Full-Electrochemical Preparation of Conducting/ Insulating Binary Polymer Films

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Binary polymer films consisting of an insulating polymer and a conducting polymer have been successfully prepared by sequential electropolymerization of the parent monomers. The insulating polymer (polyacrylonitrile or polyethylacrylate) is formed under cathodic polarization in a potential range where the growing chains are chemically grafted onto the nickel or carbon electrode. The conducting polymer (polybithiophene or polypyrrole) is formed by electrooxidation of the parent monomer. The electrochemical reactions and the electrochemical properties of the films have been analyzed by cyclic voltammetry and chronoamperometry. The influence of the main experimental parameters on the composition and morphology of the films has been investigated by X-ray photoelectron spectroscopy and atomic force microscopy. This approach strongly improves the adhesion of the conducting polymer as a result of its combination with the grafted polyacrylonitrile. This combination of insulating and conducting polymers is a way to tune the electroactivity of the conjugated chains.

1. Introduction

The discovery in the late 70s that high electrical conductivity could be imparted to doped conjugated polymers raised new application prospects for synthetic polymers. Electrochemistry proved to be an efficient technique (i) to improve the control and reversibility of the doping process[1] and (ii) to prepare directly thin conducting polymer films in the doped state.[2] Over the years, a variety of new polymers were prepared by electrochemical oxidation of monomers, such as pyrrole, thiophene, and aniline in appropriate electrolytic media.[3] Deposition of thin films of electroactive polymers (EP) on metal surfaces was proposed as a means of protecting metals against corrosion. Indeed, the electrochemical reactions responsible for corrosion no longer occur at the metal surface but rather at the polymer surface. Polyaniline[4,5] and polymethylthiophene[6] were reported to protect steel against corrosion. N-substituted polypyrrole electrodeposited on iron was also proposed[7] to act as a corrosion-inhibiting primary layer. Although the early results were encouraging, poor adhesion of the conducting polymer to the metal might be a serious limitation to the efficiency of the corrosion protection. It must be noted that the combination of an insulating polymer with an EP imparts good mechanical properties and improves the thermal stability and the processability of the electroactive polymer.[8]

This work aims at exploring a novel strategy to combine insulating and electroactive polymers, in a completely electrochemical process. This new approach leads to the direct formation of thin mixed films that combine the characteristic properties of both the polymers. The choice of the insulating polymer relies on its

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ability to be electrografted onto metallic substrates.[9] As was previously discussed, acrylonitrile (AN) and (meth)-acrylic derivatives are chemisorbed onto nickel, copper, and steel surfaces and polymerized under polarization at an appropriate cathodic potential. The striking observation is that the polymer films strongly adhere to the substrate surface, even when dipped in a good solvent for the polymer.

Two electroactive polymers have been considered in this study: polybithiophene (PBT) as a model for polymers, which are most stable in the neutral form, and polypyrrole (PPy), which is stable only in the oxidized state. The combination of these polymers with a cathodically grafted polyacrylate is expected to substantially improve the EP adhesion. This strategy will be first discussed in the case of the PAN/PBT system, with special attention paid to the effect of the electropolymerization sequence on the morphology and electroactivity of the films. In a second step, the effect of the initially grafted polymer on the morphology of mixed films with PPy will be considered. The possible tuning of the electrochemical response of PPy combined with a grafted polymer will also be discussed.

The electropolymerization and the electrochemical properties of the films will be studied by chronoamperometry and cyclic voltammetry. The microscopic morphology of the films will be observed by atomic force microscopy (AFM) and their chemical composition will be analyzed by X-ray photoelectron spectroscopy (XPS) to assess that the polymer formed in the first step is not degraded during the synthesis of the second polymer.

2. Experimental Section

Acrylonitrile (AN), ethylacrylate (EA), and acetonitrile (ACN) were dried over calcium hydride and distilled under reduced pressure. Dimethylformamide (DMF) was dried over P_2O_5 and distilled under reduced pressure. 2,2-Bithiophene (BT), which is a solid at room temperature, was dried overnight in a vacuum. Propylene carbonate (PC) was dried over molecular sieves for 24 h and distilled at 85 °C under reduced pressure. Pyrrole was distilled under reduced pressure. Tetraethylammonium perchlorate (TEAP) was heated in a vacuum at 80 °C for 12 h prior to use.

Electrochemical experiments, that is, voltammetry (CV) and chronoamperometry (CA), were carried out in a dry organic solvent (propylene carbonate or dimethylformamide) containing TEAP (5×10^{-2} M) as a conducting salt. The water content was measured by the Karl Fischer method (Tacussel aquaprocessor) and ascertained to be lower than 5 ppm. All the experiments were carried out in a glovebox under an inert and dry atmosphere at room temperature. Both the electrochemical cell and the preparation of the nickel cathode were detailed elsewhere.[9a] Because of the drastic anhydrous conditions needed for the electrografting, the use of conventional reference electrodes is precluded and the potentials have to be measured against a Pt pseudo-reference electrode. Therefore, the absolute values of the electrochemical potentials cannot be compared for processes occurring in different media.

XPS spectra were recorded with an SSI or SCIENTA apparatus. The topography of the films was studied with a Digital Instruments Nanoscope II atomic force microscope, operated in air in the contact mode and equipped with commercial Si_3N_4 tips. Several areas of each sample were analyzed to check the reproducibility of the surface topography. Under the conditions used, no tip-induced surface damage was observed.

Qualitative peeling tests were performed by using TESA 4120 scotch tape. Nickel merely coated by PBT or by binary PBT/PAN films was also tested for comparison. Cyclic voltammetry scans were recorded before and after peeling.

3. Results and Discussion

The cathodic electrochemical grafting of polyacrylonitrile and the anodic electropolymerization of bithiophene on nickel in propylene carbonate have been first examined. Nickel is a commodity metal onto which the electropolymerization of PAN has been extensively studied.[9] Mixed PAN−PBT films have been prepared in a sequential way, that is, electropolymerization of AN followed by BT or vice-versa, the monomers being dissolved separately or simultaneously in the same solution.

A. Electrochemical Deposition of Polyacrylonitrile, Polybithiophene, and Mixed Films onto Nickel Surfaces. The voltammetric response of AN in aprotic polar solvents shows two cathodic features:[9]

(1) A low intensity peak, usually referred to as the “inhibition peak”. It is assigned to the grafting of PAN onto the metal. This grafting is responsible for the strong adhesion of the film to the metal, in agreement with the insolubility of PAN in a good solvent for it (e.g., DMF).

(2) An intense peak at a more cathodic potential, which is the signature of a diffusion-controlled process.[10] AN is then polymerized in solution and no longer chemisorbed on the cathode.

Because this work aims at grafting PAN, the electropolymerization of AN has been confined to the potential range of the inhibition peak.

The anodic polymerization of BT on inert metals, such as platinum, has been extensively studied in the scientific literature.[11] Because the mixed PAN−PBT films have to be prepared on nickel, it must be assessed that BT can be electropolymerized on this oxidizable metal. The cyclic voltammetric curves (CV) that have been recorded for a BT (0.1 M) solution in propylene carbonate on nickel are essentially identical to those ones observed for anodes of inert metals.[12] A bluish film typical of doped PBT[13] is deposited on the electrode when the potential exceeds +1.5 V vs Pt. It is important to note that no signal originating from the oxidation of the nickel anode is observed.

On the basis of these data, PBT has been prepared at a constant potential of +1.75 V for 5 s. Because PAN films synthesized in PC are very thin (typical thickness of 100 Å[14]), the deposition time for PBT has been chosen such that a comparable amount of PAN and PBT has

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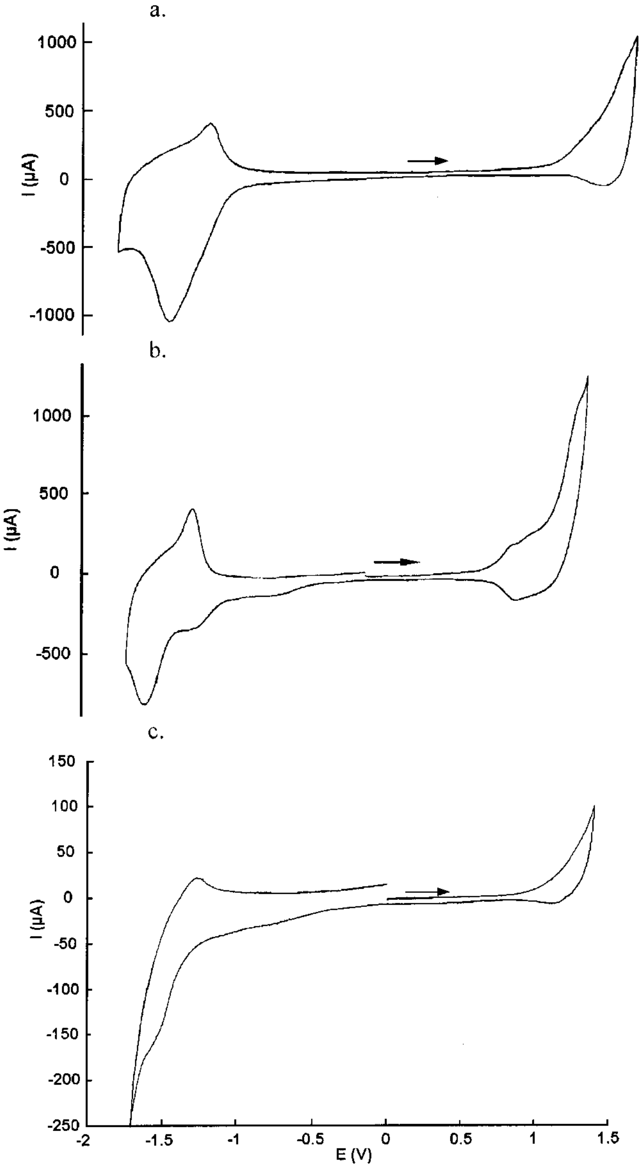

Figure 1. Cyclic voltammograms in ACN ($v = 50$ mV/s): (a) a PBT film on nickel; (b) a mixed PBT/PAN film on Ni; (c) a mixed PAN/PBT film on Ni.

been deposited. The electroactivity of the PBT films on nickel has been analyzed by cyclic voltammetry over a wide potential range (Figure 1a). The peaks that correspond to the n-doping and dedoping (on the left-hand side) and the p-doping and dedoping (on the right-hand side), respectively, are very similar to the data reported in the literature,[13,15] which indicates that the PBT films deposited on nickel exhibit the electrochemical properties expected for this polymer.

Because PBT and PAN are synthesized under anodic and cathodic polarization, respectively, it is important to assess that PAN resists anodic polarization when it is electrodeposited first. For this purpose, a PAN film has been anodically polarized under the conditions used for the deposition of the PBT films, that is, for 5 s at +1.75 V in PC. The current intensity is drastically decreased as compared with that of the bare metal, which is consistent with the effective protection of the nickel electrode by the PAN film. However, the current does not drop to zero, possibly because of some defects or pores in the PAN film. The XPS analysis of the anodically polarized PAN film (Figure 2a) shows no peak characteristic of nickel (which would appear at 660 and 870 eV) but only the signature of the polymer. Moreover, the anodic polarization of the PAN film does not change the binding energies for the C(1s) and N(1s) peaks and their relative intensity, which is a clear indication of the electrochemical stability of PAN.

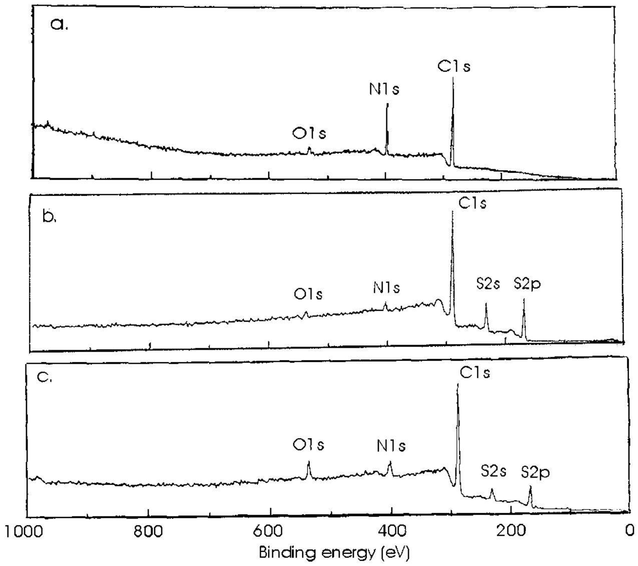

Figure 2. XPS spectra of (a) an anodically polarized PAN film, after washing with DMF; (b) a mixed PBT/PAN film deposited on Ni prepared in two separate cells; (c) a mixed PBT/PAN film deposited on Ni in a single cell.

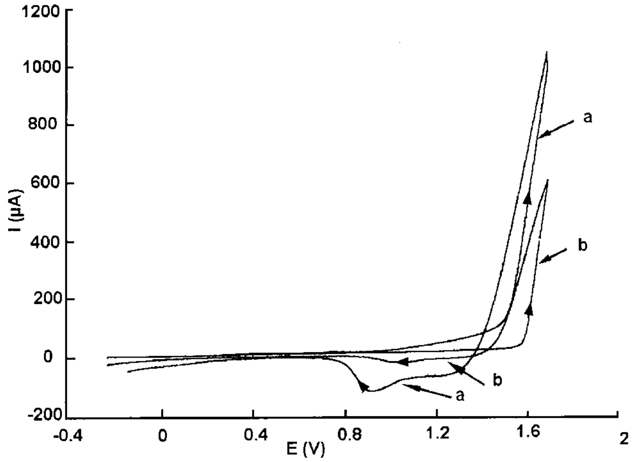

Figure 3. Cyclic voltammograms ($v = 20$ mV/s) of BT (0.1 M) in PC on (a) bare nickel and (b) PAN-coated nickel.

The originality of this work lies in the electrochemical synthesis of the two components of the film. The sequential deposition can be carried out either in two independent cells, each containing one monomer in solution, or in a single cell in which the two monomers are simultaneously dissolved. In both the cases, there are two possible polymerization sequences: PAN is electrodeposited first and BT is polymerized afterward (this sequence being referred as PBT/PAN) or vice versa (PAN/PBT).

1. Mixed PBT/PAN Films Prepared in Two Independent Cells. Figure 3 compares the CV curves for a 0.1 M BT solution in PC on bare nickel (curve a) and on

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PAN-precoated nickel (curve b). The same features are observed for the two curves, that is, a nucleation loop and a twin reduction wave, which is clear indication that a PBT film has been deposited onto the PAN-coated nickel electrode. The lower current observed in the latter case is consistent with the PAN precoating, which considerably decreases the effective electrode area.

The drastic reduction of the surface area available to BT when nickel is precoated by PAN is expected to favor the heterogeneous growth of PBT from “nucleation” spots randomly distributed on the surface. Therefore, the final binary film should have a multiphase structure formed by the coexistence of PAN and PBT domains. This tentative picture is in qualitative agreement with the XPS analysis, which shows the signature of both the polymers (Figure 2b), that is, the N(1s) peak characteristic of PAN and the S(2s) and S(2p) peaks typical of PBT. This multiphase morphology is provided by direct observation of the surface with AFM. Although the surface of a PBT film deposited on bare nickel is rather rough (Figure 4a), the roughness strongly increases when PBT is grown on the surface of PAN-precoated nickel. Grains are indeed visible on the surface, and their size increases when the PAN precoating is thicker, thus when the concentration of AN in the precoating step is higher (Figure 4b,c). It is also clear that the surface density of grains (i.e., the number of grains per surface unit area) decreases as their size increases. This evolution is consistent with less defects and pores in the PAN precoating, when it is thicker. From Figure 4a−c, it is thus reasonable to assign the large grains to PBT and the lower continuous layer to PAN. When the PAN precoating is less porous, the same amount of PBT grows from a smaller number of nucleation spots, which explains the way the roughness changes (grain size and density) from Figure 4b to Figure 4c. A multiphase morphology is also consistent with the cyclic voltammograms, which are quite similar to those ones recorded for pure PBT (Figure 1a,b).

2. Mixed PAN/PBT Films Prepared in Two Independent Cells. In this sequence, AN has been electropolymerized on PBT-precoated nickel. Figure 5 compares the voltammograms for the cathodic electrografting of PAN onto bare nickel and PBT-coated nickel. The PBT precoating of the cathode does not prevent AN from being polymerized because a current peak of comparable intensity is observed. However, the potential of this reduction peak is shifted to a less cathodic value, which results from the change of the surface (PBT instead of nickel) onto which the reaction occurs. This shift in the potential of electrografting has been confirmed by using a nickel electrode coated by PBT only on half of the useful surface. Then, the voltammogram clearly shows two peaks: the less cathodic one characteristic of the electrografting on PBT and the second one typical of the same reaction onto bare nickel. Therefore, PAN can be electrografted not only onto a metal surface but also onto an organic conducting polymer. A similar modification has once been reported elsewhere.[16]

The electroactivity of the PAN/PBT mixed films has been examined by cyclic voltammetry (Figure 1c). The intensity of the peaks is much smaller than that in the former cases (note the change in the intensity scale) and no change of color is visible. The presence of the anodic and the cathodic waves more likely results from the metal dissolution under anodic polarization and from a reaction of either the solvent or the electrolyte under cathodic polarization. The drastic decrease of the electroactivity is consistent with the hypothesis that PAN is deposited onto the PBT surface. Formation of an insulating film on the surface of PBT may indeed prevent the conducting polymer from being doped, so accounting for the loss of electroactivity. The AFM observation of the PAN/PBT film (Figure 4d) shows a morphology that is consistent with the PBT surface (Figure 4a) coated by a continuous top layer of PAN.

3. Mixed Films Prepared in a Single Cell. A cell with two compartments has been used for this purpose. The working electrode compartment contains the two monomers in solution, and the counter electrode compartment is filled with the pure electrolytic solution. In a preliminary step, we have checked that no secondary reaction occurs when the two monomers coexist in the electrochemical cell. The voltammogram for each of them is indeed quite similar to this one reported for the individual monomer (curves not shown here). This observation is in line with the lack of reaction of AN at moderate anodic potentials[17] and with the cathodic polymerization of BT only when it is complexed with transition metals.[18] Moreover, the two monomers do not mutually react.

The mixed films have been prepared by cathodic polarization at −1.8 V for 2 s (formation of PAN) followed by a 5-s-long anodic polarization at +1.75 V (formation of PBT). The XPS spectrum of those samples (Figure 2c) clearly shows that PAN and PBT coexist in the mixed film. Furthermore, cyclic voltammetry indicates that PBT is electroactive. The AFM observation of the film surface (Figure 4e) is significantly different from the morphology of the PAN/PBT film prepared in two separate cells. Instead of grains relatively homogeneous in size (Figure 4b or Figure 4c), grains with a broad size distribution are now observed. A tentative explanation might be that BT monomer is trapped in PAN. The BT polymerization can be initiated within the PAN matrix and not only from the defects in it, as is the case when the two monomers are polymerized in a sequential way. Mixed films can also be prepared via the “first PBT, then PAN” polymerization sequence in a single cell. Once again, the electrochromic properties of the film are hardly observed compared to those in the reverse sequence. It thus appears that the electrochemical activity of PBT is preserved only when PAN is first electrografted followed by PBT deposition. The mixed films have a multiphase morphology as a result of the coexistence of the polymers at the surface.

The adhesion of the PBT/PAN mixed films to nickel has been estimated by peel tests, comparatively to pure PBT. In the latter case, most of the polymer is transferred to the scotch tape, while the mixed film remains on the metal substrate except for some minor areas along the edges of the electrode. The PTB/PAN mixed film is not transferred under the same conditions. This

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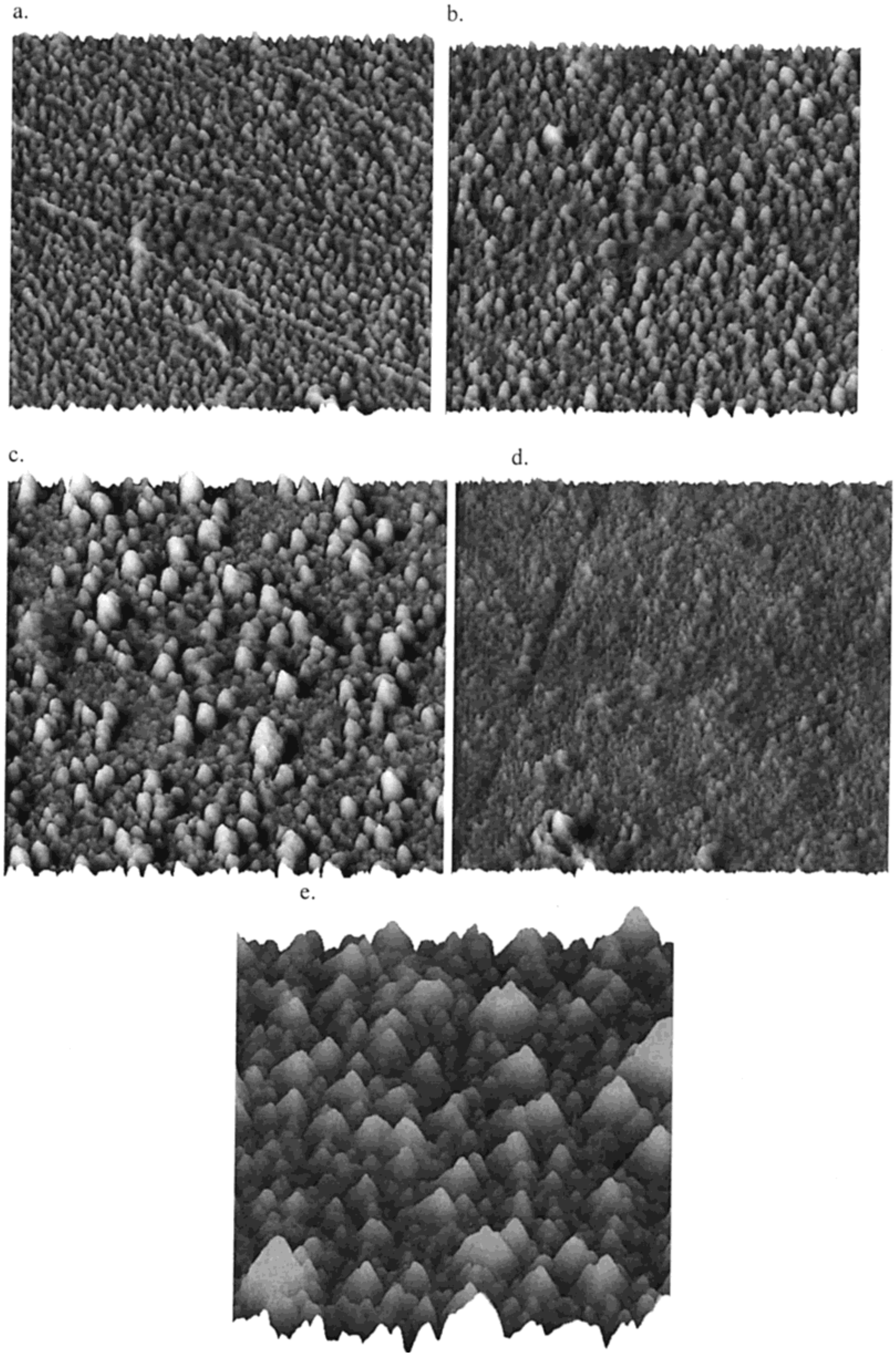

Figure 4. AFM images (horizontal size 3 × 3 μm^2, vertical size 100 nm): (a) PBT deposited on Ni; BT electrooxidized onto PAN/Ni, PAN being first electrografted (b) from a 0.5 M AN solution, (c) from a 0.2 M AN solution; (d**)** AN electroreduced onto PBT/Ni; (e) BT electrooxidized onto PAN/Ni in a single cell.

difference in behavior is confirmed by cyclic voltammetry after peeling. For pure PBT, a large signal typical of the nickel dissolution is observed. In contrast, the electrode coated by the binary mixed film shows the electrochemical signature of PBT after peeling, and no evidence for nickel dissolution is reported. The mixed film thus efficiently protects the metal against corrosion while the electrochemical activity is maintained.

In a second step, polypyrrole-containing mixed films have been prepared, polypyrrole being widely studied as an electrochemical sensor. In this case, the conducting substrate must resist anodic dissolution, which

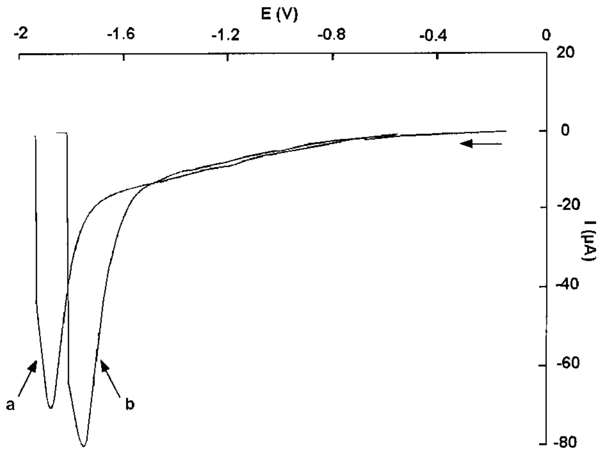

Figure 5. Voltammograms ($v = 20$ mV/s) of AN (2 M) in PC on (a) bare nickel and (b) PBT-coated nickel.

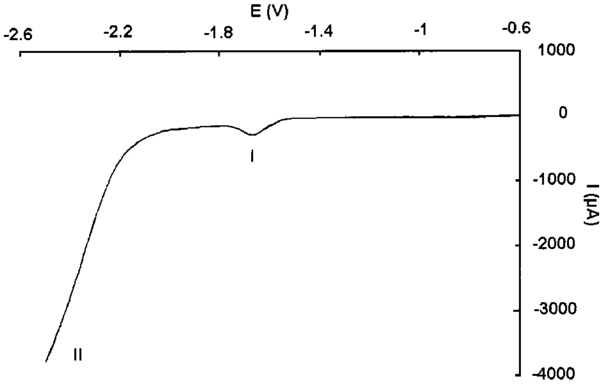

Figure 6. Voltammogram of EA (1.5 M) in DMF on carbon ($v = 20$ mV/s).

makes carbon a valuable candidate. Because electrografting of acrylic polymers was only reported onto metals, a preliminary step in this study consisted of assessing the ability of AN and ethylacrylate (EA) to be electrografted onto carbon substrates.

B. Electrochemical Deposition of Polyacrylonitrile, Polyethylacrylate, Polypyrrole, and Binary Films onto Carbon Surfaces. The electrografting of the insulating polymers (PAN and polyethylacrylate (PEA)) onto carbon has first been examined by cyclic voltammetry in DMF. A typical voltammogram is shown in Figure 6 for EA solution in DMF (1.5 M). Two reduction peaks are observed, as is the case on metal cathodes. The peak at a lower cathodic potential is the inhibition peak characteristic of the chemisorption of the growing polymer chains. Moreover, the dependence of both the intensity and the position of this peak on the scanning rate and the monomer concentration is in agreement with the observations previously reported in the case of electrografting on metals. Actually, the intensity of the inhibition peak decreases when the monomer concentration is increased, and the peak is shifted to less cathodic potentials when the potential scanning rate is lower.[19]

The permanency of the polymer film on the electrode after intense washing with DMF, a good solvent for PAN and PEA, is additional evidence for polymer grafting.

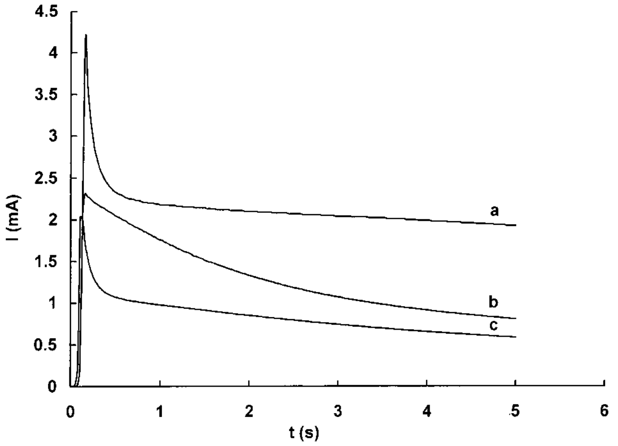

Figure 7. Chronoamperograms (+1.4 V, 5 s) of Py (0.1 M) in DMF on (a) bare carbon, (b) PAN-coated carbon, and (c) PEA-coated carbon.

The stability of this grafting toward hydrolysis has also been checked. PAN originally grafted onto a metal, such as nickel, can be detached in an ultrasonic bath containing DMF added with 5 vol % of water, although it remains grafted in anhydrous DMF. When a PAN-grafted carbon plate is similarly treated, no polymer dissolves in water-containing DMF. The film remains strongly adhering to the carbon surface. This observation indicates that PAN is chemisorbed onto the cathode by a water-sensitive organometallic bond in the case of metals, whereas the polymer is linked by a nonhydrolyzable covalent C−C bond in the case of carbon.

Pyrrole has been electropolymerized onto carbon electrodes by classical chronoamperometry ($E = 1.4$ V) in a solution of Py (0.1 M) and TEAP (0.05 M) in DMF (Figure 7a). This observation is in agreement with similar experiments reported in the literature.[20]

Polymer deposition can be observed by AFM on the glassy carbon surface, which shows low roughness (Figure 8a). As a rule, the grafting of PAN tends to increase the surface roughness of carbon (Figure 8b). Large objects are unevenly distributed on the surface. They could result from the precipitation of the grafted PAN chains when the electrode is washed by ACN, which is nonsolvent for the polymer. The surface topography completely changes when PEA is electrografted rather than PAN (Figure 8c). The surface is very smooth and quasi featureless. The carbon grains are no longer visible, and the surface consists of large-size smooth patches. This marked difference between PEA and PAN more likely originates from the low T_g of PEA (−24 °C) compared to that of PAN (155 °C). In contrast to PAN's coating, the PEA coating can flow and cover the carbon surface completely. Finally, a very rough coating with a two-layer structure is observed for PPy (Figure 8d). Apparently "exploded" spherical nodules of very large size (in the micron range) can be seen on top of a continuous sublayer of smaller-size nodules. This nodular morphology is commonly reported for conducting polymers electrodeposited on various substrates.[21]

Binary PPy/PAN films have then been deposited on carbon. The current intensity recorded during the potentiostatic deposition of PPy ($E = 1.4$ V) on PAN-

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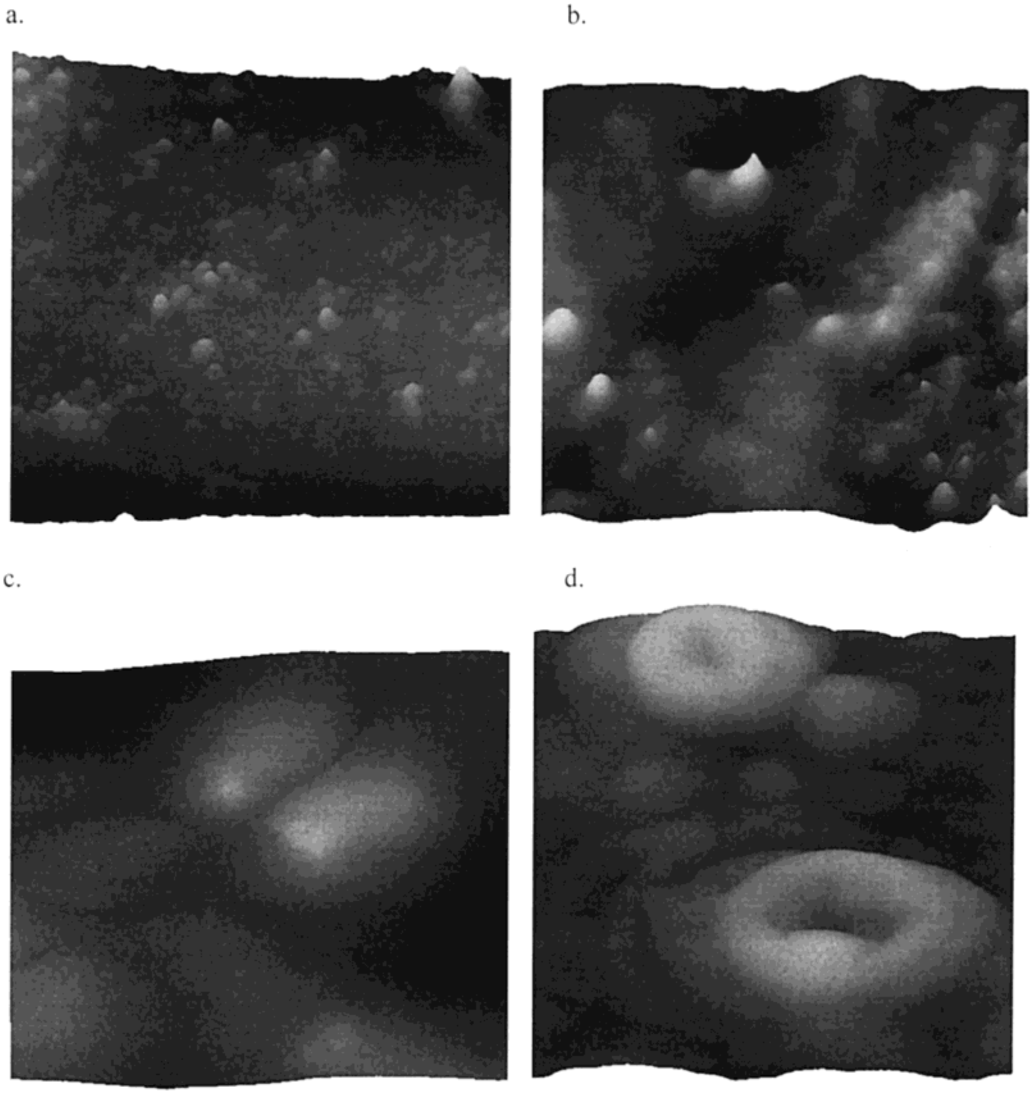

Figure 8. AFM images of (a) carbon, (b) PAN-coated carbon, and (c) PEA-coated carbon (horizontal size 3 × 3 μm^2, vertical size 100 nm); (d) PPy-coated carbon (horizontal size 5 × 5 μm^2, vertical size 1 μm).

precoated carbon electrodes in DMF is lower than that on bare carbon over the whole polarization period (curves a and b in Figure 7). This behavior is very different from that one observed for PBT deposition on PAN-precoated nickel in PC. In that case, the current reaches the same plateau value after 2 s on both bare and PAN-coated nickel (for the first 2 s, the current is however lower for the PAN/Ni substrate). The main difference between the two systems is that DMF is a good solvent for PAN and PC is a nonsolvent. Because pyrrole must diffuse through the swollen PAN layer to reach the electrode, the current intensity may be limited by the diffusion rate of the monomer. In the limits of this assumption, the PPy chains have to grow through the swollen PAN film rather than through pores or defects of the solid PAN film, as was the case for PBT in PC.

The AFM observation of the surface of the PPy/PAN film on carbon shows well-defined grains of variable size (Figure 9a). This picture is not basically different from the AFM observation of the PBT/PAN film prepared in one cell (Figure 4e). In that case, the conducting polymer is expected to grow through the PAN matrix in which some BT monomer would be trapped. Similarly, the PPy chains are expected to grow through the swollen PAN layer, thus leading to a more intimate intermingling of the two types of polymers.

For the PPy/PEA/C system, the chronoamperometric curve recorded for the pyrrole electrooxidation on PEA-precoated carbon (Figure 7c) also shows a lower current intensity compared to that on neat carbon. Because DMF is a good solvent for PEA, the explanation proposed for the chronoamperometric curve on PAN-precoated carbon remains valid. It thus means that the pyrrole chains are growing through the swollen-grafted film of PEA. The AFM images of the PPy/PEA film on carbon are consistent with the growth of small hemispherical domains beneath the featureless coating of PEA (Figure 9b,c). When the amount of PPy formed is increased (the current being increased from 45 to 110 mC), the size of these domains increases accordingly.

This unusual structure of the binary polymer film should affect the electrochemical properties of polypyrrole in relation to the solvent in which the electrode is dipped. Indeed, the PEA layer, which appears to cover the PPy domains, can either be swollen (e.g., in DMF, a good solvent of the polymer), which allows the counterions to diffuse easily, or be desolvated (e.g., in water,

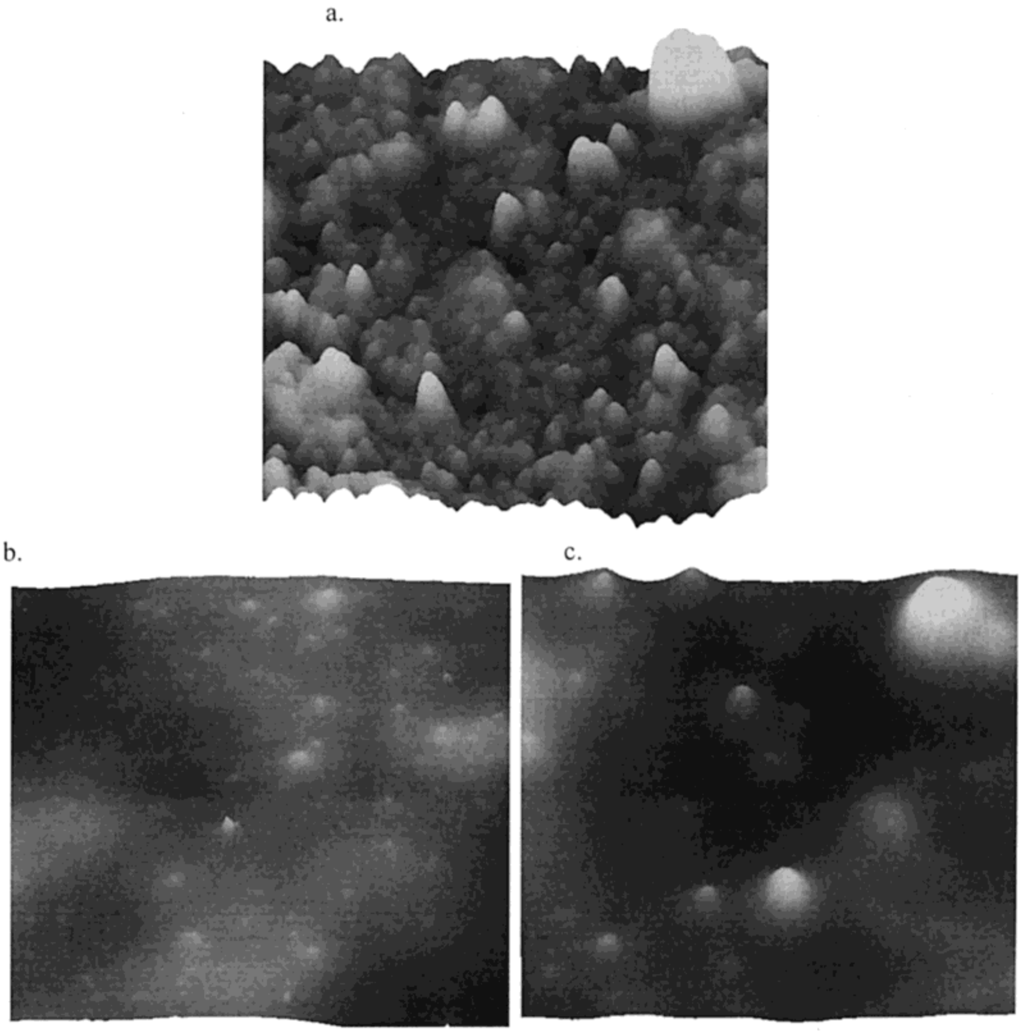

Figure 9. AFM images (horizontal size 3 × 3 μm^2, vertical size 100 nm) of the mixed films prepared by electrodeposition of PPy onto (a) PAN-precoated carbon, or PEA-precoated carbon containing an amount of PPy equivalent to (b) 45 and (c) 110 mC.

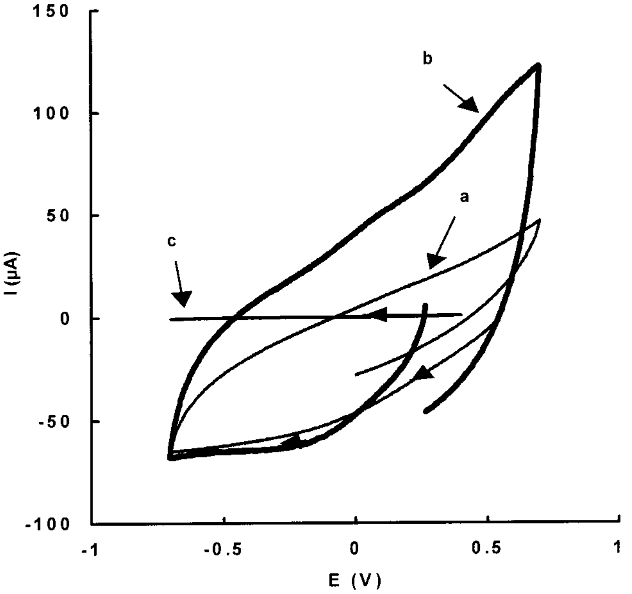

Figure 10. Cyclic voltammograms ($v = 20$ m/s) of PPy/PEA mixed films on carbon in (a) DMF, (b) ACN, and (c) water.

a nonsolvent of PEA), which can dramatically restrict the ion-exchange process. To assess this hypothesis, the electroactivity of the PEA/PPy film on carbon has been analyzed in three solvents (DMF, ACN, and water) with TEAP or $LiClO_4$ (in water) as the conducting salt. Cyclic voltammetry clearly shows that PPy can be electrochemically switched in ACN and DMF, which are good solvents for PEA (Figure 10a,b). In contrast, the redox activity of the mixed film is completely lost in an aqueous medium (Figure 10c). This behavior is not observed for PPy electrodeposited onto neat carbon, which is electroactive in water. These observations are consistent with the presence of PPy domains fully coated by PEA. Indeed, if PPy was available (at least partly) at the surface, it would be in direct contact with the aqueous electrolyte and the film would be electroactive in water.

4. Conclusions

This work has reported on the full electrochemical synthesis of mixed films containing one conducting polymer and one insulating polymer chemisorbed on the electrode. This strategy allows combination of the redox activity of the conducting constituent with the strong adherence of the insulating one to the substrate. This approach appears to be versatile, as exemplified in this work by the combination of polypyrrole or polythiophene with polyacrylonitrile or polyethylacrylate. The two components of the film are electropolymerized without mutual interference, the mechanisms being completely different and occurring in completely separated potential ranges.

The morphology of the organic film directly depends on the way the polymer deposited in the first step controls the spatial growth of the second component. If the insulating polymer is deposited first and forms a thermoplastic film nonsolvated by the solution of the second monomer, then the two polymers coexist as independent domains. If the second monomer solution swells the insulating polymer layer, then the two types of polymer tend to be mingled one with the other. In that case, the relative length and expansion of the chains determine whether the two constituents coexist at the surface of the film or not. The intimate structure of the mixed film can thus be changed at will, which allows the film electroactivity to be controlled.

The advantage of this electrochemical strategy is to combine electrochemical activity and strong adherence, as illustrated by the PBT/PAN/Ni system. This approach can also be used to tune the electrochemical activity of the conjugated polymer as described for the PPy/PEA pair. The next step of this work will be the use of a single "bifunctional" monomer, that is, a monomer that acts as a precursor of the grafted insulating polymer under cathodic polarization and that can be polymerized into a conducting compound under anodic polarization.

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