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# Density functional theory study of the electrochemical oligomerization of thiophene: transition states for radical–radical and radical–neutral pathways

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## Abstract

Accurate density-functional-theory (DFT) calculations on oligothiophenes containing up to 6 units have been performed in order to understand the various possible mechanisms of growth. There are two possible mechanisms for this process which involve the coupling of cationic radicals with either another cationic radical or with a neutral oligomer. Most of the electronic properties of these oligomers are well understood, but there is very little known about the nature of the intermediates and the transition states leading to polymerization. The initial oxidation, forming stable intermediates, releasing protons and/or further oxidations are studied in terms of the energetics, changes in the geometry, charge distributions and possible signatures in the vibrational spectra. The radical–radical pathway is found to be the more probable one between two mechanisms. Also the attack of monomers/or shorter oligomers on the longer ones is found to be faster than the coupling of equal size chains.

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**Keywords:** DFT; Oligothiophene; Mechanism

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## 1. Introduction

Electrically conducting organic polymers consisting of chains with alternating single and double bonds (conjugated polymers) are very important materials because of their wide range of applications in batteries, biosensors, coating material for metals, photoresists, optical switches, LED devices, electrochromic and electroluminescent devices [1, 2]. Most of these polymers are insoluble or less soluble in common solvents and their characterization is difficult. Among these conducting polymers polypyrroles and polythiophenes have drawn more attention due to their very wide range application areas. Theoretical calculations of these materials helped to the understanding of their formation mechanisms and made the synthesis of the materials with desired properties possible. Conjugated polymers are easily

obtained upon oxidation of monomer electrochemically or chemically. During the oxidation, reactive radical cations are generated and polymerization proceeds by a successive coupling reactions between oligomers in their neutral and charged forms. Reaction mechanisms are mostly studied by quantum chemical methods of various sophistication; however, the majority of these calculations are focused on the thermodynamical stability of different reaction products as well as the effects of the geometrical parameters.

Historically polypyrrole is the first conjugated polymer studied theoretically in detail. During the last decade; however, oligo- and polythiophenes became the choice of backbone for developing processable conjugated polymers [3,4]. There are a number of different techniques developed for synthesizing highly regular oligomers. Various substitutions as well as alterations of the thiophene backbone also allowed water-soluble polymers. With these developments, applications of the *ab initio* and density-functional-theory (DFT) techniques resulted in a thorough analysis of the bonding and electronic properties of oligothiophenes. There

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are a large number of reports on the geometry of the ground and excited states, the rotational barriers even the branching probabilities. Still there are a number of unsolved problems left regarding the thermodynamics and kinetics of growth of these systems. One problem is the extent of the charge localization upon oxidation. The extent of the charge localization is found differently from *ab initio* and DFT calculations and so far there is no conclusive evidence as we lack the highly accurate calculations including the electron correlation in sufficiently large chains [5–9]. The other important problem is the determination of the actual mechanism of the growth differentiating various coupling schemes as there is very scant experimental information for this complex phenomenon.

Couplings of the cationic radicals generated by electrochemical oxidation result in the growth of oligomers. The various crosslinked structures observed experimentally support this type of mechanisms [10]. Radical polycondensation as the initial electropolymerization is shown to be the mechanism by MALDI-TOF-MS measurements [11]. Optical spectroscopy of various oligomers together with theoretical calculations [12–15] support the generally accepted possibilities for the coupling of ionic radicals.

Oxidative coupling of oligopyrroles has been studied by Lacroix and co-workers [16–18]. They have located the transition states using semi-empirical methods and calculated the energetics with more accurate DFT calculations. In  $\alpha$ – $\alpha$  coupling of monomers/oligomers, dimerization rates have been found to decrease with oligomer length. It is also suggested that in case of the formation of long oligopyrroles a coupling of dication and nonoxidized monomer is more likely to occur. We have also presented DFT results based on the thermodynamical stability of the products comparing the radical–radical and radical–neutral pathways and concluded that the commonly accepted radical–radical mechanism is at least thermodynamically more feasible [19].

In this report, we will present our results on the energetics of each step in the growth of oligothiophenes by comparing stability of products and locating the transition states leading to these products. All possible coupling schemes between charged and neutral species of monomers and short oligomers are included in this search.

## 2. Calculations

The calculations are carried out with the Gaussian98 and Gaussian03 packages [20]. The geometry of all structures involved are optimized fully within the DFT methodology and using the three-parameter hybrid-functional of Becke [21]. The basis set is chosen to be the 6–31G(d) as this is almost the standard choice of the basis set for these molecules. Any basis set without the d functions on S would not give the correct geometry and we have in similar

problems experienced no qualitative gain by employing larger basis sets.

We have generated oligomers up to 6 units. The calculations of larger neutral oligomers do not pose any computational problems but the transition states become extremely elusive. Generally, transition states are obtained by using the QST3 formalism where geometry of the reactants and products which connect the transition state must be given as well as an initial guess to the transition state itself. Frequency analysis are carried out to make sure that proper minima and first order saddle points are located. Once the frequencies are obtained, we have computed the vibrational spectra of intermediates.

Both planar and helical structures are searched for all neutral oligomers. Even though global minima are all helical, the energy differences are too small to affect for our conclusions (around 0.1 kcal/mol). Upon oxidation all structures become planar.

To identify all the species involved in these reaction mechanisms, we used the following nomenclature.  $nT$  represents the neutral or charged oligomer containing  $n$  thiophene units;  $nTh^{++}$  is the intermediate and  $nTh^{++*}$  is the transition state leading to this intermediate. To distinguish various coupling schemes, they may be appended by (mk) where  $n=m+k$  denoting a coupling between  $mT$  and  $kT$ .

## 3. Results

Mechanism of the anodic coupling should follow the well-known coupling mechanisms of aromatic compounds. At first, singly charged radical cation is formed by the oxidation of the monomer/oligomer. Then there are two competing pathways. The more commonly accepted mechanism involves the coupling of two radicals—again these radicals can consist of more than one unit—to form the dihydrodimer ( $nTh_h^{++}$ ). In this doubly charged intermediate a bond is formed between radicals while hydrogens at the binding sites are still attached to monomers. The loss of these two protons leads to the formation of a neutral dimer (or a longer oligomer). We will denote this mechanism as the radical–radical one (RR). Since longer oligomers in general can be more easily oxidized than the shorter ones, there are a large number of coupling possibilities. One of our purposes is also to generate probabilities of such couplings.

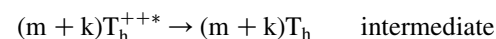
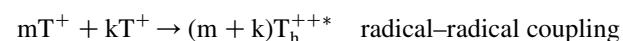
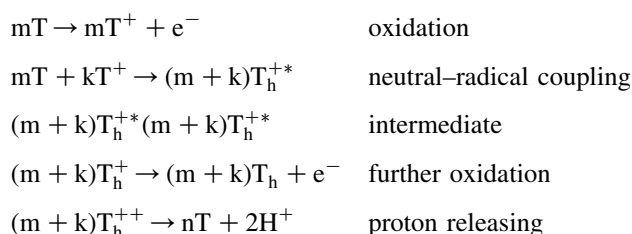


Table 1  
First and second ionization potentials (in kcal/mol) for nT

N	$nT \rightarrow nT^+$	$nT^+ \rightarrow nT^{++}$
1	196.0	
2	163.7	280.1
3	149.5	244.0
4	141.2	222.0
5	135.9	206.9
6	132.1	195.8

Another mechanism can be described as the radical–neutral attack (RN). Now, the radical can attach a neutral oligomer as a singly charged dihydrodimer which then is oxidized one more step to  $nTh^+$ . Then similar to the first mechanism, two protons are eliminated to result in the neutral dimer.



### 3.1. Oxidation

In Table 1, the first and second ionization potentials of oligomers are given.

The results presented here with DFT are different than those obtained from ab initio methods even though trends are the same [5–9]. The actual first ionization potentials are lower for SCF and higher for MP2 and CI. The differences in these methods for the second ionization potentials are smaller. The optimized geometry from DFT and SCF+MP2 also differ qualitatively from each other. DFT calculations show that the charges are delocalized over the complete oligomer in an almost symmetrical manner while

SCF shows a strong localizations of the charge over up to 5–6 units. Adding correlation effects via Moller–Plesset type perturbative techniques or configuration interaction calculations do not change these characteristics of ab initio results. However, we have noted that the trends in the energy values do not change with the method of choice and we proceed with DFT as described before.

The details of the structural and electronic changes upon oxidation of oligomers are not given here; however, they can be summarized as follows:

- The radical cations become planar. Deviations from planarity of successive thiophene units as well as the dihedral angles of hydrogens with respect to rings are less than  $2^\circ$ ,
- Monomer–monomer bond lengths become shorter with each ionization,
- Charge is delocalized to mostly S atoms almost evenly,
- Spin density in singly charged radical cations is localized on  $\alpha$  carbons. As the oligomer grows, this localization is spreading out over different units.

### 3.2. Radical–radical coupling

The dihydrodimer intermediate formed in the radical–radical coupling of two pyrrol cations has been reported before by [18,19]. For thiophene, we have obtained a very similar structure where two monomers are parallel but not on the same plane due to the steric effects of the hydrogens (Fig. 1). The distance between two planes are approximately 1.0 Å and hydrogens make an angle of  $110^\circ$  with the planes of monomers. To form longer oligomers, different combinations of cations can be coupled. Up to 6T, there are nine possibilities and we are going to label them as (11), (21), (31),(22), (41), (51), (42) and (33). In each of these intermediates, combining oligomers are aligned parallel to each other with distances varying from 1.0–1.5 Å while

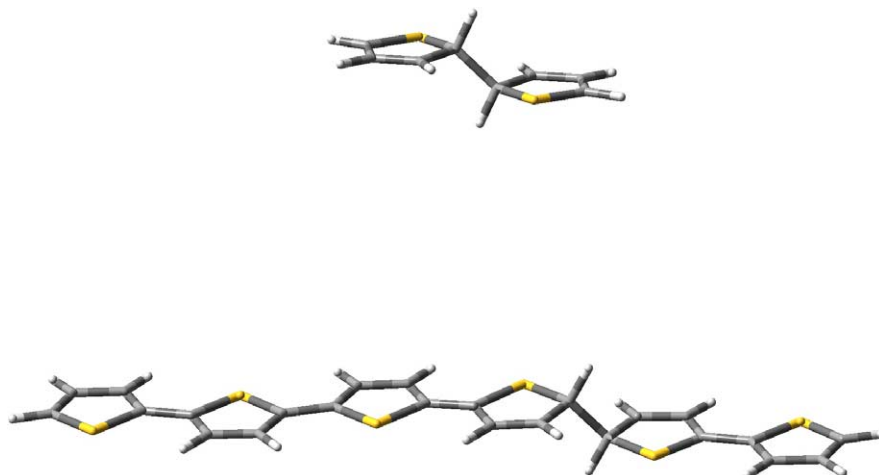


Fig. 1. Structures of the (11) and (42) intermediates.

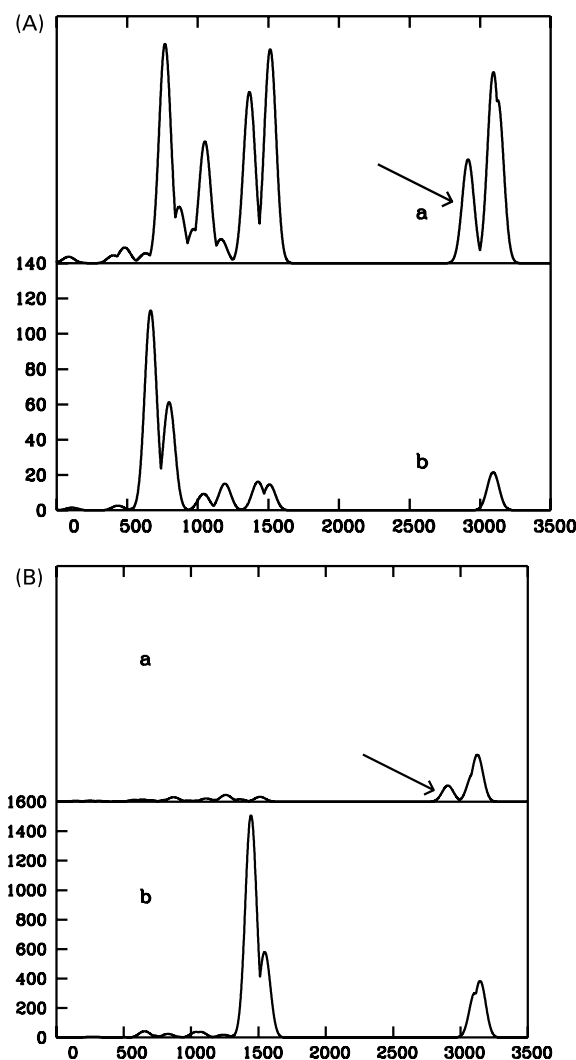


Fig. 2. (A) IR spectra of the intermediate formed in radical–radical coupling (a) and thiophene dimer (b). The arrow points out to the peak for asymmetric C–H stretching at the  $\alpha$  carbons. (B) Raman spectra of the intermediate formed in radical–radical coupling (a) and thiophene dimer (b). The arrow points out to the peak for symmetric C–H stretching at the  $\alpha$  carbons.

maintaining planar structures. An example for the (42) coupling is also given in Fig. 1.

Each of these structures is a true minimum in their

respective potential energy surfaces with all positive frequencies. The calculated IR spectra of these species are more complicated than corresponding neutral oligomers. The asymmetric stretching of two hydrogens attached to the coupling sites show strong absorption around  $2900\text{ cm}^{-1}$  (identification of peaks is done by using Gaussview). However, the vibrations involving the coupling of two oligomers are in low energy regime and they are either inactive or very weak. Raman spectra of the intermediate also shows an absorption around  $2900\text{ cm}^{-1}$  for C–H stretching (this time the symmetric coupling) in addition to the active low energy modes coupling two thiophene units. The dominant peak in the Raman spectrum of 2T belongs to the collective motion of rings described by Zerbi [22]. The calculated IR and Raman spectra are plotted in Fig. 2.

### 3.3. Structure of the transition state

The transition states (TS) corresponding to mechanism RR are searched by matching geometry of the reactants and the product intermediate states. The Hessian matrix in all cases have a single negative eigenvalue pointing out to a first order saddle and a true transition state. Transition states generally resemble reactants rather than the intermediates, that is  $\alpha$  hydrogens which are lost during the deprotonation are still in the molecular planes. The changes in the monomer–monomer distances upon oxidations and couplings are summarized in Table 2 for cations, intermediates and transition states.

As in the intermediates, in the transition states two coupling cations are in non-overlapping parallel positions. The monomer–monomer distances given in Table 2 show certain characteristics. In neutral oligomers they are shorter due to the conjugation of the monomers and as the oligomer is oxidized, these bond lengths shorten as expected. In the transition states, for small  $n$  bond lengths are rather large and only they are shortened around  $2.3\text{ \AA}$  for  $n > 4$  (for 5T we were not able to locate the transition state for the coupling (41) accurately). The abrupt change of the monomer–monomer distances in the transition states going from  $4\text{Th}^{++}$  to  $5\text{Th}^{++}$  can be explained by the total charges on each ring. In small oligomers, these charges

Table 2

C–C distances (Å) between adjacent rings. For global minima corresponding to neutral and ionic species, average distances are reported. For intermediates and transition states the distances correspond to the coupling sites of two oligomers

$n$	$n\text{T}$	$n\text{T}^+$	$n\text{T}^{++}$	Coupling	$n\text{T}_h^{++}$	$n\text{T}_h^{++*}$	$n\text{T}_h^+$
2	1.451	1.406	1.367	11	1.562	3.853	1.643
3	1.447	1.414	1.384	21	1.566	3.958	1.609
4	1.444	1.416	1.390	31	1.574	4.243	1.594
				22	1.561	3.748	1.600
5	1.444	1.421	1.398	41	1.589	–	1.586
				32	1.562	2.413	1.592
6	1.443	1.421	1.400	51	1.600	2.033	1.581
				42	1.564	2.292	1.588
				33	1.560	2.339	1.589

Table 3  
Total Mulliken charges on oligomers for the mechanism RR

Coupling	$T_h^{++}$		$T_h^{++}$	
	Long	Short	Long	Short
11	1.00	1.00	1.00	1.00
21	1.41	0.59	1.08	0.92
31	1.61	0.39	1.13	0.87
22	1.00	1.00	1.00	1.00
41			1.20	0.80
32	1.21	0.79	1.04	0.96
51	1.50	0.50	1.29	0.71
42	1.32	0.68	1.07	0.93
33	1.00	1.00	1.00	1.00

Table 4  
Charge and spin distribution (au) in the intermediate of the mechanism RN

Coupling	Charge		Spin	
	Long	Short	Long	Short
11	0.50	0.50	0.50	0.50
21	0.67	0.33	0.32	0.68
31	0.76	0.24	0.23	0.77
22	0.50	0.50	0.50	0.50
41	0.81	0.19	0.19	0.81
32	0.60	0.40	0.39	0.61
51	0.84	0.16	0.14	0.86
42	0.67	0.33	0.32	0.68
33	0.50	0.50	0.50	0.50

are very high as the total charge is distributed to fairly small number of rings and the Coulombic repulsion between units result in large separations. However, as the cations grow, the charges go below 0.35 on adjacent rings and consequently the radicals are closer in the transition state. In the intermediates the bond lengths are reduced to a C–C single bond range of 1.55–1.60 Å. In all cases considered here, the

results for 5T and 6T are very similar so we did not continue to larger cases.

In Table 3 we present the total charges on each oligomer. Short and long refer to the length of oligomers measured from the coupling site. When cations of different sizes are coupled, there is a strong charge transfer from the shorter oligomers to the longer on; however, if the charges on each ring is considered, then thiophene rings on the shorter oligomer are higher. As a general rule,  $\alpha$  carbons have charges of  $-0.1$ ,  $\beta$  carbons have  $0.1$ . The remaining charge is distributed almost equally to each S.

### 3.4. Radical–neutral coupling

In this mechanism, the radical cation attacks a neutral oligomer to form a singly charged intermediate state. Coupling occurs at the positions of highest spin density in the radical cation. Further oxidation of intermediate cation produces a dihydrodimer dication which leads to a dimer after loss of two protons and rearomatization as in the first mechanism.

Our extensive searches for the transition state leading to the intermediate did not produce any saddle point along the potential energy surface. Only likely structures correspond to large distances between the cation and the neutral species (around 4–5 Å) and they have lower energy than the reactants. Hence we conclude that this coupling does not proceed via a transition state. The structures of the

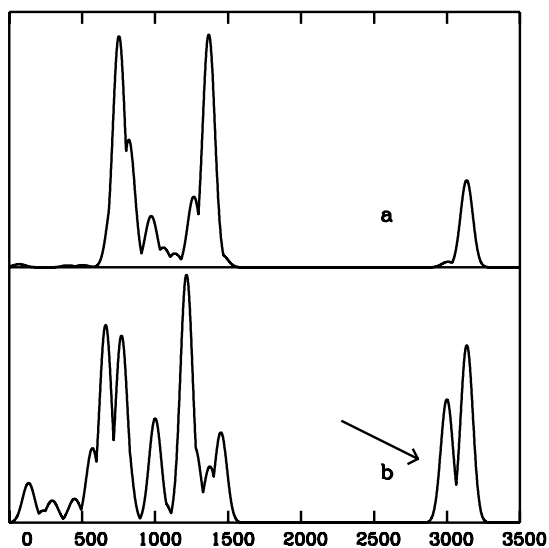


Fig. 3. (a) IR and (b) Raman spectra of  $2T_h^+$ . The arrow points out to the peak for symmetric C–H stretching at the  $\alpha$  carbons.

Table 5a

Energy of reactions for radical–radical coupling (kcal/mol)

mk	$mT \rightarrow mT^+$	$kT \rightarrow kT^+$	$mT^+ + kT^+ \rightarrow (m+k)T^{++}$	$(m+k)T^{++} \rightarrow (m+k)T^{++}$	$(m+k)T^{++} \rightarrow (m+k)T$
11	196.0	196.0	79.4	−50.0	324.5
21	163.7	196.0	54.0	−29.7	361.2
31	149.5	196.0	33.4	−14.7	380.9
22	163.7	163.7	53.4	−28.2	391.7
41	141.2	196.0	17.9	−3.9	393.8
32	149.5	163.7	46.2	−22.8	407.8
51	135.9	196.0	15.1	−5.5	403.5
42	141.2	163.7	39.7	−18.4	417.9
33	149.5	149.5	46.5	−22.7	421.4

intermediates show the same characteristics as those of the mechanism RR. Again cationic and the neutral oligomers are parallel but not on the same plane. The C–C distances at the coupling sites are around 1.6 Å and are relatively longer than the dihydrocation of the first mechanism.

In the IR spectrum, the C–H stretching at the coupling sites is shifted to  $3000\text{ cm}^{-1}$ ; however, it becomes extremely weak. Similar to the intermediate in RR, the Raman absorption of the C–H symmetric stretching at  $3000\text{ cm}^{-1}$  is very strong. Computed IR and Raman spectra are given in Fig. 3.

The charge and spin distribution of intermediates in the radical–neutral couplings are summarized in Table 4.

Again we note the strong charge transfer to the longer component in the intermediate and charges being localized on sulphur. Localization of spin shows different trends. For uneven couplings such as (21), (31), (41) and (51) radical centres are on the single monomer end of the intermediate and distributed evenly on the  $\alpha$  carbon and the opposite  $\beta$  carbon. The first of these positions lead to a linear growth while the other one forms structural defects such as kinks or branching. We have previously shown that up to 20% such structural defects can form in both polypyrroles and polythiophenes [23–25]. The radical centres on singly

oxidized oligomers are at  $\alpha$  carbons therefore it is highly likely that these defects occur from the singly charged radical cations intermediates.

### 3.5. Energetics of both mechanisms

In order to compare efficiencies of both mechanisms, we calculate the energy of reactions at each step.

In both process the most endothermic step is the loss of protons. Since this step occurs in both mechanisms, it does not affect our conclusions. The second most endothermic step is the ionizations and the secondary ionization of the singly charged intermediates is energetically the most demanding reaction. Formation of intermediates is an endothermic process in RR while that of RN is exothermic. The high energy required for further ionization of the RN intermediate shows that the reaction is most likely to proceed via RR mechanism. The comparison of various coupling schemes resulting in the same oligomer length clearly points out that the addition of a monomer to a longer oligomer is always preferred. This is in accordance with the experimental observations of Heinze [26] for  $\beta$ -substituted oligothiophenes and the theoretical conclusions of Lacroix [18] in polypyrrole.

Table 5b

Energy of reactions for radical–neutral coupling (kcal/mol)

mk	$mT \rightarrow mT^+$	$mT^+ + kT \rightarrow (m+k)T^+$	$(m+k)T^+ \rightarrow (m+k)T^{++}$
11	196.0	−17.3	242.7
12	196.0	−31.3	219.3
13	196.0	−37.9	206.1
14	196.0	−41.6	196.9
15	196.0	−44.0	189.5
21	163.7	1.0	219.3
22	163.7	−9.9	198.9
23	163.7	−14.8	187.6
24	163.7	−17.7	180.4
31	149.5	8.7	206.1
32	149.5	−0.6	187.6
33	149.5	−3.9	177.1
41	141.2	13.1	196.9
42	141.2	4.7	180.4
51	135.9	16.1	189.5



### 3.6. Solvent effects

All the calculations have been carried out in the gas phase and the solvent effects, in theory, could drastically change the conclusions. We have analyzed the effects of the solvent in a mean field philosophy. The polarizable continuum model of Tomasi and co-workers [27] is applied for processes in water. The numerical values differ from gas phase calculations to various extent; however, the qualitative conclusions remain the same (Tables 5a and b).

In a few test cases, the optimum structures of cations, intermediates and transition states in water are found to be very close to the gas phase structures so we have used the gas phase structures of all cases. The first ionization potentials are reduced by 25% and second IP by 45% almost uniformly. Similarly, the second ionization of the RN intermediate is reduced by 45%. The activation energies for RR pathway are also lower in water. The only increase (of the order of 100 kcal/mol) is observed for the loss of two protons; however, this step is present in both mechanisms and does not change the discussion. Overall, it is safe to conclude that even though the solvent effects indeed change the numerical results, the kinetic control of two pathways can be studied in the gas phase. A small set of calculation in acetonitrile produced very similar to those of in water.

## 4. Conclusion

Using highly accurate DFT calculations we compare RR and RN mechanisms for the growth of oligothiophenes. We show that the radical attack on neutral monomer does not go through a transition state. The rate determining step in the radical–neutral mechanism is the second ionization of the intermediate  $(nT)^+$ . RN coupling is less probable since it requires 180–260 kcal/mol for the further oxidation of  $(n+m)T^+$  depending on the size of the oligomer. For the RR couplings, the activation energies vary only from 15 to 80 kcal/mol and it is the preferred mechanism. The energetics of the couplings between various size oligomers shows that the fastest mechanism is the attack of monomers to longer oligomers. The most probable path is the attack of an oxidized monomer to an oxidized oligomer, forming a neutral oligomer by releasing two protons and a further oxidation of this new chain for further growth.

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## References

- [1] Skotheim TA, Elsenbaumer RL, Reynolds JR. Handbook of conducting polymers. New York: Marcel Dekker; 1998.
- [2] Nalwa HS, editor. Handbook of organic conductive molecules and polymers. Wiley; 1997.
- [3] Müllen K, Wegner G. Electronic materials: the oligomeric approach. Weinheim: Wiley-VCH; 1998.
- [4] Fichou D. Handbook of oligo- and polythiophenes. Weinheim: Wiley-VCH; 1999.
- [5] Ehrendorfer Ch, Karpfen A. J Phys Chem 1994;98:7492.
- [6] Moro G, Scalmani G, Cosentino U, Pitea D. Synth Met 2000;108:165.
- [7] Yurtsever E. Synth Met 1999;105:179.
- [8] Geskin VM, Bredas JL. Chem Phys Chem 2003;4:498.
- [9] Geskin VM, Dkhissi A, Bredas JL. Int J Quant Chem 2003;91:350.
- [10] Ohseido Y, Imae I, Shirota Y. J Polym Sci B Polym Phys 2003;41: 2471.
- [11] Estrany F, Oliver R, Garcia E, Gualba E, Cabot PL, Brillas E. Collect Czech Chem Commun 2003;68:1326.
- [12] Jiang XQ, Harima Y, Yamashita K, Naka A, Lee KK, Ishikawa M. J Mater Chem 2003;13:785.
- [13] Casado J, Miller LL, Mann R, Pappenfus TM, Higuchi H, Orti E, Milian B, Pou-Amerigo R, Hernandez V, Navarrete JTL. J Am Chem Soc 2002;124:12380.
- [14] Apperloo JJ, Groenendaal L, Verheyen H, Jayakannan M, Janssen RAJ, Dkhissi A, Beljonne D, Lazzaroni R, Bredas JL. Chem Eur J 2002;8:2384.
- [15] Hapiot P, Lagrost C, Aeiyaich S, Jouini M, Lacroix JC. J Phys Chem B 2002;106:3622.
- [16] Lacroix J-C, Valente R-J, Lacaze P-C. Chem Eur J 1998;4:1667.
- [17] Lacroix J-C, Maurel F, Lacaze P-C. Synth Met 1999;101:675.
- [18] Lacroix J-C, Maurel F, Lacaze P-C. J Am Chem Soc 2001;123:1989.
- [19] Yurtsever E. Synth Met 2001;119:227.
- [20] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery Jr., JA, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick, DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA. Gaussian 03, Revision B.05, Gaussian, Inc.: Pittsburgh PA; 2003.
- [21] Becke AD. J Chem Phys 1996;104:1040–6.
- [22] Zerbi G, Chierichetti B, Inganas O. J Chem Phys 1991;94:4637.
- [23] Yurtsever M, Yurtsever E. Synth Met 1999;98:221.
- [24] Yurtsever E, Esentürk O, Pamuk H, Yurtsever M. Synth Met 1999;98: 229.
- [25] Yurtsever M, Yurtsever E. J Phys Chem A 2000;104:362.
- [26] Smie A, Synowczyk A, Heinze J, Alle R, Tschuncky P, Götz G, Bauerle P. J Electroanal Chem 1998;452:87.
- [27] Miertus S, Scrocco E, Tomasi J. Chem Phys 1981;55:117.