

# Poly(dibenzylidenetetrathiapentalene): A Redox-Active, Linearly Extended TTF Polymer

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The  $\pi$ -conjugated polymers **poly-1** and **poly-2** composed of vinylogous tetrathiafulvalene (TTF) units were obtained by electrochemical polymerization of 2,5-di(benzylidene)-1,3,4,6-tetrathiapentalene (**1**) or of its corresponding dimer 1,2-bis(5-benzylidene[1,3]-dithiolo[4,5-*d*]1,3-dithiole-2-ylidene)-1,2-diphenylethane (**2**). The polymers were characterized by cyclic voltammetry (CV), in situ ESR spectroscopy and in situ conductivity measurements to gain insight into the charge–discharge behavior and the electronic properties as a function of applied potential. Our results suggest that both compounds behave as conducting polymers exhibiting multistep redox activity. In situ ESR studies show that charge–discharge phenomena differ in the nature of the charge storage configuration depending on whether they are investigated during a cathodic or anodic scan. Reduction of a polymer film generated at an applied potential of +1.6 V vs SCE allows for the detection of three clearly discernible maxima of the spin density at 0.60, 0.95, and about 1.25 V vs Ag, while subsequent reoxidation gives rise to only one spin density maximum at around 0.65 V vs Ag. Coulometric studies suggest that the spin density maximum at around 0.60–0.65 V vs Ag is associated with one positive charge per tetrathiapentalene unit of **poly-1** while each monomer bears up to two charges at a potential of 1.6 V vs Ag. In situ and conventional four-probe measurements of the electrical conductivity gave values of around  $5 \times 10^{-5} \text{ S cm}^{-1}$ .

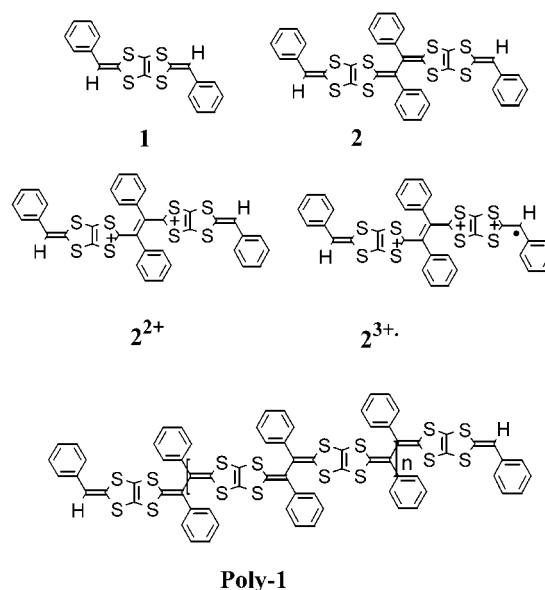
## Introduction

Considerable efforts have been made to prepare conjugated materials incorporating tetrathiafulvalene (TTF) units in oligomeric<sup>1</sup> or polymeric<sup>2</sup> structures with the objective to combine the electronic conductive properties of TTF radical salts with the processability of a polymer matrix.<sup>3</sup>

In this context, we have recently reported a novel synthetic approach to a  $\pi$ -conjugated TTF polymer composed entirely of vinylogous, linearly fused TTF moieties using 2,5-(dibenzylidene)-1,3,4,6-tetrathiapentalene (**1**) as precursor (Chart 1).<sup>4</sup> Chemical or electrochemical oxidation of **1** leads in one step to poly[(dibenzylidene)-1,3,4,6-tetrathiapentalenes], (**poly-1**), with an average molecular weight  $M_w = 19500$  and  $M_w/M_n = 3.54$ , as determined by gel permeation chromatography.<sup>5,6</sup>

The first steps of the polymerization mechanism have been elucidated and provided clear-cut evidence for a mechanism different from those known for the formation of classical conducting polymers, such as polythiophene or polypyrrole and their derivatives. Chain growth of **poly-1** starts with a radical dimerization at the benzylic carbon atoms of the TTF monomer to give the dimeric dication **2**<sup>2+</sup> as an intermediate;<sup>7,8</sup> further chain growth requires oxidation to the radical trication **2**<sup>3+</sup>.

CHART 1: General Formula of of 2,5-Di(benzylidene)-1,3,4,6-tetrathiapentalene (**1**), Dimer **2**, Various Intermediates and Neutral Polymer **poly-1**



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ESR spectroscopy is ideally suited for studies of spin–charge relations in electrochemically active polymers, especially in view of the fact that this method can be easily coupled with CV and other electrochemical techniques.<sup>9,10</sup> In situ ESR spectro-electrochemical studies on polyaniline,<sup>11</sup> polypyrrole,<sup>12</sup> and their copolymers,<sup>13</sup> as well as on dimerization<sup>14</sup> or  $\pi$ -stacking of oligothiophenes<sup>15</sup> and polythiophenes<sup>16</sup> have been reported. To

date and to the best of our knowledge, only one in situ ESR spectro-electrochemical study of a polymeric TTF derivative composed of individual TTF units attached to a polystyrene backbone has been hitherto described.<sup>17</sup>

In situ conductivity measurements have been widely used for characterizing the oxidized states responsible for the electrical conductivity of various electroactive organic materials.<sup>18</sup> In particular, electronic conducting polymers exhibit large potential windows of conductivity due to spin and spinless charges carriers<sup>19</sup> while redox polymers show narrow conductivity windows due to electron hopping between the redox sites.<sup>20</sup>

Here we discuss the redox behavior of new linearly extended TTF polymers obtained by electropolymerization of the TTP derivative **1** or its corresponding dimer **2**. To characterize the redox states created upon oxidation we have carried out detailed cyclic voltammetry and coulometric studies on **poly-1** and **poly-2**. Moreover, hyphenated techniques, such as CV-ESR and CV-electrical conductivity measurements, were employed to correlate redox and conducting states of **poly-1**.

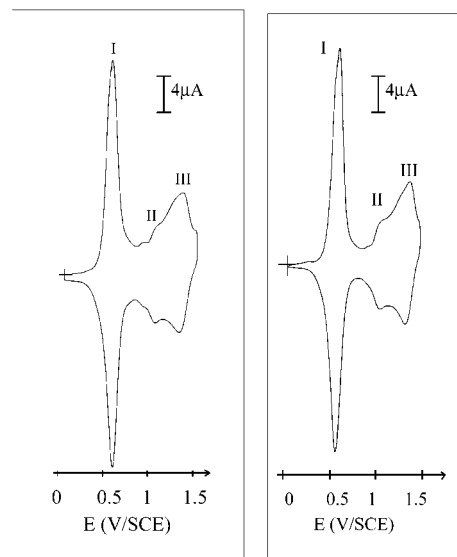
## Experimental Section

### Reagents, Chemicals, and Electrochemical Procedures.

Air- and moisture-sensitive reactions were carried out in oven-dried glassware in argon atmosphere. The monomer 2,5-(dibenzylidene)-1,3,4,6-tetrathiapentalene (**1**) and the dimer 1,2-bis(5-benzylidene[1,3]-dithiolo[4,5-*d*]1,3-dithiole-2-ylidene)-1,2-diphenylethane (**2**) were prepared as described previously.<sup>4</sup> Precursors **1** and **2** were obtained as a mixture of *cis* and *trans* (*E/Z*) isomers and used as such. CH<sub>2</sub>Cl<sub>2</sub> was distilled from P<sub>2</sub>O<sub>5</sub> and stored in a drybox in an argon atmosphere. The supporting electrolyte *n*-NBu<sub>4</sub>PF<sub>6</sub> was purchased from Fluka (puriss. p.a.) and dried at 100 °C under vacuum. Solutions and polymers were always prepared freshly before experiments. Dissolved oxygen was removed by bubbling argon through the solutions. The electrochemical syntheses of films used for in situ ESR spectro-electrochemical experiments were carried out in a drybox in an argon atmosphere. The electrochemical equipment consisted of a PAR Model 273A with a classical three-electrodes arrangement. The electrolyte solutions used for CV and CV-ESR studies were 0.1 mol L<sup>-1</sup> *n*-NBu<sub>4</sub>PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>. A 0.07 cm<sup>2</sup> platinum electrode was used as the working electrode. Potentials were measured relative to an aqueous saturated calomel electrode SCE ( $E^\circ/\text{SCE} = E^\circ/\text{SHE} - 0.2412 \text{ V}$ ) with a salt bridge containing the supporting electrolyte. The SCE was checked against the ferrocene/ferricinium couple in CH<sub>2</sub>Cl<sub>2</sub>/0.1 M *n*-NBu<sub>4</sub>PF<sub>6</sub> ( $E^\circ = +0.46 \text{ V/SCE}$ ). The working electrode was carefully polished before use with 1 μm diamond paste and cleaned in an ultrasonic bath with absolute ethanol.

Electrosynthesis of the polymer films was performed in solutions containing  $5 \times 10^{-4} \text{ mol L}^{-1}$  of **1** or **2** in the electrolyte used for CV either by continuous cycling between 0 and 1.6 V at  $\nu = 100 \text{ mV/s}$  or by potential step electrolysis at 1.67 V.<sup>4,5</sup>

**In Situ Four-Probe Resistance Measurements.** An array of gold microelectrodes was deposited on a glass substrate using an evaporation technique.<sup>21</sup> Inter-electrode spacing was of 2 μm and the surface of each microelectrode was 0.66 mm<sup>2</sup>. The deposition of a homogeneous layer of **poly-1** capable of bridging four adjacent electrodes required typically between 8 and 10 mC cm<sup>-2</sup>. A homemade stabilized power supply was used to connect the two outer electrodes. The electrical resistance was recorded with a BD91 Kipp & Zonen X-Y-Y' recorder, calibrated with a RS components ohmmeter; the sample thickness of the polymer film in the reduced state was measured using a Tencor profilometer.



**Figure 1.** Cyclic voltammogram (0.1 V s<sup>-1</sup>) in CH<sub>2</sub>Cl<sub>2</sub> + 0.1 mol L<sup>-1</sup> *n*-Bu<sub>4</sub>PF<sub>6</sub> of a freshly prepared **poly-1** (left), and **poly-2** (right) film deposited on Pt (Ø 3 mm) by scanning the electrode potential between 0 and 1.6 V vs SCE.

**Four-Probe Resistance Measurements.** Resistance measurements were carried out either on films electrodeposited on glass-substrates as described above or on compaction samples with a Jandel Universal Probe 4. In the former case, the two inner electrodes were connected to a high impedance voltmeter (Keithley 617) and the two outer electrodes to a calibrated current source (Knick-DC Calibrator J 152).

**ESR Spectro-electrochemistry.** ESR spectro-electrochemical experiments were carried out with an ER 200 X band Bruker spectrometer in a small electrochemical quartz cell with two platinum wires (working and counter electrodes) and an Ag electrode used as pseudo-reference. The Ag electrode was checked against the ferrocene/ferricinium couple ( $E^\circ = 0.44 \text{ V/Ag}$ ) after each experiment. Polymer films were grown as described previously by electropolymerization using a charge of 25 mC at 1.7 V vs SCE in a conventional three-electrodes cell. After rinsing, the film adhering to the electrode was transferred in the ESR spectro-electrochemical cell. Potential cycling was performed in monomer-free electrolyte (CH<sub>2</sub>Cl<sub>2</sub>/0.1 M *n*-NBu<sub>4</sub>PF<sub>6</sub>). The redox state of the polymer was monitored by a DC voltage applied to the working electrode over a potential window ranging from +0.3 to +1.6 V vs Ag in small increments of 0.020 V. For each experimental point the ESR susceptibility was determined by double integration of the ESR signal and by comparison with the signal of a calibrated reference placed in the same dual cavity.

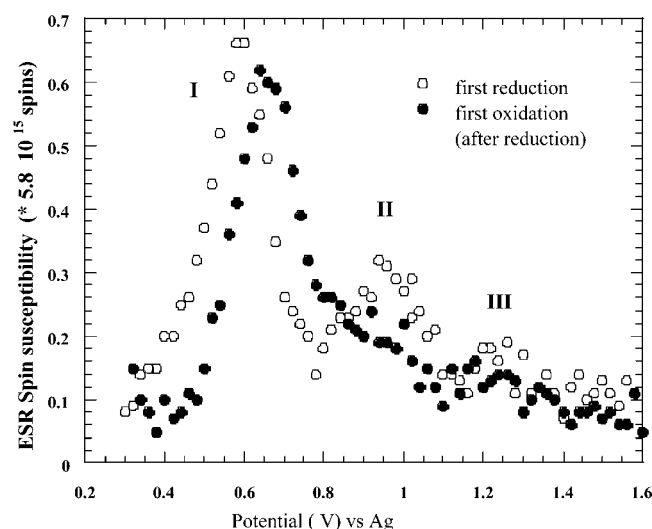
## Results

**Electrochemical Properties of poly-1 and poly-2.** The CVs of **poly-1** and **poly-2** in monomer-free solution are shown in Figure 1. The electrochemical responses consist of a narrow reversible wave (I) at +0.55 V vs SCE followed by several broad, reversible waves (II and III) between +0.9 to 1.5 V. The half sum potential values  $E_{1/2}$  of the three principal waves, defined as the half sum of the oxidation and reduction peak potentials, are given in Table 1. Both curves are very similar, suggesting a close resemblance of the polymeric products obtained from different precursors and exhibit reversible, symmetrical signals characteristic of immobilized redox species on an electrode.<sup>22</sup> This interpretation is supported further by

**TABLE 1:**  $E_{1/2}$  Values of poly-1 and poly-2<sup>a</sup>

polymers	$E_{1/2\text{I}}$ (V/SCE)	$E_{1/2\text{II}}$ (V/SCE)	$E_{1/2\text{III}}$ (V/SCE)
poly-1	0.55	1.11	1.42
poly-2	0.57	1.10	1.37

<sup>a</sup>  $E_{1/2} = (E_p^{\text{ox}} + E_p^{\text{red}})/2$  in  $\text{CH}_2\text{Cl}_2$ .



**Figure 2.** In situ ESR electrochemical experiment: ESR susceptibility versus electrochemical potential on **poly-1**; o: during the first reduction (decreasing potential from 1.6 to 0.3 V); •: during the first oxidation after reduction (increasing potential from 0.3 to 1.6 V).

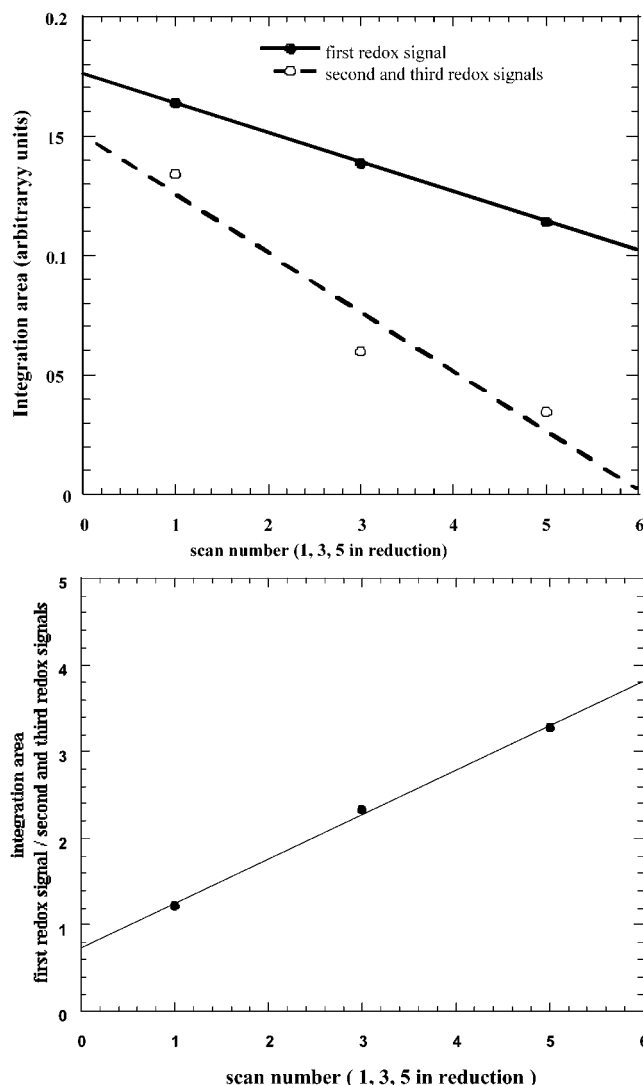
the linearity of peak intensities vs the scan rate in the range of 10 to 100  $\text{mV s}^{-1}$ .

The faradaic charge associated with redox couple (I) is roughly equal to the charge involved in the redox couples II and III. Hence, one-electron oxidation of the polymer generates a half charged state (I) at a potential of 0.9 V vs SCE, whereas a second one-electron oxidation occurs in two steps (II and III) requiring a much higher potential for completion (+1.6 V vs SCE). The application of even higher potentials results in an irreversible degradation of the film as a consequence of overoxidation.

The relaxation potential value of the oxidized polymer is about 0.6 V which corresponds approximately to the formal potential of redox system (I). In its relaxed state, the structure of the polymer may be considered to be in an equilibrium state between the half-charged polymer and a less charged state.

**ESR Measurements.** The in situ ESR experiments were carried out on **poly-1**. The electrodeposition of **1** requires a potential of 1.67 V vs SCE. To prevent overoxidation, experiments were performed on freshly deposited films in a reverse mode, i.e. the reduction scan preceded oxidation. Figure 2 shows the potential dependence of the ESR signal intensity as observed during the reduction scan in the potential range from +1.6 to +0.3 V vs Ag, as well as the subsequent oxidation scan in the reverse direction. The spin density shows three clearly discernible maxima during the cathodic scan. The potential values of the three maxima at 1.25, 0.94, and 0.64 V (Figure 2) correlate well with the oxidation peak potentials of redox waves III, II, and I observed independently in the CV of **poly-1**. Interestingly, reoxidation of the polymer film gave rise to only one spin density maximum at a potential value close to that of redox wave I.

Subsequent reduction and oxidation scans gave comparable results, albeit the intensity of all signals decreased and potential values shifted slightly. The decrease in signal intensities as a



**Figure 3.** (a) Integrated surface area (arbitrary units) of the first (•) and the second and third (o) redox peaks recorded during the reductions scans (1,3,5); (b) Ratio of the integrated surface area of the first and the second and third (together) redox systems recorded during the reduction scans (1,3,5).

function of the repetitive potential cycle  $n$  is shown in Figure 3a. The intensities of all signals diminished linearly with each completed scan, whereby the loss of signal intensity is much more pronounced for maxima II and III. Such behavior could indicate irreversible changes at higher potentials.

The ESR signal intensity of maximum I determined during the first cathodic scan is approximately equal to the sum of the signal intensity of maxima II and III (cf. Figure 3b), a result in good agreement with the CV data presented above. However, an inversion of the intensities is observed between maxima II and III and the corresponding peak currents of CV experiments. Furthermore, the ratio of the spin density intensities of maximum I over the sum of maxima II and III increases drastically with the number of scans.

ESR spectra recorded during the first cathodic scan at different potential values are presented in Figure 4. At higher potentials (1.5 V), i.e., in the completely oxidized polymer film, only a broad signal with a line width  $\Delta H = 5$  G of low intensity, tentatively assigned to the presence of residual spins, is observed. Upon lowering the potential to 0.96 V, a sharp line is superimposed on the broad signal, indicating the coexistence of two nonequivalent paramagnetic species. The line with a

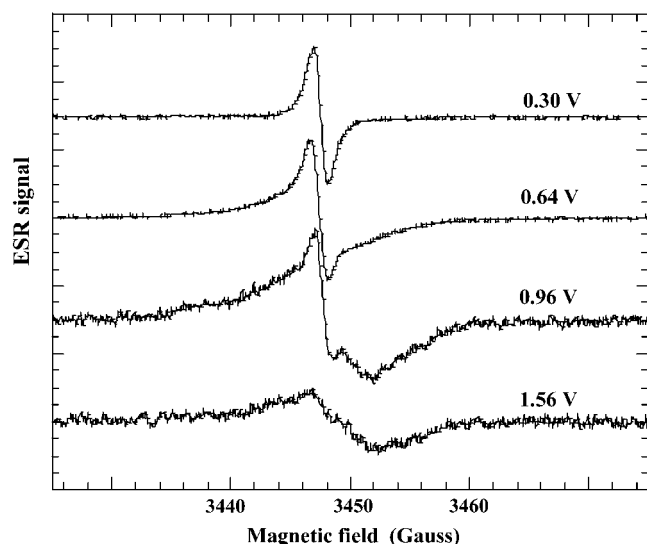


Figure 4. ESR spectra for different values of the redox potential.

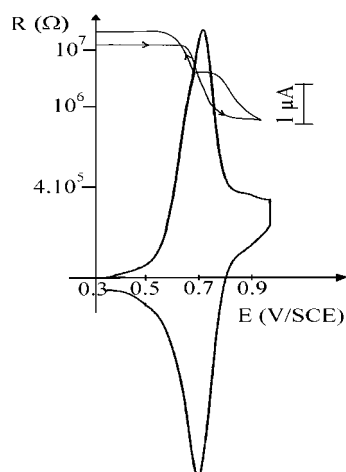


Figure 5. In situ resistance measurement and CV of **poly-1** in  $\text{CH}_2\text{-Cl}_2 + n\text{-Bu}_4\text{NPF}_6$   $0.1 \text{ mol L}^{-1} + \mathbf{1}$ ,  $5 \times 10^{-4} \text{ mol L}^{-1}$ ;  $\nu = 5 \text{ mV s}^{-1}$ ; Au electrodes; overall electrosynthesis charge:  $8 \text{ mC}$ ; film thickness:  $0.8 \pm 0.1 \mu\text{m}$ .

small value of  $\Delta H$  (about 1 G) is assigned to a single radical species, interpreted as highly mobile spins whereas the broad signal is attributed to spins localized on the polymer chain.<sup>23</sup> At 0.64 V, only one sharp signal is observed which corresponds to radicals associated with redox system I in the CV of the polymer (wave I). The signal at 0.3 V is attributed to residual spins in the reduced form of the polymer. This residual signal vanishes in the equilibrium reduced state.

**In Situ Conductivity Experiment.** To identify the redox states of **poly-1** which result in the observed electronic conductivity of the polymer, in situ cyclic voltammetry and simultaneous resistance measurements have been performed. In situ conductivity experiments performed on **poly-1**<sup>24</sup> show that the resistance reaches a minimum at a potential corresponding to the first redox wave I of **poly-1** (Figure 5) and corresponds to the first maximum of the spin concentration. The highest value of the electrical conductivity determined by in situ measurements amounts to about  $4 \times 10^{-5} \text{ S cm}^{-1}$  and is thus very close to values determined by classical four-probe measurements on compaction samples or on electrodeposited films. At higher potential values, the resistance increases rapidly with increasing potential and results eventually in insulating behavior (not shown).

## Discussion

In principle, the electropolymerization of **1** and **2** should lead to the same polymer, provided that the same type of electrochemical coupling occurs in both cases. This hypothesis is corroborated by spectroscopic and electrochemical data. First the electropolymerization of both **1** and **2** occurs at very high potential values corresponding to the trication radical  $2^{3+}$ , suggesting that the backbone of both polymers is constituted of the same dimer units. Moreover, IR spectra of **poly-1** and **poly-2** recorded for the reduced (undoped) and oxidized (doped) states are very similar and in accordance with the respective spectra of polymers containing vinyllogous extended fused TTF structural units.<sup>25</sup> Finally, the CVs of both polymers are very close and exhibit three principal redox systems (I, II, III in Figure 1) essentially identical in shape.

For clarity, it is better to discuss separately the redox couple I and the couples II and III since they distinctly differ in their electrochemical and spectro-electrochemical behavior. There are two characteristic features of the first oxidation peak of both **poly-1** and **poly-2**. First, it occurs at roughly the same potential as the corresponding peak of both the monomer **1** and the dimer **2**. Second, it is unusually narrow as compared to the oxidation peaks of other conductive polymers.

Such behavior is new when compared to the redox behavior of classical conducting polymers such as polypyrrole<sup>26</sup> or polythiophene.<sup>27</sup> For the latter, the oxidation potential of already formed polymer exhibits a cathodic shift of a few hundred millivolts in comparison to the oxidation potential of the monomer. In addition to being shifted to lower potentials, the peak significantly broadens. Similar shifts are detected for oligomers which are frequently studied as short chain models of conjugated polymers. A cathodic shift of 370 mV is observed between the oxidation potential values of the thienylenevinylene dimer and tetramer and an additional 90 mV occurs when going from the tetramer to the hexamer.<sup>28</sup>

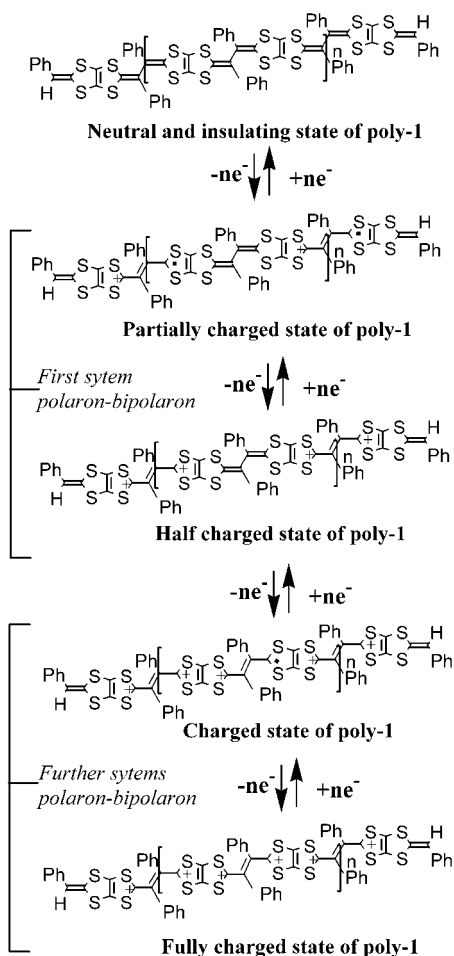
The narrow shape of the first oxidation peak (I) seems to indicate that there are no (or very little) interactions between the redox sites. Consequently, the redox centers are mutually independent and both **poly-1** and **poly-2** behave like typical redox polymers in the potential range  $0 \leq E \leq 0.8 \text{ V vs SCE}$ . As has been already stated, microcoulometric studies show that the polymer is half-charged at a potential of around 0.6 V vs SCE.

It is convenient to correlate the CV and coulometric studies with electrochemical spin response monitored by ESR for the potential range covering the first redox system. From Figure 2 it is clear that the electrochemical spin response follows the current response registered by cyclic voltammetry for both the oxidation and the reduction scans. In the relaxed oxidized state the polymer potential value corresponds to the formal potential of the first redox system and exhibits a spin-containing state.

From the experimental findings described above the following picture emerges: In the reduced state the polymer is neutral and spinless (see Chart 2). In reality, immediately after reduction the polymer shows a small number of residual unpaired spins which disappear upon relaxation. A potential increase results in the formation of radical cations whose concentration reaches a maximum at the potential of the first oxidation peak. The decrease of spin density starts at the potential greater than 0.65 V vs Ag and can be taken as evidence of the recombination of radical cations (polarons) into spinless dicationic (bipolarons). Radical cations formation and their transformation into spinless dicationic should not be considered as consecutive processes.



## CHART 2: Redox Behavior of poly-1



The recombination of radical cations into dications can in principle occur at any potential of the first redox system. The presence of the maximum in the electrochemical spin response curve shows only that the rate of radical cation formation is higher than the rate of their recombination to dications for potentials up to 0.65 V. At higher potentials, the recombination processes dominate because less and less radical cations are formed. At the end of the first oxidation process the polymer is in its half oxidized state with spinless bipolarons as charge storage configuration. Its chain microstructure can be considered as a regular alternation of oxidized vinyllogous TTF, corresponding to the dication  $2^{2+}$  entities, and reduced vinyllogous TTF units (see Chart 2). The half oxidized state is conductive as can be seen from Figure 5. The first oxidation process is accompanied by a significant drop in the resistance of the sample.

Further oxidation of the half oxidized polymer should proceed via oxidation of the remaining reduced vinyllogous-TTF units to radical cations. This process can be formally treated as the formation of trication radical in the dimeric repeat unit (see Chart 2). However, no new spins are detected upon further potential increase to the values corresponding to the II and III oxidation peaks. Evidently, the recombination of free radical cations to spinless dications is sufficiently fast so that the intermediate spin-carrying state cannot be detected in our experiment. Of course, such recombination of radical cations into spinless dications leads to a significant heterogeneity in the polymer chain since now the charge is not evenly distributed but fully oxidized units (spinless tetracations of each dimer repeat unit)

coexist with half oxidized units (spinless dications of each dimer repeat unit).

At this stage, Coulombic repulsive interactions become dominant and the drain is no longer isoenergetic as in the case of the first oxidation process where essentially no interactions existed between charges present in a rather low concentration. These interactions give rise to the observed broad and overlapping oxidation peak in CVs of **poly-1** and **poly-2**.

Note that, as evidenced by cyclic voltammetry, the oxidation of the half oxidized polymer to the fully oxidized one is a two-step process. The fully oxidized state is spinless as schematically depicted in Chart 2. This process is somehow similar to that reported for conjugated metallopolymers with strongly interacting metal-based redox sites.<sup>29</sup> In this case the oxidation of alternating Fe sites of polyferrocenes chains has been suggested as the explanation of the observed redox properties.<sup>30,31</sup> This type of alternating oxidation can also be proposed for the systems studied in this work.

Interestingly, the electrochemical spin response is different in the reversed scan, i.e., during the reduction of the fully oxidized polymer. As already stated, no spin formation was detected for the oxidation processes II and III. This is not the case for the reduction scan. In the latter case we observe two clear maxima of spin density (reduction process III and II) whose sum, in the first reduction scan, is roughly equal to the intensity of the maximum of spin density observed for the reduction process I. The spin response can be very well correlated with the three reduction peaks registered in cyclic voltammetry. It is therefore clear that the reduction of the fully oxidized polymer occurs via the formation of the trication radical in the dimeric unit  $2^{3+}$ , then via the spinless half oxidized state, radical cation of the dimeric unit  $2^{+}$  to the neutral polymer as the final reduction product, as schematically depicted in Chart 2.

The main question still to be answered is why the electrochemical spin response for the II and III redox processes is, in the reduction scan, different from that registered in the oxidation one. It is probably associated with the difference in the initial state. In the oxidation scan the initial state is half oxidized **poly-1** in which the oxidized and reduced units coexist in equal numbers. It is very probable that upon further oxidation the relaxation of the chain with simultaneous recombination of radicals is easier. As a result no free radical is detected by our rather slow ESR-potential scan experiment.

To the contrary upon reduction of fully oxidized polymer relaxation phenomena may be impeded which allows for a significant lifetime of the radical cations formed. As a result the electrochemical spin response is clear and follows the current response observed in cyclic voltammetry. The properties of the spins created upon electrochemical reduction require a more detailed discussion.

First, one must notice that the residual spins, sometimes observed by ESR, in small quantities in the totally oxidized polymer which is nominally spinless (Chart 2), give a broad line characteristic of immobilized radicals. Evidently, residual polarons which may be "trapped" between spinless domains of fully oxidized polymers are efficiently immobilized radicals. The reduction of the polymer results in the growth of the intensity of this broad line which reaches the first maximum at  $E = 1.25$  V and the second at  $E = 0.96$  V. At this latter potential, the spectrum is not homogeneous and consists of two superimposed lines: the previously described broad line and a new narrow line with  $\Delta H$  of about 1 G. The narrow line is characteristic of high spin mobility. Such picture implies a significant heterogeneity of the system at  $E = 0.96$  V. Since

the polymer is conductive at this potential (see Figure 5), it may be postulated that it consists of percolating domains of the conductive phase of **poly-1** in its half oxidized state and insulating domains of **poly-1** in the oxidation state of the trication radical. Spins in the conductive phase give rise to the narrow ESR line, whereas those in the insulating phase contribute to the broad one.

The contribution of mobile spins to the overall spin density is rather small. Thus the charge carriers in the conducting phase are predominantly spinless bipolarons which is consistent with the anodic scan results. In the anodic scan charge carriers at this potential were spinless bipolarons.

Further lowering of the potential to values corresponding to the reduction process I results in the disappearance of the broad line corresponding to fixed spins while the narrow signal due to mobile spins reaches its maximum at  $E = 0.64$  V. At this potential the polymer is still conductive. Since these mobile spin carriers are also charge carriers (polarons), it may be postulated that the polarons created at this stage of reduction contribute to the conductivity together with spinless bipolarons.

## Conclusion

In summary, we have demonstrated that electropolymerization of either 2,5-di(benzylidene)-1,3,4,6-tetrathiapentalene **1** or of the corresponding dimer **2** lead to the same polymer. This new conjugated polymer exhibits an unusual multistep electrochemical behavior, distinct from that observed for classical conjugated polymers such as polythiophene or polypyrrole.

CV studies combined with coulometry, in situ ESR electrochemistry, and in situ conductivity vs potential measurements enabled us to elucidate the electrochemical redox processes and to identify at which redox state the polymer becomes conductive. The electrochemical and in situ ESR properties show clearly that **poly-1** behaves as a redox polymer with multiple redox sites. Moreover, the conductive properties are due to the formation of polaron–bipolarons charge carriers similar to that observed for classical electrical conducting polymers.

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