Parent Polythiophene Nanofibers

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Bulk quantities of parent polythiophene nanofibers can be synthesized rapidly and in one step by chemical oxidative polymerization of thiophene by $FeCl_3$ using freeze-dried vanadium pentoxide nanofibers as seeds.

We describe a simple and rapid one-step chemical synthesis of bulk quantities of nanofibers of the electronically conducting polymer polythiophene directly from thiophene monomer using catalytic (seed) quantities of V_2O_5 nanofibers as morphology directing agents. These findings overcome an important synthetic challenge in controlling the bulk morphology of the parent polythiophene system and extends the scope of our recently described nanofiber seeding method beyond aqueous oxidative conditions (polyaniline, polypyrrole, and PEDOT) to organic solvent conditions.[1] These findings could potentially be leveraged to synthesize nanofibers of conventional (insulating) polymers.

In contrast to functionally derivatized polythiophenes (ring-substituted derivatives) where improved solubility and enhanced processability have led to significant advances in the design and development of electronic and optoelectronic devices,[2] the parent polythiophene system is relatively unexplored. For example, the chemical oxidative polymerization of unsubstituted thiophene monomer results in a black polythiophene powder that is infusible, intractable, and insoluble in common organic solvents.[3] The parent polythiophene system is also strikingly different from conducting polymer systems like polyaniline and polypyrrole in the area of nanoscale synthesis. Whereas nanofibers/tubes/spheres of polyaniline and polypyrrole are now routinely being synthesized using a wide variety of synthetic approaches,[4] to the best of our knowledge, there is no direct chemical oxidative route to parent polythiophene from thiophene monomer having bulk nanoscale morphology.

We recently described nanofiber seeding as a general synthetic approach to bulk quantities of nanofibers of all major classes of conducting polymers.[1] In one variant of this method, catalytic (seed) amounts of an aqueous sol–gel of V_2O_5 nanofibers are added prior to onset of polymerization that dramatically change the bulk morphology of the polymer precipitate, i.e., the seed nanofibers initiate fibrillar polymer growth that is transcribed across multiple length scales resulting in bulk nanofibers. Unlike other conducting polymer systems, we encountered significant challenges in extending nanofiber seeding to the parent polythiophene system. For example, we could not use aqueous solvents since it is known to cause defects along the polymer backbone,[5] and the small amount of water present in the V_2O_5 sol–gel prevented the reaction from taking place in organic solvents. In this study, we describe the use of seed quantities of freeze-dried V_2O_5 nanofibers to affect a dramatic granular to nanofibrillar change in bulk polymer morphology of polythiophene powder in the $FeCl_3$-mediated oxidative polymerization of thiophene in acetonitrile.

In a typical synthesis, freeze-dried V_2O_5 nanofibers (4 mg) were added to acetonitrile (60 mL) and stirred for 1 h at room temperature followed by addition of thiophene monomer (1 g, 11.9 mmol). After stirring for 30 min solid anhydrous $FeCl_3$ (1.9 g, 11.7 mmol) was added all at once. It is important that $FeCl_3$ is added in the solid state and not as a solution.[6] The solution darkened noticeably immediately upon addition of $FeCl_3$, and after 2 h the resulting black precipitate of poly(thiophene chloride) nanofibers was suction filtered in air, washed with acetonitrile (4×100 mL), aqueous 0.1 M HCl (4×100 mL) and dried under dynamic vacuum at 80 °C for 12 h (yield ≈200 mg). A freshly filtered precipitate of polythiophene nanofibers also forms a compact nonwoven mesh that can be removed using tweezers and manipulated as a free-standing film.[9]

Scanning electron microscopy (SEM) images show that unlike the granular morphology observed in the unseeded control reaction (Figure 1A), the V_2O_5 nanofiber seeded system yielded a near quantitative amount of 4–5 μm long nanofibers having average diameter in the 40–60 nm range (Figure 1B). The 4-probe pressed pellet room temperature DC conductivity value of polythiophene nanofibers (14 S/cm) is an order of magnitude higher than granular polythiophene (2 S/cm), although it is similar in magnitude to polythiophene synthesized previously.[7]

Whereas the elemental analysis of granular poly(thiophene chloride) (unseeded control), C, 52.16; H, 1.78; S, 34.99; Cl, 10.91; Total: 99.84%, is consistent with a doping percentage of 29% the corresponding analysis of polythiophene nanofibers, C, 49.17; H, 1.51; O, 1.21; S, 33.02; Cl, 14.18; V, 0.00; Total: 99.09%, is consistent with a significantly higher doping percentage of 39% (Scheme 1). It is possible that the high surface area of nanofibers helps facilitate polymer backbone oxidation that could also account for the small amount of oxygen found in the sample. The potential–time profile of the reaction (Figure 2) provides evidence consistent with nanofibers having a higher oxidation state, e.g., after completion of the reaction (2 h), the potential of the seeded system is higher (0.94 V) than the unseeded control (0.85 V).

It is unclear how seed quantities of V_2O_5 nanofibers help

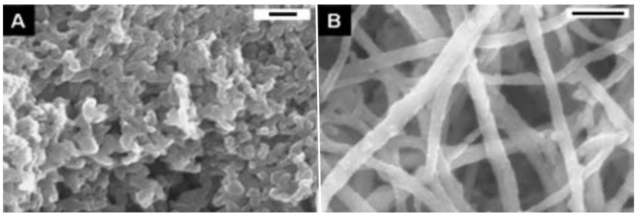
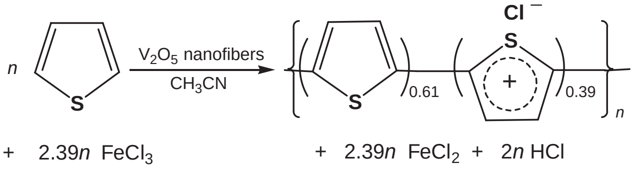


Figure 1. SEM images of conducting poly(thiophene chloride) powder: (A) unseeded control, (B) V_2O_5 seeded nanofibers. Scale bar: 200 nm.



Scheme 1. V_2O_5 nanofiber seeded polymerization of thiophene.

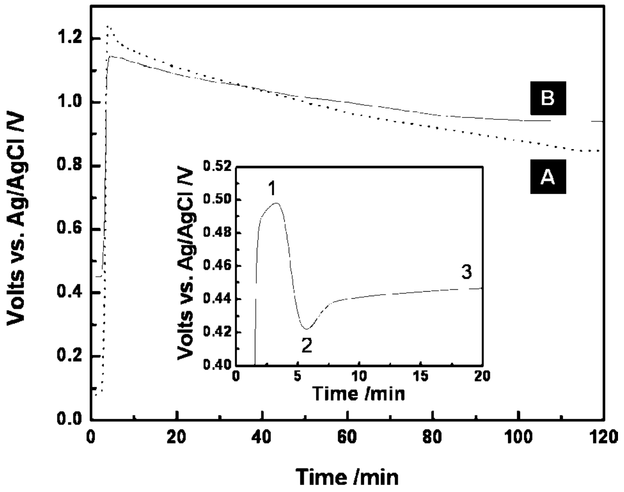


Figure 2. Potential–time profile of oxidative polymerization of thiophene using $FeCl_3$: (A) unseeded control, (B) seeded with freeze-dried V_2O_5 nanofibers. Inset: potential–time profile before the addition of $FeCl_3$.

orchestrate a granular to fibrillar change in bulk morphology in polythiophene. Like other conducting polymer seeded systems, there was no correlation between the polymer and seed fiber diameter (V_2O_5 nanofibers ≈15 nm diameter)[8] and no increase in fiber diameter as a function of reaction time. Unlike the polyaniline system, no polythiophene nanofibers are obtained when the reaction is seeded with chemically inert nanofibers such as single-walled carbon nanotubes, or other nanofibers.[1] Chemically reactive seed nanofibers, like V_2O_5, are required for nanofiber growth (like the polypyrrole system)[1] suggesting that thiophene oxidation is initiated on the surface of the V_2O_5 nanofibers with $FeCl_3$ functioning as the bulk oxidant. The potential–time profile of the system before adding $FeCl_3$ (Figure 2, inset) is consistent with this rationale, i.e., after adding thiophene to V_2O_5 nanofibers (point 1) the potential falls from 0.50 to 0.41 V (point 2), and then rises gradually over 15 min to 0.45 V (point 3) consistent with adsorption of thiophene on the V_2O_5 surface. After $FeCl_3$ is added the maximum potential in the seeded system is lower (1.15 V) than the unseeded control (1.25 V), consistent with faster reaction kinetics in the seeded system. A similar link between nanofiber formation and lower oxidation potential (faster kinetics) has also been observed in nanofiber seeding of the PEDOT system.[1]

Fibrillar and granular polythiophene exhibit different analytical, spectroscopic, and electrochemical properties unlike the polyaniline and polypyrrole systems.[9] During the polymerization a thin, strongly adherent film of polythiophene deposits spontaneously on the surface of inert substrates such as glass, plastic, etc. Observed for the first time for parent polythiophene, this film is formed by in situ adsorption polymerization and has granular morphology unlike the corresponding polyaniline and polypyrrole films that have nanofibrillar morphology.[1] These results suggest that the freeze-dried V_2O_5 nanofibers are not adhering to the walls of inert surfaces prior to the onset of polymerization, resulting in two possible pathways: (i) polymerization of thiophene adsorbed on the surface of V_2O_5 nanofibers yielding nanofibrillar polythiophene, and (ii) polymerization of thiophene adsorbed on the surface of inert surfaces yielding granular polythiophene. In the case of polypyrrole where both film and precipitate had fibrillar morphology, it is possible the aqueous V_2O_5 sol–gel disperses well in the aqueous reaction medium (within minutes) which aids in the deposition of V_2O_5 nanofibers along the substrate surface resulting in films (also) possessing fibrillar morphology. In the case of the thiophene system, it takes a much longer time (≈1 h) to fully disperse the freeze-dried V_2O_5 nanofibers.

In summary, we describe for the first time: (i) a convenient, room temperature synthetic route to bulk quantities of nanofibers of parent polythiophene directly from thiophene monomer, and (ii) the use of freeze-dried V_2O_5 nanofibers as seeds to affect a granular–fibrillar change in polymer morphology. The use of freeze-dried nanofibers as seeds also helps leverage the nanofiber seeding approach to precipitation polymerization reactions carried out in organic solvents and could open new opportunities for the synthesis of conventional polymers having preselected bulk nanoscale morphology.

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9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett.