

ORIGINAL PAPER

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Reactive groups on polymer-covered electrodes

11. Copolymerization of methyl thiophene-3-acetate with 3-alkylthiophenes

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Abstract Polythiophene films containing ester groups on the surface of electrodes are interesting potential carrier materials for reagents. Methyl thiophene-3-acetate (**3**) can be copolymerized with 3-methylthiophene (**1**) and 3-butylthiophene (**2**) by means of cyclic voltammetry (CV) at potentials of 0–2.2 V. Higher potentials (0–2.4 V) lead to overoxidation of the copolymers. The ester groups were confirmed by FTIR spectra. Electrochemical investigations of 2,2'-bithiophene (**6**) and **3** at equimolar ratios showed no successful copolymerization at potentials of 0–1.3 V. If the copolymerization experiments of **6** with **1** or **3** were carried out at molar ratios of 1:50 at 1.3 V, **6** with its low oxidation potential was polymerized without copolymerization of the other monomers. However, if the oxidation potential was increased stepwise from 1.3 V, the oxidation of **1** or **3** occurred, forming copolymers containing both monomer components. HPLC investigations of solutions containing mixtures of **6** and **3** and also **6** and **1** in acetonitrile/TEABF₄ showed, after exhaustive oxidation at a potential of 1.3 V, the complete absence of **6**; **1** and the ester **3** were not oxidized and copolymerized at these potentials. From the results of the copolymerization

experiments, as well as the HPLC investigations, it can be concluded that the dominant mechanism of the electrochemical polymerization is radical cation dimerization.

Key words Cyclic voltammetry · Electrocopolymerization · Polythiophene · Reactive surfaces · HPLC investigation

Introduction

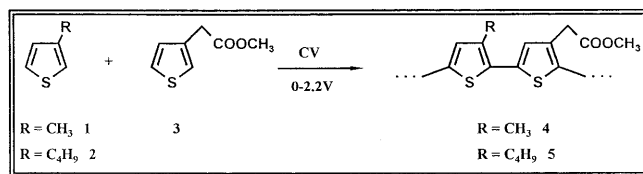
Thiophene derivatives can be oxidized electrochemically and polymerized to the corresponding polythiophenes [1, 2]. Also, the copolymerization of two different thiophene derivatives is possible and in some cases functionalized thiophene copolymers can be produced in this way [3, 4, 5]. In the literature, two different mechanisms for the electrochemical polymerization are discussed. The initiation step of the electropolymerization process occurs with the anodic oxidation of a thiophene monomer at the electrode, leading to the formation of a radical cation. Mechanistically the following reaction steps – in principle – are possible: the dimerization of one radical cation with another [6, 7] or the interaction between a radical cation and a neutral monomer molecule [8, 9]. In order to study the mechanism of the electrochemical polymerization, cyclic voltammetric (CV) copolymerization experiments with thiophene derivatives at different oxidation potentials were carried out (see Schemes 1 and 2).

For part 10, see [16]

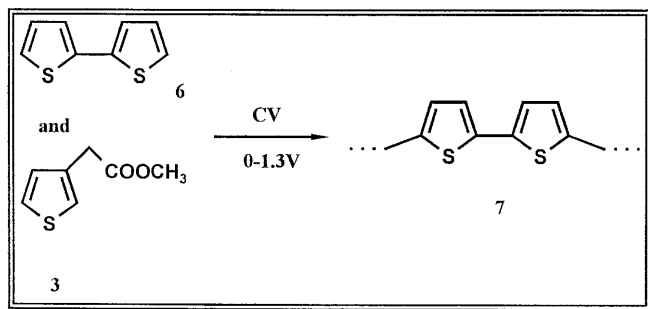
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Scheme 1



Scheme 2

Experimental

Chemicals

Commercial 2,2'-bithiophene (**6**) and 3-methylthiophene (**1**) (Aldrich), acetonitrile (AN) (Baker), tetrabutylammonium perchlorate (TBAP) and tetraethylammonium tetrafluoroborate (TEABF₄) (Fluka) were used for the electrochemical studies. 3-Butylthiophene (**2**) was synthesized starting from 3-bromothiophene [10]; methyl thiophene-3-acetate (**3**) was obtained by esterification of thiophene-3-acetic acid [11].

Analytical measurements

Reflection IR spectra were taken with a Nicolet 5 SXC FTIR spectrometer with DRIFT. Determination of the reaction products from the electrochemical oxidation of the thiophene derivatives was carried out with a Waters 510 HPLC apparatus, with a Gynkotek UV detector.

General electrochemical conditions

The peak potentials for the oxidation of the monomers **1**, **2**, **3** and **6** have been estimated to be $E_p = 1.92$ V for **1**, $E_p = 1.94$ V for **2**, $E_p = 2.12$ V for **3** and $E_p = 1.34$ V for **6** against Ag/AgCl. The copolymerization experiments were carried out in a conventional triple-electrode cell consisting of two platinum electrodes, one being the working electrode (platinum plate with an area of 5.04 mm²) and the other the counter electrode (wire, 0.5 mm diameter) to produce the polymer electrodes for recording the reflection IR spectra. A saturated (LiCl/EtOH) Ag/AgCl electrode ($E = +143$ mV vs. E_{NHE}) was chosen as the reference electrode [4, 11]. All experiments were carried out in 0.1 M TBAP/AN at a scanning rate of 100 mV/s at room temperature (23 ± 2 °C); the concentrations of the monomers are discussed below. CV experiments were performed using a BEKA electronic potentiostat/galvanostat (model PG 28) and a Siemens Kompensograph (XY C 1020). The copolymer layers were deposited by multiple potential steps under controlled conditions up to potentials of 1.3 V, 2.20 V and 2.40 V (using CV).

Electrochemical copolymerization at equimolar concentrations

A solution of **1** and **3** (both 0.05 M) was polymerized under CV conditions ($\Delta E = 0-2.2$ V, see Fig. 1; $\Delta E = 0-2.4$ V, see Fig. 2) to give copolymer **4**. A reflection IR spectrum was taken of **4** (deposited at a potential range of 0-2.2 V), showing the characteristic peaks for the heteroaromatic thiophene system, the methyl ester group and the carbonyl ester group: 3055 cm⁻¹ ($\nu_{CH\ arom}$), 2948,

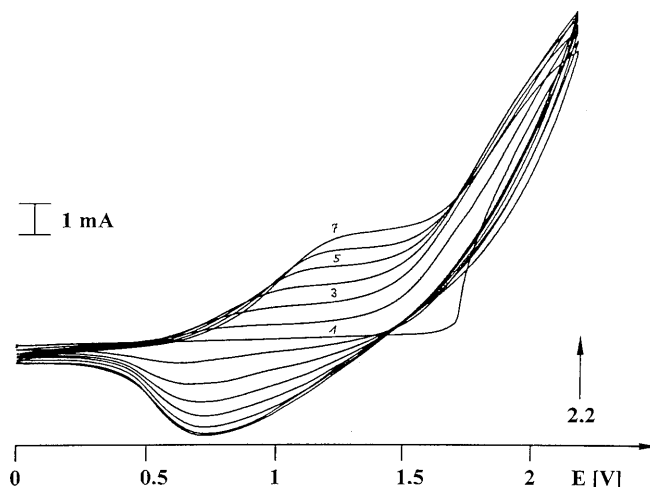


Fig. 1 Cyclic voltammogram (CV) of the copolymerization of 3-methylthiophene (**1**) with methyl thiophene-3-acetate (**3**) (first to seventh cycles, $\Delta E = 0-2.2$ V)

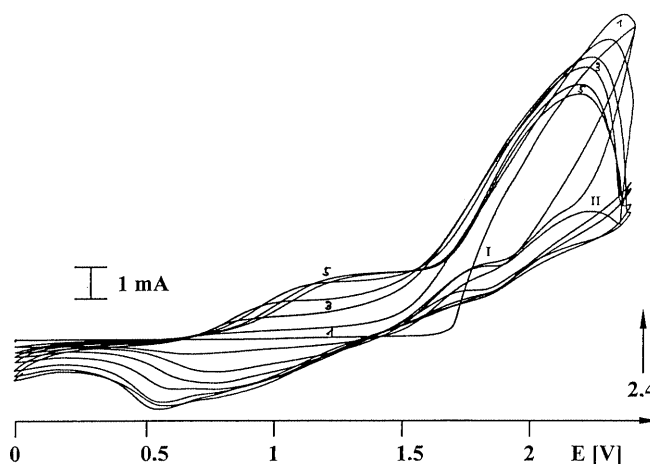


Fig. 2 CV of the copolymerization of **1** with **3** (first to seventh cycles, $\Delta E = 0-2.4$ V)

2917, 2864 ($\nu_{CH\ aliph}$), 1740 ($\nu_{C=O\ ester}$), 1326 (δ_{sCH}), 867, 829 (δ 3-subst. thiophene) (see Fig. 3).

A solution of **2** and **3** (both 0.05 M) was polymerized under CV conditions ($\Delta E = 0-2.2$ V, see Fig. 4; $\Delta E = 0-2.4$ V, see Fig. 5) to give copolymer **5**. A reflection IR spectrum was taken of **5** (deposited at a potential range of 0-2.2 V), showing the same characteristic peaks as above: 3055 cm⁻¹ (ν_{arom}), 2957, 2929, 2872, 2861 (ν_{aliph}), 1744 ($\nu_{C=O\ ester}$), 1350 (δ_{sCH}), 869, 836 (δ 3-subst. thiophene) (see Fig. 6).

A solution of **3** and **6** (both 0.05 M) was polymerized under CV conditions ($\Delta E = 0-1.3$ V). The reflection IR spectrum contains the characteristic peaks for the thiophene system: 3064 cm⁻¹ (ν_{arom}), 792 (δ 2,5-disubst. thiophene) (see Fig. 7).

Electrochemical copolymerization at different concentrations

These experiments were carried out at molar ratios of 1:50 for **6:1** or **6:3**, using 0.001 M **6** and 0.05 M **1** and **3**, with different solutions: (1) 0.001 M **6**; (2) 0.05 M **1**; (3) 0.05 M **3**; (4) 0.001 M **6** and 0.05 M **1**; and (5) 0.001 M **6** and 0.05 M **3**.

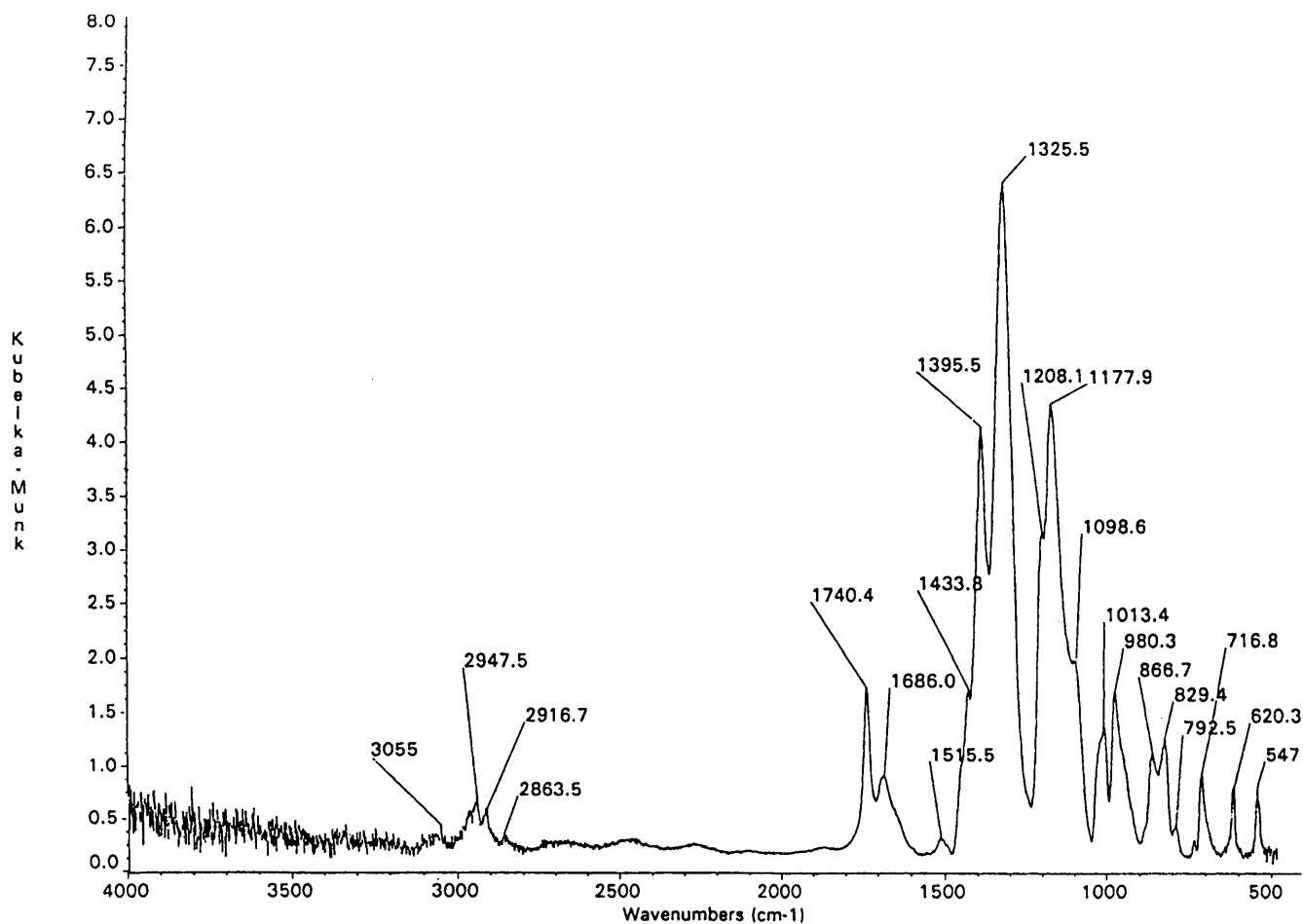


Fig. 3 Reflection IR spectrum of copolymer **4** after seven polymerization cycles ($\Delta E = 0-2.2$ V)

Solutions **1**, **2** and **3** were electrochemically oxidized in a potential range of $\Delta E = 0-1.6$ V for **1** and $\Delta E = 0-2.1$ V for **2** and **3** to compare the oxidation behavior at the beginning of the first cycle (see Fig. 8).

Solutions **1**, **4** and **5** were oxidized under CV conditions of $\Delta E = 0-1.3$ V for 10 cycles (see Fig. 9). These measurements were repeated 10 times and the average values of the anodic and cathodic currents for every cycle were noted (see Table 1 and Fig. 10). Solutions **1**, **4** and **5** were oxidized under CV conditions for 10 cycles at different potential ranges starting from $\Delta E = 0-$

1.3 V and increasing to $\Delta E = 0-1.9$ V. These operations were repeated four times and the average values of the anodic and cathodic currents for every cycle were noted (see Figs. 11, 12, 13, 14).

Oxidation experiments with **6** and HPLC studies

This study was carried out in acetonitrile with 0.1 M TEABF₄; the working electrode was a 10 cm² platinum plate. Compound **6** at a concentration of 1×10^{-3} M was mixed with the other thiophene derivatives at different concentrations (**3** and **1**, $c = 1 \times 10^{-3}$ to 5×10^{-3} M). After preelectrolysis of the electrolyte, compounds **6** and **1** or **6** and **3** were added and a sample of the solution was

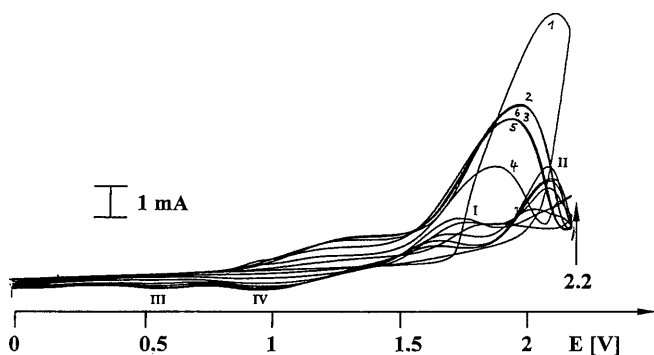


Fig. 4 CV of the copolymerization of 3-butylthiophene (**2**) with **3** (first to seventh cycles, $\Delta E = 0-2.2$ V)

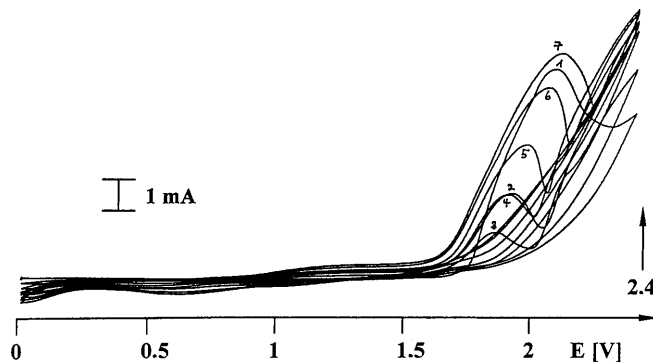


Fig. 5 CV of the copolymerization of **2** with **3** (first to seventh cycles, $\Delta E = 0-2.4$ V)

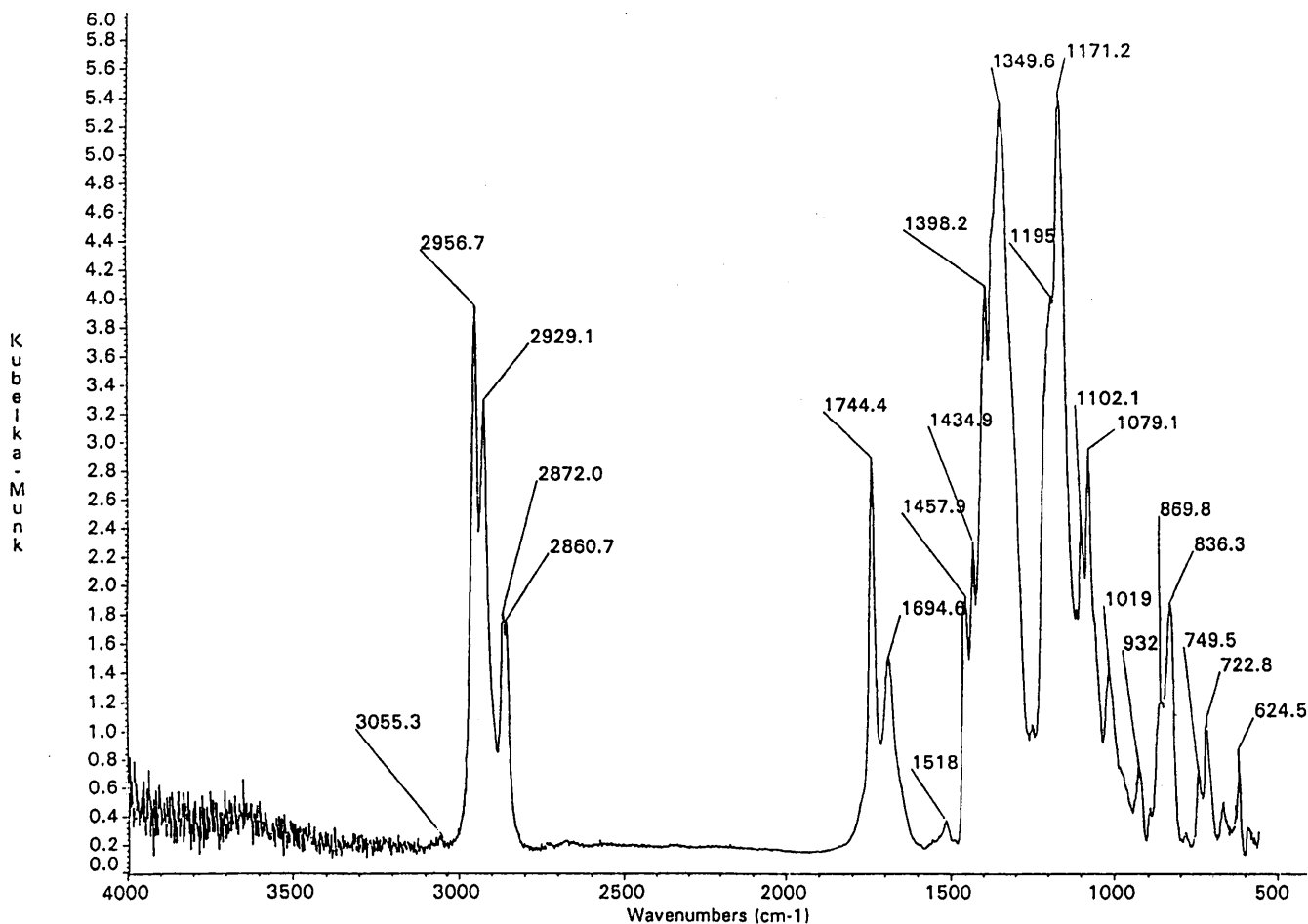


Fig. 6 Reflection IR spectrum of copolymer **5** after seven polymerization cycles ($\Delta E = 0-2.2$ V)

separated for HPLC, to detect the initial concentration of the monomers.

Compound **6** was completely oxidized at a constant potential of 1.30 V. If the current decreased to 5% of the starting value, the electrolysis was completed. Samples of the solution before starting the electrolysis and after complete oxidation of **6** were compared to ascertain the concentration of **1** or **3** after oxidation. The maximum analytical error is +5%. The results are listed in Table 1.

Results and discussion

Electrochemical copolymerization experiments at equimolar concentrations

A solution containing **1** and **3** (both 0.05 M) in acetonitrile was investigated under CV conditions between a potential of 0 to 2.2 V and 0 to 2.4 V (against Ag/AgCl, see Scheme 1). In these CVs a trace-crossing can be seen in all reverse sweeps (see Figs. 1, 2). According to Asavapiriyant et al. [12, 13], this phenomena can be interpreted as the start of the nucleation process of the corresponding polymer. Copolymerization of **1** with the ester **3** gave in both cases depositions of the expected copolymers at the two different potential ranges ($\Delta E = 0-2.2$ V and $\Delta E = 0-2.4$ V).

Figure 1 ($\Delta E = 0-2.2$ V) shows the CV for the treatment of **1** and **3** forming a deposition of copolymer **4** (see Scheme 1) as a completely reversible redoxable polymer. Copolymer deposition at a higher potential ($\Delta E = 0-2.4$ V) at the beginning also gave redoxable copolymer **4**; in addition, overoxidation was observed at such a high potential. After the fifth cycle, the current for the copolymer formation and oxidation does not follow the stepwise growing type (at the same potentials, lower currents than expected can be seen; see Fig. 2); if the experiment is continued, a nonconducting overoxidized material results. Therefore the oxidation potential for copolymerization experiments must be limited strictly at about 2.2 V to obtain conducting redoxable samples of copolymer **4**. The reflection IR spectrum of the deposited copolymer **4** (see Fig. 3) showed the carbonyl band of the ester **3** at 1740 cm^{-1} , being nearly identical with the carbonyl band of the monomeric ester at 1739 cm^{-1} . Further bands are given in the Experimental section.

Copolymerization of **2** with the ester **3** was carried out using the same procedure as described above. The resulting copolymer **5** was also conducting and redoxable (see Scheme 1), but the copolymer **5** arising from **2** is not as stable as copolymer **4**. Figure 4 shows the CV of the copolymerization at potentials of 0-2.2 V.

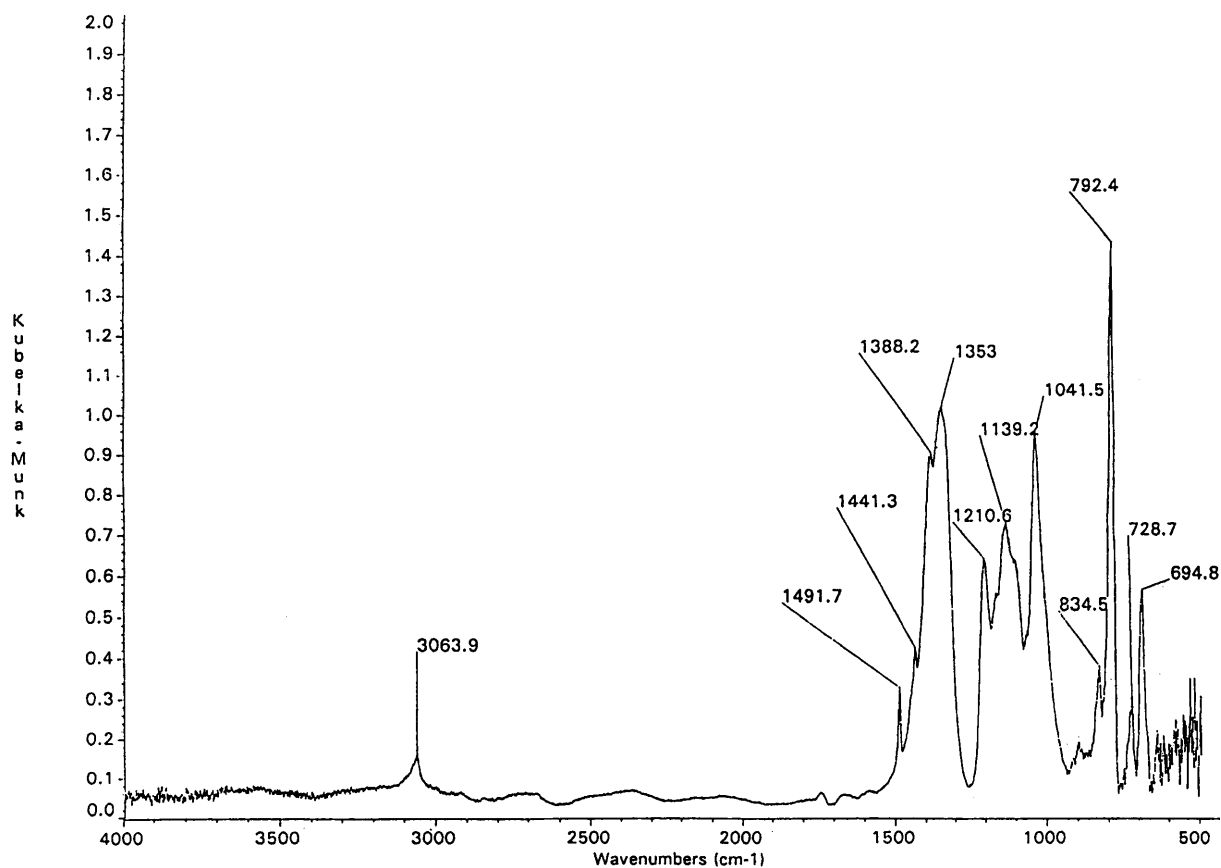


Fig. 7 Reflection IR spectrum of poly(2,2'-bithiophene-5,5'-diyl) (7) after seven polymerization cycles

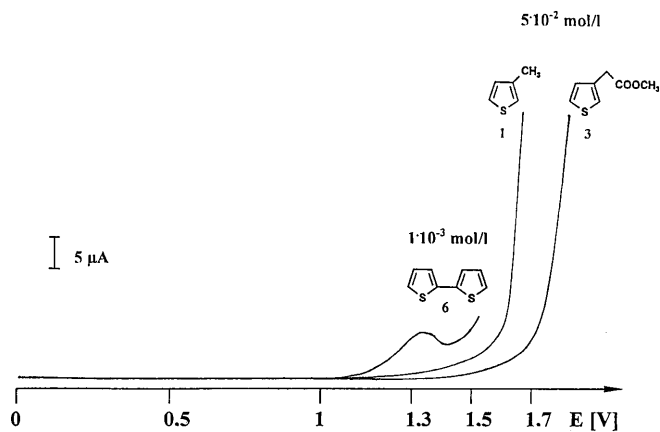


Fig. 8 Beginning of the electrochemical oxidation of 1 (0.05 M), 3 (0.05 M) and 6 (0.001 M)

After the fifth cycle the current for the polymer formation and oxidation did not increase; if the experiment was continued, the polymer was overoxidized and became nonconductive. If the copolymerization was carried out in a potential range of 0–2.4 V, deposition was observed but the conductivity of the copolymer already began to decrease during the first cycles (see Fig. 5) and the copolymer became nonconductive.

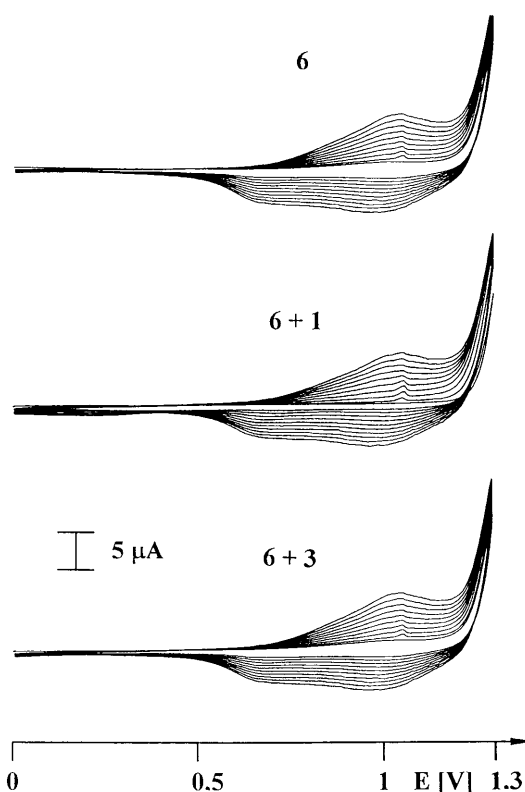


Fig. 9 CVs of the polymerization of 6 and of the copolymerization experiments of 6 and 1 and 6 and 3 (first to tenth cycles, $\Delta E = 0-1.3$ V)

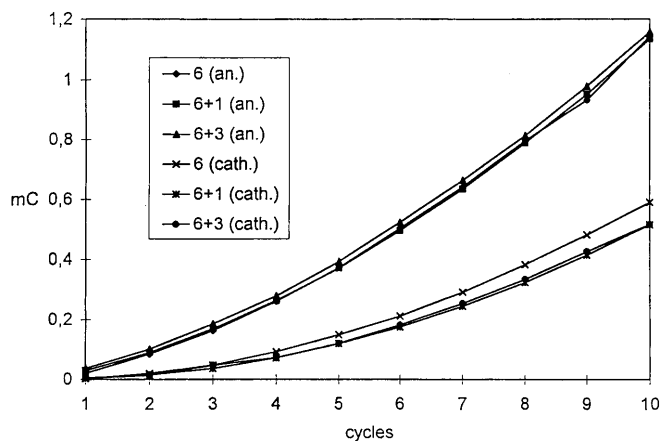


Fig. 10 Anodic and cathodic current of the polymerization of **6** and of the copolymerization experiments of **6** and **1** and **6** and **3** (first to tenth cycles, $\Delta E = 0-1.3$ V)

Table 1 Contents of the monomers **1**, **3** and **6** after oxidation, measured by HPLC^a

<i>c</i> (mol/L)	1×10^{-3}	2×10^{-3}	3×10^{-3}	4×10^{-3}	5×10^{-3}
1	97%	95%	102%	95%	98%
3	96%	95%	97%	99%	103%
6	0%	0%	0%	0%	0%

^a $c(\text{bithiophene}) = 10^{-3}$ mol/L, 0.1 M TEABF₄/AN, Ag/AgCl, Pt electrode (area = 10 cm²), oxidation potential = 1.3 V (Ag/AgCl), 25 °C

Copolymerization of **3** with **2** lead to redoxable polymers at maximum potentials up to 2.2 V, but the potential has to be limited strictly at this value and also the number of cycles.

Figure 6 shows the reflection IR spectrum of copolymer **5**. The carbonyl band at 1744 cm⁻¹ is also nearly identical with the carbonyl band of the monomeric ester **3** and confirms the incorporation of the ester into the copolymer. The ester groups of copolymers **4** and **5** can be converted to azide groups which are able to react with amino groups of various materials, e.g. enzymes [14].

The electrochemical copolymerization experiments with a mixture of **6** (with an oxidation potential as low as $E = 1.34$ V) and the ester **3** (with an oxidation potential as high as $E = 2.21$ V) were carried out under CV conditions ($\Delta E = 0-1.3$ V). At this potential, **6** was oxidized, but the oxidation potential of **3** was not reached, because the oxidation of ester **3** begins at a potential of about 1.7 V (see Fig. 8). A reflection IR spectrum was taken from the deposited polymer (see Fig. 7).

Comparison of the JR spectrum of poly(2,2'-bithiophene-5,5'-diyl) (**7**), prepared by homopolymerization, with the spectrum from the foregoing experiment showed almost exactly the same bands. This means that the resulting polymer is **7**, and no units of the ester **2** were incorporated into the polymer, because of the absence of the carbonyl band in the IR spectrum.

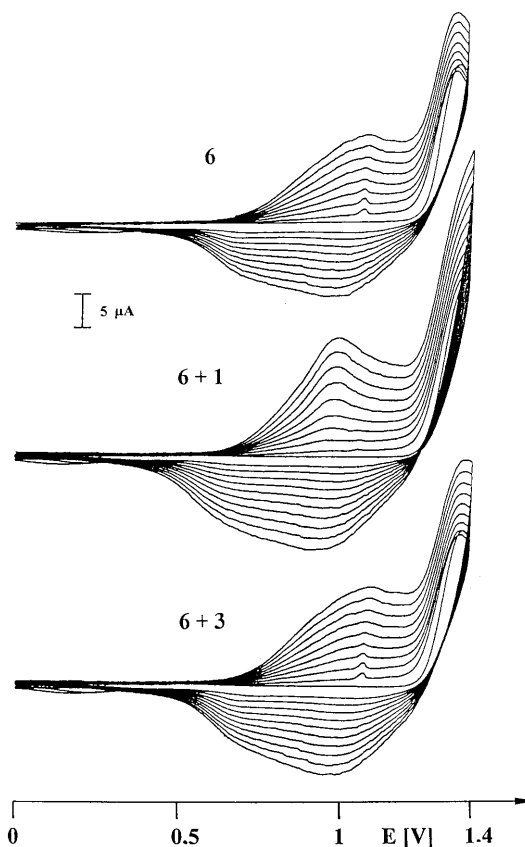


Fig. 11 CVs of the polymerization of **6** and of the copolymerization experiments of **6** and **1** and **6** and **3** (first to tenth cycles, $\Delta E = 0-1.4$ V)

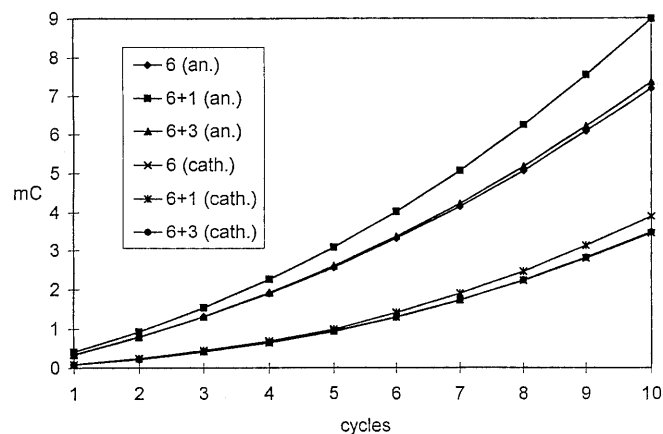


Fig. 12 Anodic and cathodic charge during the polymerization of **6** and of the copolymerization experiments of **6** and **1** and **6** and **3** (first to tenth cycles, $\Delta E = 0-1.4$ V)

Electrochemical copolymerization at different concentrations

The following experiments were carried out at molar ratios of 1:50 for **6:1** and **6:3**, using 0.001 M **6**, 0.05 M **1** and 0.05 M **3**, with different solutions: (1) 0.001 M **6**, (2) 0.05 M **1**, (3) 0.05 M **3**, (4) 0.001 M **6** and 0.05 M **1**, and (5) 0.001 M **6** and 0.05 M **3**.

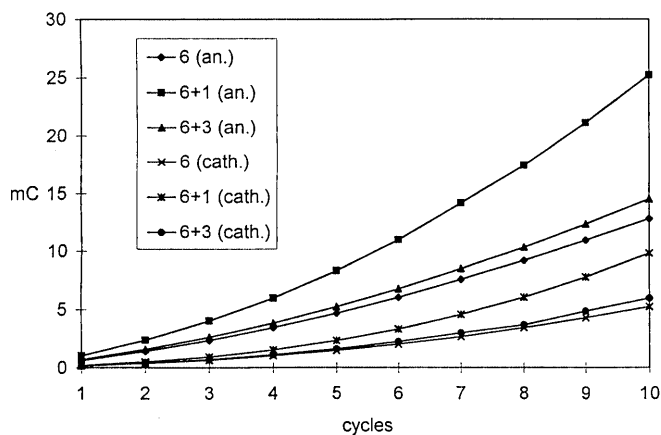


Fig. 13 Anodic and cathodic charge during the polymerization of **6** and of the copolymerization experiments of **6** and **1** and **6** and **3** (first to tenth cycles, $\Delta E = 0-1.5$ V)

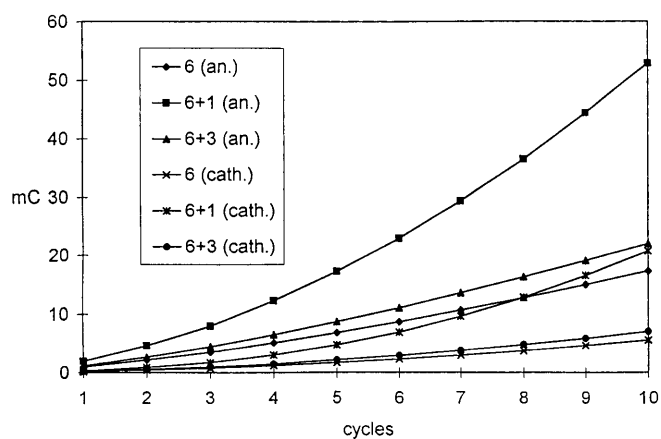


Fig. 14 Anodic and cathodic charge during the polymerization of **6** and of the copolymerization experiments of **6** and **1** and **6** and **3** (first to tenth cycles, $\Delta E = 0-1.6$ V)

In the first experiment the solutions 1, 2 and 3 were electrochemically oxidized in a potential range $\Delta E = 0-1.6$ V for 1 and $\Delta E = 0-2.1$ V for 2 and 3 to compare the oxidation behaviour at the beginning of the first cycle. Figure 8 shows the oxidation behaviour of **6**, **1** and **3** at different concentrations but at the same scale. Compound **6** was characterized by its peak potential E_p at 1.34 V; the oxidation was recorded up to 1.52 V in Fig. 8. The electrochemical study of **1** and **3** carried out at a potential range of $\Delta E = 0-2.1$ V shows that the oxidation of these monomers takes place at lower potentials: **1** ($E_p = 1.92$ V) is already oxidized at a potential higher than 1.3 V. In the case of the ester **3** ($E_p = 2.12$ V), which has a higher oxidation potential than **1**, the oxidation already starts at a potential higher than 1.4 V. This means that the oxidation of mixtures of solution 4 (**1** and **6**) or 5 (**3** and **6**) must be limited at 1.3 V if only the monomer **6** is to be oxidized without any oxidation of **1** and **3**.

Therefore the next experiment describes the electrochemical behaviour of different monomer solutions up to 1.3 V. Solutions 1, 4 and 5 were oxidized under CV conditions at $\Delta E = 0-1.3$ V for 10 cycles (see Fig. 9). These measurements were repeated 10 times and the average values of the anodic and cathodic currents for every cycle were noted.

Figure 9 shows that the CV of **6** and also of the mixtures of **6** and **1** or **6** and **3** are nearly identical at a potential range of $\Delta E = 0-1.3$ V. Only the oxidation of **6** took place without any participation of **1** or **3**. This result is also demonstrated by comparison of the anodic and cathodic currents of the CVs of solutions 1, 4 and 5, as shown in Fig. 10.

The anodic currents of solutions 1, 4 and 5 are increasingly parallel, without a significant difference between the three solutions. Also the cathodic currents of solutions 1, 4 and 5 are increasing, with little difference between solutions 1, 4 and 5, lying in the margin of error of the measurement. These experiments show that at a potential range of $\Delta E = 0-1.3$ V the electropolymerization of **6** occurs without any participation of the 50-fold excess of **1** or **3**.

In the next experiment the solutions 1, 4 and 5 were oxidized under CV conditions for 10 cycles at different potential ranges starting from $\Delta E = 0-1.3$ V and increasing to $\Delta E = 0-2.1$ V (see Fig. 11, $\Delta E = 0-1.4$ V). These measurements were repeated four times and the average values of the anodic and cathodic current for every cycle were noted (see Figs. 12, 13, 14).

The comparison of the cyclic voltammograms of solutions 1, 4 and 5 at a potential range of $\Delta E = 0-1.4$ V demonstrates a change between the solutions. The CVs of solutions 1 and 5 are again nearly identical but solution 4, a mixture of **6** and **1**, shows an extended CV (see Fig. 11). The anodic and cathodic peaks increase because **1** takes part in the electrochemical polymerization to form copolymers from **6** and **1**.

Figure 12 demonstrates clearly that the anodic and cathodic charge values are obviously higher in the case of solution 4 (**6** and **1**), whereas solutions 3 (**6**) and 5 (**6** and **3**) show lower anodic and cathodic charge values. The charge values of solutions 3 and 5 are nearly identical because the oxidation of **3** only starts at higher potentials (see Fig. 8). If the potential range is increased to $\Delta E = 0-1.5$ V, the charge values of solutions 3, 4 and 5 are more different (see Fig. 13).

The anodic and cathodic charge values of solution 4 increase and are much higher than the charge values of solution 3, but there is also a difference between solutions 3 and 5 because of the initial oxidation of ester **3**, as seen in Fig. 8. If the potential range is increased stepwise, this tendency becomes clearer up to a potential of 1.9 V.

At a potential range of $\Delta E = 0-1.6$ V the anodic and cathodic charge values of solution 4 are much higher than those of solutions 3 and 5. However, the difference between solutions 3 and 5, which is more significant than in the previous experiment at a lower potential, also

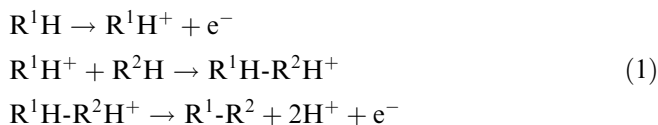
shows that ester **3** takes part in the oxidation and also in the formation of copolymer **4** (see Fig. 14).

Oxidation experiments of **6** and HPLC investigations

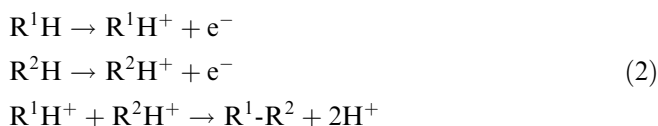
Compound **6** was mixed with **1** and separately also with ester **3**. Before starting the oxidation experiments, the electrolyte system (TEABF₄ in acetonitrile) was pre-electrolysed to remove any oxidizable substances. Then mixtures of **6** and **3** or **6** and **1** in different concentrations (see Table 1) were added. In a potentiostatic experiment the solution was oxidized at a potential of 1.3 V against Ag/AgCl up to a current of 5% of the current at the beginning of the oxidation process. At this potential, **6** was oxidized to radical cations forming homopolymer **7**, but the electrochemical oxidation of **3** and **1** was not possible. Samples of the solution before and after the electrochemical oxidation process were analysed by HPLC to detect the concentrations of **6**, **3** and **1** after the electrochemical oxidation. The error in the HPLC measurements is as accurate as 5%. The results are shown in Table 1 and clearly demonstrate that no radical cations of oxidized **6** interact at a potential of 1.3 V with neutral monomer molecules **1** or the ester **3**. Therefore no copolymerization can be observed.

Theoretical considerations

The copolymerization of monomers to form polymers via the dimeric product can principally occur by two mechanisms:



or



The experiments show that, in the case of thiophene and its derivatives, the mechanism of Eq. 1 could not be observed and that the copolymerization should follow the mechanism of Eq. 2. Smie et al. [15] found more detailed information about the coupling reaction of monosubstituted thiophenes. The film-forming process does not involve a chain propagation process with successive coupling steps of the starting radical cations to the chain. They concluded that oligomerization of the monomers in solution preferably occurs via consecutive dimerization steps, leading from a dimer to a tetramer and then to an octamer.

This statement should allow us to describe the copolymerization in a similar manner as cathodic alloy deposition or as the anodic deposition of mixed oxides.

This would imply that one should observe separate oxidation waves for **1** and **3** and for **2** and **3**. Inspection of Figs. 1 and 2 for the copolymerization of **1** and **3** shows separate waves or shoulders if the potential scan is limited to 2.2 V. However, if the limit of the oxidation potential is increased to 2.4 V, then in the backscan two anodic maxima (I and II, see Fig. 2) occur before the current passes over into the cathodic reduction region.

In the case of **2** and **3** this separation is more pronounced and appears already with the second anodic scan (I and II, see Fig. 4). Even the reduction current shows two separate waves (III and IV, see Fig. 4). If the limit of the anodic scan is increased from 2.2 to 2.4 V, then this separation is less pronounced.

From the existing results one cannot decide whether the separation into I and II is connected with the separate oxidation of the monomer **3** and the monomers **1** and **2** or has to do with overoxidation. Otherwise it is possible that the separation into two waves in the anodic region of the CV is not seen when the oxidation is diffusion controlled but will be observable if the surface becomes contaminated by overoxidation and the oxidation is kinetically controlled.

Conclusions

The polymerization of methyl thiophene-3-acetate (**3**) with 3-methylthiophene (**1**) and 3-butylthiophene (**2**) at potentials of $\Delta E = 0-2.2$ V under CV conditions gave in both cases copolymers (**4** and **5**) containing ester groups. The covalently incorporated ester units of **3** can be proved by reflection IR spectra. Copolymerization experiments of ester **3** with 2,2'-bithiophene (**6**) at equimolar concentrations and at potentials of $\Delta E = 0-1.3$ V were unsuccessful. The IR spectra showed no characteristic ester bands arising from **3**. If the copolymerization experiment is carried out at molar ratios of 1:50 for **6:1** and **6:3** at a potential range of $\Delta E = 0-1.3$ V, compound **6** with its low oxidation potential of about 1.3 V is polymerized without copolymerization of **1** or ester **3** with their higher oxidation potentials of about 2 V. If the oxidation potential is increased stepwise from 1.3 V, the oxidation of **1** or ester **3** occurred to form copolymers containing all the monomer components. HPLC studies of mixtures of **6** and **1** as well as **6** and **3**, both before and after electrochemical oxidation at a potential of 1.3 V, showed that **1**, as well as **3**, does not react during this oxidation experiment. These results lead to the conclusion that radical cation dimerization is the dominant mechanism step of the electrochemical polymerization of thiophene derivatives; the reaction of radical cations with neutral monomer molecules can be excluded (see also [7]).

Conducting thiophene copolymers with ester groups such as **4** or **5** are potential carrier materials for the immobilization of various materials, for example enzymes. The copolymerization conditions will be treated

in further studies to optimize the incorporation of ester units into the polymer.

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