

# Electrochemical Synthesis of Polypyrrole Layers Doped with Glutamic Ions

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**ABSTRACT:** Electrochemically synthesized polypyrrole thin films doped with glutamic ions were investigated as interesting materials for potential use as molecularly selective surfaces. Pyrrole and glutamate interact in aqueous solution, resulting in the formation of a prominent band at 240 nm in the absorption spectra of the solution. This feature was assigned to the formation of a complex, which significantly influences the electrochemical deposition of polypyrrole films doped with glutamate. It was also detected that oxidation of these complexes leads to the appearance of a shoulder in the absorption spectrum at 270 nm, which corresponds to the yellowish color of pyrrole aged under influence of air. A mechanism is proposed

for polymer film growth in aqueous solutions containing monosodium L-glutamate and pyrrole. It takes into account the observed influence of the pH of the solution, the concentration of reagents, the zwitterionic properties of glutamate on deposition, and results from spectroscopic measurements. It is also shown that glutamic ions can electrochemically be released from the synthesized polymer layers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 4051–4058, 2009

**Key words:** electrochemistry; polypyrrole; solution properties; UV-vis spectroscopy; morphology; L-glutamic acid ions; complex formation

## INTRODUCTION

The continuing activities in the research areas of molecular switches and molecular imprinting<sup>1–5</sup> are promising for the development of electrochemical devices, which can regulate the concentration of biomolecules in solution. A deeper understanding of the processes for manufacturing molecularly selective, biocompatible polymer layers is of broad interest for application in medical and biotechnological fields. Polypyrrole (PPy) is an interesting candidate for molecular imprinting applications due to its stability and electroactive properties. There are only a few articles<sup>6–9</sup> reporting the mechanism of the electrochemical synthesis of PPy layers intentionally doped with organic molecules, especially amino acids. Deore et al.<sup>6</sup> first demonstrated the possibility for the reversible release and uptake of L-glutamic (Glu) ions using “overoxidized” PPy films (OPPy). Recently, the enantioselective uptake and release of L-aspartic acid using OPpy films was reported.<sup>9</sup>

The structure and properties of the target biomolecules play a very important role for the development

of molecularly selective polymer layers. The behavior of amino acids in aqueous solutions, their corresponding chemical activity, and the molecular self-organization have been in the focus of recent interdisciplinary investigations.<sup>10,11</sup> McLain et al.<sup>12</sup> described the detailed structure of Glu ions and the resulting interaction with water for the first time. They found that the zwitterionic properties of Glu ions result in an extraordinary aqueous solution structure similar to bulk water at high pressure. Additionally, they found that the zwitterionic structure persists at more alkaline pH > 5.5 than it was considered earlier. Their study showed that there is a strong connection between water molecules and the charged sites of Glu molecules and that these interactions could have a significant influence on electrochemical reactions in such solutions.

In this study, electrochemical deposition of PPy layers from aqueous solutions containing monosodium L-glutamate and pyrrole has been investigated. A model is suggested for the deposition mechanism of PPy layers doped with Glu ions during the synthesis, taking into account the electrochemical behavior of Glu ions.<sup>12</sup> The release of Glu ions from the polymer layer during controlled overoxidation cycles is demonstrated.

## MATERIALS AND METHODS

Pyrrole (Py) from two commercial suppliers (99%, extra pure, Acros organics and 98%, F.C.C., Sigma-Aldrich) and L-glutamic acid monosodium salt

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monohydrate (NaGlu) (99%, Fluka) were used. Ultrapure H<sub>2</sub>O ( $R = 18 \times 10^6 \Omega \text{ cm}$ ) was obtained using a Millipore purification system. Freshly obtained Py was already yellowish and therefore vacuum distilled before use ( $10^{-2}$ – $10^{-3}$  bar). The distilled Py was colorless and stored under Ar atmosphere at  $-10^\circ\text{C}$ . Any other chemicals were used as received.

Solutions with varying concentrations of NaGlu and Py were prepared by adding Py to NaGlu water solution and mixing in an ultrasonic bath. The PPy films were deposited potentiostatically in a three-electrode cell from the freshly prepared solutions. The working electrodes were prepared by thermal deposition of Au (150 nm) on a thin Cr (2 nm) layer on glass substrates. For the experiments, which involved variation of pH of the solution, Pt working electrodes (CH Instruments), a standard cell (CH Instruments) and standard buffer solutions for pH = 3, 7, and 9 were used. The reference electrode was a Ag/AgCl electrode in 3 mol L<sup>-1</sup> KCl water solution obtained from CH Instruments. Platinum wire or Pt electrodes purchased from CH Instruments were used for the auxiliary electrode. The cell setup was constructed using glass and polypropylene tetraethylene (PPTE) to allow efficient cleaning of the cell components and a fixed geometry for the electrodes.

All electrochemical data were obtained with a CH Instruments 660C workstation with accompanying software, Version 6.28. The voltammetric curves [electrical current vs. time,  $I(t)$ ] were recorded before deposition in the range  $-0.8$  to  $+0.8$  V against Ag/AgCl electrode. Potentiostatic deposition was performed at 0.8 V against Ag/AgCl for 1–2 h. All experiments were repeated several times with fresh solutions at ambient temperature ( $20.0^\circ\text{C} \pm 2^\circ\text{C}$ ) in air. The synthesized PPy films were thoroughly washed with Millipore water and then were cycled in Millipore water in the range  $-0.3$  to  $+0.8$  V for 10–40 cycles. The cycling and “overoxidation” (Deore et al.<sup>6</sup>) result in release of incorporated Glu ions from the polymer layer. The thickness of the PPy films was determined using a Dektak profilometer. The morphology of the synthesized films was investigated using SEM imaging with a Focused Ion Beam from the FEI Company. The UV-vis properties of the solutions were studied before deposition and after cycling using a Cary Varian 100 Scan with the accompanying software.

## RESULTS AND DISCUSSION

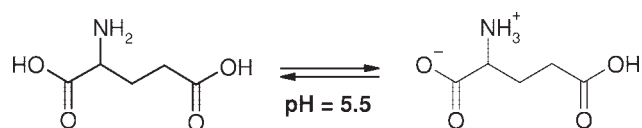
### Electrochemical deposition

The mechanism of the electrochemical synthesis of PPy layers from aqueous solutions not containing glutamate has been studied in detail<sup>13,14</sup> using both

potentiodynamic and potentiostatic procedures for the deposition of the polymer layers. However, we found that the synthesis of PPy from solutions containing Glu ions using a potentiodynamic procedure was not reproducible; therefore, the potentiostatic deposition was preferred here.

### Influence of the pH value on PPy film deposition

The electrochemical deposition of PPy layers depends on the pH value of the electrolyte.<sup>11</sup> Additionally, the net charge on the Glu ions varies with pH. L-glutamic acid is a zwitterion in aqueous solutions in the pH range 2.2–4.3 and exists as monovalent anion in the range 4.3–9.7.<sup>6</sup> Nevertheless, Glu ions still demonstrate zwitterionic properties at pH = 5.5 without the addition of a buffer solution<sup>12</sup>: the amino group is protonated to  $-\text{NH}_3^+$ , and the C<sub>α</sub> carboxylate group is deprotonated to  $-\text{COO}^-$  [eq. (1)]. The bifunctionality of Glu ions should affect the PPy deposition process because the Glu ions, while mixed with pyrrole, have a zwitterionic structure.

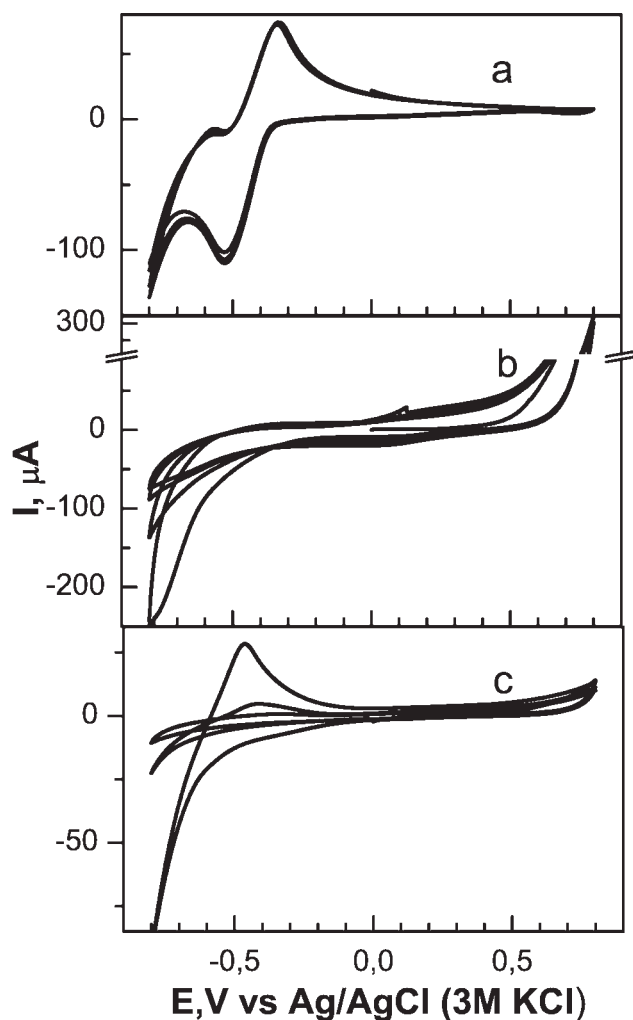


Eq. 1. Zwitterionic structure of Glu ions

Taking this behavior into account, mechanism of the deposition of PPy in the presence of Glu should be studied more carefully.

Buffer solutions with pH = 3, 7, and 9 were used to adjust the pH values in the deposition solutions. The pH value of the solution containing only Py and NaGlu was not stable due to the oxidation of Py and shifted from pH = 6.5 to pH = 8 during 1-h period of measurement. Figure 1 presents the cyclic voltammetric characteristics of the solutions before the deposition at the different pH values. The  $I(E)$  characteristics show some similarities to those for solutions containing pyrrole without NaGlu.<sup>15</sup> In general, cyclic voltammograms are a helpful diagnostic tool for processes occurring due to electrostimulation at various potentials.<sup>16</sup>

Voltammetric curves for the solution at pH = 3 [Fig. 1(a)] show two peaks at  $-0.36$  and  $-0.55$  V, and one minimum at  $-0.52$  V. Signals at potentials lower than  $-0.5$  V correspond to a reduction of pure polymer fragments to their neutral state; and the broad peak at  $-0.35$  V is assigned to the oxidation of the pure polymer.<sup>15</sup> The peak corresponding to the oxidation of the monomer Py (above 0.7 V)<sup>15</sup> and polymer film growth was not detectable. These peaks would indicate the formation of a polymer layer in the NaGlu electrolyte. The exponential



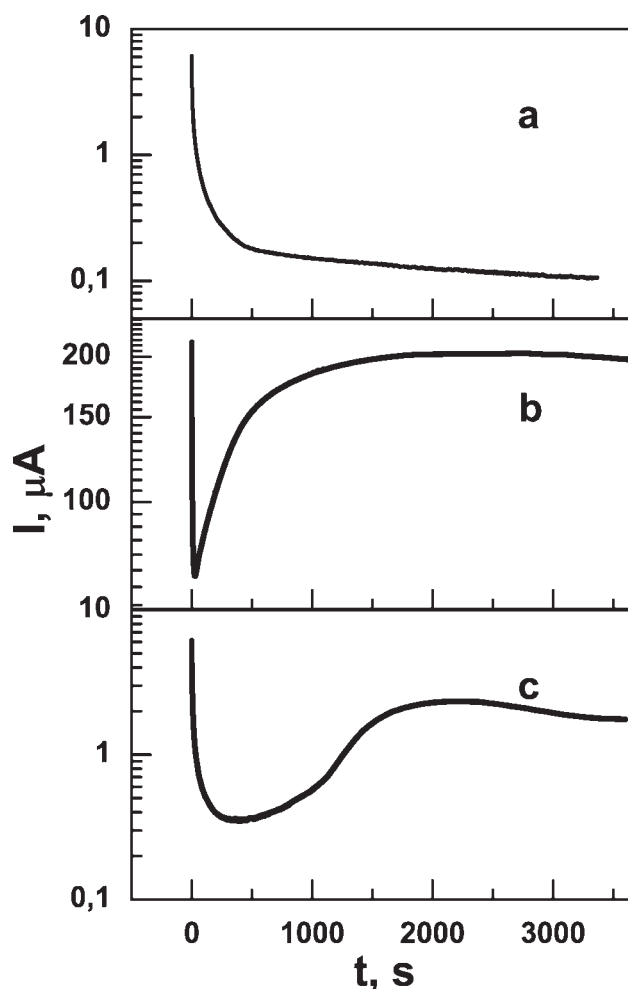
**Figure 1** Cyclic voltammograms for solutions containing  $0.2 \text{ mol L}^{-1}$  Py and  $0.5 \text{ mol L}^{-1}$  NaGlu at: (a) pH = 3; (b) pH = 7; and (c) pH = 9. The scan rate was  $0.1 \text{ V s}^{-1}$ .

kinetics of deposition [Fig. 2(a)] demonstrates a first-order process, probably the electrochemical adsorption-desorption of glutamic ions. Nevertheless, some precipitation took place and a very thin film could be detected. The film was transparent yellow, barely visible to the eye, and its position could be determined by the hydrophilic properties of the film. The Au-coated working electrode is nonhydrophilic, and so the polymer film could be observed due to the behavior of water drops on the substrate surface. After several days in air the film oxidized, and it became a yellow-brownish color, which corresponds to the film thickness less than  $100 \text{ nm}$ .<sup>13</sup>

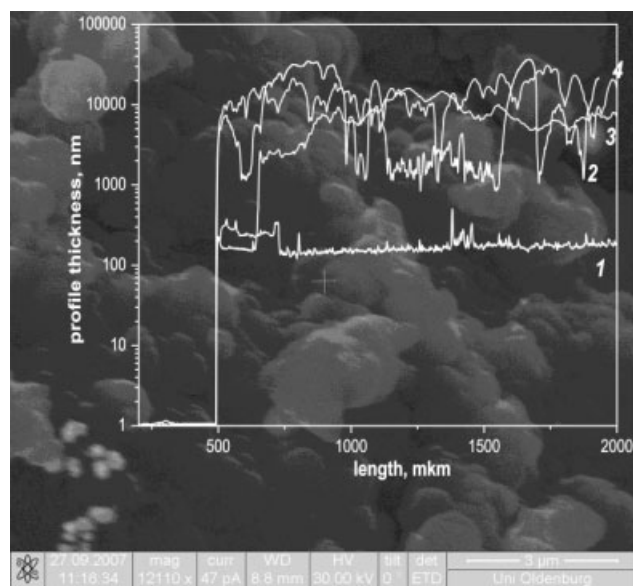
This result can be explained by taking into account the zwitterionic form of Glu and the supposed mechanism of PPy deposition without Glu.<sup>13</sup> Because of zwitterionic structure, the glutamic molecules could interact with pyrrole molecules and prevent their oxidation. For positive potentials in acidic solution, the sufficient concentration of any

anions is necessary for deposition of polymer film, to compensate a positive charge of the growing polymer chain. This suggestion explains low current densities during film deposition. Thus, the zwitterionic form of Glu ions leads to less efficient formation of PPy chains.

In neutral solutions (pH = 7), the cyclic voltammograms [Fig. 1(b)] could be compared with the curves described by Smela<sup>15</sup> for PPy deposition from solutions containing sodium dodecylbenzenesulfonate (NaDBS). The nonrelevant region between 70 and  $250 \mu\text{A}$  was omitted in the chart to show the most important part of the curve. There is a strong peak at  $E > 0.6 \text{ V}$  corresponding to oxidation of the monomer. There is also a low intensity broad peak at  $0.2\text{--}0.3 \text{ V}$ , which can be assigned to the oxidation of PPy oligomers shifted due to the Glu ions. The current was approximately 7 times stronger than the current observed for the solution with pH = 3 ( $350$  and  $50 \mu\text{A}$ , respectively) and points to a larger



**Figure 2** Deposition kinetics  $I(t)$  in double logarithmic scale for solutions containing  $0.2 \text{ mol L}^{-1}$  Py and  $0.5 \text{ mol L}^{-1}$  NaGlu at: (a) pH = 3; (b) pH = 7; and (c) pH = 9. The deposition voltage was  $0.8 \text{ V}$  against Ag/AgCl.



**Figure 3** Morphology and thickness profile (inset) of the PPy films, synthesized at pH = 7 and different ratios (mol · L<sup>-1</sup>) NaGlu/Py: (1) gray film, ratio = 0.1 : 0.2 for 1 h; (2) black film, ratio = 0.1 : 0.2 for 2 h; (3) black film, ratio = 0.5 : 0.2 for 1 h; and (4) black film, ratio = 0.5 : 0.2 for 2 h. The morphology is shown for the Sample 2.

amount of charged particles (molecules) in the solution. This situation results in thicker PPy films.

The deposition kinetics  $I(t)$  [Fig. 2(b)] consists of an exponential decay at the start, and then a nearly exponential rise corresponding to polymerization and the beginning of PPy film growth, followed by a plateau in the current, and finally a very small decay in the current at later deposition times. The constant current over time (plateau) indicates the growth of a conductive PPy film. The voltage applied to the working electrode drops over the thickness of the PPy film, and the current begins to drop slightly after the film has reached a certain micrometer thickness. The synthesized films were black and more than 2  $\mu\text{m}$  thick (Fig. 3). This fact indicates that the unbounded Glu ions show the anionic structure, which supports the growth of polymer chain.

For the solutions made with a buffer with pH = 9, the voltammetric curves demonstrated a small peak corresponding to PPy growth in the voltage range  $\geq 0.6$  V [Fig. 1(c)]. There is also an additional cathodic peak observed at  $-0.42$  V. The current intensity is in the same range as for acidic solutions [Figs. 1(a) and 2(a)]. This low current intensity indicates a limitation of the deposition process. The deposition kinetics [Fig. 2(c)] shows a noticeable increase in current after 200 s of deposition followed by a small decrease in current, quite similar to the kinetics for film deposition in solutions with pH = 7. However, both the form of the

$I(t)$  curve and the lower current intensity during deposition lead to a formation of thinner layers than those deposited in solutions with pH = 7. These films were taupe-black and are less than 500 nm thick. At alkaline pH values, the Glu ions tend to have less effective negative charge. The lower current intensity during the deposition could be explained taking this into account or by the prevalent oxidation in the solution in comparison with oxidation at the working electrode.

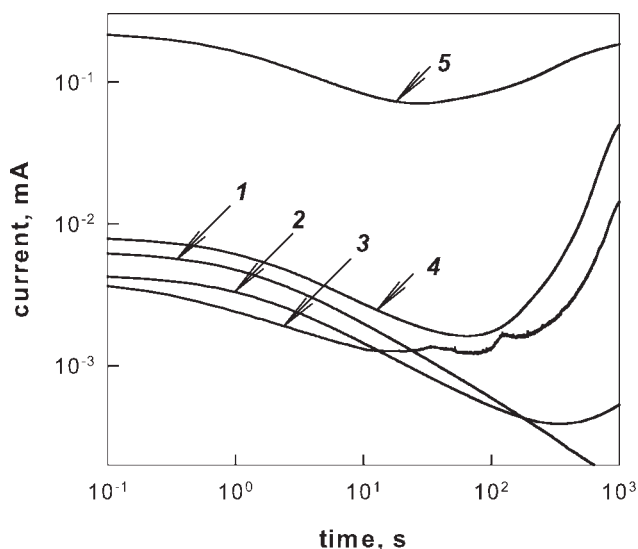
#### Morphology and thickness of PPy films doped with Glu ions

The morphology of PPy films synthesized at pH = 7 is presented in Figure 3. It can be seen that the surface of the film consists of globules roughly 500 nm by 1  $\mu\text{m}$  in size. The picture was taken from a film which was black in color, approximately 2  $\mu\text{m}$  thick (inset on the Fig. 3), synthesized at a NaGlu : Py mol ratio = 0.1 : 0.2 for 2 h. Films of about 200 nm (Curve 1 on the inset on Fig. 3) have a gray color and a very flat profile. Films thicker than 1  $\mu\text{m}$  are black and have very rough surfaces (Curves 2–4 on the inset on the Fig. 3), as can also clearly be seen on the electron microscope image in Figure 3. The thinnest films were synthesized in the shortest deposition times. The results indicate that film growth is uniform up to several hundred nanometers, after which columnar hills of up to 200  $\mu\text{m}$  in size will form. This observation points to a possible formation of some oligomeric aggregates also in the solution during the synthesis. They could precipitate on an already existing PPy film at the later stages. It was also observed that films grow thicker in solutions containing higher concentrations of the compounds.

The rough surface of the PPy films doped with Glu ions could potentially be more effective for the controlled release and uptake of a large amount of Glu due to the large surface area. This may be an interesting characteristic for medical and biological applications.

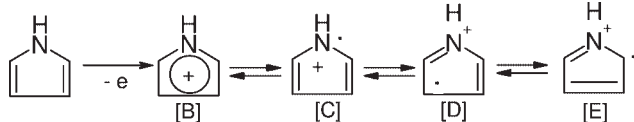
#### Mechanism of Glu-doped PPy film deposition

To characterize the mechanism of the deposition of Glu-doped PPy films, the polymer synthesis was performed in solutions with different concentrations of components. The deposition kinetics  $I(t)$  at various component concentrations and ratios are presented in double logarithm coordinates in Figure 4. All curves show an exponential trend at the start of the deposition process. This fact indicates a possible identical initial stage of polymer growth for all deposition conditions—the nucleation phase, which is limited by the



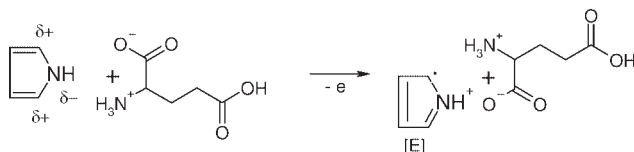
**Figure 4** Kinetics of deposition of PPy films at pH = 7 and different concentrations of NaGlu : Py in double logarithmic scale, mol L<sup>-1</sup>: (1) 0.1 : 0.05, (2) -0.1 : 0.1, (3) -0.1 : 0.2, (4) -0.1 : 0.5, and (5) 0.2 : 0.5. The deposition voltage was 0.8 V against Ag/AgCl.

oxidation process of the Py monomer. Larger Py concentration results in higher concentration of oxidized pyrrole (Fig. 4, Curves 1–4). Oxidized Py has several isomeric resonance states of cation-radical forms<sup>13</sup> [eq. (2)]:



Eq. 2. Oxidation of the pyrrole monomer and resulting isomeric cation-radicals

The most stable cation-radical form of oxidized pyrrole is [E] and zwitterionic Glu ions could react with them [eq. (3)]. The zwitterionic form of Glu is mentioned in every equation, because Py is added to NaGlu solution, where Glu ions show the zwitterionic form prior mixing with Py. This suggestion, in turn, results in geometry-oriented course of the reaction:

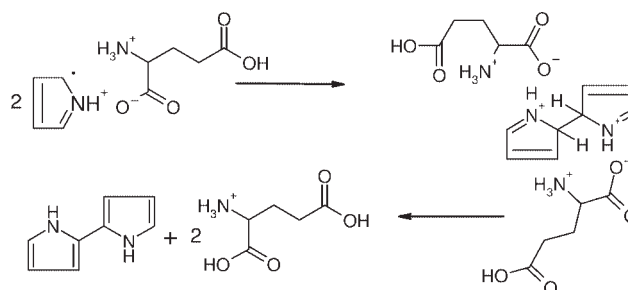


Eq. 3. Oxidation of pyrrole in the presence of L-Glu ions

The initial current decreased with an increase in Py concentration from 0.05 to 0.2 mol L<sup>-1</sup> for the same concentration of Glu ions (0.1 mol L<sup>-1</sup>). This is attributed to the polar Glu ions being bound to

polar Py molecules before electrostimulation, corresponding to eq. (3). If the concentration of Py is further increased up to 0.5 mol L<sup>-1</sup> at the same constant concentration of Glu, some Py molecules appear to be unbound. The doubling of Glu ions concentration ( $c(\text{NaGlu}) = 0.2 \text{ mol L}^{-1}$ ) also results in an increase of solution conductivity of more than 10 times (Fig. 4, Curve 5). Thus, in the NaGlu/Py ratio range 1:0.5 until 1 : 4 the most Glu and Py molecules seem to interact strongly. However, the initial trend of the kinetics curve remains the same for all ratios, which point to the same initials stage. An excess of Glu ions in the electrolyte seems to support film deposition rather than an increase of the Py concentration, increasing the Glu concentration led to black and several micrometers thick synthesized films. This confirms the suggestion that Glu ions show strong affinity to pyrrole molecules.

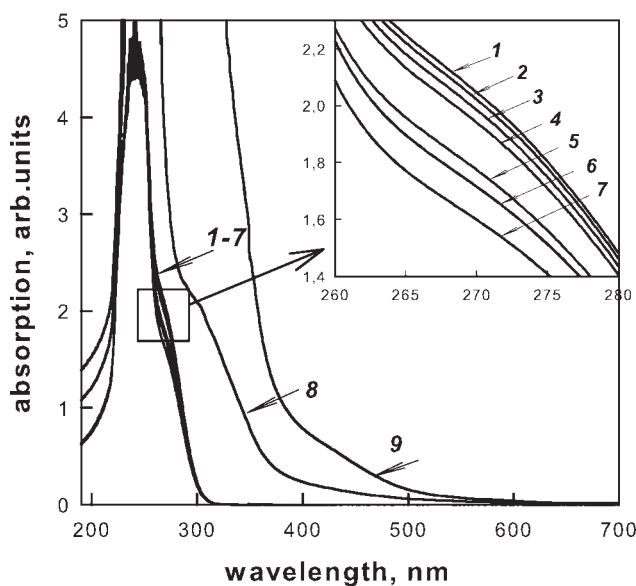
In the range of 10–100 s, the trends of the curves begin to divert from one another, and with increasing electrical current the resulting films become thick and black in color (Fig. 4, Curves 2–5). The second stage of PPy deposition without Glu ions is a dimerization of cation-radicals oxidized pyrrole.<sup>13</sup> Because the Glu ions seem to stabilize the resonance form [E], the next stage of polymerization is the same [eq. (4)].



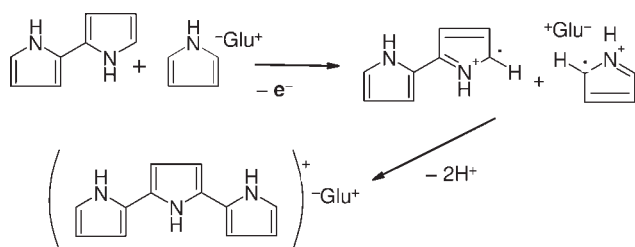
Eq. 4. Dimerization of pyrrole radicals in the presence of Glu ions

Protons are produced during this stage; this could affect the film growth because Glu takes on the zwitterionic structure. The zwitterionic form of the Glu ions in this case could stabilize the polymeric oligomers and not support the further film growth. This situation takes place in acidic solutions. Thus, this stage [eq. (4)] could be a limitation stage for the oxidation process.

The further oxidation of the dimers results in a chain growth in which Glu ions could also play a supporting role [eq. (5)]. This suggestion is supported by Smela,<sup>15</sup> where the structural analysis of PPy films doped with Glu ions has given that the Glu/Py ratio is 1 : 3. The Glu ions are incorporated into the PPy film during synthesis for charge compensation.



**Figure 5** UV-vis spectra of ageing solutions: (1) (1–7)  $0.1 \text{ mol L}^{-1} \text{ NaGlu} + 0.2 \text{ mol L}^{-1} \text{ Py}$ ; (1) at the start, (2) after 15 min, (3) after 34 min, (4) after 60 min, (5) after 150 min, (6) after 180 min, (7) after 248 min, (8) old yellow Py, and (9) very old brown Py.



Eq. 5. PPy chain growth in presence of Glu ions

The aforementioned description of the deposition process explains why neutral pH solutions resulted in the most successful deposition. The strong interaction between the zwitterionic Glu ions and Py molecules already during the preparation of the solution leads to a complex formation, where Py is forced into its induced dipole form, which is easier to oxidize. Because at  $\text{pH} > 5.5$  the Glu ions tend to show an anionic form, the unbounded Glu ions play a role of anions compensating the positive charge of the oligomeric chains and by this way support the further growth of oligomers.

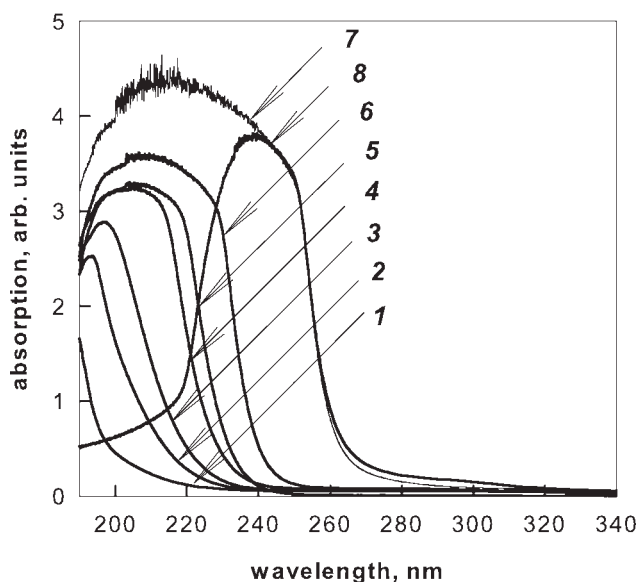
At alkaline pH values, the anionic structure of Glu results in less interaction between the Glu ions and Py monomers and subsequently in less stabilized monomer or oligomer radicals. The oligomers seem to be preferably in solution and in this case compensated by Glu positive charge of the oligomers does

not support chain growth on the electrode. This causes thinner deposited PPy films.

### UV-vis measurements of the solutions for the synthesis of PPy films

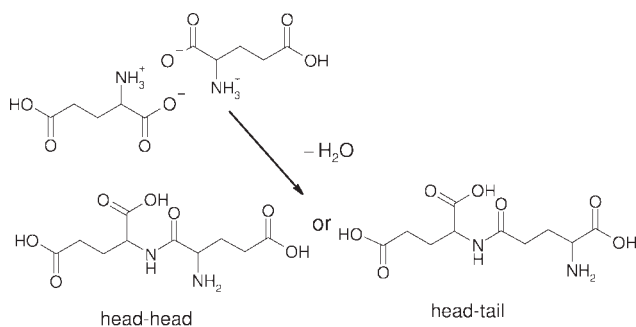
Spectroscopic studies were performed in an attempt to acquire more information about the composition and evolution of the deposition solutions. Pyrrole is unstable in contact with air, where oxidation accompanied by polymerization occurs and increases with exposure time. Because oxidation in air is slower than electrochemical oxidation and their initial oxidation stages seem to be similar, the initial stages of electrochemical oxidation could be observed during the exposition of such solutions in air. The UV-vis spectra were recorded for the solutions containing  $0.2 \text{ mol L}^{-1} \text{ Py}$  and  $0.1 \text{ mol L}^{-1} \text{ NaGlu}$  for approximately 4 h. As can be seen from Figure 5, there is a strong absorption in the 200–300 nm range: a large peak at 240 nm and a shoulder at 270 nm (inset in Fig. 5, Curves 1–7). The shoulder appears after the solution was exposed to air for 30 min, therefore Stage 1 [eq. (2)] has already taken place and some oligomers have been produced. The intensity of this shoulder decreases during the absorption measurements (inset in Fig. 5). This means that these substances take part in the further polymerization stages, which is confirmed by spectra of old polymerized pyrrole (Fig. 5, Curves 8–9). There is a broad absorption range within 300–500 nm, which corresponds to large polymer fragments in old pyrrole.

The shape of the spectra can be explained by taking into account spectra of the solutions of the single components (Fig. 6, Curves 1–7). A solution containing only NaGlu (Fig. 6, Curves 1–6) has strong absorption band in the range 190–240 nm; its maximum is shifted from 190 to 210 nm with an increase of the NaGlu concentration from 0.005 to  $0.5 \text{ mol L}^{-1}$ . The width at the half of this peak accordantly increases from approximately 20–40 nm with increasing of NaGlu concentration. The broadening of the peak at larger concentrations indicates the formation of dimers, trimers, or oligomers of glutamate [eq. (6)]. Wang et al.<sup>17</sup> detected the oligomerization of L-glutamic acid in the presence of *N,N*-carbonyldiimidazole using HPLC method without electrostimulation, and the process was enhanced in the presence of sodium chloride. In the electrochemical cell, chloride ions are always present due to their diffusion through the membrane from the KCl solution in the Ag/AgCl reference electrode. Because pyrrole molecules are quite similar to imidazole molecules, the oligomerization of glutamic ions could be also expected in the electrochemical cell as a parallel reaction. This corresponds to a broadening of the absorption peak and slight shift in the position of its maximum.



**Figure 6** UV-vis spectra of the freshly prepared water solutions of compounds with different concentrations, mol L<sup>-1</sup>: (1) 0.001 NaGlu; (2) 0.005 NaGlu; (3) 0.01 NaGlu; (4) 0.05 NaGlu; (5) 0.1 NaGlu; (6) 0.5 NaGlu; (7) 0.2 Py; and (8) 0.1 NaGlu + 0.2 Py.

The solutions containing only Py (0.2 mol L<sup>-1</sup>) show a strong and very broad absorption band in the range 190–260 nm with a maximum around 210 nm (Fig. 6, Curve 7). In mixed solutions containing 0.1 mol L<sup>-1</sup> NaGlu and 0.2 mol L<sup>-1</sup> Py, there are no prominent peaks that can be assigned to pure NaGlu or pyrrole, and a new strong peak appears at 240 nm (Fig. 6, Curve 8). This fact indicates a strong interaction between pyrrole and glutamate molecules, possibly resulting in a formation of a kind of complex [Py<sub>x</sub>Glu<sub>y</sub>]. Taking these results into account, the first stage of polymerization [eq. (3)] takes place already with the participation of this complex. This result also supports the suggestion that the Glu ions stabilize the monomer or oligomer radicals.



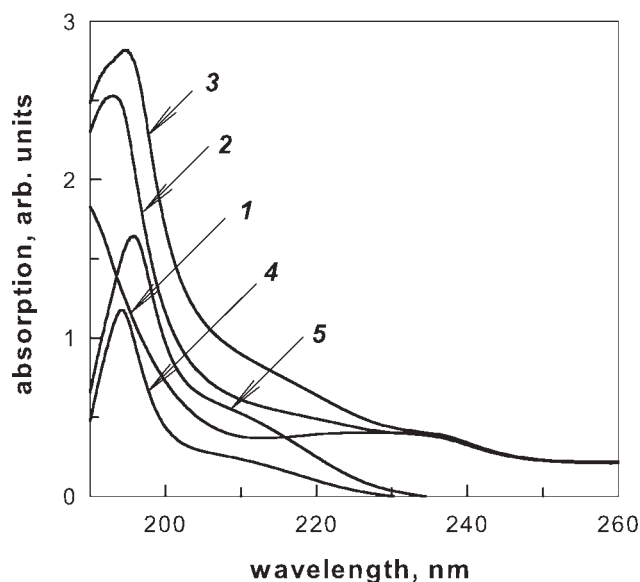
Eq. 6. Dimerization of glutamate

According to these results, the mechanism of the polymerization reaction would be different than that for PPy synthesis with other anionic species. The structure and composition of these complexes has a

significant impact on the kinetics of the electrochemical deposition of PPy layers at different pH of the solution, as was shown in influence of the pH value on PPy film deposition section. These complexes in the solution slowly oxidize over time in air, accompanied by the formation of oligomeric fragments, resulting in the appearance of a new absorption band at 270 nm (Fig. 5, Curves 1–7). Most likely, these oligomeric fragments grow further, so that the intensity of the absorption band of smaller fragments (270 nm) decreases (inset in Fig. 5), and a new low-intensity broad absorption band appears in the range more than 300 nm. The spectra of pure (not in solution) pyrrole oxidized up to different grades have a strong absorption in the same range and additionally broad prominent absorption in the range of more than 300 nm. The intensity and width of this absorption band increases with higher oxidation grade of pyrrole. The substance first becomes yellow in color (Fig. 5, Curve 8), turning darker with time (Fig. 5, Curve 9) due to the formation of larger PPy chains in liquid pyrrole.

#### Properties of synthesized PPy films doped with Glu ions

The electrochemical stimulation of biocompatible substances can be applied for the controlled uptake and release of biological molecules.<sup>18</sup> As was shown by Deore et al.,<sup>6</sup> glutamic acid ions can be removed from the PPy films by overoxidation of the polymer layer. After the removal of Glu ions, the PPy films contain cavities that demonstrate a possibility to serve for the enantioselective uptake/release of glutamic acid ions. The PPy layer is possibly partially overoxidized already during the synthesis. In this work, the synthesized films were thoroughly washed with Millipore water and then additionally “soft” cycling in the range -0.3 to +0.8 V was applied. Immediately after the treatment, the spectra of the resulting solutions were recorded (Fig. 7). The additional cycling was performed in pure Millipore water at pH = 7, supported by a buffer solution (Fig. 7, Curve 1). The release of glutamic acid ions was detected (Fig. 7, Curves 4 and 5). It was observed that 10 complete voltammetric cycles resulted in a strong absorption peak with a maximum at 193 nm (Fig. 7, Curve 2). Further cycling resulted in an increase of the peak intensity and a shift of its maximum to 196 nm (Fig. 7, Curve 3). The subtraction of the spectrum of the buffer solution from the spectrum after additional voltammetric cycles shows that these solutions most likely contain glutamate (Fig. 7, Curves 4 and 5), because the shape of these spectra is very close to the spectrum of solution containing only pure sodium glutamate with a concentration of 0.005 mol L<sup>-1</sup> (Fig. 6, Curve



**Figure 7** UV-vis spectra of the solutions: (1) before overoxidation (only buffer solution), (2) after 10 overoxidation cycles, (3) after 20 overoxidation cycles, (4) subtraction of spectrum of buffer solution from spectrum after 10 overoxidation cycles, and (5) subtraction of spectrum of buffer solution from spectrum after 20 overoxidation cycles.

2). At this low concentration ( $0.005 \text{ mol L}^{-1}$ ), glutamate molecules are very well diluted and most likely present in single molecular form. This assumption would mean that glutamic ions could individually be incorporated in PPy films.

### CONCLUSIONS

The mechanism of the electrochemical deposition of PPy films doped with L-glutamic ions was investigated. The synthesis conditions, including the concentration and concentration ratio of reagents, and pH value of the deposition solution were varied. It was demonstrated that the mechanism of the deposition of PPy films, doped during synthesis with glu-

tamic ions, is unique and differs from the deposition of pyrrole with other anionic species. It was found that thicker PPy films could be deposited at neutral pH than under acidic or basic conditions and that an excess of Glu ions is helpful for film deposition. The Glu ions were found to interact strongly with Py molecules, apparently in form of a complex  $[\text{Py}_x\text{Glu}_y]$ . It was additionally shown by UV-vis spectra that these glutamic ions could be released from the film using additional cyclic voltammetry.

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