

ORIGINAL ARTICLE

Toward a trace-free oxidant—insight into unexpected high yields of vapor phase polymerized polyterthiophene

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Vapor phase polymerization (VPP) of conducting polymers has been widely reported as a versatile technique to obtain thin films with high conductivity and order. One oxidant commonly used for VPP is iron(III) *para*-toluenesulfonate (Fe(III)PTS) owing to its outstanding film-forming properties. The polymerization mechanism using Fe(III)PTS has been believed to follow the normal route, where (at least) two Fe(III) is needed for oxidizing one monomer unit to form the polymer. Surprisingly, when polymerizing terthiophene (TTh) monomers at 100 °C using Fe(III)PTS, it was found that ~2.3 times more the expected amount of PTTh was produced, when long polymerization times were used. An explanation for the phenomenon was found when VPP of TTh was successful using only *para*-toluenesulfonic acid (PTSa) as oxidant. It is believed that PTSa is gradually converted to SO₃ and toluene at elevated temperature and that reduction of SO₃ is driving the oxidation of the TTh monomers. This finding also opens a useful oxidative polymerization route where the oxidant can be converted to volatile compounds leaving no trace in the end product.

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INTRODUCTION

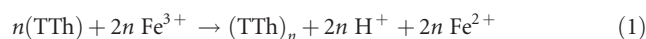
Intrinsically conducting polymers (ICPs) are currently being intensively researched, not only for their conductivity but also for their unique properties such as their ability to work in catalytic, electrochromic and light harvesting applications.^{1–6} Polythiophene is one ICP recognized for its high stability and tunable properties. By attaching different side groups to polythiophene, polymers with different band gaps and solubilities can be obtained, making it suitable for a wide range of applications.^{7–9}

As many uses of ICPs, for example, electrodes require them as films, and most ICPs are hard or impossible to melt or dissolve after synthesis,² significant research has focused on directly polymerizing smooth, ordered films of ICPs. Two well-known methods to do this are electrochemical polymerization and vapor phase chemical polymerization.¹⁰ However, electrochemical polymerization requires electrically conducting substrates, making this method unsuitable for coating of nonconducting surfaces. In addition, the production rate of this method is low and its cost is high. Vapor phase polymerization (VPP) is able to create smooth, highly conducting films without requiring a conducting substrate.^{11,12}

During chemical polymerization of most ICPs, an oxidant is used to oxidize the monomer. For most common monomers, this requires

removal of two hydrogen atoms from each monomer molecule. A mechanism for this reaction is shown in Figure 1¹³ for thiophene being oxidized using Fe(III)Cl₃.

From Figure 1, it can be seen that 2 mol of Fe(III) oxidant are required to produce 1 mol of polymer repeat units. For terthiophene (TTh) the equation would be:



The 2:1 oxidant:monomer ratio has been experimentally confirmed in the case of VPP of pyrrole.¹² The same ratio is expected for polymerization of other monomers proceeding by the same mechanism. This ratio has also been seen in electropolymerization and oxidative chemical polymerization, where at least 2 mol of electrons (oxidant) are required to produce 1 mol of polymer.^{10,13,14}

In this report, measurement of the masses of iron(III) *para*-toluenesulfonate (Fe(III)PTS) oxidant used and polymer produced during chemical VPP of TTh showed that more polymer was produced than expected according to equation (1). In other words, the molar amount of polymer produced was more than half the molar amount of oxidant. Further, the difference of polymers made at different polymerization times were studied, which could indicate different mechanisms of polymerization over the course of the

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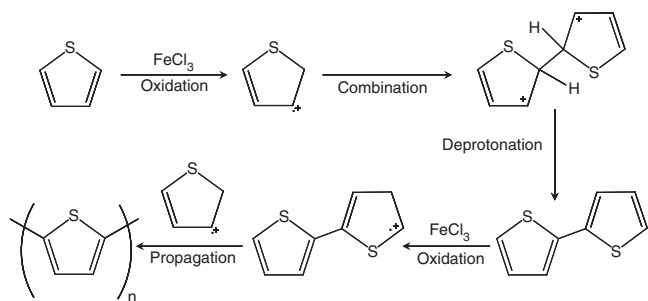


Figure 1 Chemical polymerization of thiophene using FeCl_3 as oxidant.¹³

polymerization. It was found that the PTS contributes to the oxidation of TTh.

EXPERIMENTAL PROCEDURE

The chemicals used were 2,2':5',2''-terthiophene from Sigma-Aldrich (Castle Hill, NSW, Australia), and Fe(III) tosylate, marketed as CLEVIOS C-B 40 V2 from H.C. Starck (Goslar, Germany). The Fe(III) tosylate was delivered as a solution of 40 wt% in butan-1-ol, which was then diluted with an equal volume of butan-1-ol to produce a 25 wt% solution (for the 140- μg oxidant coating), and three times the volume of butan-1-ol to produce a 14 wt% solution (for the 59- μg oxidant coating). 3,4-Ethylenedioxythiophene (EDOT) was purchased from Yacoo Chemical Reagent Co., Ltd. (Suzhou, China) *Para*-toluenesulfonic acid (PTSA) was purchased from Sigma-Aldrich.

The oxidant solution was spin-coated onto glass slides or quartz crystal microbalance (QCM) crystals at 1500 r.p.m. for 30 s. The oxidant-coated substrate was then dried at 70 °C for 1 min before being placed in the polymerization chamber for various lengths of time. The polymerization chamber containing TTh monomer was immersed in a silicone oil bath at a controlled temperature. QCM samples were polymerized at 104 °C while all other samples were polymerized at 98 °C. The polymerization setup is illustrated in Figure 2.

After polymerization, the samples were rinsed in ethanol and the mass of the polymers were determined using QCM. QCM measurements were made with a Stanford Research Systems QCM200 (Sunnyvale, CA, USA). The area measured on each QCM crystal was 1.37 cm²¹⁵ and the variation in deposited Fe (III) PTS was <5%. The sensitivity of QCM used in the experiments was 18 ng Hz⁻¹¹⁵ whereas the minimum mass of oxidant on the quartz was ~59 μg . Therefore the experimental error from the weight was considered very low. The masses measured were converted into the number of moles using the molar masses of 248.4 and 569.5 g mol⁻¹ for TTh and Fe(III) tosylate, respectively. Ultraviolet–visible (UV–vis) spectrophotometry was done with a Jasco V-670 Spectrophotometer (Jasco, Tokyo, Japan).

Samples for differential scanning calorimetry (DSC) and elemental analysis were prepared by drop casting the oxidant solution onto glass slides, allowing excess to flow off, then drying and polymerizing as before. Two types of samples were prepared for DSC: one was polymerized for 3 h and another for 16.5 h. After polymerization, the polymer was rinsed off into a suspension of ethanol. The ethanol was changed several times to remove excess oxidant and monomer. The resulting polymer was then dried at room temperature before performing DSC measurements. Measurements were made using a TA-Q100 DSC (TA Instruments, Rydalmere, NSW, Australia). Heating and cooling rates were 10 °C min⁻¹, and nitrogen purge rate was 50 ml min⁻¹. C, H and S were analyzed by Campbell Microanalytical Laboratory, University of Otago, New Zealand using a Carlo Erba Elemental Analyser EA 1108 (Carlo Erba, Lakewood, NJ, USA) and a Mettler UMT2 microbalance (Mettler Toledo, Auckland, New Zealand).

All Raman spectra are recorded using a Renishaw in Via Raman microscope (Renishaw, Sandringham, VIC, Australia), operating at a wavelength of 514 nm with 500 mW of power at the laser head. A 6% neutral density filter between

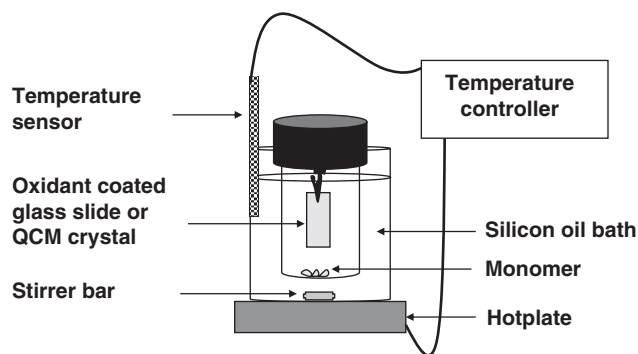


Figure 2 Schematic of VPP setup for TTh polymerization. A full color version of this figure is available at *Polymer Journal* online.

the laser and instrument is also used. All data are analyzed using the software package Grams AI 8.0 by Thermo Electron Corporation (Sydney, NSW, Australia).

Conductivity measurements were performed according to the procedure described previously.¹¹ Two PEDOT films separated by an ~6-mm gap were polymerized on a single glass slide using VPP. PTTh was then polymerized to cover one of the PEDOT films and extend across the gap to within ~2–3 mm of the other PEDOT film. The ionic liquid propyl methyl pyrrolidinium bis(trifluorosulfonamide) (C3mpyr(Tf)₂N), synthesized in-house, was applied over the PTTh film, the gap and the exposed PEDOT film. The two-electrode cell was cycled between –1 and +3 V twice and subsequently held at 3 V until the current leveled off after ~3–5 min. The applied potential was then removed, the cell disconnected and the film rinsed with ethanol to remove the ionic liquid, followed by drying under N₂. Immediately, the surface conductivity was measured with a Jandel four-point probe (Jandel, Linslade, UK). The film thickness was analyzed using a DekTak profilometer (Veeco, Plainview, NY, USA) and the bulk conductivity was calculated.

RESULTS AND DISCUSSION

QCM results (Figure 3) showed that the expected amount of PTTh was produced after ~2 h of polymerization. However, the amount of PTTh continued to increase until an amount about 2.3 times higher than expected was reached. To ensure the excess mass was polymer and not remaining oxidant or monomer, different samples were soaked for 1 h in ethanol, acetone or distilled water, and rinsed in butan-2-one, a good solvent for the monomer. This did not result in any significant change in mass. Samples were also dried over silica gel to remove moisture, which still did not change their mass.

Clearly, more polymer was produced than expected, up to ~2.3 times that expected according to equation (1), corresponding to a molar Fe(III):polymer(unit) ratio of 1:1.15. This 2.3-times limit did not change when using 140 μg of oxidant (instead of 59 μg) on the QCM crystals or purging the polymerization chamber with nitrogen gas or air during polymerization. The fact that the 2.3 actual/expected limit is the same for different amounts of oxidant shows that the polymerization is stopping, and not just very slow.

This ratio of 1:1.15 seems almost magic and is not fitting with any polymerization mechanism for thiophenes found in the literature. If some kind of free-radical-like polymerization route was in play, it is not explainable why the reaction should stop at this (or any) well-defined ratio. The same argument can be used if regeneration of the oxidant by atmospheric oxygen was thought to be responsible and, as already mentioned, performing the polymerization under nitrogen or air did not change the result.

In order to further investigate the phenomenon, samples at different polymerization times were prepared and analyzed to clarify

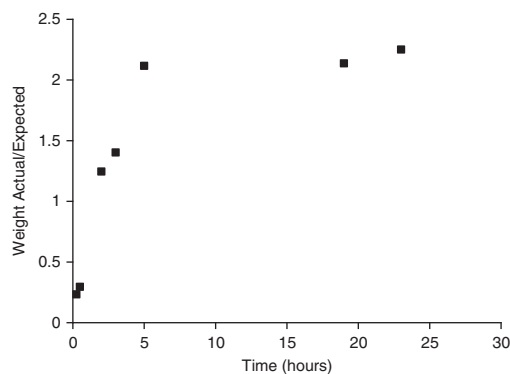


Figure 3 Mass of polymer produced over time after wash, as a multiple of expected mass according to equation (1), using $\sim 59 \pm 3 \mu\text{g}$ of oxidant on the QCM crystal. Each point represents a separate experiment.

if there would be any change in the properties of PTTh produced with different polymerization times, that is, 3 and 16.5 h. These times were chosen to produce two polymers corresponding to the time when (3 h) and long after (16.5 h) the Fe(III) oxidant was ‘used up’ according to equation (1).

Elemental analysis of the samples showed the ratio of C:H:S 4.3:3.1:1 and 4.2:2.6:1 for 3 h and 16.5 h, respectively. The C to S ratio is thereby very close to the theoretical value (4:1) for both samples. The H content is somewhat higher for the shorter polymerization time, which indicates a lower average chain length. Conductivity of PTTh in its undoped state was very low and not possible to be measured using four-point probe technique.¹¹ The conductivity values of the doped PTTh films were 17 ± 1 and $42 \pm 4 \text{ S cm}^{-1}$ for 3 h and 16.5 h, respectively, following the previously reported procedure.¹¹ The conductivity for the 3-h samples is in very good agreement with earlier reports on VPP PTTh.¹¹ However, the 16.5-h samples showed higher conductivities, which may be assigned to slightly longer chain length as indicated from the elemental analysis.

The DSC scans of both samples show a peak within the range 130–140 °C (Figure 4). The DSC trace indicates a solid–solid phase transition, where the material is going from a more-ordered to less-ordered state.^{11,16} The presence of this peak shows that the material is intrinsically ordered after polymerization. In the second scan, the peak disappeared, meaning the order was lost. These phenomena have been reported earlier for different ICPS^{11,16} and is also reported to reappear (reorder) after 3–5 days.

The sample polymerized for 16.5 h had a broader peak, with a lower transition energy of 63.67 J g^{-1} , compared with 122.3 J g^{-1} for the 3-h sample. The width of the peak is believed to correspond to the distribution of ordered structures in the material, with a broader peak arising from a broader distribution. Having a lower transition energy means that the sample polymerized for 16.5 h has less order. It is an unexpected result to see that the 16.5-h samples have higher conductivity given that they possess a lower degree of order—this indicates that there is no direct correlation between high degree of π -stacking/order and conductivity for these samples. Taking the QCM results into account, the mass ratio between 3-h and 16.5-h samples should be about 1:2 and this could mean that most-ordered polymer in the 16.5-h sample was obtained during the first 3 h of polymerization. This change in the order obtained during the polymerization at and after 3 h indicates that there could indeed be a change in polymerization mechanism during the course of polymerization. It

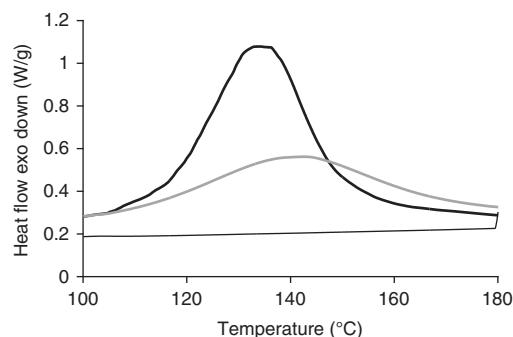


Figure 4 DSC scans of PTTh polymerized for 3 h (thick black curve) and 16.5 h (gray curve). The thick black line represents the first scan, while the thin black line represents the second scan for the 3-h sample. Solid–solid transition energies were 122.3 J g^{-1} for the 3-h sample and 63.67 J g^{-1} for the 16.5-h sample.

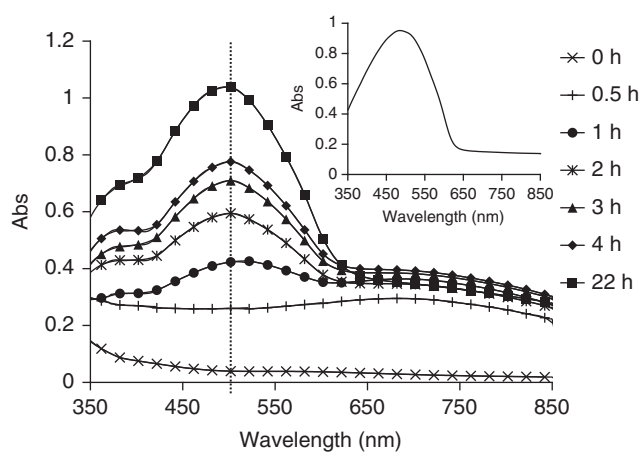


Figure 5 UV-vis spectrum of samples polymerized for various lengths of time without wash. Inset shows the spectrum of a sample polymerized for 22 h and washed in ethanol.

has previously been shown that the Fe(III) salt used for VPP has a templating influence on the order in PEDOT,¹⁶ resulting in significantly more order than in electropolymerized samples with the same cation. Imagining a shift in polymerization mechanism from a Fe(III)PTS templated to a non-templated route could result in the changes in DSC traces as seen for different polymerization times.

The UV-vis spectrum of unwashed samples during the polymerization in Figure 5 shows two peaks, at ~ 500 and ~ 700 nm corresponding to the π - π^* transition and the polaron absorption and thereby to reduced and oxidized PTTh. These transitions also indicate the conjugation length of the conducting polymer.¹⁷ The oxidized peak at 700 nm stops growing after ~ 2 h (around the time that the oxidant is expected to be used up as shown in Figure 3). The peak at 500 nm continues to grow, showing that reduced PTTh continues to be produced, possibly by a different mechanism. However, it is worth noticing that the position of the ~ 500 -nm peak is not changing during the period of polymerization, indicating that the conjugation length remains the same for all polymers polymerized independent of polymerization time. It is also remarkable that the amount of oxidized PTTh remains unchanged and is not decreasing after 2 h of polymerization, excluding the possibility of one oxidized part of the polymer driving further polymerization after the

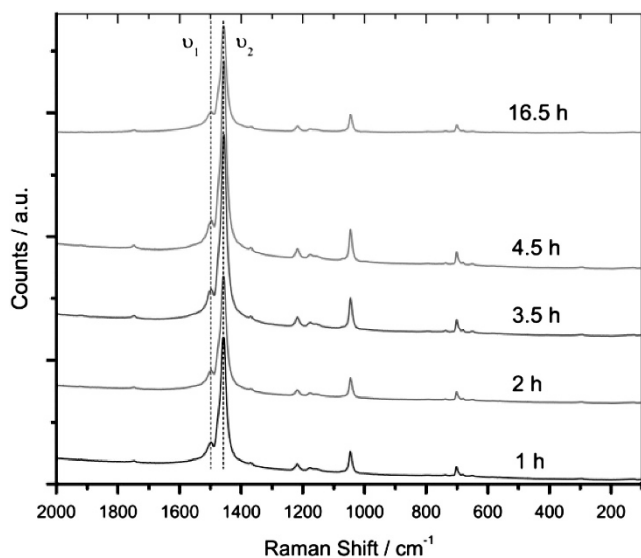


Figure 6 Raman spectra of PTTh with varying VPP time.

Fe(III) source of oxidant has been used up. The inset in Figure 5 shows the PTTh polymerized for 22 h after wash in ethanol. The polaronic band around 700 nm has disappeared, leaving a reduced form of the material.

Figure 6 displays the Raman spectra of the samples polymerized for various times after wash. All spectra show the features of polythiophene in the reduced state¹⁸ and, typical of the Raman spectra of polyconjugated materials, the relatively sparse bands originate from totally symmetric modes.^{19,20} The spectra are dominated by the bands in the 1500–1450 cm^{-1} region owing to the strong enhancement caused by electron–phonon coupling.¹⁹ The ν_1 mode indicated in Figure 6 appears at $\sim 1500 \text{ cm}^{-1}$ and is associated with the ring deformation of the ends of the polymer chains, while the ν_2 mode situated at 1455 cm^{-1} is associated with ring deformation in the central part of the polymer chain.^{10,21,22} Through the deconvolution of this region, the integrated area intensity ratio between the ν_1 and ν_2 modes provides an indication of the length of the polymer chains.¹¹ Although an apparently slight increase in chain length is seen as the polymerization proceeds up to 4.5 h, the difference is far too small to draw any conclusions and well within the experimental/statistical errors, and is therefore not included in the presented data.

Frequency dispersion in conjugated polymers is well known¹⁰ and it has been shown that the ν_1 mode in polythiophene is sensitive to the conjugation length of the polymer chains.^{21,23} Increased conjugation causes enhanced electron–phonon coupling that causes the Raman frequency of the ν_1 mode to shift to lower values.²¹ In the present study, however, there was no significant or systematic change in the ν_1 mode, indicating that between the samples there is no real change in the average conjugation length as also noticed above in the UV–vis measurements. It is interesting to note that the 16.5-h sample exhibited more fluorescence than the shorter polymerization times and required a quadratic baseline correction for display in Figure 6.

Combining the results, a few hypotheses can be made: first, during initial VPP, oxidized PTTh is formed, which has an ordered structure owing to Fe(III)PTS templating. Second, this occurs with Fe(III) as the oxidation agent as per usual understanding according to equation (1). Last, with continued polymerization, when the Fe(III) oxidant is ‘used up’ according to equation (1), a reduced and non-templated, less-ordered form of PTTh is formed.

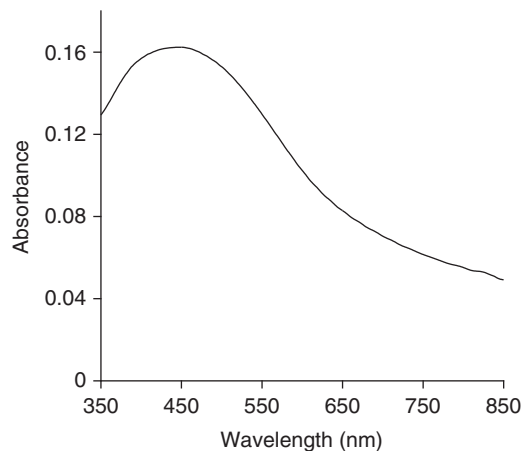


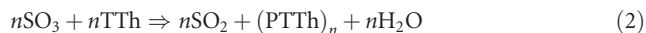
Figure 7 UV–vis spectra of VPP PTTh polymerized on glass with only PTSa as oxidant at $98 \text{ }^\circ\text{C}$ for 6 h.

The main observation that requires explanation in the present study remains that we are reaching a maximum polymerization point, where the polymerization stops—and that this point is about 2.3 times higher than one would expect from the common known polymerization route(s). It has earlier been shown that some thiophene derivatives can be polymerized by an acidic route to a nonconjugated form, that later can be converted to the conjugated form in a post-oxidation step.¹⁰ However, the UV–vis spectra clearly show that the reduced PTTh formed is conjugated and that the conjugation length remains unchanged with longer polymerization times (which is also confirmed with the Raman measurements), undermining this tempting explanation of an acidic polymerization route.

The unusual conditions used for VPP of TTh, $\sim 100 \text{ }^\circ\text{C}$ and no solvent (apart from liquid TTh), allow the possibility that some more ‘exotic’ reduction reactions could take place. It is worth reminding that the sulfur in the PTS actually is in a relatively high oxidation state and may have the potential to contribute to the TTh oxidation. In separate experiments, PTSa or poly(4-styrenesulfonic acid) (PSS) was coated onto glass substrate from a 0.1 M ethanol solution and then dried. PTSa and PSS films were then exposed to TTh vapor at $98 \text{ }^\circ\text{C}$. Indeed coloration started to occur on the PTSa samples shortly after they were inserted into the VPP chamber, but no reaction could be detected on the PSS film. Figure 7 shows the UV–vis spectra of the PTSa-initiated film (6 h polymerization) after wash in ethanol, confirming that PTTh is formed.

PTSa is normally not considered an oxidant. However, desulfonation of PTSa at elevated temperatures is well known. The desulfonation of PTSa and other aromatic sulfonic acids was originally studied in detail by Wanders and Cerfontain,^{24,25} and was found to be a first-order process with respect to the initial sulfonic acid concentration. Increase in temperature (over $100 \text{ }^\circ\text{C}$) and acid concentration increased the rate constant of the desulfonation. The products of the desulfonation were confirmed to be toluene and SO_3 . This reversibility of the sulfonation process allows us to suggest that SO_3 is formed during the VPP, after some of the initial Fe(III)PTS has been converted to Fe(II)PTS and PTSa (where the added proton is a product from the polymerization of TTh).

Sulfuric acid and SO₃, on the other hand, has been reported to be able to oxidize thiophenes at elevated temperatures, itself being reduced to H₂SO₃ or SO₂, respectively.^{26,27} For SO₃ and TTh:



In the absence of aqueous conditions—as under VPP at ~100 °C—SO₂ and H₂O would then evaporate from the samples during VPP (equation (2)). Further, the gradually ‘available’ PTSa is converted to SO₃, and SO₃ is reduced to SO₂ owing to the oxidation of TTh monomer. We are hereby suggesting the most likely scenario where the polymerization mechanism is maintained (as oxidative polymerization) but where a second oxidant than Fe(III) comes into play, namely the sulfur being reduced from oxidation state 6⁺ to 4⁺.

QCM data for the PTTh polymerization with Fe(III)PTS were then considered as following. During the reduction of Fe(III) to Fe(II), one PTS per Fe(III) is ‘released’ from the iron complex; some of this is incorporated as counter ions in the doped PTTh formed during the ‘use’ of Fe(III) as oxidant (Figure 5). Normally a doping level of ~0.25 is reported for thiophenes.^{10,14} For TTh, this means that 8 (for the polymerization) + 3 (for the oxidation) Fe(III) is needed to polymerize four units of TTh ⇒ that 1 mol of Fe(III) would produce 0.36 mol of polymerized and oxidized TTh units containing 0.27 mol of PTS as dopant. This would then leave 0.73-mol PTS (that is not participating in the Fe(II) complex) per mole of initial Fe(III), that is now ‘free’ to form PTSa with a proton eliminated from TTh in the polymerization process. The possible amount of SO₃ formed, according to the route suggested above, would then also be 0.73 mol per mole of initial Fe(III) and should so be able to polymerize a further 0.73 mol of (reduced) TTh units per mole of initial Fe(III), leading to a total of (0.36 + 0.73) = 1.09 mole of TTh units per mole of initial Fe(III). This value is indeed close to values measured in the QCM experiments reported above (1:1.15).

These findings open a one-step polymerization route for VPP of thiophenes where the oxidant is not leaving any trace (apart from eventually as dopant) in the final product. This route is very attractive because it eliminates the possibility of iron contamination and saves a washing step to remove unwanted products from the conducting polymer material (that is, Fe(II) and excess of anions).

CONCLUSIONS

The polymerization of PTTh by VPP has been studied using a standard Fe(III)PTS oxidant and it was surprisingly found, when long polymerization times were used, that more than twice the amount of PTTh was produced compared with the expected amount according to the common understanding of the oxidative polymerization route using Fe(III) salts. The produced PTTh had similar conjugation length independent of polymerization time but showed less-ordered structure at longer polymerization times (more than ~3 h). The explanation for the large amount of PTTh polymerized was found to be owing to the PTS component of the oxidant and it is suggested that part of the PTS is converted to SO₃ under VPP conditions and that the SO₃ is capable of oxidizing the TTh monomer, itself being converted to SO₂ and H₂O.

This finding is of importance as it is not only explaining the unexpected high yield of PTTh produced from more than 3 h polymerization but is also a discovery of an alternative oxidative polymerization route where the oxidant is converted to volatile compounds leaving no trace on the end product. Further development of this method will be reported in separate communications.

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