Synthesis of Adherent Hydrophilic Polypyrrole Coatings onto (Semi)conducting Surfaces

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Hydrophilic and adherent polypyrrole coatings were prepared by a two-step electrochemical method. First, α-pyrrole, ω-acrylate polyethylene oxide (Py-PEO-A) dual macromonomer was synthesized by anionic polymerization and electrografted onto (semi)conducting substrates by cathodic polymerization of the acrylic end-group. The obtained adherent coating is hydrophilic and thus swells in water and bears a pyrrole ring, a precursor of the conducting polymer. In a second step, the coating is anodically polarized in a mixture of Py and Py-PEO to give the hydrophilic and adherent polypyrrole. Properties such as morphology, adherence, electroactivity, and hydrophilicity of these coatings were investigated by conventional methods and compared to those of pure polypyrrole coatings. These novel coatings exhibit efficient protein adsorption repellency and are thus good candidates for applications in biomaterials and biosensors.

Introduction

Polymer coating of inorganic surfaces is a technology of the utmost importance, in which conjugated polymers are playing a steadily increasing role.[1] Indeed, conjugated polymers offer the advantage to easily tune the thickness of electrodeposited films and to be electroactive. Additionally, the use of functional monomers is a very simple way to impart functionality to the final coating. Promising developments of these conducting polymer coatings in biotechnology have resulted in a number of studies that treat their biocompatibility issue.[2−7] Polypyrrole (PPy) is by far the most extensively investigated electrically conductive polymer for biocoating purposes, because of high electrical conductivity, flexible method of preparation,[8] easy surface modification,[9] and excellent environmental stability.[10] However, in order to increase the biocompatibility, there is a need to develop new functional pyrrole monomers with as high hydrophilicity as possible.[11] In this respect, pyrrole derivatives with pendent hydrophilic groups such as poly(ethylene glycol) have been prepared and polymerized as coatings of implantable medical devices for protecting them against thrombosis and restenosis.[5,12] However, the major limitation of these coatings is the lack of adherence to the metal onto which it has been electrodeposited, which is a critical issue in the case of expandable devices, such as intravascular stents. Moreover, PPy and derivatives have aroused much interest in the design of biosensors because of the well-suited redox potential of PPy and the possibility of growing PPy from an aqueous solution. For example, Cosnier[13] prepared amphiphilic pyrrole and used it for the entrapment of redox enzymes. To the best of our knowledge, the electropolymerization of hydrophilic pyrrole in aqueous medium with formation of conductive films strongly adherent onto conductive substrates has not been reported yet.

This paper aims at reporting on a two-step electrochemical process that consists of the cathodic polymerization of a

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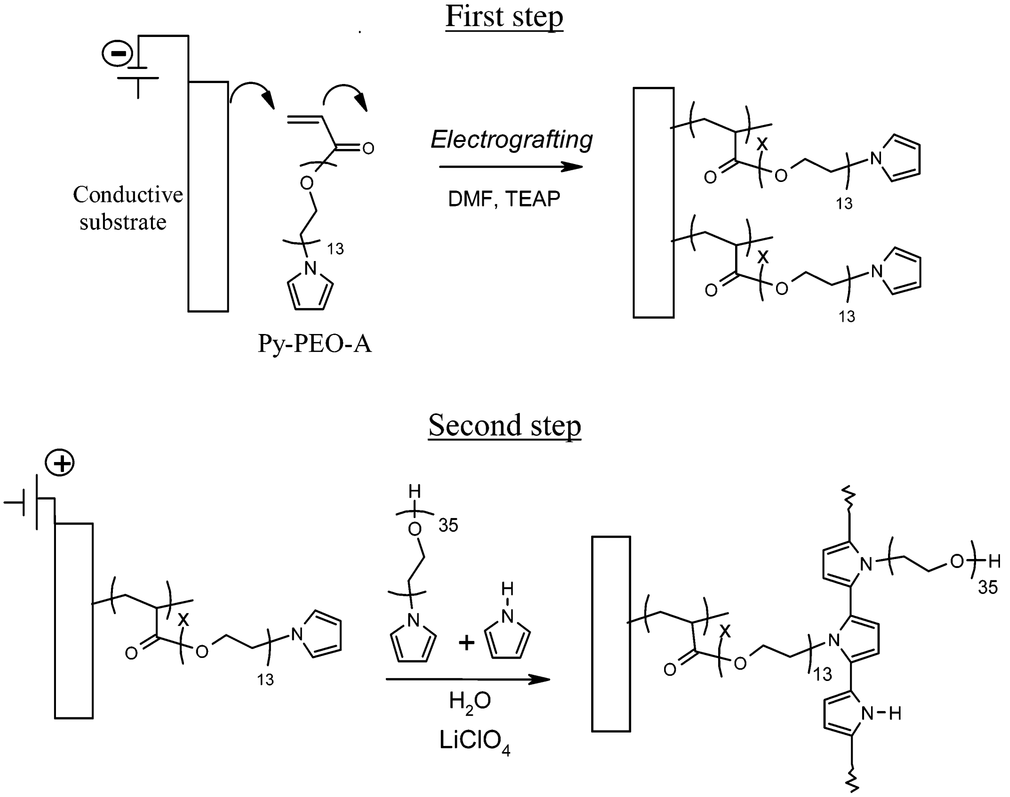
Scheme 1. Cathodic Polymerization of Py-PEO-A Macromonomer in DMF and Chemisorption of the Chains at the Potential of the Passivation Peak (First Step) and Anodic Polymerization of a Mixture of Py and Py-PEO in Water (Second Step)



pyrrole-containing acrylate with the simultaneous chemisorption of the chains, followed by an inversion of the electrode polarization and the anodic copolymerization of the pyrrole units of the polyacrylate film with pyrrole and pyrrole-PEO dissolved in water (Scheme 1).

The PPy film, formed in the second step, is expected to be firmly anchored to the polyacrylate layer through the incorporation of the pyrrole units that it contains. For these units to participate to the growth of the PPy chains in water, they must be hydrated and enjoy enough freedom. For this reason, they have been attached to the acrylate through a hydrophilic poly(ethylene oxide) spacer. Thus, a novel dual macromonomer has been synthesized and used in the first electrochemical step, i.e., a poly(ethylene oxide) chain α-end-capped by a pyrrolyl group (anodically polymerizable) and ω-end-capped by an acrylate group (cathodically polymerizable), referred to as Py-PEO-A. Finally, for the PPy film to be not only adherent but also hydrophilic and thus protein repellent, a hydrophilic macromonomer, Py-PEO, has been used in the second electropolymerization step.

Experimental Section

Pyrrole (Aldrich) was distilled before use. Potassium hydroxide (Fluka) and ethylene oxide (EO, Messer) were used as received. Toluene was dried by reflux over sodium and distilled prior to use. EO was polymerized in a 1 L reactor (Autoclave Engineers Europe) equipped with a stirrer and a pressure gauge. All the experiments were carried out under dry nitrogen. Acryloyl chloride (Aldrich) and triethylamine (Aldrich) were dried over calcium hydride and distilled under reduced pressure. Dimethylformamide (DMF, Aldrich) was dried over P_2O_5 and distilled under reduced pressure. Acetonitrile (ACN, Aldrich) was dried over calcium hydride and distilled. Tetraethylammonium perchlorate (TEAP, Fluka) was heated in vacuo at 80 °C for 12 h, prior to use. β-Lactamase (BlaP, 32 kDa) from *Bacillus licheniformis* was supplied by Progenosis (Belgium). Nitrocefin (Unipath, Belgium) was dissolved in a phosphate buffer (pH 7.4) in order to prepare a 100 μM solution.

α-Pyrrolyl-ω-hydroxy-poly(ethylene oxide) (Py-PEO) was synthesized as follows. To a 500 mL bi-neck flask, 8 g of KOH (0.14 mol) and 12 mL of pyrrole (0.17 mol) were added, followed by 300 mL of toluene. The mixture was kept under magnetic stirring at 80 °C for 24 h. Water formed as a byproduct and the excess pyrrole were distilled off together with toluene under reduced pressure. The white reaction product (Py^-K^+) was dried by three azeotropic distillations of toluene. A suspension of this prepared salt (14 g) in toluene was injected in the stainless steel reactor followed by 100 g of EO. Polymerization was carried out under vigorous stirring at 80 °C. When the pressure was dropped to zero, the reaction was terminated by addition of 0.15 mol of HCl (3 M) and the reactor was maintained at 40 °C for 1 h. PEO was collected by elimination of toluene, then dissolved in CH_2Cl_2, and KCl was extracted from this solution by water. CH_2Cl_2 was finally distilled off, and the polymer was dried by azeotropic distillation of toluene. Finally, 109 g of a light yellow product was collected. ^{1}H NMR spectrum in $CDCl_3$ showed resonances at δ (ppm) = 6.69 (2H, pyrrole), 6.12 (2H, pyrrole), 4.04 (2H, CH_2-N), 3.63 (52H, EO). M_n (640 g/mol) was calculated from the intensity of the ^{1}H NMR resonances for EO (at 3.63 ppm) and Py (at 6.69 ppm). The molecular weight distribution was narrow (M_w/M_n = 1.12), as measured by SEC calibrated by PEO standards. Under the same experimental conditions, α-pyrrolyl-ω-hydroxy-poly(ethylene oxide) with M_n 1600 and polydispersity = 1.10 was prepared from 31 g of KOH, 55 mL of pyrrole, and 150 g of EO. α-Pyrrolyl-ω-acrylate-poly(ethylene oxide) (Py-PEO-A) was synthesized by reaction of 3.9 mL of acryloyl chloride with 10 g of Py-PEO in the presence of 6.6 mL of triethylamine in 200 mL of dried CH_2Cl_2 at room temperature for 30 h. The organic phase was twice extracted by 80 mL of a saturated aqueous solution of $NaHCO_3$. The Py-PEO-A macromonomer was collected by solvent evaporation with a rotavapor. Before electropolymerization, the Py-PEO-A macromonomer was dried by three azeotropic distillations of toluene. ^{1}H NMR ($CDCl_3$): δ (ppm) = 6.69 (2H, pyrrole), 6.40 (1H, acrylate), 6.12 (3H, pyrrole and acrylate), 5.85 (1H, acrylate), 4.31 (2H, $CH_2-O-C{=}O$), 4.04 (2H, CH_2-N), 3.63 (52H, EO). M_n (780 g/mol) was calculated from the ^{1}H NMR spectrum (cf. supra).

All the electrografting experiments were carried out in a glovebox under dry nitrogen. Electrochemical measurements were carried out in a three-compartment cell equipped with a Pt pseudoreference electrode, a Pt counter electrode, and a working electrode (1 cm^2) and with a PAR EG&G potentiostat (model 273A). The working electrodes were used, i.e., glassy carbon (Carbone Lorraine, contact angle of water = 82°), stainless steel (316L, Goodfellow, contact angle of water = 91°), and n-type silicon wafers (contact angle of water = 63°), with a specific electric resistance of 0.004−0.005 $\Omega\cdot$cm (ACM). Carbon and stainless steel electrodes were cleaned with heptane, acetone, and 2-propanol. Silicon electrodes were treated with a HF solution (40%) for 30 s. The chemisorbed polyacrylate films were prepared by two scans of potential between the initial potential at open circuit and the potential at the top of the first reduction peak, at which it was kept constant for 5 s. Pure Py and mixtures were anodically electropolymerized by chronoamperometry (500 mC/cm^2); the potential was adjusted in each case based on voltammetry. The conducting films were electropolymerized and characterized in a three-electrode-containing cell. Saturated calomel was used as the reference electrode and a Pt disk as counter electrode. All the experiments were carried under nitrogen and by using double-distilled water.

Films were analyzed by X-ray photoelectron spectroscopy (XPS) (Al Kα X-ray source) after reduction at −0.9 V for 3 min in an aqueous solution of KCl (0.1 M) in order to remove the ClO_4^- counterions, then rinsed with double-distilled water and ACN, respectively, and then dried.

The resistance of the films was determined from the voltammograms recorded at different scanning rates by plotting E_{ox} versus I_{ox}, where E_{ox} and I_{ox} stand for the potential and the current at the maximum of the oxidation wave, respectively.[14]

The protein adsorption test consisted in incubating the electrode coated by the PPy film in a phosphate buffer solution containing 0.1 mg/mL of β-lactamase at 4 °C for 1 h. After washing with water and buffer, the film was incubated in buffer solution at 4 °C for 4 h in order to eliminate the loosely adsorbed protein prior to UV−vis quantification. Then, the film was dipped in an aqueous solution of nitrocefin (100 μM), and the absorbance of the solution was measured as a function of time. A calibration curve allowed the absorbance to be converted into the actual mass of adsorbed active β-lactamase (see the Supporting Information).

Results and Discussion

The cathodic electrografting of the new dual PEO macromonomer (first step, Scheme 1) has been first studied on glassy carbon, i.e., an inert substrate well-suited to electrografting,[15,16] by voltammetry in DMF containing a conducting salt (0.05 M TEAP). Curve A in Figure 1 shows the typical peak of electrografting, or peak I, at −1.47 V. It is indeed characteristic of a passivation peak as the result of the chemisorption of an insulating polyacrylate film.[15,17]

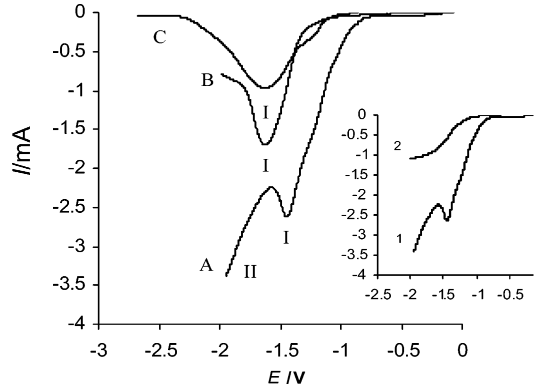


Figure 1. Voltammograms for the reduction of Py-PEO-A (0.5 M) in DMF containing TEAP (0.05 M) at 20 mV/s on (A) glassy carbon, (B) stainless steel, and (C) silicon: (I) passivation peak; (II) reduction without passivation. Inset: reduction of Py-PEO-A (0.5 M) on glassy carbon: (1) first scan, (2) second scan.

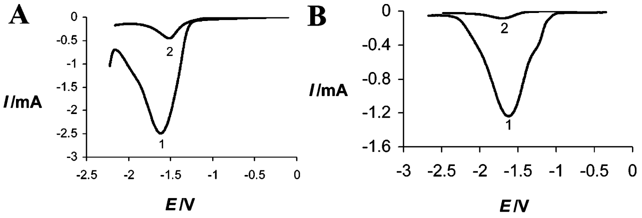


Figure 2. Voltammograms on stainless steel (A) and silicon (B) for the reduction of Py-PEO-A (0.1 M) in a TEAP solution (5×10^{-2} M) in DMF at 20 mV/s.

This film is formed in DMF, and it resists dissolution in a good solvent for the polymer. Peak I is no longer observed when the scanning of the cathodic potentials is repeated until the top of this peak, which confirms the electrode passivation (curve 2 in the inset of Figure 1). At a higher cathodic potential, a second electrochemical reaction occurs (peak II of curve A, Figure 1), which is merely controlled by the monomer diffusion to the cathode. The originally grafted chains are thus been desorbed, and the monomer reduction results in species that are no longer adsorbed onto the electrode and initiate the acrylate polymerization in solution.

The cathodic electrografting of the Py-PEO-A macromonomer has also been studied on stainless steel and n-doped silicon. Indeed, comparison of the electrografting process on different substrates, (i) conducting and organic for C, (ii) conducting and inorganic for stainless steel, and (iii) semiconducting and inorganic for Si, is expected to provide useful pieces of basic information. Moreover, 316L stainless steel is commonly used for the fabrication of implants and silicon is a common constituent of microelectronic devices. Figure 1 compares the voltammograms for the reduction of Py-PEO-A (0.5 M) on glassy carbon (curve A), stainless steel (curve B), and n-doped silicon (curve C). The grafting peak is observed in all cases, and Figure 2 confirms the passivation whenever the metal and the semiconductor are used as the cathode. Indeed, the intensity of peak I is dramatically decreased when the potential

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Table 1. Current Intensity at the Potential of Peak I (Passivation Peak) in Relation to the Py-PEO-A Concentration in a DMF Solution of TEAP (0.05 M) at 20 mV/s

[Py-PEO-A]	0.1 M	0.25 M	0.5 M
Ip1 on carbon (mA)	−3.55	−3.29	−2.65
Ip1 on stainless steel (mA)	−2.44	−2.18	−1.82
Ip1 on Si (mA)	−1.23	−1.12	−0.96

Table 2. Thickness and Contact Angle of Water (at 3 min) at the Surface of Chemisorbed Poly(Py-PEO-A) Films

[Py-PEO-A]		0.1 M	0.25 M	0.5 M
carbon	thickness [nm]	34 ± 4	47 ± 5	54 ± 7
	contact angle [deg]	43 ± 2	42 ± 2	41 ± 2
stainless steel	thickness [nm]	30 ± 4	44 ± 5	51 ± 6
	contact angle [deg]	47 ± 3	44 ± 3	41 ± 2
Si	thickness [nm]	23 ± 3	27 ± 4	36 ± 4
	contact angle [deg]	50 ± 3	48 ± 2	45 ± 3

scanning is repeated until the potential at the maximum of peak I. Again, the films cannot be dissolved in any good solvent of the polymer.

An additional evidence for the electrografting and the associated cathodic passivation can be found in the systematic decrease in the intensity of peak I (Ip1) when the Py-PEO-A concentration is increased. The data summarized in Table 1 show that an increase in monomer concentration results in smaller Ip1.

This observation confirms the success of grafting, because it is related to the chain growth from the (semi)-conducting surface, which is as fast as the monomer concentration is high, and thus results in the earlier passivation of the cathode and in lower electrografting peak intensity, as previously reported for the electrografting of other acrylates.[17,18]

That the chemical insulating film is the expected poly-(Py-PEO-A) has been confirmed by ATR-FTIR analysis (see the Supporting Information) of the surface after extensive washing of the cathode by DMF, a good solvent for both the macromonomer and the polymer. The three main absorptions at 2861, 1730, and 1109 cm^{-1} are characteristic of the CH_2, $C{=}O$, and $C{-}O{-}C$ vibrations of poly(Py-PEO-A), respectively. The absorption at 1619 cm^{-1} is typical of unreacted pyrrole units to be polymerized in the second step.

The thickness of the poly(Py-PEO-A) films has been measured by ellipsometry. Table 2 shows a direct dependence of the film thickness on the macromonomer concentration in the electrochemical bath.

As a rule, the film thickness increases with the macromonomer concentration, in agreement with previously reported results and in line with the more rapid propagation at higher concentration.[17] The substrate also has an effect on the film thickness. At constant macromonomer concentration, thicker polymer films are formed on glassy carbon and on stainless steel electrodes compared to the silicon electrode, which reflects a difference in the grafting density (i.e., number of chains/cm^2). On the assumption that chain propagation, and thus chain length, are independent of the substrate, the thinner film on the silicon substrate can be explained by a grafting density which is low enough for the chains to lay on the surface rather than to form a brush.

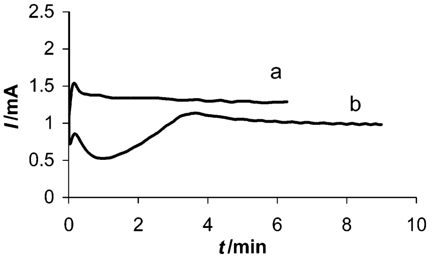

Figure 3. Chronoamperograms (0.65 V, 500 mC) of a Py/Py-PEO mixture (0.05 M/0.05 M) in an aqueous solution of $LiClO_4$ (0.2 M), on bare glassy carbon (curve a) and on a chemisorbed poly(Py-PEO-A) film (curve b).

Contact angles of water measured for the poly(Py-PEO-A)-coated surfaces are in good agreement with the thickness measurements. Table 2 shows that the hydrophilicity is as high as the film is thick. Furthermore, when the film thickness reaches a value of ~35 nm, whatever the substrate, the contact angle does not change significantly, which indicates that the surface is completely coated by the polymer.

Very importantly, as result of the hydrophilicity of the dual Py-PEO-A macromonomer, all the polyacrylate grafted films have a contact angle of ~40−45°, thus polar enough to be swollen by water and for the pyrrole units to be anodically polymerized in this solvent. Otherwise, the insulating polyacrylate chains would be precipitated on the surface, so preventing monomer and salt from diffusion to the anode and polymerization from occurring.

The electropolymerization of Py and Py-PEO has been studied by voltammetry on neat carbon. The oxidation potential of the macromonomer is shifted toward more anodic values (0.95 V/SCE) as compared to Py (0.6 V/SCE). Substitution of the nitrogen atom of Py is the usual explanation for such a shift.[19] This difference in reactivity together with a smaller diffusion rate of the macromonomer accounts for a Py enrichment in the films compared to the comonomers feed composition.

The electrodes coated by an adherent poly(Py-PEO-A) film have been dipped in a solution of a mixture of Py and Py-PEO (0.05 M each) in $H_2O/LiClO_4$ (0.2 M) and anodically polarized. The electrodeposition of PPy has been first investigated by chronoamperometry. Figure 3 shows that the nucleation and growth of the aromatic chains is perturbed by the chemisorbed poly(Py-PEO-A) chains. In comparison to curve a for neat glassy carbon, curve b shows an additional characteristic feature beyond the maximum observed at short reaction time. Indeed, the current increases slowly, and so does the chain growth, before reaching the plateau regime.

Nucleation and growth of PPy would occur first within the chemisorbed chains, mainly the hydrated PEO segments to which Py units are attached, and later on at the extreme surface of the poly(Py-PEO-A) film. The first part of this two-step process depends on the applied potential and the

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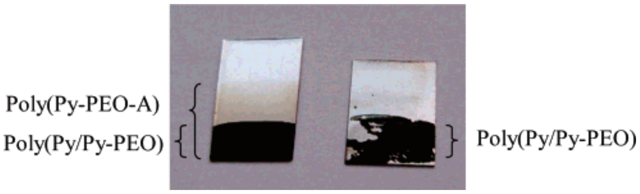

Figure 4. Pictures of stainless steel surfaces modified by poly(Py/Py-PEO) (50/50) electropolymerized on a bare electrode (right-hand side) and on an electrode premodified by poly(Py-PEO-A) (left-hand side).

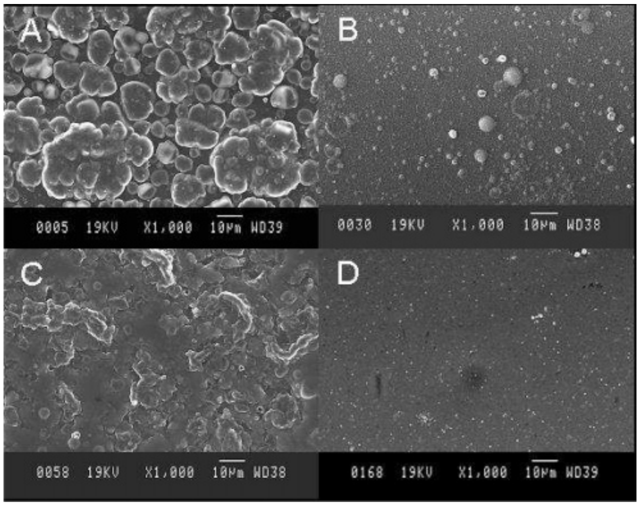

Figure 5. SEM pictures of PPy films prepared on (A, C) bare glassy carbon and (B, D) chemisorbed poly(Py-PEO-A) films. (A, B) Py (0.1 M) was the monomer; (C, D) a 0.05 M/0.05 M mixture of Py and Py-PEO were the comonomers, in aqueous solution of $LiClO_4$ (0.2 M). The films were grown under constant potential with a total charge of 500 mC/cm^2.

Py concentration. A similar observation was reported elsewhere for the electrodeposition of PPy on a decanethiol brush at the surface of a gold electrode.[20]

Figure 4 is a direct evidence of the beneficial effect that the chemisorbed poly(Py-PEO-A) layer has on the adherence of the mixed poly(Py/Py-PEO) film formed in the second step. Indeed, when the PPy film is prepared from a 50/50 Py/Py-PEO mixture on neat stainless steel, the adherence of the coating is weak, being easily detached after few cycles of wetting and drying (Figure 4, right-hand side). This is not the case when the electrode surface has been premodified by chemisorbed poly(Py-PEO-A); then, the PPy film has strong adhesion to the substrate (Figure 4, left-hand side).

In the specific case of the anodic polymerization of Py-PEO (no Py added) on bare electrode, no film is deposited because of the water solubility of the formed polymer (poly(Py-PEO)). This polymer imparts a dark color to the solution. In contrast, the poly(Py-PEO) is anchored to the surface of the premodified electrode. Nevertheless, it is not useful for sensoring applications, because the full N-substitution of the Py units is responsible for poor electroactivity.

The morphology of the PPy and poly(Py/Py-PEO) (50/50) films that has been observed by scanning electron microscopy (SEM) depends on whether the electrode has been premodified by poly(Py-PEO-A) or not. In comparison to electrodeposition on pristine carbon (Figure 5, parts A and C), the surface roughness is hardly observed in the case of the premodified glassy carbon (Figure 5, parts B and D), consistent with formation of a large number of nucleation spots, and thus individual grains, as previously observed for PPy films electrodeposited on substrate premodified by poly(*N*-(2-acryloyloxy ethyl) pyrrole).[21]

The morphology of the PPy films also depends on the Py-PEO/Py molar ratio, the films being smoother at higher ratios. Smoothness of the films and lack of defects are highly desirable for a variety of applications that require high mechanical strength, homogeneous drug loading (e.g., drug-eluting stents), homogeneous electroactivity, etc.

Content of the Py-PEO macromonomer in the PPy films has been estimated by XPS. The relative surface area of the C, N, O peaks confirms that this content increases with the Py-PEO concentration in the electrolytic bath. The C1s peak is shown in Figure S2 in the Supporting Information for films of different compositions. They can be deconvoluted into two main components at 284.8 and 286.6 eV assigned to PPy and PEO, respectively. The Py/Py-PEO molar ratio of the films has been determined from the atomic percentage of C1s (at 284.6 eV) or N1s for PPy and C1s (at 286.6 eV) or O1s (at 532.9 eV) for PEO. Data in Table 3 show that the macromonomer content increases from 4% to 8% in the films when the Py-PEO content is increased from 25% to 75% in the electrolytic bath. This rather low content of Py-PEO of the copolymer films more likely results from the higher oxidation potential and the lower diffusion rate in solution of the Py-PEO macromonomer as compared to those of Py. A copolymer with a comblike architecture as described in Scheme 2 should thus be formed. Even though Py is preferentially incorporated in the copolymer, the degree of polymerization (DP) of the PEO grafts (=35) is higher than the theoretical mean DP of the PPy segments between two macromonomers, thus the Py/Py-PEO molar ratio in the copolymer, which can account for the effective coating of the electrode by hydrophilic PEO (Scheme 2).

The electrochemical properties of the two-layered films have been studied by voltammetry in aqueous solution of $LiClO_4$ (0.2 M) and when possible (i.e., on C) compared to those of the unmodified substrate. Figure 6 illustrates the cyclic voltammograms of poly(Py/Py-PEO) films on glassy carbon, stainless steel, and silicon. When pure Py was electropolymerized on bare and premodified electrodes, the electroactivity in the doping/undoping process in water is very comparable (Figure 6A, curves a, a′).

This observation indicates that the diffusion of the counterions and the redox properties of PPy are basically independent of the premodification of the electrodes by poly(Py-PEO-A). It is thus clear that the chemisorbed chains of the dual PEO macromonomer are highly hydrated, which allows Py and Py-PEO to have a direct access to the electrode in the second electropolymerization step (Scheme 1). This very desirable effect was not, however, observed in the case of gold modified by a hydrophobic self-assembled monolayer.[20]

However, when the macromonomer Py-PEO is incorporated into the films (Figure 6, curves b, b′, c), the oxidation

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Table 3. Physicochemical Characteristics of the Homo- and Copolymer Films

comonomer composition of the solution	resistance (Ω)[a]	Py/Py-PEO mol ratio in solution	Py/Py-PEO mol ratio in the film[b]	contact angle (deg)[c]	mass of adsorbed active protein (ng/cm²)[d]
PPy	27 ± 4			74 ± 3	84.5 ± 6.5
poly(Py/Py-PEO) (75/25)	42 ± 8	3/1	25/1	50 ± 5	8.3 ± 1.5
poly(Py/Py-PEO) (50/50)	53 ± 9	1/1	18/1	41 ± 5	2.1 ± 0.8
poly(Py/Py-PEO) (25/75)	67 ± 11	0.33/1	12/1	40 ± 5	1.2 ± 0.7
poly(Py-PEO)				38 ± 6	0.8 ± 0.4

[a] Resistance of copolymer films (0.5 C/cm^2) grown from a poly(Py-PEO-A) film chemisorbed onto glassy carbon, in an aqueous solution of $LiClO_4$ (0.2 M). [b] As determined by XPS analysis for poly(Py/Py-PEO) copolymers prepared by chronoamperometry (0.5 C/cm^2). [c] Contact angles of water (at 30 s) on undoped Py/Py-PEO copolymer films on premodified glassy carbon. All the films were previously reduced at −0.6 V for 30 s in an aqueous solution of $LiClO_4$ (0.2 M). [d] Quantitative adsorption of active β-lactamase onto doped Py/Py-PEO (co)polymer films deposited on premodified glassy carbon.

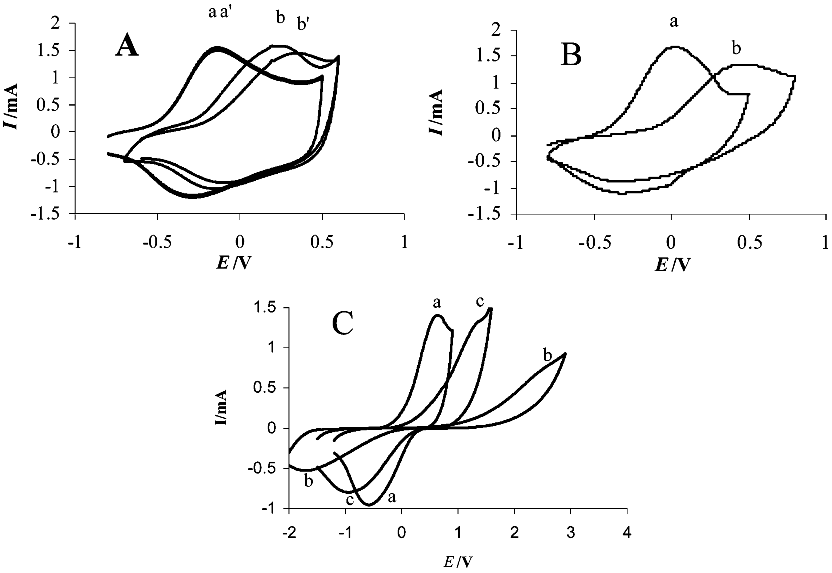
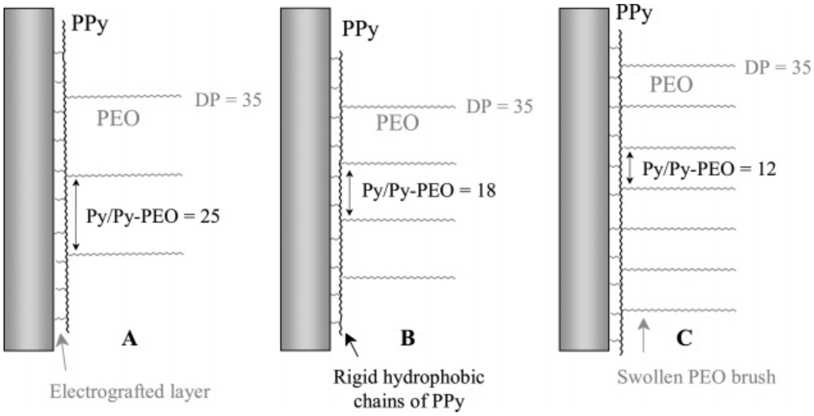


Figure 6. Cyclic voltammograms recorded at 20 mV/s on glassy carbon (A), stainless steel (B), and n-doped silicon (C) in an aqueous solution of $LiClO_4$ (0.2 M). Films were prepared in an aqueous solution of Py (0.1 M) on a bare electrode (curves a′) and on a premodified electrode (curves a), a mixture of Py and Py-PEO (0.05 M/0.05 M) on a bare electrode (curves b′) and on a premodified electrode (curves b), and a mixture of Py and Py-PEO (0.075 M/0.025 M) on a premodified electrode (curve c). These films were grown under constant potential with a total charge of 500 mC/cm^2.

Scheme 2. Tentative Sketch of the Poly(Py/Py-PEO) (75/25) (A), (50/50) (B), and (25/75) (C) Copolymer Films in Water Based on the XPS Analysis



potential of PPy is shifted toward more positive values, which is consistent with a decrease in the oxidation degree and conductivity when PPy is N-substituted by alkyl groups. This phenomenon is more pronounced in the case of the poorly conducting n-doped Si substrate. It must be mentioned that the very poor adhesion of the nongrafted films to stainless steel and Si prevented reliable voltammograms from being recorded and compared to those of the grafted counterparts.

The aging of copolymer films has been studied by cyclic voltammetry. Above all, the premodification of the electrodes by poly(Py-PEO-A) is of the utmost importance for the adherence of the aged films. As shown in Figure S3 in the Supporting Information, where the copolymer is directly electrodeposited on a bare electrode, the electroactivity has decreased after 2 days of storage in an aqueous solution of $LiClO_4$ or in the dry state, as a result of the poor adherence

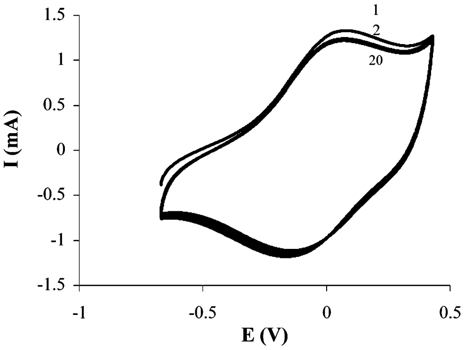


Figure 7. Electroactivity of the 25/75 poly(Py/Py-PEO) film grown from a poly(Py-PEO-A) film chemisorbed onto glassy carbon, in an aqueous solution of $LiClO_4$ (0.2 M) at 20 mV/s: (1) first, (2) second, and (20) 20th scans.

of the hydrophilic PPy, which is seen to detach from the electrode. Moreover, the electrochemical stability of the PPy films, chemisorbed onto the electrode, has been qualitatively confirmed by the full persistent adherence to the substrate and CV characteristics upon multiple CV scans (Figure 7).

Conversely, the strong adherence of the films to the substrate prevent them from being detached as free-standing films and conductivity from being measured by the traditional four-points technique. An electrochemical technique reported by Zoppi and De Paoli allows, however, the film resistance to be roughly estimated, from voltammograms recorded at different scanning rates (see Supporting Information Figure S4).[14] The slope of the plot of potential versus current intensity at the maximum of the oxidation wave (Figure S5 in the Supporting Information) is indeed the ohmic resistance of the film. Data in Table 3 show that the conductivity of the films decreases as result of the increasing content of Py-PEO in the PPy chains. This effect is, however, of a low magnitude, the conductivity being decreased by only a factor of 2 for the film with the higher Py-PEO content.

The hydrophilicity of the coatings has been estimated from the contact angle of water recorded for neutral (undoped) PPy films, thus after polarization at -0.6 V for 30 s in a 0.2 M $LiClO_4$ aqueous solution, followed by careful washing with double-distilled water and then with ACN. Data in Table 3 show that the hydrophilicity is higher when the Py-PEO/Py molar ratio is increased. Interestingly, when PPy is oxidized, the hydrophilicity of the films increases sharply, as testified by the contact angle of water which is then lower than 10°. This characteristic feature is desirable for enhancing the protein repellency, as previously observed for surfaces onto which poly(acrylate-PEO) was chemisorbed.[18]

Finally, the protein repellence property of the hydrophilic coatings has been quantified by UV−vis analysis by substituting the commonly used albumin and fibrinogen by β-lactamase, i.e., a protein with enzymatic activity.[22] Indeed, the physical adsorption of a β-lactamase on a surface can be easily quantified by immersing the surface in an aqueous solution of nitrocefin (yellow) which is hydrolyzed into a red product ($\lambda_{max} = 482$ nm) as result of the catalytic activity of the adsorbed protein. The reaction product is quantified by UV−vis spectroscopy after setting up a calibration curve (see the Supporting Information). A first visual evidence of the protein repellency by the electrodeposited coating is the persistent yellow color of the nitrocefin solution upon immersion of the poly(Py/Py-PEO) film previously incubated in a β-lactamase solution. In sharp contrast, whenever the experiment is repeated with a PPy film, a fast yellow to red change is observed (see the Supporting Information). Table 3 confirms that the incorporation of Py-PEO in the conducting film is very efficient in preventing protein adsorption.

Even if the amounts of adsorbed proteins reported in this table are probably underestimated because the catalytic activity of the adsorbed protein decreases as compared to that of the free protein in solution[21] (as used for the calibration), the comparison of the different samples is, however, relevant. The hydrophilic poly(Py/Py-PEO) films decrease the β-lactamase adsorption compared to that of the pure PPy film by 90.5%, 97.5%, 98.5%, and 99% for poly(Py/Py-PEO) (75/25), (50/50), (25/75), and (0/100), respectively. The small size of the β-lactamase (32 kDa) compared to albumin (67 kDa) and fibrinogen (340 kDa) emphasized the high efficiency of the protein repellency and confirmed again the high density of the PEO chains at the surface.[23]

Ohmic resistance and protein repellency data in Table 3 show that the Py-PEO macromonomer has an antagonistic effect on these properties. The 50/50 poly(Py/Py-PEO) film is a good compromise of low resistance and high protein repellency. Nevertheless, a further increase in protein repellency should not result in a dramatic loss of conductivity.

Conclusions

α-Pyrrole, ω-acrylate PEO dual macromonomer has proved to play a key role in the surface modification of electrically conducting substrates, such as glassy carbon, stainless steel, and silicon semiconductor. Indeed, the cathodic polymerization of the acrylate end-group at the appropriate potential (at the maximum of the passivation peak) results in the chemisorption of polyacrylate chains substituted by the hydrophilic α-pyrrole PEO. This first layer is solvated by water without being detached from the surface. This solvation makes the α-pyrrole end-group available to anodic copolymerization with Py and Py-PEO macromonomer in water. This terpolymerization is the key issue for anchoring the PPy chains formed in the second step (Scheme 1) to the chemisorbed poly(Py-PEO-A) chains. The dual macromonomer is thus an ideal bridging agent between PPy and the conducting surface. The premodification of the electrode surface by chemisorbed chains has an impact on the deposition and growth of the PPy chains and the morphology of the related film. Moreover, the PEO chains, which are incorporated into the PPy films by the Py-PEO macromonomer, are very efficient in repelling proteins from the surface, whereas only a slight decrease in conductivity is observed. Interestingly, the PEO chains involved in the second step are end-capped by a hydroxyl group, which is

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an opportunity to attach molecules of interest, including biomolecules, as demonstrated by preliminary tests of esterification of these −OH groups by ferrocene−COOH (see the Supporting Information). The strategy reported herein thus paves the way to bioactive coatings, e.g., endowed with biosensoring property. This fully electrochemical process is thus very promising in the coating of biomedical devices, such as stents and biosensors.

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Supporting Information Available: ATR-FTIR spectra of poly(Py-PEO-A), cyclic voltammograms, details of the protein adsorption test, observation of nitrocefin solution 30 min after glassy carbon immersion. This material is available free of charge via the Internet at http://pubs.acs.org.

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