Deprotonation and Dehydration of Pristine PPy/DS Films during Open-Circuit Relaxation: an Ignored Factor in Determining the Properties of Conducting Polymers

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The relaxation process of pristine polypyrrole/dodecyl sulfate (PPy/DS) films at open circuit, immediately after electropolymerization, was studied by in situ spectroelectrochemical, alternating-current conductance, electrochemical quartz crystal microbalance, and pH-metric techniques. A new phenomenon, called irregular reduction, involving apparent redoping and resulting in a polymer with a lower conjugation length is observed, which may occur if the pristine film is reduced without a waiting period. During this waiting period at open circuit, the film is deprotonated and partially desolvated with concurrent stacking of the polymer chains. The length of the waiting period allowed for the newly made polymer is of utmost importance, and ignorance of the relaxation of the film may explain the well-known irreproducibility in the fabrication of conducting polymers.

Introduction

The realization of the electronically conducting state of polymeric films has been described already in the early 1980s by the polaron/bipolaron model.[1] Since that time, many efforts have been made to reveal the details of the process and to provide a chemical picture formulating the transformation into the conducting state.[2−10] Previous studies on polythiophene films gave direct evidence for the involvement of nonfaradaic steps in the undoubtedly electrochemically induced transformation by demonstrating the conductance increase under currentless circumstances.[11] These studies were initiated by the observation of an increase in the in situ conductance of the pristine film after electropolymerization at open circuit (OC). Recently, an irregular behavior of pristine polypyrrole/dodecyl sulfate (PPy/DS) films during their electrochemical reduction was reported.[12] It was observed that the time spent at OC before the reduction greatly influences the properties of the polymer.

This observation is considered very important in the context of the large variation in the reported properties of the films made essentially under similar conditions. The importance of proper washing of the pristine PPy film by a fresh electrolyte solution was already suggested in the early "history" of conducting polymers,[13−15] and the effect of the composition of the polymerization solution on the behavior of the film was presented.[3] However, the later appearance of such different or even contradictory reports on the "same" polymer has to indicate that the films were not identical. They were only thought to be identical because they were prepared under the same conditions by applying the same electrochemical parameters, using the same solvent, and using the supporting electrolyte in the same concentration. This paper demonstrates that allowing a properly long waiting period for the pristine film to relax in the solution before its first reduction is a necessary and crucial factor to receive a polymer which behaves regularly, that is, according

to the expectations based on prior knowledge. It is assumed that the same effect may also be achieved by proper rinsing of the film,[14] but the lack of relaxation leads to anomalous behavior.

It is believed that the recognition of this new factor may serve as an interpretation of the diverse and often even contradictory results. Our aim was to study systematically the relaxation process of the pristine film to give an interpretation of the steps taking place at OC and a description of the process during the irregular reduction caused by the lack of relaxation.

The phenomena were studied by applying different in situ [optical, electrochemical quartz crystal microbalance (EQCM), alternating-current (ac) conductance, and pH-metric] techniques with the purpose of connecting the relaxation process to the gradual transition into the well-conducting state.

Experimental Section

The monomer solution was prepared using pyrrole (Sigma) distilled freshly under vacuum, sodium dodecyl sulfate (SDS, Merck) as received, and MilliQ water deaerated by nitrogen or argon. The concentration of the solutions was 0.05 M for both SDS and pyrrole.

The spectroelectrochemical experiments were carried out at room temperature in a three-electrode spectroelectrochemical cell that was described previously.[16] The spectra were registered on a diode-array spectrophotometer (HP 8452A). The working electrode was indium−tin oxide ($A = 0.28$ cm^2), and the reference electrode and counterelectrode were an Ag/AgCl microelectrode and a gold-plated steel electrode, respectively. The PPy films were deposited galvanostatically at a 3-mA/cm^2 current density and a 67.5-mC/cm^2 charge density. The electrochemical experiments were done on a PGSTAT 10 (Autolab) instrument. In the OC experiments, the films were left to relax for different time periods in the polymerization solution. All the films were reduced uniformly at a −0.6-V, constant potential. Following a thorough washing, cyclic voltammetric experiments were performed in the 0.05 M SDS solution at a

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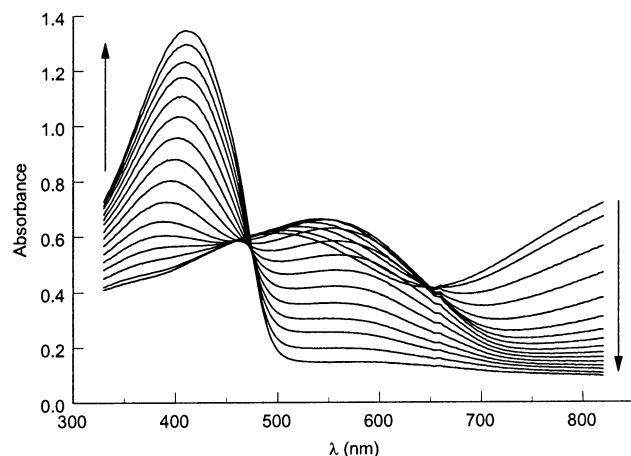† University of Szeged.
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Figure 1. Spectral changes of the pristine PPy/DS film during its reduction at −0.6 V in the polymerization solution after a 5-min relaxation at OC. The spectra are taken at 1-s intervals.

20-mV/s sweep rate. In the in situ ac conductance measurements, the working electrode was a double-band platinum electrode ($A = 0.005$ cm^2) with a 15-μm gap width. The reference electrode and the counterelectrode were a calomel electrode saturated with sodium chloride (SSCE) and Pt wire, respectively. In this case, the polymerization charge was 18 C/cm^2 and the potentiostatic reduction time was 400 s. The reference signal for the ac conductance measurement was a 130-Hz sine wave, and the response was measured on a lock-in amplifier (model SR830, Stanford Research Institute).

The EQCM measurements were carried out by using a quartz-crystal analyzer (model QCA917, EG&G Seiko). The working electrode was a Pt-coated quartz crystal with a resonance frequency of 8.9 MHz. The electrochemical measurements were done on a potentiostat/galvanostat (model 283, EG&G PAR) using the software M270. The films were deposited by applying the same current and charge density as was applied in the case of the spectroelectrochemical measurements.

The pH measurement of the stirred solution was carried out in the anodic part of a two-compartment cell by a special needle-shaped SENTEK glass electrode (type P13) placed in the very vicinity of the films, which were prepared by applying different charge densities up to 1.5 C/cm^2.

Results and Discussion

In the first part of this section, the phenomenon is presented in connection with the in situ UV−visible spectroelectrochemical results. To get a regular film to behave according to the general theoretical expectations, a certain relaxation period in the polymerization solution has to be allowed for our film and it must not be reduced until after a 5 min waiting time at OC. The spectra registered during the potentiostatic reduction are presented in Figure 1 for reference.

Figure 2 shows the absorbance changes at three characteristic-wavelength values (400, 550 and 800 nm), which are generally connected to the excitation of neutral, polaronic (monocationic), and bipolaronic (dicationic) segments, respectively. These spectral changes are generally interpreted by the consecutive reduction of bipolarons to polarons and then to neutral species. However, the identical rate of the increase in absorbance at 400- and 550-nm wavelengths may indicate the parallel formation of the two reduced forms in a dissociation-type step.[17−19]

If we do not wait until after polymerization but start the electrochemical reduction of the identically prepared film without allowing a properly long relaxation time, a more
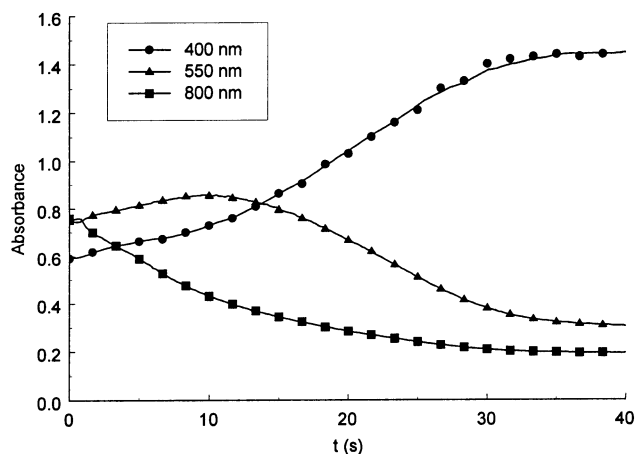

Figure 2. Absorbance changes versus time of the reduction according to Figure 1 at the three characteristic wavelengths.
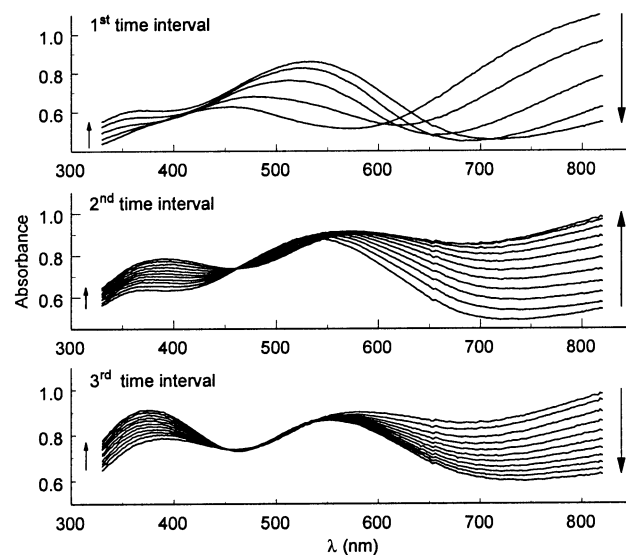

Figure 3. Spectral changes of the pristine PPy/DS film during its reduction at −0.6 V without relaxation at OC: first time interval, 0−5 s; second time interval, 6−15 s; third time interval, 16−40 s. The arrows indicate the direction of the changes.

complex optical change can be recorded during the reduction. To clearly present the different regions of the spectral changes, they are divided into three parts (Figure 3).

During the first time interval of the reduction, the tendency of the spectral changes is according to the expectations: the absorbance decrease at 800 nm is accompanied by the two increases at smaller characteristic wavelengths. During the next period of time, however, the absorbance at 800 nm increases back, although the film is continuously reduced at −0.6 V. The absorbance decrease takes place only during the third time interval, but the final spectrum still represents a mixture of oxidized and reduced species, although the charge passed during the process was about 30% larger than that in the case of the regular reduction. The kinetic curves at the characteristic wavelengths presented in Figure 4 undoubtedly show the irregularities of the spectral changes in two senses: (i) the original absorbance value at 800 nm is reobtained, and (ii) the amount of the species absorbing at 550 nm is not reduced after the maximum but becomes almost constant despite the continued reduction.

The two films that were electropolymerized and electro-reduced identically in the polymerization solution but with different waiting periods at OC were put, after proper washing,
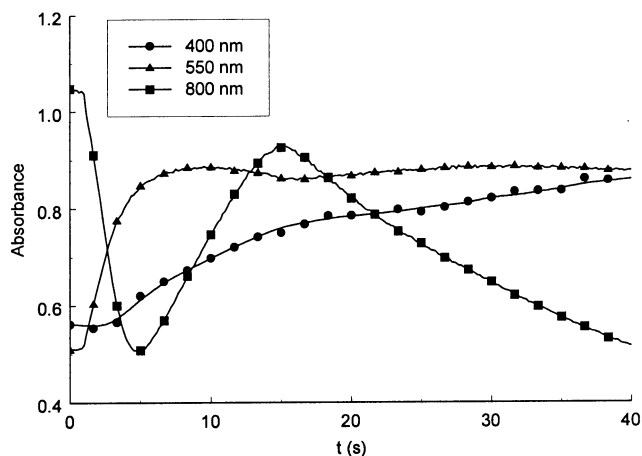
Figure 4. Absorbance versus time curves during the reduction according to Figure 3 at the three characteristic wavelengths.
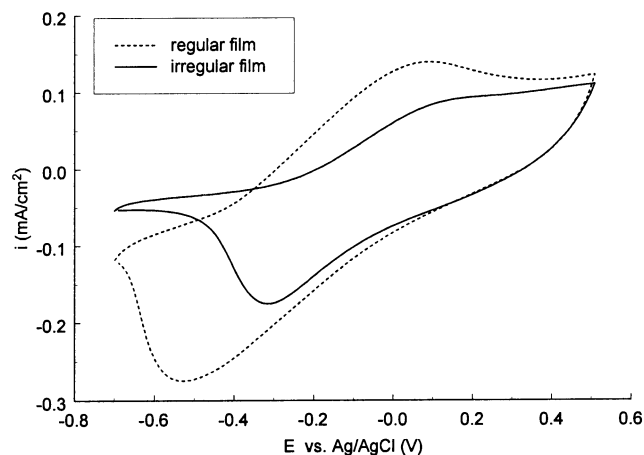

Figure 5. Comparison of the voltammetric curves of the identically prepared, reduced, and washed PPy/DS films taken after relaxation (regular case) and without relaxation (irregular case). The voltammograms were registered in a 0.05 M SDS solution and at a 20-mV/s sweep rate.

Figure 6. Cumulative curves of the absorbance changes at 800 nm of films obtained in different polymerization processes by applying different relaxation times. Each curve covers the preparation, relaxation, and reduction of a new film.

Figure 7. Potential dependence of the absorbance versus time curves at 800 nm during irregular reduction.

into the 0.05 M solution of SDS, and their redox behavior was compared by using cyclic voltammetry. As Figure 5 shows, the difference in the charge capacity is striking.

The figure also illustrates that the cyclic voltammetric data, such as the peak potential or peak current, are significantly modified not only by a change in the solution composition[3] but also by a change in the waiting period at OC by a few minutes.

To study the effect of the time spent at OC, in the next series of independent experiments the time allowed for the relaxation of the film was systematically increased. The cumulative results can be seen in Figure 6. Here, the absorbance of different films at 800 nm is presented as a function of time and includes three time intervals: the polymerization, the waiting period at OC (increased systematically in the different experiments), and the potentiostatic reduction. It is clearly demonstrated that the "feedback" behavior starts at a constant optical density, but its extent is changing. The longer the time period that is allowed for the film to relax after polymerization, the smaller the extent of spontaneous redoping that occurs during the cathodic reduction. If the film spends enough time at OC, its reduction exhibits the theoretically expected behavior without any feedback. Thus, the irregular behavior can be avoided just by allowing the properly long relaxation time for the pristine film. Because the monomer and its oligomers are also present in the system during the regular reduction, which can be achieved after
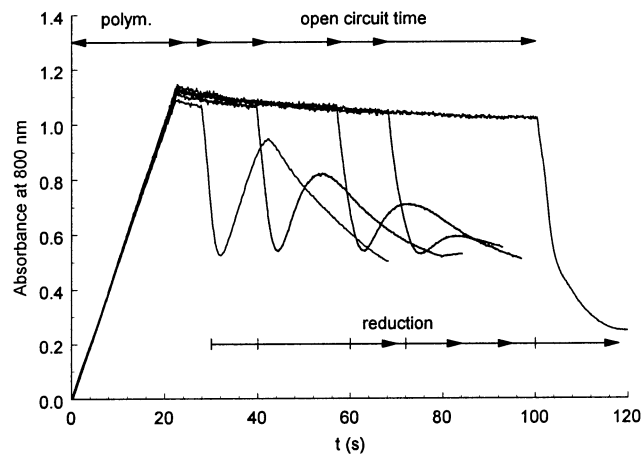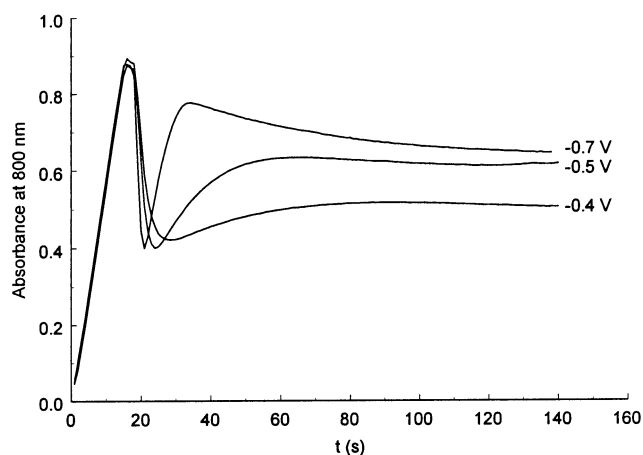
a certain waiting period, the components of the polymerization solution cannot be attributed to the observation of the irregular spectral behavior during reduction. The regular reduction results in a film that can be characterized by the same spectroelectrochemical behavior (see Figures 1 and 2) as the one washed thoroughly after electropolymerization and studied in a clean electrolyte solution.

The feedback pattern is potential-dependent, as is demonstrated by Figure 7. To achieve spontaneous reoxidation, a certain cathodic threshold potential is needed. Comparing this value with the voltammetric curve of the irregular film, we may state that the phenomenon similar to self-reoxidation is coupled with the reduction of the film.

If this is so, it should also occur in the case of the frequently used potentiodynamic polymerization (when the film is prepared by cycling between the potentials of the monomer oxidation and the film reduction) because this technique does not allow time for relaxation, except at extremely slow scan rates. In Figure 8, such polymerization curves are presented together with the absorbance change at 800 nm. As the potential is swept in the potential region of the monomer oxidation, the spectra indicate the formation of oxidized species that are reduced during the cathodic scans. Although there is no absorbance increase in the reduction section, a clear slowing down or interruption of the absorbance decrease could be monitored at all cycles. This observation may induce a reconsideration of
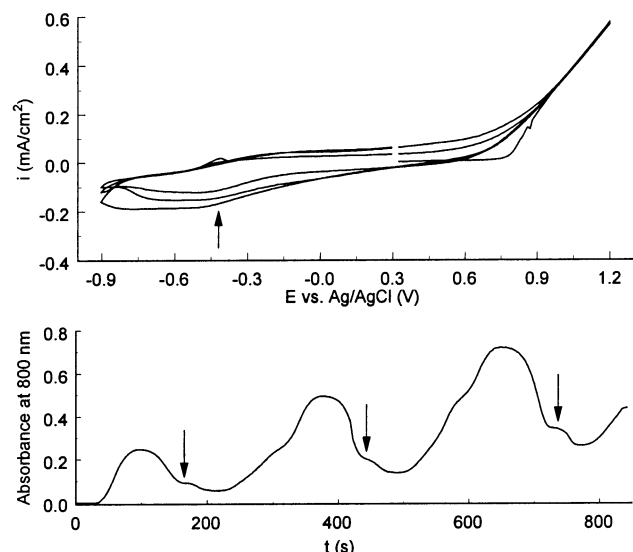
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Figure 8. Potentiodynamic polymerization in a 0.05 M pyrrole−0.05 M SDS solution at a sweep rate of 15 mV/s and the concurrent absorbance changes at 800 nm during the first three cycles. The arrows indicate the appearance of irregular reduction.
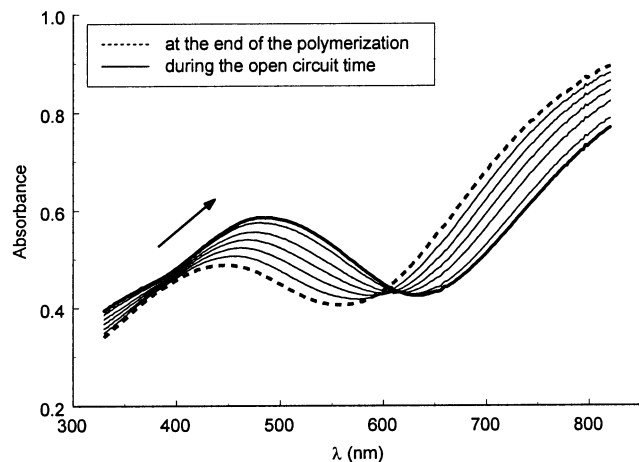

Figure 9. Spectral modification of the pristine PPy/DS film during relaxation at OC.

the information[20,21] that potentiodynamic polymerization by cycling is very good or preferable over stationary electrochemical methods.

After having demonstrated the importance of the OC relaxation, in the second part of our work we try to answer the question of what is going on during this important waiting period at OC. It has to be emphasized that these measurements are carried out at OC after electropolymerization so that the observations cannot originate from the electrochemical signals from the monomeric or oligomeric species. To characterize the relaxation from several aspects, the optical, ac conductance, and mass changes during the process were measured and completed by monitoring the pH of the solution in the anodic compartment of a divided cell.

As is shown in Figure 9, the spectrum typical for the pristine film changes at OC. There is a clear bathochromic shift from 430 to approximately 500 nm and a change in the absorbance range above 600 nm. Matrix-rank analysis[16,22] of the spectral modifications provided evidence of the appearance of one optically new species, which has an absorbance that also extends into the near-infrared region.
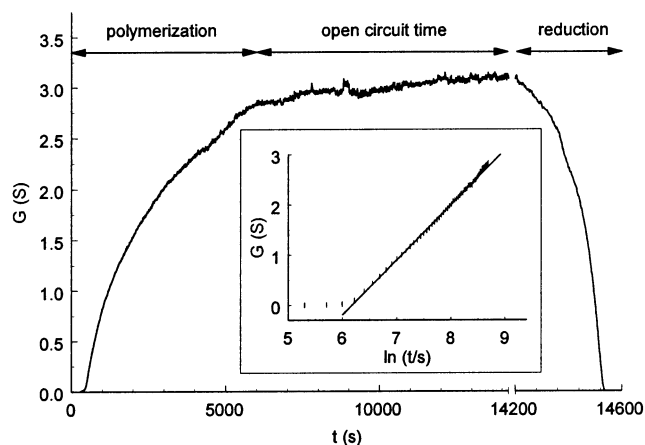

Figure 10. Conductance versus time curve from in situ ac measurements during and after polymerization as well as during potentiostatic reduction. The inset shows the G−ln t curve for the determination of conductivity.

In Figure 10, the conductance of the film versus time is presented, including the period of electrochemical polymerization, the relaxation at OC, and the potentiostatic reduction. The conductance increase in the second region proves the transformation into the conducting state during OC relaxation. On this basis, the process occurring at OC can be described as an extension of the conjugation, which can take place through either intra- or interchain interactions:

$$2PPy^+ \rightarrow PPy_2^{2+}$$
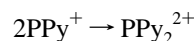
and the new optically independent species discussed in the previous paragraph is called a bipolaron or π or σ dimer in the literature.[23,24]

In Figure 10, the inset shows the data according to the equation derived in ref 25. The obtained linear behavior makes it possible to calculate the conductivity of the layer, and the value of 17 S/cm agrees well with those found in the literature.[25,26]

The constant slope in Figure 10 shows also that the layer, although "extremely" thick compared to those used in the spectroelectrochemical and EQCM measurements, can be characterized with a constant conductance value even toward the end of polymerization.

In the next part of the experiments, the mass change of the film during the waiting period at OC was studied. The linearity of the frequency change during electropolymerization and the low viscosity−low density product of the medium[27] ensure the validity of the Sauerbrey equation. In Figure 11, the mass change vs time is presented during both the galvanostatic deposition and the waiting period at OC. From the first part, where the linearity is perfectly fulfilled, the film formation can be characterized by a slope of 0.7437 ± 0.0013 μg/mC (obtained from m_1 in Figure 11). During the relaxation at OC, an approximate 10% mass decrease was measured. When the layer was reduced in the same solution after the relaxation period, the mass of the film increased (presented as an inset in Figure 11, curve a), as it should do in the case of films containing immobile anions but mobile cations. During the first section of regular reduction, the constant slope of 0.427 ± 0.003 μg/mC (m_2) is larger than the value connected to Na$^+$ incorporation. This value may reflect the movement of hydrated Na$^+$ species, whose pattern has been already reported for PPy/DS films.[28] Actually, from the slope of the first section, the uptake of monohydrated Na$^+$ ions can be deduced. Later on, the slope of
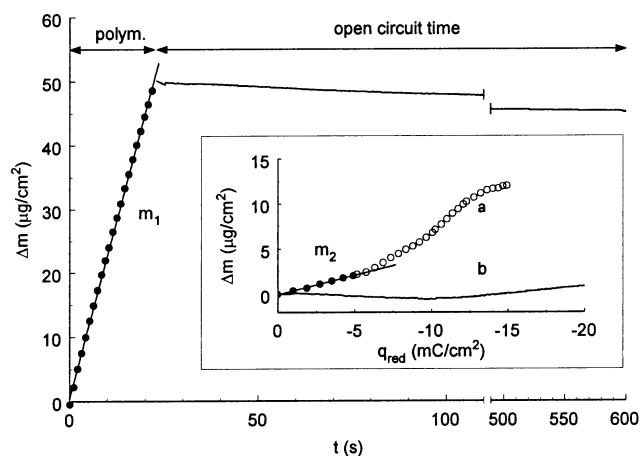
Figure 11. Mass change of the electrode obtained from EQCM data during and after polymerization. The inset shows the mass changes during the regular (curve a) and irregular (curve b) reductions that both registered in the polymerization solution. The slope of the curve is m_1 = 2.231 μg/(cm^2 s).
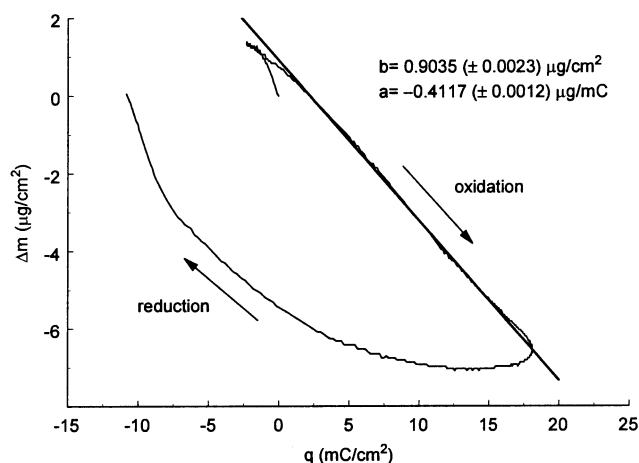

Figure 12. EQCM data during the cyclic voltammetric transformation of the regular PPy/DS film in a basic solution at a sweep rate of 20 mV/s. The results of a linear regression delivered the intercept (b) and the slope (a) with a correlation of R = 0.9989.

the mass increase becomes larger, which may indicate the formation of a more hydrated layer.

When this PPy film was studied by a cyclic voltammetric method in the clean supporting electrolyte solution, the EQCM results presented in Figure 12 were obtained. Restricting our discussion only to the oxidation section of the data, we could observe that the slope of the $\Delta m - q$ curve is identical with that determined during the regular reduction, because a value of -0.4117 μg/mC was obtained together with a regression parameter of R = 0.9989. This means that, in accordance with the expectations, the redox transformations of the PPy/DS film are accompanied by the movement of (mono)hydrated Na$^+$ ions.

Let us compare the above-mentioned observations with the EQCM data registered during the irregular reduction completed right after polymerization. The most unexpected pattern in Figure 11 (inset, curve b) is the almost constant mass of the film during the whole reduction. This means that the discharge of the polymeric layer did not cause an overall mass change! Again, it has to be emphasized that curves a and b were obtained in the polymerization solution and that curve a, registered after the relaxation period, reflects regular behavior.

As for the identification of the process that takes place at OC relaxation, we may start from the mass decrease of 4.7 μg/
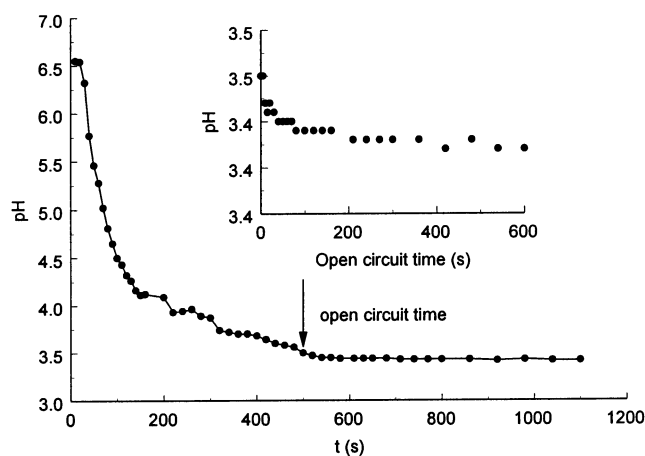

Figure 13. Change in the pH of the solution in the anode compartment of the cell during and after electropolymerization. The inset shows the enlarged section of the relaxation period at OC in the polymerization solution.

cm^2 (Δm_{relax}). Keeping in mind that the rule of electroneutrality requires the preservation of equal charges in both the film and the solution at OC, this mass decrease has to be connected to the removal of species with a zero overall charge, in which the possible cations are Na$^+$ or H$^+$ ions. Because one of the elementary steps during electrochemical polymerization is the H$^+$ removal from the coupling monomeric units, the assumption of in situ formation of the protons in the polymer is obvious.[29] On the other hand, PPy films are known as pH sensors as well,[30] for which the interaction of the polymer with the protons is involved.[31] To control the possible deprotonation of the layer during OC, the pH of the solution in the anode compartment of the divided cell was measured during and after polymerization. As is demonstrated in Figure 13, electropolymerization coupled with deprotonation, which causes an acidification of the solution, also continues during the relaxation period after electrochemical deposition. Although the measurements that resulted in a delayed pH decrease in the solution were also done with thin films, Figure 13 shows the results obtained with a thicker film. In this case, the pH changes connected to the relaxation of the film could be more accurately separated from those due to a slow response of the glass electrode to a very fast process.

Thus, the oxidized form of the film possessing positive chain segments still expels protons during the relaxation period after electropolymerization. The realization of this process and its connection with relaxation received further support by a new electropolymerization when the film was prepared in a sulfuric acid solution of pH = 1.85. In this case, irregular reduction was preserved despite a properly long waiting period at OC, indicating that the deprotonation of the film, which is inhibited by the very acidic medium, is a fundamental event of relaxation.

These protons have to leave the layer by preserving the electroneutrality, that is, in the form of ion pairs formed with the anions, DS$^-$ in this case. It is assumed that these anions are not incorporated into the bulk but are adsorbed close to the surface of the polymer.

To connect the mass decrease taking place during the relaxation to the more exactly formulated species, the average molar mass (M_{meas}) of one monomeric unit in the polymer was calculated from Faraday's law:

$$M_{meas} = \frac{m_{pol}}{n_{pol}} = m_1 \frac{(2 + y)F}{i}$$

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where m_1 is the slope in Figure 11, F is the Faraday constant, y is the doping level of the film, and i is the current density used during polymerization.

We assumed that the extent of oxidation is the same at the end of both the polymerization and the oxidation processes (it is a generally accepted and applied approximation).[32] Thus, the doping level can be calculated from the charge values consumed during polymerization (Q_{pol}) and oxidation (Q_{ox}) in the clean electrolyte solution:

$$y = \frac{2Q_{ox}}{Q_{pol} - Q_{ox}}$$

Our calculation gave a value of 0.2524 for the doping level, y, which agrees with the results reported in the literature for PPy/DS films.[29] By using this value, the average molar mass of the monomeric units in the layer at the end of electropolymerization, $M_{meas} = 158.44$ g/mol, was obtained.

If we compare this value with the theoretical value

$$M_{cal} = M_{Py-2H} + yM_{DS} = 131.89 \text{ g/mol}$$

there exists an extra mass of $\Delta m = 26.55$ g/mol in the film. On the basis of the previous results, we may state that protons and extra DS$^-$ ions are also in the film, which come out during the waiting period at OC. Their amount depends on the protonation of the film, which can be characterized by a protonation degree, z, of the monomeric units. Taking into account the protonation, the average molar mass can be given as

$$M_{cal} = zM_H + M_{Py-2H} + (z + y)M_{DS} = 158.44 \text{ g/mol}$$

from which $z = 0.0998$ is obtained if no other species are in the layer.

The value of z can also be calculated from the mass decrease during relaxation. The observed mass decrease is $\Delta m_{relax} = 4.7$ μg/cm^2, which gives the amount of protons by taking into consideration the H$^+$DS$^-$ units as the leaving species:

$$n_{H^+} = \frac{\Delta m_{relax}}{M_{H^+} + M_{DS^-}} = 3.457 \text{ nmol}$$

This gives for the protonation degree

$$z = \frac{n_{H^+}}{n_{Py}} = 0.057$$

where n_{Py} can be calculated from the polymerization charge and doping level.

The difference between the two z values indicates that the previous protonation degree of 0.0998 is really a maximum for z if no other species except pyrrole and H$^+$ and DS$^-$ ions are the components of the layer. However, it is an obvious assumption that the coming-out ion pairs, and also the film itself, are hydrated, and it is a rational approximation that the H$^+$DS$^-$ pairs are similarly hydrated inside the layer as well as when they are leaving the film. An iterative calculation leads to the average composition of H$^+$DS$^-$·2.5H$_2$O. These units are incorporated into the layer during polymerization and are expelled from it during relaxation. With these values, M_{meas} can be obtained as
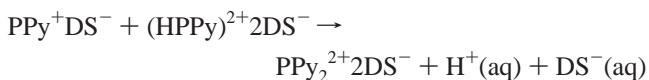
$$M_{cal} = zM_H + M_{Py-2H} + (z + y)(M_{DS} + 2.5M_{H_2O}) =$$
$$158.44 \text{ g/mol}$$

Conclusions

In the previous chapter, we presented that during the waiting period at OC, or during the "relaxation time", the following changes at the pristine polymeric film were observed: a spectral bathochromic shift, which reflects an increase in the effective conjugation length; an increase in the ac conductance of the film; a decrease in the mass of the film by approximately 10%; and the further acidification of the solution in the anode compartment.

We were unable to connect these observations coherently to a possible chemical reaction with the monomeric or oligomeric molecules in the polymerization solution. Instead, as a rational interpretation, all these results are described as the relaxation of the films when a deprotonation and coupled partial dehydration take place. During this process, the layer may transform to the well-conducting or, as it is generally called, quasi-metallic state by the extension of the conjugation through either a more favorable charge distribution along the chains or the development of interchain interactions. If this relaxation is not ensured, the reduction generates unusual reactions. These results are also in conformity with those obtained with polythiophenes, where desolvation was found to play an essential role in the development of the conducting state during oxidation of the film in the supporting electrolyte solution.[11,19] Relaxation of the film in which the neighboring monocationic segments are involved can be formulated as

$$\text{PPy}^+\text{DS}^- + (\text{HPPy})^{2+}2\text{DS}^- \rightarrow$$
$$\text{PPy}_2{}^{2+}2\text{DS}^- + \text{H}^+(\text{aq}) + \text{DS}^-(\text{aq})$$

where the formula of PPy$_2{}^{2+}$ indicates the increased conjugation level in the dications formed through interchain interactions by π stacking. According to our calculations, the average hydration degree of the ion pairs expelled from the layer is 2.5. As for (HPPy)$^{2+}$2DS$^-$, this species may be the protonated form of a monocationic segment or it might be assumed that this form is a polymerization intermediate that still contains one α proton originating from the coupling of cation radicals according to the well-known and generally accepted polymerization mechanism. The removal of the proton with the concurrent stacking of chains involves a change of the sp^3 hybridization of the α carbon to sp^2 with the concomitant conformational changes. These changes are slow because of the solid-state environment, leading to the long relaxation times observed. Still another slow step is the diffusion-limited expulsion rate of the dodecyl sulfate anions. The delayed simultaneous expulsion of the protons, anions, and solvent into solution, accompanied by the stacking of the polymer chains, leads to the gradual increase in density and anisotropy of the layer with a simultaneous increase in the capacitance. In the OC, the electric charge is constant and, consequently, the potential over the capacitor is lowered, as was observed.

From all these observations, an interpretation of the irregular reduction can begin from the fact that immediately after electropolymerization the film is composed of polarons, bipolarons, and their partially protonated forms. If the reduction is now started without a waiting period, the protons remaining in the film induce a side reaction. When the neutral polypyrrole is formed in the reduction, it is immediately protonated, and the protonated form has an absorption spectrum that is similar to the spectrum of bipolarons. This phenomenon is the well-known acid doping,[33,34] and it gives rise to the anomalous maximum at 800 nm shown in Figures 3 and 4. Finally, at certain cathodic potentials, the protonated pyrrole units in the chain are irreversibly reduced to pyrrolidine rings, resulting in a polymer with a lower degree of conjugation. This interpretation may explain the facts that the film exhibits the mixed optical behavior in

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the third time interval and a decreased charge capacitance and that the mass of the film did not increase during its reduction, which should take place in the case of a cation uptake.

During relaxation, the transformation into the stacked state is accomplished and the regular reduction, which starts with the more conjugated form $PPy_2^{2+}2DS^-$, creates monocationic and neutral segments in parallel, in a dissociation-type step:

$$PPy_2^{2+}2DS^- + e^- + Na^+{}_{hydr} \rightarrow$$
$$PPy^+DS^- + PPy^0 + (Na^+DS^-)_{hydr}$$
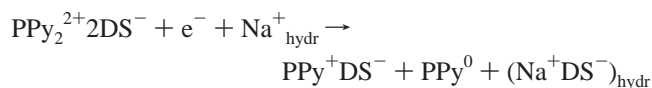
Because there are no protonated segments in the film anymore, the acid doping cannot take place and the film can be totally reduced.

Finally, it is assumed that the recognition of the crucial effect of the relaxation process may solve many obscure contradictions among the observations or may initiate the reconsideration of some prior incoherent results.

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