

# Electrografting via Diazonium Chemistry: The Key Role of the Aryl Substituent in the Layer Growth Mechanism

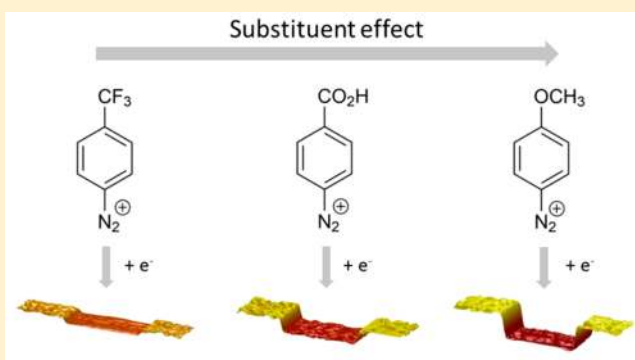
Thibaud Menanteau,<sup>†</sup> Marylène Dias,<sup>†</sup> Eric Levillain,<sup>†</sup> Alison J. Downard,<sup>‡</sup> and Tony Breton<sup>\*,†</sup>

<sup>†</sup>MOLTECH-Anjou, Université d'Angers, UMR CNRS 6200, 2 Boulevard Lavoisier, 49045 Angers, France

<sup>‡</sup>MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Chemistry, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand

## S Supporting Information

**ABSTRACT:** A series of diazonium salts bearing different para substituents was used to functionalize glassy carbon (GC) and pyrolyzed photoresist film (PPF) under electrografting conditions in the absence and presence of the radical scavenger diphenyl-1-picrylhydrazyl (DPPH). Depositions were monitored by electrochemical quartz crystal microbalance (EQCM) and the grafted layers were analyzed by atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). DPPH was used to selectively suppress film growth by radical coupling and thereby to reveal the existence of secondary mechanisms involved in the polymerization. Differences in grafting behaviors between various diazonium ion derivatives can be explained by the influence of the para substituent's electronic properties on the electrophilic aromatic substitutions of diazonium ions on already grafted aromatic groups.



## INTRODUCTION

The use of diazonium salts is now a recognized route to attach functionalities<sup>1</sup> or sustainably change surface properties of carbon<sup>2,3</sup> and various metals.<sup>4–6</sup> The flexibility of the implementation and the stability of the materials has led to an increasing interest of the scientific community for various applications.<sup>7–11</sup> It is now well-known that the grafting process rests on the production of a highly reactive aryl radical at the substrate–solution interface by reduction of the corresponding diazonium ion.<sup>2,12</sup> The subsequent coupling of this radical to the surface generates a covalently linked molecular layer.<sup>3,13</sup> However, in most cases, when no strategy is used to control the radical process, the aryl radical also reacts on already grafted aryl groups, leading to the formation of a polyaryl layer.<sup>14,15</sup> The homogeneity of the layer is generally quite low depending on the substrate roughness and the deposition conditions but its thickness is typically between 1 and 20 nm.<sup>16</sup>

Several studies have underlined the steric effect of the arylsubstituent on the grafting efficiency of diazonium ions.<sup>17–20</sup> When bulky substituents are used, the surface coverage is lowered and the polymerization is limited. This aspect has been exploited to generate monolayer or near monolayer films adapted to nanotechnology uses.<sup>21</sup> In contrast, electronic activation/deactivation effects of the substituents have been significantly less investigated. This lack of studies can be explained by the fact that the mechanism is generally considered to be radical<sup>14</sup> and consequently poorly dependent on the activation/deactivation effect of the arylsubstituents.

However, the existence of secondary electrophilic mechanisms has been tentatively proposed to explain some experimental results such as the presence of azo links in the layer. Azo groups appear to be incorporated in films under all deposition conditions.<sup>22–24</sup> The real impact of this type of mechanism on the layer growth and the consequences on the film composition remains difficult to evaluate and has most often been neglected.

In this work, a series of diazonium salts with para substituents which are activating or deactivating for electrophilic addition was used to investigate the variable grafting behaviors of diazonium salts. A radical scavenger, 2,2-diphenyl-1-picrylhydrazyl (DPPH), was used to selectively suppress the radical polymerization<sup>25,26</sup> and to assess the role of nonradical mechanisms in the layer formation.

## EXPERIMENTAL SECTION

**Products and Reagents.** 4-Nitrobenzenediazonium tetrafluoroborate (D-NO<sub>2</sub>, Aldrich), 4-methoxybenzenediazonium tetrafluoroborate (D-OCH<sub>3</sub>, Aldrich), 2,2-diphenyl-1-picrylhydrazyl (Aldrich), tetrabutylammonium hexafluorophosphate (Aldrich) and acetonitrile (HPLC grade, Carlo Erba) were used as received.

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**Surfaces.** Glassy carbon (GC) electrodes used for cyclic voltammetry were obtained from Bioanalytical Systems Inc. (Model MF-2012; diameter 3 mm). GC sheets ( $10 \times 10 \times 2$  mm) used for XPS experiments were obtained from Good-Fellow. Preparation of pyrolyzed photoresist film (PPF), used for atomic force microscopy (AFM) experiments, has been described previously.<sup>15</sup>

**Synthesis of 4-Trifluoromethylbenzene Diazonium (D-CF<sub>3</sub>), 4-Carboxybenzene Diazonium (D-CO<sub>2</sub>H), and 4-Chloromethylbenzene Diazonium (D-CH<sub>2</sub>Cl).** Para-CF<sub>3</sub> or -CO<sub>2</sub>H substituted aniline (18 mmol) was dissolved in 10 mL of tetrahydrofuran. Then boron trifluoride diethyl etherate (28 mmol) was slowly added to the mixture. After the solution was cooled to 0 °C, 22 mmol of *tert*-butyl nitrite was slowly added. After 20 min the solution was filtered by suction. The precipitate was washed with cold ether and finally dried under vacuum overnight. D-CH<sub>2</sub>Cl was synthesized as described by Pinson and co-workers.<sup>27</sup>

**Electrochemistry.** A potentiostat/galvanostat model SP150 (from Bio-Logic) monitored by ECLab software was used for the electrochemical experiments on GC. All potentials are reported versus Ag/AgNO<sub>3</sub> (10 mM in acetonitrile). Electrochemical experiments on PPF were performed using an Eco Chemie Autolab PGSTAT302 potentiostat/galvanostat. The GC surface was cleaned by polishing with Buehler 1 and 0.04 μm alumina slurry. After each polishing step, the electrode was washed with Nanopure water (18.2 MΩ cm) by sonication. Prior to each derivatization, the electrode was sonicated in acetonitrile for 1 min. All electrolytic solutions were deaerated by nitrogen bubbling for 15 min before cyclic voltammetry (CV) or potentiostatic experiments. Modification of surfaces was achieved at a fixed potential of -0.8 V (Ag/AgNO<sub>3</sub>) in deaerated acetonitrile containing 0.1 M NBu<sub>4</sub>BF<sub>4</sub> and 1 mM diazonium salt. When present, the concentration of DPPH was 2 mM. After each derivatization, the electrode was sonicated in acetonitrile for 1 min.

**Electrochemical Quartz Crystal Microbalance.** Electrochemical quartz crystal microbalance (EQCM) measurements were performed with a QCA922 system (Seiko-EG&G, Princeton Applied Research) equipped with a carbon-coated quartz crystal (Biologic SE-9C-M) in a closed cell (Biologic SE-CL3 model). The cell was used in vertical set up equipped with a platinum wire as counter electrode and a Ag/AgNO<sub>3</sub> reference electrode. Considering that the deposited layer is rigid and that no viscoelastic changes occur at the electrode interface, the relationship between the frequency change and the mass change was calculated by integration of the Cu-stripping voltammetric curves of a CuSO<sub>4</sub> aqueous solution ( $1 \times 10^{-3}$  M/KCl 0.1 M) recorded at 10 mV/s in the range 0–1 V (Ag/AgNO<sub>3</sub>). Subsequently, EQCM experiments were carried out to monitor the mass change of the electrode during the electrochemical reduction of the diazonium cation under the electrochemical modification conditions described above. Typically, the carbon coated quartz was maintained at 0 V (Ag/AgNO<sub>3</sub>) in the cell containing supporting electrolyte and DPPH while the diazonium salt was injected. Then, a -0.8 V (Ag/AgNO<sub>3</sub>) potential was applied to observe the diazonium reduction. Two control experiments were conducted: (1) Injection of an acetonitrile/NBu<sub>4</sub>BF<sub>4</sub> solution (final concentration in the cell = 2 mM) at a fixed potential of -0.8 V (Ag/AgNO<sub>3</sub>) and (2) injection of a 4-nitrobenzene diazonium solution (final concentration in the cell = 2 mM) at open-circuit potential. In both cases, no significant frequency change

was noted. For the second case, the absence of spontaneous grafting is due to the high open-circuit potential recorded (+0.2 V) for carbon coated quartz, contrary to that observed for classical vitreous carbon electrode. Surface coverage was calculated from the mass increase ( $1 \text{ Hz} = 5 \text{ ng cm}^{-2}$ ) by considering the molecular weight of the aryl derivative moiety without azo group.

**X-ray Photoelectron Spectroscopy.** XPS data were collected using a Kratos Axis Ultra spectrometer on modified GC sheets (Goodfellow, model VC 551). Films were deposited in the presence of 1 mM diazonium without and with 2 mM DPPH, at a controlled potential of -0.8 V for 60 min. The X-ray source was monochromated Al Kα working at 1486.6 eV. Spectra were accumulated at a take off angle of 90°, using a spot size of  $0.7 \times 0.3 \text{ mm}^2$  at a pressure of less than  $10^{-8}$  mbar. High resolution scans (N 1s, C 1s, and O 1s) were carried out with 0.1 eV step size and pass energy 20 eV. All spectra were calibrated taking C 1s as a reference binding energy of 284.5 eV (graphitic carbon component of the vitreous carbon substrates), without internal standard. XPS spectra were analyzed with the curve fitting program CASA XPS and involved background subtraction using Shirley and a subsequent pseudo-Voigt function mixing Gaussian–Lorentzian functions. Atomic ratios of the surfaces were calculated from core level spectra normal area divided by number of scans and the element sensitivity factor. For the elements considered, the sensitivity factors are O 1s 2.93, N 1s 1.78, C 1s 1.00, F 1s 4.43, and Cl 2s 1.69.

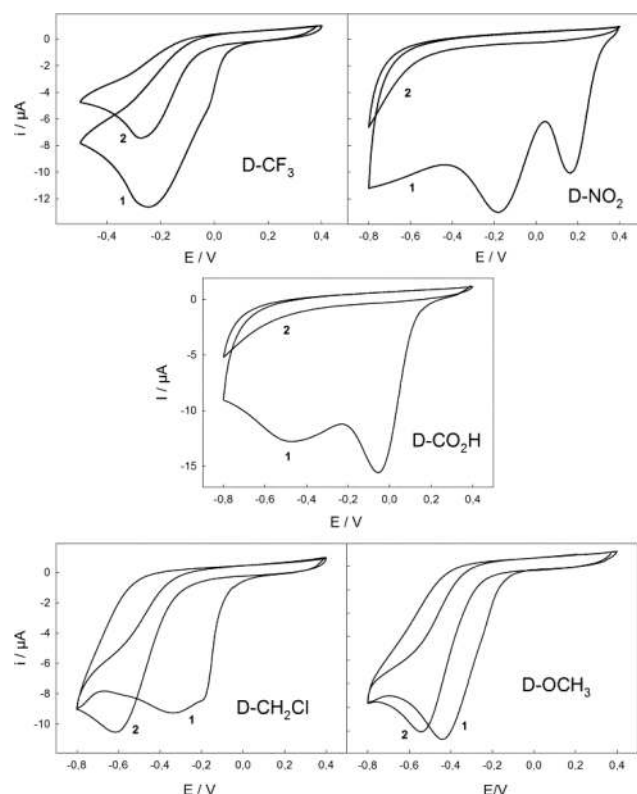
**Atomic Force Microscopy.** Film thickness measurements were made on modified PPF working electrodes by depth profiling using an AFM instrument and technique as described previously.<sup>15</sup> A section of film was removed by scratching with the AFM tip (silicon cantilever, NSC 12 model, Ultrasharp) and the scratch was imaged using noncontact tapping mode (silicon cantilever NSC 14 model, Ultrasharp). The grafting of D-NO<sub>2</sub>, D-CF<sub>3</sub>, and D-CO<sub>2</sub>H was repeated 5 times, giving quasi-identical results. The grafting of D-CH<sub>2</sub>Cl and D-OCH<sub>3</sub> was repeated 3 times, giving small differences (max 15%) and similar images.

## RESULTS AND DISCUSSION

The grafting of five para substituted diazonium salts, all having a low steric hindrance, was investigated: 4-nitrobenzene diazonium (D-NO<sub>2</sub>), 4-trifluorobenzene diazonium (D-CF<sub>3</sub>), 4-carboxybenzene diazonium (D-CO<sub>2</sub>H), 4-chloromethylbenzene diazonium (D-CH<sub>2</sub>Cl), and 4-methoxybenzene diazonium (D-OCH<sub>3</sub>). Prior to the study, electrochemical reactivity of the compounds was evaluated by cyclic voltammetry on vitreous carbon (Figure 1).

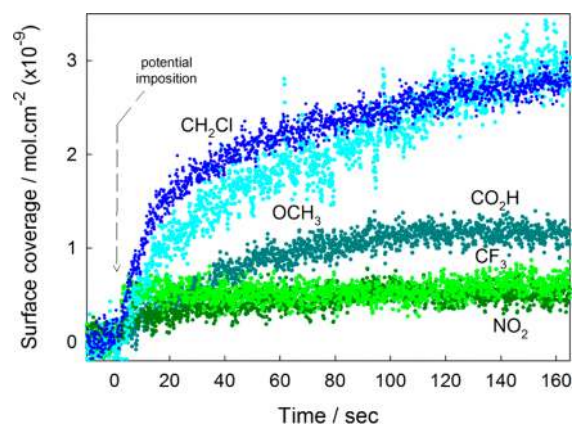
For each salt, a typical reduction wave of the diazonium function is observed on the first forward scan. The changes observed during the second cycles are consistent with the grafting process.<sup>28</sup> The extent of electrode passivation appears to be dependent on the substituent. For D-NO<sub>2</sub>, D-CO<sub>2</sub>H, and to a lesser extent D-CF<sub>3</sub>, the low reduction current recorded during the second cycle indicates that an insulating layer has been formed. For D-CH<sub>2</sub>Cl and D-OCH<sub>3</sub>, only a potential shift is visible, which can be interpreted as a weaker passivation of the electrode due to a thinner and/or porous layer.

The gravimetric monitoring of a potentiostatic electro-deposition of the five diazonium salts was achieved using an electrochemical quartz crystal microbalance equipped with a carbon coated resonator (roughness 0.06 μm). In all cases, a



**Figure 1.** First and second CV cycles recorded at 50 mV/s on a GC electrode ( $0.07 \text{ cm}^2$ ) in  $\text{CH}_3\text{CN}$  0.1 M  $\text{NBu}_4\text{BF}_4$  containing 1 mM of diazonium salt. Potential is reported versus  $\text{Ag}/\text{AgNO}_3$ ,  $10^{-2}$  M.

rapid mass increase was observed, corresponding to multilayer grafting with surface coverage exceeding  $3 \times 10^{-9} \text{ mol}\cdot\text{cm}^{-2}$  (not shown). Experiments were repeated with diazonium salt solutions containing 2 equiv of DPPH to prevent the radical polymerization<sup>25</sup> and obtain information on a possible secondary grafting mechanism. Figure 2 shows the evolution of the calculated surface coverage as a function of the deposition time at controlled potential. It must be noted that EQCM in situ measurements only give access to surface coverages corresponding to unwashed films which can include

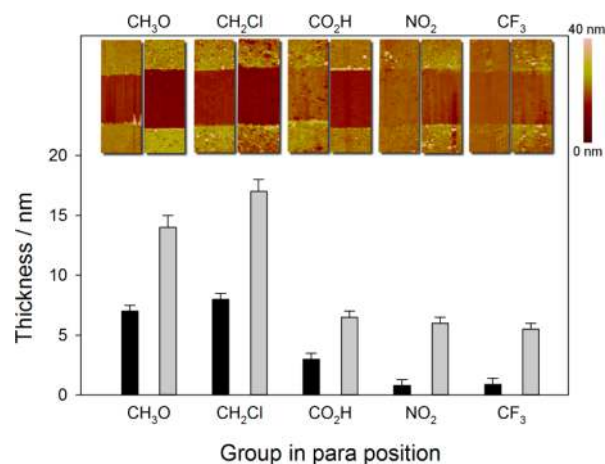


**Figure 2.** Surface coverage variation vs time on a carbon-quartz measured by EQCM for the electrochemical grafting using 1 mM of  $\text{D-NO}_2$  (dark green),  $\text{D-CF}_3$  (light green),  $\text{D-CO}_2\text{H}$  (blue-green),  $\text{D-CH}_2\text{Cl}$  (dark blue), and  $\text{D-OCH}_3$  (light blue) in  $\text{CH}_3\text{CN}$ , 0.1 M  $\text{NBu}_4\text{PF}_6$  at a fixed potential of  $-0.8$  V with 2 mM of DPPH.

some noncovalently attached material contrary to XPS and AFM experiments presented later.

Three different behaviors are observed. For  $\text{D-NO}_2$  and  $\text{D-CF}_3$ , a rapid mass increase is noted after the potential imposition, followed by a stabilization at approximately 5 to  $6 \times 10^{-10} \text{ mol cm}^{-2}$ . The grafting kinetics of  $\text{D-CH}_2\text{Cl}$  and  $\text{D-OCH}_3$  are similar at the initial stage, but the deposition is characterized by a continuous mass increase during 160 s, reaching a surface coverage of  $2.8 \times 10^{-9} \text{ mol cm}^{-2}$ . In the case of  $\text{D-CO}_2\text{H}$ , an intermediate behavior can be observed with stabilization at  $1.2 \times 10^{-9} \text{ mol cm}^{-2}$  after 120 s. Considering the surface coverages reached, the grafting of nitro and trifluoro derivatives in the presence of the radical scavenger is consistent with the formation of a near monolayer. In contrast, chloromethyl and methoxy diazonium grafting behaviors are consistent with a polyaryl layer formation despite the presence of the radical trap.

To complement these experiments, AFM measurements of film thickness were achieved on modified pyrolyzed photoresist film (PPF) with the diazonium salts series. The deposition was carried out with and without DPPH, under a controlled potential of  $-0.8$  V during 60 min to ensure that a steady state of the growth was reached in every case. Current–time plots are presented in the Supporting Information Figure S1. This time duration limits the risk of partial coverage in case of a heterogeneous multilayer growth (presence of unmodified PPF areas). The thickness of films grafted on PPF was measured by removing small sections of attached film by scratching with an AFM tip, followed by profiling perpendicularly to the scratch. Figure 3 presents the images obtained with thicknesses depicted in chart form. Note that corresponding depth profiles are presented in the Supporting Information, Table S1.



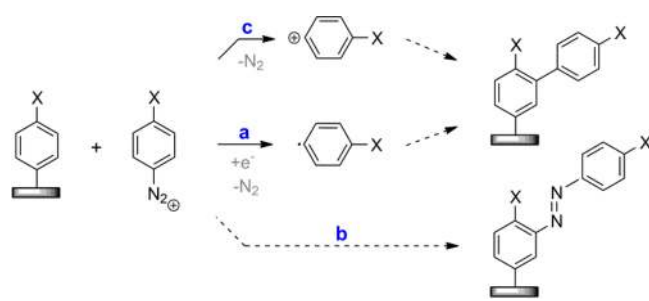
**Figure 3.** Atomic force microscopy images ( $6 \times 1.4 \mu\text{m}$ ) and corresponding thicknesses measured on scratched modified PPF surfaces with various diazonium salts grafted at  $-0.8$  V for 60 min with (black) and without (gray) DPPH in the deposition solution.

The thicknesses measured on modified PPF generated from the reduction of  $\text{D-NO}_2$  and  $\text{D-CF}_3$  are very similar, whether or not in the presence of DPPH. Without radical trap, a thickness of 5–6 nm is obtained. This result is consistent with previously reported results on nitrophenyl-modified PPF and is characteristic of a multilayer formation.<sup>15</sup> When DPPH is added to the deposition solution, the thicknesses of the grafted films are drastically lowered to a subnanometer level (i.e., 0.8 nm for  $\text{D-NO}_2$  and 0.9 nm for  $\text{D-CF}_3$ ). Considering the size of the

immobilized molecules, this layer thickness is consistent with a monolayer formation. In this case, the radical scavenger prevents the radical polymerization of the reduced diazonium ions following the process recently described.<sup>26</sup> The AFM results obtained from the grafting of D-OCH<sub>3</sub> and D-CH<sub>2</sub>Cl are drastically different to those of D-NO<sub>2</sub> and D-CF<sub>3</sub>. In the absence of DPPH, the very thick layers obtained (i.e., 14 nm for D-OCH<sub>3</sub> and 17 nm for D-CH<sub>2</sub>Cl) are consistent with an extended polymerization. In the presence of DPPH, although the layer growth is limited, the thickness goes far beyond the monolayer threshold. The grafting behavior of D-CO<sub>2</sub>H is close to that of D-NO<sub>2</sub> and D-CF<sub>3</sub> when no radical trap is used, illustrated by a layer thickness of 6.5 nm, but in the presence of DPPH, an intermediate value of 3 nm is measured, probably corresponding to a moderate polymerization.

Gravimetric and AFM measurements in the presence of DPPH are very well correlated and show that the layer growth is stopped after the deposition of a monolayer for D-CF<sub>3</sub> and D-NO<sub>2</sub>, but layer growth continues for D-OCH<sub>3</sub>, D-CH<sub>2</sub>Cl, and, to a lesser extent, D-CO<sub>2</sub>H. Assuming the radical polymerization (Scheme 1, route a) is drastically suppressed

**Scheme 1. Proposed Pathways Leading to the Formation of Multilayers in the Presence of Substituted Diazonium Salts**



in the presence of the radical scavenger, differences in the thickness of the films must involve a nonradical mechanism. One of the main assumptions to explain layer growth excluding radical polymerization from diazonium ions is to consider the nonradical formation of -N=N- links between aryl groups. The presence of azo bridges in the layers formed from diazonium ions has been evidenced in many works and is now recognized as inherent to the technique and independent of the diazonium ion substitution.<sup>22,23,29</sup> The proposed mechanism responsible for the formation of azo bridges involves the condensation of nonreduced diazonium ions on already grafted aryl groups<sup>22</sup> (Scheme 1, route b). However, due to the low electrophilicity of diazonium ions, only activating substituents such as alcohol and amino derivatives undergo efficient azo condensations under the usual homogeneous (solution) conditions.

A second polymerization route, based on the nonradical spontaneous decomposition of the diazonium salt, has been proposed to account for differences of grafting efficiency depending on the light conditions and temperature.<sup>30</sup> This second possibility involves the reaction of a spontaneously dediazoniated aryl carbocation in solution on a grafted group (Scheme 1, route c).

Since both routes b and c proceed via an electrophilic attack of a cation (diazonium ion or dediazoniated carbocation), we speculate that the layer growth should be controlled by the activation of the aromatic ring positions, which is dependent on the ring substituent. The activating effect is very low for

electron withdrawing substituents, low for carbonyl functions, neutral for halogens, and high for O- and N- substituents thanks to their mesomeric effect on the aromatic ring. In the case of route c, two additional parameters must be considered: the dediazonation rate and the lifetime of the generated aryl carbocation. The dediazonation kinetics of 4-substituted aryl diazonium ions has been intensively studied. The classical Hammett equation cannot describe the evolution of the reactivity since mesomeric and field (inductive) effects must be independently considered.<sup>31,32</sup> Experimentally, it was found that electron withdrawing substituents, as well as substituents inducing mesomeric effects (alcohols, amines, and derivatives) are rate retarding with respect to dediazonation, in contrast to alkyl groups. In our study, this parameter should not be determining since all the substituents used are rate retarding. With respect to the carbocation lifetime, once formed the Hammett equation can be used to evaluate the stabilization induced by the substituent.<sup>33</sup> Thus, this stabilization effect follows the same rules as those involved in the activation of the aromatic electrophilic substitution (vide supra).

To explore the film growth pathways, XPS was used to determine the composition of grafted layers. Films were deposited using the same conditions as for AFM measurements (with and without DPPH, at a controlled potential of -0.8 V for 60 min). Table 1 summarizes atomic compositions,

**Table 1. Atomic Composition of the GC Surface Modified by Electrochemical Reduction of Diazonium Salts**

	C 1s <sup>a</sup>	O 1s	N 1s <sub>400</sub> <sup>b</sup>	charact. signal
bare	88.9	11.0	0.1	
NO <sub>2</sub>	73.2	18.3	2.1	6.4 (N 1s <sub>406</sub> ) <sup>c</sup>
NO <sub>2</sub> -DPPH	87.0	10.1	1.6	1.3 (N 1s <sub>406</sub> ) <sup>c</sup>
CF <sub>3</sub>	74.1	4.4	0.4	21.1 (F 1s)
CF <sub>3</sub> -DPPH	87.9	8.0	1.0	3.1 (F 1s)
CO <sub>2</sub> H	74.5	19.0	1.3	5.2 (C 1s <sub>288</sub> ) <sup>d</sup>
CO <sub>2</sub> H-DPPH	75.9	17.2	2.6	4.3 (C 1s <sub>288</sub> ) <sup>d</sup>
CH <sub>2</sub> Cl	82.9	12.4	2.6	2.1 (Cl 2s)
CH <sub>2</sub> Cl-DPPH	89.6	8.4	1.2	0.8 (Cl 2s)
OCH <sub>3</sub>	83.7	15.1	1.2	
OCH <sub>3</sub> -DPPH	84.5	14.1	1.4	

<sup>a</sup>C 1s corresponds to the peak at 284.5 eV. <sup>b</sup>N 1s<sub>400</sub> corresponds to the peak attributed to azo-bridge. <sup>c</sup>N 1s<sub>406</sub> corresponds to the peak attributed to nitro groups. <sup>d</sup>C 1s<sub>288</sub> corresponds to the peak at 288.3 eV (attributed to the CO<sub>2</sub>H groups).

obtained from XPS measurements, of the layers formed from D-NO<sub>2</sub> and D-CF<sub>3</sub> with and without DPPH. In both cases, the concentration of the characteristic element (i.e., N 1s(406 eV) for the NO<sub>2</sub> group and F 1s(687 eV) for the CF<sub>3</sub> group) drastically decreases when grafting in the presence of DPPH and is thus consistent with AFM data. XPS data can also provide information on the concentration of azo links in the layer using the signal located at 400 eV, classically assigned to the corresponding reduced nitrogen atoms.<sup>22</sup> Note that traces of NBU<sub>4</sub><sup>+</sup> were detected in every sample thanks to the signal located at 401.8 eV.<sup>34</sup> This signal did not exceed 10% of the 400 eV signal and was excluded from the surface concentration calculations. N 1s(406 eV)/N 1s(400 eV) and F 1s(687 eV)/N 1s(400 eV) ratios were respectively used for D-NO<sub>2</sub> and D-CF<sub>3</sub> modified surfaces to estimate the proportion of aryl groups bonded through azo linkages. For the nitrophenyl layer, the proportion of azo bonded groups increases from 16% to 62%

when DPPH is added to the grafting solution. In the same way, the proportion of azo bonded groups in the trifluoromethylphenyl layer increases from 3% to 50% when DPPH is added. Assuming that there is just a monolayer of aryl-NO<sub>2</sub> and aryl-CF<sub>3</sub> groups when the radical scavenger is used (vide supra), the azo groups must link the rings to the GC surface. In that case, 3 in 5 aryl-NO<sub>2</sub> groups and 1 in 2 aryl-CF<sub>3</sub> groups are attached through an azo link. In agreement with our previous work,<sup>26</sup> this increase in the proportion of azo linked groups provides evidence of the decreasing role of the radical mechanism in the direct grafting to the surface. NO<sub>2</sub> and CF<sub>3</sub> groups are strongly deactivating groups for aryl substitution due to their pronounced electron withdrawing effect. Thus, polymerization by electrophilic attack of diazonium ions or aryl carbocations on grafted groups (respectively via route b or c) to generate a multilayer should be disfavored. The absence of multilayer grafting evidenced by AFM and EQCM for both diazonium ions in the presence of DPPH is consistent with this hypothesis. When no radical scavenger is used, the multilayered modification predominantly arises from electroreduction of diazonium ions followed by the classical radical mechanism. Film growth is self-limited for thickness exceeding 5 nm due to a negligible rate of reduction of diazonium ion.

In the case of the surface modified with D-CO<sub>2</sub>H, the C 1s signal located at 288 eV, assigned to the + III oxidized state of the carboxy function, unambiguously demonstrates the functionalization. The N 1s signal, located at 400 eV, reveals the presence of azo links in the layer. By calculating the ratio between N 1s and C 1s(288 eV) signals, the proportion of Ar-CO<sub>2</sub>H functions grafted through azo links for the layer prepared without DPPH was estimated to be 13%. This result is consistent with that extracted from data obtained by Baranton et al. on Ar-CO<sub>2</sub>H modified glassy carbon (8%).<sup>24</sup> When DPPH is added, this percentage increases to 30%. The film being multilayered in both cases, the determination of the azo links location is almost impossible, unless techniques such as secondary ion mass spectrometry (SIMS), is used in dynamic mode.<sup>22</sup> Without radical trap, the multilayer formation evidenced by EQCM and AFM can mainly be attributed to the radical polymerization (route a) as it is the case for D-NO<sub>2</sub> and D-CF<sub>3</sub>. In the presence of DPPH, the electronic properties of the carboxy group have to be considered to explain the layer growth. CO<sub>2</sub>H is a moderately deactivating group for electrophilic addition and does not allow the reaction, under homogeneous (solution) conditions, with diazonium ions. Consequently, polymerization following route b remains possible but unlikely. Polymerization following route c appears more favorable because the electrophilic character of an aryl carbocation is higher than that of a diazonium ion and could be sufficient to react with a moderately deactivated ring. The approximate doubling of the azo group proportion while the film thickness halves when DPPH is added to the grafting solution could then be explained by azo links mainly bonding Ar-CO<sub>2</sub>H groups to the surface, rather than within the film, as observed for Ar-NO<sub>2</sub> and Ar-CF<sub>3</sub> layers.

For D-CH<sub>2</sub>Cl modified surfaces, the Cl 2s signal confirms the grafting. The chlorine surface concentration appears surprisingly low in both layers prepared without and with DPPH (2.1 and 0.8% respectively) despite the high surface coverage measured by EQCM, the large thickness measured by AFM and the strong blocking behavior highlighted during the grafting (see the Supporting Information Figure S1). No clear explanation was found but one suggestion to explain this result

and the anomalously high oxygen percentage (based on film thickness) is a partial hydrolysis of the chloromethyl functions into hydroxyl groups under the reductive conditions of the prolonged electrografting.<sup>35,36</sup> Assuming, for simplicity, that all O in the D-CH<sub>2</sub>Cl film arises from hydrolysis of CH<sub>2</sub>Cl groups, the (Cl 2s + O 1s)/N 1s ratio allows the proportion of Ar-CH<sub>2</sub>Cl and Ar-CH<sub>2</sub>OH groups attached through azo links to be estimated. Calculations give 9% of Ar-CH<sub>2</sub>Cl and Ar-CH<sub>2</sub>OH groups bonded via azo links when the grafting is carried out without DPPH and 7% when DPPH is used (note that the latter value is expected to be an underestimate because surface O is expected to contribute to the XPS signal from the thinner film). Chloromethyl and hydroxymethyl groups are considered to be neutral for aromatic electrophilic substitution activation since the electron withdrawing effect of chlorine and oxygen atoms is counterbalanced by the inductive effect of the methylene group. The low proportion of Ar-CH<sub>2</sub>Cl and Ar-CH<sub>2</sub>OH bonded via azo links and the higher electrophilicity of dediazoniated cations compared to diazonium cations are consistent with the predominance of route c. Furthermore, considering the thickness of the layers, the small difference between the measured proportion of azo-linked groups without and with DPPH is not surprising if we assume that the electrochemical reduction of D-CH<sub>2</sub>Cl becomes very limited when the layer reaches 5–6 nm thickness. This means that there should be no radicals being generated during film growth (in the absence of DPPH) beyond 5–6 nm. Consequently, for the outermost ~10–12 nm of the 17 nm thick Ar-CH<sub>2</sub>Cl/Ar-CH<sub>2</sub>OH film grown in the absence of DPPH, the growth mechanism should be the same nonradical mechanism as in the presence of DPPH. Assuming that XPS only probes the outermost ~10 nm of the film, the similar composition of the films grown with and without DPPH is to be expected.

For Ar-OCH<sub>3</sub> modified surfaces, the increase of the oxygen atomic percentage (15% and 14% for modified surfaces without and with DPPH, respectively) compared to that of a bare carbon surface (i.e., 11%) is consistent with the functionalization. The atomic percentage of nitrogen involved in azo links (calculated from the N 1s(400 eV) signal) was found equal to 1.2% for the layer prepared without radical scavenger and 1.4% for the layer prepared with scavenger. It can be assumed, as for the Ar-CH<sub>2</sub>Cl modified surface, that the outermost 10 nm of the Ar-OCH<sub>3</sub> film grown without DPPH will mostly have grown via a nonradical mechanism and should present a similar composition to the film formed in the presence of DPPH. The methoxy group is a strongly activating group for electrophilic substitution but the low electrophilicity of the diazonium involves low reactions rates compared to that of -OH or -NH<sub>2</sub> groups that are commonly used for azo coupling under homogeneous conditions. Furthermore, the methoxy group can strongly stabilize the dediazoniated carbocation. Considering those points and the low nitrogen atomic percentage measured, the multilayer obtained could consequently be mainly due to route c.

Considering the hypothesis of a grafting efficiency promoted by the substituent activation, the results agree with the continuous growth process reported by Kariuki et al.<sup>37</sup> for the deposition of diethylaniline and Simons et al. for the deposition of aminophenyl films.<sup>38</sup> Indeed, amino substituents are also known to strongly activate aromatic positions for electrophilic substitutions due to the stabilizing mesomeric effect produced on the cationic transition state.

## CONCLUSION

In view of the results presented, the grafting behavior of aryldiazonium salts is strongly dependent on the substituent in the para position on the aryl ring, suggesting that the influence of secondary mechanisms proposed by several authors is more important than typically acknowledged.<sup>22,23</sup> For diazonium salts having strongly electron withdrawing substituents, the grafting is only governed by the widely recognized radical process. For diazonium ions substituted by a less electron withdrawing group (i.e., CO<sub>2</sub>H) the layer growth can occur by secondary mechanisms in addition to the radical process but their impact remains limited. In the case of neutral or activating groups, thick films can be grafted via secondary mechanisms. This substituent effect points to polymerization via an electrophilic aromatic substitution mechanism by diazonium ion or dediazoniated carbocation on already grafted groups. A consequence of this result is that the control of the layer growth via the use of radical scavenger will be dependent on the substituent on the diazonium ion, a monolayer functionalization being only possible by the use of withdrawing substituents. More generally, this study significantly advances understanding of the mechanism of film formation from diazonium salt solutions. The results indicate that, through careful selection of the diazonium ion derivative, thick films can be grafted under conditions where reduction of the diazonium ion is not possible, for example at nonconducting substrates or at conducting substrates once the grafted film prevents further reduction of diazonium ions and production of radicals.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b12565.

Current–time curves recorded at  $-0.8$  V for the electrografting of the diazoniums on PPF (Figure S1) and AFM depth profiles of scratched modified PPF after grafting with diazonium salts (Table S1) (PDF)

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [tony.breton@univ-angers.fr](mailto:tony.breton@univ-angers.fr).

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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