

Emese Kriván · Csaba Visy

New phenomena observed during the electrochemical reduction of conducting polypyrrole films

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Abstract Properties of polypyrrole/dodecyl sulfate films were studied by different spectroelectrochemical, ex situ alternating current conductance and IR techniques. It was demonstrated that the open-circuit time after the accomplishment of the electropolymerisation has a key role in the redox behaviour of the film. Layers reduced immediately after the deposition exhibit different charge capacity, conductance and reducibility: once the film was reduced in this manner, it could be transformed into either the totally neutral or the quasimetallic state anymore. The pristine film can reach the quasimetallic state only after a certain period of time at open circuit. The reduction of this film can be interpreted by a dissociation-type first step, instead of the classical consecutive two-step mechanism.

Keywords Polypyrrole · Electrochemical reduction · UV-vis · Conductance · Open-circuit relaxation

Introduction

Owing to their high stability and good conductance, polypyrrole (PPy) films grown in the presence of surfactants such as dodecyl sulfate (DS) [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11] and dodecylbenzene sulfonate [11, 12, 13, 14] have been widely investigated. Moreover, in the case of these anions the polymerisation can be conveniently achieved in aqueous solution.

The effect of the synthesis conditions on these polymers was examined from many aspects in earlier studies

[15, 16, 17] which revealed that these bulky anions are captured in the film during its synthesis. It is well known that the electrochemical parameters have crucial importance as well as the concentration of the monomer or the supporting electrolyte. Recently, it was observed that the conductance of polymer films reasonably changes in time after the polymerisation [18]: just waiting at open circuit after the accomplishment of the electrochemical polymerisation of 3-methylthiophene, the conductance increases in time. It means that a fundamental property of the polymer layer might be determined also by a post-polymerisation factor. The aim of the present work was to study the effect of this postpolymerisation factor upon the most important properties of the PPy film, such as electrochemical, optical and conductance behaviour. As will be demonstrated, the open-circuit time (OCT) following the polymerisation has a key role in the redox activity of the film. Under special circumstances, the film cannot be reduced completely, while after enough OCT the film is perfectly reducible. These two kinds of films – reducible and nonreducible – are called “regular” and “irregular” films throughout this article.

Experimental

The monomer solution was prepared by using pyrrole (Sigma) distilled freshly in vacuum, sodium dodecyl sulfate (SDS, Sigma) as received and MilliQ water. The concentrations of the solutions were 0.05 M for both pyrrole and SDS. The spectroelectrochemical experiments were carried out at room temperature in a three-electrode spectroelectrochemical cell. The PPy films were electrodeposited galvanostatically onto an ITO working electrode ($A=0.28\text{ cm}^2$) at 3 mA/cm^2 current density and at 67.5 mC/cm^2 charge density. The reference and the counter electrodes were an Ag/AgCl microelectrode and a gold-plated steel electrode, respectively. UV-vis spectra were acquired with an HP 8452A diode-array spectrophotometer and the electrochemical experiments were executed using a PGSTAT 10 (Autolab) instrument. Further experimental details have already been published [10, 19].

In the OCT experiments the films were reduced in the monomer solution after the polymerisation. Following the reduction, the monomer solution was exchanged by 0.05 M SDS solution.

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E. Kriván (✉) · C. Visy
University of Szeged, Institute of Physical Chemistry,
P.O. Box 105, 6701 Szeged, Hungary
E-mail: krivan@chem.u-szeged.hu
Tel.: +36-62-544616
Fax: +36-62-544652

Results and discussion

It is well known that PPy films can be reversibly switched between conducting and nonconducting states; thus, their oxidation/reduction charge ratio should be close to 1. If the reduction charge is significantly lower than the oxidation one, degradation of the film – originating, for example, from its overoxidation – has to be taken into account; however, in certain circumstances it can be that the ratio is smaller than 1. As Fig. 1 shows, the oxidation charge integrated during a stationary scan is almost constant in the sweep rate range studied. At the same time, the reduction charge starts to increase with the decrease in the scan rate. These two tendencies result in a sharp increase in the charge ratio at small sweep rates. A similar extra reduction charge was demonstrated [18] and connected to a non-Faraday process taking place in the oxidised state. The observation in Fig. 1 supports the assumption that slow perturbations, when the film spends a longer time in the oxidised state, give an opportunity for the occurrence of a similar transformation in case of the PPy/DS film.

Since this behaviour may be connected to the phenomenon observed after the accomplishment of the electropolymerisation, we decided to study the effect of the OCT for “relaxation” processes before the electrochemical reduction of the pristine film.

In Fig. 2a we can see the spectrum of the PPy film at the end of the polymerisation process (curve 1). In the case of the regular reduction – when the film is reduced after 180 s OCT – the absorbance at the higher wavelengths decreases quickly, while the absorbance increases significantly around 400 nm (curve 2). At the end of the complete reduction (curve 3) only one wide band can be seen, which belongs to the π – π transition of the neutral polymer. Figure 2b shows absorbance versus time curves at three characteristic wavelengths (550, 800,

400 nm) which are widely attributed to the polaron, bipolaron and neutral forms of PPy, respectively.

However, when we reduced the film immediately after the accomplishment of the electrochemical polymerisation (irregular reduction), it could not be reduced completely (Fig. 3a, curve 2), although this film was polymerised exactly in the same way as the previous one – proved by the identical final spectrum (curve 1). Curve 2 shows that the film could not reach its neutral form (see Fig. 2a, curve 3) – characterised by one wide absorption at 400 nm. Thus, it seems that depending on the OCT, during which the film may relax between the polymerisation and the reduction, the spectral development during the reduction is greatly different. It seems as if the irregular film was a mixture of reduced and non-reduced parts.

The absorbance versus time curves (Fig. 3b) clearly show that – though the reduction has been started – a new process takes place later, resulting in a spectrally different film. These unusual spectral changes – the absorbance at 800 nm is “fed back” in parallel with the absorbance increase at 400 nm at constant optical

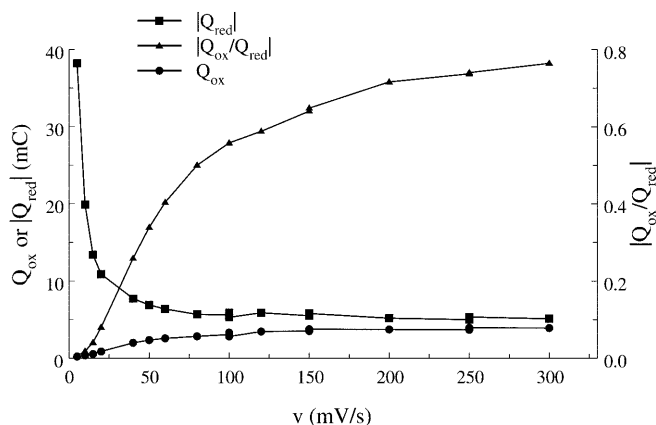


Fig. 1 The oxidation charges and the absolute values of the reduction charges (*left*) and their ratio (*right*) versus sweep rate curves obtained during the redox transformation of polypyrrole (PPy)/dodecyl sulfate (DS) film in sodium dodecyl sulfate (SDS) solution

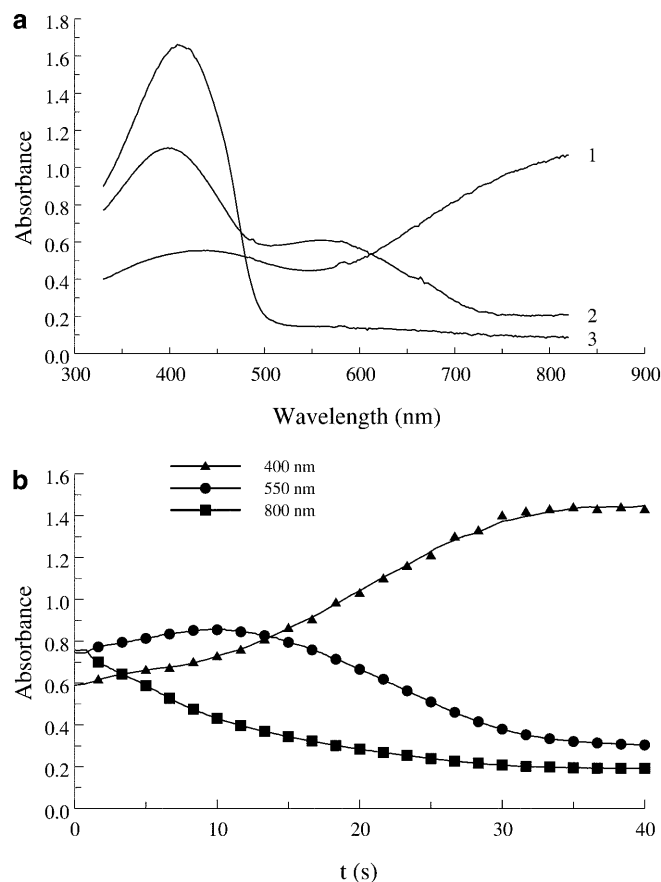


Fig. 2 **a** Spectra of PPy/DS film at the end of the polymerisation (1), during (2) and at the end of the reduction (3). The film was reduced at -0.6 V (versus Ag/AgCl) in the monomer solution 3 min after the polymerisation. **b** Absorbance changes at three characteristic wavelengths during the regular reduction at 400, 550 and 800 nm

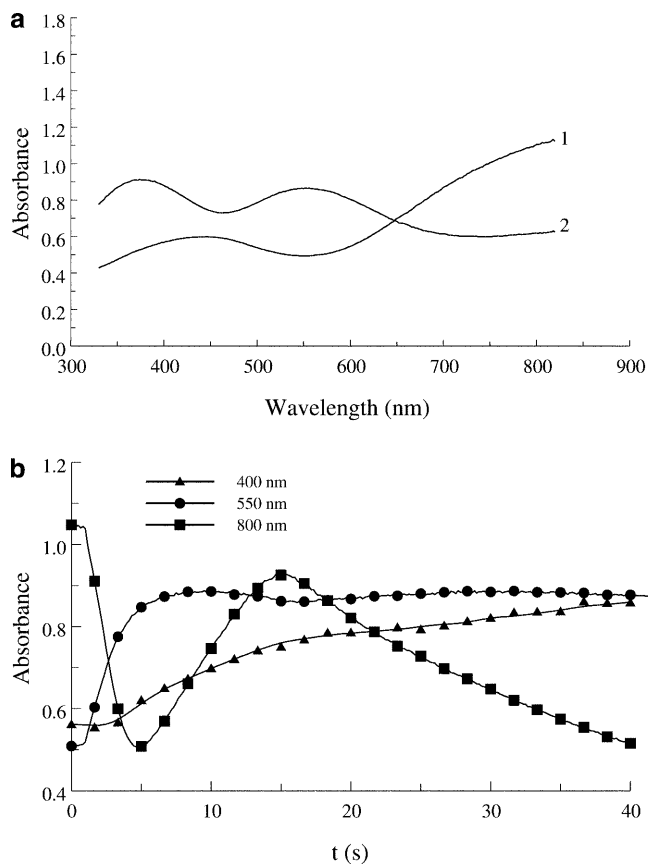


Fig. 3 **a** The spectrum of PPy/DS film at the end of the polymerisation (1) and at the end of the immediately applied reduction (2). The film was reduced at -0.6 V (versus Ag/AgCl) in the monomer solution. **b** Absorbance changes at the three characteristic wavelengths during the irregular reduction

density at 550 nm – cannot belong to the conventional redox transformation of PPy.

The chronoamperometric and chronocoulometric curves – registered during the reductions following the polymerisation (Fig. 4) – show that the reduction charge for the irregular reduction (-4.44 mC) is significantly higher than that of the regular one (-3.30 mC).

In order to get further information about the effect of the OCT after the polymerisation, the OCT was systematically changed in several independent experiments (Fig. 5). Figure 5 shows the absorbance at 800 nm versus time curves including the change during the polymerisation process. All the polymerisations were carried out under the same circumstances. As can be seen, the curves are very tendentious: the longer the OCT, the smaller the feedback of the absorbance curve and as a result a more and more complete reduction is achieved.

PPy films reduced regularly and irregularly exhibit different electrochemical features during their redox transformations in the base solution. Cyclic voltammograms performed in 0.05 M SDS solution show that the irregular film is oxidised only at more positive potentials and that it has much less redox capacity than the regular one (Fig. 6). This fact seems to be inconsistent with

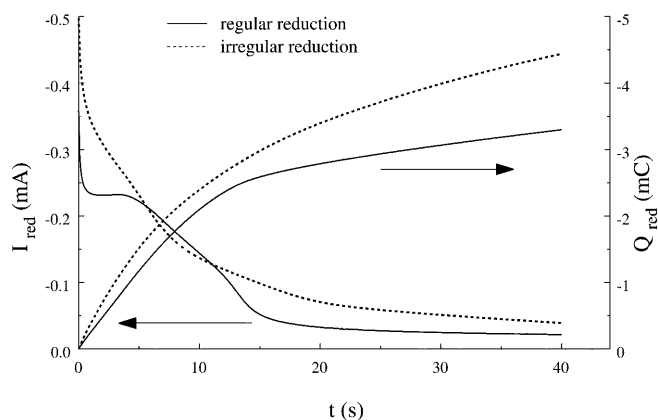


Fig. 4 Chronoamperometric (left) and chronocoulometric (right) curves performed at -0.6 V in the monomer solution during the regular (solid lines) and irregular (dashed lines) reduction

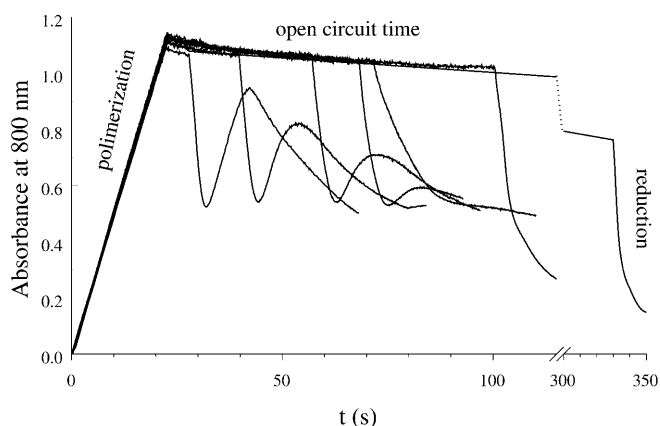


Fig. 5 Cumulative absorbance changes at 800 nm versus time from the beginning of the polymerisation throughout the open circuit time to the end of the reduction

Fig. 4, where it is seen that more charge is needed for the reduction of the nonreducible film than for that of the reducible one.

As an interpretation it can be taken into consideration that the open circuit potential decreases rapidly from a very positive polymerisation potential (about 2 V) until it reaches the rest value. Thus, the reduction starts from different initial states of the polymer (Figs. 2b, 3b). As a consequence, the film partially discharges during the OCT. After a longer OCT a smaller reduction charge is needed in the case of the regular reduction.

At the same time, as can be seen in Fig. 3a curve 2, the most “reduced” spectrum of the irregular film exhibits an absorption originating from midgap excitation. In other words the irregular film is a mixture of reduced and nonreduced parts. Moreover, we found that the irregular film could not be reduced totally either during a longer reduction time or at more negative potentials. From this fact it follows that the film can never be completely reduced if it has not spent enough time at the

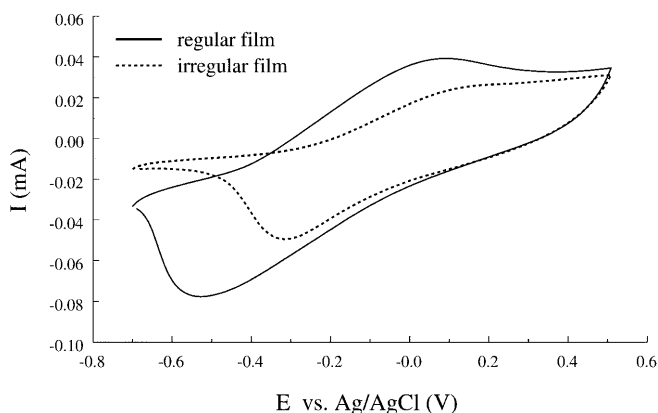


Fig. 6 Cyclic voltammograms in 0.05 M SDS solution at 20 mV/s sweep rate registered with the regular film (*solid lines*) and the irregular (*dashed lines*) film

open circuit after the polymerisation in the monomer solution.

In this context the results in Fig. 6 can be easily interpreted: the partially nonreduced film is coupled with less charge during its oxidation and the electrochemically unavailable parts cannot be reduced either.

This complex pattern of the irregular film was also supported by ex situ alternating current conductance measurements. The regularly reduced films – while standing in air – are readily reoxidised and their resistance decreases below 0.2 k Ω [19]. Ex situ conductance data of the two types – measured under the same conditions – showed that the alternating current impedance of the irregular film is 2 orders of magnitude larger than that of the regular film.

On this basis we assume that in the course of the irregular reduction, where the OCT is short, the extension of the interaction among chains or segments cannot take place. This assumption gained experimental support by registering the spectral changes during the OCT. As Fig. 7 shows the spectrum registered at the end of the electropolymerisation exhibits a redshift in the whole visible range during the OCT. The local maximum of the spectrum moves from 450 to 480 nm and the midgap absorption shifts correspondingly into the near IR region. These changes are considered as the manifestation of the transformation into the quasimetallic state. This phase transition is in accordance with the observation obtained with polythiophenes [18], where the in situ conductance was found to increase after the accomplishment of the electrochemical polymerisation. Without applying a long enough OCT, this transformation cannot occur and the irregular reduction is achieved with a film in which the conjugation between neighbouring segments has not developed. As a consequence, the irregular reduction leaves behind “isolated” non-reduced spots within the film. Since these spots, being isolated, cannot come into electrical contact with the rest of the electrode, they did not take part in the redox transformation. That is the reason why the redox ca-

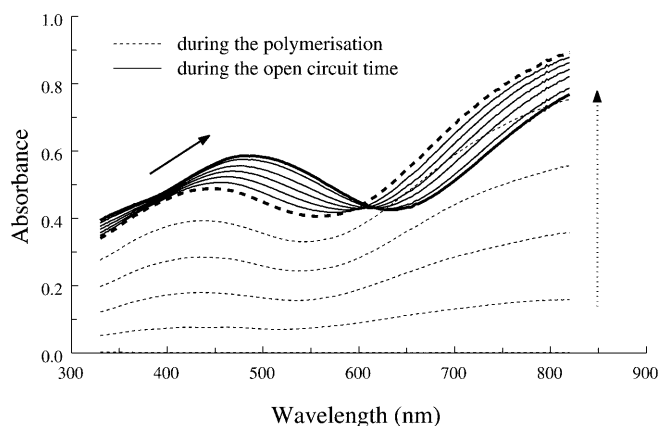


Fig. 7 Spectral changes of the PPy film registered during (*dashed lines*) and after (*solid lines*) the electropolymerisation at the open circuit potential

capacity of the irregular film is much smaller than that of the regular one.

On this basis we may assume that the OCT is necessary for the development of the well-conducting quasimetallic state. In the case of irregular reductions this nonfaradic transformation cannot take place, and these types of films can never reach the quasimetallic state. The regular reduction of the film was studied in the base solution by the potential multistep method combined with spectral measurements. The voltabsorptiometric curves obtained from the stationary spectra acquired at different potentials during the reduction are shown in Fig. 8. As can be seen, the reduction causes an absorption increase at around 400 nm from the very beginning, and the derivative curve has an extreme point at a more positive potential value than the one at 550 nm. This observation excludes the classical consecutive two-step mechanism which describes the reduction as a process from bipolaron to neutral form through a polaronic intermediate. Instead, we may assume that the

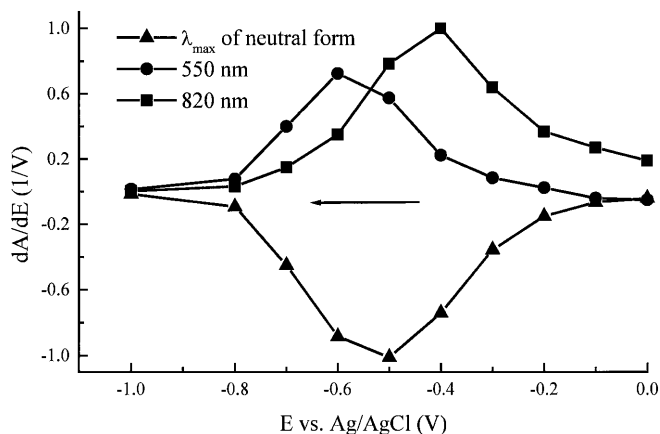


Fig. 8 Voltabsorptiometric curves at around 400 (λ_{\max} of the neutral form), 550 and 820 nm obtained from the potential multistep measurements during the reduction of the regular film

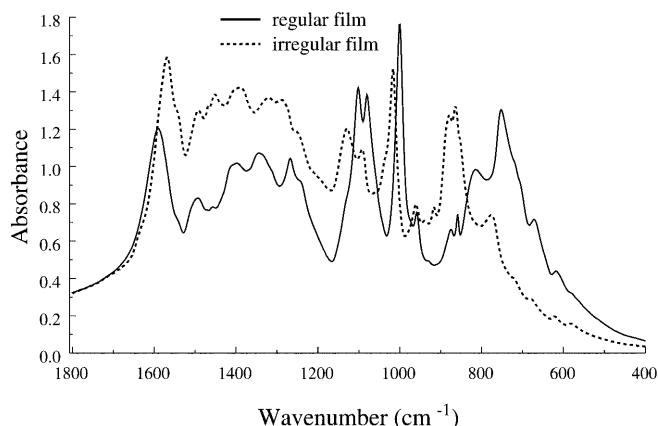
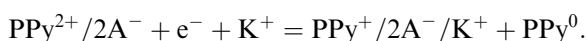


Fig. 9 IR spectra of the regular (*solid line*) and irregular (*dashed line*) PPy film enlarged in the 1,800–400 cm^{-1} range

reduction of a PPy/DS film in the quasimetallic state starts with a dissociation-type step:



As for the interpretation of the feedback-type pattern of the spectral change during the irregular reduction, the great difference in the state of the two types of polymers has to be taken into consideration.

In order to see the differences between regular and irregular PPy/DS films, IR spectra were registered with both polymers in the 4,000–400 cm^{-1} wavenumber range. We found a spectral difference in the 1,800–400 cm^{-1} region (Fig. 9), where the regular and irregular films have a band around 750 and 870 cm^{-1} , respectively. Further studies in this respect are in progress.

Conclusion

In our study we found that a postpolymerisation factor (the OCT) also has great influence on the properties of the PPy/DS film.

In analogy with polythiophenes [18], where the conductance increased drastically at the OCT (non-Faraday process), a significant modification takes place in the PPy film during the OCT. Although this behaviour may be connected at least partially to an ordering effect of the immobilised anion, the conductance increase at open

circuit – also observed with mobile anion-doped polythiophene – suggests a more general pattern. In case of a very short OCT, the film is unable to transform into the well-conducting state. With irregular reduction the extension of the interaction among chains or segments is prevented and the reduction leaves behind “isolated” nonreduced spots within the film, causing the decrease in the charge capacity. Once the film is irregularly reduced, it cannot be transformed into either the totally neutral or the quasimetallic state anymore.

The feature of the voltabsorptometric curves obtained during the reduction of the regular film cannot be interpreted by the classical (bipolaron, polaron, neutral form) consecutive reaction scheme. The reduction of PPy films which have achieved the quasimetallic state starts with a dissociation-type step.

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