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Metastable Reaction Mixtures for the *in Situ* Polymerization of Conducting Polymers

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ABSTRACT: The widespread use of conducting polymers in technological applications has been hindered by poor processability; strong intermolecular interactions prohibit thermal processing and reduce solubility in conventional solvents. To date, there has been a focus on the disruption of these interactions through the functionalization of the polymer backbone or the stabilization of colloidal polymer. In this work, we present a generalized approach to the synthesis of conducting polymers that uses an easily processable mixture of monomer and oxidant that is metastable in solution, yet rapidly polymerizes upon solvent evaporation. This procedure was originally used for the polymerization of pyrrole and is now demonstrated as a general approach by extending the method to the polymerization of thiophene. The method allows the casting and spin-coating of films with similar conductivities and redox properties to those of electrochemically generated thin films, without the need for a conducting substrate. Films produced via spin-coating are smooth with a thickness of 100−200 nm and show conductivities in the range 0.2−0.3 S cm^{-1}. Microscopic and spectroscopic characterizations are also presented.

Introduction

Over the past several decades, there has been a surge of interest in the synthesis and properties of conducting polymers. These polymers are typically synthesized by one of three general methods: chemical,[1] electrochemical,[2] and plasma polymerization.[3] Numerous applications for conducting polymers have been proposed, ranging from organic light-emitting diodes[4] to chemiresistor-type detectors.[5,6] Despite the promise of these new materials and their widespread study, relatively few viable technologies have emerged from the laboratory proof-of-concept stage. Lack of processability has been one of the biggest impediments to successful industrial application of these polymers, although several elegant approaches have been developed over the years to improve their processability. For example, the addition of bulky side chains along the backbone can disrupt $\pi-\pi$ interactions, resulting in soluble conducting polymers.[7] However, this approach tends to diminish ring coplanarity which invariably leads to lower conductivities[8] due to reduced π-orbital overlap along the backbone.[9] Furthermore, these side chains can have undesired influences on the polymer's electronic properties and also add layers of synthetic complexity to the process. Alternative approaches use emulsions or suspensions that can be processed; however, these approaches typically retain the original microstructure present in solution.[10] Recently, it was demonstrated that homogeneous polymer structures can be created by flash-welding films consisting of nanoparticles of conducting polymers;[11,12] however, it is not clear how this thermal processing impacts the electronic properties of the polymer since the observed conductivities were decreased by an order of magnitude.

In this work we explore an alternative strategy involving the use of metastable mixtures of monomer and oxidant that enable processability followed by *in situ* polymerization initiated by solvent evaporation. This method was first demonstrated with pyrrole/phosphomolybdic acid mixtures that were used to produce well-behaved polypyrrole films[13] that could be deposited on a variety of substrates. This enabled previously unknown applications including composite polymer-based sensing arrays[14] and hybrid electronic devices.[15] The proposed mechanism is presented in Figure 1. This process involves the formation of a metastable mixture of oxidant and monomer by selecting an oxidant whose formal potential in close to, but lower than, the oxidation potential of the monomer. In accordance with the Nernst equation, this ensures that the concentration of oxidized monomer (a radical cation) is relatively low, thereby resulting in a relatively slow polymerization rate (a radical coupling reaction). While the solutions are metastable under dilute conditions, concentration by solvent evaporation allows the rate-limiting radical coupling step to become significantly faster. The first successful completion of the cycle produces dimers that in turn have lower oxidation potentials owing to their increased conjugation length.[16] This condition shifts the balance of the first step to produce relatively more radical cations. The increased concentration of radical cations, resulting from both the more favorable thermodynamics and loss of solvent, causes a further increase in the polymerization rate as the reaction cascades.

Since this process relies solely on the thermodynamic balance of neutral vs oxidized monomer and concentration-based kinetics, this synthetic strategy should be general and applicable to any polymer system involving a similar redox-driven polymerization; in principle, all that is required is a suitable oxidant for a given monomer and a solvent which evaporates in such a way that the polymerization rate is initially slow. To illustrate this point, the concept previously demonstrated for polypyrrole is adapted here for the polymerization of thiophene. Polythiophene is a conducting polymer that has shown to be a useful material in a wide range of technologies, including charge-dissipating films,[17] light-emitting diodes,[4] electrochromic devices,[18] and organic vapor sensors.[19] Since the oxidation

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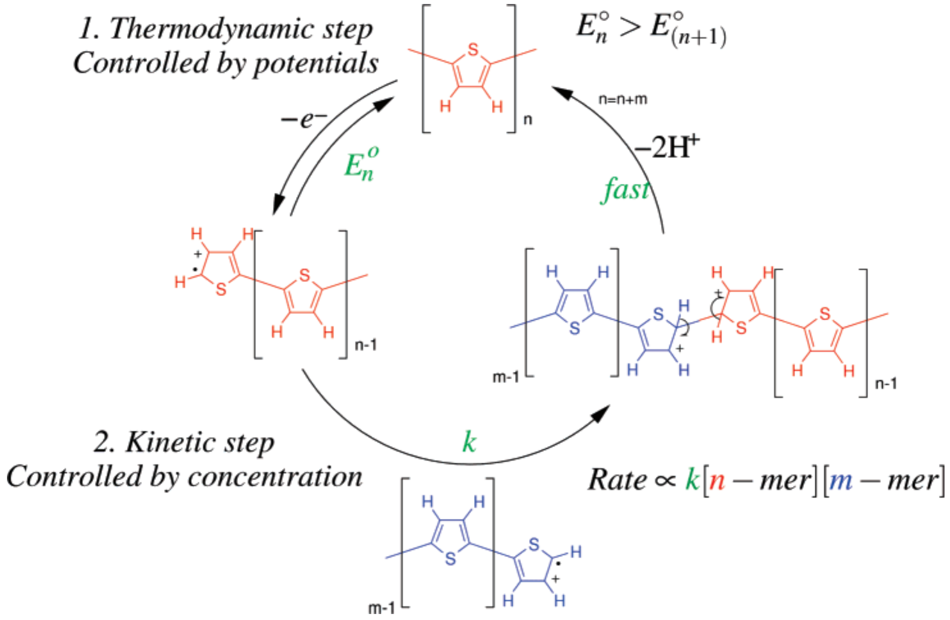

Figure 1. Proposed cascade polymerization mechanism with pyrrole as the monomer.

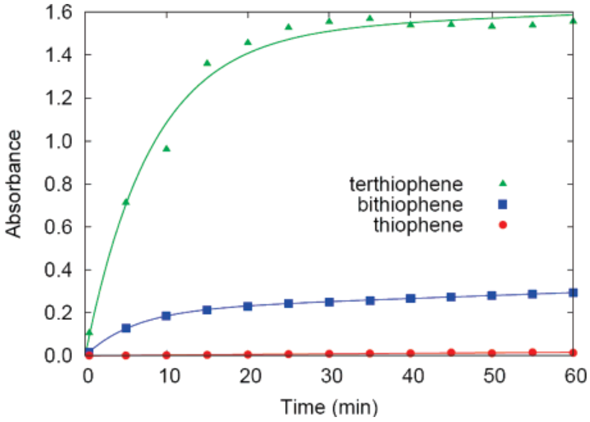

Figure 2. Evolution of spectra at 700 nm as a function of time during the polymerization in acetonitrile in the presence of 0.05 M phosphomolybdic acid.

potential for thiophene is higher than pyrrole (2.07 and 1.30 V vs SCE, respectively),[3] the previous synthetic approach must be modified by altering the oxidation potential of either the monomer or the oxidant. In this case it is straightforward to manipulate the oxidation potential of the monomer by utilizing either bithiophene (1.31 V)[3] or terthiophene (1.05 V),[3] which have redox potentials nearer to that of pyrrole. This is advantageous since the same oxidant that was successfully employed previously (phosphomolybdic acid, 0.36 V)[13] can be here as well, avoiding the potential pitfalls of changing too many experimental variables at once.

Experimental Section

Material and Chemicals. Phosphomolybdic acid hydrate ($H_3PMo_{12}O_{40}$), pyrrole, thiophene, 2,2′-bithiophene, 2,2′:5′,2″-terthiophene, acetonitrile (HPLC grade), and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) were purchased from Aldrich and used without any further purification. Indium-doped tin oxide (ITO, 6 ± 2 Ω/square) glass slides were purchased from Delta Technologies Limited.

Synthesis. The polymerization mixture for synthesizing spin-coated polythiophene consisted of 0.2 M bithiophene in acetonitrile and 0.1 M phosphomolybdic acid in acetonitrile. The chemically synthesized films were spin-coated onto either plain glass substrates (nonconducting) or ITO glass at 2000 rpm for 10 s and then left to dry at room temperature for 40 min before rinsing with acetonitrile. The resulting films were blue-gray and in the conductive oxidized state as illustrated by four-point probe measurements.

For purposes of comparison, polythiophene films were grown electrochemically on ITO glass slides from a solution of an acetonitrile solution containing 0.01 M bithiophene and 0.1 M $TBAPF_6$. This was done using the common electrochemical procedure of sweeping between 0 and 1.0 V (vs $Ag/AgNO_3$) at a scan rate of 0.05 V/s.

Characterization. *UV−vis Spectroscopy*. The chemical polymerization of thiophene, bithiophene, and terthiophene with phosphomolybdic acid as oxidant in acetonitrile was studied in bulk solution in a 1.0 cm quartz cuvette. Spectra were acquired at room temperature on an Agilent 8453 UV−vis spectrometer.

Cyclic voltammetric measurements were performed using a CH Instruments CHI-660 workstation controlled by a PC. Unless otherwise noted, a three-electrode setup was used, using a platinum coil auxiliary electrode, a Pt disk (2 mm diameter) working electrode, and a $Ag/AgNO_3$ reference electrode. These measurements were performed in acetonitrile using $TBAPF_6$ (0.1 M) as supporting electrolyte.

Four-point probe measurements were performed using a Signatone four-point probe apparatus device attached to a Fluke 87 True RMS multimeter and constant-current source system (CH instrument, CHI-660 workstation controlled by a PC). The probe contacts were spaced 0.040 in. apart.

The electrical conductivity σ (Ω^{-1} cm^{-1}) was expressed by

$$\sigma = \frac{\ln 2}{\pi d}\frac{i}{V}$$

where d is the thickness of the films, i is current passed through outer probes, and V is voltage across inner probes. Current was applied within the range of 1.0×10^{-8}−8.0×10^{-7} A.

Scanning electron microscopy (SEM) images were collected using a Cambridge Sterescan 120 SEM, equipped with a secondary electron (SE) detector, a four-quadrant semiconductor backscatter electron (BSE) detector, and an EDAX Genesis 4000 energy dispersive X-ray spectrometer (EDS). No Au/carbon coating was necessary unless otherwise specified.

Atomic force microscopy (AFM) images were recorded in tapping mode using a Dimension 3100 from Veeco/Digital Instruments with a Nanoscope VI controller. The tapping mode was selected in order to capture topographical images without damaging the films. Tapping mode also allowed us to measure film thickness where a

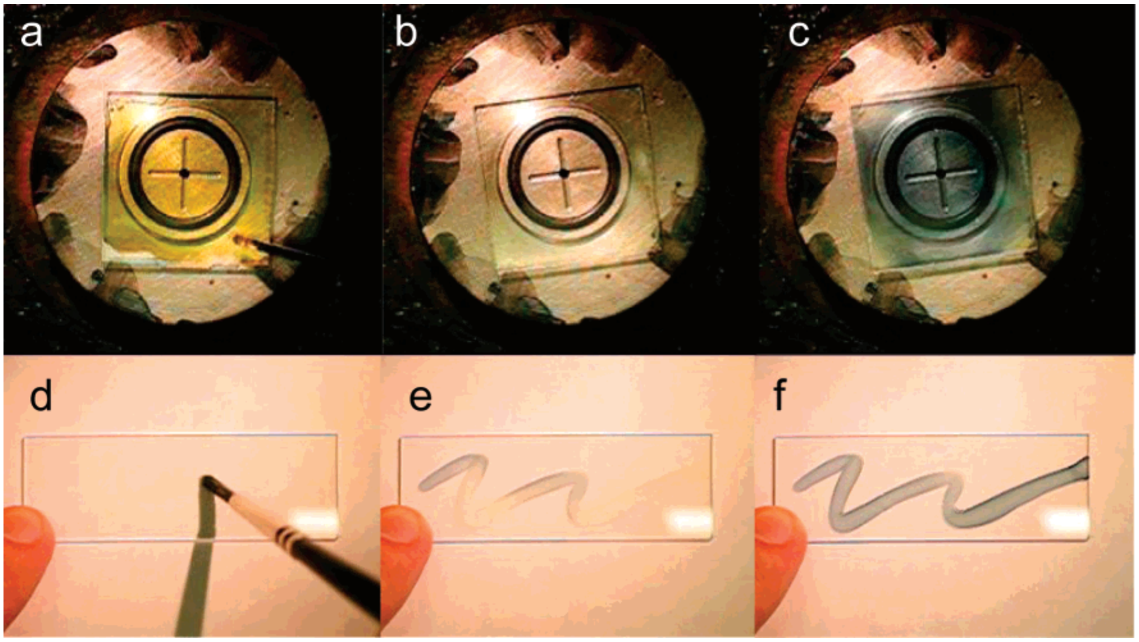

Figure 3. Optical images of the spin-coating process: (a) mixture deposited onto substrate; (b) following spin-coating; (c) following solvent evaporation (~7 s) and the painting process: (d) application of mixture; (e) 3 s of solvent evaporation; (f) 5 s of solvent evaporation. Mixture contained 0.2 M bithiophene and 0.2 M phosphomolybdic acid in acetonitrile.

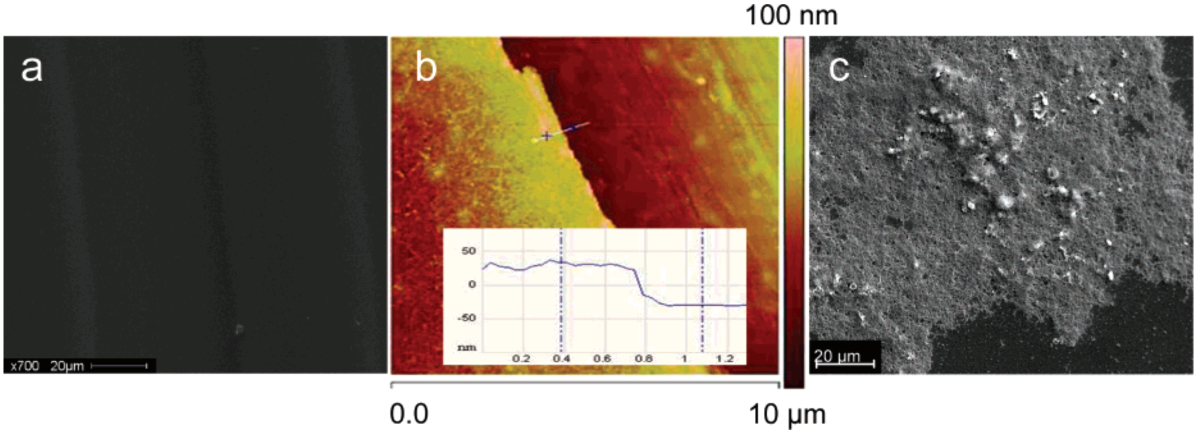

Figure 4. (a) Scanning electron and (b) AFM micrograph of spin-coated polythiophene film onto a glass substrate (inset graph shows the cross section of a thin film adjacent to exposed substrate); (c) scanning electron micrograph of polythiophene generated with a strong oxidant, $FeCl_3$.

portion of the polymer is removed. Images were taken by using an n+ Si cantilever (Nanosensors PPP-NCH) at a resonance frequency of 300 kHz, and the spring constant was 42 N/m. Samples were purged with high-purity N_2 gas to minimize moisture in the samples. Images were captured and analyzed using the Nanoscope software (Version 6.13r1).

Results and Discussion

The appearance of peak near 700 nm in the UV−vis spectrum is an indicator of the formation of polythiophene in its doped state.[20] The degree of polymerization in solution was monitored by following the evolution of this band with time, as shown in Figure 2. Solutions containing thiophene (0.1 M) or bithiophene (0.1 M) and phosphomolybdic acid (0.05 M) were monitored in this way. Attempts to follow the polymerization of 0.1 M terthiophene were unsuccessful due to the rapid precipitation of polymer, so a much lower concentration of terthiophene (0.01 M) was used, though the concentration of phosphomolybdic acid was kept at 0.05 M for consistency.

As expected from the large difference between the oxidation potentials of thiophene and phosphomolybdic acid, no polymerization was observed for this monomer, even after 12 h. In contrast, both bithiophene and terthiophene resulted in successful production of polythiophene, but the rate of bithiophene polymerization is considerably slower.

As was the case for polypyrrole,[13] polymerization of bithiophene occurs rapidly from the metastable solution only after partial evaporation of the solvent. This ultimately leaves behind a smooth film of polythiophene. This straightforward method is illustrated in Figure 3, where the polymerization mixture can be spin-coated, cast, or painted onto insulting substrates such as a glass slide.

The morphology of the spin-coated films was studied with scanning electron microscopy (SEM) and atomic force microscopy (AFM). SEM and AFM of the polythiophene films spin-coated onto glass substrates demonstrated that they were smooth and free of pinholes on the micron scale (Figure 4a). This is in contrast to polythiophene grown using a strong oxidant such as $FeCl_3$ and thiophene (Figure 4c) which leads to rough and amorphous deposits, consistent with rapidly formed and precipitated material. Figure 4b shows a typical AFM image of a spin-coated film and confirms the thickness to be about 100 nm.

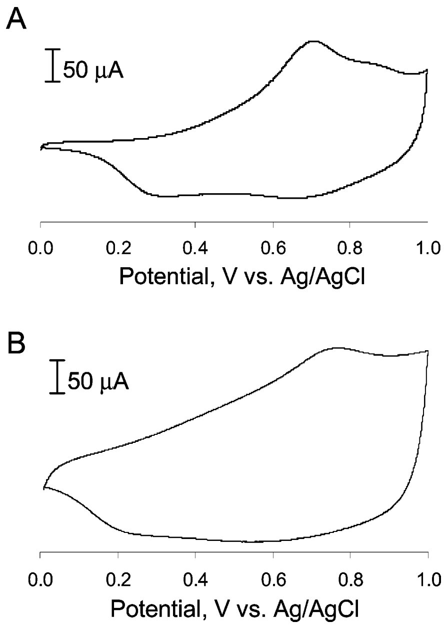

Figure 5. Cyclic voltammogram of polythiophene grown (A) electrochemically and (B) chemically (under conditions described in Figure 3) on ITO in 0.10 M TBAPF$_6$/ acetonitrile; scan rate = 0.05 V s^{-1}.

Electrochemistry. The typical voltammetry of an electrochemically generated polythiophene film on an ITO substrate is shown in Figure 5A. The broad non-Nernstian wave is typical of polythiophene derivatives.[21] The oxidation peak observed near 0.7 V/AgCl corresponds to the electrochemical p-doping process, and the reverse undoping processes occur over a wide range. The voltammetric response of a polythiophene film grown by *in situ* chemical polymerization is compared in Figure 5B. The behavior of the films is similar, with a somewhat broader envelope at the extremes for the *in situ* growth film. The behavior is more capacitive in nature, and the enhanced currents at the edges could be explained by more facile ion transport in the film due to pores and channels introduced by the templating action of the Keggin structure. The absence of a redox current associated with phosphomolybdic acid suggests that the acid (and/or its products) is either completely removed or not redox active. The similarity of the cyclic voltammograms indicates that the polythiophene grown by slow *in situ* chemical polymerization is of a quality comparable to polythiophene grown by established methods.

UV−vis Spectroelectrochemistry. Polythiophene was deposited either electrochemically or chemically onto ITO substrates, rinsed in acetonitrile, and let dry at room temperature. Films were subjected to oxidation by applying potential in steps. Figure 6A shows the disappearance of the peak at ∼450 nm due to the oxidation of the electrochemically grown polythiophene film. There is a concomitant increase in the broad band in the vicinity of 700 nm. The chemically deposited film (Figure 6B) shows a similar response. The optical properties of polythiophene at various stages of doping have been discussed extensively in the literature,[21] and the present experiments agree well with previous findings. This again illustrates that good quality polythiophene films can be produced via the *in situ* chemical polymerization method.

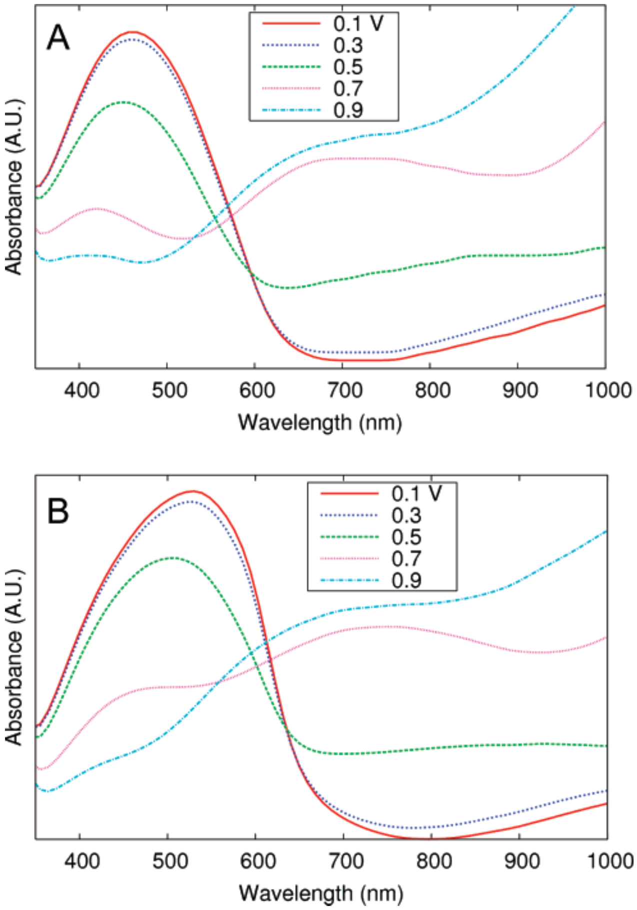

Figure 6. Spectroelectrochemistry of both polythiophene grown (A) electrochemically and (B) chemically (under conditions described in Figure 3) on ITO in 0.10 M TBAPF$_6$/acetonitrile.

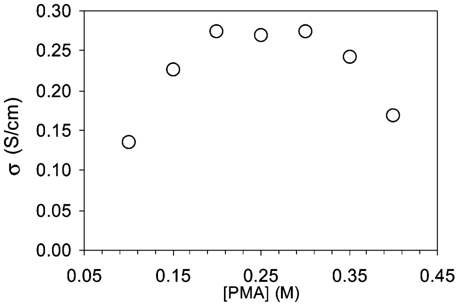

Figure 7. Conductivity as a function of concentration of oxidant (phosphomolybdic acid) used during polymerization.

Conductivity. Conductivity measurements were performed using a four-point probe device, and the results are presented in Figure 7. The concentration of phosphomolybdic acid was varied while the starting concentration of bithiophene was held constant at 0.2 M. The conductivity of the resulting films reached a maximum of nearly 0.3 S cm^{-1} when the initial oxidant concentration lay between 0.2 and 0.3 M, i.e., somewhat beyond a 1:1 molar ratio of oxidant to dimer. This suggests that adding quantities of oxidant below this stoichiometric ratio leads to incomplete polymerization and/or production of polymer mostly in a reduced nonconductive state.

Conductivity roll off occurs when the initial concentration of oxidant surpasses the ratio of around 1.5:1 PMA:bithiophene. Reasons for this are not entirely clear, since overoxidation by this weak oxidant is unlikely. We suspect that a more diffuse, porous structure arising from the templating effect of surplus PMA could be responsible for the diminished conductivity.

Conclusions

In summary, we have demonstrated that the polymerization approach utilizing metastable monomer/oxidant mixtures for *in* *situ* polymerization is a general approach that can be used to produce conducting polymer films with excellent quality. Polythiophene films spin-coated from bithiophene monomer exhibit similar electrochemical behavior as the polythiophene films grown using conventional electrochemical methods. Films obtained by *in situ* growth were smooth and conductive and did not need a conducting substrate, supporting electrolyte, or electrochemical equipment. Also, by increasing the concentration of oxidant (phosphomolybdic acid) in the initial mixture, it is possible to obtain conducting polythiophene films in the doped conductive state. The films obtained here have lower conductivities than those reported in the literature, which may be due to increased porosity associated with the Keggin structure present during polymerization. This may be addressed with further optimization of the reaction parameters. The clear advantage of the *in situ* approach demonstrated here is that this method should be easily adapted to make any oxidation-growth conducting polymer in a processable manner.

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