

Polyaniline nanofibers: chemical synthesis using surfactants†

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Nanofibers of doped polyaniline.HCSA having diameters 1–2 nm are observed in TEM images of bath sonicated aqueous dispersions of larger nanofibers (30–50 nm diameter) synthesized by surfactant-assisted chemical oxidative polymerization of aniline in dilute aqueous organic acids.

We describe a simple and rapid one-phase surfactant-assisted chemical method to synthesize bulk quantities of analytically pure nanofibers of polyaniline doped with D,L-camphorsulfonic acid (emeraldine.HCSA) and with 2-acrylamido-2-methyl-1-propane-sulfonic acid (emeraldine.AMPSA). A conventional chemical oxidative polymerization of aniline in 1.0 M HCSA or AMPSA using ammonium peroxydisulfate oxidant, when carried out in the presence of added non-ionic surfactant results in a precipitate of doped emeraldine salt composed almost entirely of nanofibers having average fiber diameter in the range 30–50 nm and exhibiting a room temperature DC conductivity of 1–5 S cm⁻¹. Fiber diameter can be driven even lower by bath sonication to yield what we believe from TEM images to be the first report of a single molecule fiber of emeraldine.HCSA (1–2 nm diameter).

While polyaniline with fibrillar morphology has been chemically synthesized using insoluble (hard) templates,¹ soluble (soft) templates,^{2,3} pseudo-templates like large organic dopant anions,³ and more recently, by interfacial polymerization,⁴ the use of surfactants during the polymerization, *i.e.*, micellar and emulsion polymerization systems has largely yielded polyaniline having particulate (non-fibrillar) morphology.⁵ There are very few instances where fibrillar morphology has been observed in surfactant-assisted polymerization of aniline,⁶ and to the best of our knowledge, there has not been any report on the use of non-ionic surfactants to generate polyaniline having bulk nanofiber morphology. The present study describes: (i) the use of a combination of large organic dopants and non-ionic surfactants such as polyoxyethylene(10) isooctylphenyl ether, Triton-X 100 (TX100) to synthesize highly conducting nanofibers of polyaniline, and (ii) attempts to drive down the fiber diameter closer to the one-dimensional (single molecule fiber) regime.

Experimental details are described elsewhere.⁷ The polyaniline precipitate obtained by chemical oxidative polymerization of aniline in aq. 1.0 M HCSA or AMPSA in the presence of TX100 is composed almost entirely of nanofibers having average diameter in the range 30–50 nm (Fig. 1). The insets in Fig. 1 describe the morphology of polyaniline obtained under identical conditions in the absence of TX100. Polyaniline nanofibers synthesized using TX100 for both HCSA and AMPSA systems are analytically and spectroscopically similar to corresponding samples synthesized without TX100. The doping percentage, calculated from elemental analyses (sulfur/nitrogen ratio) was 43% for emeraldine.HCSA and 45% for emeraldine.AMPSA.⁷ The elemental analyses also showed slightly elevated oxygen levels which persist even upon several doping/dedoping cycles and extended drying under dynamic vacuum at 80 °C, suggesting its origin to water of hydration, or to water trapped inside the fiber should the fibers be hollow. For both systems, vibrational spectra (KBr pellet), cyclic voltammetry

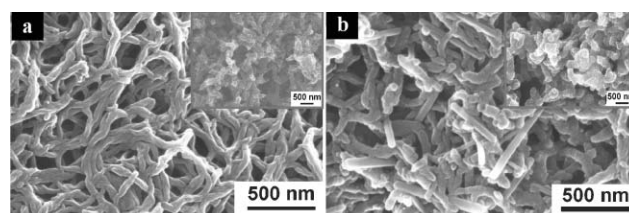


Fig. 1 SEM images of nanofibers of (a) emeraldine.HCSA and (b) emeraldine.AMPSA synthesized in the presence of TX100 (inset: conventional synthesis, without TX100).

(aq. 1.0 M HCl vs. SCE) and pressed pellet four-probe room temperature conductivity values (1–5 S cm⁻¹) are essentially identical to the corresponding emeraldine salts synthesized without TX100. Expectedly, significantly higher capacitance values are obtained for polyaniline nanofibers synthesized using TX100 which is consistent with its high surface area.⁷

Polyaniline nanofibers obtained in this study are chemically robust and retain their fibrillar morphology even after repeated doping and dedoping cycles using aqueous acids and bases, although they deform readily under mechanical stress and fragment to smaller pieces under strong probe sonication. TEM images obtained after moderate mechanical agitation, *e.g.*, bath sonication for 2 h in water show very small diameter nanofibers (1–2 nm) distributed among fragmented clusters of the original larger nanofibers (Fig. 2a, inset). An expanded section of this image (Fig. 2a) shows a thin, 2–5 nm fiber bridging two regions of fragmented fiber clusters. At the center of the bridge, over a length of 40 nm, the fiber appears to become so thin that its image does not register which is consistent with a fiber having diameter in 1–2 nm range (instrument limit). When the electron beam was focused on this area (see arrow in Fig. 2), the fiber begins to vibrate and then breaks cleanly into two independently vibrating fibers (Fig. 2b, also seen in video imaging) confirming the presence of a very thin fiber in this region. Molecular models and crystal structure studies of emeraldine.HCSA show that the ‘diameter’ of a single chain is in the range 1.0–1.8 nm,⁸ suggesting that the TEM image, in this region of the sample, is consistent with that of a single molecule fiber of doped polyaniline. Size exclusion chromatography of the corresponding emeraldine base powder in NMP/LiBF₄ eluent

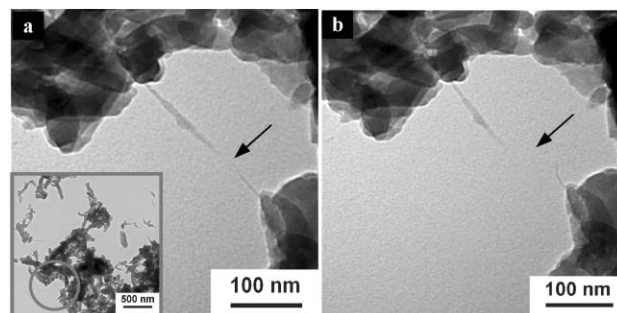


Fig. 2 TEM images of a emeraldine.HCSA nanofiber ‘bridge’ (a) before, and (b) after the e-beam was focused on the area (arrow). Inset: larger area image with circle describing area of interest.

† Electronic supplementary information (ESI) available: Synthetic procedure, elemental analyses, enlarged SEM and TEM images. See <http://www.rsc.org/suppdata/cc/b4/b409309g/>

(60 °C/polystyrene standards) shows a unimodal Gaussian peak and $M_w = 20\,000$ (PD 2.2) indicating that the chains are long enough to form 40 nm long fibers. A close observation of the TEM images reveals that these very small diameter nanofibers are present in all parts of the sample and may even be present in emeraldine.HCSA reported in previous studies.⁴ Alternatively, if gentle bath sonication is in some way responsible for the formation of these very small diameter fibers from larger fibers, this method could be an attractive post-synthesis 'processing step' to synthesize smaller diameter fibers in larger quantities.

The role of TX100 in promoting fibrillar polymer growth is not clear, e.g., a close examination of SEM images of polyaniline synthesized without TX100 (Fig. 1 insets) show regions already having fibrillar, or quasi-fibrillar morphology. This suggests that mechanisms that promote fibrillar polymer growth are intrinsic to the synthesis rather than to added TX100, and these pre-existing mechanistic pathways are favored in systems that contain TX100. Intrinsic fiber-forming mechanisms have also been reported to be favored at the aqueous/organic interface.⁴ Our working hypothesis is that the chemical environment in the vicinity of the micelle-water interface in our system could be qualitatively similar to the organic-aqueous interface in interfacial polymerization.

There appears to be a connection between the the critical micelle concentration (c.m.c.) of TX100 in the reaction mixture and fiber formation. Longer, more uniformly distributed and smaller diameter fibers are produced at TX100 concentrations in the range 2500–4000 ppm for the HCSA system and 800–1200 ppm for the AMPSA system. The typically low c.m.c. values observed in aqueous TX100 solutions (100–200 ppm in inorganic acids)⁹ increases significantly to 1100 ppm in 1.0 M HCSA and 620 ppm in 1.0 M AMPSA. When aniline is added the c.m.c. increases even further, i.e., to 2200 ppm (HCSA system) and 866 ppm (AMPSA system) (Fig. 3). The initial increase in c.m.c. is caused presumably by mixed micelle formation and/or incorporation of these large organic anions in the micelle. The subsequent increase in c.m.c. is consistent with cation exchange between protons and anilinium ions at the Stern layer. There is also a significant increase in surface tension consistent with charge buildup in the micellar aggregate from the negatively charged sulfonate headgroup. The best nanofibers are obtained above the composite c.m.c. of the system suggesting that micelle-water interface is playing an important role.⁹

It is important to note that unlike typical aniline polymerization reactions, our reactions were not stirred or mechanically agitated in any way. Polymerization is expected to be initiated at the micelle-water interface because of the increased local aniline concentration and since our system is not agitated, aniline dimer and higher oligomers are expected to accumulate at the micelle-water interface. We believe that these dimers and oligomers could be responsible for orchestrating fibrillar polymer growth. This is consistent with nanofibrillar morphology previously observed in chemical and electrochemical polymerization of aniline in the presence of added aniline oligomers.¹⁰

Precisely how aniline oligomers promote fibrillar polymer growth is unclear, although we believe that the nascent polyaniline precipitate formed during the early stages of the reaction must also possess fibrillar morphology. Since aniline polymerization has been shown to be autocatalytic with the loci of polymerization shifting from bulk solution to the nascent oligomeric chains, the morphology of these 'seed' oligomers is transcribed to the bulk precipitate. This is analogous to our recently reported 'nanofiber seeding' synthesis of polyaniline.¹¹

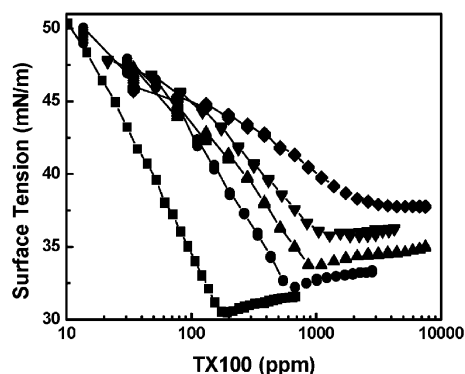


Fig. 3 Surface tension vs. concentration plots for TX100 in aq. 1.0 M HCl (■), AMPSA (●), AMPSA + aniline (▲), HCSA (▼), HCSA + aniline (◆).

In summary, we demonstrate (i) the use of nonionic surfactants to synthesize rapidly, and in one step, bulk quantities of doped polyaniline nanofibers without the need for conventional templates, polymers or organic solvents, (ii) unusually high composite c.m.c. values for TX100 in organic acid-aniline systems and its role in orchestrating bulk nanofibrillar morphology, and (iii) a simple method to 'process' larger polyaniline nanofibers into smaller, 1–2 nm fibers in what we believe is the first report of a single molecule fiber of a doped conducting polymer.

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