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Scheme for the Anodic and Cathodic Transformations in Polythiophenes[†]

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ABSTRACT: The unique symmetric voltammetric behavior of anodically and cathodically conducting 3′-thienylterthiophenes supports the analogous interpretation of the anodic and cathodic transformations of thiophene type polymers. The splitting of the anodic current peak during the reoxidation of the cathodically transformed film is connected to the presence of more conjugated segments presumably because of the side-chain thiophenyl ring. According to the scheme both the anodic and cathodic processes leading to conductive forms start with the electrochemical oxidation or reduction of more conjugated segments. This can explain the blue shift in the absorbance of the neutral polymer in the UV–visible spectra during the insulating–conducting transformation.

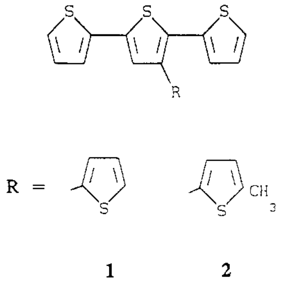
Introduction

In a recent work[1] spectroelectrochemical observations for the redox switching processes of anodically and cathodically conducting poly(3-methylthiophene) have been presented. On the basis of the results and thermodynamic considerations, a mechanism to describe the anodic and cathodic doping/undoping processes has been suggested[1] based on electrochemical, spectroscopic, and ESR studies of this polymer.[1–16]

It was thought that by studying poly(3′-substituted-2,2′:5′,2″-terthiophenes), new information can be obtained about the anodic and cathodic switching mechanism of polythiophenes. In a recent work[2] a series of substituted terthiophenes were systematically studied with the aim of finding such substitutent which has a determining effect on the extent of conjugation in the polymer. New results with films obtained by electrochemical polymerization of 1 and 2 (Figure 1) are presented in this paper.

Experimental Section

The experimental setup has been already described.[1,17] The synthesis of the monomers will be published elsewhere.[18] Electrochemical polymerization was achieved under galvanostatic conditions at a current density of 5 mA/cm^2, applying a short current pulse (i_0 = 25 mA/cm^2 for 100 ms) at the beginning of the deposition to a total charge of 50 mC/cm^2. The monomer concentration was 0.05 mol/dm^3; the concentration of the conducting electrolyte was 0.1 mol/dm^3 Bu_4NPF_6 in propylene carbonate(PC) whose water content was less then 30 ppm. After the reduction of the freshly prepared polymer film, the solution was changed to Bu_4NPF_6 in acetonitrile (AN) solution, and spectrovoltammetric measurements were performed to study both the anodic and the cathodic conduction of the polymer. The potential is given *vs* that of the applied Ag pseudoreference electrode, the potential of which had been determined with ferrocene: E = 0.60 V *vs* the Fc/Fc$^+$ redox couple.[17] Spectra were recorded on the optical multichannel analyzer OMA (PAR 1461 and 1463, EG&G) equipped with an extra memory card capable of storing up to 121 spectra. The OMA was controlled and the spectra were transferred to the computer via a GPIB bus. The potentiostat/galvanostat was connected to the 16-bit A/D–D/A data acquisition board DT2823 within the computer. All data acquisition was carried out using the ASYST language programming package.



Structure of 3'-substituted 2,2':5',2''-terthiophenes

Figure 1. Structure of 3′-substituted-2,2′:5′,2″-terthiophene monomers.

Results

Figure 2a shows the voltammetric curve obtained with 1 in both the anodic and the cathodic directions. The experimental results implicate that polythiophenes can be cathodically transformed to their conductive forms not only at low temperatures and/or NH_3 solution[14] but under the generally applied conditions,[13] as well.

The voltammetric curve (Figure 2a) showed an exceptional feature: the doubling of the current peak on the reverse branch of the voltammogram can be seen not only at the anodic but also at the cathodic side. The potential was cycled from −0.4 V to +1.3 V, then returned to −1.6 V, and finally back to −0.4 V, and the spectra were registered at each 100 mV. During this cycle the neutral polymeric layer was first oxidized (Figure 3) and then reduced (Figure 4), while in the cathodic potential region the neutral film was reduced (Figure 5) and reoxidized (Figure 6).

As for the spectral changes, the anodic transformation of the neutral polymer is accompanied by the well-known changes[1,13,14] in the visible spectrum (Figure 3) where the blue or hypsochromic shift for the absorbance of the neutral form is clearly observable.

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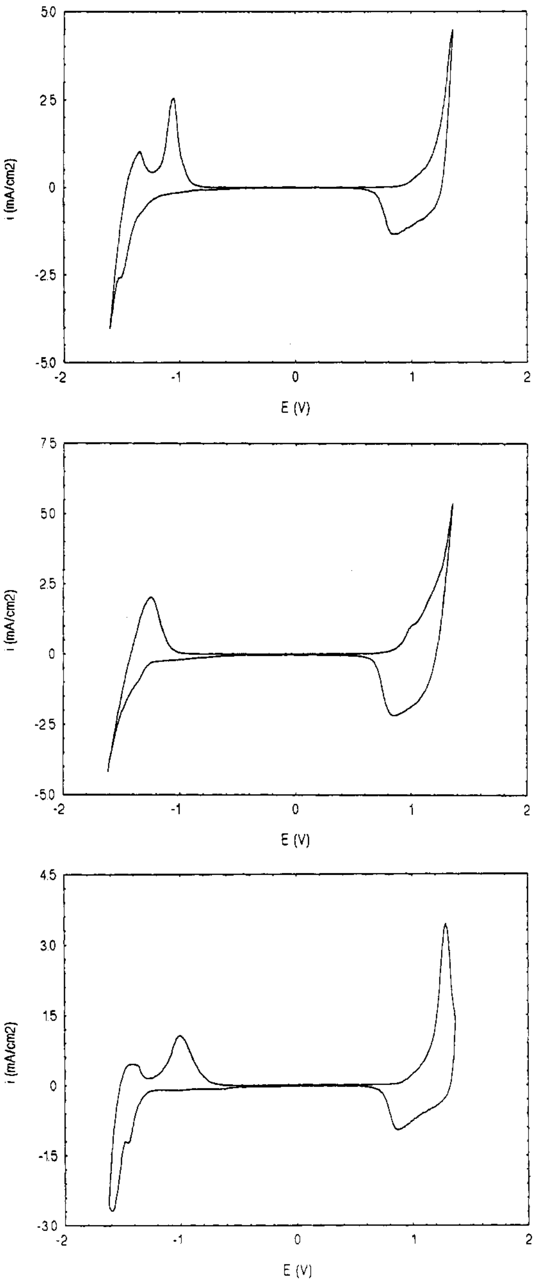

Figure 2. Voltammetric curves obtained with poly[3′-(2-thienyl)-2,2′:5′,2″-terthiophenes] in Bu_4NPF_6/AN solution. v = 100 mV/s: a (top), voltammogram of 1; b (middle), voltammogram of 1 after long-time cycling; c (bottom) voltammogram of 2.

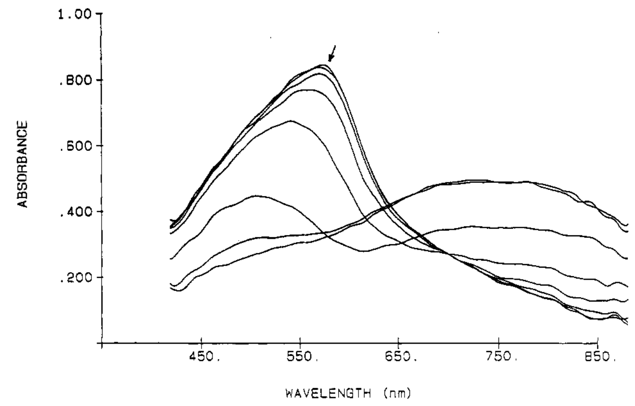

Figure 3. Spectral changes accompanying the anodic transformation of the neutral film of 1 during the potential cycle in the range of −0.4 to +1.3 V.

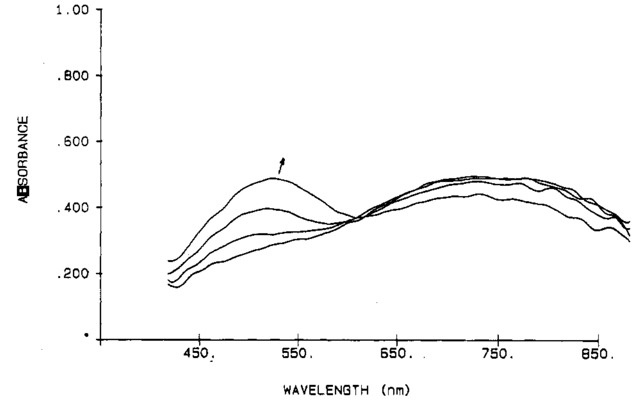

Figure 4. Spectral changes during the first section of the reduction of the anodically conducting polymer of 1 in the potential range of +1.3 to +1.0 V.

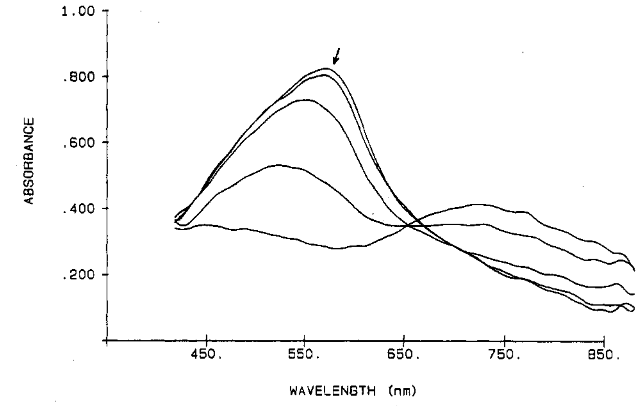

Figure 5. Spectral changes during the cathodic transformation of the neutral polymer of 1 in the potential region of −0.4 to −1.6 V.

After the anodic turning point during the first period of the reduction above +1.0 V, the absorption of the neutral form is increasing exhibiting a red or bathochromic shift, but there is no proportional decrease in the amount of mid-gap excitations (Figure 4). In the second section of the reduction in the potential range of +1.0 to +0.8 V, the film is returned to its neutral form.

During the cathodic sweep the spectral changes clearly show the achievement of the conducting state (Figure 5)—as the cathodic current alone does not necessarily mean the formation of a cathodically doped film[20]—and the transformation is reversible (Figure 6).

If we examine the cathodically conducting film in detail, we can observe the appearance of a reduction prepeak (Figure 2a)—similar to some cases of the anodic doping[7] which is connected to the applied consecutive anodic and cathodic polarization. The reoxidation process occurs in two separate steps, and the potential regions are below −1.22 and −0.90 V, respectively. By increasing the frequency of spectral data acquisition (Figure 6), we can see that—similar to the anodic "undoping"—the spectral changes are characteristic for the different potential regions: they follow the same stepwise feature as in the anodic case, and the very fast return to the neutral form takes place only in the second potential region.

After long-term cycling the two processes gradually overlap and the doubling or splitting of both the anodic and the cathodic reverse sections disappears (Figure 2b). This observation might be connected to some irreversible changes in the polymeric film.

The structure of 1 gives possibility for easy cross-linking. In order to see whether the previously observed character is somehow connected to the possibility of such two-

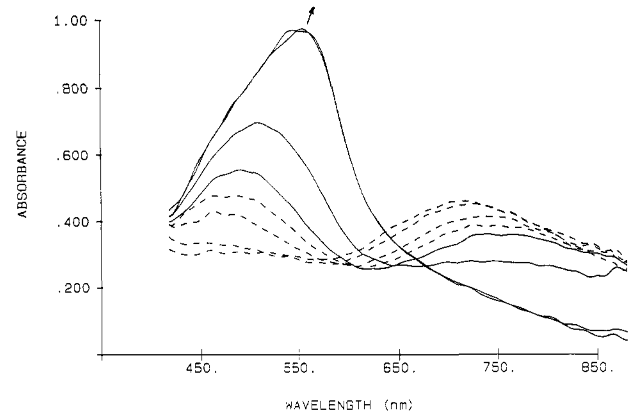

Figure 6. Spectral changes during the first (dashed) and the second (solid) anodic peak of the reoxidation of the cathodically conducting polymer of 1.

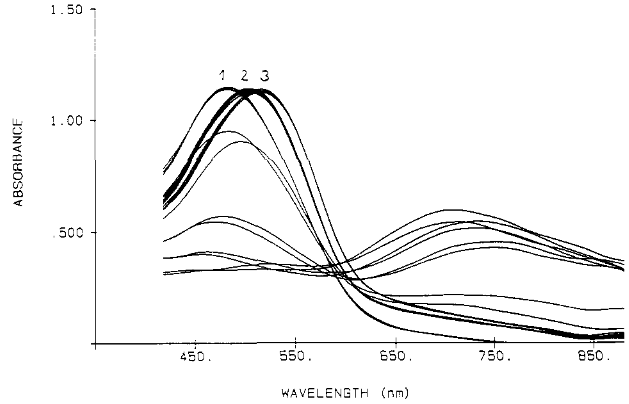

Figure 7. Spectral modification of the neutral form of a freshly prepared 1 polymer during the first cycle into the anodic and cathodic conducting potential regions: 1, before the voltammetric cycle; 2, after the anodic; 3, after the subsequent cathodic polarization.

dimensional effects, its methyl derivative **2** was also studied. Figure 2c shows that the same doubling of the voltammetric peaks can be seen at both sides of the curve with this polymer as well, where the opportunity for such an easy cross-linking is excluded by the blocking methyl group.

The bathochromic or red shift in the absorption maximum after the first cyclings with the freshly prepared **1** indicates (Figure 7) an increase in the effective conjugation length.[1,16] Thus, the presence of the side-chain thiophene ring along the polymer ensures an increase in conjugation in both derivatives, and this enhanced ability for conjugation is assumed to be responsible for the observed stabilization of the intermediate compound during the reoxidation of the cathodically conducting polymeric film.

Conclusions

On the basis of the symmetric voltammetric and spectral behavior of anodically and cathodically conductive polythiophenes, the similarity of their chemistry is concluded. The experimental facts allow extending the mechanistic conclusions made for the 3-methylthiophene[1] to all of the thiophene-type polymers (Schemes I and II).

Scheme I

INSULATING ⟶ CONDUCTING
TRANSFORMATIONS

TO CATIONIC FORM

$$A^{+} + n1 \longrightarrow A^{2+} + e^{-} \qquad E_{a,2/1}$$

$$n2 \longrightarrow A^{2+} + 2\,e^{-} \qquad E_{a,2}$$

$$n1 \longrightarrow A^{+} + e^{-} \qquad E_{a,1}$$

TO ANIONIC FORM

$$A^{-} + n1 \longrightarrow A^{2-} - e^{-} \qquad E_{c,2/1}$$

$$n2 \longrightarrow A^{2-} - 2\,e^{-} \qquad E_{c,2}$$

$$n1 \longrightarrow A^{-} - e^{-} \qquad E_{c,1}$$

Scheme II

CONDUCTING ⟶ INSULATING
TRANSFORMATIONS

FROM CATIONIC STATE

$$A^{2+} + e^{-} \longrightarrow A^{+} + n1 \qquad E_{a,2/1}$$

$$A^{2+} + 2\,e^{-} \longrightarrow n2 \qquad E_{a,2}$$

$$A^{+} + e^{-} \longrightarrow n1 \qquad E_{a,1}$$

FROM ANIONIC STATE

$$A^{2-} - e^{-} \longrightarrow A^{-} + n1 \qquad E_{c,2/1}$$

$$A^{2-} - 2\,e^{-} \longrightarrow n2 \qquad E_{c,2}$$

$$A^{-} - e^{-} \longrightarrow n1 \qquad E_{c,1}$$

According to the scheme in the case of both the anodic and the cathodic doping processes (I) the first thermodynamically possible process would be the transformation of the monoion. Thus, starting from the neutral form of the polymer—as there is no monoion—in both cases the first possible step of the reaction involves the species of higher effective conjugation length **n2**. The transformation of species of lower effective conjugation length **n1** takes place stepwise with the involvement of a neighboring neutral segment, but these two processes—for thermodynamic reasons—occur closely together.

The blue/hypsochromic shift during both types of transformation of the neutral film can be explained by the prior participation of species of higher effective conjugation in the reaction.

The opposite processes from the conducting to the insulating state (Scheme II) always take place stepwise, but the monoions are now considerably more stable. This can explain the doubling of the voltammetric current peak on the reverse branch of the curves. During these processes, the segments of shorter conjugation length are obtained back first *via* a dissociation reaction of the diions. This causes the observed red or bathochromic shift in the visible spectra. The reverse order of the electrochemical steps during the insulating–conducting and the opposite conducting–insulating transformations of the polymer provides a reasonable explanation for the hysteresis observed even under steady-state circumstances.

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