Surface Electroinitiated Emulsion Polymerization: Grafted Organic Coatings from Aqueous Solutions

Guy Deniau,* Laurent Azoulay, Luc Bougerolles, and Serge Palacin

CEA-Saclay, DSM-DRECAM-SPCSI, F-91191 Gif-sur-Yvette Cedex, France

Received March 29, 2006. Revised Manuscript Received July 25, 2006

The surface electroinitiated emulsion polymerization (SEEP) protocol, described here for the first time, combines the advantages of the electrografting process, which delivers thin organic coatings chemically bonded to conducting surfaces, with polymerization in emulsion, which allows synthesizing hydrophobic polymers in aqueous solutions. From the mechanistic point of view, SEEP combines the "grafting to" and "grafting from" methods in one fast electrochemical step at room temperature, taking advantage of the ability of diazonium salts to (i) be easily electrografted on conducting surfaces under moderate cathodic conditions and (ii) act as an initiator for the radical polymerization of vinylic monomers in emulsion. This work is a preliminary description of this process applied to various vinylic monomers like acrylic acid (AA), acrylonitrile (AN), and butyl methacrylate (BUMA). Experiments showed that the process works correctly whatever the surfactant used. In all cases, the surface initiation was obtained via the electrochemical reduction of nitrobenzenediazonium tetrafluoroborate salts. The resulting grafted copolymer (poly(nitrophenylene, vinylics)) was obtained and characterized by infrared and photoelectron spectroscopies.

1. Introduction

The modification of the surface of materials is a very important issue since a great part of their properties is expressed via their surfaces. It is thus the case for adhesive properties, wettability, decoration, protection against corrosion, or biocompatibilization, for instance. It is also the case in electronics, where patterning of surfaces with respect to conducting or insulating zones is crucial. Thus, a large scientific community is working on various methods of synthesis of organic, mineral, or composite layers to induce new properties for materials.

Two major routes can be highlighted for the organic modification of minerals: (i) The first is physisorption including for example painting, spin coating, vacuum evaporation, or the Langmuir–Blodgett technique. Generally, those coatings are poorly organized (except the Langmuir–Blodgett layers) and in all cases rather fragile, in particular, in their interfacial zone, where organics meets mineral materials. Their properties very often deteriorate with time but there is almost no limitation for choosing the couple substrate layer. (ii) The second is chemisorption, which creates actual chemical bonds between the organic matter and the mineral substrate and includes plasma polymerization, mono- and multilayers formation by self-assembly, and in situ surface polymerization. The former gives highly cross-linked structures whose thickness is generally close to 1 μm; self-assembled monolayers can be easily built, but are fragile and limited to a few substrate–molecule couples; the latter technique gives strongly adherent films and offers the possibility of controlling the grafting densities, the orientation of the organic chains, and the thickness of the organic films.[1]

Covalent attachment of polymer chains to the surface can be obtained by either "grafting to" or "grafting from" techniques. The "grafting to" method involves the bonding of a preformed end-functionalized polymer to reactive surface groups on the substrate. The "grafting from" technique involves the immobilization of initiators onto the substrate followed by in situ surface polymerization to generate the grafted polymer chains.[2] For better control of the molecular weight and thicknesses of the grafted polymers brushes, living radical, anionic, cationic, ring-opening metathesis polymerization (ROMP), atom-transfer radical polymerization (ATRP),[2] and cathodic electrografting[1] have been used in the "grafting from" scheme.

Cathodic electrografting of activated vinylic monomers on conducting surfaces proceeds thanks to an electroinitiation of polymerization starting from the surface, followed by a growth of the polymer chains, monomer by monomer. The reaction mechanism of the electrografting was in particular described by C. Bureau et al.[3–5] The growth of the grafted chains proceeds by purely chemical polymerization, i.e., independently of the polarization of the conducting surface, which gave place to the initial grafting. Thus, the layer thickness, ranging between 10 and 500 nm, is not controlled by the amount of charge injected in the system, as for the electrodeposition of metals or conducting polymers, but fully tuned by the characteristics of the monomer solution (type

* Corresponding author. Tel.: +33 1 69 08 21 11. Fax: +33 1 69 08 64 62. E-mail: guy.deniau@cea.fr.

(1) Palacin, S.; Bureau, C.; Charlier, J.; Deniau, G.; Mouanda, B.; Viel, P. *ChemPhysChem* **2004**, *5*, 1468–1481.
(2) Edmondson, S.; Osborne, V. L.; Huck, W. T. S. *Chem. Soc. Rev.* **2004**, *33*, 14–22.
(3) Bureau, C.; Deniau, G.; Viel, P.; Lécayon, G. *Macromolecules* **1997**, *30*, 333.
(4) Bureau, C.; Delhalle, J. *Surf. Anal.* **1999**, *6*, 159 and references therein.
(5) Bureau, C.; Deniau, G.; Viel, P.; Lécayon, G.; Delhalle, J. *J. Adhes.* **1996**, *58*, 101.

of monomer, concentration, solvent, salt, temperature, and possible side reactions). This growth is particularly sensitive to protons, and water traces, and more generally the acidic protons of protic solvents, were shown to be detrimental for the anionic growth of the grafted chains.[6]

The advantages of electrografting, which applies on any conducting and semiconductor substrates,[7−9] are as follows: process in one step at room temperature, clear spectroscopic evidence of the grafting[10] and very good control of the density of grafting and thickness of films as well as the great stability of the samples in use conditions (friction, corrosion, etc.). The inconveniences are related to anionic polymerization: the use of an anhydrous medium (although a small amount of water (≤500 ppm) in the organic solution does not inhibit the growth[11]) and a limited choice of vinylic monomers.

Controlled radical polymerization, especially atom-transfer radical polymerization (ATRP),[12] is the most used method to graft polymer chains of controlled molecular weight onto, e.g., silicon wafers, gold particles, and nonconductive substrates. The ATRP method offers a large choice of functional monomers and substrates leading to a variety of polymeric materials (from simple linear macromolecules to more sophisticated architectures such as star brush copolymers[13]). Surface-initiated ATRP[2] (SI-ATRP) allows developing new thermo-responsive systems,[14] semiconductor−polymer hybrids for the control of cell adhesion,[15] separation materials based on nanofilms of molecularly imprinted polymer brushes,[16] dispersible carbon nanotubes in common solvents,[17] etc. SI-ATRP can be performed using, e.g., initiator-functionalized silanes,[12] thiols,[18,19] and polyelectrolyte macroinitiators.[20] Recently, Chehimi and co-workers proposed ATRP initialization of vinyl monomers by electrografted brominated aryl species based on diazonium salts at the surface of iron.[21−23] The use of aryl diazonium salts

is indeed a simple and elegant way of modifying conducting substrates such as metals, semiconductors, and carbon. When halogenated functional groups are grafted to surfaces via the electrochemical reduction of diazonium salts, a platform can be obtained for the grafting of polymer brushes by ATRP from the surface. That latter method is anyway a two-step process, generally performed at high temperature (∼100 °C) and in organic solvents which makes industrial applications difficult.

The objective of our work is thus to graft organic polymer films on conducting surfaces in one step, at room temperature by using water as solvent. We thus combined cathodic electrografting and emulsion polymerization in a new process named: "surface electroinitiated emulsion polymerization" (SEEP). SEEP applies to all vinylic monomers, in water and at room temperature. Moreover, the resulting grafted polymer coatings are obtained in one short step (a few minutes).

We will show that applying cathodic potentials to an aqueous emulsion containing a diazonium salt, a vinylic monomer (soluble or not in water), and a surfactant leads to (1) the formation of a primer grafted layer, (2) the initiation of radical polymerization of the vinylic monomers within the emulsion, (3) the grafting of the growing macroradicals onto the primer layer to form the final coating. The first step is thus related to the "grafting from" scheme, while the second one behaves as the "grafting to" mechanism.

This work is a preliminary description of this process applied to various vinylic monomers like acrylic acid (AA, totally miscible in water), acrylonitrile (AN, maximum solubility ∼ 2 mol dm^{-3} in water), and butyl methacrylate (BUMA, very poorly soluble in water), which demonstrate that the water monomer solubility is not a restricting parameter. In the same way, several surfactants were used and demonstrate the versatility of the process. In all cases, the first grafting layer and the initiation were obtained via the electrochemical reduction of nitrobenzenediazonium tetrafluoroborate (NBD) salts.

2. Experimental Section

2.1. General Methods. The synthesis was carried out in a three-electrode electrochemical cell under argon bubbling. The experiments were conducted in deionized water. The tested surfactants were either anionic [tetraethylammonium *p*-toluenesulfonate (TEPTS Aldrich 97%) or sodium dodecyl sulfate (SDS Aldrich 98.5%)], cationic [trimethyl tetradecyl ammonium bromide (TTAB Aldrich 99%)], or neutral [poly oxyethylene 23 lauryl ether (POE23 or Brij 35 Aldrich)]. Three different monomers were used in this work: acrylonitrile (AN, Aldrich ≥99%), acrylic acid (AA, Aldrich 99%), and butyl methacrylate (BUMA, Aldrich 99%). 4-Nitrobenzenediazonium tetrafluoroborate (NBD, Aldrich 97%) was used as electrochemical initiator for the vinylic radical polymerization. All those reactants were used as received and, in particular, vinylic monomers were not distilled to remove the inhibitors.

The emulsions were prepared by mixing the surfactant and the monomer in water. Then, a small quantity of mineral acid (H_2SO_4 Aldrich 95%) was added to lower the pH down to 2 (because the diazonium salts are stable in water only if pH ≤ 2.5). Just before

(6) Bureau, C. *J. Electroanal. Chem.* **1999**, *479*, 43.
(7) Deniau, G.; Lécayon, G.; Viel, P.; Hennico, G.; Delhalle, J. *Langmuir* **1992**, *8*, 267−276.
(8) Defever, T.; Deniau, G.; Goux-Capes, L.; Barrau, S.; Mayne, M.; Bourgoin, J.-P.; Palacin, S. *J. Electroanal. Chem* **2006**, in press.
(9) (a) Charlier, J.; Ameur, S.; Bourgoin, J.-P.; Bureau, C.; Palacin, S. *Adv. Funct. Mater.* **2004**, *14*, 125−132. (b) Charlier, J.; Baraton, L.; Bureau, C.; Palacin, S. *ChemPhysChem* **2005**, *6*, 70−74.
(10) Deniau, G.; Azoulay, L.; Jégou, P.; Le, Chevallier, G.; Palacin, S. *Surf. Sci.* **2006**, *600*, 675−684.
(11) Bureau, C.; Gonzales, J.; Deniau, G. French Patent No. FR0311491, 2003-10-01.
(12) Matyaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.
(13) Matyaszewski, K.; Qin, S.; Boyce, J. R.; Shirvanyants, D.; Sheiko, S. S. *Macromolecules* **2003**, *36*, 1843.
(14) Perruchot, C.; Khan, M. A.; Kamitsi, A.; Armes, S. P.; von Werne, T.; Patten, T. E. *Langmuir* **2001**, *17*, 4479.
(15) Xu, F. J.; Zhong, S. P.; Yung, L. Y. L.; Tong, Y. W.; Kang, E. T.; Neoh, K. G. *Biomaterials* **2006**, *27*, 1236.
(16) Wei, X.; Li, X.; Husson, S. M. *Biomacromolecules* **2005**, *6*, 1113.
(17) Hong, C.-Y.; You, Y.-Z.; Wu, D.; Liu, Y.; Pan, C.-Y. *Macromolecules* **2005**, *38*, 2606.
(18) Jones, D. M.; Smith, J. R.; Huck, X. T. S.; Alexander, C. *Adv. Mater.* **2002**, *14*, 1130.
(19) Cai, Q. J.; Fu, G. D.; Zhu, F. R.; Kang, E.-T.; Neoh, K.-G. *Angew. Chem., Int. Ed.* **2005**, *44*, 1104.
(20) Chen, X.; Armes, S. P. *Adv. Mater.* **2003**, *15*, 1558.
(21) Matrab, T.; Chehimi, M. M.; Perruchot, C.; Adenier, A.; Guillez, A.; Save, M.; Charleux, B.; Cabet-Deliry, E.; Pinson, J. *Langmuir* **2005**, *21*, 4686.
(22) Matrab, T.; Chehimi, M. M.; Boudou, J. P.; Benedic, F.; Wang, J.; Naguib, N. N.; Carlisle, J. A. *Diamond Relat. Mater.* Available online on www.sciencedirect.com.
(23) Matrab, T.; Chehimi, M. M.; Pinson, J.; Slomkowski, S.; Basinska, T. *Surf. Interface Anal.* **2006**, *38*, 565.
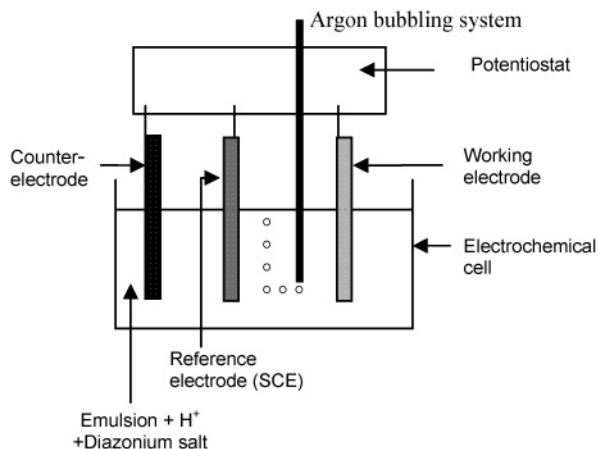
SEEP: Grafted Organic Coatings from Aqueous Solution

Chem. Mater., Vol. 18, No. 23, 2006 5423

Figure 1. Electrochemical setup scheme.

Figure 2. Cyclic voltammetry (ten cycles) registered on a stainless steel cathode with an aqueous solution containing 5.0 M AN, 1.46 M TEPTS, 1.8 mM NBD, pH = 2. 0, argon bubbling, scan rate 10 mV/s.

the electrochemical operation, the diazonium salt was added to the emulsion. In each studied case, the emulsion was immediately transferred in the electrolysis cell and stirring conditions were kept by continuous argon bubbling inside the cell. A scheme of the experimental setup is presented in Figure 1.

The working electrodes were stainless steel plates (8.0×1.0 cm^2) polished with 1 μm diamond powder and rinsed by sonication in acetone and ethanol. The auxiliary electrode was a glassy carbon foil of large surface area. The reference electrode was a saturated calomel electrode (SCE).

Cyclic voltammetry was used to perform the electrochemical polarization of the working electrode. All the potentials given in this work were with respect to the SCE. Electrochemical analysis was done using an EG&G potentiostat, model 273A, with automatic correction for ohmic drop. After polarization, the surfaces were rinsed (with H$_2$O and acetone and by sonication in DMF, 2 min) and studied ex situ by X-ray photoelectron spectroscopy (XPS) and by infrared reflection absorption spectroscopy (IRRAS).

2.2. Spectroscopic Studies. Photoemission studies were performed with a Vacuum Generator Escalab 210 spectrometer, using the monochromatized Al Kα line at 1486.6 eV for XPS. A fixed analyzer pass energy of 20 eV was used for C 1s core level scans. The photoelectron takeoff angle was 90° with respect to the sample plane, which provides an integrated sampling depth of approximately 15 nm for XPS. The energy scale of the instrument was calibrated by setting Au 4f$_{7/2}$ = 84.00 eV, Ag 3d$_{5/2}$ = 368.70 eV, Cu L$_3$M$_{4,5}$M$_{4,5}$ = 567.90 eV, and Cu 2p$_{3/2}$ = 932.65 eV.[24] During XPS measurements, those levels were not shifted in energy, thus suggesting that no charging phenomena occurred in these films.

Infrared spectra were obtained with an IFS-66 Bruker spectrometer, by reflection-absorption spectroscopy (IRRAS) at grazing angle (85°). The detector was a MCT working at liquid nitrogen temperature. The spectra were obtained after 256 scans at 2 cm^{-1} resolution and contribution from H$_2$O and CO$_2$ (gas) were subtracted.

3. Results and Discussion

Several pairs of monomer/surfactant were studied, keeping NBD as the radical initiator. To study in detail the polymerization process, two types of experiments were carried out. First, the effect of the monomer solubility was studied, using three monomers selected among a large range of water solubility. Indeed, it is well-known that polymerization in
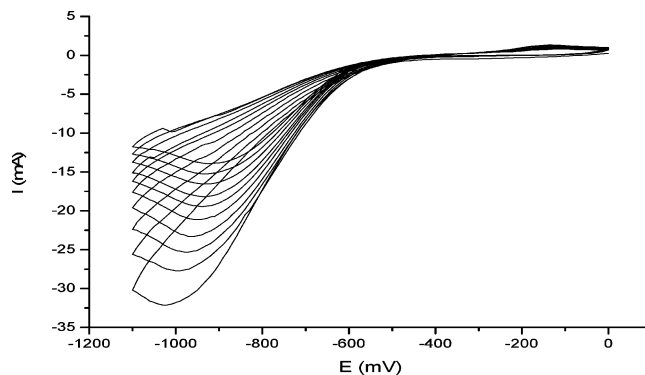
emulsion works better with insoluble monomers.[25] Second, three types of emulsifiers (anionic, cationic, and neutral) were tested with the same monomer.

3.1. Effect of the Vinylic Water Solubility. Three vinylics compounds were chosen: AN, which has medium to high solubility (2 mol dm^{-3}); BUMA, which has very low solubility in water ($\sim$10^{-2} mol dm^{-3}); AA, which is totally miscible in water.[26]

(1) The first case concerns the (AN; TEPTS) couple. The reaction medium was obtained by mixing deionized water with 5 mol dm^{-3} AN and 1.45 mol dm^{-3} TEPTS. After the formation of the emulsion, a small quantity of sulfuric acid was added to adjust the pH at 2, and finally, 1.8×10^{-3} mol dm^{-3} NBD was dissolved in the medium. The molecular structures of the reactants are shown in the Supporting Information (SupFig. 1).

Ten voltammetric cycles were carried out between the rest potential (ca. +0.05 V/SCE) and -1.10 V/SCE at a 10 mV s^{-1} scan rate. The resulting voltammogram is shown in Figure 2. The curve is dominated by the protons reduction regime starting near -0.6 V, followed by a reduction peak centered on -1.0 V. This peak decreases in intensity versus the number of cycles and could not be interpreted as NO$_2$ reduction, which starts after the protons reduction (nearby -1.3 to -1.5 V/SCE). This behavior is rather characteristic of an electrode passivation resulting from its progressive coating by a polymer film.[27] The coating is indeed not soluble in water and acts as an insulating barrier toward the redox reactions, leading to a vinylic reduction peak and a decrease of the electrolysis current observed for the successive cycles.

After the electrochemistry, the sample was rinsed (as described in the Experimental Section) and analyzed by IRRAS (Figure 3). The spectrum exhibits the major absorption bands of the expected polyAN (PAN): 2940 and 2870 cm^{-1} attributed to the stretching vibration of CH$_2$ groups, 2245 cm^{-1} for the stretching vibration of the nitrile group, and 1450 cm^{-1} for the bending of CH$_2$ group. The absorption bands at 1530 and 1350 cm^{-1} are attributed to the NO$_2$ group while the one at 1600 cm^{-1} signs the presence of phenyl

(24) Briggs, D.; Seah, M. P. *Practical Surface Analysis, 2nd ed. Vol. 1*; Wiley: New York, 1990.

(25) Schork, F. J.; Luo, Y.; Smulders, W.; Russum, J. P.; Butté, A.; Fontenot, K. *Adv. Polym. Sci.* **2005**, *175*, 129−255.

(26) Chai, X.-S.; Schork, F. J.; DeCinque, A.; Wilson, K. *Ind. Chem. Res.* **2005**, *44*, 5256−5258.

(27) Tanguy, J.; Deniau, G.; Augé, C.; Zalczer, G.; Lécayon, G. *J. Electroanal. Chem.* **1994**, *377*, 115−123.
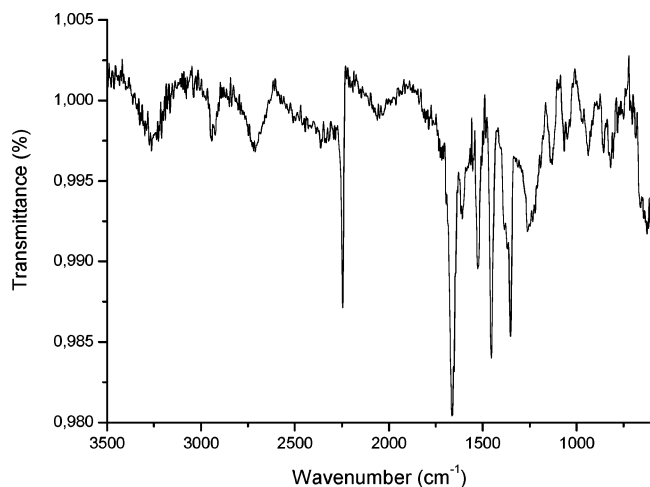
Figure 3. Infrared reflection-absorption spectrum of a metallic surface obtained after electrochemical operation with an AN/TEPTS emulsion.

groups. Thus this spectrum is characteristic of a poly-(nitrophenylene, acrylonitrile) copolymer.

We can obtain an estimation of the equivalent thickness of the two polymer components from the IRRAS spectrum (transmittance % of the CN group for PAN and NO_2 group for polynitrophenylene PNP) and from abacuses previously obtained by combining independent thickness measurements (ellipsometry, profilometry) and IRRAS analysis of pure PAN and PNP grafted films. In that case, we found ∼5 nm of PNP and ∼50 nm of PAN.

A XPS analysis carried out in the N 1s energy range (nearby 400 eV) reveals a peak centered on 400.5 eV, characteristic of a nitrile group. The spectrum is presented in Figure 4a. As XPS is only sensitive to the outer 15 nm of the coating (mean escape depth of electrons in a polymeric material), the lack of a line at 406.5 eV, characteristic of N 1s in the NO_2 group, demonstrates that pure PAN constitutes the outer 15 nm of the sample. Consequently, it is likely that the inner part of the coating should be richer in PNP than the outer part. We believe that a primer layer of almost pure PNP is first grafted, followed by chemical coupling with macroradicals formed within the emulsion.

To test this hypothesis, a thinner PAN sample was prepared with the same procedure by applying only five voltammetric cycles at a 20 mV s^{-1} scan rate. This sample was analyzed by XPS after the rinsing step. The N 1s

spectrum is presented in Figure 4b. Two lines are observed: a weak one centered on 406.5 eV was attributed to the polynitrophenylene (PNP) NO_2 groups, while the second one, centered on 400.5 eV, is characteristic of the nitrile PAN groups.

This spectrum is in good accordance with a sample constituted by a few nanometers of PNP coated by 10 nm thick PAN.

(2) The second case concerns the (BUMA; SDS) couple. The reaction medium was obtained by mixing deionized water with 0.69 mol dm^{-3} BUMA and 8 × 10^{-3} mol dm^{-3} SDS. The pH was then adjusted between 1.7 and 2.2, and finally, 2 × 10^{-3} mol dm^{-3} NBD was dissolved in the medium. The molecular structures of the reactants are shown in the Supporting Information (SupFig. 1).

Two voltammetric cycles were carried out between the rest potential (ca. +0.25 V/SCE) and −1.10 V/SCE at a 10 mV s^{-1} scan rate. The voltammogram is given in the Supporting Information (SupFig. 2). On this curve we can observe the reduction of the diazonium salt near −0.1 V, followed by the protons reduction regime starting around −0.6 V.

After the electrochemistry, the sample was first rinsed with water and acetone (without sonication), analyzed by IRRAS, then sonicated in DMF, and analyzed again by IRRAS. Figure 5 gives the spectra before (a) and after (b) sonication. The two spectra are similar, even in their transmittance intensities, clearly pointing out that no matter was extracted by the sonication. Such results point very likely to a coating chemically grafted onto the metallic surface, or less likely (in our opinion) to insoluble and strongly interpenetrated polymer networks. The spectrum exhibits the major absorption bands of the expected poly(butyl methacrylate) (PBUMA): 2980 and 2940 cm^{-1} attributed to the stretching vibration of CH_3 and CH_2 groups respectively, 1735 cm^{-1} for the stretching vibration of the ester carbonyl group, and 1150 cm^{-1} for the C−O−C stretching group. The absorption bands at 1530 and 1350 cm^{-1} are attributed to the NO_2 group while the one at 1600 cm^{-1} is a sign of the presence of phenyl groups. Thus, this spectrum presents all the features of a poly(nitrophenylene, butyl methacrylate) copolymer.

The thickness of the film was estimated as above from the IRRAS spectrum using the C=O and NO_2 signatures.
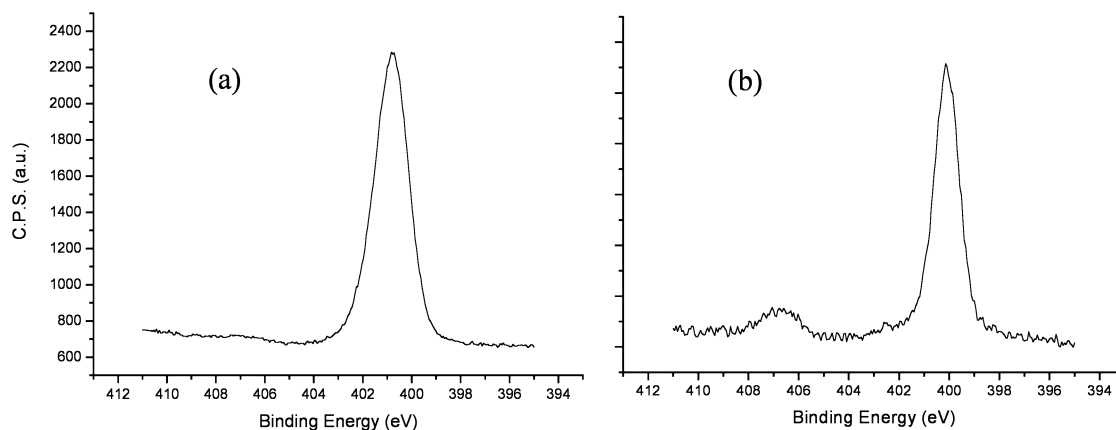

Figure 4. X-ray photoelectron spectra of N 1 s level of a metallic surface obtained after electrochemical operation with an AN/TEPTS emulsion: (a) thick PAN film; (b) thin PAN film.
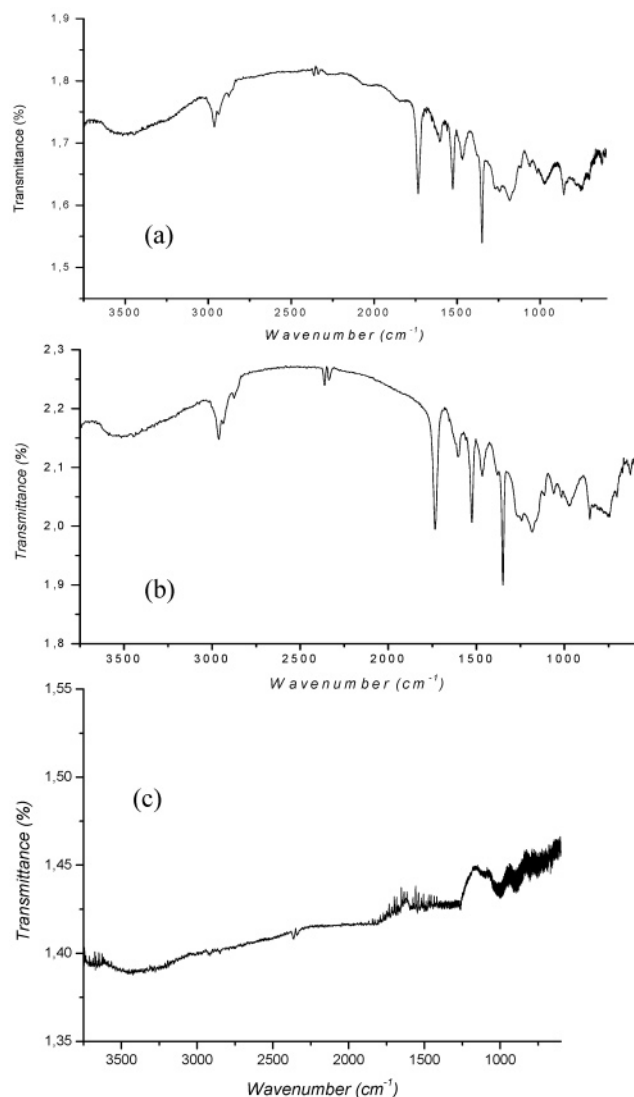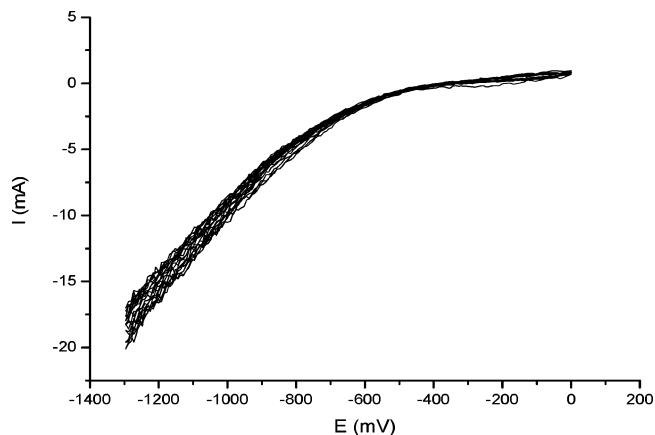
Figure 6. Cyclic voltammetry (ten cycles) registered on a stainless steel cathode with an aqueous solution containing 5.0 M AA and 1.8 mM NBD, pH = 1.7, argon bubbling, scan rate 10 mV/s.

the pH already being equal to 1.7. The molecular structures of the reactants are shown in the Supporting Information (SupFig. 1).

Ten voltammetric cycles were carried out between the rest potential (± 0.00 V/SCE) and -1.30 V/SCE at a 10 mV s^{-1} scan rate. The voltammogram is shown in Figure 6. The curve reflects only the protons reduction regime starting near -0.6 V. On this curve, the reduction peak previously described in the cases of BUMA and AN was not observed. Indeed, as poly(acrylic acid) (PAA) is soluble in water, grafted PAA is totally swelled by water and no insulating layer is formed on the electrode during the polymer film growth. Consequently, the curves were practically the same between the first and the tenth cycle. This result could also be interpreted as a protons transfer, by hopping from one COOH to the other, toward the electrode. After the electrochemical step, the sample was rinsed (as described in the Experimental Section) and analyzed by IRRAS (Supporting Information: SupFig. 3). The spectrum exhibits the major absorption bands of the expected PAA: a broadband at 3250 cm^{-1} attributed to the stretching vibration of OH groups, 1750 cm^{-1} for the stretching vibration of the C=O group, and 1450 cm^{-1} for the bending vibration of the CH$_2$ group. The PNP characteristic bands at 1530 and 1350 cm^{-1} attributed to the NO$_2$ group are not clearly seen on that spectrum. This suggests either a PNP signal dilution by a thick layer of PAA or a chemical transformation of the nitro group during the radical polymerization and leading to $-$NOHOR or NOROR groups (band at 1590 cm^{-1}).

The equivalent thickness of the PAA layer deduced from the IRRAS spectrum (transmittance % of the $-$C=O group) was about 150 nm.

We have shown that whatever the water solubility of vinylic monomers, the SEEP process leads to grafted thin copolymer layers onto the stainless steel surface. The copolymers are likely to be composed of a first thin layer of pure PNP, followed by a second one of almost pure poly-(vinylic) polymer.

3.2. Effect of the Surfactant. Three types of surfactant were studied by SEEP to graft the same polymer (PBUMA) onto the metallic surface. This study allows observing the versatility of the process toward the nature of the surfactant

Figure 5. Infrared reflection-absorption spectra of a stainless steel surface obtained after electrochemical operation with a BUMA/SDS emulsion. (a) Spectrum obtained before sonication in DMF (13% transmittance for the carbonyl group); (b) spectrum obtained after sonication in DMF (12.5% transmittance for the carbonyl group); (c) IRRAS spectrum obtained after electrochemical reduction without NBD.

The poly(nitrophenylene, BUMA) grafted film contains about 15 nm of PNP and about 100 nm of PBUMA.

A similar electrochemical experiment was carried out without the diazonium salt in the emulsion. In that case, H$^\bullet$ was the only compound able to initiate the radical polymerization of BUMA, but that initiator, contrary to NBD, does not give rise to any grafted film on the cathode. Logically, PBUMA was found in solution, but no polymer was observed on the metallic surface, as shown by the IRRAS spectrum of the resulting sample after the same rinsing procedure as above (Figure 5c). That experiment strongly suggests that the first PNP layer is necessary to graft the second polyvinyl one.

(3) The third example concerns the particular case of acrylic acid. This case is indeed particular because AA is totally miscible in water and as a consequence no surfactant was used to prepare the electrolytic medium. This one was obtained by mixing deionized water with 5 mol dm^{-3} AA and 1.8×10^{-3} mol dm^{-3} NBD. No sulfuric acid was added,

(anionic, cationic, or neutral). SDS has already been associated with BUMA (second example in section 3.1). Trimethyl tetradecyl ammonium bromide (TTAB) and poly oxyethylene-23 lauryl ether (POE23) were used as cationic and neutral surfactants, respectively.

Cationic Surfactant: (BUMA; TTAB) Couple. The reaction medium was obtained by mixing deionized water with 0.69 mol dm^{-3} BUMA and 8×10^{-3} mol dm^{-3} TTAB. After the formation of the emulsion, the pH was adjusted at 1.7, and finally 4×10^{-3} mol cm^{-3} NBD was dissolved in the medium. The molecular structures of the reactants are given in the Supporting Information (SupFig. 1).

Five voltammetric cycles were carried out between the rest potential (ca. +0.05 V/SCE) and −1.10 V/SCE at a 10 mV s^{-1} scan rate. The voltammogram (not presented here) shows the reduction of the diazonium cation near −0.3 V, followed by the protons reduction regime starting around −0.6 V. After the electrochemistry, the sample was rinsed (as described in the Experimental Section) and analyzed by IRRAS (not presented here). As in the SDS case, this spectrum presents all the features of a poly(nitrophenylene, butyl methacrylate) copolymer.

We obtained an estimation of the equivalent thicknesses of the two polymer components by using the previously described method. We found about 5 nm of PNP and about 20 nm of PBUMA. This very low thickness probably explains why no reduction peak was observed on the voltammogram in that case.

Neutral Surfactant: (BUMA; POE23) Couple. As previously (same concentrations and experimental setup), an emulsion was prepared. The molecular structures of the reactants are given in the Supporting Information (SupFig. 1).

One voltammetric cycle was carried out between the rest potential (ca. +0.30 V/SCE) and −1.10 V/SCE at a 10 mV s^{-1} scan rate. The voltammogram, given in the Supporting Information (SupFig. 4), shows the reduction of the diazonium cation near −0.35 V and the protons reduction regime followed by a reduction peak. As already explained, this latter peak is attributed to a temporary locking of the electronic transfer due to the organic film construction.

After the electrochemistry, the sample was rinsed (as described in the Experimental Section) and analyzed by IRRAS (not presented here). As above, this spectrum presents all the features of a poly(nitrophenylene, butyl methacrylate) copolymer. The deduced thicknesses were about 15 nm of PNP and about 100 nm of PBUMA.

Thus, whatever the surfactants type, the SEEP process delivers thin grafted copolymers onto metallic surfaces.

3.3. Proposed Mechanism. In this section, we describe one tentative mechanism for the copolymer coating synthesis, which fully explains our experimental results, in particular, the resistance to sonication of the two new interfaces (between metal and PNP and between PNP and polyvinyl).

Our results clearly show the following; (i) a copolymer containing both PNP and the vinylic polymer is electrografted from the aqueous emulsion, whatever the surfactant or the vinylic monomer used within the present study; (ii) the outer part of the copolymer coating is purely vinylic, without any

trace of PNP, but PNP can be detected when very thin vinylic polymer layers are obtained; (iii) no grafting occurs in the absence of NBD.

We thus propose the following mechanism to explain our results, where the SEEP process can be split in three steps:

(i) The first one is purely electrochemical and leads both to a first grafted layer of almost pure PNP and the formation of radicals within the emulsion (initiating the vinylic radical polymerization).

(ii) The second one is purely chemical: it is the vinylic radical polymerization, starting within the micelles (except for AA, of course).

(iii) In the third one, the growing vinylic radical chains interact chemically with the PNP primer layer to give the final copolymer coating.

This mechanism is detailed below taking as an example the (BUMA; SDS) couple electroinitiated by the NBD salt.

The cathodic current flow produces nitrophenyl radicals from NBD in the vicinity of the cathode (reaction 1), which immediately graft onto the electrode surface (reaction 2).

Reaction 1
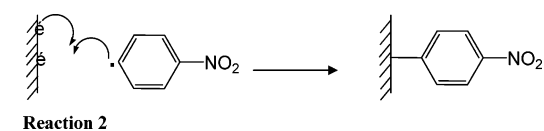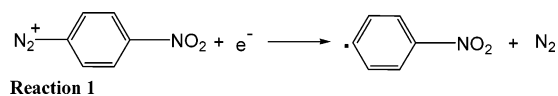
Reaction 2

The excess of nitrophenyl radicals can either contribute to the thickening of the grafted layer[28,29] as described by reactions 3 and 4 or initiate the BUMA radical polymerization within the micelles (reaction 5). This step is schematized in Figure 7.

Reaction 3

Reaction 4
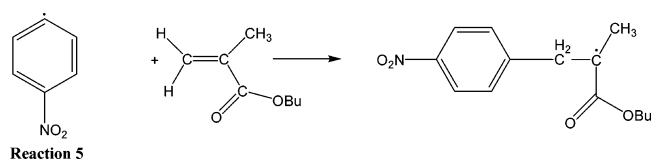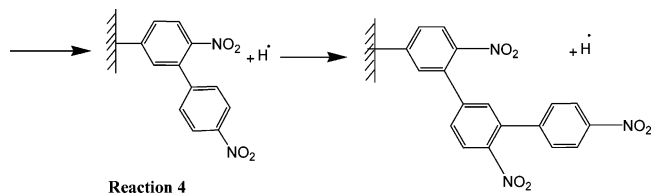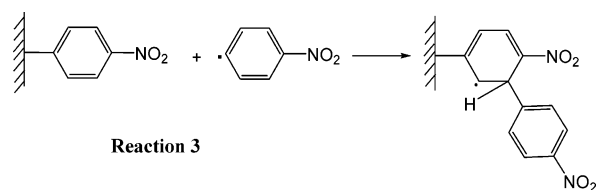
Reaction 5

As we are working in an acidic medium, we observe the protons reduction (reaction 6). One part of the hydrogen

(28) D'Amours, M.; Bélanger, D. *J. Phys. Chem.* **2003**, *107*, 4811−4817.
(29) Combellas, C.; Kanouffi, F.; Pinson, J.; Podvorica, F. *Langmuir* **2005**, *21*, 280−286.
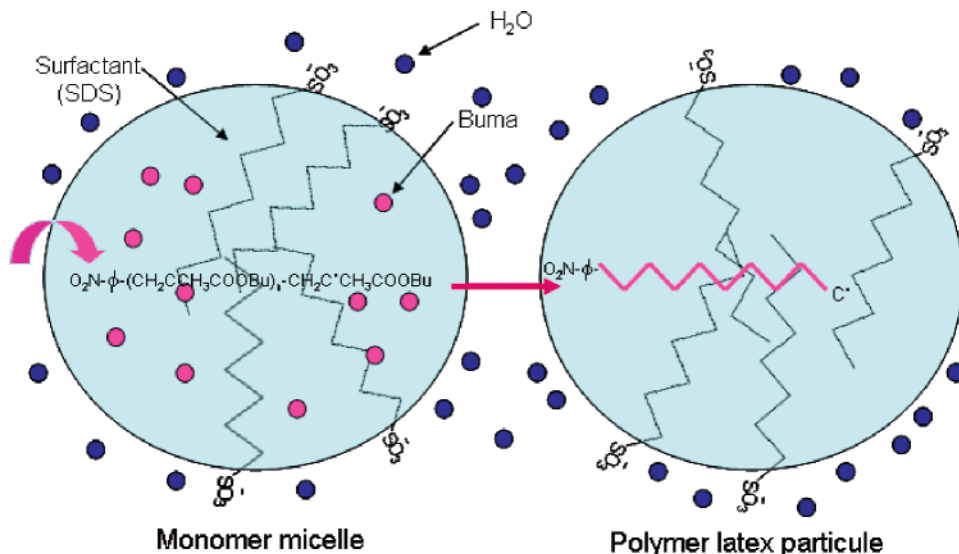
Figure 7. Scheme of emulsion polymerization step in the BUMA/SDS case.

radicals give gaseous hydrogen (reaction 7) and the other may participate in the initiation of the radical polymerization (reaction 8) followed by the propagation step, either in water phase for the very short chains, and then within the micelles (reaction 9). As the medium contains probably a large quantity of hydrogen radical, a termination reaction can take place and lead to the observed polymer formation in solution (reaction 10).

Reaction 6

Reaction 7

Reaction 8

Reaction 9
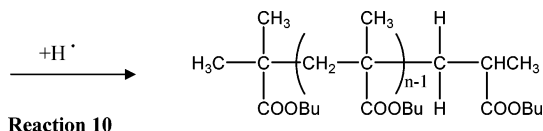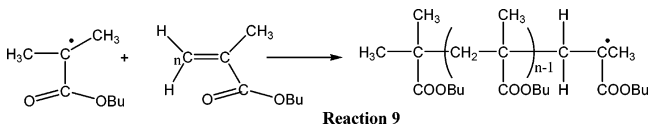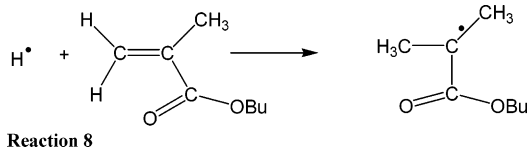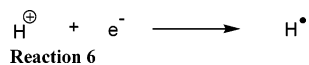
Reaction 10

At the end of the propagation reaction, macroradicals (initiated with either H$^\bullet$ or NO$_2$−C$_6$H$_4^\bullet$ radicals) react with the previously grafted polynitrophenylene layer (reactions 11 and 12) to form the final grafted copolymer as schematized in Figure 8.

The proposed mechanism is supported by the absence of PNP signature on the outer part of the coating when the total thickness exceeds the average detection length of XPS, and
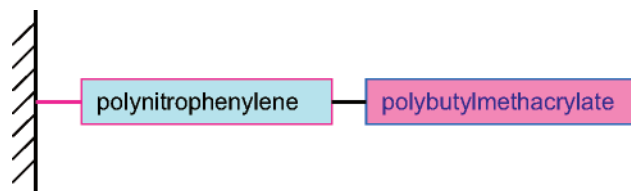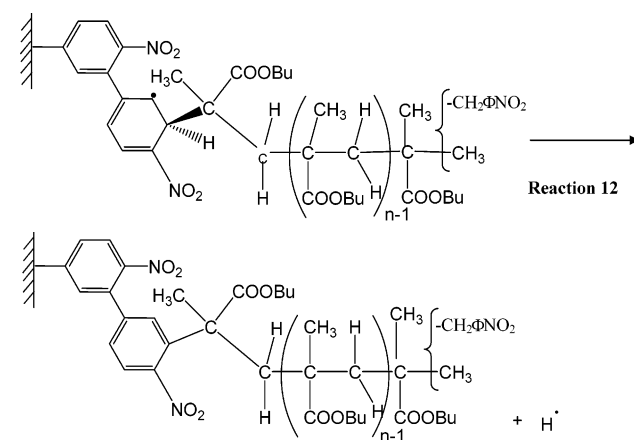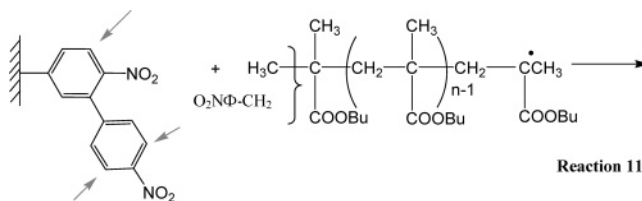

Figure 8. Scheme of the grafted copolymer obtained by SEEP.

the already described mechanism for the thickening of PNP layers.[28,30]

Reaction 11

Reaction 12

4. Concluding Remarks

Synthesis of grafted copolymers on a metallic surface was studied by SEEP including several vinylic compounds and surfactants. In each case, SEEP leads to a stable grafted organic coating. SEEP is a one-step process characterized by the mixing of "grafting to" and "grafting from" techniques

(30) Charlier, J.; Laudé, M.; Palacin, S. *ChemPhysChem,* submitted.

and consequently offers the advantages of both techniques. Using SEEP allows us to synthesize grafted organic polymers coatings on conductive or semiconducting surfaces, with a large range of thicknesses and chemical composition, thus opening a whole range of potential applications. As an example, SEEP could be used for the biocompatibilization of cardiovascular stents, grafting the biocompatible PBUMA

from aqueous precursor solutions. Indeed, SEEP directly competes with already described stent coatings, which require several steps and a very toxic (mutagen) solvent (DMF).[31]

Supporting Information Available: Chemical structures of molecules used in this study, cyclic voltammetry registered on stainless steel cathodes with (BUMA, SDS) and (BUMA, POE23) couples, and an IRRAS spectrum of PAA. This material is available free of charge via the Internet at http://pubs.acs.org.

CM060739T

(31) Jérôme, C.; Aqil, A.; Voccia, S.; Labaye, D. E.; Maquet, V.; Gautier, S.; Bertrand, O. F.; Jérôme, R. *J. Biomed. Mater. Sci.* **2006**, *76A*, 3, 521−529.