J. Am. Chem. Soc. **2001,** *123,* 1989−1996

Oligomer−Oligomer versus Oligomer−Monomer C_2−C_2' Coupling Reactions in Polypyrrole Growth

Jean-Christophe Lacroix,* Francois Maurel, and Pierre-Camille Lacaze

Contribution from the Institut de Topologie et de Dynamique des Systèmes, Université de Paris 7-Denis Diderot, associé au CNRS (UPRES-A 7086), 1 rue Guy de la Brosse, 75005 Paris, France

Received July 14, 2000. Revised Manuscript Received November 7, 2000

Abstract: The C_2−C_2' coupling reactions of oligopyrrole radical-cations of increasing length generated by electrochemical oxidation have been modeled by transition state calculations. The modeling approach takes into account solvent effects and (i) shows that the coupling distance in the transition state decreases with oligomer length, (ii) demonstrates that dimerization rates in the gas phase decrease with oligomer length but increase in water, (iii) suggests that in a less solvating medium the dimerization rates could be equivalent, (iv) indicates that in all solvents quaterpyrrole and sexipyrrole formation is faster through a coupling reaction between oligomer and monomer radical-cations than two oligomer radical-cations, and (v) suggests that for the formation of a long oligopyrrole from oligopyrrole−pyrrole reactions the mechanism might involve the coupling of the oligopyrrole dication with a non-oxidized pyrrole unit instead of the coupling of two radical-cations or that of the oligopyrrole dication with a pyrrole radical-cation.

Introduction

Electropolymerization is one of the most valuable techniques for obtaining conductive polymers. The first step of the process is a one-electron electrooxidation of the monomer which leads to the formation of a very reactive radical-cation in the vicinity of the electrode. The polymer is generated through a succession of coupling reactions involving this radical-cation. Several electrochemical studies, focused on the dimerization step,[1−6] have led to the conclusion that it involves coupling between two radical-cations (RC/RC mechanism).[7] The subsequent coupling reactions which generate the polymer are little known and are generally considered to be similar to the dimerization step. When electropolymerization is performed with a dimer as the starting molecule (instead of a monomer) important structural differences are observed in the materials. Indeed, poly(bipyrrole), poly(bithiophene), and poly(parabiphenylene) have more structural defects than polypyrrole, polythiophene, and poly(paraphenylene).[8] This tendancy is even greater when a trimer is used as the starting aromatic molecule and in this case polymerization stops after a few coupling steps. These differences have been considered as indirect proof that conductive polymer growth involves mainly monomer−oligomer coupling reactions. This idea is compatible with the recent work of Barbarella et al.[9] concerning the oligomerization of 3-(alkylsulfanyl)thiophene but can be questioned since it has recently been demonstrated that terpyrrole, bipyrrole, and pyrrole radical-cations have similar lifetimes in acetonitrile[4,5] (the rate constants for their dimerization being 5×10^8, 1.2×10^9, and 1×10^9 $M^{-1}\ s^{-1}$, respectively, and are very close to the diffusion-limit rate constant) whereas tetrapyrrole has a much longer lifetime. Moreover, some electrochemical data have been interpreted as clear indications that the electropolymerization of donor-substituted thiophene is not a chain propagation process but a series of successive "dimerization" steps.[10a] Therefore, two alternative pathways can be considered for the synthesis of long polymer chains, i.e., monomer−oligomer or oligomer−oligomer reactions. It is generally accepted that the former is predominant but the latter cannot be excluded as contributors to the growth of conductive polymers and probably compete with monomer−oligomer reactions.[10]

Development of molecular modeling methods makes it possible to investigate alternative mechanisms involving very reactive species that can hardly be isolated. Theory can therefore potentially make a valuable contribution to the understanding of the factors which affect electropolymerization. There have been few quantum chemical studies.[11−17] Most of them were

---

* Address correspondence to this author. E-mail: lacroix@paris7.jussieu.fr.

(1) Andrieux, C. P.; Audebert, P.; Hapiot, P.; Savéant, J.-M. *J. Am. Chem. Soc.* **1990**, *112*, 2439.

(2) Audebert, P.; Hapiot, P. *Synth. Met.* **1995**, *75*, 95 and references therein;

(3) Yang, H.; Bard, A. J. *J. Electroanal. Chem.* **1992**, *339*, 423.

(4) Guyard, L.; Hapiot, P.; Neta, P. *J. Phys. Chem. B* **1997**, *101*, 5698.

(5) Andrieux, C. P.; Hapiot, P.; Audebert, P.; Guyard, L.; Nguyen Dinh An, M.; Groenendaal, L.; Meijer, E. W. *Chem. Mater.* **1997**, *9*, 723.

(6) (a) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Synth. Met.* **1993**, *61*, 81. Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 430. (b) Zotti, G.; Martina, S.; Wegner, G.; Schlüter, A.-D. *Adv. Mater.* **1992**, *4*, 798.

(7) (a) The alternative coupling mechanism involving the attack of a cation radical on a neutral substrate molecule (CR−S) has been suggested until very recently,[6b,c] but will not be considered in this study. (b) Wei, Y.; Chan, C.-C.; Tian, J.; Jang, G.-W.; Hsueh, K. F. *Chem. Mater.* **1991**, *3*, 888. (c) Qiu, Y. J.; Reynolds, J. R. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1315.

(8) *Handbook of Organic Conductive Molecules and Polymers*; Nalva, H. S., Ed.; John Wiley and Sons: New York, 1997; Vol. 2.

(9) Barbarella, G.; Zambianchi, M.; Di Toro, R.; Colonna, M.; Iarossi, D.; Goldoni, F.; Bongini A. *J. Org. Chem.* **1996**, *61*, 8285.

(10) (a) Smie, A.; Synowczyk, A.; Heinze, J.; Alle, R.; Tschuncky, P.; Götz, G.; Bäuerle, P. *J. Electroanal. Chem.* **1998**, *452*, 87. (b) Andrieux, C. P.; Audebert, P.; Hapiot, P.; Savéant, J.-M. *J. Phys. Chem.* **1991**, *95*, 10158. (c) Bäuerle, P.; Segelbacher, U.; Maier, A.; Mehring, M. *J. Am. Chem. Soc.* **1993**, *115*, 10217.

(11) Davis, T. P.; Rogers, S. C. *Eur. Polym. J.* **1993**, *29*, 1311.

(12) Lacroix, J.-C.; Garcia, P.; Audière, J. P.; Clement, R.; Kahn, O. *New J. Chem.* **1990**, *14*, 87.

(13) Lacroix, J.-C.; Mostefai, M.; Havard, G.; Pham, M. C.; Doucet, J. P.; Lacaze, P.-C. *New J. Chem.* **1995**, *19*, 979.

(14) Lacroix, J.-C.; Havard, G.; Aaron, J. J.; Taha-Bouamri, K.; Lacaze, P.-C. *Struct. Chem.* **1997**, *8*, 177.

10.1021/ja0025954 CCC: $20.00

based on the Frontier Orbital Model and have shed some light on the process. Indeed, prediction of the predominant structure of the polymers seems to be attainable within the framework of this simple model and the influence of several parameters, such as the doping level of the material, can be described. More sophisticated calculations have also been performed. The polymerizability of aniline derivatives was examined by using density functional calculations (DFT) and discussed in terms of the softness−hardness concept, the study being restricted however to the dimerization reaction.[16] Recently, we examined pyrrole polymerization[17] with the assumption that the growth process involves oligomer−monomer reactions. Quantum chemical calculations were used to describe the successive coupling reactions between pyrrole radical-cation and oligopyrrole radical-cation of increasing length, and the combined use of AM1 semiempirical calculations for transition states searches and B3LYP/6-31G* single point calculations for energy was shown to be a reasonably economical method, in terms of calculation time and accuracy.

In this paper, we have used the same modeling strategy to investigate the alternative growth pathway for polypyrrole, i.e., oligomer−oligomer reactions. We have therefore described the C_2-C_2' coupling of oligopyrroles of increasing length and compared the findings of these calculations with those of ref 17. Several aims underlie this work. The first objective is to understand what factors affect the relative dimerization rates of pyrrole, bipyrrole, and terpyrrole. Second, we require an understanding of what factors affect the competition between the oligomer−oligomer and the monomer−oligomer mechanisms. Can we predict what experimental conditions will favor one of these two possible mechanisms over the other? A third aim is to understand intermediate reactions involved in the growth of conductive polymers. These reactions are generally described as being analogous to the dimerization reaction, despite the fact that the electronic structure of oligomers of different length must evolve. Almost no experimental data are available concerning these intermediate reactions, though their understanding is crucial for the appreciation of effects that favor the synthesis of defect-free chains.

Modeling Strategy

The modeling strategy is based on transition state calculations. Owing to the size of the molecules to be handled a semiempirical method is required for TS searches. We have used, as in our previous study,[17] a combination of AM1 semiempirical calculations[18] for TS searches and B3LYP/6-31G*[19,20] single-point calculations for energy. The results of applying the semiempirical method AM1(UHF) to the C_2-C_2' coupling reactions between oligopyrroles give potential/energy coordinate curves of the same general form, there being an energy barrier corresponding to a well-defined transition state (the diagonalized force-constant matrix contains only one negative eigenvalue and animation of the vibration indicates that the transition states located connect the correct reactants and products, i.e., C_2-C_2' formation or bond breaking corresponding to the forward or the backward reactions for all coupling reactions under study, including those involving the longest oligomers). According to this procedure, absolute activation energies are not calculated accurately but one assumes that errors in the evaluation of the activation energies of two similar reactions are similar and that the calculated differences (relative activation energies) are significant. This must be kept in mind when analyzing results. Even though tremendous progress has been made, accurate computation of absolute activation energies remains a major challenge, needs excessive calculation times, and is beyond the scope of this work.

All semiempirical calculations were performed with the MOPAC 7 program.[21] Gaussian 94 was used for DFT calculations.[22] Unless stated otherwise, all calculations refer to the gas phase. Solvent effects were modeled by AMSOL V5.4 software[23,24] with the SM2 (water) and SM4 (alkane) solvation models on the basis of the optimized gas-phase geometry.[25] The SM2 and SM4 methods are based on atomic charges derived from the AM1 semiempirical Hamiltonian and calculate the solvation energies by using a cavity adapted to the shape of the solvated molecule. For a wide range of neutral and ionic molecules they yield solvation energies with an average error of only 1−2 $\text{kcal}\cdot\text{mol}^{-1}$. The use of these two methods makes it possible to analyze solvent effects in two extreme situations, i.e., solvation in water, in which radical-cations and charged TS are highly solvated, and alkane, in which radical-cations and charged TS are very poorly solvated. Of course, this last case is purely hypothetical since in such a solvent ion pairing, which has not been modeled, occurs and reduces electrostatic interactions. Nevertheless, reactivity results in alkane are interesting because they can be considered as a tool to investigate specific counterion effects. Extrapolation for an intermediate solvent (i.e. acetonitrile, DMF) is then used.

Results and Discussion

Gas-Phase Results. Gas-phase results will be presented first. They act as the starting point of the modeling approach to show trends within the two series of reactions, i.e., oligomer dimerization and oligomer−monomer reactions. These trends do not reproduce what really happens in the growth process since at this stage the calculations do not include solvent effects. The results are therefore distorted by overestimation of the electrostatic interactions between the reacting species. Nevertheless, these results are the starting point on which solvent effects will be added to reach a modeling level that allows direct comparison with experiment and makes it possible to separate electronic and solvent effects on the whole process. Table 1 shows the absolute energy barriers at the AM1 and B3LYP/6-31G*//AM1 level and the C_2-C_2' distance in transition states (AM1 results), for various oligomer−oligomer and oligomer−monomer reactions.

We will first focus on the differences in the absolute energy barriers of the various dimerization reactions.

Absolute energy barriers calculated at the AM1 and B3LYP/6-31G*//AM1 level for the C_2-C_2' dimerization reactions appear to fall as the oligomer length increases. It thus appears that pyrrole dimerization is much slower than terpyrrole dimerization in the gas phase through a RC/RC coupling mechanism.[26] A similar evolution was observed with oligomer−monomer reactions (Figure 1). This effect can be correlated with the evolution of the electrostatic repulsion between the two

---

(15) Smith, J. R.; Cox, P. A.; Campbell, S. A.; Ratcliffe, N. M. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2331.

(16) D'Aprano, G.; Proynov, E.; Lebeuf, M.; Leclerc, M.; Salahub, D. R. *J. Am. Chem. Soc*, **1996**, *118*, 9736.

(17) Lacroix, J.-C.; Valente, R. G.; Maurel, F.; Lacaze P.-C. *Chem.: Eur. J.* **1998,** *4*, 1667.

(18) Dewar, M. J. S.; Zoebisch, E. G.; Hearly, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc*. **1985**, *107*, 3902.

(19) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(20) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 786.

(21) Seiler, F. J.; Research Labortory, U.S. Air Force Academy, 1994.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision E.1

(23) Cramer, C. J.; Truhlar, D. G. *Science* **1992**, *256*, 213

(24) Hawkins, G. D.; Lynch, G. C.; Giesen, D. J.; Rossi, I.; Storer, J. W.; Liotard, D. A.; Cramer, C. J.; Truhlar, D. G. QCPE program 606, version 5.4.

(25) In doing so we assume that the TS can be considered as implastic species and that solvation has only a slight effect upon their geometries.[28,29]

Table 1. C_2-C_2' Distance in TS and Gas-Phase Activation Energy for Oligopyrrole C_2-C_2' Dimerization and Oligopyrrole/Pyrrole C_2-C_2' Coupling Reactions at AM1//AM1 and B3LYP/6-31G*//AM1 Levels

reaction type	C_2-C_2' coupling reactions	C_2-C_2'distance in TS (Å)	AM1//AM1 gas-phase energy barriers (kcal·mol^{-1})	B3LYP/6-31G*//AM1 gas-phase energy barriers (kcal·mol^{-1})
dimerization reactions	Pyr + Pyr	2.20	74.5	60.5
	Bipyr + Bipyr	2.05	59.1	48.8
	Terpyr + Terpyr	1.99	50.6	47.5
oligomer−monomer reactions	Pyr + Bipyr	2.14	59.7	46.6
	Pyr + Terpyr	2.09	44.1	35.0
	Pyr + Tetrapyr	2.01	31.6	25.9
		2.11	90.9	83.4
	Pyr + Pentapyr	1.97	22.3	15.2
		2.10	77.7	68.0
	Bipyr + Terpyr	2.03	51.5	46.3
	Bipyr + Tetrapyr	2.02	43.2	42.7

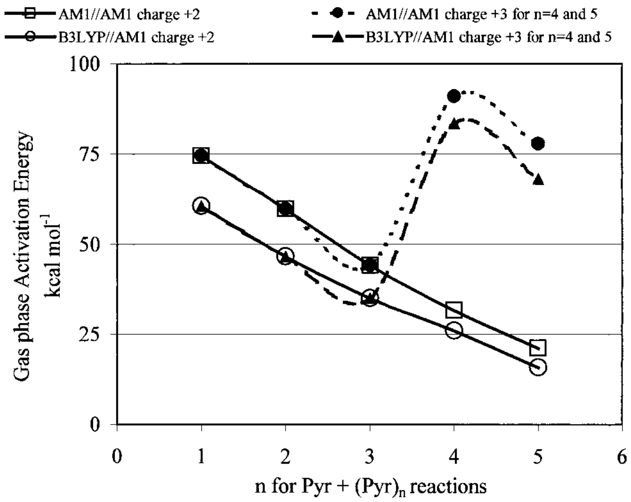

Figure 1. Gas-phase activation energy for C_2-C_2' coupling of pyrrole and oligopyrrole radical-cations.

reacting molecules. The charge is distributed over the whole oligomer chain, which implies that the net charge on each atom decreases and that the distance between the charge distribution barycenters on each interacting fragment increases when the oligomer length increases. This markedly reduces electrostatic interactions between the two molecules; consequently, the gas-phase energy barriers appear to fall. Note that in the oligomer−monomer series this effect is amplified by a strong partial charge transfer from the pyrrole radical-cation toward the oligopyrrole radical-cation (which explains why the decrease is steeper in this series than in the oligopyrrole dimerization series).[17] This calculated trend is in contradiction with the experimental results reported in acetonitrile, and clearly indicates that solvent effects will have, as expected, a marked impact upon the relative coupling rates of these reactions. In other words, it might not be quite correct to consider that the pyrrole radical-cation is inherently more reactive than oligopyrrole radical-cation in RC/RC dimerization, since the difference in solvent effects is the main reason pyrrole radical-cations dimerize faster than oligopyrrole radical-cations.

Some results must be discussed. First, it seems that the modeling strategy is not performing well for the calculation of the terpyrrole dimerization energy barrier at the B3LYP/6-31G*//AM1 level. Indeed, at the AM1 level a smooth decrease in the barriers is seen within the series, whereas the same trend is not observed in the single-point B3LYP/6-31G*//AM1 calculations, the terpyrrole dimerization energy barrier being only slightly smaller than that of bipyrrole. On the contrary, in the oligomer−monomer series a smooth variation of the absolute energy barriers with oligomer length is observed at both the AM1 and B3LYP/6-31G*//AM1 levels (Figure 1). This might indicate that the absolute energy barrier of terpyrrole dimerization calculated at the B3LYP/6-31G*//AM1 level is overestimated. Second, comparison of the two reactions that lead to quaterpyrrole, i.e., pyrrole + terpyrrole and bipyrrole + bipyrrole radical-cation couplings, indicates that the pyrrole + terpyrrole reaction is associated with a smaller gas phase absolute energy barrier than bipyrrole + bipyrrole dimerization. In the former reaction the electrostatic repulsion term is probably smaller than in the latter because of partial charge transfer from pyrrole to terpyrrole[17] and a longer C_2-C_2' distance in the TS. The same trend is found for the terpyrrole + terpyrrole and bipyrrole + quaterpyrrole reactions that lead to sexipyrrole. In other words, gas-phase results indicate that monomer−oligomer reactions are inherently faster than oligomer−oligomer reactions (when comparing reactions with the same number of pyrrole units). Third, the oligopyrrole doping level has a marked impact upon the gas-phase activation energy of the coupling reactions. Indeed, when pentamerization or hexamerization is modeled with a +2 overall charge, the activation energies are relatively low whereas when a +3 charge is used, to mimic the high doping level for the oligopyrrole, the calculated activation energy rises considerably, as depicted in Figure 1b. Finally, correlation effects appear to be similar for the treated reactions or to slightly decrease with the oligomer length, since the AM1//AM1 and B3LYP//AM1 curves are almost parallel (see Figure 1) and come closer as the oligomer length increases.

Let us now focus on the differences in the transition state geometries of the different dimerization reactions. The AM1-calculated geometries for the TS of the C_2-C_2' coupling of the supermolecule formed by the two pyrrole, two bipyrrole, and two terpyrrole radical-cations are shown in Figure 2.

One of the interesting aspects of this study is that it allows a relatively precise description of the geometry of the transition states for these coupling reactions even though the calculated C_2-C_2' distance in each TS is probably underestimated, as judged by the TS localization at the CASSCF(2,2)/6-31G* level for pyrrole dimerization.[27] In all cases treated, the major interaction between the two radical-cations involves the π-orbitals. When two oligopyrrole radical-cations approach, the carbon $2p_z$ orbitals overlap significantly, and the two molecules come together with their planes roughly parallel. Consequently, these orbitals are brought approximately into a σ-type overlap. This

---

(26) In the gas phase, the attack of a radical-cation on a neutral substrate molecule (RC−S mechanism) is much faster than the RC−RC mechanism studied here.[17]

(27) CASSCF(2,2)/6-31G* level for pyrrole dimerization, unpublished results.

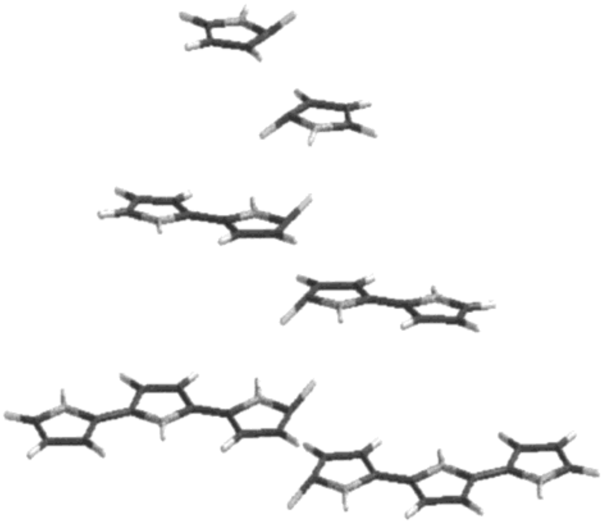

Figure 2. TS geometry for C_2-C_2' coupling of (a) two pyrrole radical-cations, (b) two bipyrrole radical-cations, and (c) two terpyrrole radical-cations.

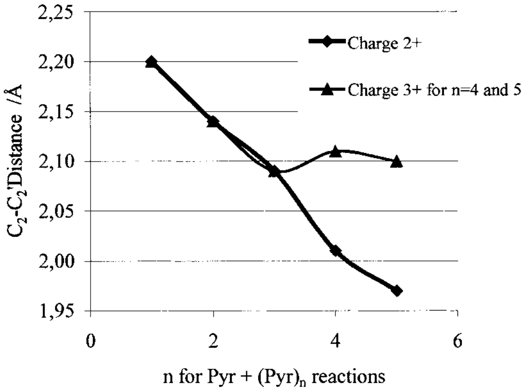

Figure 3. C_2-C_2' distance in TS for coupling of pyrrole and oligopyrrole radical-cations.

induces ring deformation, and the hydrogen atoms linked to the coupling carbons move out of the molecular planes, as shown in Figure 2. The intermediate dimer dication has tetrahedral carbons which are sp^3 hybridized and prevent conjugation between the rings. This sequence is confirmed by analyzing the variations in the interatomic distance and π-electron delocalization during the formation of quaterpyrrole starting either from two bipyrrole radical-cations or from pyrrole and terpyrrole radical-cations.[17]

More interesting is the evolution of the TS geometry with the length of the starting oligomer. The C_2-C_2' distance in the transition state is 2.20, 2.05, and 2.00 Å for pyrrole, bipyrrole, and terpyrrole dimerization, respectively, and is thus predicted to decrease as the starting oligomer length increases. The angle between the hydrogen atoms linked to the coupling carbons and the plane of the rings exhibits a similar trend, that is, it increases as the length of the oligomer increases (32.6°, 35.3°, and 36.8° for pyrrole, bipyrrole, and terpyrrole dimerization, respectively). It seems therefore that the pyrrole dimerization TS is sooner than the terpyrrole dimerization TS. The same trend is seen if one compares the C_2-C_2' distance of the reaction between the pyrrole radical-cation and oligopyrrole radical-cations of increasing length (Figure 3). Although higher level calculations (TS geometry optimization at the ab initio level) might be needed to confirm this geometry evolution, this trend is most probably significant and reflects a simultaneous decrease of the electrostatic repulsion and of the frontier orbital interactions (for the same C_2-C_2' distance) as the oligomer length increases.

This variation is at first sight surprising. Indeed, it is generally observed that as the absolute energy barrier increases, the transition state is reached later in the reaction,[28,29] i.e., for a reaction involving the formation of a chemical bond, the length of this bond in the transition state increases when the absolute energy barrier decreases. This is clearly not the case here since the pyrrole dimerization energy barrier is much higher than that of terpyrrole dimerization whereas the pyrrole dimerization TS is sooner than that of terpyrrole. The same trend is seen when one compares oligomer−monomer reactions with oligomers of increasing length.

In a simplistic description, the C_2-C_2' distance in the TS is such that electrostatic repulsion (ESR > 0) is balanced by a stabilizing frontier orbital interaction (FOI < 0) so that a further reduction of the C_2-C_2' distance makes the variation of the frontier orbital interaction term greater (it varies exponentially with the coupling distance) than the variation of the electrostatic repulsion (it is inversely proportional to the square of the coupling distance) and allows a decrease of the total energy of the system ($E \approx \mathrm{ESR} + \mathrm{FOI}$). In other words, the TS is reached when $|d(\mathrm{ESR})/dr| = |d(\mathrm{FOI})/dr|$ whereas if $|d(\mathrm{ESR})/dr| > |d(\mathrm{FOI})/dr|$ the system is located on the reactant side of the potential vs reaction coordinate curve.

Starting at the pyrrole + pyrrole radical-cation TS_1 located at a C_2-C_2' distance r_1 where $[|d(\mathrm{ESR})/dr|]r_1 = [|d(\mathrm{FOI})/dr|]r_1$, it can be qualitatively demonstrated that if the electrostatic repulsion decreases i.e., $\Delta(\mathrm{ESR}) < 0$ (because of an increase in the oligomer length inducing an increase in the distance between the charge barycenter of the two interacting oligomers), at a constant C_2-C_2' distance with no modification of the FOI, the system reaches a situation where $[|d(\mathrm{ESR})/dr|]r_1$ is smaller than $[|d(\mathrm{FOI})/dr|]r_1$ and thus is located on the product side of the potential vs reaction coordinate curve. A new TS (TS_2) will occur at a new distance $r_2 > r_1$ where $[|d(\mathrm{ESR})/dr|]r_2 = [|d(\mathrm{FOI})/dr|]r_2$. On the contrary, at constant C_2-C_2' distance and constant electrostatic repulsion, if the frontier orbital interaction decreases, i.e., $\Delta(\mathrm{FOI}) > 0$ (because of an increase in the oligomer length inducing a decrease of the coefficient in the C_2 atomic p_z orbital in the SOMO molecular orbital), the system reaches a point located on the reactant side and the new TS (TS_3) will occur later (that is for shorter C_2-C_2' distance). In other words, ESR and FOI decreases have the opposite effect on the coupling distance in the TS. Moreover, energy barriers to reach TS_2 or TS_3 will be smaller than that of TS_1 if $\Delta(\mathrm{ESR})_{TS1,TSn} < -\Delta(\mathrm{FOI})_{TS1,TSn}$. In this expression both terms are negative, indicating that the energy barrier of the coupling reaction will decrease if $|\Delta(\mathrm{ESR})_{TS1,TSn}| > |\Delta(\mathrm{FOI})_{TS1,TSn}|$ i.e., if the electrostatic repulsion decrease is higher than that of the frontier orbital interaction.

The predicted evolution of the C_2-C_2' distance in TS within the dimerization and the monomer−oligomer reaction series (later TS when oligomer length increases) reflects the simultaneous decrease of the ESR and the FOI terms but strongly suggests that the later counts for more in the geometry differences of the successive transition states than the former. On the other hand, the predicted evolution of the absolute energy barriers (smaller energy barrier when oligomer length increases)

---

[28] Hehre, W. J. *Practical Strategies for Electronic Structure Calculations*; Wavefunction Inc.: Irvine, 1995.

[29] Shaik, S. S.; Schlegel, H. B.; Wolfe, S. *Theoretical Aspects of Physical Organic Chemistry*: *The SN2 Mechanism*; Wiley: New York, 1992.

Table 2. Calculated Variations with Chain Length for Solvation Effect on Oligopyrrole Radical-Cations and Dimerization TS at AM1-SM4//AM1 and AM1-SM2//AM1 Levels

radical-cations	pyrrole	bipyrrole	terpyrrole	tetrapyrrole	pentapyrrole
(ΔG° solv)SM2[a]	−60.6	−49.4	−45.5	−44.4	−45.3
(ΔG° solv)SM4[a]	−29.9	−25.8	−26.4	−27.9	−30.3

C_2–C_2′ TS dimerization	pyrrole	bipyrrole	terpyrrole
(ΔG° solv)SM2[a]	−184.6	−141.2	−121.8
(ΔG° solv)SM4[a]	−94.3	−77.6	−71.9

[a] kcal·mol^{-1}.

indicates that $|\Delta(\mathrm{ESR})_{\mathrm{TS1,TSn}}| > |\Delta(\mathrm{FOI})_{\mathrm{TS1,TSn}}|$ and thus confirms that the ESR term has a greater bearing on the value of the gas-phase absolute energy barrier.

Solvent Effects. The results of the preceding section refer to the gas phase. The transition state energies calculated for the radical-cation/radical-cation mechanism are high because of the very high electrostatic repulsion that accompanies the approach of two +1 charged species in the gas phase (approaching two point charges at a distance of 4 Å requires as much as 83 kcal mol^{-1}). However, in the vicinity of the electrode a solvent is present, and this plays a very important role in decreasing these interactions.

AM1-SM2 and AM1-SM4 calculations of the energy on the basis of the gas-phase optimized geometry were first performed to investigate solvent effects in the two extreme cases, i.e., water and alkane. The ΔG°solv of the species under study are gathered in Table 2.

Variations of the calculated ΔG°solv with oligomer chain length indicate the following: First, in water, the oligopyrrole radical-cation/solvent interaction is mostly controlled by the electrostatic interaction, and ΔG°solv decreases smoothly when the oligomer length increased because the +1 charge is delocalized over a greater number of atoms. Solvation of the radical-cations in hexane is, as expected, smaller than that in water but one observes that after an initial decrease when the oligomer length increases, solvation increases for longer oligomers. Indeed, for a short oligomer, the solvation is mainly due to electrostatic interaction because the charge is delocalized over a small number of atoms and, as in water, this interaction decreases with oligomer length. On the other hand, the cavity-dispersion and the entropic terms increase on going from pyrrole radical-cation to terpyrrole radical-cation. Consequently, solvation of oligopyrrole radical-cation in hexane starts to decrease then increases as the oligomer length increase. A similar effect is observed in water but occurs for much longer oligopyrroles since the solute–solvent electrostatic interaction is much higher in this solvent.

Second, in all cases, the solvent stabilizes the 2+ charged transition states more than the reactants (two +1 charged oligopyrroles) which traduces the fact that the +2 charge is more concentrated in the transition states than in the reactants. Moreover, in the TS the +2 charge is pushed away from the coupling rings toward the extreme pyrrole units to minimize electrostatic repulsion (see Figure 4). In other words, approaching two +1 oligopyrrole induces an additional dipole moment on each oligopyrrole due to the polarizability of the π-electron structure. The appearance of this induced dipole moment gives an extra-stabilization in the TS–solvent interaction that is not present in the oligopyrrole–solvent interaction. As expected the different TS are less solvated in alkane than in water, and one observes a smoothly decreasing variations of ΔG°solv as the oligomer length increases in both solvents.

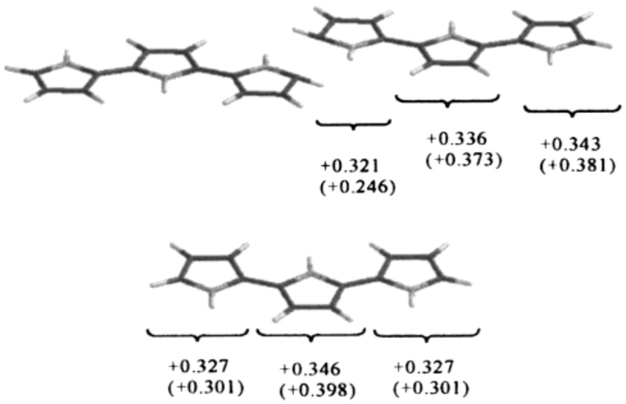

Figure 4. Mulliken and electrostatic fit (in bracket) charge analysis in the TS of terpyrrole radical-cation dimerization (top) and in the terpyrrole radical-cation (bottom).

Table 3. Calculated Variations with Chain Length for Oligopyrrole Dimerization: Approximate Gas-Phase Energy Barriers, Δ(ΔG°solv)SM2, Δ(ΔG°solv)SM4, and Approximate Energy Barriers in Water and Alkane, Using B3LYP/6-31G*//AM1 and AM1//AM1 (*in parentheses and italics*) Gas-Phase Results

dimerization	pyrrole	bipyrrole	terpyrrole
gas-phase energy barriers[a]	60.5 (*74.7*)	48.8 (*59.1*)	47.6 (*50.6*)
Δ(ΔG° solv)SM2[a]	−63.4	−42.4	−30.8
Δ(ΔG° solv)SM4[a]	−34.5	−26.1	−19.2
energy barriers in water[a]	−2.9 (*11.3*)	6.4 (*16.6*)	16.7 (*19.8*)
energy barriers in alkane[a]	26 (*40.3*)	22.7 (*32.9*)	28.3 (*31.4*)

[a] kcal·mol^{-1}.

Table 3 shows the gas-phase energy barriers, Δ(ΔG°solv), and the estimated energy barriers in solution for the dimerization reaction, obtained at the AM1-SM2 and AM1-SM4 levels and by combining the B3YP/6-31G*//AM1 gas-phase absolute energy barriers with the calculated Δ(ΔG°solv).

The dimerization of two radical-cations, which appeared very difficult in the gas phase, becomes perfectly feasible when solvent effects are included. They reduce dramatically the activation energy for the radical-cation/radical-cation reactions. Pyrrole dimerization in water might even be diffusion-controlled, since the solvent effect (Δ(ΔG°solv)) is greater than the gas-phase activation barrier. However, it has to be noticed that solvent effects on the dimerization reactions decrease sharply with the length of the oligomers that couple (for very long chains it is reasonable to expect that the electrostatic part of the solvation effect for the +2 charged TS will tend toward twice that of the +1 charged oligomer). Consequently, two opposite effects are demonstrated and balanced each other, i.e., a reduction of the gas-phase energy barriers and a reduction of the solvent effects as the oligomer length increases. The relative rates for pyrrole, bipyrrole, and terpyrrole dimerization will thus depend on the electrolytic medium. In water, solvation of the +2 charged TS is very important and pyrrole dimerization is predicted to be much faster than bipyrrole or terpyrrole dimerization. Solvation in water makes it therefore possible to reverse the calculated gas-phase trend (i.e., pyrrole dimerization slower than terpyrrole dimerization). On the contrary, solvation in alkane is not strong enough to reverse this trend. Indeed, in such a solvent, the lifetime of the bipyrrole radical-cation could be much shorter than that of the pyrrole radical-cation, whereas the terpyrrole radical cation could have a lifetime either longer than (B3LYP//AM1 +AM1-SM4) or similar to (AM1//AM1 +AM1-SM4) that of the bipyrrole radical-cation.[30] Furthermore,

---

(30) Remember that the terpyrrole dimerization gas-phase energy barrier might be overestimated at the B3LYP//AM1 level.

Table 4. Tetrapyrrole Formation through Oligomer−Monomer and Oligomer−Oligomer Reactions: Approximate Gas-Phase Energy Barriers, Δ(Δ*G*°solv)SM2, Δ(Δ*G*°solv)SM4, and Approximate Energy Barriers in Water and Alkane, Using B3LYP/6-31G*//AM1 and AM1//AM1 (*in parentheses and italics*) Gas-Phase Results

	gas-phase energy barriers (kcal·mol^{-1})	Δ(Δ*G*°solv)SM2 (kcal·mol^{-1})	Δ(Δ*G*°solv)SM4 (kcal·mol^{-1})	energy barriers in water (kcal·mol^{-1})	energy barriers in alkane (kcal·mol^{-1})
Pyr + Terpyr	35.0 (*44.1*)	−34.3	−21.2	0.65 (*9.8*)	13.8 (*22.9*)
Bipyr + Bipyr	48.8 (*59.1*)	−42.4	−26.1	6.4 (*16.6*)	22.7 (*33*)

Table 5. Sexipyrrole Formation through Oligomer−Monomer and Oligomer−Oligomer Reactions: Approximate Gas-Phase Energy Barriers, Δ(Δ*G*°solv)SM2, Δ(Δ*G*°solv)SM4, and Approximate Energy Barriers in Water and Alkane, Using B3LYP/6-31G*//AM1 and AM1//AM1 (*in parentheses and italics*) Gas-Phase Results

	gas-phase energy barriers (kcal·mol^{-1})	Δ(Δ*G*°solv)SM2 (kcal·mol^{-1})	Δ(Δ*G*°solv)SM4 (kcal·mol^{-1})	energy barriers in water (kcal·mol^{-1})	energy barriers in alkane (kcal·mol^{-1})
Terpyr RC + Terpyr RC	47.5 (*50.6*)	−30.8	−19.2	16.7 (*19.8*)	28.3 (31.4)
Bipyr RC + Tetrapyr RC	42.7 (*43.2*)	−28.1	−18.5	14.6 (*15.1*)	24.2 (25.1)
Pyr RC + Pentapyr RC	15.2 (*22.3*)	−15.6	−11.8	−0.4 (*6.5*)	3.4 (10.4)
Pyr + Pentapyr^{2+}	1.5 (*0.3*)	+ 12.7	+3.1	14.3 (*13.0*)	**4.6 (*3.4*)**
Pyr RC + Pentapyr^{2+}	68.0 (*77.7*)	−65.0	−38.0	**2.96 (*12.7*)**	30.0(39.7)

in this solvent the three radical-cations lifetimes (assuming that no other mechanism occurs[26]) will be much higher than in water. Of course, this last case is purely hypothetical since in such a solvent ion pairing, which has not been modeled, occurs and reduces electrostatic interactions. Even though accurate prediction of the absolute energy barriers requires higher level calculations, it can nevertheless be suggested that solvent effects have an important influence on the relative lifetime of the three radical-cations under study. Experimental lifetimes of such species measured in different electrolytic media but also in the same electrolytic medium cannot therefore be used as a measure of the intrinsic reactivity of the species. Solvent effects are strong enough in water to make oligopyrrole radical-cation dimerization slower as the oligomer chain length increases, while in apolar aprotic solvents additional reduction of the electrostatic interaction by counterion effects or ion pairing will be needed to reach a similar situation. Moreover, it can be suggested that there might be a solvent, somewhere between water and alkane, in which solvent and counterion effects might just be strong enough to make pyrrole, bipyrrole, and terpyrrole radical-cation lifetimes identical. (It has recently been shown experimentally that dimerization of pyrrole, bipyrrole, and terpyrrole proceeds at roughly the same rate in acetonitrile[4,5] even though the measured rate constants are very close to the diffusion-limit rate constant.)

The energy barrier of the two coupling reactions giving quaterpyrrole, i.e., pyrrole + terpyrrole and bipyrrole dimerization, are compared in Table 4. This allows a crude estimation of the competing alternative pathways for the synthesis of long polymer chains, i.e., monomer−oligomer or oligomer−oligomer reactions.

It can be seen that in water quaterpyrrole formation is predicted to occur with an energy barrier of 0.65 kcal·mol^{-1} when coupling of pyrrole and terpyrrole radical-cations occurs, whereas it is 6.4 kcal·mol^{-1} through bipyrrole radical-cation dimerization. Such a difference (which indicates that at ambient temperature 10^5 quaterpyrrole molecules will be generated through the former mechanism when one is generated by the latter, if one assumes similar local concentration for the three radical-cations) is most probably significant even though a higher level of calculations might be needed as confirmation. The reason for this lies mainly in the gas-phase energy barrier which is 14 kcal·mol^{-1} lower for tetramerization via the monomer/oligomer mechanism than for bipyrrole dimerization. Indeed, the electrostatic repulsion is lower in the former case because the +1 charge on the terpyrrole moiety is more delocalized than that on bipyrrole moieties and because the partial charge transfer occurring in the pyrrole/terpyrrole TS reduces electrostatic interaction between the two species. This effect is only partially compensated by solvent effects which increase with a higher charge localization: as a consequence, the two bipyrrole radical-cations are less solvated (−98.9 kcal·mol^{-1}) than one pyrrole radical-cation and one terpyrrole radical-cation (−106.1 kcal·mol^{-1}) whereas the two TS are similarly solvated (−141.2 and −140.4 kcal·mol^{-1}, respectively). Overall, solvent effects in water are higher for the reaction between two bipyrroles (−42.4 kcal·mol^{-1}) than between pyrrole and terpyrrole radical-cations (−34.3 kcal·mol^{-1}) but the difference in solvent effects (8.1 kcal·mol^{-1}) is not enough to fully compensate the gas-phase energy barrier difference (14 kcal·mol^{-1}) and to make bipyrrole/bipyrrole dimerization faster than pyrrole/terpyrrole coupling. The same trend is observed for the synthesis of sexipyrrole when one compares bipyrrole/quaterpyrrole coupling and terpyrrole dimerization (Table 5), with the former being the faster even though the difference between the two pathways decreases as expected (it seems reasonable to expect that formation of dodecapyrrole by coupling reactions between oligopyrroles 6+6 or 5+7 will be energetically equivalent). It can thus be concluded that, in water, polymer growth goes through the monomer/oligomer mechanism rather than the oligomer/oligomer mechanism (assuming similar local concentrations for the three radical-cations).

Results of the competition between the two mechanisms in alkane are similar. Indeed, in such a solvent it is again predicted that the monomer/oligomer mechanism is the faster. The Δ(Δ*G*°solv) for the two competing reactions is lower than that in water, the two TS which have roughly the same molecular size have similar ΔG°solv (−77.6 and −77.4 kcal·mol^{-1} for bipyr + bipyr and pyr + terpyr, respectively), and the pyrrole/terpyrrole initial state is only slightly more solvated (−55.3 kcal·mol^{-1}) than that of bipyrrole/bipyrrole (−51.6 kcal·mol^{-1}). Overall, the difference in solvent effects for the two competing reactions is smaller than that in water. As a result, in alkane monomer/oligomer reactions are again predicted to be the main polymer growth mechanism (assuming similar local concentrations for the three radical cations).

It thus appears that solvent effects are not capable of modulating the polymer growth mechanism even though the use of a protic, polar solvent will reduce the energy gap between the two mechanisms.

There is a third coupling pathway which yields sexipyrrole, that is pyrrole + pentapyrrole reaction. However, when dealing with such a coupling step one needs to take into account the

Table 6. Calculated Variations with Chain Length between S_1 = (pyr + oligopyr $^{2+}$) and S_2 = (pyr$^+$ + Oligopyr$^+$) Systems: Approximate Gas-Phase Energy Difference, $\Delta(\Delta G°\text{solv})$SM2, $\Delta(\Delta G°\text{solv})$SM4, and Approximate Energy Difference in Water and Alkane, Using B3LYP/6-31G*//AM1 and AM1//AM1 (*in parentheses and italics*) Gas-Phase Results

$S_1 - S_2$	gas-phase energy diff (kcal·mol^{-1})	$\Delta(\Delta G°\text{solv})$SM2 (kcal·mol^{-1})	$\Delta(\Delta G°\text{solv})$SM4 (kcal·mol^{-1})	energy diff in water (kcal·mol^{-1})	energy diff in alkane (kcal·mol^{-1})
tetrapyrrole	29.2 (*37.5*)	−38.0	−21.3	−8.8 (*−0.5*)	7.9 (*16.2*)
pentapyrrole	14.3 (*21.9*)	−28.4	−14.9	−14.1 (*−6.5*)	0.6 (*7.0*)

fact that pentapyrrole is oxidized to a dication at a lower potential than that needed for the one-electron oxidation of pyrrole (solvated pentapyrrole dication + pyrrole is therefore more stable than solvated pentapyrrole radical-cation + pyrrole radical-cation). We have therefore performed the calculation in three different situations, i.e., with a +2 overall charge on the system but starting either from pentapyrrole and pyrrole radical-cations or from a +2 pentapyrrole and a non-oxidized pyrrole. In the third situation a +3 overall charge on the system is used; this mimics the reaction between a pentapyrrole dication and a pyrrole radical-cation.

Table 5 compares the activation energies of these three situations with the two previous ones which yield sexipyrrole. Let us first compare the three RC/RC reactions (pyrrole RC + pentapyrrole RC coupling; bipyrrole RC + quaterpyrrole RC; terpyrrole RC dimerization). It is clear that in all solvents, sexipyrrole is formed much more rapidly by the first reaction. The gas-phase activation energy is way below that of the other two reactions and even though solvent effects on this reaction are smaller they are not enough to make oligomer−oligomer faster than monomer−oligomer RC/RC coupling reactions. This analysis holds as long as one does not examine carefully the charge distribution in the pyrrole RC + pentapyrrole RC transition state and what are the reactants connected to this TS. In doing so either by animation of the imaginary vibration connecting the reactants and products or by performing calculations for a C_2-C_2' distance slightly greater than that in the TS, we come to the conclusion that the localized TS connects the product to non-oxidized pyrrole + pentapyrrole dication. Indeed, when a total +2 charge is used in the pentamerization, hexamerization steps, etc. and when the two reactants are far from each other, the +2 charge is on the oligopyrrole and the monomer is neutral. This recalls the well-known experimental result that it is easier to oxidize tetrapyrrole or pentapyrrole to the dication than pyrrole to the monocation. Table 6 highlights this point in comparing the stability of the two possible initial states, i.e., oligopyrrole RC + pyrrole RC (S_2 system) and oligopyrrole dication + non-oxidized pyrrole (S_1 system) in various environments and for various oligomer lengths.

It is clear that as the oligomer length increases, the oligopyrrole dication + non-oxidized pyrrole gas-phase energy comes closer to that of oligopyrrole RC + pyrrole RC. Moreover, when solvent effects are added, it is predicted that at some point, depending on the solvent used and the length of the oligopyrrole, the former system will be more stable than the latter. It is therefore difficult and probably not significant to calculate activation barriers for the RC−RC coupling between pyrrole and pentapyrrole as in Table 5 (line 3), because in many solvents this is not the initial state of the coupling reaction yielding sexipyrrole and because the localized TS is probably that of the reaction between pentapyrrole dication and non-oxidized pyrrole.

If we now look at the two other reactions that can yield sexipyrrole starting from pyrrole, it appears that, depending on the solvent, the fastest reaction will not be of the same type. In water, the reaction will mainly involve 2+ charged pentapyrrole and the pyrrole RC whereas in alkane this reaction will be much slower than coupling between pentapyrrole dication and non-oxidized pyrrole. Table 5 highlights in bold type the predicted predominant reaction in each environment. In other words, molecular modeling suggests that for the electrosynthesis of long oligopyrroles from a solution containing pyrrole, the predominant mechanism may change during the growth process at some point which will depend on the solvent and on the oligomer length. Pyrrole oxidation might not always be necessary and polymer growth may occur as long as the polymer chains are doped at a high doping level. This effect, which was already proposed on the basis of frontier orbital considerations,[12−14] is a possible explanation of the catalytic effect observed in the electrosynthesis of many conducting polymers. In any case, oligomer−monomer reactions remain faster than oligomer−oligomer reactions.

Conclusion

In this work we have compared the C_2-C_2' coupling reactions of oligopyrroles of various lengths generated by electrochemical oxidation. Despite the severe limitations inherent to the theoretical approach and numerous approximations used (TS localized at a semiempirical level with the C_2-C_2' distance too short when compared to the more sophisticated level;[27] absolute energy barriers were still not calculated accurately; solvent effects were calculated on the basis of the gas-phase geometry, i.e., TS and radical-cations were considered as implastic species; there was no modeling of counterion effects; and branching ratios were estimated on the basis of the height of the activation barriers, i.e., no rate constant calculation, no reversible σ or π dimerization, and finally, similar radical-cation concentrations in the vicinity of the electrode), molecular modeling suggests or indicates the following:

(a) The gas-phase transition state geometries of oligopyrrole dimerization reactions are similar but the C_2-C_2' distance decreases as the oligomer length increases. In other words, the TS are later for terpyrrole dimerization than for pyrrole dimerization. On the other hand, the gas-phase energy barriers decrease on going from pyrrole to terpyrrole. These results suggest that the TS geometries are controlled by frontier orbital interactions whereas the gas-phase energy barriers are mainly due to electrostatic repulsion. The same evolution is seen in the oligopyrrole−pyrrole RC/RC coupling series which leads to an unusual situation, i.e., the hardest radical cation (pyrrole RC) reacts more rapidly on the softest radical-cation than on himself. This effect, which is due to the strong electrostatic repulsion between two hard radical-cations, is probably general and will be addressed with more details in a further publication.

(b) Solvent effects have been modeled in two extreme cases, water and alkane, on the basis of the gas-phase geometry (assuming therefore that the species are not plastic). This makes it possible to qualitatively describe their impact on the coupling reactions. It is found that the dimerization of two radical-cations, which appeared very difficult in the gas phase, becomes perfectly feasible when solvent effects are included. Furthermore, the relative lifetimes of the three oligopyrrole radical-cations are predicted to be highly dependent on the electrolytic medium, and might be reversed. Dimerization rate constant are predicted to be very close or even above the diffusion-limit kinetics rate constant in water.

(c) Comparing the different reactions yielding quaterpyrrole and sexipyrrole indicates that the polymer growth tends to involve oligomer−monomer coupling (assuming that the local concentrations of the radical-cations are similar) which gives some grounds for the general belief based on indirect proofs. The alternative mechanism, i.e., oligomer−oligomer reactions, seems not to be competitive in any solvent even though solvent effects can reduce the energy gap between these two mechanisms.

(d) Moreover, molecular modeling suggests that for the electrosynthesis of long oligopyrroles from a solution containing pyrrole, a modification of the predominant mechanism may occur during the growth process at some point which will depend on the solvent and on the oligomer length. Pyrrole oxidation might not always be necessary and polymer growth may occur as long as the polymer chains are doped at a high doping level. This effect is a possible explanation of the often observed catalytic effect.

We do believe that our results could be of great help as guidelines for future experimental work both for understanding the processes involved in the making of the polymers and for improving the quality of these materials even though electropolymerization is a very subtle process and a small change in a single experimental variable influences drastically the properties of the resulting polymers.[31]

JA0025954

---

(31) Zhou, M.; Heinze, J. *Electrochim. Acta* **1999**, *44*, 1733.