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Why is pristine PEDOT oxidized to 33%? A density functional theory study of oxidative polymerization mechanism

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Abstract

Currently, theoretical understanding of thermodynamics and kinetics of oxidative polymerization of poly(3,4-ethylenedioxythiophene) (best known as PEDOT) is missing. In the present study step-by-step density functional theory calculations of the radical polymerization of PEDOT with tosylate counterions (PEDOT:TOS) using $\text{Fe}^{3+}(\text{TOS}^-)_3$ as oxidant and dopant are performed. We calculate the Gibbs free energy for the conventional mechanism that consists of polymerization of neutral PEDOT oligomers first, followed by their oxidation (doping). We also propose an alternative mechanism of polymerization in which already oxidized oligomers are used as reactants, leading to doped (oxidized) oligomers as products during polymerization. Our calculations indicate that the alternative mechanism is more efficient for longer PEDOT oligomers (chain length $N > 6$). We find that the oxidation of EDOT monomer is the rate-limiting step for both mechanisms. Another focus of our study is understanding of the maximum oxidation level that can be achieved during polymerization. Our calculations provide a theoretical explanation of “the magic number” of 33% for the oxidation level typically reported for the pristine (i.e. as polymerized) materials and relate it to the change of the character of the bonds in the oligomers (aromatic to quinoid) that occurs at this oxidation level.

Keywords: PEDOT, oxidative polymerization, oxidation level, density functional theory

1. Introduction

Poly(3,4-ethylenedioxythiophene) (best known as PEDOT) is the one of the most important conducting polymer due to its superior features such as high electronic and ionic conductivities, versatile optical properties, as well as stability against oxidants and air-humidity¹⁻⁵. (For recent reviews on PEDOT see e.g. Refs. ⁶⁻⁸) Owing to these properties, PEDOT has been utilized for a number of applications such as photovoltaic cells⁹⁻¹⁰, supercapacitors¹¹, organic electronic ion pumps¹², light-emitting diodes and electrochromic displays¹³, field effect transistor¹⁴⁻¹⁵ and many others. Moreover, simple and well-established synthesis methods¹⁶⁻²¹ make PEDOT attractive material not only for academic research but also for industrial applications.

In contrast to most other conjugated polymers, a pristine (i.e. as polymerized) PEDOT is heavily oxidized (p-doped). The positive charge of p-doped PEDOT are compensated by negative counterions. One of the most popular counterions is a polyanion of polystyrene sulfonate (PSS), where sulfonyl groups are deprotonated and thus negatively charged. Also, PEDOT with molecular counterions, in particular, p-toluenesulfonate, (also called tosylate, TOS), has gained lots of interests because of its (PEDOT:TOS) high conductivity and semi-metallic behavior²²⁻²⁴. Oxidative polymerization of PEDOT with TOS counterions (PEDOT:TOS) using $\text{Fe}^{3+}(\text{TOS}^-)_3$ as oxidant and dopant is a well-established method^{1, 25-27}, known to proceed via a step-by-step mechanism. In the oxidative polymerization, the first step is to oxidize 3,4-ethylenedioxythiophene (EDOT) monomers to radical cations followed by a coupling process between two radical cations of EDOT, and subsequently

radical cations of EDOT and radical cations of PEDOT oligomers. Although many efforts have been devoted to optimization of synthesis conditions^{5, 17, 26, 28}, understanding optical properties and electronic structure²⁹⁻³⁴, and clarifying mechanism of conductivity³⁵⁻³⁷ of PEDOT, only a very few studies have so far focused on its polymerization mechanism. Kirchmeyer et al.²⁵ experimentally studied the reaction kinetics of in-situ oxidative polymerization of PEDOT:TOS. They revealed that first step, oxidation of the EDOT monomer to a radical cation, is the rate determining step, and oxidation of neutral oligomer to the radical cation is much faster than that of the EDOT monomer. A mechanism of HO⁺ induced polymerization of EDOT up to a dimer (i.e. EDOT₂) was studied by Coletta et al.³⁸ using a pulsed radiolysis combined with thermodynamic calculations and spectrokinetic analysis.

Currently, theoretical understanding of thermodynamics and kinetics of PEDOT:TOS oxidative polymerization is completely missing. This understanding is in the critical demand, because there are many aspects of PEDOT structure and morphology that are well established experimentally but remain unexplained theoretically. For example, it is generally accepted that PEDOT polymerizes into relatively short oligomers consisting of 10-20 monomer units.³³ The factors that limit the chain length are not understood, and, to our knowledge, has never been discussed in the literature. At the same time, this understanding is of the utmost importance because the chain length affects the polymer morphology,³³ which, in turn, influences the electron conductivity.³⁷ Another important property of PEDOT is its oxidation level. In most studies the oxidation level of pristine PEDOT is typically found to be 33%, i.e. one charge per three monomer unit.²⁵ Currently, the understanding of this “magic number” of 33% is not available. Apparently, understanding of the factors that determine and limit the oxidation level during polymerization is instrumental for design and improvement of charge storage material and devices such as supercapacitors and batteries with the enhanced performance.

Motivated by the need for theoretical understanding of the thermodynamics and kinetics of the oxidative polymerization, in the present study we perform step-by-step density functional theory calculations of the radical polymerization of PEDOT:TOS. To this end, we calculate the Gibbs free energy change during oxidative polymerization of a single PEDOT oligomer with Fe³⁺(TOS⁻)₃ as an oxidant. We investigate the conventional mechanism²⁵ that consists of polymerization of a neutral PEDOT oligomers followed by its oxidation (doping). We also suggest an alternative mechanism of polymerization in which highly oxidized oligomers are used as reactants, leading to already doped(oxidized) oligomers as products during polymerization. Our results indicate that the alternative mechanism can be dominant for longer PEDOT oligomers (chain length N>6). Another focus of our study is understanding of the maximum oxidation level that can be achieved during polymerization. Our calculations provide a theoretical explanation of “the magic number” of 33% for the oxidation level, and relate it to the alternation of the character of the bonds from the aromatic to quinoid that occurs at this oxidation level. We hope that the results of our computational study will lead to better understanding of this important material and will guide corresponding experimental synthesis efforts aiming at improvement of the material properties.

2. Computational Methods

The geometry optimization of molecules involved in the oxidative PEDOT polymerization by Fe³⁺(TOS⁻)₃ were carried out by using density function theory with ωb97xd³⁹ functional and 6-31G(d)⁴⁰ basis set as implemented in Gaussian 09 package. For the case of the singlet (S=0) spin multiplicity (M=2S+1=1) the restricted (close-shell) spin calculations were performed. For all other multiplicities M>1 the unrestricted (open-shell) spin calculations were performed (for further details see Ref.³⁴). The solvent effect of water was taken into account implicitly by using the polarizable continuum model (PCM) reference.⁴¹ The thermochemistry calculation for all optimized molecules were conducted at 373.15K in order to corroborate the condition of in-situ chemical polymerization, which is typically performed at this temperature.

In the calculations of the Gibbs energies all neutral PEDOT oligomers, oxidants Fe³⁺(TOS⁻)₃, Fe²⁺(TOS⁻)₂, and protonated tosylate (TOSH), were geometrically optimized separately. For calculations of the conventional polymerization mechanism (Sec. 3A) the charged species (EDOT^{•+}, PEDOT_N^{•+}, PEDOT_{N+1}²⁺-2H, PEDOT_{N+1}⁺-H) were optimized and calculated together with TOS⁻ or

2TOS⁻ counterions to account for the formation of the corresponding complexes (PEDOT_N^{•+} + TOS⁻, etc.) with bounded positive and negative species, see Figure S1 in Supplementary information. Accounting for counterions in the calculations is very expensive computationally. We therefore also performed calculations in which all the species were optimized separately, and found that the difference in energetics is relatively small, with the largest difference of ~15% being for the case of EDOT^{•+} + TOS⁻. That is the oxidation energy of EDOT monomer $\Delta G \approx 1.2$ eV for the case of optimization with counterions, and $\Delta G \approx 1.02$ eV for the case of a separate optimization. Hence, all calculations for the case of the alternative polymerization mechanism (Sec. 3B) are performed with separate geometrical optimization of all species.

3. Result and Discussion

A. Conventional Mechanism of the Oxidative Polymerization of PEDOT by Fe³⁺(TOS⁻)₃

The conventional mechanism of the synthesis of highly doped PEDOT:TOS by means of oxidative polymerization by Fe³⁺(TOS⁻)₃ is believed to consist of two consecutive processes.²⁵ First, an oxidative polymerization of neutral oligomers, PEDOT_N⁰, takes place (here N stands for the number of monomer units, and 0 indicates charge). Then, after the polymerization of neutral species is completed, the oligomers are oxidized to (typically) 33% oxidation level.

The oxidative polymerization to neutral oligomers, PEDOT_N⁰. The first process (the oxidative polymerization of neutral oligomers, PEDOT_N⁰), takes place via 3 repetitive steps: 1) oxidation of EDOT monomer and PEDOT_{N-1}⁰ oligomers, 2) coupling between EDOT⁺ and PEDOT_{N-1}⁺ radical cations, 3) deprotonation resulting in a neutral oligomer, PEDOT_N⁰.²⁵ These three steps are outlined in Scheme 1 and illustrated in the insets of Figure 1. Structure of all molecules involved in the reactions is visualized in Figure S1 in the Supplementary information.

Step 1. Oxidation

(a) Oxidation of EDOT

(b) oxidation of PEDOT

Step 2. Coupling of oxidized PEDOT and EDOT

Step 3. Deprotonation

(a) first deprotonation

(b) second deprotonation

Scheme 1: Conventional mechanism of oxidative polymerization of neutral PEDOT oligomers, PEDOT_N⁰ → PEDOT_{N+1}⁰ (chain length N ≥ 1).²⁵ A sign “•+” describes a radical cation. PEDOT_{N+1}²⁺ - 2H and PEDOT_{N+1}⁺ - H correspond to respectively doubly and singly protonated PEDOT. Parentheses (... + TOS⁻) indicate that TOS⁻ forms a complex with a corresponding positively charged

cation/oligomer as illustrated in the insets to Figure 1. $\text{Fe}^{2+}(\text{TOS}^-)_2$ in step 2 and 3 are presented in light grey to outline that they do not participate in the polymerization at these steps.

Note that in the experimental study of Kirchmeyer et al,²⁵ it was assumed that the oxidative polymerization of neutral oligomers takes place by coupling between radical cations of oligomers since oxidation of oligomers can be much faster than that of the monomer. To keep our calculations conceptually simple, in our study we assumed that polymerization of neutral oligomers, PEDOT_N^0 , occurs via a consecutive addition of EDOT radical cation to radical cation of oligomer such that the chain length during polymerization grows in increments of one monomer unit. Note that it is expected that EDOT monomers have much higher diffusivity than N-oligomers, and therefore EDOT radical cations are most likely to encounter its oligomer cation counterpart to continue polymerization reaction.

The Gibbs free energy change, ΔG , for each polymerization step is calculated as

$$\Delta G = \sum G(\text{products}) - \sum G(\text{reactants}), \quad \text{Eq. (1)}$$

where the products and reactants are those outlined in Scheme 1.

Let us first discuss the thermodynamics of the polymerization, focusing on the changes in the Gibbs energy of the system required to form neutral oligomers, PEDOT_N^0 . The Gibbs energy change for this process including all the reaction steps is shown in Figure 1a for the chain length from $N=1$ to $N=4$. The Gibbs energy change for the chain length from $N=1$ to $N=15$ (excluding intermediate steps) is shown as a grey curve in Figure 2a. The Gibbs energy of the system decreases as the polymer chain grows longer, signifying that the oxidative polymerization of neutral PEDOT oligomers is a spontaneous process which is thermodynamically favorable. This decrease is practically linear, with the difference of the Gibbs energy between N and $N+1$ oligomer being rather independent on the chain length, $\Delta G^{N \rightarrow N+1} \approx -0.49$ eV. This finding indicates that thermodynamically, there is no limitation on how long PEDOT oligomers can grow. In turn, this means that the limitation of the experimentally observed chain lengths (10-20 monomer units) is not related to the thermodynamics of the single PEDOT chain polymerization, but due to other factors such as diffusion and supply of the reactants and oxidants in a course of polymerization. Note that because of the computational limitations we did not consider polymerization of oligomers with the chains longer than $N=15$. We however expect that the calculated $\Delta G^{N \rightarrow N+1}$ would be the same even for $N \geq 15$ (i.e. chain length independent). Indeed, because of the covalent character of the bonds, the energetics of the polymerization is not affected by the monomers situated away from the polymerization site.

Let us now discuss the kinetics of polymerization, which is determined by the reaction barriers during reaction steps and the reaction barrier due to the transition states. Figure 1b, c shows a detailed energetics of the oxidative polymerization of neutral PEDOT oligomers for all polymerization steps (oxidation, coupling, and deprotonation), as well as the transition states for two representative cases of dimer ($N=2$) and tetramer ($N=4$) polymerization.

Figure 1b shows the energetics of polymerization from EDOT^0 to the dimer PEDOT_2^0 . The energetical barrier at the first step, which is the oxidation of two EDOTs to the EDOT^+ radical cations, is the largest energy surge during all three steps of polymerization ($\Delta G \approx 1.2$ eV for each EDOT^0 monomer). Subsequent coupling of two radical cations results in an intermediate product, a doubly oxidized protonated dimer, $\text{PEDOT}_2^{2+}-2\text{H}$, which is less favorable compared to the initial reactants.

In the deprotonation step, it was found that only one proton at a time is taken away by a TOS^- counterion. The energy barrier of the first deprotonation ($\Delta G \approx 0.21$ eV) is by a factor of about 4 higher than that of the second deprotonation ($\Delta G \approx 0.054$ eV). After the deprotonation step, an energetically favorable neutral PEDOT_2^0 is obtained, which is used as a reactant for further polymerization.

The polymerization reaction from a trimer to a tetramer (PEDOT_3^0 to PEDOT_4^0) is shown in Figure 1c. Its energetics exhibits a similar behavior as compared to the case of the dimer. As in the case of the dimer, the first polymerization step exhibits the highest energy barrier due to the oxidation of EDOT monomer, meaning that the oxidation of EDOT monomer is still the rate determining step even

for longer chains. The main difference is that the step 1(b), (i.e. oxidation of the oligomer), is energetically favorable ($\Delta G \approx 0.28$ eV) compared to that of EDOT ($\Delta G \approx 1.2$ eV), which can be related to a higher HOMO level of the oligomer in comparison to the monomer due to a longer π conjugation length. The oxidation step is followed by the coupling step, where two radical cations get bound together to form intermediate species, the doubly charged tetramer ($\text{PEDOT}_4^{2+} - 2\text{H}$). When it comes to the deprotonation of the oligomer that is longer than $N = 2$, the first deprotonation can take place either at the oligomer side or at the edge side. We calculated the change of the Gibbs energy for both cases, and we found that the first deprotonation from the edge side is more energetically preferable. (The energetics of the deprotonations starting from oligomer or the edge sides is discussed in Figure S2 in supporting information). It is noteworthy that the fact that the oxidation energy of EDOT^0 monomer was much higher than that of other steps, is in a good agreement with the experimental result.²⁵ Our calculations confirm the conclusion of the experimental studies that the oxidation of EDOT^0 is the rate determining step in the PEDOT polymerization.^{25, 38}

Oxidation of neutral oligomers. Let us now discuss the second process in the conventional oxidative polymerization mechanism, namely, the oxidation of neutral oligomers. The oxidation takes place via repetitive steps,

starting with the neutral oligomer $n=0$, where n denotes the number of positive charges in the chain (see an illustration in the inset in Figure 2a).

Figure 2a shows the change of the Gibbs energy for different oligomer lengths N for the case of the oxidation level $\text{ox}=33\%$ and 66% (i.e. one and two charges per three monomers respectively). For the oxidation level $\text{ox}=33\%$, the Gibbs energy of the oxidized oligomer is practically the same as for the neutral one. However, for the oxidation level $\text{ox}=66\%$, the Gibbs energy of the oxidized oligomer significantly exceeds the one for the neutral monomer. This trend is further specified in Figure 2b, which shows the energetics of the oxidation for representative N -oligomers ($N=6, 9, 12$). During successive oxidation steps, the Gibbs energy does not increase until the oxidation level reaches $\text{ox} \approx 33\%$. After that, the Gibbs energy starts rapidly increasing. These findings show that the oxidation of the polymers chains up to $\text{ox} \approx 33\%$ is energetically allowed process, but further oxidation is not energetically preferable.

The rapid increase of the energy needed for the polymer oxidation above 33% would be attributed to the effect of the charge carrier localization and corresponding changes in the bond length alternation and the lattice energy. Because of a one-dimensional character of the conjugated PEDOT backbone, the bond length l_B exhibits the alternation caused by the Peierls instability^{29-30, 34}. The double- and single bond alternation is illustrated in Figure 3a-f, where for the case of a neutral oligomer $l_B \approx 1.37\text{\AA}$ for the double bonds and $l_B \approx 1.42\text{\AA}$ or $1.44\text{\AA}$ for the single bonds. This character of the bond alternation (corresponding to the neutral oligomer) is referred to as aromatic (grey lines in Figure 3a-f). When a charge is removed (or added) to the chain, the character of the bond alternation alters in the places where the charge is localized, with the single bonds transforming into double bonds and vice versa. The new character of the bond alternation is referred to as quinoid (red lines in Figure 3a-f). (Note that for some cases the difference between single- and double bond alternation vanishes, e.g. $Q=+1$, bonds 13-23). Typical localization length of one state in PEDOT is 3-4 monomer units.^{23, 34} Hence, for the oxidation levels $\text{ox} < 33\%$, there are always parts of the backbone that are in the aromatic configuration. This is illustrated in Figure 3 which shows the bond length alternation for a PEDOT chain $N=9$ for different oxidation levels. (The bond length alternations for the chains $N=6$ and $N=12$ are shown in Figure S3). When a new charge is added, the chain can easily change the bond alternation from aromatic to quinoid in the place where the charge becomes localized. However, as soon as the oxidation level $\text{ox} = 33\%$ is exceeded, the entire chain is already mostly in the quinoid state, and the calculations show that one needs additional energy to squeeze new charges into the chain, such that further oxidation becomes energetically unfavorable, see Figure 2b. This explains why the oxidation level of the pristine (i.e. as polymerized) PEDOT is typically 33% . It is noteworthy that all the above conclusions are equally applied to the alternative polymerization mechanism discussed in the next

section, because the calculated Gibbs energy profiles correspond to the products that are the same for both mechanisms. It is also important to stress that this conclusion also applies to the oxidation level of PEDOT:PSS, because the charge carriers localization length in PEDOT chains is primarily determined by the electron-lattice interaction (i.e. properties of the backbone), and is rather insensitive to the character of the counterions.

Note that in order to study the conjugation and aromaticity in polycyclic conjugated molecules and graphene nanoribbons, the resonant-theoretic models based on the Clar's theory have been used in the past⁴²⁻⁴³. In order to gain better insight into the bond alternation pattern obtained from the DFT approach^{29-30, 34}, it would be interesting to apply the above models to PEDOT where the challenge would be to include electron interaction and spin effects for the case of oxidized oligomers.

Finally, we note that the Gibbs energy of the oligomers within the range of $0 < \text{ox} < 33\%$ is not constant but varies as a charge is added to the chain. That is, ΔG can be both positive and negative between two consecutive charged states n and $n+1$. For example, for the chain length $N=9$, $\Delta G \sim -0.31\text{eV}$ between $n=0$ and $n=1$, and $\Delta G \sim 0.14\text{eV}$ between $n=1$ and $n=2$, see Figure 2b. We can relate this to the change of the electronic energy due to the change of the spin state in the chain when a new electron is added/removed, as well as to the change of the lattice energy due the change of the bond length alternation (A detailed analysis of the evolution of electronic structure of PEDOT as the oxidation level changes is reported in Ref. ³⁴).

B. Alternative polymerization mechanism where both reactants and products are doped oligomers

The conventional mechanism of polymerization described in the previous section presumes that polymerization of neutral oligomers takes place first. After this stage is completed, the neutral oligomers are oxidized to (typically) 33% oxidation level. However, in a real experimental situation there is a constant supply of oxidants $\text{Fe}^{3+}(\text{TOS}^-)_3$ as well as EDOTs. Hence, one can expect that the oxidation of neutral oligomers is possible from the very beginning, and the highly oxidized oligomers can be reactants in a subsequent oxidative polymerization process. Therefore, in this section we explore an alternative polymerization mechanism where already doped oligomers are both the reactants and products, in contrast to the conventional mechanism, where the reactants and products are neutral oligomers. The alternative polymerization mechanism is thus described by a following Scheme,

Step 1) Oxidation of EDOT

Step 2) Coupling of already oxidized PEDOT and oxidized EDOT.

Step 3) Deprotonation

(a) first deprotonation

(b) second deprotonation

Step 4) oxidation of $\text{PEDOT}_{N+1}^{(n-1)+}$

Scheme 2: Alternative mechanism of oxidative polymerization of PEDOT oligomers where both the reactants and the products are doped oligomers, $\text{PEDOT}_N^{n+} \rightarrow \text{PEDOT}_{N+1}^{n+}$. $\text{PEDOT}_{N+1}^{2+}-2\text{H}$ and $\text{PEDOT}_{N+1}^{+}-\text{H}$ correspond to respectively doubly and singly protonated PEDOT. Parentheses (... + TOS⁻) indicate that TOS⁻ forms a complex with a corresponding positively charged cation/oligomer. Note that in the alternative mechanism the oxidation step (4) is the same as in the conventional mechanism (described by Eq. (2) and illustrated in the inset to Figure 2).

Note that a ground state of a doubly charged PEDOT oligomers, PEDOT_N^{2+} , can be whether triplet or singlet. The former corresponds to a dication, whereas the later corresponds to a biradical, also called a “polaron pair”. (A detailed discussion and analysis of the electronic structure of PEDOT oligomers for different levels of doping is given in Ref. ³⁴). The grounds states of the reactants and the product in Scheme 1 and Scheme 2 (i.e. PEDOT_N^{n+} , where $n=0,1,2,3$; $\text{PEDOT}_N^{3+}-2\text{H}$, $\text{PEDOT}_N^{2+}-\text{H}$, $\text{PEDOT}_N^{2+}-2\text{H}$, $\text{PEDOT}_N^{+}-\text{H}$) are presented in Table S1 in the Supplementary information.

The Gibbs energy change for the alternative polymerization route and its comparison to the conventional one is shown in Figure 4 for one polymerization step $N \rightarrow N+1$ for two representative chain lengths, $N=6$ and $N=12$. For the case of the conventional mechanism we first polymerize neutral PEDOT_N^0 to PEDOT_{N+1}^0 , and then oxidize it to PEDOT_{N+1}^{2+} . For the alternative mechanism we first oxidize PEDOT_N^0 to PEDOT_N^{3+} and then polymerize it to PEDOT_{N+1}^{2+} . The calculations are done according to Eq. (1) where the products and reactants are those outlined in Scheme 1 and Scheme 2. For the sake of comparison, in both cases we consider the same initial and final states, namely the neutral PEDOT_N^0 and oxidized PEDOT_N^{2+} respectively. (Note that Scheme 2 considers already oxidized oligomer as the initial state. Thus, the energy diagrams for the alternative mechanism include an additional step with the oligomer oxidation, $\text{PEDOT}_N^0 \rightarrow \text{PEDOT}_N^{3+}$).

Regardless of the chain length, the rate-limiting step for both polymerization mechanisms is always the oxidation of EDOT during the first step, $\Delta G \approx 1.02$ eV, see Figure 4 (see a comment concerning calculations of ΔG in the last paragraph of Sec. 2, Computational Methods) For the short oligomer $N=6$, the change of the Gibbs energy required for the oxidation of PEDOT_6 to PEDOT_6^{3+} ($\Delta G \approx 0.53$ eV) in the alternative mechanism is higher than that of PEDOT_6 to PEDOT_6^{+} ($\Delta G \approx -0.27$ eV) for the conventional one. Therefore, highly doped short oligomer such as PEDOT_6^{3+} is less favourable reactant compared to PEDOT_6^{+} , and thus for short chains the polymerization likely proceeds via the conventional mechanism. In contrast, for the long oligomer, $N=12$, the change of the Gibbs energy required for the oxidation of PEDOT_{12} to PEDOT_{12}^{3+} ($\Delta G \approx -0.56$ eV) in the alternative mechanism is lower than that of PEDOT_{12} to PEDOT_{12}^{+} ($\Delta G \approx -0.32$ eV) in the conventional one, see Figure 4b, and therefore the alternative polymerization mechanism might be more preferable.

Note that kinetics of the polymerization depends not only on the reaction energetics (such as the height of the rate-determining steps), but also on a number of other factors, including availability of reactants (such as EDOTs) and oxidants ($\text{Fe}^{3+}(\text{TOS}^-)_3$), local concentration of oligomers, local supply of the energy, diffusion rates of the reactants and many other. Also, oxidized PEDOT oligomers are accumulated in time, which might favor the alternative mechanism. Because of this, the DFT calculations alone cannot provide a definite answer on which mechanism is more preferential, and more studies, e.g. based on the molecular dynamics approaches that can account for the above-mentioned factors are needed in order to fully clarify this question.

Conclusion

By using the density functional theory, each step of the oxidative polymerization of PEDOT:TOS using $\text{Fe}^{3+}(\text{TOS}^-)_3$ as the oxidant was corroborated in terms of both thermodynamics and kinetics by calculating the Gibbs free energies of the reactants and products. We first considered a conventional mechanism consisting of two successive processes, first the polymerization of neutral PEDOT oligomers, and then their oxidation (doping). In addition to the conventional mechanism, we suggested an alternative mechanism in which reactants are already highly oxidized oligomers, leading to doped (oxidized) oligomers as products, which become reactants for next polymerization steps. The

calculated reaction energetics indicates that for short chains ($N \lesssim 6$) the polymerization likely proceeds via the conventional mechanism, whereas for longer chains the alternative mechanism can be dominant. For the both mechanisms the rate-limiting step is the oxidation of EDOT monomer, which energy is always higher than the barriers in the subsequent deprotonation steps. This conclusion is in good agreement with the previous experimental results^{25, 38}.

It is known experimentally that PEDOT polymerizes into relatively short oligomers consisting of 10-20 monomer units.³³ Our calculations show that thermodynamically, there is no limitation on how long PEDOT oligomers can grow. This means that the limitation of the experimentally observed chain lengths is not related to the thermodynamics of the polymerization, but due to other factors such as e.g. diffusion and supply of the reactants and oxidants in a course of polymerization.

The oxidation level of pristine (i.e. as polymerized) PEDOT is typically 33%, i.e. one charge per three monomer unit.²⁵ Our calculations provide the theoretical understanding of the “magic number” of 33%: We demonstrate that during successive oxidation steps, the Gibbs energy does not increase until the oxidation level reaches $ox \approx 33\%$, and starts rapidly increasing after that. We relate this to the change of the character of the bond alternation from the aromatic to quinoid that occurs at this oxidation level for all bonds in the backbone, which makes further oxidation energetically unfavorable. Note that this conclusion is not limited for the case of PEDOT:TOS, but is valid for any counterions including the case of PEDOT:PSS.

We hope that the results of our computational study, providing new theoretical insight into the polymerization that has not been available previously, would be instrumental for the experimental efforts towards further improvement and functionalizing of this important material.

Figure 1. The color bars are guide for eye and corresponds to the polymerization steps of Scheme 1 as outlined in the figure. (a) The Gibbs energy change for the oxidative polymerization of neutral oligomers, PEDOT_N⁰ for the chain length from N=1 to N=4 according to Scheme 1. (b)-(c) Detailed energy diagrams for polymerization (b) EDOT⁰ → PEDOT₂⁰, (c) PEDOT₃⁰ → PEDOT₄⁰. Insets show illustrations of products/reactants according to Scheme 1. Note that the position of TOS⁻ near PEDOT radical cation is schematic, and TS denotes transition state.

Figure 2. (a) The Gibbs energy change of the PEDOT oligomers as a function of the chain length N for different oxidation level of the product (Ox=0%, 33.3%, 66.6%). Inset illustrates the oxidation of an oligomer as described by Eq. (2). (b) The Gibbs energy change as a function of the number of the positive charges in a chain for different oligomer lengths, $N=6, 9, 12$. The oxidation levels ox=33.3% and 66.6% are marked in the figures

N=9

Figure 3. Red lines: Bond length alternation in the backbone of PEDOT chain of the length $N=9$ for the different number of charges in the chains $n = 1-6$ (as indicated in (a)-(f) respectively). Grey lines correspond to the undoped oligomer. Oxidation levels $ox=33.3\%$ and 66.6% correspond to $n=3$ and 6 respectively.

Figure 4. Comparison of the reaction energy profiles for polymerization of (a) PEDOT_6 and (b) PEDOT_{12} via conventional (blue) and alternative (orange) mechanisms.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX.
Content:

- Figure S1. Structure of molecules for geometry optimization.
- FigureS2. Comparison the effect of the order of deprotonation on the reaction energy in the conventional mechanism.
- Figure S3. C-C bond length alternation for PEDOT oligomers N=6 and N=12 for different oxidation levels.
- Table S1. Charge and Spin multiplicity ($M=2S+1$) of PEDOT oligomers of different lengths and oxidation levels in the ground state.

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Table of Content

Supplementary Information

Why is pristine PEDOT oxidized to 33%? A density functional theory study of oxidative polymerization mechanism

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EDOT

PEDOT₂

PEDOT₃

PEDOT₄

TOS⁻

TOSH

EDOT⁺:TOS⁻

PEDOT₂²⁺ : TOS⁻

PEDOT₃³⁺ : TOS⁻

PEDOT₂²⁺ - 2H : 2TOS⁻

PEDOT₃²⁺ - 2H : 2TOS⁻

PEDOT₄²⁺ - 2H : 2TOS⁻

PEDOT₂²⁺ - H : TOS⁻

PEDOT₃³⁺ - H : TOS⁻

PEDOT₄⁴⁺ - H : TOS⁻

Fe³⁺(TOS⁻)₃

Fe²⁺(TOS⁻)₂

Figure S1. Structure of molecules for geometry optimization. The color code of atom types is as follows: C (grey), O (red), S (yellow), H (light grey; small spheres), Fe(purple).

Figure S2. Comparison the effect of the order of deprotonation on the reaction energy in the conventional mechanism for a) PEDOT₃²⁺-2H and b) PEDOT₄²⁺-2H

Figure S3. C-C bond length for PEDOT_6^{n+} and PEDOT_{12}^{n+} (red line) for different number of positive charges in the chain, n (indicated in the figures). Grey lines indicate the bond length for corresponding neutral oligomers PEDOT_6^0 and PEDOT_{12}^0 .

molecule	Charge	Spin Multiplicity	molecule	Charge	Spin Multiplicity
EDOT	0	Singlet	PEDOT ₁₂	0	Singlet
EDOT ⁺	1	Doublet	PEDOT ₁₂ ⁺	1	Doublet
PEDOT ₆	0	Singlet	PEDOT ₁₂ ³⁺	3	Doublet
PEDOT ₆ ⁺	1	Doublet	PEDOT ₁₃ ²⁺ - 2H	2	Singlet
PEDOT ₆ ²⁺	2	Singlet	PEDOT ₁₃ ⁴⁺ - 2H	4	Singlet
PEDOT ₆ ³⁺	3	Doublet	PEDOT ₁₃ ⁺ - H	1	Singlet
PEDOT ₇ ²⁺ - 2H	2	Singlet	PEDOT ₁₃ ³⁺ - H	3	Singlet
PEDOT ₇ ⁴⁺ - 2H	4	Singlet	PEDOT ₁₃	0	Singlet
PEDOT ₇ ⁺ - H	1	Singlet	PEDOT ₁₃ ²⁺	2	Triplet
PEDOT ₇ ³⁺ - H	3	Singlet			
PEDOT ₇	0	Singlet			
PEDOT ₇ ²⁺	2	Singlet			

Table S1. Charge and Spin multiplicity (M=2S+1) of PEDOT oligomers in the ground state.