# Investigation of Styrene−Methacrylic Acid Block Copolymer Micelle Doped Polypyrrole Films by Scanning Electrochemical Microscopy

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The preparation of a novel type of polypyrrole films is described. Spherical styrene−methacrylic acid block copolymer micelles with a hydrophobic core of 18 nm and a hydrophilic corona of 100 nm were incorporated in polypyrrole films by electropolymerization from a mixed solvent with 80 vol % of dioxane and 20 vol % of water. The properties of the block copolymer micelle doped polypyrrole films were investigated by cyclic voltammetry and scanning electrochemical microscopy (SECM). It was found that the self-assembled block copolymer micelles in polypyrrole behave as polyanions and the charge compensation by cations has been identified during electrochemical switching of the polymer films. The ejection of cations from the films was monitored by SECM using an amperometric or potentiometric ultramicroelectrode tip during different potential programs (potential step and cyclic voltammetric scans) applied on the block copolymer micelle doped polypyrrole modified substrate electrodes. The incorporation of self-assembled block copolymer micelles into the polypyrrole structure can represent an interesting way to change its properties. Different kinds of hydrophobic molecules can be dissolved in the core of the micelle and thus incorporated into the polypyrrole films.

## Introduction

Electrochemically formed conductive polymer films have been used widely for preparing chemically modified electrodes of different functions. In these works most often freshly distilled pyrrole served as a reagent for the electrochemical oxidation, which resulted in an insoluble polypyrrole electrode modifying film. The differently prepared polypyrrole films show electroactivity. Considerable interest has been focused on the elucidation of the mechanism of charge transport in polypyrrole films, as well as toward the redox characteristics of the films.[1]

The electrochemically formed, cross-linked polypyrrole matrixes can entrap different molecules as enzymes,[2,3] antibodies,[4] or electrochemically active compounds.[5] Biosensors, electrocatalytic electrodes, or analyte preconcentrating probes can be prepared in this way. Another way to modify the character and the behavior of conductive polymer films is offered by the selection and the replacement of the charge-compensating ions. As it is known the electrochemical switching of the polymer films induces the exchange of ionic species between the film and the fluid media. Taking advantage on this exchange process, the polymer films with different practically useful functions can be obtained. For example, the amperometric detection of electrochemically inactive[6] ions has been carried out with conductive polymer coated electrodes in ion chromatographic separations.[7] Drug-delivering conductive polymer coated electrodes can be prepared, which enable the introduction of different molecules into a certain target area with coulometric precision and with spatial and time resolution.[8] Interestingly the ion-exchange character of specially designed and prepared polypyrrole films can be switched from anionic to cationic by changing the redox state of the polymer matrix.[9]

The charge transport character and the electrochemical behavior of polypyrrole films depend very much on the conditions of their preparation and on the nature of species entrapped in the matrix. A great number of publications[10−13] deal with the study of injection and ejection of the charge balancing ions occurring during electrochemical oxidation or reduction of the polymer films, i.e., during electrochemical switching of the polymer. It was found that if polyanions are incorporated into the polypyrrole films, then, in contrast to polypyrrole with small anions, polyanions due to their large size and their encapsulation into the polypyrrole chains cannot take part in the charge balancing ion-transport process during the electrochemical switching of the films. In this case small cations moving opposite direction are involved in the charge compensation.[10,14]

In recent years the self-assembling molecules attracted considerable attention, because of their specific characters and perspective application in coatings, adhesives, thin films, microfabrication of electronic devices, pharmaceuticals, photographic technology, and biosensor research. The block copolymers made by joining blocks of different monomer molecules show an interesting feature when dissolved in selective solvents, which are good solvents for one block but poor for the other. They form self-assembled spherical micelles with a dense core composed of the insoluble blocks and a corona consisting of the soluble blocks.[15,16] These micelles differ from the classical detergent micelles by their larger size and greater stability.

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Micelle-Doped Polypyrrole Films

*J. Phys. Chem. B, Vol. 102, No. 49, 1998* **9935**

It was expected that the block copolymers or block copolymer micelles can be incorporated in electrochemically formed polypyrrole films. It was also reasonable to believe that by the incorporation of the specially tailored block copolymer units into polymers the properties of the polymer films can be modified and made it proper for certain kinds of applications.

Different methods have been employed to study the charge transport processes in doped conductive polymer films. Among them different electrochemical and spectroelectrochemical techniques,[17,18] ellipsometry,[19] and electrochemical quartz crystal microbalance[20–23] need to be mentioned.

Scanning electrochemical microscopy (SECM) is a powerful new technique for studying local concentration profiles in microscale. Recently Arca and co-workers[24] investigated the ion and electron transfer in polypyrrole films by SECM with amperometric ultramicro platinum disk measuring tip. In their experiments the *in* and *out* fluxes of different kinds of charge balancing ions from the polypyrrole films during electrochemical redox processes were clearly detected. In this way the anion exclusion and cation absorption ratio during electrochemical switching of the polypyrrole film under different experimental conditions could be estimated. It was also proved by SECM that the location of the charge exchange reaction is at the polymer–electrolyte interface.

Denuault and co-workers[25,26] used SECM for monitoring the changes in chloride concentrations close to the polyaniline film modified substrate electrode. In this work potentiometric silver chloride coated silver microdisk electrode was used as a measuring tip. Anson and Kwak[27] have investigated the ejection and incorporation of $Fe(CN)_6^{3-/4-}$ counterions at protonated poly(4-vinylpyridine) films, while in another work Anson and Lee[28] report on the monitoring of the ejection of $Os(bpy)_3^{3+/2+}$ from Nafion coatings.

In the work to be reported here, block copolymer micelles of styrene and methacrylic acid blocks were incorporated as dopants in electrochemically polymerized polypyrrole films. The behavior of this new, electrode-modifying film was investigated by cyclic voltammetry and SECM.

In the block copolymers used the styrene block is hydrophobic while the methacrylic acid one is hydrophilic.[29,30] They are mutually incompatible and interact differently with solvents. The formation of self-assembly of the micelles is facilitated in 80:20% (v/v) dioxane/water solvent mixture. Dioxane is a good solvent for both blocks, while the water is a precipitant for the polystyrene block. In this solvent mixture the micelles have narrow size distribution and the polystyrene core is substantially swollen in dioxane.

## Experimental Section

**Chemicals.** Pyrrole (Ventron, Karlsruhe, Germany) was distilled under vacuum and stored under nitrogen atmosphere at low temperature. The ion-selective membrane components, except the ligand BME-44 (2,2′-bis[3,4-(15-crown-5)-2-nitro-phenylcarbamoxymethyl]tetradecane), poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (oNPOE), potassium tetrakis(4-chlorophenyl) borate (KTpClPB), and tetrahydrofuran (THF) were obtained from Fluka AG (Buchs, Switzerland). The potassium selective ligand BME-44 was designed and synthesized at the Department of Organic Chemical Technology, Technical University of Budapest, Budapest, Hungary.[31]

Styrene–methacrylic acid block copolymer (PS-*b*-PMMA) was synthesized and characterized in the Department of Chemistry and Biochemistry and the Center for Polymer

Research of the University of Texas at Austin as in refs (30, 32, 33), and it was the generous gift of Professor Petr Munk.

Physical properties of the block copolymer (PS-*b*-PMMA): molecular weight measured with gel chromatography, 47 700; weight fraction of the polystyrene measured by NMR, 55.0%; molar mass of micelles in dioxane/water mixture of 80:20% (v/v), $3.7 \times 10^6$; core size, 18 nm.

Inorganic chemicals such as KCl, $CaCl_2$, and $Cd(NO_3)_2$ were purchased from Fluka AG (Buchs, Switzerland) and were used as received. All solutions were prepared with doubly quartz-distilled water.

**Electrodes.** For SECM studies platinum and gold microdisk ultramicroelectrodes were fabricated as described previously.[34] The radius of the insulating ring was always chosen to be 10 times the radius of the microtip (RG = 10). They were wet polished with 0.05 $\mu$m alumina before each experiment. The gold microdisk electrodes were amalgamated by immersing them in a Hg pool for a few seconds.

Micropipet type potassium selective electrodes prepared as in ref 35 were used to monitor potassium ion fluxes. The composition of the ion-selective cocktail was the following: 4 wt % BME-44; 10 wt % PVC; 86 wt % oNPOE; 70 mol % KTpClPB.

For the electrochemical deposition of pyrrole a Pt disk electrode was used as substrate electrode. A Pt wire with 500 $\mu$m diameter (Goodfellow, Cambridge, U.K.) was sealed in glass tube under vacuum in a section of 5 mm, leaving one end of wire free for electric contact. The sealed end of the glass tube was polished by sandpaper until the wire cross section became visible, and then it was polished successively with finer and finer alumina suspension from 1 to 0.05 $\mu$m diameter. The electrodes were rinsed with distilled water before further use.

In the amperometric SECM experiments Pt wire served as counter electrode while a double junction saturated calomel electrode (SCE) with 0.1 M $KNO_3$ bridge electrolyte was used as reference. The switching of the substrate electrode potential (500 $\mu$m diameter Pt electrode covered with block copolymer micelle doped polypyrrole film) and current recording (amalgamated gold electrode) was performed simultaneously with a bipotentiostat (BIPAD, Tacussel, Lyon, France).

In the potentiometric SECM measurements a home-built high-impedance voltmeter was used for potential recording. A double junction saturated calomel electrode (SCE) with 0.1 M lithium acetate bridge electrolyte was employed as reference electrode. The potential switching of the substrate electrode was made with a special battery driven, home-built potential programmer.

The SECM apparatus, built in our laboratory, was described in detail previously.[36] This apparatus incorporates three step motor-driven high-resolution positioning stages (Newport, Evry, France) controlled through a PC-Lab 812 interface (Advantech, Sunnyvale, CA) by a Pentium personal computer.

**Preparation of Polypyrrole Films.** To prepare the polypyrrole films on the Pt disk surface, 5 mg of styrene–methacrylic acid block copolymer was dissolved in 5 mL of mixed solvent (80 vol % dioxane and 20 vol % water). A 15 min time was given for self-assembled micelle formation. During this time period the solution was sonicated to prevent cluster formation. Then 500 $\mu$L of freshly distilled pyrrole was added to the micelles containing solution, and it was purged with high-purity nitrogen. The higher the pyrrole concentration, the higher the film formation rate; however, the stability of the micelle-containing solution decreases with the increasing pyrrole content. The pyrrole concentration used in the experiments was selected as a compromise between the acceptable film formation

time and the necessary stability of the micelles in the solution. It was determined by trial and error.

The polymer film loaded with micelles was prepared by potentiostatic oxidation of the pyrrole for at least 90 min at a 500 $\mu$m diameter Pt disk at 1.9 V using a BAS-100 B/W electrochemical workstation (Bioanalytical System, West Lafayette, IN) in the micelles containing a partially nonaqueous pyrrole solution. Ag/AgCl wire was used as a reference electrode during polymerization. The thickness of the polypyrrole film was determined by atomic force microscopy. For the measurements, the tip was positioned in close proximity to the polypyrrole covered Pt/glass shielding interface. A 70 × 70 $\mu$m portion of the electrode surface was scanned with the $x$ axis perpendicular to the separation line of the polypyrrole/glass insulator layers. The thickness of the polymer film was estimated from the difference of the average $z$ coordinate values obtained for the glass and for the polypyrrole film. The thickness of the black polymer film obtained after 1.5−3 h of electropolymerization was found usually within 1−15 $\mu$m by AFM. Before measurement the films were rinsed with deionized water.

**SECM Procedure.** The polypyrrole/polystyrene−methacrylic acid films were loaded with cations in two different ways. In the first kind of experiments the polypyrrole-modified films were reduced (−0.6 V versus SCE) in the presence of 0.01 M Cd(NO$_3$)$_2$ solution, while, in the second type of the experiments, the freshly prepared film was kept in 0.1 M KCl overnight. The films were rinsed with deionized water before incorporating them into the SECM cell.

To perform the SECM experiments, the substrate covered with the polymer film was mounted into the base of the SECM cell (of 15 mL; made of Perspex glass). As a background electrolyte 0.1 M KCl was used in the Cd$^{2+}$ ion ejection monitoring experiments, while 0.1 M CaCl$_2$ was used in the K$^+$ ion outflow monitoring experiments. In the amperometric Cd$^{2+}$ monitoring experiment the oxygen was eliminated from the KCl background electrolyte either by purging it out with ultrahigh purity nitrogen or by the addition of a few crystals of Na$_2$SO$_3$ and trace amounts of Cu$^{2+}$.

The monitoring of ion release from polypyrrole/polystyrene−methacrylic acid (PPY/PA) films was carried out at preselected substrate potential or by redox cycling. The ultramicro tip was positioned close to the film/solution interface. Depending on the nature of the cations to be monitored, potentiometric ion−selective or amperometric measuring tips were used.

During the amperometric measurements the potential of the amalgamated gold electrode was held at − 0.8 V versus SCE. An amalgamated gold ultramicro electrode was positioned in the close proximity of the film, and the amperometric tip current was recorded. In the cation ejection experiments we selected dissolved O$_2$ as an electroactive species for the estimation of tip to substrate distance and to achieve the precise positioning of the tip, as described previously.[3,4] In voltammetric SECM experiments the determination of the tip to substrate distance always preceded the oxygen elimination step.

In potentiometric SECM measurements the tip to substrate distance was adjusted in an empirical way. The micropipet was carefully moved toward the target from $z$ direction until it contacted the electrode surface. During this downward movement of the tip, the tip potential was continuously monitored. As the tip touched the substrate, a potential jump was observed and concomitantly its forward movement was stopped. Subsequently the tip was withdrawn usually with 1 $\mu$m, adjusting in this way the tip to substrate distance.

To detect the potential dependent feedback character (insulator, conductor) of electrochemically prepared polymer films by SECM, 2 mM ruthenium hexamine chloride (Ru(NH$_3$)$_6$Cl$_3$) as a mediator, 0.1 M KCl solution as background electrolyte, and a 25 $\mu$m platinum ultramicro electrode as a measuring tip were used.

## Results and Discussion

**Electrochemical Investigation of the Polypyrrole/Polystyrene−Methacrylate Film.** The electropolymerization of polypyrrole onto metal surface proceeds in the presence of negatively charged counterions. In analogy we incorporated styrene-methacrylate copolymer micelles as large polyanions (PA) into the polypyrrole polymer matrix by electrochemical polymerization of pyrrole in block copolymer containing mixed solvent:
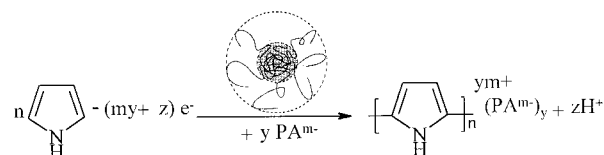


In connection with this, the possibility that during the long electropolymerization time, the Cl$^-$ ions leaking out from the reference electrode may facilitate the polypyrrole film formation even in the absence of the negatively charged copolymer micelles needs to be addressed. To clarify this, the electrochemical polymerization of polypyrrole was attempted under the same experimental conditions as described in the Experimental Section, in the absence of the styrene−methacrylic acid block copolymer micelles also. The result of this experiment has proved that if no anions are added into the polypyrrole containing solution, no polypyrrole film is formed on the Pt substrate electrode. This result clearly proves that the incorporation of the block copolymers in the polypyrrole structure during electropolymerization was successful.

The mechanism of redox reaction of polypyrrole film depends strongly on the structure of the anion incorporated. As in our experiments, the polypyrrole film was prepared in the presence of large polyanions and it is expected that the mobility of the incorporated anions in the matrix is low. Consequently during the electrochemical switching of the polypyrrole (PPY) the charge is assumed to be compensated by cations:

$$\text{PPY}/n\text{PA}^{m-}p\text{C}^{q+} \xrightleftharpoons{pq\text{e}^-} \text{PPY}^{qp+}n\text{PA}^{m-} + P\text{C}^{q+}$$
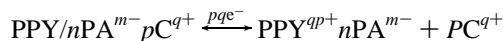
Here C$^{q+}$ stands for cation.

In Figure 1, the cyclic voltammograms of differently prepared polypyrrole films are shown. Curve A is obtained with polypyrrole film prepared in the presence of small size Cl$^-$ counterions (in 1 M KCl at 0.8 V for 30 s), and its shape agrees well with that reported for small, mobile anion doped polypyrrole film.[37] Curve B is the CV of the block copolymer doped polypyrrole film. The difference is obvious. The electrochemical oxidation of the block copolymer micelles containing film results in two "peaks" in the CV (curve B), with relatively small $i_p$ values and the shift of the peak potential to higher positive values. This indicates that the transport of the charge balancing ion during oxidation is hindered.

In SECM with amperometric active measuring tip, the information about the chemical nature of the target surface can be obtained by studying the character of the "feedback" effects. A conductive surface amplifies the current response of the
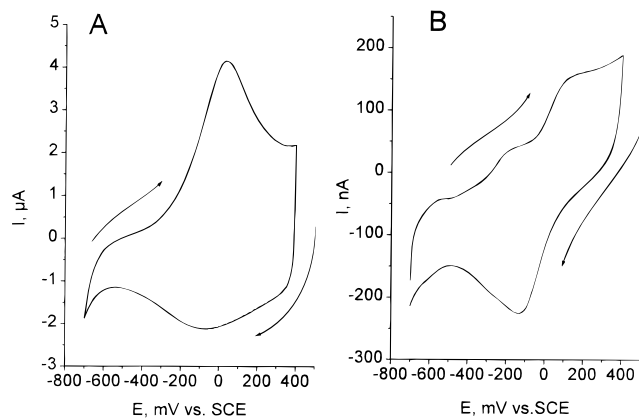
Micelle-Doped Polypyrrole Films

*J. Phys. Chem. B, Vol. 102, No. 49, 1998* **9937**



**Figure 1.** Steady-state cyclic voltammograms of differently prepared polypyrrole-modified Pt disk ($d = 500 \, \mu$m) electrodes: (A) polypyrrole film doped with Cl$^-$ as mobile counterions (sweep rate: 50 mV/s, background electrolyte: 0.1 M KCl); (B) polypyrrole film doped with styrene−methacrylic acid block copolymer micelles as charge-compensating ions (sweep rate: 50 mV/s, background electrolyte: 1 M KNO$_3$).



**Figure 2.** Approaching curves to a 500 $\mu$m diameter platinum disk electrode covered with styrene−methacrylic acid block copolymer micelles containing polypyrrole film. The tip was scanned at 3.5 $\mu$m/s. In case A the film was reduced at −0.4 V versus SCE, and in case B the film was oxidized at 0.4 V versus SCE prior the measurements. Tip: 25 $\mu$m diameter platinum microdisk electrodel. Tip potential: −0.4 V versus SCE. Mediator: 2 mM Ru(NH$_3$)$_6$Cl$_3$ in 0.1 M KCl.

ultramicro amperometric electrode, corresponding to the electrochemical reaction of a reversible electroactive redox couple by regenerating the electroactive species (*positive feedback*). In contrast, with the approach to the insulator surface by the ultramicro measuring tip, the current decreases due to the hindered diffusion of the electroactive species (*negative feedback*). The feedback character of the reduced and oxidized block copolymer doped polypyrrole film can also be questioned. To study this experimentally, the polypyrrole coating was reduced at −0.4 V or oxidized at +0.4 V versus SCE and then was mounted in the SECM cell base with the coated surface upside. Using 2 mM Ru(NH$_3$)$_6$Cl$_3$ as a reversible redox couple, the Pt disk ultramicro electrodes with 25 $\mu$m diameter were moved toward the doped polypyrrole film surface (in the meantime the PPy/PA film was held at open circuit potential), while the current was recorded at −0.4 V versus SCE tip potential in the oxygen-free 0.1 M KCl background electrolyte. The relevant approaching curves are shown in Figure 2. Figure 2A was recorded with reduced film, while Figure 2B shows the current−tip distance dependence obtained in case of the oxidized block copolymer micelle doped polypyrrole film.

The comparison of the two curves clearly indicates the difference in the feedback character of the reduced and oxidized block copolymer doped polypyrrole films. In the case of reduced polymer films, negative feedback effect, while, in the case of the oxidized films, positive feedback effect influenced the amperometric tip current. Although the feedback character of the film could clearly be observed, by fitting the theoretical approach curves to the experimental data discrepancies were found between the theoretical and experimental curves. The deviation is most likely caused by the porosity and roughness of the block copolymer micelle doped polypyrrole films. The substrate is very far from the ideal "smooth" surface for which the theoretical approach curves were derived.

**Monitoring the Ionic Transport from the Polypyrrole/Polystyrene−Methacrylate Film.** SECM is an excellent method for the study of local ion fluxes. In this work our intention was to investigate the charge balancing counterion fluxes during redox cycling of the block copolymer micelle doped polypyrrole films using this technique. It was reasonable to believe that if we incorporate negatively charged block copolymer spheres into the polypyrrole matrix, then the role of charge balancing will be played by mobile cations as it is in
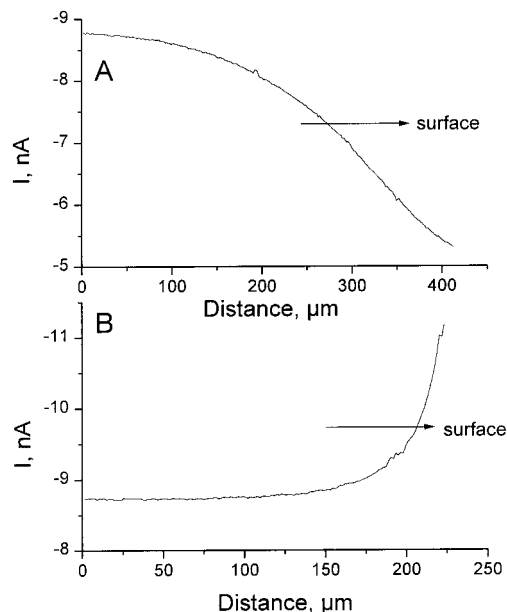
the case of other large anion doped polymer films. To follow the cation fluxes, Cd$^{2+}$ ions were selected, because the oxidation state of the Cd$^{2+}$ ions does not change in the potential range employed during redox cycling of the polymer film substrate. Small concentrations of Cd$^{2+}$ ions can be conveniently measured with amalgamated gold ultramicroelectrodes in oxygen-free media. Thus, in our studies block copolymer doped polypyrrole films on Pt disk substrates were loaded with Cd$^{2+}$ ions by immersing them in oxygen-free 10$^{-2}$ M Cd(NO$_3$)$_2$ solution at −0.6 V versus SCE for 15 min.

After rinsing of the film with deionized water, the PPy/PA covered platinum disk sample substrate was introduced into the SECM cell filled with 0.1 M KCl solution. A 25 $\mu$m amalgamated gold tip was positioned about 10 $\mu$m away from the film and biased at −0.8 V versus SCE, where the Cd$^{2+}$ ions could be detected through their reduction current. The tip current recorded reflects the flux of Cd$^{2+}$ ions ejected from the PPy/PA film.

Figure 3 shows a sequence of recordings relevant to the ejection of Cd$^{2+}$ ions from the Cd$^{2+}$ ions loaded PPy/PA film, at subsequent substrate potential scans from −0.7 to +0.5 V. The data presented clearly show that parallel with the oxidation of the film a considerable amount of cadmium ion outflows from the polymer film. As the reduction of the film proceeds, the uptake of the cadmium ions can occur; however, a part of the released cadmium ions diffuses into the bulk of the solution and the cadmium ion content of the film is gradually decreasing. These are indicated in Figure 3 by the decreasing heights of the subsequent current−time recordings corresponding to repeated scans. At the same time it is supposed that in the reduced state the compensation of the excess of negative charges due to the presence of immobile polyanions in the film is− most likely−gradually overtaken by the K$^+$ ions.

The outflow of Cd$^{2+}$ ions from the PPy/PA films was also checked at constant oxidation potential of the substrate. For this an accumulation time of 20 min in a 0.01 M Cd(NO$_3$)$_2$
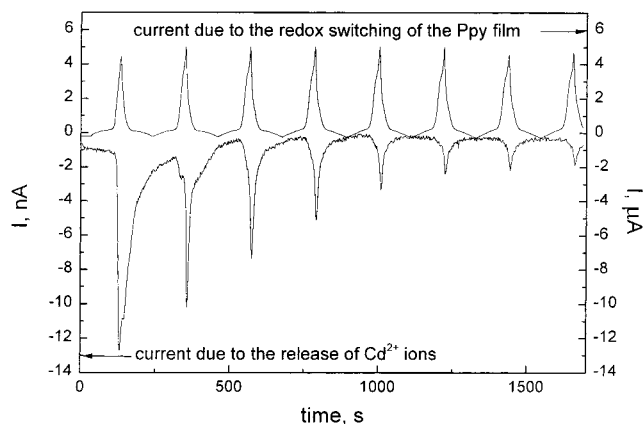
**Figure 3.** Simultaneous recording of the substrate electrode (500 $\mu$m diameter PPY/PA film covered Pt electrode loaded with $Cd^{2+}$ at $-0.6$ V versus SCE for 15 min in $10^{-2}$ M $Cd^{2+}$) current and tip (25 $\mu$m diameter amalgamated gold microelectrode) current during subsequent potential cycling of the substrate electrode between $-0.7$ and $+0.5$ V (tip potential: $-0.8$ V versus SCE, background electrolyte: 0.1 M KCl). Negative current represents the reduction of cadmium ions on the tip. Positive current was measured during the redox switching of the polypyrrole film.
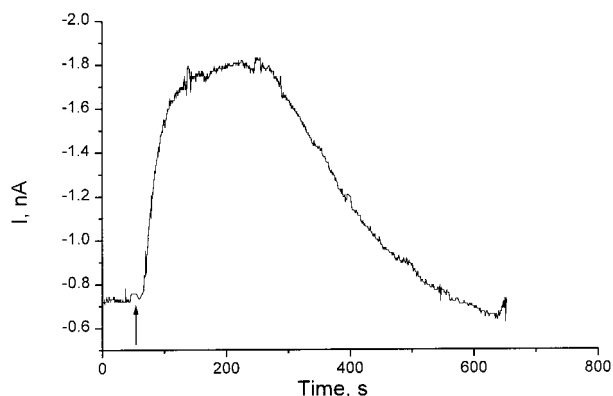


**Figure 4.** Ejection of cadmium ions during the oxidation of the polypyrrole film. The constant oxidation potential of the film was 0.5 V. The arrow indicates the potential switching of the polypyrrole electrode to 0.5 V. Tip: $r = 50$ $\mu$m amalgamated gold microdisk electrode. Tip potential: $-0.8$ V versus SCE. Background electrolyte: 0.1 M KCl.

solution at $-0.5$ V versus SCE was employed. The experimental setup was the same as it was employed for the previous experiment. The relevant experimental results presented in Figure 4 show a continuous release of the $Cd^{2+}$ ions in time from the PPy/PA film until the $Cd^{2+}$ ion "reserve" accumulated in the PPy/PA has become exhausted. One can distinguish three different regions on the curve shown in Figure 4: a relatively sharp rising part followed by a broad current maximum and a slow descending part. The rising part is due to a relatively fast initial release of $Cd^{2+}$ ions. Most likely the diffusion through the relatively thick membrane used for this study is responsible for the time delay of the maximum current. The descending part of the curve is primarily affected by the gradual depletion of the $Cd^{2+}$ content of the polypyrrole film but can be influenced by solution diffusion also.

Amperometric detection is very sensitive; however, its selectivity is considered rather poor. Therefore, the ion-flux experiments were repeated by loading the film with an ion, which can be detected with an ion-selective potentiometric electrode. For this study potassium ions were selected as mobile charge balancing cations. As known, the potentiometric detection of single charged ions is more sensitive and also ionophores
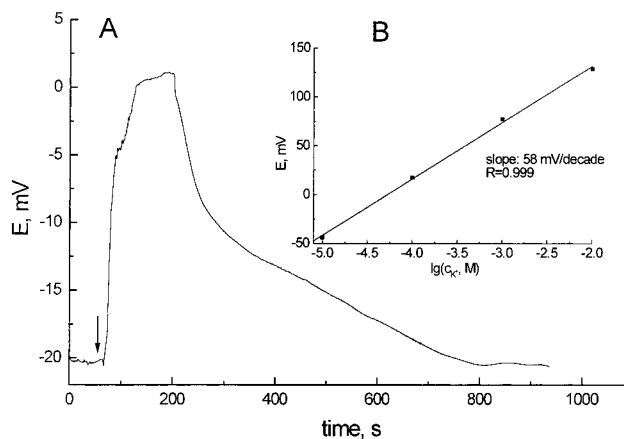


**Figure 5.** Curve A: Ejection of potassium ions from oxidized polypyrrole film. The constant oxidation potential of the film was 0.5 V. The arrow indicates the potential switching of the polypyrrole electrode to 0.5 V (measuring tip: potassium ion-selective microelectrode; background electrolyte: 0.1 M $CaCl_2$). Curve B: Calibration curve of the potassium ion-selective microelectrode

for ion-selective electrodes with good selectivity toward potassium ions are readily available. In our work a highly selective ionophore, BME-44, was selected to prepare potassium ion-selective microelectrodes.

In this experiment, similarly with the amperometric ones, first the PPy/PA films were loaded with potassium ions. In this case the freshly prepared films were immersed in 0.1 M KCl solution overnight. Before the SECM measurements the modified polypyrrole films were carefully rinsed with deionized water, and then the substrate electrode was mounted in the SECM cell in the same way as described for amperometric measurements. The cell was filled with about 10 mL of 0.1 M $CaCl_2$ solution. The potassium ion-selective tip was positioned over the PPy/PA surface within 5 $\mu$m distance, and the potential of the ion-selective electrode was recorded in time. After a steady-state reading was obtained, the potential of the substrate was switched from the open circuit potential to $+0.5$ V. The relevant potential versus time recording obtained is shown in Figure 5A. The data presented clearly indicate that the oxidation of the PPy/PA film induces the $K^+$ ion outflow. The recorded curve very much resembles the one obtained during $Cd^{2+}$ release. However, when comparing the shape of the two curves, one should keep in mind the difference in the concentration dependence of analytical signals of the two types of sensors, which is linear for amperometric detectors, while logarithmic for potentiometric ones. Although exactly the same experimental conditions (from objective reasons) for amperometric and potentiometric monitoring could not be set, some careful conclusions may be drawn. When using an amperometric tip, because of the glass shielding, a thin solution layer channel like gap is formed between the substrate and the tip. Furthermore the substrate electrode cannot be considered as a point source of $Cd^{2+}$; initially there is no concentration gradient between the solution in the channel and the outer solution just above the polypyrrole layer. All these increase the transit time of the detected molecule in the proximity of the sensing area as their diffusion is hindered. Most likely this is the explanation for the broad maximum in case of amperometric detection. The fact that potentiometric detection is less affected by diffusion proves that the falling part of the curve is mainly due to a gradual depletion of potassium from the film.

It is well-known that polypyrrole films doped with small anions present a potentiometric response toward anions.[38] As

Micelle-Doped Polypyrrole Films

*J. Phys. Chem. B, Vol. 102, No. 49, 1998* **9939**

in the PPy/PA films, the cations are the main charge balancing ions; it was interesting to verify whether the PPy/PA shows an anionic or a cationic potentiometric response. The potential response of the Pt electrode covered with the $K^+$-loaded PPY/PA film was measured in $KNO_3$ solutions of different concentrations. The electrode potential vs log $a_{KNO_3}$ plot obtained in the range of $10^{-3}-10^{-1}$ M was linear with a $+39$ mV/decade positive slope value. This clearly validates that the charge compensation during electrochemical oxidation or reduction of a copolymer micelle containing polypyrrole film involves the movement of cations, in this case potassium ions.

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