Vapor-Phase Polymerization of 3,4-Ethylenedioxythiophene: A Route to Highly Conducting Polymer Surface Layers

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ABSTRACT: A new synthetic route to poly-3,4-ethylenedioxythiophene (PEDT) with a conductivity exceeding 1000 S/cm is described. The method is based on base-inhibited vapor-phase polymerization, where a surface covered with ferric *p*-toluenesulfonate as oxidant mixed with a volatile base (pyridine) is exposed to 3,4-ethylenedioxythiophene (EDT) vapors. The base is added to suppress an acid-initiated polymerization of EDT, leading to a product with little or no conjugation. The product of the base-inhibited vapor-phase polymerization is confirmed to be virtually identical to PEDT obtained by wet chemical oxidation by both spectroscopic and electrochemical methods. A possible reaction scheme for the acid-initiated polymerization is discussed.

Introduction

Among the different conducting polymers used in practical applications, poly-3,4-ethylenedioxythiophene (PEDT) is known as a particularly robust and well conducting system.[1] PEDT is available from Bayer AG as an aqueous suspension (Baytron P) that can be conveniently coated onto a number of different surfaces by printing or spinning techniques. The resulting bluish, transparent polymer layer can obtain conductivities[1] in the range of up to 10 S/cm, which is more than sufficient for applications as antistatic coatings, for which it was originally developed. Today the focus has shifted toward the use of PEDT as hole injection layers in polymer electronic devices. The availability of this easily applied polymer hole conductor has been instrumental for the present development of polymer LED's and polymer electronics in general, although PEDT in most applications must be combined with better conducting layers, because the conductivity that can be achieved does not meet the requirements for current conducting paths to and from the devices.

PEDT is by itself insoluble, but the use of a water-soluble polyelectrolyte, poly(styrene sulfonic acid) (PSS), as the charge balancing counterion has made it possible for Bayer AG to formulate Baytron P as a stable PEDT/PSS suspension that at the same time shows excellent film-forming properties. Although the conductivity of the resulting films can be increased in a number of ways, e.g., by changing the solvent,[2] Baytron P does not express the full possibilities of PEDT in terms of conductivity. This is not surprising as the requirements for high conductivity (first of all long, unperturbed polymer chains) may be difficult to combine with solution processing.

It has previously been shown that in situ formation by electropolymerization can lead to conducting polymers with a high conjugation length, providing that the synthesis conditions are chosen properly.[3] Aleshin et al produced PEDT-PF_6 by electropolymerization from acetonitrile at −30 °C and obtained conductivities up to[4] 300 S/cm. Electropolymerization can, however, only be used to coat surfaces that are already conducting, which limits the practical use of this method. Alternatively, PEDT can be produced by direct chemical oxidation of the monomer. This is mostly used for the production of bulk polymers, but de Leeuw[5] developed a direct oxidative polymerization method suitable for formation of surface films. By an adaptation of this method, conductivities up to 550 S/cm have been reported for PEDT.[6] It is, however, not trivial to obtain reproducible, homogeneous films using this method.

Bayer AG ships both the 3,4-ethylenedioxythiophene (EDT) monomer (Baytron M) and an oxidative solution of ferric *p*-toluenesulfonate (Fe(III) tosylate) in butanol (Baytron C). Spinning a mixture of these two ingredients onto a surface enables one to obtain PEDT films. However, to get a homogeneous film requires great skill, and the pot-life of the polymerization mixture is only 10−20 min before PEDT forms insolvable flocculates in the solution. This makes practical use difficult and made us look for alternative routes to highly conducting PEDT surface films.

Vapor-phase polymerization (VPP) has been used for making conducting polymers. The method was originally described by Mohammadi et al.[7] as a CVD process using $FeCl_3$ or H_2O_2 as oxidizing agents for polymerization of polypyrrole films. It was later adapted for the formation of well-defined surface patterns of polypyrrole using patterned copper converted to $CuCl_2$ as the oxidation agent.[8] VPP has also been used for in situ polymerization of polypyrrole inside a number of different nonconducting polymers and rubbers. This was first reported by Ueno et al.,[9] who made a conducting composite by exposing PVC blended with $FeCl_3$ to pyrrole vapors. In 1998 Fu et al.[10] showed promising results using Fe(III) tosylate as oxidizing agent for VPP of pyrrole in a polyurethane foam, but no further results were reported. Recently the first use of VPP to produce PEDT has been reported.[11] Films with conductivities around 70 S/cm were obtained using $FeCl_3$ as oxidizing agent.

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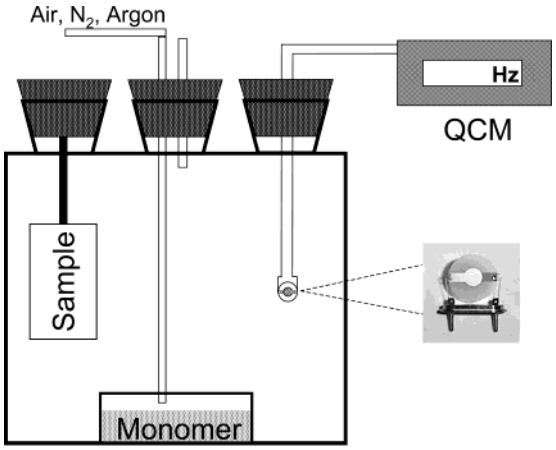


Figure 1. Schematic drawing of polymerization chamber.

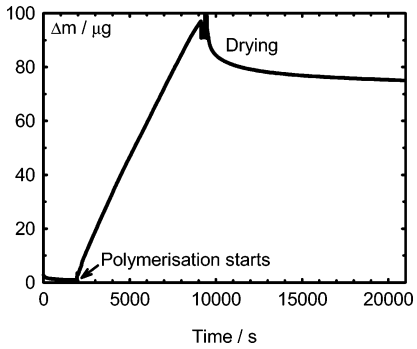


Figure 2. Response of quartz crystal microbalance during vapor-phase polymerization of EDT on Fe(III) tosylate in air. EDT temperature = 30 °C; airflow rate = 260 mL/min. The frequency change is transformed into mass change by the Sauerbrey equation.

The present paper presents a new route to highly conducting PEDT surface films based on vapor-phase polymerization. The aim of the work has been to develop a process that is amenable to patterning and compatible with the processes used to produce microfluidics and electronic devices.

Experimental Section

The EDT monomer (Baytron M) and Fe(III) tosylate (40% solution in butanol, Baytron C) was received from Bayer AG. *p*-Toluenesulfonic acid (PTSa) and pyridine were obtained from Aldrich. All chemicals where used as received.

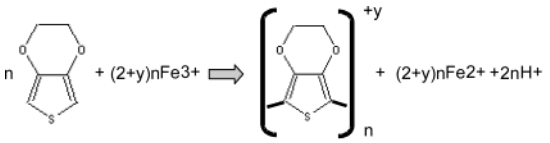
Vapor-phase polymerization was carried out in a simple single-chamber setup as shown on Figure 1. The chamber can be flushed with air, nitrogen, or argon during the polymerization, and a heater provides the possibility to raise the temperature of the monomer reservoir (30−50 °C) in order to speed up the process. The samples to be covered with PEDT are initially coated with the oxidant, e.g., a butanol or ethanol solution of Fe(III) tosylate. After drying at 60 °C in air, the samples are transferred to the polymerization chamber.

The polymerization chamber can be equipped with a quartz crystal microbalance (QCM) that is used to monitor the progress of the polymerization process. It is based on a 10 MHz crystal (from ICM, Oklahoma City) that can be coated with the same oxidant as the substrates prior to exposure to EDT vapor. Weight changes in the surface film on the crystal can then be detected as changes in the resonant frequency of the crystal. An oscillator (Lever Oscillator, ICM) connected to a frequency counter (FLUKE PM6680B) excites the crystal, and the change in frequency is followed by logging the analogue output from the frequency counter. The lever oscillator also outputs a signal that allows estimation of the damping of the oscillation due to nonrigid deposits.

The polymer coatings on the substrates were characterized by UV−vis spectroscopy (Shimadzu UV1700), FTIR (Perkin-Elmer, Spectrum One with an STI "Thunderdome" ATR system), and Raman spectroscopy (Lab Raman Infinity Spectrometer with a confocal microscope; spectra obtained with an excitation wavelength of 676 nm). Some coatings were further characterized by cyclic voltammetry (CV) in a standard three-electrode cell using an Autolab potentiostat. The conductivity of the samples was measured using a four-point probe from Jandel Engineering Ltd. connected to a Keithly 2400 source meter. The probe is equipped with four spring-loaded tungsten carbide needles spaced 1 mm apart. During a measurement sequence the current through the sample is changed from a low level where the potential drop over the sample is in the μV range to the current level where the potential is well above 10 mV. To eliminate errors from thermovoltages and voltmeter offsets, two current pulses of opposite signs are used for each measurement point. Both high and low currents may lead to relatively large measurement errors, and the surface resistivity is extracted from an intermediate current range where the resistivity is independent of the applied current. The bulk resistivity of the films is calculated from the surface resistivity using the film thickness measured by a DekTak profilometer.

Results and Discussion

Direct Polymerization of EDT on Fe(III) Tosylate and PTSa. Initially direct oxidation using the commercially available Baytron C solution of Fe(III) tosylate in butanol was tried because this oxidant is known to produce highly conducting PEDT.[1] Exposing Fe(III) tosylate to EDT vapor could be expected to give PEDT



(1)

Assuming that the overoxidation, *y*, is 0.25,[12] one would then expect to gain ≈63 g of PEDT per mol of Fe(III) tosylate. The results from the QCM measurements, however, gave a very different result as illustrated on Figure 2. In this experiment 22.1 nmol of Fe(III) tosylate was initially coated onto the quartz crystal, and the expected mass gain from polymerization is 1.4 μg. At time 2000 s, the quartz crystal with Fe(III) tosylate is transferred to the polymerization chamber and the mass on the crystal starts to increase. At time 9100 s, the QCM stops oscillating due to a combination of high mass loading and a high damping from a viscous (nonrigid) deposit. The QCM is subsequently taken out of the polymerization chamber and placed in a drying chamber flushed with air (260 mL/min) where nonreacted EDT is allowed to evaporate. Soon after the QCM starts oscillating again and after 20 000 s, the total mass increase is 71 μg. This is 50 times more than that expected from reaction 1, indicating that the polymerization is not only caused by oxidation by Fe(III) tosylate. The experiment was repeated in both nitrogen and argon atmosphere with similar results, ruling out the possibility that oxygen is driving the polymerization reaction. The brownish coatings obtained from direct vapor-phase polymerization of EDT on Fe(III) tosylate turned green after Fe(III) and Fe(II) tosylate was removed by washing in ethanol. The resistivity of the

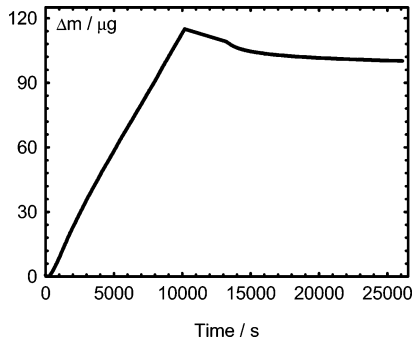


Figure 3. Response of quartz crystal microbalance during vapor-phase polymerization in nitrogen of EDT on a crystal coated with *p*-toluenesulfonic acid. EDT temperature = 30 °C; flow rate = 260 mL/min.

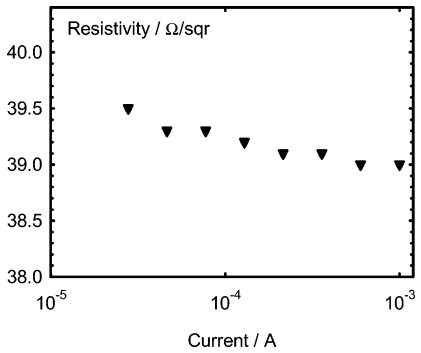


Figure 4. Surface resistance of a BI VPP PEDT-film on glass measured at different currents. The thickness of this sample is 250 nm, and the bulk conductivity calculated from the surface resistivity at 1 mA is 1025 S/cm.

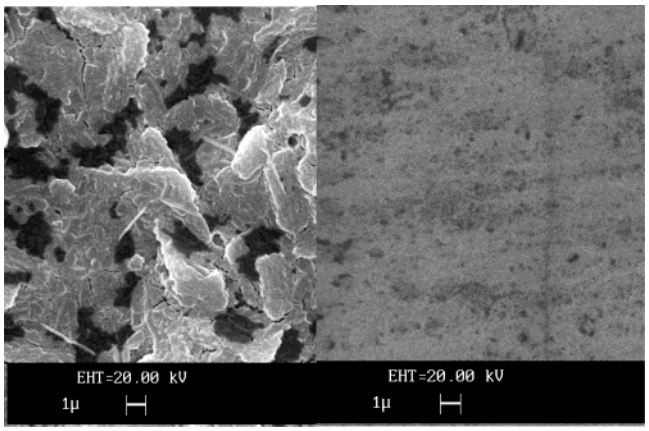


Figure 5. SEM micrographs of BI VPP PEDT before and after ethanol rinse.

deposits was very high (>1 GΩ/sq), indicating that the product was not PEDT. In an attempt to perform NMR analysis on the VPP films, dissolution was attempted with different solvents (chloroform, methanol, ethanol, acetone, water, and acetic acid) but without success. This supports the notion that the films are indeed polymeric.

As the polymerization process is not driven by oxidation by Fe(III) or oxygen, the high acidity of Fe(III) tosylate might be the critical factor. To test this hypothesis, a quartz crystal coated with 3470 ng (18.9 nmol) of *p*-toluenesulfonic acid (PTSa) was placed in the vapor-phase polymerization chamber; the QCM curve is shown on Figure 3. Again, the polymerization continues until the QCM crystal is removed from the polymerization chamber at time 10 000 s. After drying, the gain in mass is 96.8 μg or 36 mol of EDT polymerized per mol of PTSa employed. When PTSa is exchanged with poly(acrylic acid), no film is formed. This indicates that a strong acid is needed to drive this kind of polymerization.

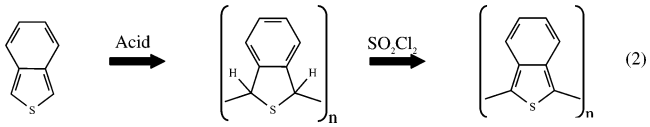
Base-Inhibited VPP of EDT. The results above show that acid-initiated polymerization of EDT requires a pH lower than what can be provided by poly(acrylic acid). On the other hand, a low pH is essential for the use of Fe(III) tosylate, which is preferred to other oxidation agents such as ammonium peroxydisulfate because of its good film-forming properties. The question is whether there is a pH range where reaction 1 is preferred over the acid-initiated polymerization?

Using an alkaline inhibitor the pH of the Fe(III) tosylate solution in butanol can be raised, which at the same time decreases the redox activity of Fe(III).[5] By choosing a liquid base with a relatively high vapor pressure, the pH at the substrate will slowly decrease until the polymerization according to reaction 1 starts. If the sample is then removed before the acid-initiated polymerization takes over, a conducting PEDT film should be formed.

Pyridine was chosen as the basic inhibitor, and the pH of the Fe(III) tosylate solution was raised (to 2.5 measured by a pH probe, but the low water content of the solution makes the absolute value uncertain) by adding 0.5 mol of pyridine per mol of Fe(III) tosylate. Samples where prepared using poly(ethylene terephthalate) (PET) foils and platinum-coated PET foils as substrates. The Fe(III) tosylate/pyridine solution was applied to the substrates and dried in air at room temperature until the solvent, butanol, had evaporated. The samples were then further dried for 3 min in an oven at 75 °C before it was exposed to EDT vapor in the vapor polymerization chamber (EDT liquid temperature, 50 °C; N_2 flow rate, 50 mL/min). After 1 h the samples were removed from the chamber. After another 30 min. in air the samples where washed twice in ethanol for 10 min (hereafter referred to as "BI VPP PEDT").

Using this method light blue films were obtained with conductivities that routinely exceeded 1000 S/cm, see Figure 4. The films are very smooth and without characteristic substructures after a rinse in ethanol to remove the Fe(II) tosylate content, but as seen from the SEM pictures in Figure 5, the pristine films are quite rough. QCM measurements performed under these synthesis conditions showed only rather small weight changes because the growth of the polymer is counteracted by pyridine evaporation. The total weight change after the crystal is rinsed in ethanol is consistent with reaction 1.

Mechanism of Acid-Initiated Polymerization. Acid-initiated polymerization of thiophene derivates has been reported for polymerization of benzo[*c*]thiophene (isothianaphthene).[13] The proposed polymerization leads to a nonconjugated polymer, which can be oxidized in a second step, e.g., by sulfuryl chloride (SO_2Cl_2)[14]



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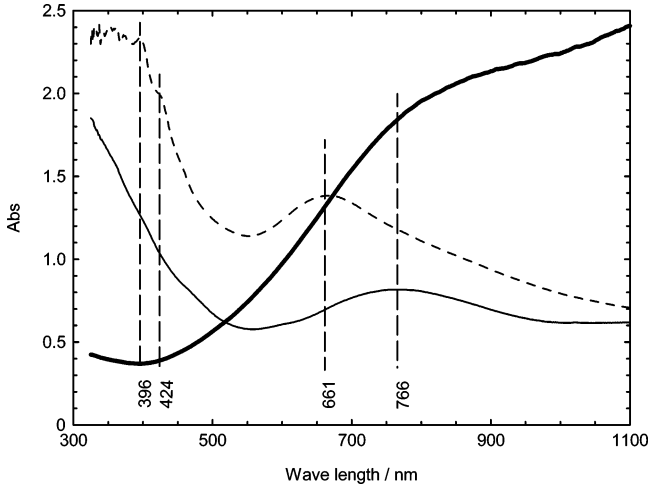
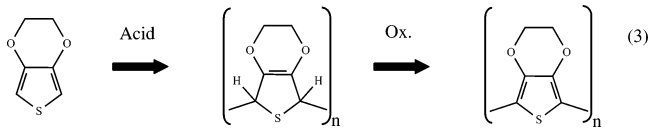


Figure 6. UV−vis spectra of BI VPP PEDT (thick full line) deposited onto a PET foil compared to VPP PEDT deposited on a PET foil with Fe(III) tosylate, washed in ethanol (broken line), and post-Ox VPP PEDT (thin full line).

A similar reaction scheme might be possible for PEDT. In that case the intermediate polymer and the oxidation step should have the structure



(3)

To explore whether this reaction is actually taking place, films obtained from direct vapor polymerization on Fe(III) tosylate and PTSa were subsequently oxidized in an Fe(III) tosylate solution in ethanol (pH regulated to 1.5 with pyridine). After oxidation the films were washed twice in ethanol for 10 min.

This treatment causes the films to change color from green to bluish-black, and the films became slightly conducting (1−5 MΩ/sqr), although not in the same range as the films obtained from base-inhibited vapor polymerization. Films made by this method are in the following dubbed "post-Ox VPP".

These results called for further investigations of polymerized EDT films obtained by the different routes. New thicker samples for further analysis were made on PET and platinum-coated PET. These samples were exposed in the vapor polymerization chamber (EDT temperature 50 °C, N_2 flow 50 mL/min) for 2 h, dried for 30 min, and subsequently washed twice in ethanol.

UV−Vis. Figure 6 shows the UV−vis spectra of VPP films of EDT polymerized on Fe(III) tosylate, postoxidized VPP of EDT on Fe(III) tosylate, and BI VPP PEDT. The spectrum of BI VPP PEDT fits well with the spectrum reported for electrochemically oxidized PEDT at potentials around 1000 mV.[15] The spectrum of the post-Ox VPP film, which according to reaction 3 also should be oxidized PEDT, has a minor absorption peak at 766 nm and an increasing absorption in the lower UV range but no significant similarity to spectra reported for oxidized PEDT.

The VPP P-EDT films on Fe(III) tosylate and PTSa (not shown) have similar characteristics, although the ratio between the peeks are different. The VPP P-EDT films are clearly different from the BI VPP PEDT, showing significant absorbance in the 325−450 nm range, around 661 nm and—as post-ox VPP P-EDT—

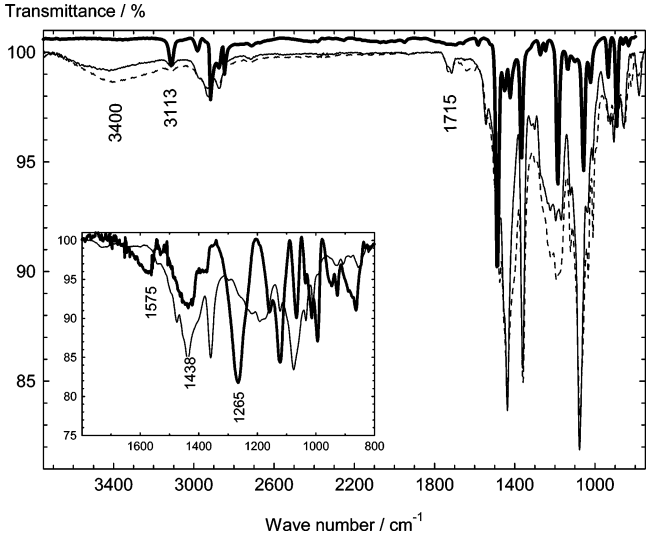


Figure 7. FTIR spectra of the EDT monomer (thick full line) on a PE membrane compared to VPP PEDT deposited on a aluminum foil (with Fe(III) tosylate) washed in ethanol (broken line) and post-Ox VPP PEDT (thin full line). The insert is a comparison of BI VPP PEDT (thick full line) with post-Ox VPP PEDT in the frequency interval.

very low absorbance over 700 nm. The lack of absorbance above 700 nm shows that the density of the polaronic states, which in oxidized PEDT gives rise to a broad absorption above 600−700 nm, is low, which corresponds with the fact that the two VPP PEDT films are poor conductors. Reduced PEDT has an absorption peak at around 600 nm corresponding to excitation of electrons across the band gap of the delocalized, semiconducting states. Neither VPP P-EDT nor post-ox VPP P-EDT shows appreciable absorbance in this region.

FTIR. The FTIR spectra of VPP PEDT on PTSa and post-ox VPP PEDT show only minor differences and are compared to the spectra of the EDT monomer on Figure 7. The peak at 3116 cm^{-1} is due to the 2,5-hydrogen atoms on the thiophene ring and is seen both in the EDT monomer and VPP PEDT and (to some extent) in the post-ox VPP PEDT. The peak at 1715 cm^{-1} is due to a carbonyl group (C═O), and the broad peak around 3400 cm^{-1} is due to −OH groups—neither of these are found in the EDT monomer. Reaction 3 does not account for the appearance of these peeks in VPP PEDT and post-Ox VPP PEDT. This indicates that reaction 3 is not the only reaction in play! The carbonyl and the hydroxy groups can only originate from the oxygen in the monomer's dioxane ring. This shows that part of the monomers has undergone a reaction in the dioxane ring, presumably starting with an ether cleavage during the polymerization reaction.

The FTIR spectra in the interval from 800 to 1700 $cm^{-1}$of post-ox VPP PEDT show some similarity to both BI VPP PEDT and what is described for PEDT in the literature.[16] However, especially the peaks at 1542 and 1438 cm^{-1} (C═C region) are different from what was earlier reported.

If the acid-initiated polymerization follows reaction 3, the spectra of post-ox VPP PEDT and BI VPP PEDT should be identical, which they apparently are not! The peak at 1575 cm^{-1} is due the conjugated C═C system and is seen clearly in BI VPP PEDT but not in post-ox VPP P-EDT. Again, this is consistent with the poor conductivity of post-ox VPP PEDT.

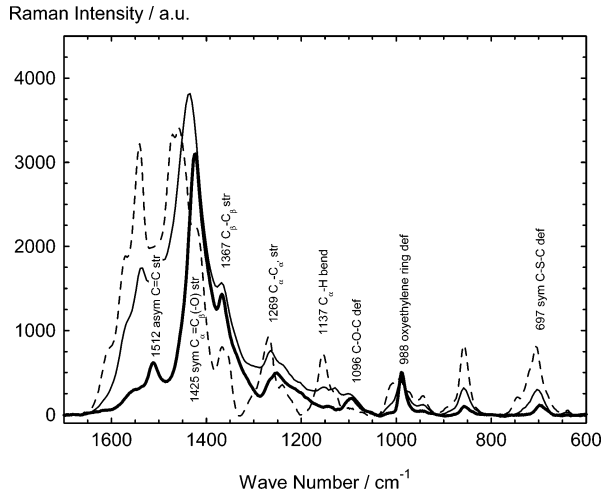


Figure 8. Raman spectra of BI VPP PEDT (thick solid line) compared with VPP PEDT deposited on a PET foil with Fe(III) tosylate, washed in ethanol (broken line), and post-Ox VPP PEDT (thin full line).

Raman Spectroscopy. Data from Raman spectroscopy (excitation wavelength 676 nm) are shown in Figure 8. The spectra of BI VPP PEDT correspond very well with what is reported in the literature[15] for electrochemically oxidized PEDT at positive potentials in the 300−500 mV range. Peaks from pyridine are not seen. Raman spectra of VPP PEDT on Fe(III) tosylate and VPP PEDT on PTSa (not shown) are nearly identical.

At 1137 cm^{-1} the band from $C_\alpha-H$ bend found in the EDT monomer is also present in VPP PEDT. Another peak in the C−H region at 1155 cm^{-1} (neither present in the EDT monomer nor in PEDT) appears. These two peaks are also found in the post-ox VPP PEDT but with lower intensity. The hydrogen ($C_\alpha-H$) on the thiophene ring is not (totally) removed, which shows that vapor-phase polymerization followed by chemical oxidation does not lead to the formation of a highly conjugated system.

In the C═C stretching region the peaks in post-Ox VPP P-EDT are quite similar to BI VPP PEDT—just shifted to higher wavenumbers. In this part of the spectra post-ox VPP PEDT shows all the bands one would expect from a conjugated polymer, which indicates that at least some parts of the polymer are formed according to reaction 3.

Cyclic Voltammetry. Cyclic voltammetry (CV) is a sensitive method to characterize the redox states and thereby the electronic properties of conjugated polymers. The voltammetry current is proportional to the number of sites that can be reduced or oxidized at a given potential, and this quantity is dependent not only on the chemical composition of the polymer but also on structural factors such as conjugation length and local order. CV's can thus be used as a kind of fingerprint to identify a given polymer type. On Figure 9 cyclic voltammograms of BI VPP PEDT and post-Ox VPP PEDT on pTSa are compared. The CV's are recorded at a sweep rate of 100 mV/s with the polymers deposited on Pt-coated PET immersed in a nonaqueous electrolyte (0.1 M tetrabuthylammonium hexafluorophosphate in acetonitrile). It is seen that the electrochemical response of the two polymers are vastly different. BI VPP PEDT shows the larger response, with a shape that is identical to what has previously been reported for electropolymerized PEDT.[15] The post-Ox VPP PEDT electrode, on the other hand, shows a much smaller, nonspecific response indicating that this material has very few conjugated double bonds that can be oxidized or reduced in this potential interval. This is not a kinetic effect as the same difference is also seen at much lower sweep rates and is consistent with the low conductivity of this polymer compared to BI VPP PEDT.

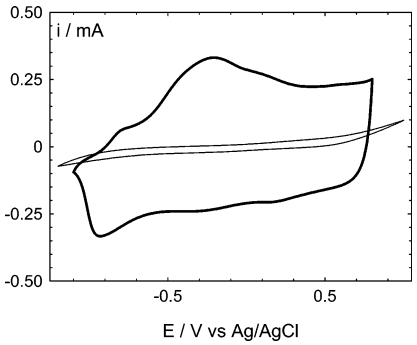


Figure 9. Cyclic voltammograms of Pt-coated PET foils with BI VPP PEDT (thick solid line) compared to post-Ox VPP PEDT (thin line). Electrolyte = 0.1 M tetrabuthylammonium hexafluorophosphate in acetonitrile; scan rate = 100 mV/s.

Alternative to chemical oxidation by Fe(III) VPP PEDT on pTSa can also be oxidized electrochemically under CV conditions. In the first cycles an irreversible oxidation bends the curve upward at potentials higher than 0.2 V, but after a few cycles, the curve becomes identical to the curve for post-Ox VPP PEDT in Figure 9. The electrode changes color from green to black during the oxidation process.

In summary, the different analyses of the product of acid-initiated polymerization of EDT give contradicting results. It is likely that reaction 3 describes the main reaction route, but it is not the only reaction involved. The conjugation is broken by thiophene rings with saturated bonds, and the dioxyethylene ring occasionally undergoes a cleaving reaction. As a result, this reaction does not lead to PEDT in the wanted highly conjugated form essential for obtaining a good conductivity.

Conclusion

A side reaction for the polymerization of EDT under acidic condition has been identified. A possible reaction scheme is given as the first part of reaction 3, but several indications in the analysis above suggests that the reaction is more complex. Most important is the fact that the reaction product of the acid-initiated polymerization cannot be oxidized to highly conjugated PEDT. Furthermore, it seems that the dioxane ring in the EDT monomer is unstable at very low pH (pH < 1/2).

A route to prevent the side reaction has been demonstrated, simply by raising the pH during the VPP with, e.g., pyridine. The polymer films obtained with base-inhibited VPP show very high conductivity, exceeding 1000 S/cm.

Direct chemical polymerization of PEDT film from EDT and an Fe(III) containing oxidant has been widely used. The films are typically cast from a solution with an organic solvent. The presence of Fe(III) normally results in a very acidic solution (a 40% Fe(III) tosylate solution has a pH less than −1). When the solvent evaporates, the acid concentration goes up and the environment becomes more favorable for the described side reaction. The fact that the side product cannot be

oxidized/reacted to PEDT with Fe(III) then leads to films with "non-PEDT" impurities. It also means that the polymerization conditions (concentration, solvent, temperature, etc.) have an unexpected high influence on the quality of the polymerized films, because these conditions influence the acidity during the polymerization.

Very different values for the conductivity of PEDT are reported in the literature. One might wonder if this may be due to uncontrolled side reaction caused by too acidic conditions as it is reported here for vapor-phase polymerization of EDT.

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