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Abstract

Properties and behavior of a group of four newly synthesized derivatives of terthiophene and terthienylvinylene was studied. All four investigated monomers bear a 1,3-indandione substituent at the central thiophene ring and two of them (ThIV, ThIVM) have additional vinyl bonds introduced between the thiophene rings. In addition, ThIM and ThIVM have 5 positions of the two terminal rings blocked with methyl groups. The measurements were done using cyclic voltamperometry (CV) in solutions of 0.1M Bu₄NBF₄ in CH₂Cl₂. It was found that ThI and ThIV polymerise easily. CV of ThI reveals a reduction peak resulting probably from the abstraction of a proton. During polymerisation of ThIV a group of peaks is observed indicating its stepwise oxidation process. The polymerisation potential of ThIV was found to be lower than that of ThI which could mean that formation of radical-cation is easier in the former. Stability measurements indicated that polymer films of ThI are electrochemically stable in CH₂Cl₂ and films of ThIV are not. Efforts to polymerise ThIM and ThIVM failed. Their CVs revealed only peaks coming from oxidation of the monomers, some of which were semi-reversible.

Keywords

electrochemical, 1, 3, indandione, study, terthiophenes, derivatives

Disciplines

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Electrochemical study of 1,3-indandione derivatives of terthiophenes

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Abstract: Properties and behavior of a group of four newly synthesized derivatives of terthiophene and terthienylvinylene was studied. All four investigated monomers bear a 1,3-indandione substituent at the central thiophene ring and two of them (ThIV, ThIVM) have additional vinyl bonds introduced between the thiophene rings. In addition, ThIM and ThIVM have 5 positions of the two terminal rings blocked with methyl groups. The measurements were done using cyclic voltamperometry (CV) in solutions of 0.1M Bu₄NBF₄ in CH₂Cl₂. It was found that ThI and ThIV polymerise easily. CV of ThI reveals a reduction peak resulting probably from the abstraction of a proton. During polymerisation of ThIV a group of peaks is observed indicating its stepwise oxidation process. The polymerisation potential of ThIV was found to be lower than that of ThI which could mean that formation of radical-cation is easier in the former. Stability measurements indicated that polymer films of ThI are electrochemically stable in CH₂Cl₂ and films of ThIV are not. Efforts to polymerise ThIM and ThIVM failed. Their CVs revealed only peaks coming from oxidation of the monomers, some of which were semi-reversible.

Introduction

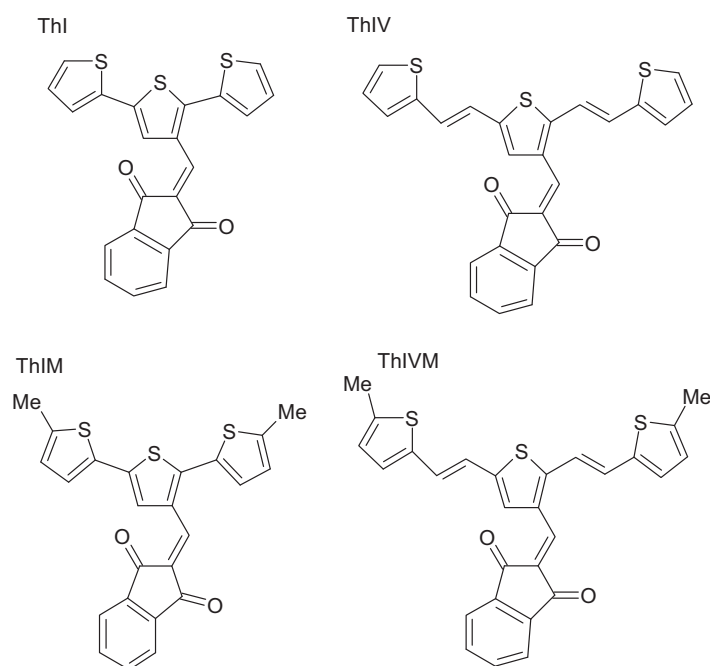
Polythiophene and its derivatives belong to the group of conducting polymers where π -electron delocalization along their backbones causes interesting optical and nonlinear optical properties and allows them to become good electrical conductors. Wide range of possible applications requires good mechanical properties of the material together with its environmental stability and susceptibility to modification [1, 2].

Polythiophene may be obtained by using thiophene, bithiophene or terthiophene as a starting monomer. Although thiophene – derived polymers show high conductivities, they tend to be less stable during electrochemical cycling [3]. Because of this reason attention was paid to the terthiophene units, which are known to form more stable films. In the same time the presence of two additional thiophene units increases ability of the monomer to polymerise.

One of the essential issue concerning conducting polymers is electronic structure of the forming films. It depends largely on the chemical structure of the monomer, which in turn can be tailored for example by addition of electron donating or accepting substituent in the specific positions of molecule or spacing apart the core building blocks of the monomer [4, 5].

Considering all above mentioned facts, the behavior of a group of four newly synthesized derivatives of terthiophene and terthienylvinylene was investigated. They are: 2-[2,2';5',2'']Terthiophen-3'-ylmethyleneindan-1,3-dione (ThI), 2-(5,5''-Dimethyl-[2,2';5',2'']terthiophen-3'-ylmethylene)indan-1,3-dione (ThIM), (E,E) 2-(2,5-Bis-(2-thiophen-2-ylvinyl)-thiophen-3-ylmethylene)indan-1,3-dione (ThIV), (E,E) 2-(2,5-Bis-(2-(5-methyl-thiophen-2-yl)vinyl)thiophen-3-ylmethylene)indan-1,3-dione (ThIVM). All of them contain 1,3-indandione substituent, which is known to be strongly electron accepting group [6, 7]. The advantages of including the 1,3-indandione group might be indicated. Firstly, it creates intramolecular charge transfer effect and secondly, its presence may lead to the reduction of the energy gap in the polymer. On the other hand due to the size of the substituent it may cause steric interactions. The solution to this problem might be attachment of the substituent to the middle ring of terthiophene. Another important fact is that owing to the structure of the molecules some steric interactions between thiophene rings and substituent are possible. The way of diminishing it was introducing vinyl bonds between the rings to expand them spatially.

The research effort has been focused on the preparation of well-defined conjugated polymers with improved processability and stability characteristics. Structures of investigated compounds are presented below.



Results and discussion

ThI and ThIV

Electrochemical oxidation of ThI and ThIV leads to formation of conducting polymer films in both cases, which is evidenced by current increase in the potential range between 0.0 V to 0.6 V in successive cycles. The ThI solution is orange and the polymer of ThI is brown. The polymer can be switched between its reduced form, which is light brown and its oxidised form, which is dark brown. The ThIV solution is dark red and the polymer of ThIV is brownish-violet. In case of ThI the colour change was easier to observe as the solution was less coloured compared to ThIV. The colour change of the polymers is connected with changes in electronic structure

resulting from oxidation of the molecules. The layers formed at the Pt surface were uniform and did not change after rinsing with solvents. No soluble products were observed in the vicinity of the electrode.

The value of the polymerisation potential is lower for ThIV than for ThI, which means that it is easier to create radical cation in the former. The reason for that might be the presence of vinyl bonds elongating the delocalisation length of the radical cation and facilitating conformational rearrangements within the molecule upon oxidation.

There are however differences, in the way films are formed. As far as ThI is concerned, during electropolymerisation no well defined peaks are observed on the CV, which may indicate large variation of the length of polymer chains. In addition to that they are probably not regioregular. At the same time CV of ThI reveals a reduction peak which may result from monomer reaction, since the peak disappears during stability measurements of the film.

At the beginning of electropolymerisation of ThIV, some peaks at 0.33 V and 0.41 V are observed, which vanish in the course of polymerisation. They could be evidence to the formation of the oligomers, synthesized as more defined structures. Oligomers could be the first stage of polymerisation, combining later to give a polymer.

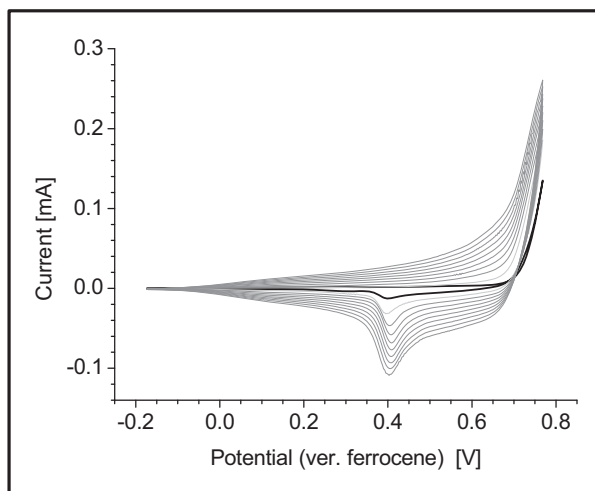


Fig. 1. Cyclic voltammogram of 2 mM solution of ThI in 0.1M (Bu)₄NBF₄ in CH₂Cl₂ at Pt electrode. Scan rate: 50 mV/s

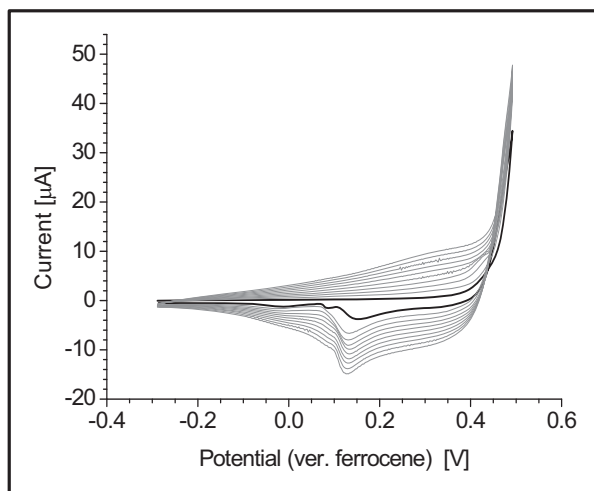


Fig. 2. Cyclic voltammogram of 2 mM solution of ThIV in 0.1M (Bu)₄NBF₄ in CH₂Cl₂ at Pt electrode. Scan rate: 50 mV/s

ThIM and ThIVM

As it was expected in case of ThIM and ThIVM, electrochemical polymerisation failed due to blocking of the 5 positions of the thiophene rings. CVs of ThIM and ThIVM reveal oxidation peaks of the monomers at potentials similar to their non-blocked analogues. Oxidised ThIVM molecule appears to be more stable than a corresponding ThIM one as its CV is more reversible. In the potential range of the experiment, the oxidation of ThIM reveals one oxidation peak whereas for ThIVM a two-step process is observed. At higher potentials the CVs showed some additional peaks resulting probably from the decomposition of the monomer units. The degradation potential is once again lower for ThIVM than for ThIM.

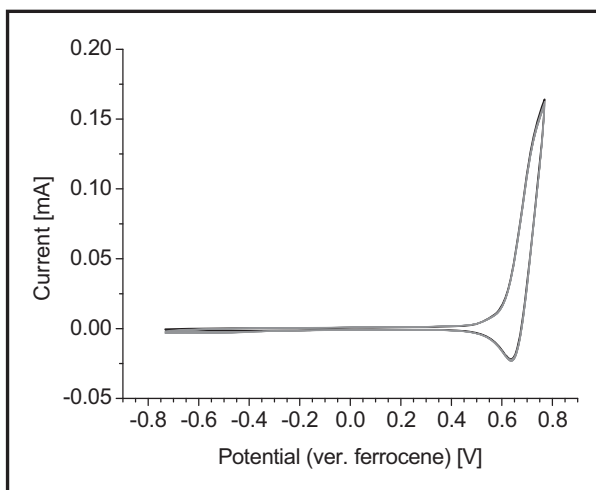


Fig. 3. Cyclic voltammogram of 2 mM solution of ThIM in 0.1M (Bu)₄NBF₄ in CH₂Cl₂ at Pt electrode. Scan rate: 50 mV/s

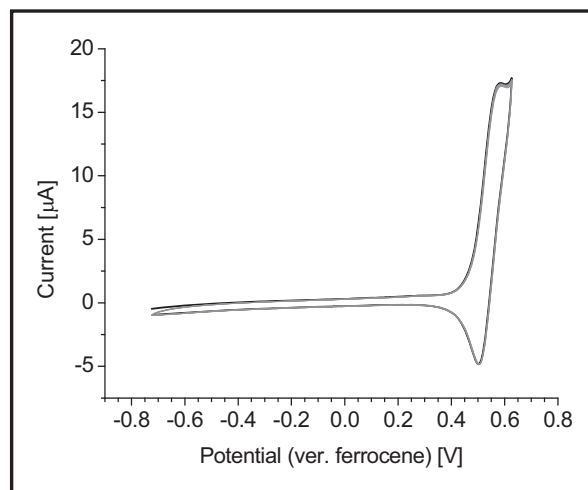


Fig. 4. Cyclic voltammogram of 2 mM solution of ThIVM in 0.1M (Bu)₄NBF₄ in CH₂Cl₂ at Pt electrode. Scan rate: 50 mV/s

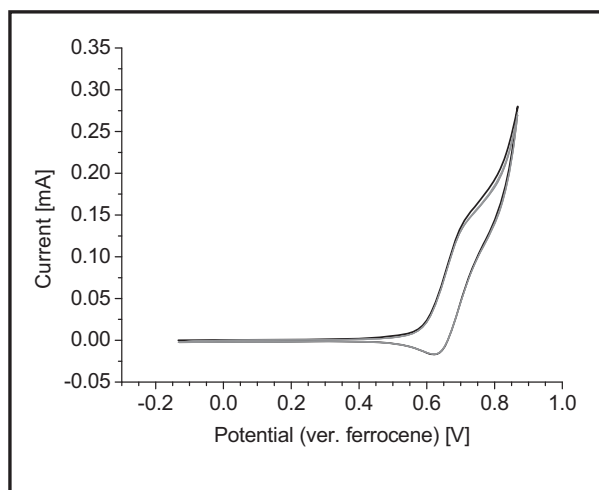


Fig. 5. Cyclic voltammogram of 2 mM solution of ThIM in 0.1M (Bu)₄NBF₄ in CH₂Cl₂ at Pt electrode. Scan rate: 50 mV/s

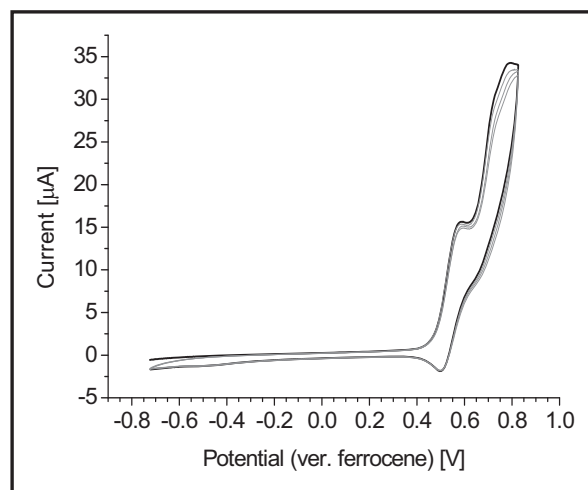


Fig. 6. Cyclic voltammogram of 2 mM solution of ThIVM in 0.1M (Bu)₄NBF₄ in CH₂Cl₂ at Pt electrode. Scan rate: 50 mV/s

Stability of the films

The conductivity of the films in the electrolyte solutions is relatively high, what can be deduced from the sharp drop of the current value at the beginning of the reduction half-cycle in the CVs of the films. CV of the ThI film is stable in the potential range applied during the polymerisation process, whereas the CV of ThIV film is not.

PolyThIV reveals peaks indicating the presence of the oligomers whose redox potentials are below the polymerisation one. Probably the presence of the vinyl bonds facilitates the oxidation of the monomer unit but in the same time decreases the stability of the film. Perhaps structure of the ThIV monomer hinders the formation of longer chains compared to the structure of ThI, as the ThIV molecule is longer than ThI one. This could cause steric hindrances.

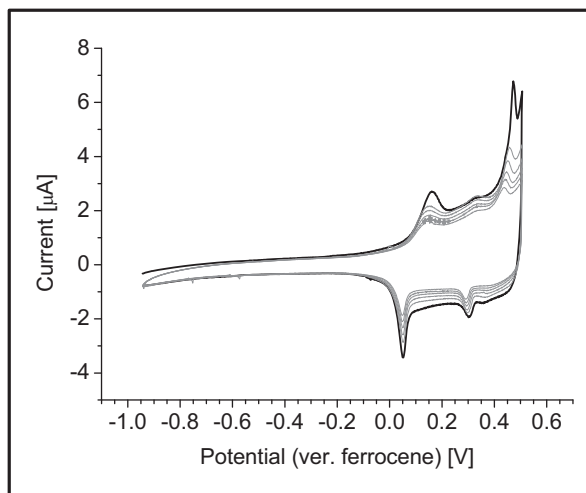
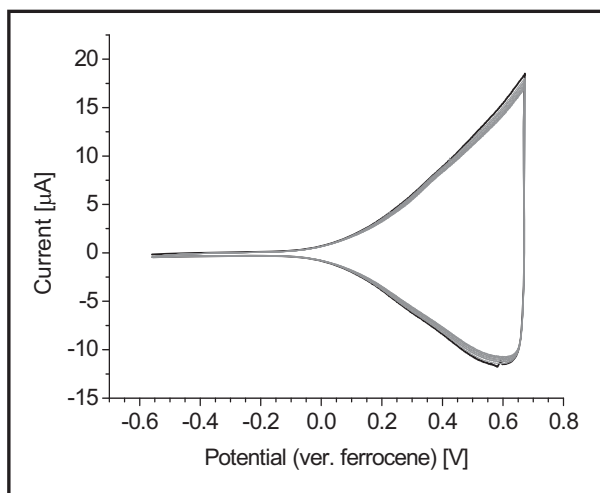


Fig. 7. Cyclic voltammogram of film of polyThI in 0.1M $(\text{Bu})_4\text{NBF}_4$ in CH_2Cl_2 at Pt electrode. Scan rate: 50 mV/s

Fig. 8. Cyclic voltammogram of film of polyThIV in 0.1M $(\text{Bu})_4\text{NBF}_4$ in CH_2Cl_2 at Pt electrode. Scan rate: 50 mV/s

To summarise the obtained results it might be stated that electrochemical oxidation of ThI and ThIV leads to formation of conducting films. In comparison to the polyThI the electrodeposition of polyThIV requires lower potential, from which can be deduced that the presence of the vinyl bonds facilitates the process. However, it is polyThI film that seems to be more stable during electrochemical cycling.

As far as the ThIM and ThIVM are concerned the molecules oxidation was not followed by film formation.

Experimental part

Reagents and materials

ThI, ThIM, ThIV, ThIVM were synthesised by P.Wagner at Massey University, New Zealand. The synthesis of investigated compounds will be published elsewhere.

Electrolyte solution was prepared by dissolving tetrabutylammonium tetrafluoroborate Bu_4NBF_4 (Janssen Chimica, 99%) in dichloromethane CH_2Cl_2 (CH_2Cl_2 for spectroscopy (stab. with amylene), water < 0.01%, POCh, Gliwice, Poland). Concentration of the solution was 0.1 M. The measurements were carried out at room temperature.

Concentration of the compounds was 2mM and the measurements were done in three – electrode cell, using 2 mL sample solution. CVs of electrodeposited polymers were taken in monomer-free solutions, of the same supporting electrolyte as used for polymerisation.

Instrumentation

Electrosynthesis and studies of polymer films were performed on Ecochemie AUTOLAB potentiostat – galvanostat model PGSTAT20 driven by a computer. Results were analysed using GPES program (*General Purpose Electrochemical System*).

Polymer films were synthesised directly on the Pt electrode, which was used as a working electrode. Ag wire served as a pseudoreference electrode and platinum spiral was employed as an auxiliary electrode.

Cyclic voltammetry (CV) was used for all measurements performed in this study.

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