

Grafting Polymers on Surfaces: A New Powerful and Versatile Diazonium Salt-Based One-Step Process in Aqueous Media

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Covalent surface modification of conductive, semiconductive, and insulating substrates with thin organic polymers films induced by redox activation of aryl diazonium salts in the presence of vinyl monomers has been investigated in acidic aqueous media. This new process, called diazonium-induced anchoring process (DIAP), is an efficient technique to impart covalent adhesion of polyvinyl coatings onto raw inorganic or organic surfaces without any conductivity requirement. Typically, aryl diazonium salts are reduced with iron powder to give surface-active aryl radicals leading (i) to the formation of a grafted polyphenylene-like film on the substrate surface and (ii) to the initiation of the radical polymerization of the vinylic monomer in solution. The resulting radical-terminated macromolecular chains formed in solution are then able to react with the polyphenylene primer layer to form a very homogeneous thin organic film on the surface. The final organic thin coating is strongly grafted on materials surfaces, as evidenced by its persistence after a long ultrasonic treatment in a good solvent of the polymer. We speculate this process is supported by the large concentration of aryl and hydrogen radicals formed when iron powder is added in the acidic aqueous solution. The thickness of the polymer film can be controlled as a function of time, typically a few minutes, and was measured between 10 and several hundred nanometers. Infrared reflection–absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), and contact angle measurements were used to characterize the surface modification of metals, glass, carbon nanotubes, or polytetrafluoroethylene (PTFE). This very simple and efficient grafting method provides a powerful tool for the covalent coating of organic or inorganic surfaces possessing complex geometrical shapes.

1. Introduction

The grafting of polymer films on various surfaces (metal, glasses, etc.) has attracted considerable attention in the past two decades in many fields of application. In fact, the surface modification of materials reveals a crucial issue since a great part of their properties is expressed via the phase that resides at the boundary between the substrate and the outer environment. For instance, adhesive properties, wettability, protection against corrosion, or biocompatibilization requires a good control of surfaces modification. Thus, many research teams are working on various methods in order to synthesize organic or composite layers and also induce new properties for materials.

The major problem to be tackled is however the usually weak and short-term adhesion between organic polymers and materials of a completely different nature. Many routes included in “physisorption techniques” such as painting, spin coating, vacuum evaporation, or the Langmuir–Blodgett technique lead to rather fragile coatings. The most desirable situation is then by far the covalent bonding of the thin organic layers generally induced by “chemisorption techniques” such as plasma polymerization,^{1,2} self-assembled

mono- and multilayers,^{3,4} and cathodic^{5,6} or anodic^{7,8} electropolymerization. The former gives highly cross-linked structures whose thickness is generally close to 1 μm ; self-assembled monolayers are known to be fragile and limited to few substrate–molecule couples;^{3,4,9} cathodic electropolymerization initiated from conductive surface gives strongly adherent films¹⁰ and offers the possibility of controlling the grafting densities, the orientation of the organic chains, and the thickness of organic films but remains restricted to (meth)acrylic derivatives on conductive materials.^{11,12} Recent developments have been issued to overcome these limitations of the electrografting technique such as the combination of

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electropolymerization with radical polymerization to broaden the nature and the properties of organic coatings. In this way, covalent attachment of polymer to the surface can be obtained by “grafting from” techniques involving the immobilization of initiators onto the substrate followed by in situ surface polymerization. Atom-transfer radical polymerization (ATRP),¹³ ring-opening metathesis (ROMP),¹⁴ or nitroxide-mediated polymerization (NMP)¹⁴ has been used to control the molecular weight and the thickness of grafted polymer brushes. Nevertheless, the first layer remains an electrografted primer layer and limits this approach to conductive or semiconductive surfaces. Alternatively, the “grafting to” approach involves the bonding of a preformed end-functionalized polymer to reactive surface groups on the substrate. For instance, plasma treatment can introduce active species on the surface of materials, followed by the polymerization of monomers. The limitation on this grafting-to method is that plasma treatment is expensive and has found only limited applications, even though the surface properties can be changed in a few minutes. Despite the large scale of coating processes listed here, to our knowledge, no one-step, universal method for the covalent grafting of polymer on raw conductive, semiconductive, or insulator surfaces under mild conditions is yet available.

The objective of the work presented in this paper is grafting organic polymer films onto raw surfaces, conductive or not, with a simple one-step reaction, at room temperature and open air using water as solvent and without any specific apparatus. We will show that a simple spontaneous redox activation of aryl diazonium salts with iron powder as reducing agent in presence of vinylic monomers in aqueous solution leads to very homogeneous thin polymer films strongly grafted on various surfaces. On the basis of literature, electrochemical reduction of diazonium^{15–20} salts is an attractive method which has been applied to carbon,^{21–23} metals,^{24–26} and semiconductors.^{27–29} The mechanism of the electrografting of aryl diazonium salts has been extensively

reported in the literature.^{30–33} It involves a reductive electron transfer to the diazonium salt concerted with the cleavage of dinitrogen³⁴ leading to the generation of aryl radicals, followed by the binding of those radicals to the surface via carbon–carbon or carbon–metal covalent bonds.^{26,35} Recent works have shown the spontaneous surface reactivity of aryl diazonium salts toward reducing metals such as iron,^{36,37} copper,³⁷ or zinc,³⁷ leading to the spontaneous formation of a polyphenylene-like layer at the metal surface. On the basis of this observation, we will show how this heterogeneous electron transfer can be used as an homogeneous active radical generator in aqueous media. In addition, with the already described mechanism of the aryl diazonium electrografting, we will first demonstrate that aryl radicals formed by redox activation at a reducing metal surface are not only able to covalently bond to this surface but equally to any surfaces present in the reaction media. In the second hand, we will describe the formation of copolymer films obtained by adding a vinylic monomer to this solution.

A mechanism of DIAP could be proposed as follows: (1) generation of highly concentrated aryl radicals after redox activation of the diazonium salt by iron particles, (2) formation of a polyphenylene-like primer grafted layer, (3) at the same time, initiation of the radical polymerization of the vinylic monomer in solution, and (4) trapping of the growing macroradicals onto the aromatic rings of the primer layer to form the final coating. A detailed mechanism will be proposed in the discussion.

This work is a preliminary description of this process applied to various vinylic monomers like acrylic acid (AA), hydroxyethyl methacrylate (HEMA), acrylonitrile (AN), or butyl methacrylate (BUMA) and various substrates like metals (Au, Zn, Ti, stainless steel), glasses, carbon (nanotubes), or PTFE. In all cases, the first grafting layer and the initiation were obtained via the redox activation of various aryl diazonium salts, used as received or synthesized in situ from the corresponding aryl amine, by iron powder. The thickness of the resulting polymer films was measured between 20 and 300 nm in the range of the studied reaction time (from 5 to 30 min). By this way, we proposed for the first time a powerful and versatile polymer grafting process which can be applied to numerous materials without any conductivity or pretreatment requirements.

2. Experimental Section

2.1. General Methods. The syntheses were carried at open air and room temperature in a simple flask. The experiments were

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conducted in acidic deionized water ($\text{pH} \leq 2$, because the diazonium salts are stable in water only if $\text{pH} \leq 2.5$). Four different monomers were used in this work: acrylonitrile (AN, Aldrich $\geq 99\%$), acrylic acid (AA, Aldrich $\geq 99\%$), butyl methacrylate (BUMA, Aldrich $\geq 99\%$), and hydroxyethyl methacrylate (HEMA, Aldrich $\geq 99\%$). Three aryl diazonium salts were used as initiators for the vinyl radical polymerization: 4-nitrobenzenediazonium tetrafluoroborate (NBD, Aldrich, 97%) used as received; 4-aminobenzyl diazonium chloride (ABD) and 4-aminophenyldiazonium chloride (APD) both synthesized in situ from the corresponding aryl diamine and sodium nitrite (NaNO_2) in 0.5 M HCl solution, as already described.³⁸ All those reactants were used as received, and in particular, vinylic monomers were not distilled to remove commercial inhibitors. Iron particles were purchased from VWR Prolabo (98%, mean particle size 45–100 μm).

2.2. Grafting of Aryl Diazonium Salts on Au. In a typical experiment, commercial NBD (59.2 mg) was dissolved in 5 mL of 0.5 M HCl. For ABD and APD, the diazonium salts were synthesized in situ from the corresponding aryl diamine (2.5 mL, 0.1 M in 0.5 M HCl) by reaction with 1 equiv of sodium nitrite NaNO_2 (2.5 mL, 0.1 M). Then, a gold plate was introduced, and a small amount of iron powder (150 mg, 10 equiv vs NBD) was added. Instantaneously, small bubbles were observed in the flask corresponding to dihydrogen and dinitrogen evolution, as iron reduced protons and diazonium salts in solution. After the desired reaction time, the surface was rinsed (with DMF and acetone and by sonication in DMF, 3 min, 120 W) and studied ex situ by XPS and IRRAS.

2.3. Grafting of Polymers on Surfaces. First, the aryl diazonium salt was dissolved in acidic aqueous solution to obtained 5 mL at 5×10^{-2} M as described for the grafting of aryl diazonium salts on Au surface. Then, the monomer (AN, AA, or HEMA, 1 mL, 30 equiv) was introduced into the solution. For BUMA (insoluble in water), the acidic mixture was sonicated for 15 min to obtained a good dispersion of the insoluble organic phase prior to use. Then, the substrate (metal, glass, multiwall carbon nanotubes brushes, or PTFE) was introduced into the flask, and a small amount of iron powder (150 mg) was added. After the desired reaction time, the surfaces were rinsed (with DMF and acetone and by sonication in DMF, 5 min) and studied ex situ by XPS, IRRAS, contact angle measurement, and electron microscopy. The thickness of the resulting polymer films was measured with a mechanical profilometer Dektak 30 ST using a lateral resolution of 50 μm .

2.4. Spectroscopic Studies. Photoemission studies were performed with a Vacuum Generator Escalab 210 spectrometer, using the monochromatized Al K α 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 ~ 15 nm for XPS. The energy scale of the instrument was calibrated by setting Au 4f_{7/2} = 84.00 eV. 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 a Vertex 70 spectrometer by ATR-IR spectroscopy. The detector was a MCT working at liquid nitrogen temperature. The spectra were obtained after 256 scans at 2 cm^{-1} resolution, and the contributions from H₂O and CO₂ (gas) were subtracted.

2.5. Microscopy Studies. The transmission electron microscopy (TEM) studies were conducted using a Philips CM12 transmission electron microscope operating at 120 keV. Samples were prepared by a dropwise addition of the suspended carbon nanotubes in isopropanol onto a copper mesh covered with holey carbon film.

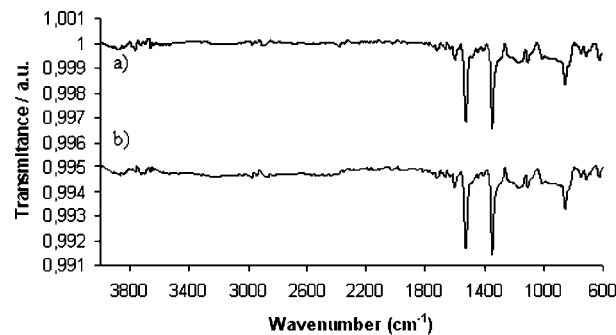


Figure 1. Infrared reflection-absorption spectrum of a polynitrophenylene (PNP) film grafted on Au with the DIAP process (a) before and (b) after a 3 min sonication time in DMF. The curves were shifted vertically for sake of clarity.

The scanning electron microscope (SEM) studies were conducted using a Léo-Gémini field emission gun microscope.

3. Results and Discussion

First, the iron redox activation of various aryl diazonium salts (NBD, ABD, or APD) and the formation of the primer grafted polyphenylene-like layer were studied on model Au surface in order to confirm the covalent bonding of the organic film. Then, several pairs (diazonium/monomer) were studied on Au to compare the activities of those systems. Finally, a large range of surfaces have been tested using the APD/HEMA couple as a reference system. A mechanism of the coating process will then be proposed on the basis of these results and recent work published by our research team.³⁹

3.1. Grafting of Aryl Diazonium on Au. Three aryl diazonium salts were chosen: NBD was used as received from Aldrich; APD and ABD were synthesized in situ from the corresponding aryl diamine in aqueous HCl solution.

The first case concerns the NBD grafting on Au surface. The Au substrate was immersed into the aryl diazonium solution, and iron powder was added. After 15 min the Au surface was removed and rinsed several times with DMF and acetone before a 3 min sonication time in DMF.

The resulting polynitrophenylene (PNP) film was analyzed by IRRAS (Figure 1) in two steps, before and after the ultrasonic treatment. The spectra exhibit the major absorption bands of the expected PNP: 1530 and 1350 cm^{-1} were attributed to the NO₂ group while the one at 1600 cm^{-1} signals the presence of phenyl groups. Thus, this spectrum is characteristic of a polynitrophenylene film. The insignificant variation of the intensity of the NO₂ peaks before and after sonication reveals a strong covalent bonding between PNP and the Au surface, together with the efficiency of the rinsing steps.

The second example concerns APD and ABD grafting on Au. APD and ABD were synthesized in situ from the corresponding aryl diamine. After the DIAP step, the resulting polyaminophenylene (PAP) and polyaminobenzyl (PAB) films were analyzed by IRRAS (see Supporting Information). The spectra show the absorption bands at 1619

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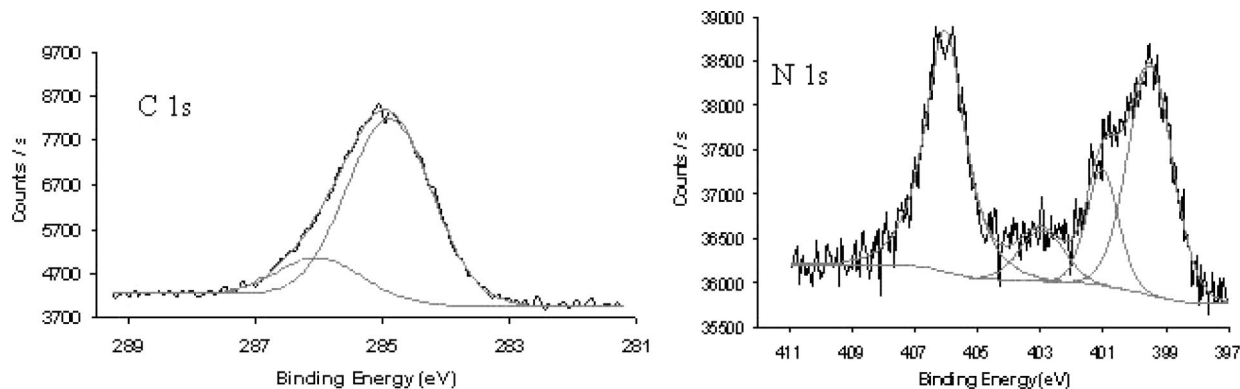


Figure 2. C 1s and N 1s X-ray photoelectron spectra of a PNP film grafted on Au with the DIAP process.

and 1602 cm^{-1} (large) characteristic of the NH_2 groups in PAP and PAB, respectively. In these two cases, the phenyl absorption band at 1600 cm^{-1} is observed, and the intensity of the absorption bands remains unchanged even after sonication, characterizing a strong covalent bonding between the organic layer and the substrate. These three aryl diazonium salts seem to have a similar surface reactivity according to the measured thickness of the resulting organic layer, close to 20 nm.

To confirm the attachment of the polyphenylene-like films, the surfaces were examined by XPS. Figure 2 displays XPS spectra recorded on PNP polyphenylene-like layers. The C 1s core level shows a peak centered at 285 eV, which mainly corresponds to aromatic carbons of the phenyls groups. However, numerical adjustment of this peak leads to a high binding energy component at 286 eV, indicating carbons carrying nitro groups ($-\text{NO}_2$).

Analysis of the N 1s core level gives two perfectly separated peaks centered at 400 and 406 eV, together with a small peak near 403 eV. The peak at high binding energy obviously corresponds to the nitro groups. An analysis based on the calculation of the atomic concentrations of the total carbon compared to total nitrogen gives roughly a 6C for 1N stoichiometry. Thus, a part of nitro groups has to be converted in a new chemical form expressed by the 400–403 eV peaks. The detailed analysis of the broad peak around 400 eV shows that it is clearly composed of two components of unequal proportions at 399.4 and 400.9 eV. According to the literature, the former can be attributed to a mixture of amino groups ($-\text{NH}_2$) and azo groups ($\text{N}=\text{N}$). Indeed, as originally proposed by McCreery⁴⁰ and more recently by Bélanger⁴¹ and Pinson⁴² in chemical and electrochemical grafting of diazonium salts, azo bridges are actually inserted in the molecular structure of the polyphenylene-like grafted films, arising from an alternate electroreduction pathway that does not lead to dinitrogen evolution. We assume a similar process occurs here to account for part of the 399.7 eV peak. In the same time, it is possible to assign part of that same peak to the presence of amines arising from the reduction

products of nitro groups in acidic aqueous medium and in the presence of reducers.^{31,43} Hence, the peak near 403 eV can be attributed to ammonium groups ($-\text{NH}_3^+$) resulting from protonation of those amino groups by the acidic medium.

The second component of that broad peak is generally not observed upon (electro)grafting of NBD. However, the recorded energy (close to 401 eV) is fully compatible with nitroso moieties, which could result from incomplete reduction of the nitro group. A similar assignment was postulated by Belanger for electrochemically reduced NBD films⁴⁴ and confirmed on nitroso-bearing thin organic films.^{45,46} Hence, both XPS peaks at 406 and 401 eV are specific of the NBD reagent.

The XPS spectra recorded on the ABD and APD grafted layers (see Supporting Information) exhibit similar features (except for the 406 and 401 eV peaks, of course), indicating the mechanism is the same. It is noteworthy that none of those XPS spectra exhibit any trace of iron remaining within the grafted films.

The first step of this study clearly shows that aryl diazonium salts are able to form a very thin and strongly grafted polyphenylene-like layer on Au substrate after iron redox activation in aqueous media. Similar experiments performed on nickel, stainless steel, and glass confirm that result (see Supporting Information for examples). These results are consistent both with the numerous studies on the electro-induced grafting of aryl diazonium salts leading to polyphenylene-like multilayers on the electrodes and with the spontaneous grafting of aryl diazonium salts on reducing metallic surfaces.^{36,37} However, our results show that the covalent grafting occurs also on any surface available in the reaction medium, and not only on the reducing metal surface. That indicates that the production of aryl radicals at the surface of iron particles is efficient enough to provide active phenyl radicals able to link with other surfaces.

These first results confirm the reactivity of aryl radicals formed at the iron surface toward the surfaces immersed in the solution. The second step of our study will focus on the

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Table 1. Grafting of Polymers on Au

entry	couple diazonium/monomer	time (min)	IR absorption band (cm ⁻¹)
1	NBD/HEMA	15	νNO_2 (1530), $\nu\text{C}=\text{O}$ (1729)
2	NBD/AA	15	νNO_2 (1530), $\nu\text{C}=\text{O}$ (1726)
3	APD/HEMA	15	νNH_2 (1619), $\nu\text{C}=\text{O}$ (1729)
4	APD/AN	15	νNH_2 (1619), νCN (2240)
5	APD/BUMA	15	νNH_2 (1619), $\nu\text{C}=\text{O}$ (1735)
6	ABD/HEMA	15	νNH_2 (1602), $\nu\text{C}=\text{O}$ (1729)
7	ABD/AA	15	νNH_2 (1602), $\nu\text{C}=\text{O}$ (1726)

formation of polymer coating on Au surface by adding vinylic monomers into the system.

3.2. Grafting of PAN, PAA, PHEMA, and PBUMA on Au. Similar experiments were carried out using the three aryl diazonium salts coupled with several monomers such as AN, AA, HEMA, and BUMA in order to form the corresponding polymer films on Au surface. Table 1 reports the results obtained with the following couples: NBD/HEMA, NBD/AA, APD/HEMA, APD/AN, APD/BUMA, ABD/HEMA, and ABD/AA. In all cases, the organic film obtained was analyzed by IRRAS after a 3 min sonication time in DMF.

The polyphenylene-like layer can be observed through the NO_2 and NH_2 absorption bands near 1530 cm^{-1} for NO_2 (entries 1, 2), 1619 cm^{-1} for Ar-NH_2 (entries 1–3), and centered at 1602 cm^{-1} for $\text{Ar-CH}_2\text{-NH}_2$ (entries 6, 7 large bands). The absorption bands of $\text{C}=\text{O}$ for HEMA, BUMA, and AA near 1700 cm^{-1} and CN for AN near 2240 cm^{-1} confirm the presence of the vinylic polymer film.

XPS analysis was carried out for APD/HEMA (entry 3) copolymer taken as a reference couple to confirm the nature of the grafted film (Figure 3). The peak C 1s is clearly characteristic of a polyacrylate film with the main peak at 285 eV corresponding to the polymethylene skeleton of the polymer. The secondary peaks at 286 and 288 eV correspond respectively to the C–O and C=O bonds. The double structure of the O 1s peak (not shown) confirms the presence of the ester group. The atomic concentrations are in agreement with the molecular structure of PHEMA.

The very low intensity of the N 1s peak (ratio C/N close to 150; Figure 3, inset) attests that the diazonium salt reduction products are in small proportion compared to the vinylic polymer. This is consistent with the location of the polyphenylene-like layer (as a primer layer directly in contact with the metal surface) but could also be compatible with the presence of isolated APD reduction products within the PHEMA chain structure.

In addition, a survey of the polymer formation vs time has been carried out for the APD/HEMA couple. Figure 4 shows the IRRAS spectra of the film after 1, 3, 5, 10, and 15 min reaction time. The absorption bands of the carbonyl group at 1729 cm^{-1} increased with reaction time, from 0.8% for 1 min to 9% after 15 min, and the thickness of the corresponding polymer films was measured between 20 and 300 nm. This observation reveals a good control of the film thickness which can be easily tuned as a function of time.

The role of the polyphenylene-like primer layer was evidenced by the following experiments. First, the same grafting procedure was used with HEMA alone (i.e., without diazonium salt). In that case, only hydrogen radicals coming

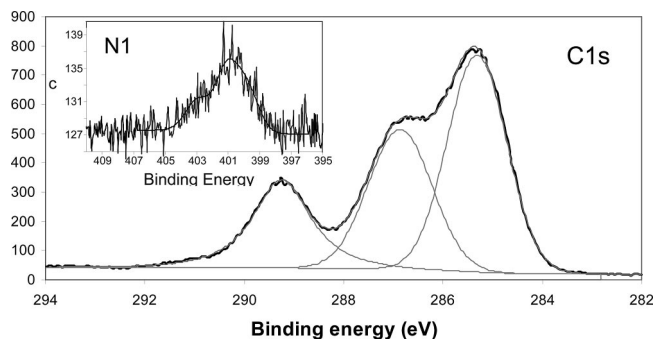


Figure 3. X-ray photoelectron spectra of C 1s levels and N 1s levels (inset) of an Au surface after DIAP grafting with the APD/HEMA couple.

from the reduction of protons by iron could initiate the polymerization of HEMA in solution. After a 15 min reaction time no film was observed on the Au surface according to the IRRAS analysis (Figure 5a). In a second experiment, a PAP layer was first grafted on Au surface using the procedure described in section 3.1. Then, the surface was washed and immersed into an acidic solution of HEMA (without diazonium salt) and iron was added. After 15 min, a very thin layer of poly(HEMA) was observed on the Au sample surface, as evidenced by the 1.2% absorbance recorded on the IRRAS C=O band (Figure 5b). Again, only hydrogen radicals coming from the reduction of protons by iron could initiate the polymerization of HEMA in solution. But in that latter case, the resulting macroradicals were able to graft on the primer polyphenylene-like layer. These experiments prove that the polyphenylene-like primer layer is essential for the grafting of macroradicals formed in solution and act as an efficient radical trapping agent. Moreover, the very thin HEMA film obtained without diazonium salt shows that aromatic radicals originating from the reduction of the diazonium salt are crucial for the efficient growth of the polymer film. Indeed, the same experiment performed in the presence of APD gives a 9% absorbance for the C=O peak in the same conditions (Figure 5c). Thus, we assume that aromatic rings originating from the reduction of the diazonium salt are actually embedded in the polymer matrix and act as anchoring points for the vinylic macroradical chains formed in solution.

3.3. Metals, Glasses, and Carbon Nanotubes One-Step Functionalization. In the same way, many conductive (Zn, Ti, stainless steel), semiconductive (carbon nanotubes), and insulating (glass) surfaces were functionalized with the APD/HEMA reference couple. In all cases, the substrate was rinsed after reaction several times in water, DMF, and acetone before being kept under ultrasound for 3 min in DMF. The resulting surfaces were analyzed by IRRAS to confirm the formation of the grafted organic layer. In addition, carbon nanotubes were analyzed by TEM and SEM in order to visualize directly the polymer film grafted along the nanotube sidewall. Contact angle measurement was carried out for glass substrates to show the hydrophilic modification of the surface.

The same procedure previously described was used for conductive surfaces, e.g., nickel, titanium, and stainless steel. After 15 min reaction time, the substrate was rinsed and a thin homogeneous film could be observed to the naked eye.

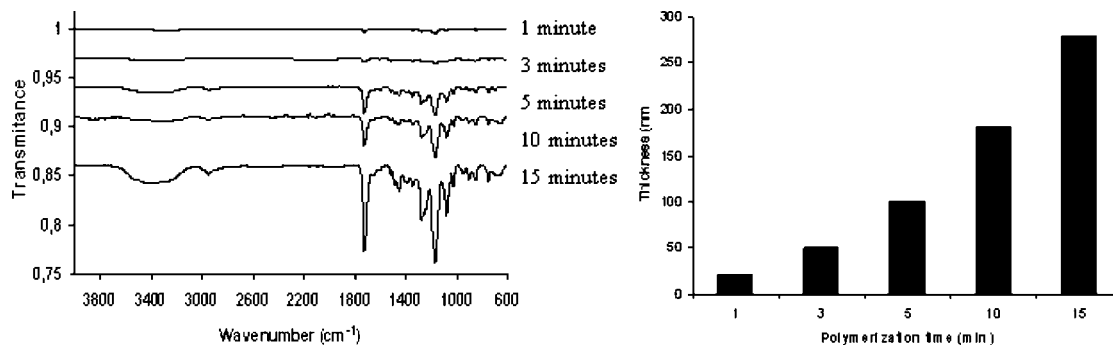


Figure 4. Infrared reflection-absorption spectra of DIAP APD/HEMA grafting on Au surface as a function of time. The histogram presents the thickness measured by profilometry as a function of polymerization time.

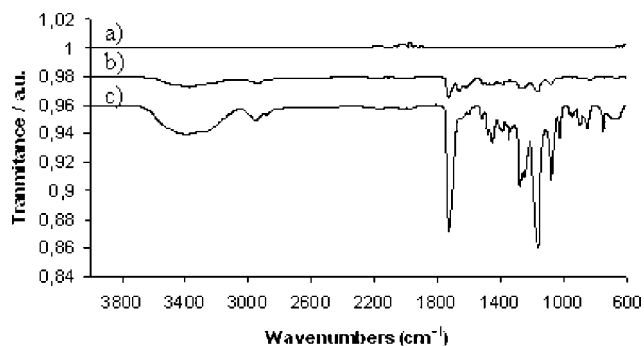


Figure 5. Infrared reflection-absorption spectra of Au plates (a) after treatment with HEMA/Fe/H⁺, (b) after the DIAP grafting of a pristine PAP layer and then treatment with HEMA/Fe/H⁺, and (c) after DIAP grafting with APD/HEMA couple (15 min reaction time) (from top to bottom).

In all cases, the IRRAS absorption bands of the HEMA ester carbonyl group at 1729 cm⁻¹ confirm the presence of the polymer network as already observed on Au surface. The NH₂ band at 1619 cm⁻¹ remains very difficult to observe due to the small amount of aromatic ring embedded in the polymer film (see Supporting Information for IRRAS analysis).

Multiwall carbon nanotubes (MWNTs) used in this study were obtained by aerosol-assisted catalytic chemical vapor deposition on Si substrate.⁴⁷ We directly used the resulting MWNT brushes as substrates for DIAP. The MWNTs brushes were analyzed by TEM and SEM after a 10 min reaction time. Scanning electron microscopy (SEM) images (Figure 6) of control and grafted MWNTs revealed that the polymer film is very homogeneously grafted to the nanotube sidewalls. The polymer can be observed from the top to the bottom of the substrate showing that both diazonium salts and vinylic monomers can penetrate easily inside the MWNT brush. Transmission electron microscopy (TEM) analysis was performed on MWNTs after a strong ultrasonic treatment of the MWNT brush in ethanol to obtain a good dispersion. Figure 7 shows the MWNT structure tightly embedded in the PHEMA matrix, even after a long sonication time in a good solvent of the polymer. This observation confirms the covalent bonding of the polymer onto MWNTs. The thickness of the polymer film can be easily observed, about 10

nm after 5 min reaction time, and looks very homogeneous along the nanotube sidewall.

Finally, we extended this procedure to a glass substrate in order to modify the hydrophilic properties of the surface. Typically, a glass plate was cleaned in a piranha solution (mixture of 60/40 by volume of concentrated sulfuric acid and concentrated hydrogen peroxide) for 30 min. Then the surface was functionalized with the (APD, BUMA) couple as previously described. To put in evidence the surface modification of the glass surface, contact angle measurement was carried out. Table 2 gives the result: the contact angle was measured at 17.8° for pristine glass and 83.9° after functionalization. The modification of the hydrophilic properties reveals that hydrophobic BUMA polymer is coated on the glass surface.

3.4. PTFE One-Step Functionalization with Poly (acrylic acid). Perfluorinated polymers possess outstanding properties comprising excellent chemical resistance, high-temperature stability, and very low friction coefficient. For instance, poly(tetrafluoroethylene) (PTFE) materials are applied widely for the production of medical devices. For that reason, there is a strong demand to tailor their surface properties for specific applications. Thus, a large scale of surface modification strategies were developed in particular plasma-assisted techniques^{48,49} or scanning electrochemical microscopy methods (SECM).⁵⁰ Nevertheless, all these techniques require strong operational conditions associated with a high cost of the functionalization process.

The grafting of poly(acrylic acid) (PAA) on PTFE surface was carried out using DIAP. Because of the excellent chemical resistance of the PTFE, the substrate was kept in the reaction mixture for 30 min. The resulting PAA-coated PTFE surface was analyzed by IRRAS, and contact angle measurement was carried out to exhibit the surface properties modification of the PTFE. The observed C=O absorption band at 1726 cm⁻¹ reveals the presence of the poly(acrylic acid) (see Supporting Information). Figure 8 shows a water drop deposited on untreated and functionalized PTFE substrate. The contact angle (see Table 2) was measured at 110° for untreated PTFE and 52° after functionalization

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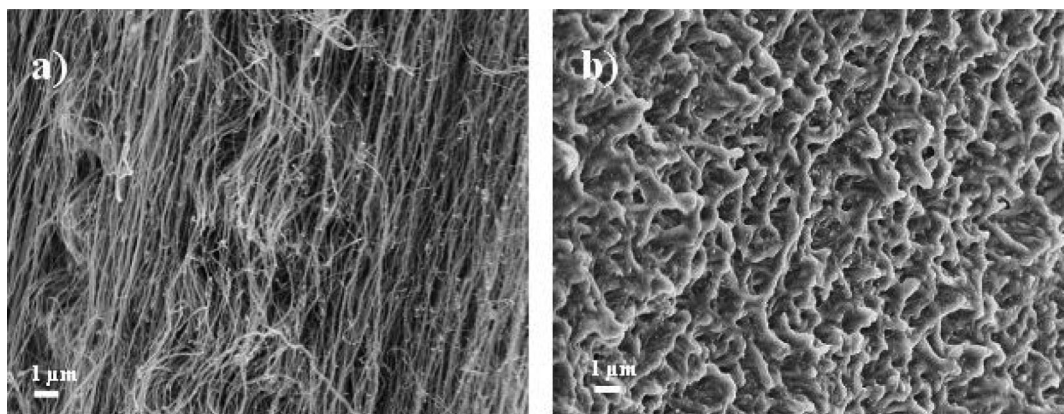


Figure 6. Scanning electron microscopy images of multiwall carbon nanotubes brushes (a) before and (b) after DIAP grafting with the APD/HEMA couple.

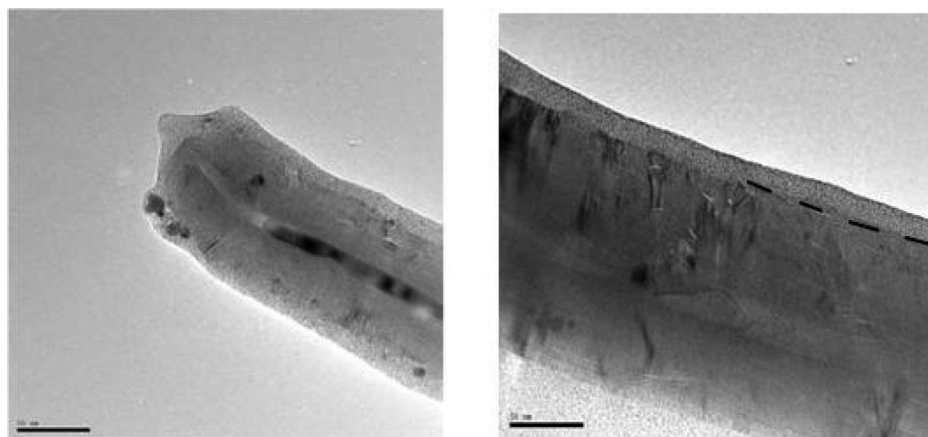


Figure 7. Transmission electron microscopy images of multiwall carbon nanotubes after DIAP grafting with the APD/HEMA couple. Dashed line corresponds to the interface polymer/nanotube.

Table 2. Contact Angle Measurements (Water)

substrate	contact angle before DIAP (deg)	contact angle after DIAP (deg)
glass	17.8	83.9
PTFE	110	52

characterizing a good modification of the PTFE hydrophobic surface properties.

The surface reactivity of this process has been studied for a large range of materials. The results obtained show some differences of reactivity depending of the substrate or the monomer nature. For instance, hydrosoluble monomers have shown to react faster than non soluble ones. Moreover, some substrates are more difficult to functionalize such as glasses or PTFE and require a longer reaction time. Nevertheless, in all cases, the formation of a thin organic polymer film has been observed and fully characterized.

3.5. Proposed Mechanism. In this section, we describe one tentative mechanism for DIAP, which fully explains our experimental results, in particular the resistance to sonication of the metal/polymer interface.

The first part of our study clearly shows that aryl diazonium salts are able to form a polyphenylene-like film strongly bound at the substrate surface. Then, we have demonstrated the formation of a polymer film by adding a vinylic monomer into the solution. We thus proposed the following mechanism to explain these observations, where

the process can be split in four steps: (i) chemical reduction of aryl diazonium salts and protons at iron surface leading to the formation of the corresponding radical species; (ii) formation of the grafted polyphenylene-like layer together with the initiation of the vinylic radical polymerization in solution both by aryl and hydrogen radicals formed in step i; (iii) interaction of growing macro-radical chains with the polyphenylene-like primer layer to give a grafted copolymer film, which can be assimilated to a “trapping step” (Scheme 1); (iv) growth of the polymer film induced by the successive grafting of macro-radical chains and phenyl groups embedded in the already grafted chains (Scheme 2). In that scheme, the presence of N=N linkages between the aryl rings, arising from a noncomplete reduction of the diazonium group,³⁸ was eluded for sake of clarity. The final coating is thus a statistical copolymer containing both vinylic monomers and aryl groups from the former diazonium salts, covalently grafted on a polyphenylene-like primer layer. As the medium contains probably a large quantity of hydrogen and aryl radicals, termination reactions can take place and lead to the observed polymer formation in solution. The proposed mechanism is supported by well-known mechanism for the thickening of polyphenylene layer^{30–33} and the already described reactivity of alkyl radicals toward polycondensed aromatic rings.^{51–54}

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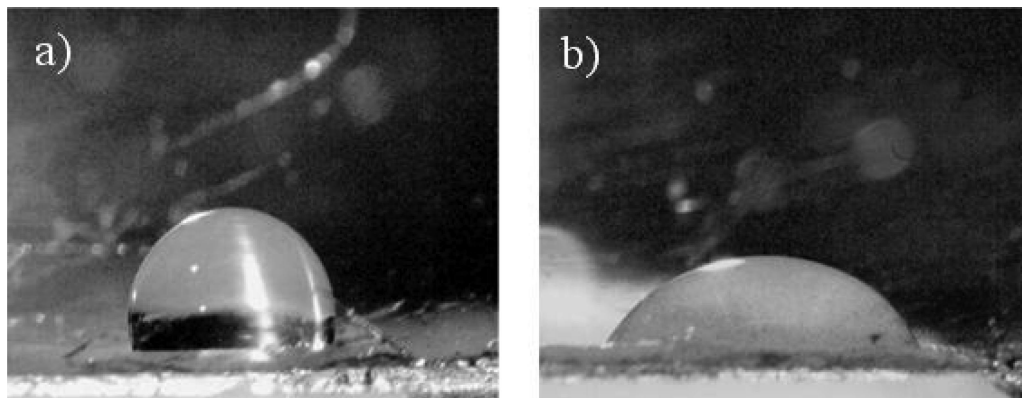
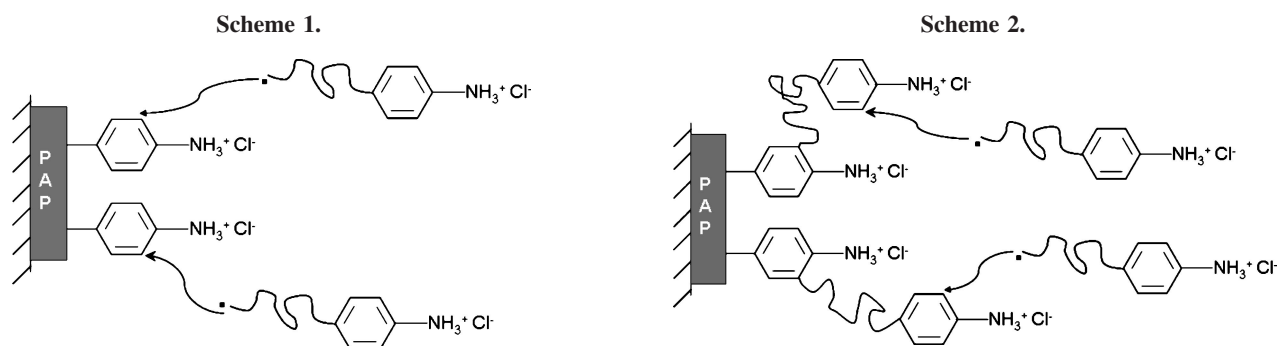


Figure 8. Water droplet on PTFE (a) before and (b) after DIAP grafting with the APD/AA couple.



4. Concluding Remarks. Synthesis of grafted copolymers on raw conductive, semiconductive, and insulating surfaces was studied using a new spontaneous aqueous redox activation of aryl diazonium salts in the presence of vinylic monomers. In each case, this new process leads to a stable organic grafted film. Using this technique allows us to graft organic polymers on various raw substrates without any restriction of conductivity, with a large range of thicknesses and chemical composition, thus opening a whole range of applications. To our knowledge, this is the first technique which can be used for so different surfaces nature working

in water, ambient temperature, and without any apparatus requirement. Investigations are currently in progress to test several homogeneous activators for the aryl diazonium reduction such as hydrogen carbonate or hypophosphorous acid. The first results obtained show that surfaces functionalization occurs with comparable reactivity as already observed with iron activation.

Supporting Information Available: Schemes of the grafting mechanism, IRRAS spectrum, and XPS (N 1s) spectrum of PBA and PAP grafted on Au; IRRAS spectrum of PNP grafted on stainless steel; IRRAS spectrum of PAP grafted on nickel; and IRRAS spectrum of APD/HEMA grafted on Ti, Zn, stainless steel, and PTFE surfaces. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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