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Jerzy Zak · Mieczyslaw Lapkowski
Stephane Guillerez · Gerard Bidan

State of partial oxidation of the regioregular sexi (3-octyl thiophene) oligomer in solid phase on electrode surface

Abstract An existence of a new, stable oligomer state of the solid film is reported, which is produced under electrochemical conditions. In this state, a formal charge exchanged in the redox process is about one-half of electron per oligomer molecule. The procedure, which allows controlling precisely the amount of oligomer on the electrode surface, is proposed that together with the coulometric evaluation of the electric charge provides the number of electrons involved in a redox process. This is demonstrated for a case of α-monochloro-substituted regioregular sexi (3-octylthiophene) oligomer (6OTCl). The electrochemical results are discussed together with UV–Vis–NIR spectroelectrochemical data obtained for both solution and solid phase that support the proposed interpretation.

Keywords Oligothiophenes · Conjugated polymers · Spectroelectrochemistry · Thin oligomer films

Introduction

Intense research efforts are focussed currently on more defined polymeric materials and structures like mono-

Dedicated to Professor M. A. Vorotyntsev on the occasion of his 60th birthday

J. Zak · M. Lapkowski (✉)
Department of Chemistry, Silesian University of Technology, 44-100 Gliwice, Poland
E-mail: lapkowsk@zeus.polsl.gliwice.pl
Tel.: +48-32-2371743
Fax: +48-32-2371509

M. Lapkowski
Institute of Coal Chemistry, Polish Academy of Sciences, Sowinskiego 5, 44-121 Gliwice, Poland

S. Guillerez · G. Bidan
Département de Recherche Fondamentale sur la Matiere Condensée SI3M/EM, CEA Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 09, France

disperse, various length and regioregular oligomers. A strong motivation for the studies is a potential application of both, π-conjugated polymers and oligomers in molecular electronics and non-linear optics that are an objective of numerous considerations [1–8]. Much of the research on this area has been addressed to conjugated thiophene oligomers [9, 10]. A wide spectrum of aspects are discussed for this important model system including a nature of optical transitions in charged oligothiophenes [11], formation of ordered monolayers in self-assembly process [12], formation [13, 14], chains interactions [15], and description of charged oligothiophene π-dimers [16] and π-stacks [17], large size oligothiophenes functionalisation [18, 19].

Our group has been investigating electrochemical and related aspects, like doping process of a series of α-monochloro-substituted regioregular (3-octylthiophene) oligomers in last years [20–22]. In this paper we present a finding of a stable oligomer state, which is produced under electrochemical conditions. In this state, a formal charge exchanged in the redox process is about one-half of electron per oligomer molecule. This state can be observed for the solid phase film on the electrode surface during voltammetric scans, as one of, generally multi-step redox processes. The procedure used in this study makes possible to measure the amount of reacting species with a fair precision that together with coulometric assessment of the electric charge it provides an important factor, that is the number of electrons involved in a particular redox process. This is demonstrated for a case of α-monochloro-substituted regioregular sexi (3-octylthiophene) oligomer (6OTCl) used for the purpose of the study.

The electrochemical results are discussed together with UV–Vis–NIR spectroelectrochemical data obtained for both solution and solid phase. These measurements evidently support the presented finding of the formation of dimeric species having single positive charge being a stable form, which in fact is the first stage preceding formation of cation radical and dication forms of single oligomer molecule during its oxidation.

Experimental

3,4′,4″,4‴,4⁗,4⁗′-hexaoctyl-5⁗′-chloro-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′-sexithiophene was synthesised according to the procedure described earlier [23]. For all solid-state measurements the oligomer film was deposited on Au electrode according to a procedure described below. This electrode of the active surface area of 0.3 cm² was attached to a Teflon electrochemical cell using a kelres o-ring. The counter electrode was a Pt grid, whereas as a reference, Ag /AgCl electrode was used. The last one was placed in the Teflon tubing filled with 0.2 M Bu₄NClO₄ in propylene carbonate (PC), (Aldrich) and separated from the cell-solution using a frit. The cell was filled with 0.2 M Bu₄NPF₆ (Fluka) in PC solution. Under conditions of experiments, 6OTCl appeared to be practically insoluble in this solution as found from separate electrochemical, spectroscopic (UV–Vis) and QCM tests. All electrochemical processes were controlled, and the data were processed using CHI620A (USA) potentiostat and its software.

To prepare the solid-oligomer film, a measured volume, from 1 to 10 µL of the 6OTCl solution of controlled concentration in dichloromethane (MeCl₂) (Aldrich), was placed in the centre of the Au electrode using a 10-µL syringe (Hamilton) and allowed to evaporate. To avoid a water vapour condensation on the surface, the electrode was slightly heated during deposition and evaporation. It was an important part of the procedure that concentration of the oligomer in the solution has been monitored spectroscopically, directly before using the solution for deposition of the film.

For spectroelectrochemical measurements the oligomer film was cast onto ITO/quartz (Delta Technologies, USA) electrode, which was cut to a size fitting the standard 1 cm quartz cuvette. Pt-wire counter, and Ag/Ag + reference electrodes were mounted in the Teflon cover of the cuvette. These measurements were performed using GBC Cintra-5 UV–Vis–NIR spectrometer and Cypress Omni 90 potentiostat.

For the solution phase electrochemistry and spectroelectrochemistry 6OTCl was dissolved to 0.5 mM concentration in MeCl₂ solution containing 0.2 M Bu₄NPF₆. Similar counter and reference electrodes as given above were used. The working electrode in electrochemical measurements was Au disc (0.1 cm diameter, BAS). Spectroelectrochemistry was carried out in the thin-layer cell, in which 80-µm-thick spacer (Teflon) together with cuvette wall and ITO/quartz have created the cell cavity. In all spectroelectrochemical measurements the steady state spectra were recorded at a constant potential that was gradually adjusted to a required level.

All the data reported in text were obtained for the system at room temperature. Commonly used procedures were applied to prepare and to protect all the solutions as free of water contaminations.

Results and discussion

During potential scan the solid film of 6OTCl on electrode undergoes multiple redox processes as shown in Fig. 1a. As discussed in detail below, this voltammetric behaviour is substantially different from that observed for 6OTCl in solution phase, where, within the same potential range, this oligomer reveals evidently three reversible redox processes as shown in Fig. 1b.

The case of the solution phase was earlier described in literature for this particular oligomer [21], or for other oligothiophenes, e.g. [24]. It is well established, at least for the first two steps in the solution phase that formation of radical cation takes place, which then leads to dication formation according to the reactions: $6T \rightarrow 6T^{\bullet +} + e^-$ and $6T^{\bullet +} \rightarrow 6T^{2+} + e^-$. The third step in solution is also one electron oxidation as may be seen from the insert to the Fig. 1b, where the differential pulse curve clearly shows three peaks of same height when the current curve is background-corrected. This third step was assigned to formation of the second radical cation in the molecule [21].

The current voltage curve obtained for the solid oligomer, which is shown in Fig. 1a, can be recorded in such a shape for the first scan only. Further scanning (not shown here) within the range of potential applied in this measurement confirms more evidently the irreversibility of processes. This irreversibility is observed clearly during the first scan, when the cathodic portion of the CV curve is analysed. The anodic portion of the curve at a first glance indicates, similar to the case of solution, three-step oxidation, however some important differences might be easily found. The first anodic peak is very sharp and usually a small pre-peak accompanies it. The peak position, E_{pa1}, which appears to be well reproducible, is moved of nearly 0.120 V towards positive potentials as compared to E_{pa1} for solution species. The separation between the first and the second peak is substantially larger for the solid oligomer. The last value, as can be seen from literature data [21] for solution electrochemistry, depends on the number of thiophene units in the oligomer, thus it should remain unchanged. However, in contrast to the potential of the first anodic peak, E_{pa1}, the position of E_{pa2} for the solid film is very unstable, it varies even about 0.060 V for different films, probably due to irreproducible morphology of the films. Whereas in solution the peak separation between E_{pa1} and E_{pa2} is 0.145 V, in case of the solid film it might be even twice as large. For the data in Fig. 1a, it is equal to 0.241 V. Also the position of the third peak in case of solid oligomer is not as stable as in its solution.

All these observations strongly suggest that the mechanism of oxidation in solid films might be different from that known for oligothiophenes in solution phase. It is important to add that cyclic scanning in solution phase provides still the same voltammograms as this shown in Fig. 1b, whereas the reproducible CV curves in

Fig. 1 Cyclic voltammetry curves recorded at 0.05 V/s for: **a** Au electrode covered with solid film of 6OTCl in 0.2 M Bu_4NPF_6/PC solution; **b** Au electrode, 1 mM 6OTCl + 0.2M Bu_4NPF_6 in CH_2Cl_2; the *inset* is differential pulse graph obtained in the same solution as for CV; **c** film obtained from 1 μL of oligomer solution containing 0.15 nmol of 6OTCl; *dashed line* is obtained in electrolyte solution; **d** films like in (**c**) obtained from 2 to 20 μL of oligomer solution
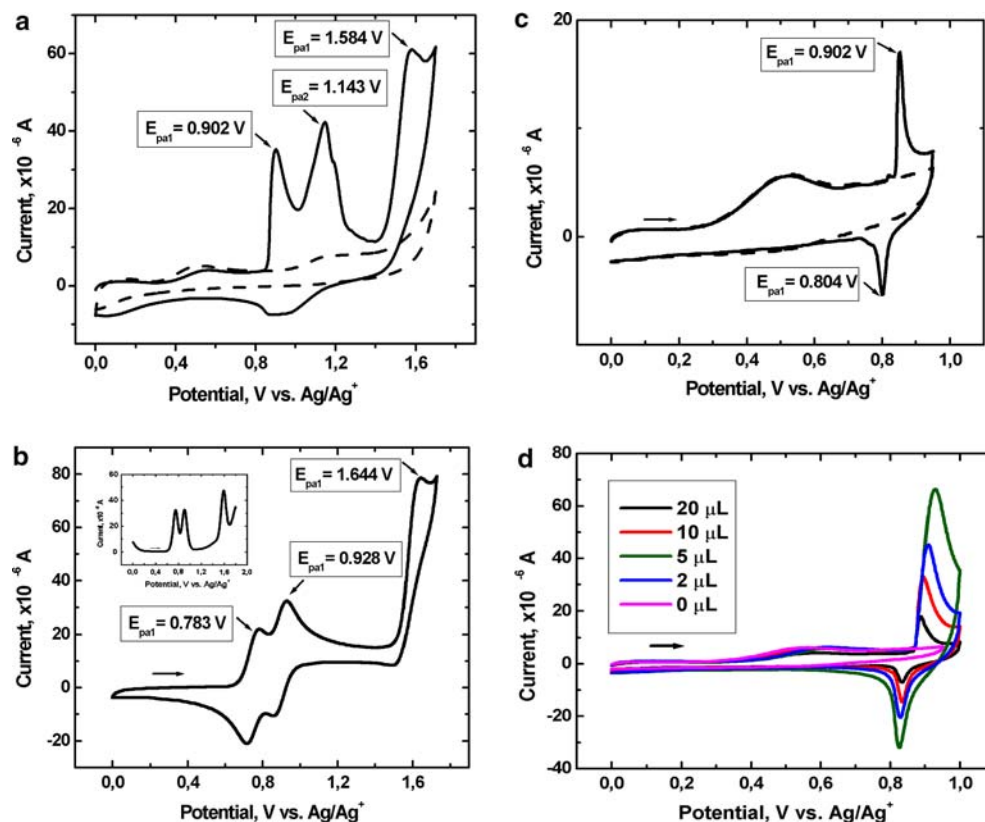
case of solid 6OTCl can be obtained only if the potential range is limited to the region of the first oxidation step.

The last situation is shown in Fig. 1c for the controlled amount of oligomer on the gold electrode. The electrode potential was swept here exactly to the point, where minimum of anodic current occurs after passing the sharp peak at E_{pa1}. The voltammogram recorded under such condition is fairly stable during several scans. Over the large portion of the recorded curve it matches the background current line. This makes possible an accurate evaluation of the charge responsible for the conversion of the oligomer from the neutral form to the state in which it exists at that applied potential limit. As already mentioned, the position of the peak maximum is well reproducible, besides, it is very characteristic for the number of thiophene units in the oligomer molecule[1]. The peak shape is an attribute of the observed process; the characteristic rapid increase of the peak current takes place in case of both monolayer-like and relatively thick films covering the electrode surface. The apex of the peak may, however change its shape and position which is evidently a result of irregularities in the film thickness. Though an appearance of the anodic pre-peak is not clear at the moment, it must be the result of a physical process on solid–solid interface, since its height is always negligibly small and independent of the

amount of the oligomer film. All the features described here for the gold electrode supporting the oligomer film appear to be essentially the same in case of any other electrode surfaces tested, like Pt, HOPG or glassy carbon.

To explain the differences between the electrochemical behaviour of 6OTCl in solid and solution phase, an attempt was undertaken to determine the number of electrons involved in the redox reactions in the solid oligomer phase. This approach could be important in solving the detailed mechanism of the processes in solid oligomer film. In fact, most of the results in this area presented in literature have focussed on solution rather than solid systems, if one excludes conductive polymers. In case of a structurally well-defined oligomer molecule a quantitative approach to this important task should be much more straightforward than in the case of a corresponding polymer.

Shown in Fig. 1d is a set of voltammograms recorded for a known, and increasing amount of oligomer moles on the electrode surface. Generally, this set of voltammetric curves demonstrates two basic experimental facts. The first is the observed simple relation between the volumes of the oligomer solution used to prepare the film and the magnitude of the recorded peak of the first step of oligomer oxidation. The magnitude of the peak should be understood as the charge under the CV curve rather than the peak height, since the above-mentioned irregularities in film thickness may affect the recorded peak height. Secondly, the uniform shape of the peaks

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[1]Detailed studies on partial oxidation of solid state for each in the series of regioregular oligomers nOTCl at n=4–8 are under way and the results will be published soon.
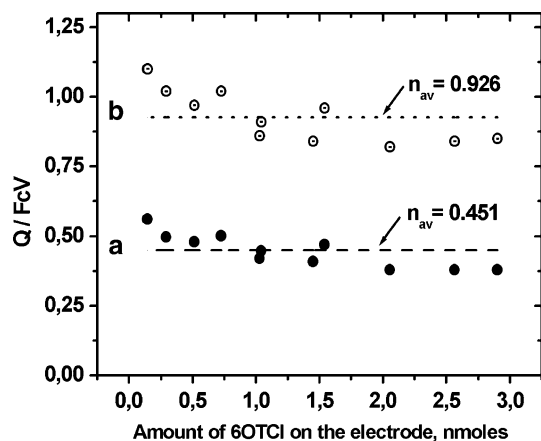
Fig. 2 Q/FCV versus number of moles of 6OTCl on the Au electrode

over the range of used oligomer quantities proves that no other process takes place in the considered range of potentials.

Thus, the magnitude of the recorded peaks was evaluated in terms of number of coulombs for the films formed at controlled amount of oligomer. The measurement of the number of oligomer moles was based on spectroscopic control of 6OTCl solution absorbance at 406 nm, taking into account that the absorption coefficient found in a separate measurement for 6OTCl/CH_2Cl_2 is equal to $37,650 \pm 2\%$ (cm^{-1} L mol^{-1}). Measured volume of this solution was then used to cast the film on the gold electrode. Both the experimental values, the number of coulombs and the number of oligomer moles were then used to calculate the number of electrons involved in particular redox step of oligothiophene.

The main interest of this study was focussed on the oligomer state that is determined by the fully reversible process, which takes place at the potential E_{pa1}. However, to have a full description of the oxidation, besides the charge under the voltammetric peak at E_{pa1}, the total charge under two peaks E_{pa1} and E_{pa2} was also measured. The results were then compared with the calculated charge that would be expected for one e^- process. Data from different experiments are collected in Fig. 2, where the quotient Q/FCV is plotted against the number of 6OTCl moles (Q is corrected electric charge, C and V are concentration and volume of the oligomer solution used to prepare the film).

The dashed line (a; Fig. 2) on the plot represents the average value of number of electrons that was found to be equal to 0.451 at the standard deviation of 0.059. Other set of data plotted in the figure represents the number of electrons involved, as a sum, in two consecutive oxidation processes taking place at E_{pa1} and E_{pa2}. Again the dashed line (b; Fig. 2) reflects the average value of Q/FCV calculated here for the total charge under these two peaks. Since it is equal to 0.915, it may be assumed that the total charge under the peaks at E_{pa1}

and E_{pa2} corresponds to the value, which is close to one electron per one oligomer molecule.

These results suggest that in the reversible, electrochemical process taking place at the potential denoted as E_{pa1}, a number close to 0.5 electrons per 6OTCl molecule is involved. Therefore the oligomer can be considered as partially oxidised at that potential. Moreover, this state may be considered as a stable state of the solid oligothiophene. This state of partial oxidation may also suggest an existence of the dimeric form of radical cation, which could be formed at E_{pa1} according to the reaction scheme:

$$2(6OTCl) \leftrightarrow (6OTCl)_2^{\bullet+} + 1e^-$$
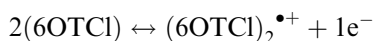
Thus, during the first stage of oxidation of solid oligomer one electron is presumably withdrawn from each two molecules of the oligomer. Then, formation of the single molecule radical cation $6OTCl^{\bullet+}$ or a corresponding state for the dimeric form, $(6OTCl^{\bullet+})_2$ would occur in two distinguishable steps, as shown in Fig. 1a at E_{pa1} and E_{pa2}. The corresponding state in solution phase is attainable in one oxidation step. Although, (in solid) due to more complicated background current at the anodic limit, it is difficult to determine the charge related with the peak at E_{a3}, the estimated number of electrons involved in this process was found to be always close to one. Thus, the peak appearing at E_{pa3} for the solid oligomer could be assigned to the process of dication formation.

The phenomena observed in the electrochemical measurements should affect spectra of corresponding states of 6OTCl. A set of UV–Vis–NIR spectra recorded at different potentials of solid film on OTE and the solution phase in thin layer cell is shown in Fig. 3a and b, respectively.

In the neutral, reduced form the main absorption peak of the solid film has a maximum at 447 nm and its width at the half of maximum (WHM) is equal to 175 nm. As compared to the spectra obtained in the thin solution layer shown in Fig. 3b, the peak is shifted in solids towards lower energies and evidently broader since the corresponding values are 406 nm for the absorbance maximum and 100 nm for WHM. These differences are generally expected as a result of strong interactions in the solid state as compared to the situation in the solution. When the oxidation is progressing within the potentials corresponding to E_{pa1}, then, besides the decreasing absorbance at 447 nm, a significant shift of the peak maximum is observed, towards larger energies. For the stable spectrum recorded at 0.950 V this shift is about 20 nm, which is in contrast to solution spectra having a stable peak position in course of oxidation. This shifted peak has still almost a half of its initial height. In case of solution species the corresponding absorbance decrease is practically accomplished at 0.850 V, where radical cation already exists. For the solid film such a decrease of the peak is attained for its second oxidation state. The blue-shifted

absorbance maximum and the non-zero absorbance value at this wavelength can support the existence of partially oxidised oligothiophene state.

At the same time, as oxidation progresses, the absorbance in the region above 600 nm gradually increases, forming a wide band with maximum being shifted towards larger energies for each following spectrum. Finally, for the state corresponding to E_{pa1}, the stable spectrum recorded at 0.950 V has maximum at 659 nm. Again, this is in contrast to the situation of 6OTCl in solution, since a corresponding increase of absorbance occurs at the constant wavelength for the maximum at 764 nm. When the film is oxidised at potentials closer to E_{pa2}, then a relative absorbance in the region of 450 nm decreases and the maximum starts to move back, towards lower energies. This is consistent with a model in which the partially oxidised dimer forms the single radical cation, when undergoes further oxidation at E_{pa2}. The observed increase of absorbance over the entire region of spectrum recorded at 1.150 V, shown in Fig. 3a, is a result of a scattering of the light beam accompanying the morphology changes of the film. The phenomenon that takes place at higher potentials, was observed earlier using ECAFM measurements for the 6OTCl film [22]. More detailed interpretation of the spectroelectrochemical results will be published separately.

Besides the qualitative interpretation of the spectroelectrochemical data, indicating generally effects of stronger interactions in solid state, an approach to estimate the number of electrons exchanged in the considered redox steps was also possible, based on the Nernst plots. To evaluate the number of electrons by applying Nernst equation, absorbance values at $\lambda = 446$ nm were used. Plotting potential versus logarithm of the ratio of absorbance values corresponding to oxidised and reduced forms allows estimating the number of electrons n from the equation:

$E = E^{0\prime} + 0.059/n \log ([O]/[R])$. From the slope of the line obtained for the range of potential 0.850–0.890 V, a value of n was calculated as equal to 0.55 (± 0.012). These calculations were possible by finding a minimum absorbance at 446 nm for the most oxidised state of the film from the spectrum recorded at $E = 1.150$ V. However, this spectrum has elevated background line due to effects mentioned above, thus transferring it to the level of initial spectrum for 0 V makes these approach possible. Therefore, the obtained result may be considered only as a rough estimation. In case of solution spectroelectrochemistry the recorded spectra make possible more reliable calculations using absorbance values at $\lambda = 406$ nm, or at $\lambda = 764$ nm, or both ranges at the same time. Using absorbance at 764 nm, for potentials between 0.500 and 0.600 V the Nernst equation is: $E = E^{0\prime\prime} + 0.059/n \log ([O]/[R])$. From the slope of the line, a value of n is equal to 1.03 (± 0.011). In both solution- and solid-state, linearity of the Nernst plot is better than 0.990. The values of $E^{0\prime}$ and $E^{0\prime\prime}$ in the Nernst equation cannot be expected to be
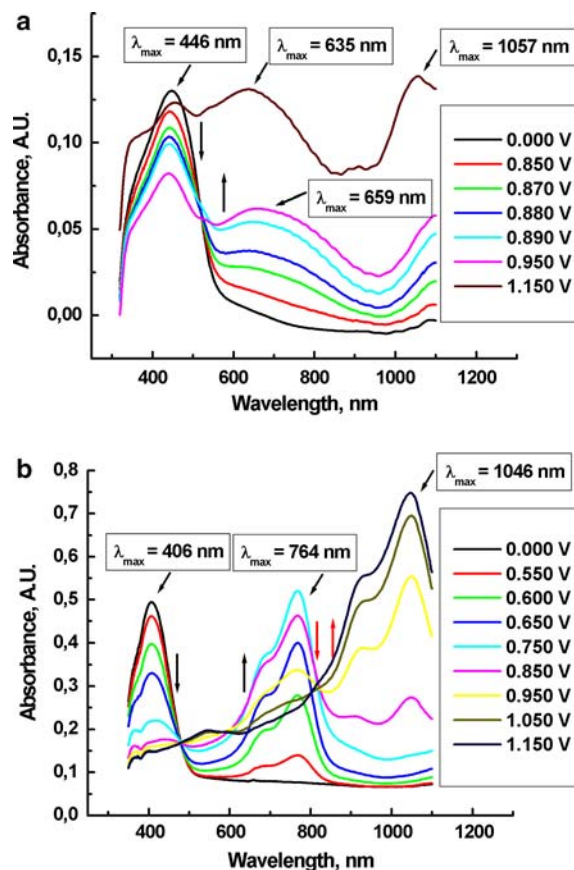

Fig. 3 a Spectra of the solid film of 6OTCl on ITO electrode in 0.2 M Bu$_4$NPF$_6$/PC solution recorded in equilibrium state at given potential in range of potential 0/1.150 V; **b** spectra of 6OTCl as the solution phase on ITO electrode in the thin layer cell (80 μm thickness); solution contains 1 mM 6OTCl in 0.2 M Bu$_4$NPF$_6$/CH$_2$Cl$_2$. Spectra recorded in equilibrium state at given potential; the range of applied potentials is 0/1.150 V

equal for the cases of solid and solution states, since they are referred to two different redox states of the system. Besides, they consist the reference electrode potential which is different under conditions of these two experiments. Thus, although their quantitative character is limited due to estimation of base line spectra for the solid state, the spectroelectrochemical data may only support the suggested difference in the redox mechanism of 6OTCl found for solid film phase versus solution species in electrochemical measurements.

According to literature data [25] it was postulated for poly(3-alkylthiophenes) that charge of one electron is delocalised along four to five thiophene units and, in that state, the polymer reaches the highest conductivity. From this point of view the result presented here is unexpected, however one must take into account the evident structural differences between these two systems. On the other hand, the earlier postulated formation of π-dimers [13] could be now supported by the presented results. It is also worth mentioning that a concept of mixed valence was postulated earlier for some solid α-oligothiophene salts [26]. The nature of interactions that are responsible for the differences in electrochemical

properties of crystalline structures of solid films will be presented soon for the oligothiophene molecules shorter and longer than presented in this paper. A wider review of important issues of these kinds of systems was recently presented for conducting polymers in [27].

Conclusions

A reversible electrochemical oxidation of the solid oligomer 6OTCl may lead to its dimeric form of radical cation $(6OTCl)_2^{\bullet+}$, which is postulated as the result of 0.5 electron per molecule process. This partially oxidised state is stable under electrochemical conditions and might be detected in UV–Vis spectral region. Mechanism of the oligothiophene oxidation is substantially different for the solid and solution phase.

References

1. Skotheim TA, Elsenbaumer RL, Reynolds JR (1998) Handbook of conducting polymers. Marcel Dekker, New York
2. Heeger AJ (2001) Current Appl Phys 1:247
3. Nyberg T, Zhang F, Inganas O (2002) Current Appl Phys 2:27
4. Carrol LR, Gorman CB (2002) Angew Chem Int Ed 41:4378
5. Videlot C, Ackermann J, Blanchard P, Raimundo JM, Frere P, Allain M, Bettignies R, Levillain E, Roncali J (2003) Adv Mater 15:306
6. Dimitrakopoulos CD, Malenfant PRL (2002) Adv Mater 14:2
7. Shaw JM, Seidler PF (2001) IBM J Res Dev 45:3
8. Shim HK, Jin JI (2002) Adv Polym Sci 158:19
9. Bäuerle P (1998) Electronic materials: the oligomer approach. In: Müllen K, Wegner G (eds). Wiley-VCH, Weinheim p 105
10. Tour JM (1996) Chem Rev 96:537
11. Cornil J, Brédas JL (1995) Adv Mater 7:295
12. Azumi R, Götz G, Bäuerle P (1999) Synth Met 101:569
13. Miller LL, Mann KR (1996) J Am Chem Soc 29:417
14. Hong Y, Yu Y, Miller LL (1995) Synth Met 74:133
15. Brocks G (2000) J Chem Phys 112:5353
16. Brocks G (2001) Synth Met 119:253
17. Cornil J, Calbert JP, Beljonne D, Silbey R, Brédas JL (2001) Synth Met 119:1
18. Apperloo JJ, Janssen RAJ, Malenfant PRL, Groenendaal L, Fréchet JMJ (2000) J Am Chem Soc 122:7042
19. Odobel F, Suresh S, Blart E, Nicolas Y, Quintard JP, Janvier P, Le Questel JY, Illien B, Rondeau D, Richomme P, Häupl T, Wallin S, Hammarström L (2002) Chem Eur J 8:3027
20. Lapkowski M, Gullierez S, Bidan G, Chauvet O (2001) J Electroanal Chem 501:166
21. Barth M, Guillerez S, Bidan G, Bras G, Lapkowski M (2000) Electrochim Acta 45:4409
22. Lapkowski M, Kolodziej-Sadlok M, Zak J, Guillerez S, Bidan G (2001) Adv Mater 13:803
23. Bidan G, De Nicola A, Enée V, Guillerez S (1998) Chem Mater 10:1052
24. Roncali J, Giffard M, Jubault M, Gorgues A (1993) J Electroanal Chem 361:185
25. Nessakh B, Horowitz G, Garnier F, Deloffre F, Srivastava P, Yassar A (1995) J Electroanal Chem 399:97
26. Tabakovic I, Maki T, Miller LL (1997) J Electroanal Chem 424:35
27. Levi MD, Cohen YS, Gofer Y, Aurbach D (2004) Electrochim Acta 49:3701–3710