Huang and R. B. Kaner, *Nat. Mater.*, 2004, **3**, 783–786.
- 24 D. Li and R. B. Kaner, *Chem. Commun.*, 2005, 3286–3288.

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