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Sequential anodic oxidations of aliphatic amines in aqueous medium on pyrolyzed photoresist film surfaces for the covalent immobilization of cyclam derivatives

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Abstract We investigate here the derivatization of pyrolyzed photoresist film (PPF) surface by anodic oxidations of amino-containing linkers in aqueous medium. As an example of application, nitrogen macrocycles are then covalently immobilized by chemical reactions with the modified surface. The surface coverage is estimated by X-ray photoelectron spectroscopic analyses and cyclic voltammetry using redox probes, and the thickness of the film is measured by atomic force microscopy from scratching experiments. The surface coverage increases when two successive grafting processes are carried out and stops after the third electrolysis. The influence of the electrolyte medium on the thickness of the film is also highlighted.

Keywords Carbon · Immobilization · Covalent grafting · Cyclam · Amines

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Introduction

Electrochemical methods are attractive for modifying conductive surfaces [1, 2]. It consists of the electrochemical generation of radicals, reacting with the surface to form stable covalent bonds. Many electrografting reactions have been explored, such as the reduction of diazonium salts [3, 4], the oxidation of aryl acetates [5], and the oxidation of amines [6, 7]. Different molecular structures have been immobilized by anodic oxidation of amines [7–9]. The reaction is usually carried out in anhydrous solvents. However, it has been noticed that aqueous solutions also support this process [7, 8].

The mechanism of the grafting process has been studied. A number of observations supported that the amine is covalently attached to the surface [6, 7]. Thus, sonicated and soaking modified GC electrodes in a variety of aqueous and non-aqueous solutions did not change the X-ray photoelectron spectroscopic (XPS) spectra. Moreover, it has been clearly demonstrated that it is the neutral radical, formed after deprotonation of the radical cation, which reacts with the electrode surface, leading to an amine linkage (Scheme 1) [6, 7, 9].

Even if the formation of monolayers has been reported under some well-defined conditions [10–12], the radical grafting process is known to preferentially form multilayers on the electrodes [11, 13, 14]. For aryl diazonium salts, this phenomenon has been explained by the addition of the aryl radicals to the already grafted phenyl groups, leading to polyphenylene structures [13]. Multilayers have also been reported for the anodic oxidation of amines with the formation of two to five molecular layers [14]. Whereas an electrochemical polymerisation mechanism proposed for diamines [15] can give a possible explanation to multilayers formation, it is not clear for aliphatic monoamines.
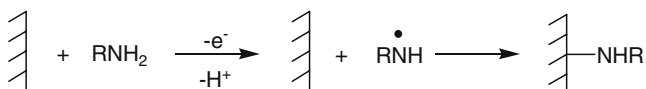
Scheme 1 Mechanism for the electrochemical immobilization of amines

Different natures of electrodes have been derivatized by this electrochemical process, such as metal and carbon surfaces [2]. More recently, pyrolyzed photoresist films have proven to be good supports for electrochemical grafting [14, 16]. These surfaces, a form of glassy carbon, containing randomly oriented graphitic crystallites have a very low rugosity (<0.5 nm) and have been used to make patterned electrodes [17–20].

In this work, we investigated the anodic oxidations of aliphatic amines on pyrolyzed photoresist film (PPF) in aqueous medium. The modified surfaces were analyzed by XPS and cyclic voltammetry using redox probes. These analyses showed that the surface covering (about 2–6% of a compact monolayer) increased when two successive grafting processes were carried out. Surprisingly, the thickness of the organic layer measured by atomic force microscopy (AFM) scratching was consistent with the formation of one layer on the surface for aqueous medium, whereas quantitative analyses indicated that the coverage was lower than a monolayer. Since the modification of electrodes with nitrogen macrocycles is very useful for many applications such as redox catalysis [21–25] and electrochemical analysis [26, 27], we investigated the introduction of cyclam derivatives by this process. The results presented here give rise to a general method for the covalent immobilization of nitrogen macrocycles.

Experimental section

Reagents and materials

The PPF surfaces (10×10 mm) were purchased from the MacDiarmid Institute for advanced Materials and Nanotechnology, Department of Chemistry, University of Canterbury, New Zealand (A. Downard) [28]. 5-Amino-pentanoic acid, thionyl chloride, 1,4,8,11-tetraazacyclotetradecane (cyclam), triethylamine, 4-bromobenzyl alcohol, and tetrabutylammonium tetrafluoroborate were purchased from Acros and methyl 6-aminohexanoate hydrochloride was from Fluka. 1,4,8-Tris(trifluoroacetyl)-1,4,8,11-tetraazacyclotetradecane has been prepared according to the literature [29]. Ultrapure water (18.2 MΩ, Millipore Simplicity) was used for the preparation of all aqueous solutions and for washing surfaces. All solvents used were of analytical or HPLC grade.

Instrumentation

Electrochemical experiments were performed with an EDAQ potentiostat unit using the EChem software package. A standard three-electrode electrochemical cell with a Pt plate as counter electrode and a saturated calomel electrode (SCE) as a reference was used for the derivatization step. Contact to the PPF substrate was made with an alligator clip to the top surface of the PPF. The electrochemical analysis of the modified PPF surfaces was carried out in a Teflon cell (4.6 mm in diameter) containing a SCE as reference electrode and a Pt plate as counter electrode. The modified electrodes were analyzed by cyclic voltammetry in degassed H_2SO_4 0.5 M under nitrogen. First, electroreduction of the nitro groups into hydroxylamines was performed by cycling the potential twice between 0 and −500 mV_{SCE} at 100 mV s^{-1}, and then the nitrosohydroxylamine reversible system was observed by cycling the potential between 0 and 600 mV_{SCE}. The cathodic reduction of hydroxylamines occurred at more cathodic potential.

XPS analyses were performed under a base pressure of 7× 10^{-10} mbar using a VSW HA100 spectrometer. The analyzer was operated with constant pass energy of 22 eV. X-ray source used Mg Kα excitation radiation at 1,283.6 eV. The spectrometer binding energy scale was initially calibrated against the Au 4f (84.0 eV) level. C1s level (284.4 eV) on fresh PPF served as a reference for all spectra.

Topographic images were acquired with an AFM Picoplus (Molecular Imaging, Phoenix, USA) in intermittent contact mode (ACAFM) using silicon tips. The spring constant of the tips was 25–50 N m^{-1} and the image size was 512×512 pixels. The surfaces were imaged in air with a scan rate of about 2 Hz. Topographic measurements were made in intermittent contact mode and scratches in contact mode with the same tip. The force set point used for scratches was set as to obtain a topographic image of the nude PPF surface. The tip was replaced after several scratches and its resonance frequency was checked frequently to evaluate tip damage or presence of adhering organic residue on it. For each sample, a series of scratches was realized as to obtain averaged height values. Topographic images, 3D representations, and height estimations were obtained with the Gwyddion SPM data visualization tool (http://gwyddion.net), free software under the GNU General Public License.

Nanoscale secondary ion mass spectrometry (NanoSIMS) analyses were performed on a NanoSIMS 50 standard ion microprobe (CAMECA). Samples were cut and directly introduced into the instrument. A cesium primary ionic source was used for the measurement of $^{19}F^{-}$. A 16-keV Cs^{+} beam (~2 pA) was focused and raster-scanned on the surface sample. Sputtered negative secondary ions were extracted for mass analysis and collected in an electron multiplier. A mass resolving power of ~3,000 ($M/\Delta M$) enabled to remove potential mass interferences. All $^{19}F^{-}$ images (70×70 μm) of

Scheme 2 Preparation of the modified PPF surfaces
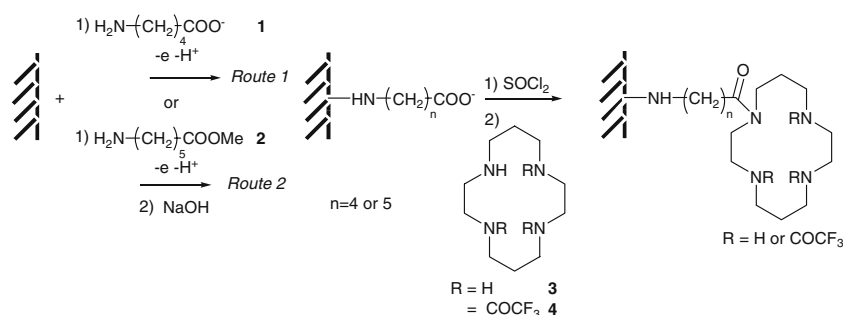
the same set were recorded under the same primary ion current and with the same parameters (diaphragms, slits, time/pixel). The spatial resolution for all images was around 0.12 μm. At least two places on each sample have been imaged.

Derivatization of PPF

Methyl 6-aminohexanoate hydrochloride was added to 1 eq. of triethylamine in dichloromethane. After 10 min of stirring, the solution was filtered and evaporated to give a mixture of methyl 6-aminohexanoate and triethylammonium chloride. The mixture was used in the following experiments since the salts did not perturb the electrolysis.

The derivatization of PPF was performed in a standard electrochemical cell (see above). Twenty milligrams of 5-amino-pentanoic acid **1** or methyl 6-aminohexanoate **2** (with $Et_3N^+Cl^-$ salts) in 20 mL of a carbonate buffer solution of pH 10.3 (Na_2CO_3 0.25 M, $NaHCO_3$ 0.25 M) or 0.1 M $Bu_4NBF_4^-$ acetonitrile (HPLC grade) were oxidized at 0.8 V_{SCE}. The electrolyses were done consecutively and the total reaction time varied from 5 to 125 min (see text). The modified PPF surfaces were sonicated in water ($6×30$ min) at the end of each electrolysis ((5 min +sonication)+ (30 min + sonication) + (60 min + sonication) + (30 min + sonication)).

Saponification of the amino ester-modified PPF surfaces was performed with 0.1 M NaOH at room temperature for 3 h.

Modified surfaces were then heated at 40 °C for 3 h in 20 mL of toluene in the presence of 0.5 mL of thionyl chloride. They were dried in vacuum before being refluxed overnight in 10 mL of anhydrous dichloromethane with 15 mg of cyclam **3** or 1,4,8-tris(trifluoroacetyl)-1,4,8,11-tetraazacyclotetradecane **4** or 4-nitrobenzylamine and Na_2CO_3. The PPF surfaces were successively sonicated in dichloromethane ($3×30$ min), water ($3×30$ min), and HPLC grade MeOH ($3×30$ min) before being analyzed.

Results

PPF surfaces [28] were derivatized by two consecutive anodic oxidations of 5-amino-pentanoic acid **1** (Scheme 2, route 1) or 6-amino-hexanoic acid methyl ester **2** [29] (Scheme 2, route 2) at 0.8 V_{SCE} in a pH 10.3 carbonate (0.5 M) buffer solution for 5 min and then 30 min. The modified surfaces were carefully cleaned between electrolyses. The same experiment was also performed in a continuous electrolysis for 60 min.

Compounds **1** and **2** were used here as linkers to avoid steric hindrance and increase the accessibility of the anchoring sites. Surfaces modified by the electrochemical grafting of **2** were saponified with NaOH. The carboxylate-functionalized surfaces were allowed to react with thionyl chloride and then with cyclam **3** or its fluoro derivative **4**.

The success of the grafting process was checked by XPS (Table 1).

Surfaces derivatized by anodic oxidation of **1** (route 1) and **2** (route 2) and subsequent attachment of fluoro macrocycle **4** were analyzed after 4.5 h of ultrasonic baths in different solvents. The presence of fluorine was clearly highlighted by F1s analysis, showing that the covalent attachment of fluoro compound **4** was successful for routes 1 and 2. A higher intensity of the F1s signal and an increase of the intensity of the N1s signal, compared with a fresh PPF, were observed with the sequential grafting process. These results indicated that a low coverage was obtained after the continuous electrolysis of 60 min, whereas the coverage increased when two successive electrolyses of 5 and then 30 min were performed. An estimation of the maximum coverage of about $2×10^{13}$ chains per square centimeter, corresponding to a surface concentration of $3× 10^{-11}$ mol cm^{-2}, can be deduced from X-ray photoemission spectra. It is given by the ratio of the nitrogen signal reported to the signal corresponding to a plane of glassy carbon. This value is probably slightly overestimated since a fresh PPF surface already contains nitrogen (Table 1). Fluorine and nitrogen contents were similar for derivatization performed via routes 1 and 2, showing that the grafting process was as efficient with amino acid **1** as amino ester **2**.

These results were confirmed by cyclic voltammetry analyses. After derivatization of PPF surfaces by the ester **2**, 4-nitrobenzylamine was immobilized instead of fluoro macrocycle 4. The nitro group serves as a redox probe and allows the estimation of the surface concentration, Γ, of

Table 1 Nitrogen and fluorine values as deduced from XPS analyses of modified PPF surfaces

Nitrogen and fluorine/carbon ratio	Fresh PPF surface	PPF surfaces modified with 4	
		Via route 1[a]	Via route 2[a]
% N_{1s} 400–401 eV	0.6	1.1 (0.6)	1.1 (0.5)
% F_{1s} 688–689 eV	0	1.3 (0.5)	1.3 (0.6)

[a] Consecutive electrolyses in carbonate buffer solution of pH 10.3, at 0.8 V_{SCE}, for 5 and then 30 min. The XPS data after 60 min of continuous electrolysis are given in parentheses

immobilized aryl groups, calculated from cyclic voltammetry analysis of the NHOH/NO reversible system (Fig. 1).

The estimated values of Γ were 2×10^{-12} mol cm^{-2} for 60 min of continuous electrolysis and 8×10^{-12} mol cm^{-2} for two successive electrolyses of 5 and then 30 min. This increase of the surface concentration of immobilized nitro groups with the sequential process is also observed with XPS analyses. The estimation of the surface concentrations is consistent with the XPS analyses. It is interesting to note that three successive electrolyses of 5, 30, and then 60 min led to a surface concentration of $8–9 \times 10^{-12}$ mol cm^{-2}, showing that further electrolysis did not improve the surface coverage anymore.

Fresh PPF surfaces modified with amino ester **2**[1] and surfaces post-functionalized with the cyclam **3** were then imaged by AFM (Fig. 2).

The fresh PPF exhibited a morphology and a rms roughness of 4 Å, which corresponded with other reported PPF surfaces (Fig. 2a) [16]. The PPF surface observed in Fig. 2b was derivatized by two successive anodic oxidations of amino ester **2** for 5 and then 30 min. The surface exhibited a topography comparable to the nude PPF with nodules of about 20 nm and a rms roughness of 4 to 7 Å. The cyclam-modified PPF surface imaged by AFM (Fig. 2c) had a rms roughness of 17 Å, with additional disperse nodules of approximately 30 nm in diameter. The presence of such nodules can be due to aggregations of free cyclam molecules on the surface in spite of the ultrasonic baths steps.

The thicknesses of the films were estimated by AFM from scratching experiments[2] using the procedure previously described by Anariba et al. [11]. Considering the scratched region as the ground level, the measured thicknesses of the amino ester **2** and cyclam-modified films were about 11 and

16 Å, respectively (Fig. 2d). Since the chain length of spacer **2** was estimated to be around 10 Å, these values are in agreement with one layer of amino ester with cyclam covalently attached via the extended spacer on the surface. Indeed, the crystal structure of [H$_2$cyclam]$^{2+}$ (the predominant form at pH • 7) [30] showed that the distance between a nitrogen atom and an opposite carbon atom is around 5–6 Å.

To better understand this phenomenon, a PPF surface was derivatized by successive anodic oxidations of **2** and analyzed at different electrolysis times (5, 35, 95, and 125 min). The surface was thoroughly washed by ultrasonic baths after each electrolysis. The resulting film thicknesses, measured by AFM scratching of the molecular film, were represented in Fig. 3.

As seen above, the film thickness obtained after a total of 35 min of two successive electrolyses corresponded to one layer coverage. Interestingly, similar values were measured after 95 and 125 min of successive electrolyses, showing that the electrochemical grafting was self-stopped after the second electrolysis. This result is in agreement with the electrochemical analysis since we measured the same surface concentration after two and three successive electrolyses. Moreover, the anodic oxidation of **2** was also carried out in a continuous electrolysis of 125 min. The measured film thickness was around 5 Å, as measured after 5 min of electrolysis. This result showed that the sequential process was necessary to obtain a better coverage of the surface and confirmed the XPS and electrochemical analyses.

Since multilayers (2 to 5) have been previously reported in the literature for anodic oxidation of amines on PPF in organic medium [14], we grafted amino ester **2** under the same conditions using anhydrous acetonitrile instead of the carbonate buffer solution. The thickness reached values of
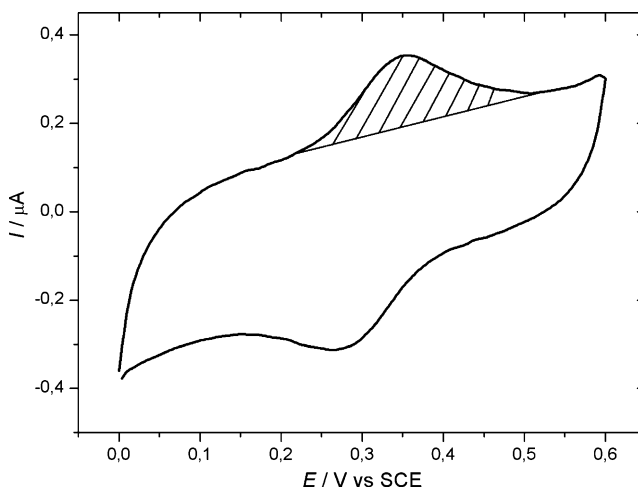
Fig. 1 Voltammogram of NHOH/NO system obtained in 0.5 M H$_2$SO$_4$ after reduction of NO$_2$ into NHOH at −0.5 V_{SCE}. The 4-nitrobenzylamine-modified surface was obtained via route 1 after two successive electrolyses of **5** and then 30 min. Scan rate, 0.1 V s^{-1}. Only the bottom of the wave (*hatched area*) was considered for the calculation of the surface concentration using the Faraday law

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[1] We could not obtain well-defined images of surfaces modified with amino acid **1**, probably because of the presence of charges (COO$^-$ groups).

[2] To our knowledge, ellipsometry measurements on PPF surfaces have never been reported. The different experiments we performed were not successful because of the difficulty to model such surfaces.
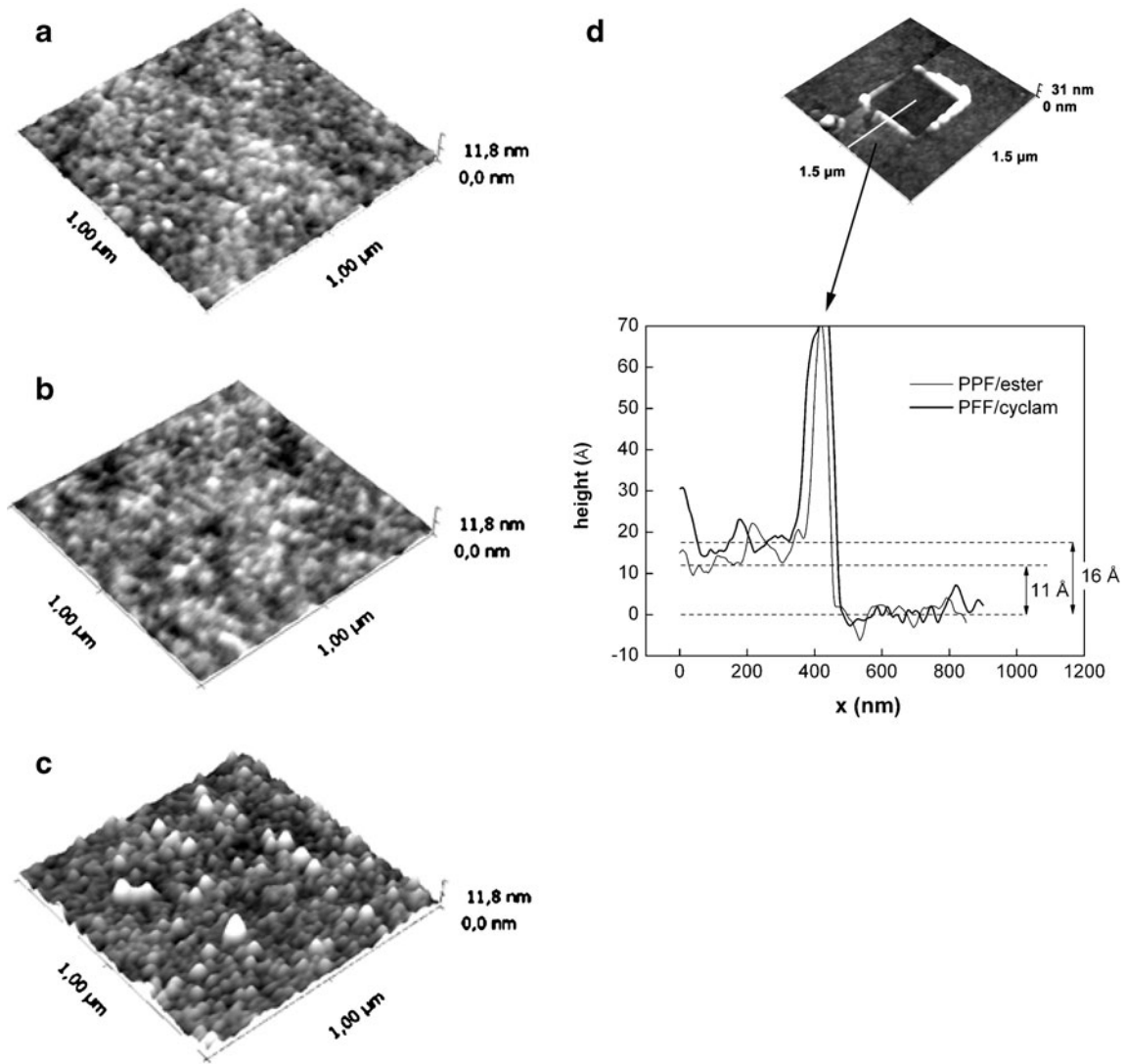
Fig. 2 Tri-dimensional 1×1 μm AFM images of PPF surfaces: bare surface (**a**), derivatized by successive anodic oxidations of amino ester **2** for 5 and then 30 min (**b**), and after addition of the cyclam **3** (**c**). Comparison of profiles extracted from scratching experiments (**d**)

Fig. 3 AFM film thickness (measured by AFM depth profiling) versus time used to graft amino ester **2** to PPF surface in aqueous (*square*) or organic (*circle*) medium. *Error bars* are estimated from roughness variations observed on AFM profiles. *Inset* Example of scratching experiment on an amino ester-modified PPF surface
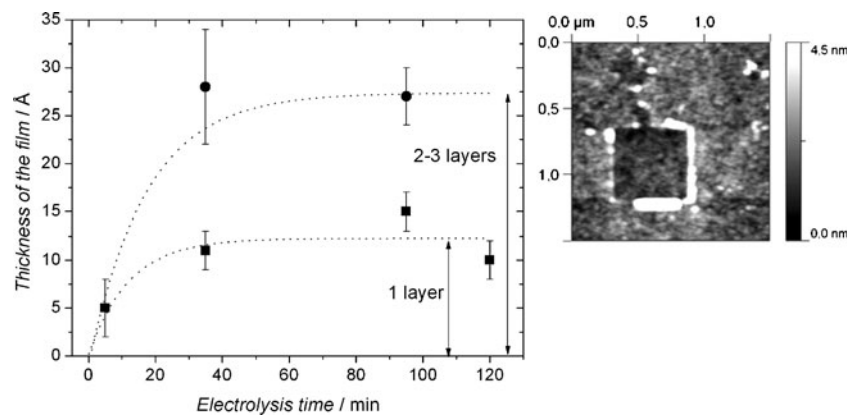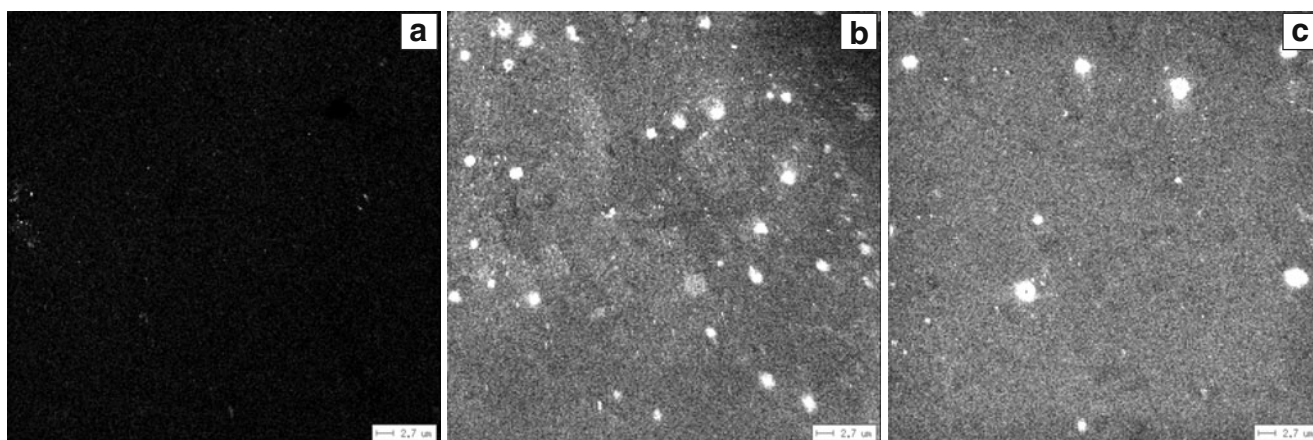
Fig. 4 F⁻ maps obtained by NanoSIMS analysis of PPF derivatized by anodic oxidation of amino ester **2** for 60 min (**a**) and PPF modified by fluoro compound **4** after derivatization by anodic oxidation of amino ester **2** for 60 min (**b**) or amino acid **1** for 60 min (**c**)

25 Å (20 Å) after 35 min (95 min) of electrolysis, which corresponds to two to three molecular layers. The thickness of the film obtained after 5 min of electrolysis was too small to be measured by our method. These results are in agreement with the literature and underline the difference of efficiency between the aqueous and the organic media.

A PPF sample was also dipped in a carbonate buffer solution of amino ester **2** for 5 and then 30 min at open circuit. The thickness was measured to be also 10 Å, showing that the spontaneous grafting of the amine [31] also occurred during the electrochemical process.

NanoSIMS was also used to check the repartition of fluorine on surfaces derivatized by the anodic oxidation of amino ester **2** and then modified with fluoro compound **4** (Fig. 4b).

A sample modified with amino ester **2** without fluoro compound **4** was used as a reference (Fig. 4a). As expected, the F⁻ map showed a high intensity of fluorine on the sample containing the fluoro derivative compared with the reference, confirming the success of the grafting process. Interestingly, the repartition of fluorine was uniform with some fluoro-enriched spots up to 2 μm in diameter (Fig. 4b). These spots probably corresponded to the same kind of smaller nodules previously observed by AFM and can be attributed to aggregated cyclam molecules, which were not eliminated by the ultrasonic baths. A PPF surface modified by fluoro compound **4** via route 1 was also imaged (Fig. 4c). The spatial localization of fluorine was similar to image B, showing that both grafting methods had the same efficiency. This result is in agreement with XPS analyses since the fluorine content was nearly the same for both samples (Table 1).

Discussion

The electrografting of aliphatic primary amines **1** and **2** on PPF surfaces in aqueous medium led to a surface coverage of

2–6% of a compact monolayer, as shown by XPS and cyclic voltammetry analyses. Scratching experiments performed in AFM differed on the estimation of the amount of this surface coverage since the measured layer was consistent with the formation of a monolayer. A possible explanation would be a poor efficiency of the three chemical reactions used to introduce the redox probe or the cyclam derivative **4**. Indeed, quantitative yields are usually difficult to obtain because of the heterogeneous reaction medium and the steric hindrance. Since the estimation of the thickness of the layer by the scratching experiments is approximate on PPF surfaces (rms roughness, 4 Å), an additional explanation would be the formation of a non-compact layer of ester **2** after the electrochemical treatment, with molecules lying flat on the surface. Thus, the layer thickness measured by AFM would be overestimated.

Despite the overestimation of the layer thickness, the tendency observed by scratching experiments is in agreement with XPS and cyclic voltammetry analyses: There is a positive influence of the sequential grafting process on the surface coverage. The increase of the surface concentration after the second electrolysis is not clear, but can be explained by the elimination of adsorbed species from the surface by the intermediate washing procedure. Indeed, after the first anodic
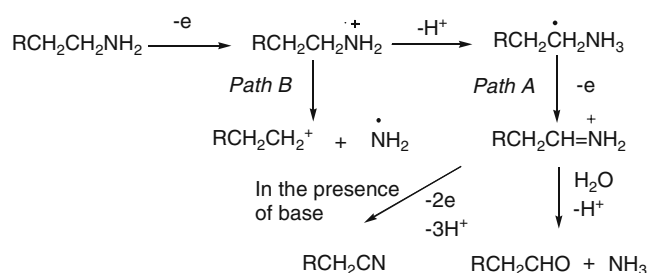
Scheme 3 Mechanism for anodic oxidation of aliphatic primary amines

oxidation of amino ester **2**, the modified surface was observed in AFM before the washing procedure. The surface exhibited a heterogeneous morphology with large blisters, corresponding to surface-adsorbed species, which were eliminated by the ultrasonic baths. These adsorbed species probably prevented the grafting process.

The estimated surface concentrations after the sequential grafting process $(0.8–3 \times 10^{-11}\ \mathrm{mol\ cm^{-2}})$ are significantly lower than those reported for the most close-packed monolayer of 4-substituted phenyl groups $(4.8 \times 10^{-10}\ \mathrm{mol\ cm^{-2}})$ [31]. The layer thickness measured by AFM was higher for the grafting process performed in acetonitrile (25 Å) than in water (10 Å), showing that the grafting process is less effective in water than in organic medium. This result is consistent with literature since surface concentrations around $10^{-9}\ \mathrm{mol\ cm^{-2}}$ have been reported for carbon electrodes modified by anodic oxidation of aliphatic primary amines in acetonitrile [32].

This behavior can be explained if we consider the mechanism for anodic oxidation of amine-containing compounds. It proceeds via the one-electron oxidation of the amino group to the corresponding cation radical (Scheme 3) [33].

Then two paths are opened, either a deprotonation leading to the formation of an iminium cation (path A) or C–N bond cleavage if a relatively stable carbenium ion can be formed (path B) [34]. It has been established that path B mechanism is favored at low potentials, whereas higher potentials lead to path A. The iminium ion can hydrolyze and form aldehyde, ammonium, and nitrogen, or it adds to a nucleophile, giving a substitution product. Under basic conditions, the formation of nitrile by oxidation of an imine intermediate has also been reported [35]. It has been demonstrated than in acetonitrile, the mechanism responsible of the grafting process is the attack of a radical formed after deprotonation of the radical cation [9]. XPS analyses have shown that some immobilized amines are protonated by the proton released during the oxidation process. In water, the grafting process is less effective since a smaller amount of radicals are electrogenerated on the vicinity of the electrode compared with acetonitrile. Indeed, at the potential used to oxidize the amine ($0.8\ \mathrm{V_{SCE}}$), path B is favored.

Spontaneous grafting of the amine also occurred during the grafting process, as shown by the thickness layer (10 Å) measured by the scratching experiments. The value is similar to those measured after the electrochemical process. A proposed mechanism for this spontaneous reaction involves a Michael-like, nucleophilic addition of the amine on a double bond of the carbon surface adjacent to an electron withdrawing group such as carboxyl or carbonyl functional groups [36]. It is difficult to know at this stage the part of the chemical and electrochemical processes. However, since AFM and electrochemical experiments showed that the grafting process was self-stopped after the second electrolysis, when the surface coverage is only of 2–6%, it is consistent with a reaction involving only activated double bonds of the electrode surface.

Conclusions

In conclusion, we have shown that anodic oxidation of amines in aqueous medium led to their covalent grafting on PPF surfaces. The derivatization has been carried out with a heterobifunctional linker, allowing the subsequent covalent immobilization of nitrogen macrocycles. Comparison of the electrochemical grafting performed in water and in acetonitrile showed the influence of the reaction medium on the thickness of the film. The influence of the sequential process on the surface coverage (around 2–6%) of the PPF was also underlined by XPS and cyclic voltammetry using redox probes and AFM from scratching experiments. After the second electrolysis of the amine, the film did not increase anymore with the electrolysis time. It would be interesting to investigate the influence of mixed aqueous–organic media and applied potentials on the surface coverage.

References

1. Downard AJ (2000) Electroanalysis 12:1085
2. Pinson J, Podvorica F (2005) Chem Soc Rev 34:429
3. Delamar M, Hitmi R, Pinson J, Saveant JM (1992) J Am Chem Soc 114:5883
4. Allongue P, Delamar M, Desbat B, Fagebaume O, Hitmi R, Pinson J, Saveant J-M (1997) J Am Chem Soc 119:201
5. Andrieux CP, Gonzalez F, Saveant JM (1997) J Am Chem Soc 119:4292
6. Barbier B, Pinson J, Desarmot G, Sanchez M (1990) J Electrochem Soc 137:1757
7. Deinhammer RS, Ho M, Anderegg JW, Porter MD (1994) Langmuir 10:1306
8. Geneste F, Moinet C (2005) New J Chem 29:269
9. Adenier A, Chehimi MM, Gallardo I, Pinson J, Vila N (2004) Langmuir 20:8243
10. Allongue P, De Villeneuve CH, Pinson J, Ozanam F, Chazalviel JN, Wallart X (1998) Electrochim Acta 43:2791
11. Anariba F, DuVall SH, McCreery RL (2003) Anal Chem 75:3837
12. Combellas C, Kanoufi F, Pinson J, Podvorica FI (2008) J Am Chem Soc 130:8576
13. Adenier A, Combellas C, Kanoufi F, Pinson J, Podvorica FI (2006) Chem Mater 18:2021
14. Cruickshank AC, Tan ESQ, Brooksby PA, Downard AJ (2007) Electrochem Commun 9:1456
15. Lakard B, Herlem G, Fahys B (2001) J Chem Phys 115:7219
16. Ranganathan S, McCreery RL (2001) Anal Chem 73:893
17. Ranganathan S, McCreery R, Majji SM, Madou M (2000) J Electrochem Soc 147:277

18. Downard AJ, Garrett DJ, Tan ESQ (2006) Langmuir 22:10739
19. Garrett DJ, Lehr J, Miskelly GM, Downard AJ (2007) J Am Chem Soc 129:15456
20. Brooksby PA, Downard AJ (2005) Langmuir 21:1672
21. Kashiwagi Y, Kikuchi C, Anzai J (2002) J Electroanal Chem 518:51
22. Manriquez J, Bravo JL, Gutierrez-Granados S, Succar SS, Bied-Charreton C, Ordaz AA, Bedioui F (1999) Anal Chim Acta 378:159
23. Roslonek G, Taraszewska J (1992) J Electroanal Chem 325:285
24. Jarzebinska A, Rowinski P, Zawisza I, Bilewicz R, Siegfried L, Kaden T (1999) Anal Chim Acta 396:1
25. Taraszewska J, Roslonek G, Darlewski W (1994) J Electroanal Chem 371:223
26. Ferrer SJ, Granados SG, Bedioui F, Ordaz AA (2003) Electroanalysis 15:70
27. Taniguchi I, Matsushita K, Okamoto M, Collin JP, Sauvage JP (1990) J Electroanal Chem 280:221
28. Brooksby PA, Downard AJ (2004) Langmuir 20:5038
29. Yang W, Giandomenico CM, Sartori M, Moore DA (2003) Tetrahedron Lett 44:2481
30. Nave C, Truter MR (1974) J Chem Soc Dalton Trans, p 2351
31. Gallardo I, Pinson J, Vila N (2006) J Phys Chem B 110:19521
32. Ghanem MA, Chretien JM, Pinczewska A, Kilburn JD, Bartlett PN (2008) J Mater Chem 18:4917
33. Lund H, Hammerich O (2001) Organic electrochemistry. Marcel Dekker, New York
34. Barnes KK, Mann CK (1967) J Org Chem 32:1474
35. Luczak T (2007) J Appl Electrochem 37:269
36. Buttry DA, Peng JCM, Donnet JB, Rebouillat S (1999) Carbon 37:1929