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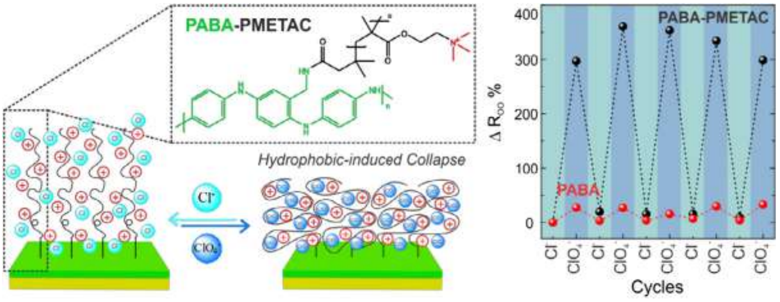
Regular Article

# Reversible modulation of the redox activity in conducting polymer nanofilms induced by hydrophobic collapse of a surface-grafted polyelectrolyte

Gonzalo E. Fenoy [a,b], Juan M. Giussi [a], Catalina von Bilderling [a,c], Eliana M. Maza [a,d], Lía I. Pietrasanta [c,e,f], Wolfgang Knoll [g], Waldemar A. Marmisollé [a,*], Omar Azzaroni [a]

[a] Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), Departamento de Química – Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP), CONICET, 64 and 113, La Plata 1900, Argentina
[b] Instituto de Investigación e Ingeniería Ambiental, Universidad Nacional de San Martín, 25 de Mayo y Francia, 1 piso (1650), Buenos Aires, Argentina
[c] Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, C1428EHA Buenos Aires, Argentina
[d] Soft Matter Nanotechnology Group, CIC biomaGUNE, Paseo Miramón 182, 20009 San Sebastián, Gipuzkoa, Spain
[e] Instituto de Física de Buenos Aires (IFIBA, UBA-CONICET), Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, C1428EHA Buenos Aires, Argentina
[f] Centro de Microscopías Avanzadas Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, C1428EHA Buenos Aires, Argentina
[g] Austrian Institute of Technology, Donau-City-Strasse 1, 1220 Vienna, Austria

## GRAPHICAL ABSTRACT



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## ABSTRACT

We present the covalent modification of a Pani-like conducting polymer (polyaminobenzylamine, PABA) by grafting of a polyelectrolyte brush (poly [2-(methacryloyloxy)-ethyl-trimethylammonium chloride], PMETAC). As PABA has extra pendant amino moieties, the grafting procedure does not affect the backbone nitrogen atoms that are implicated in the electronic structure of the conducting polymers. Moreover, perchlorate anions interact very strongly with the quaternary ammonium pendant groups of PMETAC through ion pairing. Therefore, the grafting does not only keep the electroactivity of PABA in aqueous solutions but it adds the ion-actuation properties of the PMETAC brush to the modified electrode as demonstrated by contact angle measurements and electrochemical methods. In this way, the conjugation of the electron transfer properties of the conducting polymer with the anion responsiveness of the integrated brush renders perchlorate actuation of the electrochemical response. These results constitute a rational integration of nanometer-sized polymer building blocks that yields synergism of functionalities and illustrate the potentialities of nanoarchitectonics for pushing the limits of soft material science into the nanoworld.

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* Corresponding author.
*E-mail address:* wmarmi@inifta.unlp.edu.ar (W.A. Marmisollé).

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## 1. Introduction

Nanoarchitectonics is an emerging field that refers to the rational design and construction of nanostructures into functional materials with control at the nanoscale [1–3]. Within nanoarchitectonics, polymer brushes have become versatile building blocks for the construction of more complex hybrid materials as they constitute thin polymer films in which the individual chains are tethered by one end to an interface [4,5]. Moreover, the incorporation of polymer brushes by surface-initiated polymerization techniques has become a powerful approach to tailor the chemical and physical properties of different surfaces [4]. Furthermore, in the case of polyelectrolyte brushes, environmental changes in ionic strength, pH or solvent nature can promote sharp changes in surface characteristics due to transitions between the stretched and collapsed states of the polymer chains [6]. The capability of the brushes to respond to both ionic strength and the specific nature of the electrolytes in solution can be used for controlling the state of brushes and therefore their application as nanoactuators [7].

On the other hand, conducting polymers (CPs) have attracted significant attention from the scientific community in recent decades owing to their excellent electronic and electrochemical properties. Particularly, Polyaniline (Pani) has been one of the most studied CPs, owing to its high electronic conductivity, low cost, simple synthesis, and chemical stability. Polymer brushes grafted from conducting polymer thin films are a promising class of materials for the design of functional and stimuli-responsive surfaces for applications including organic electronics, micro/nanofluidics, and biomedical applications [8]. For instance, over the last years, a special emphasis has been given to the need to realize a successful marriage between conducting polymers and polymer brushes with the aim of allowing the development of complex integrated chemical systems with perfect mastery of composition, film nanoarchitecture, and functionality [9–12].

Several synthetic strategies have been explored for the integration of polymer brushes and conducting polymers with different purposes. For example, composite films were obtained by via Surface Initiated Atom Transfer Radical Polymerization (SI-ATRP) of poly-N-isopropylacrylamide (p-NIPAM) on the holes of a surface patterned by electropolymerization of a conducting polymer (polycarbazole) [13]. Also the synthesis of poly(3,4-ethylenedioxythiophene (PEDOT) by chemical oxidation of EDOT confined to a polystyrene (PS) brush was reported to give conducting composite film [14]. More recently, the synthesis of a polymer brush on electropolymerized PEDOT-based polymer was reported. In this case, a Br-functionalized co-monomer was employed for the brush anchoring via SI-ATRP. However, as the focus of that study was on protein adsorption and cell interactions with the platforms, neither the electrochemical response nor the influence of the brush layer on the redox behavior of the PEDOT layer was reported [15].

The grafting of polyampholyte brushes on polypyrrole has also been reported [16,17]. In this case, the copolymerization of pyrrole and a COOH-appended-pyrrole was performed to obtain a conducting polymer with pendant COOH groups, which could be then used for the covalent anchoring of an ATRP initiator. They showed how the swelling behavior of zwitterionic brushes depends on the oxidation state of the conducting polymer.

Strover et al. reported the synthesis of a novel monomer containing both thiophene and pyrrole units and an initiator moiety as sidechain and its electropolymerization to give a conducting polymer [18]. The brush grafting by SI-ATRP was proved with different monomers and the influence of the oxidation state on the contact angle of the brush-modified surfaces was shown. The same conducting polymer was employed for electrochemically mediated ATRP synthesis of methacrylic brushes [8]. More recently, they explored a different approach for the integration of brushes on conducting polymers [19]. In this case, the ATRP of brushes was performed from a macroinitiator previously incorporated to the conducting polymer as a counter-polyelectrolyte (dopant) during the electrosynthesis.

The integration of brushes on Pani-based polymers has been also explored. The anchoring of polymethyl methacrylate (PMMA) brush on Pani powder dispersed in solution was reported to give core-shell structures [20]. In this case, previous covalent anchoring of initiator moieties on backbone N atoms of Pani was performed (N-grafting-from). Similarly, the polymerization of NIPAM was also performed on Pani powder particles by ATRP yielding composites with enhanced solubility in polar solvents but poor electrochemical response [21]. In the same line, Massoumi et al. synthesized N-grafting-from polyacrylic brushes on Pani particles with enhanced solubility and appreciable electroactivity in acidic aqueous solution [19]. Using a different approach, these authors performed the grafting-to synthesis of a polyacrylic brush on the Pani particles (N-grafting-to), which reduced its intrinsic conductivity [22].

The problem is that backbone N atoms in Pani are implicated in the electron delocalization responsible for the particular electronic structure of the CPs. As all these reported procedures involve the chemical modification of nitrogen atoms of the polymer backbone, the grafting of the brush significantly affects electronic and electrochemical properties of the conducting material.

We have recently chemically [23] and electrochemically [24] synthesized modified polyanilines with extra pendant amino groups, generically referred as PABA, from polyaminobenzylamine. PABA, unlike Pani, shows appreciable electroactivity in neutral solutions. By varying the proportion of 3-aminobenzylamine (ABA) and aniline (ANI), we are able to control the proportion of pendant amino groups by using an easy electro-copolymerization method [24]. These pendant amino groups also allow modifying the conducting copolymer by using the extra $NH_2$ as anchoring sites, giving rise to the possibility of incorporating new functionalities and moieties.

Following this concept, we have modified the surface of an electrosynthesized PABA film with poly[2-(methacryloyloxy)-ethyl-trimethylammonium chloride] (PMETAC) brushes via SI-ATRP. It is well-known that the interaction between the quaternary ammonium groups in the PMETAC brushes and the surrounding counterions plays a major role in determining the change in the wetting characteristics. In contrast to hydrated $Cl^-$ anions, $ClO_4^-$ anions are large, poorly hydrated and highly polarizable. So, they can interact very strongly with the quaternary ammonium pendant groups through ion pairing. As a result, significant changes are introduced in the physicochemical properties of the brush layer [6].

We show that, in the present case, the conducting polymer remains electroactive in aqueous solution after the brush anchoring, allowing the anion responsiveness from the PMETAC moieties to combine with the electrochemical capability in the composite nanofilms. This yield enhanced anion actuation of the electron transfer behavior in the hybrid polymer coatings.

## 2. Experimental section

### 2.1. Chemicals

[2-(Methacryloyloxy)ethyl] trimethylammonium chloride solution (75 wt% in $H_2O$) was from Aldrich. THF (Sintorgan) was dried by reflux in sodium and benzophenone presence and simple distillation after blue-violet coloration. Triethylamine (99.9%, Merck), α-Bromoisobutyryl bromide (98%, Aldrich), 2,2′-bipyridine (99%, Merck), $CuCl_2$ (99.999%, Aldrich), CuCl (99.999%, Aldrich).

Aniline (ANI) and 3-aminobenzylamine (ABA) were purchased from Sigma Aldrich. $NaClO_4$ was purchased from Merck. Sodium chloride, hydrochloric acid and sulfuric acid were purchased from Anedra. All chemicals were employed as-received except for ANI, which was vacuum distilled. All solutions were prepared with Milli-Q water.

For anion-responsiveness experiments, 50 mM sodium salt solutions were employed (NaCl or $NaClO_4$). The pH of these solutions was adjusted to 3 by adding HCl or $HClO_4$ in order to assure the electrochemical stability and long-term cyclability of the conducting polymer.

### *2.2. Instrumentation*

Electrochemical measurements were performed in a Gamry Reference 600 potentiostat. The electrochemical cell consisted of three electrodes in a Teflon-lined cell with 2 mL volume capacity. The counter electrode was a Pt wire and the reference electrode was an Ag/AgCl (3 M NaCl) electrode. All the potentials in this work are referred to this electrode. Gold electrodes were prepared by sputtering a thin layer of Ti on glass substrates to improve the adhesion. The electrodes were cleaned with soft basic piranha solution ($1NH_4OH{:}1H_2O_2{:}7H_2O$) prior to the electrochemical experiments. Before the electrosynthesis of the conducting copolymer, the Au electrodes were cycled in 0.5 M $H_2SO_4$ between −0.2 and 1.5 V to obtain a clean surface for reproducible electropolymerization conditions.

Contact angles were measured using a Rame-Hart contact angle system (Model 290) at 25 °C. Four measurements at different positions on the substrates were performed and average values are reported. For anion-responsiveness contact angle measurements, the substrates were previously rinsed water and immersed in 50 mM sodium salt solution for 30 min to allow the ionic equilibrium in each medium and, finally, they were dried with nitrogen. In each contact angle measurement, a 2 μL droplet of the corresponding sodium salt solution was dispensed onto the surface of the electrode.

X-ray Photoelectron Spectroscopy (XPS) was performed using a SPECS SAGE HR 100 system spectrometer. A Mg Kα (1253.6 eV) X-ray source was employed operating at 12.5 kV and 10 mA. The take-off angle was 90° and operating pressure was $8 \cdot 10^{-8}$ mbar. Quantitative analysis of spectra was carried out by using the Casa XPS 2.3. 16 PR 1.6 software, employing Shirley baselines and Gaussian\Lorentzian (30%) product functions. Surface-charging effects were corrected by setting the binding energy (BE) of the main component of the core level C1s at 285 eV [25]. The full width at half maximum (fwhm), was kept fixed for different components of a given element.

Tapping mode Atomic Force Microscopy (AFM) images were acquired in a dry nitrogen environment using a Nanoscope V, Multimode 8 AFM (Bruker, CA) with a vertical J scanner having a maximal lateral range of approximately 150 μm. RTESPA AFM probes (Bruker, CA) with a nominal spring constant of 40 N/m and a nominal tip radius of 2 nm were used. Image processing and roughness analysis was performed with the NanoScope software. Images were processed by flattening to remove the background slope.

### *2.3. Conducting polymer electrosynthesis*

Firstly, the gold substrates were cycled in 0.5 M $H_2SO_4$ between −0.2 and 1.5 V to check the absence of contamination on the electrode. The voltammetric electropolymerization was performed by potential cycling in presence of 0.07 M ABA and 0.03 M ANI in 0.5 M $H_2SO_4$ solution from −0.15 to 0.95 V at 50 mV $s^{-1}$ up to 20 voltammetric cycles. The film thickness was determined to be about 17 nm in previous works by E-QCM measurements under the same electropolymerization conditions [26]. Also, by employing this feed ratio, a film composition of approximately 30% in ABA is expected [24]. The extra amino moieties of the PABA films are much more reactive to the initiator anchoring reaction, so the brushes are expected to grow-up preferentially from these groups.

### *2.4. Controlled growth of PMETAC brushes*

PMETAC brushes were obtained by ATRP technique, which allows the surface initiated polymerization. The complete PMETAC brushes synthesis requires a number of steps, depicted in Scheme 1. These steps are grafting of ATRP initiator (Reaction with α-bromoisobutyryl bromide) and ATRP procedure to obtain the PMETAC brushes. For this, after the electropolymerization (Scheme 1, left), the PABA-modified electrodes were cycled in $H_2SO_4$ 0.5 M and dried under vacuum for 3 hs. The ATRP initiator grafting was started by immersing the electrodes in an erlenmeyer with 40 mL of dry THF. Later, 2 mL of triethylamine was added and the reaction solution was put in an ice bath. The solution was bubbled with $N_2$ and later 2 mL α-Bromoisobutyryl bromide was added slowly via syringe. After 2 h, the electrodes were removed and washed with acetone and Milli-Q water.

The modified electrodes with ATRP initiator was placed in a Schlenk tube (tube 1) and 5 vacuum/nitrogen cycles of 10 min each one were carried out. In a separated Schlenk tube (tube 2) the polymerization mixture was prepared. For this, 416 mg of 2,2′-bipyridine, 14 mg of $CuCl_2$, 10 mL of METAC and 10 mL of a 4:1 mixture of MeOH and water were mixed and purged with bubbled $N_2$ for 45 min. Then 105 mg of CuCl was incorporated and the brown mixture was allowed to stabilize for 10 min with $N_2$. Then, the mixture of tube 2 was quickly transferred to tube 1 via syringe under $N_2$. The polymerization was conducted at room temperature for 24 hs and the substrates were later washed with Milli-Q water and dried under vacuum overnight.

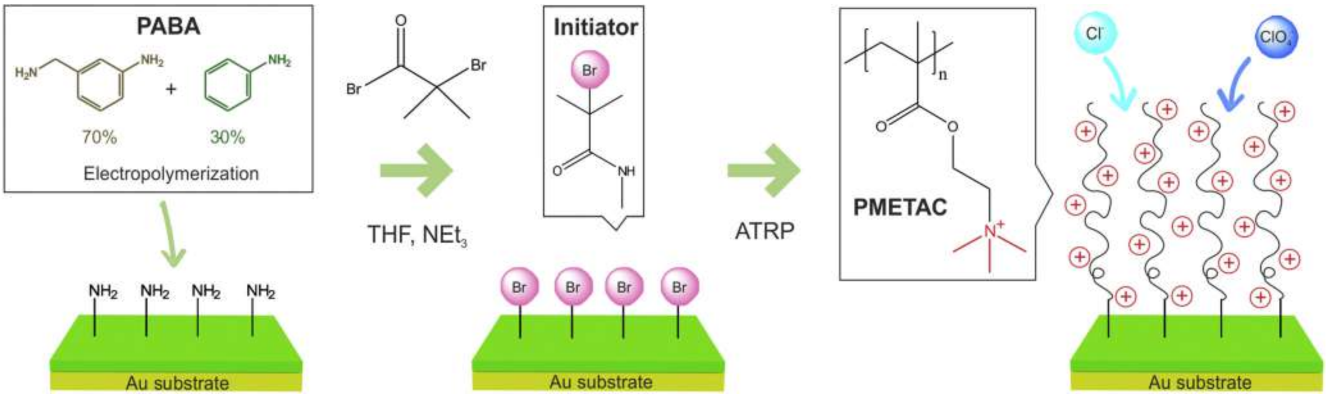
## 3. Results and discussion

In Fig. 1 the voltammograms for the PABA copolymer electropolymerization are shown. The high anodic current values at about 0.9 V are owing to the oxidative electropolymerization, whereas the previous voltammetric peaks can be assigned to redox transitions of the copolymer films [24]. The main redox couple appears at about 0.45 V. As the redox couple of pure poly(3-aminobenzylamine) is at about 0.5 V [24], this peak are probably convoluted with the so-called “middle peak” of Pani [26]. The peaks at about 0.7 V corresponds to the second redox couple of Pani (emeraldine to pernigraniline state). Finally, the peaks appearing at 0.22 V are described as an overlapping of the first redox couple for pure poly(3-aminobenzylamine) and Pani (leucoemeraldine to emeraldine state, see Fig. 5). The presence of the extra amino groups was confirmed also by XPS.

## 4. Dry brush characterization

The PABA, PABA-Initiator and PABA-PMETAC modified electrodes were studied by XPS to verify the anchoring of the initiator and the subsequent polymer brush polymerization on the PABA films. The N1s core region spectra for each modification step are shown in Fig. 2.

The PABA N1s spectrum can be deconvoluted into five components, as reported before [24]. A complete list of the N1s assignments is presented in Table 1. The peak at 398.4 eV has been assigned to the neutral imine in the polymer backbone (=N—), while the one at 399.4 eV is ascribed as neutral amines, reported to appear at BE 1 eV higher than the imine [27]. The next three



**Scheme 1.** Successive steps for PABA, PABA-Initiator and PABA-PMETAC modification.

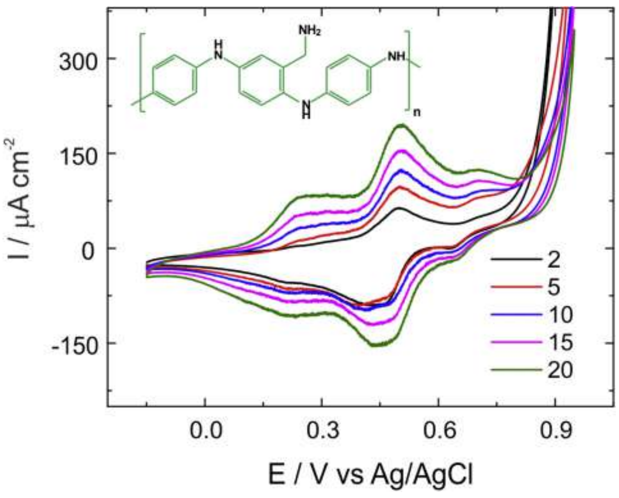


**Fig. 1.** Cyclic voltammetry curves of the PABA electropolymerization for different cycle numbers, indicated in the plot. $v = 50\ \mathrm{mV\ s^{-1}}$.

components at higher energy correspond to charged nitrogen species. The one at 400.1 eV has been attributed to secondary oxidized amines, existing at delocalized polaron-type structures in the polymer. The following two correspond to protonated amine and imine. For the first species, the peak is found at 401.1 eV [28]. The protonated imine from the localized bipolaron-type structure appears at 402.4 eV [29]. Being so many nitrogen components, the determination of the co-monomers proportion in the films becomes difficult. However, the composition can be obtained from the analysis of the XPS spectra of a series of copolymers with different feed ratio. We have previously determined the composition for the present feed ratio (and the same electropolymerization conditions) to be about 30% molar of ABA [24].

In the PABA-Initiator spectrum the neutral imine and the neutral amine peaks can be assigned at 398.5 eV and 399.6 eV, respectively. The component at 400.4 eV is attributed to the N in the polaron structure. Moreover, neither the protonated primary amine (extra amino groups) nor imine components can be found in the spectrum. This fact indicates the successful initiator anchoring on the extra amino groups of PABA, involving an amide bond generation. On the other hand, the absence of the protonated imine components could be owing to the deprotonation of the polymer induced by the modification conditions.

The presence of the bromine (Br3d, which is the unique elemental marker due to the ATRP initiator) in the XPS spectrum also confirms the initiator anchoring onto the conducting polymer (inset in Fig. 2) [13]. On the other hand, the Br3d peak was detected neither in the case of PABA nor in the PABA-PMETAC spectrum (in the latter case, probably due to exchange by chlorine).

Finally, the PABA-PMETAC N1s core spectrum displays a major difference emerging from higher energies, which is originated by a peak at 402.3 eV. This band has been assigned to protonated quaternary amines, corresponding to the polyelectrolyte brush [16,30]. This result corroborates the effective anchoring of the polymer brush on the conducting copolymer.

Atomic force microscopy (AFM) was also performed to study the brush grafting. Fig. 3 shows the AFM topography images (1 μm × 1 μm) of PABA and PABA-PMETAC modified substrates in a dry nitrogen environment. Note the scale differences in each case. The AFM reveals that after brush grafting, the surface presents higher globular domains which can be ascribed to brushes, as previously reported [31]. Typical height profiles are also shown in this figure. The root mean square (rms) roughness values measured by AFM increased from 1.43 nm for PABA to 8.0 nm for PABA-METAC, which clearly indicates the effective modification of the conducting polymer by the brush grafting. Moreover, the height of the globular domains can be estimated from the AFM height profiles to be about 30 nm.

## 5. Anion responsiveness

It is well-known that some salts with hydrophobic anions ($ClO_4^-$, $PF_6^-$, and $Tf_2N^-$) induce brush collapse via solubility changes [30,32,33]. In PMETAC brushes, the positively charged quaternary amino groups can be strongly coordinated by hydrophobic anions leading to insoluble brushes [33–36]. By varying the anion in the sodium salt solution from $ClO_4^-$ to $Cl^-$ (pH = 3, 50 mM salt concentration), we can switch from a collapsed PMETAC conformation to an extended one. The conformational changes for PMETAC are depicted in Fig. 5.

Contact angle measurements were made to confirm the anion responsiveness of the modified electrodes. In Fig. 4, we see that the contact angle for PABA-PMETAC in chloride solution is lower than in PABA (42° vs 72°). As expected, the PMETAC brushes make the surface more hydrophilic, causing a decrease in the measured contact angle. The higher hydrophobicity (contact angle 81°) evidenced in PABA-Initiator can be explained by the Br-bearing initiator anchoring during the modification.

Regarding the anion responsiveness, we can note that upon switching between $Cl^-$ and $ClO_4^-$ in PABA and PABA – Initiator modified electrodes, the change in the contact angle is minimum ($\leq 2°$). Doing this in PABA-PMETAC generates a 14° increase in the contact angle while using perchlorate as an anion. The coordination of the quaternary amino groups by the perchlorate anions

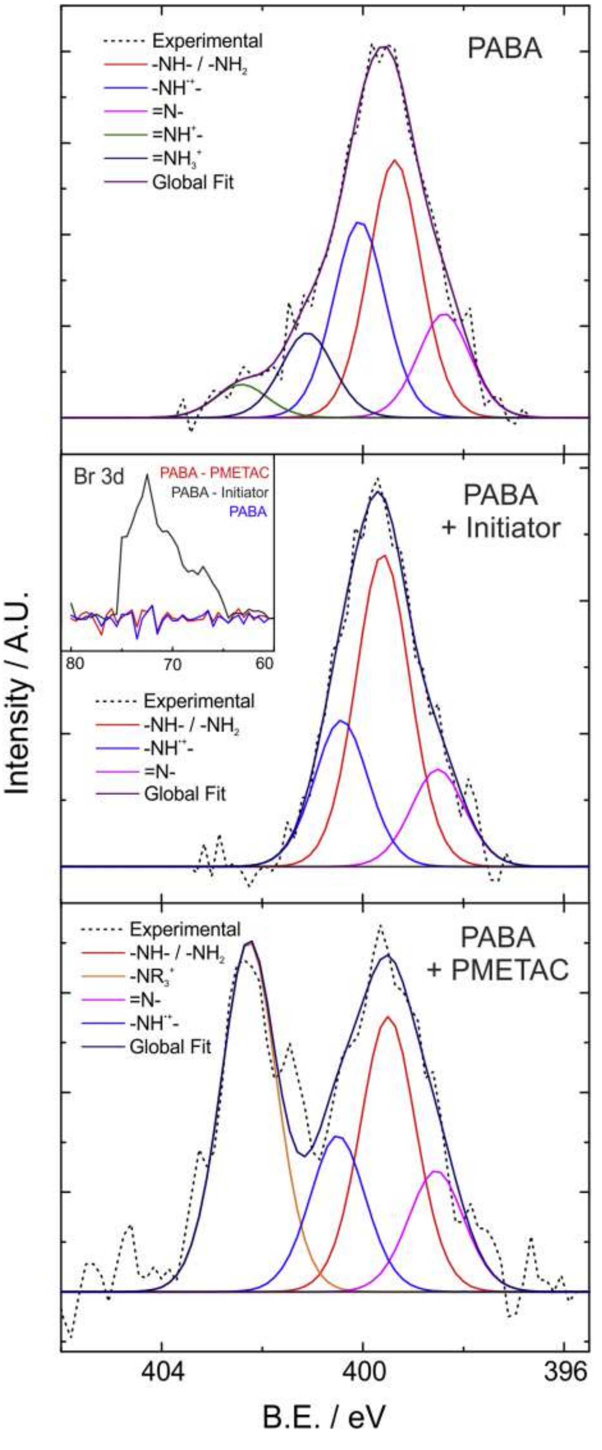


**Fig. 2.** XPS N1s spectra of PABA, PABA-Initiator and PABA-PMETAC modified electrodes.

makes the surface more hydrophobic and gives the surface an anion responsiveness behavior. The change in the angle is lower than the one observed in other similar systems [35,37] and could be explained by a low grafting density, which reinforces the idea that the brush anchoring takes place on the extra pendant amino groups. As the brush anchoring does not affect the backbone nitrogen atoms, this grafting procedure allows keeping the electrochemical activity of the conducting copolymer without blocking the electrode surface while incorporating the PMETAC responsiveness behavior.

## 6. Anion responsive electrochemical behavior

We then studied the effect of switching the anions on the electrochemical behavior of the brush-modified conducting copolymer. We performed cyclic voltammetry measurements to probe the PABA and PABA-PMETAC modified electrodes response while changing the anion from chloride to perchlorate. The measurements were performed in 50 mM NaCl or $NaClO_4$ solutions at pH 3.

In Fig. 5 the cyclic voltammetry curves for PABA and PABA – PMETAC modified electrodes are shown. We can see that the PABA response remains almost unaltered by switching the anion from $Cl^-$ to $ClO_4^-$, while in PABA-PMETAC modified electrodes the polymer response is clearly affected by the change of the electrolyte solution and, consequently, by the brush collapse. Voltammograms at different scan rates are presented in Fig. 5(A) and (C). The insets in these show the linear dependence of the peak current on the sweep rate, which is characteristic of a film-confined redox couple. On the other hand, the PABA-PMETAC modified electrode shows lower electroactivity in perchlorate solution, while preserving it in the presence of chloride. So, the anchoring of the polymer brush onto the conducting polymer confers anion selectivity to the voltammetric response of PABA. Moreover, we can see that the brush modification does not totally block the ionic transport through the film, preserving the electroactivity of the films and giving rise to a new functionality.

Besides the possibility of performing the brush anchoring, the extra $NH_2$ moieties of PABA improve the electroactivity of the copolymer in the pH 3 solution. It is well-known that the electroactivity of Pani diminishes by increasing pH. The incorporation of pendant amino groups modifies the leucoemeraldine to emeraldine transition by shifting the redox potential to higher values, owing to the steric effect of the alkyl substituent that induces non-planar conformations in the emeraldine chains [24,38]. Then, we originated a platform which is electroactive in pH 3 solutions and presents anion responsiveness.

Electrochemical Impedance Spectroscopy (EIS) is an effective method to probe the generalized resistance properties of a polymer-functionalized surface [39]. In this work, we have grafted PMETAC brushes on a PABA modified electrode, so EIS becomes an adequate tool to study the differences in the charge transport through the polymer-polymer array when changing the nature of the ions in solution.

**Table 1**
N1s components used for fitting the PABA, PABA-Initiator and PABA-PMETAC spectra. (fwhm = 1.3 eV).

| | *PABA* | | *PABA-Initiator* | | *PABA-PMETAC* | |
|---|---|---|---|---|---|---|
| *Assignment* | BE (eV) | At% | BE (eV) | At% | BE (eV) | At% |
| Neutral Imine | 398.4 | 15.4 | 398.5 | 17.5 | 398.5 | 13.4 |
| Neutral Amine | 399.4 | 38.1 | 399.6 | 56.2 | 399.5 | 30.5 |
| Polaron Structure | 400.1 | 29 | 400.4 | 26.3 | 400.5 | 17.3 |
| Protonated 1° Amine | 401.1 | 12.6 | – | – | – | – |
| Protonated Imine | 402.4 | 4.9 | – | – | – | – |
| 4° Amine | – | – | – | – | 402.3 | 38.8 |

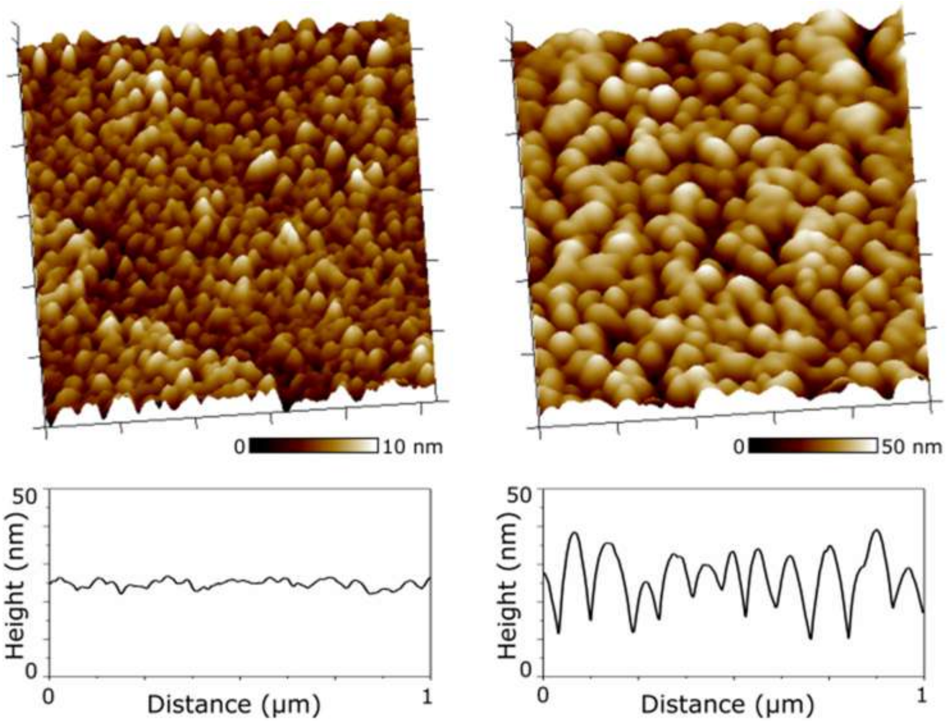


**Fig. 3.** AFM topography images and height profiles corresponding to PABA-modified Au substrates before (left) and after (right) the PMETAC brush-grafting. Note the scale differences in the height of the images.

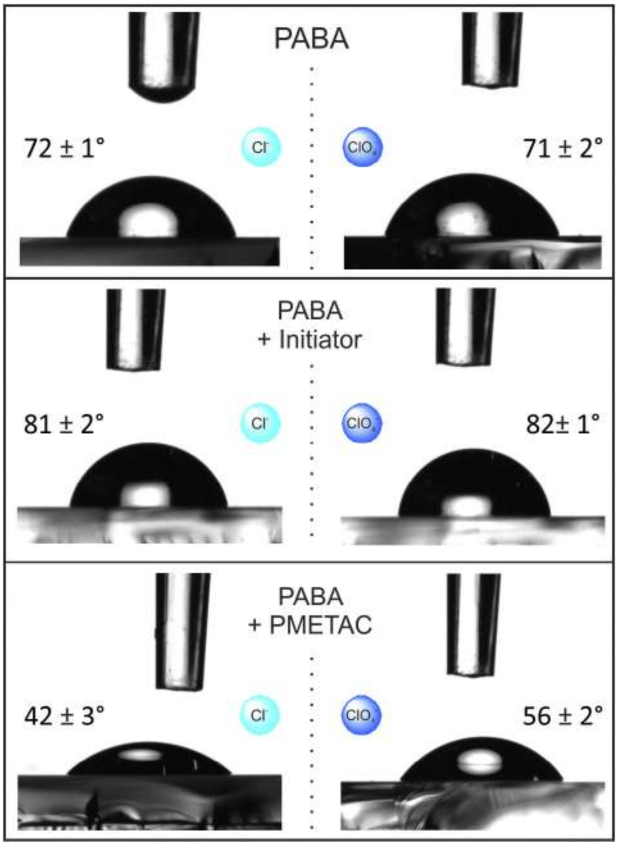


**Fig. 4.** Contact angles measurements for PABA, PABA-Initiator and PABA-PMETAC modified electrodes. Sodium salt concentration: 50 mM, pH = 3.

The effect of $ClO_4^-$ on the impedance response of quaternary ammonium brushes has been previously studied on other architectures [39–41]. As the brushes employed were non-electroactive, an external redox couple was added in those cases. In the present case, however, the redox response of the base conducting polymer is employed and no additional redox compounds are needed. In this way, we can abolish any possible interference in the analysis caused by interactions of the brushes with the external redox couple.

When polymer brushes are fully collapsed, an increase in the impedance modulus due to the blocking of transport to the PABA surface is expected, whereas when PMETAC is in a fully stretched state there would be additional pathways for charge/mass transport. So, we performed potentiostatic EIS measurements in each electrolyte (50 mM NaCl or $NaClO_4$, pH = 3) to explore the changes in the response of the brush-modified conducting polymer.

The interpretation of the EIS response of conducting polymers is not simple and several models have been developed [42,43]. In the present work, we kept the minimum complexity of the equivalent circuit to account for the changes in the experimental EIS response when changing the nature of the anion in solution. In Fig. 6(A) Bode plots for PABA and PABA-PMETAC modified electrodes are shown. The impedance response exhibits a single capacitive relaxation behavior, which can be interpreted in terms of the equivalent circuit depicted in Fig. 6(B). The physical meaning of each circuit component can be considered as follows.

The high frequency resistance ($R_{oo}$) can be assigned to the series combination of the film and solution resistances [44,45]. Even further splitting of the film resistance into the electronic conductivity of the polymer and the ionic conductivity of the pores has been proposed [46]. It is widely accepted that for highly conducting polymers (e.g. Pani emeraldine state in acidic solutions) the film resistance is negligible compared with the solution resistance and this high frequency resistance does coincide with the resistance measured using bare gold electrodes without polymer films

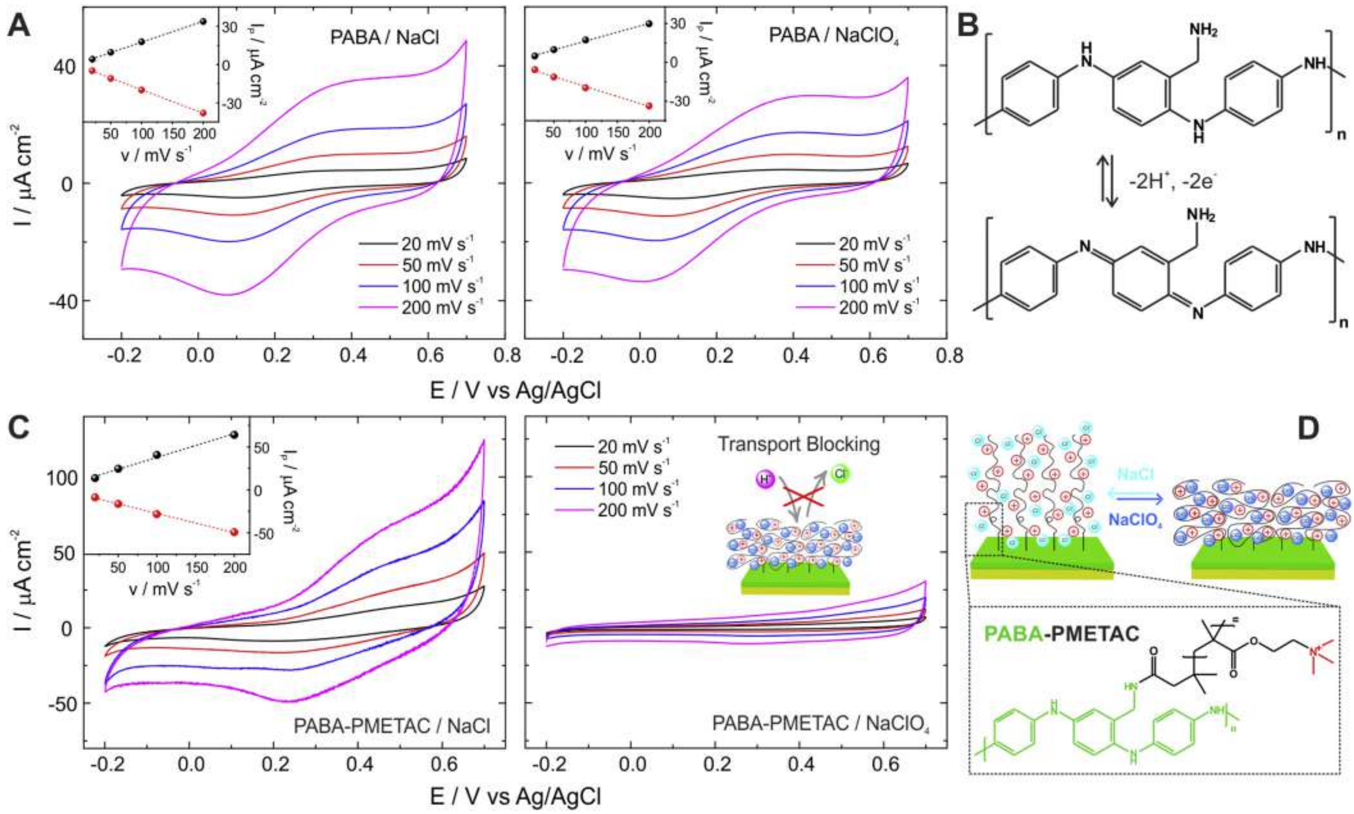


**Fig. 5.** (A) Cyclic voltammetry of PABA modified electrodes in NaCl solution (left) and $NaClO_4$ (right). (B) Redox process occurring at PABA. (C) Cyclic voltammetry of PABA-PMETAC modified electrodes in NaCl solution (left) and $NaClO_4$ (right). (D) Schematic representation of the conformational changes that occurs at PABA-PMETAC modified electrodes. Insets in panels A and C show the dependence of the current peak on the sweep rate.

[47]. However, as the polymer becomes less conducting (higher pH or reduction degree), the film resistance increases and $R_{oo}$ becomes higher than the resistance of the solution [48]. In this case, results show that the $R_{oo}$ values are higher than those measured on a bare electrode (114 and 120 Ohm for NaCl and $NaClO_4$ respectively) and they depend on the nature of the polymer coating, which indicates that the polymer resistance is not negligible.

On the other hand, the potential-dependent arrangement of charges around the interface is usually described in terms of a capacitance. Sometimes, particularly when the electrode surface is rough, the electronic properties of the interface cannot be described sufficiently well with a capacitive element, and a constant phase element (CPE) is employed. The CPE reproduces non-homogeneity of the layer and the frequency dispersion is generally attributed to "capacitance dispersion". The extent of the deviation from the Randles model is controlled by the parameter $n$ in Eq. (1). The CPE has meaning of capacitance when $0.8 \leq n < 1$ and the coefficient $Y_o$ becomes equal to the double-layer capacitance when $n = 1$ [49].

$$Z_{CPE} = Yo^{-1}(j\omega)^{-n} \tag{1}$$

A *polarization* resistance ($R_p$) in parallel connection to the CPE has been also included. The origin of $R_p$ remains controversial. It has been associated to a charge transfer resistance at the substrate and, also, to the occurrence of any parasitic electrochemical reaction that could take place at defect sites in the film giving rise to a shunt resistance [50]. In this work, however, there are no electroactive species with a decomposition potential in the studied potential window. On the other hand, in the case of electroactive polymers films, there is also the possibility of ionic transfer in the interface polymer/solution. This polarization resistance has been also considered as a charge transfer resistance due to the ionic exchange between the polymeric and the electrolytic solution phases and even Butler-Volmer-type equations have been proposed [46,51,52]. This latter interpretation is supported by the comparison of the EIS responses of PABA and PABA-PMETAC in NaCl solution. As the brush chains are highly charged, the incorporation of the brush on PABA promotes the increase in the concentration of ionic species within the interface, which yields both an increase in the double-layer capacitance and a decrease in the ionic charge transfer resistance.

The changes in the impedance response when replacing NaCl by $NaClO_4$ are clear from analysis of Fig. 6(A). In the presence of perchlorate, the impedance of the PABA-METAC electrodes increases. The difference in the $R_{oo}$ values in PABA and PABA-PMETAC modified electrodes while changing the electrolyte can be directly seen in the Bode plots (note the logarithm scale).

In Fig. 7(A) the $R_{oo}$ values from the EIS fittings for PABA and PABA-PMETAC modified electrodes are shown. The changes in the $R_{oo}$ values of PABA films by changing the anion are higher than the expected ones from the difference between bulk solution resistances of each electrolyte, which reaffirms the fact that the charge transport within the film is also different (different film resistance). This can be ascribed to the difference in the hydrophobicity of the anions and also to variations in the structure of the polymer, as it has been reported that $ClO_4^-$ promotes a more compact structure, while $Cl^-$ induces a more open state in Pani-like polymer films [53]. However, we can see that the variation in $R_{oo}$ when switching from $ClO_4^-$ to $Cl^-$ in PABA-PMETAC is much larger than in the case of PABA. Evidently, the collapse induced by the more hydrophobic $ClO_4^-$ anion on the PMETAC brush makes the films

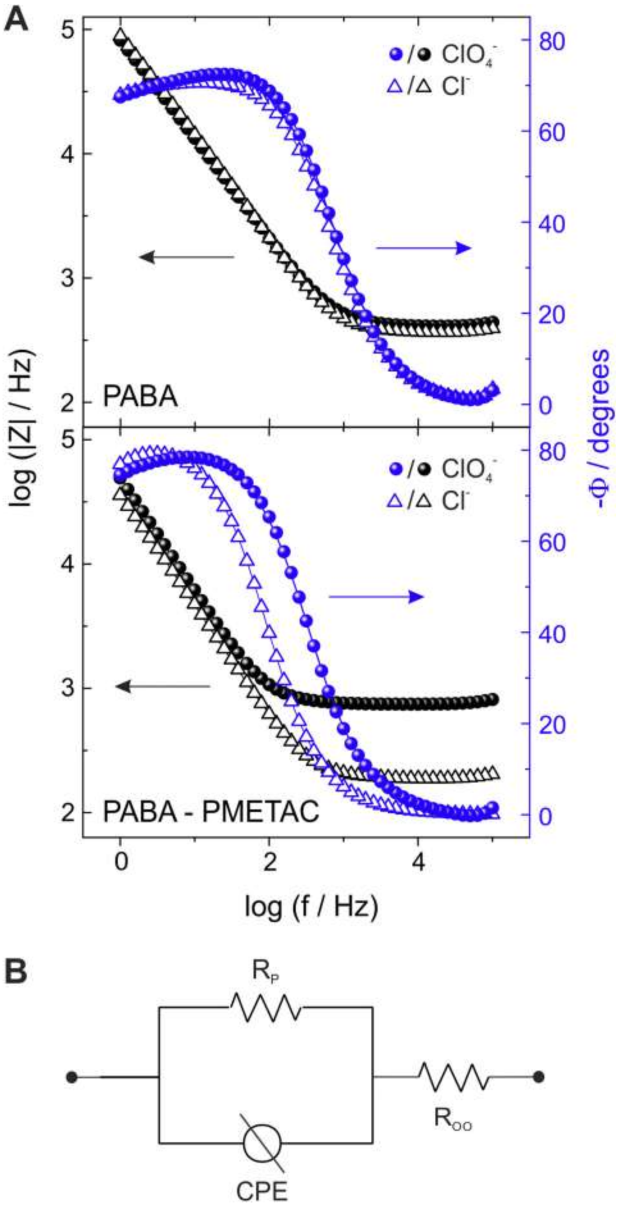


**Fig. 6.** (A) Bode plots for PABA and PABA-PMETAC modified electrodes (E = 0.4 V). Circles correspond to $NaClO_4$ and triangles to NaCl solutions. (B) Equivalent circuit used for fitting the EIS results.

more hydrophobic and hinders the charge transport through these brushes, as reported before [6]. The reversibility of the EIS response was checked up to 10 cycles, showing excellent results (Fig. 7).

The same situation takes place in the analysis of $R_p$, which also increases more pronouncedly in the presence of perchlorate due to the grafting with the brush (150% in the case of PABA-PMETAC vs. 10% in the case of PABA films, Fig. 7(B)). Changes in both resistances, $R_{oo}$ and $R_p$, reflect the hindering of the charge transfer by the collapse of the brush.

Interestingly, both voltammetric and impedimetric results indicate that the collapse of the brushes does not lead to a total blockage of the ionic transport. From previous XPS studies, the final ABA ratio in the conducting copolymer is expected to be approximately 30% [24]. This proportion would allowed us to graft a low density of brushes onto PABA electrodes, keeping the electrochemical response of PABA and incorporating the responsiveness of the PMETAC brushes without abolishing the ionic transport.

More remarkably, the incorporation of the METAC brush on the PABA film inverts the anion responsiveness of the capacitive behavior. The mean fitted values of *n* are 0.85 and 0.92 for PABA and PABA-PMETAC respectively and do not appreciably depend on the anion. Taking into account these values, the parameters of the CPE can be analyzed in capacitive terms. The corrected values of the capacitance presented in Fig. 7(C) were obtained from the CPE parameters as suggested by Orazem et al.[54]. Whereas the capacitance increases when changing chloride by perchlorate in PABA films, the behavior of the brush-modified film is the opposite. The reduction of the capacitance is likely to be related to the partial blockage on the interface caused by the brush collapse in the presence of perchlorates.

The impedance study of the brush-modified conducting polymer electrode shows that it is possible to confer anion responsiveness without completely blocking the electrochemical behavior of the platform. That is, the anion responsiveness can be integrated to the electroactivity yielding multifunctional interfacial architectures.

## 7. Conclusion

We have presented the covalent modification of a Pani-like conducting polymer (PABA) by grafting of a polyelectrolyte brush using SI-ATRP. As PABA has extra pendant amino moieties, the grafting procedure does not affect the backbone nitrogen atoms that are implicated in the electronic structure of the conducting polymers. So, the electrochemical properties of the base polymer are retained. The grafting does not only keep the electroactivity

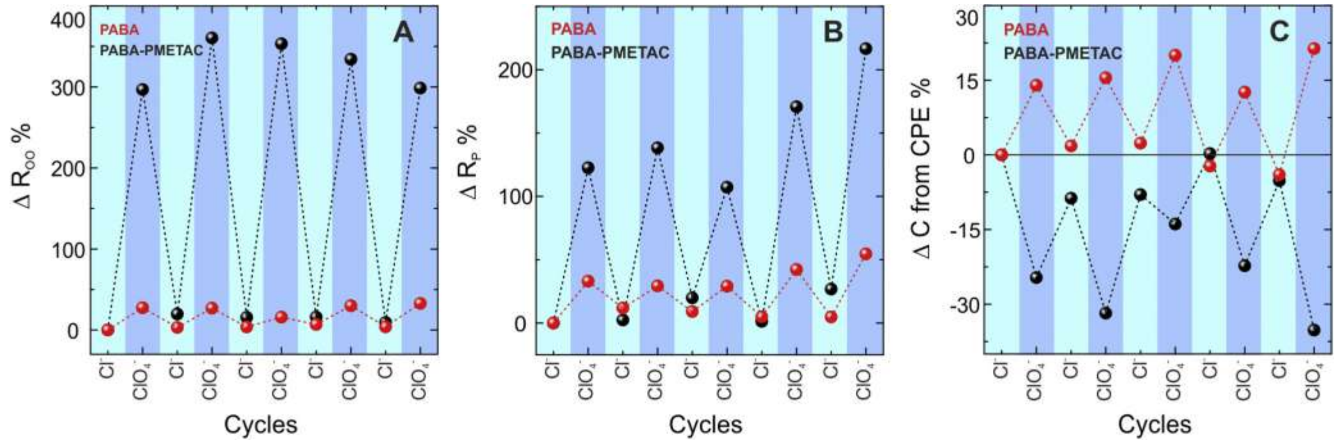


**Fig. 7.** Relative variations of the fitted EIS parameters: high frequency resistance, $R_{oo}$ (A); polarization resistance, $R_p$ (B); and corrected capacitance, C (C), for sucessive electrolyte changes between NaCl and $NaClO_4$.

of PABA in aqueous solutions but it adds the ion-actuation properties of the PMETAC brush. Thus, the conjugation of the electron transfer properties of the conducting polymer with the anion responsiveness of the integrated brush renders perchlorate actuation of the electrochemical response. Additionally, being PABA electroactive at near neutral pH, the anion actuation of the electrochemical response also presents potential applications in biosensing.

These results show how the rational integration of nanometer-sized polymer building blocks yields synergism of functionalities and illustrate the potentialities of nanoarchitectonics for pushing the limits of soft material science into the nanoworld.

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