

The Electrochemical Reduction of Diazonium Salts on Iron Electrodes. The Formation of Covalently Bonded Organic Layers and Their Effect on Corrosion

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Electrochemical reduction of aryldiazonium salts on an iron electrode in acetonitrile leads to the attachment of aryl groups to the iron surface. We investigated aryl groups substituted with 4-alkyl chains ($-\text{CH}_3$, $-\text{C}_4\text{H}_9$, $-\text{C}_{12}\text{H}_{25}$, $-\text{OC}_{12}\text{H}_{25}$, $-\text{OC}_{16}\text{H}_{33}$), with 4-halogeno substituents ($-\text{I}$, $-\text{F}$, $-\text{CF}_3$, $-\text{OCF}_3$, or $-\text{C}_6\text{F}_{13}$), or with five fluorine atoms (pentafluorophenyl, $-\text{C}_6\text{F}_5$). Attachment of these groups was characterized by FTIR, XPS, and capacity measurements. It is shown by measuring the polarization resistance and the corrosion current that these layers provide a significant protection against corrosion.

Introduction

The main observable process during the electrochemical reduction of diazonium salts on carbon electrodes is the attachment of aryl groups on the surface^{1–15} of the electrode rapidly leading to the blocking of the electrode.^{1,2} This grafting reaction can be performed in

acetonitrile (ACN)^{1–15} but also in dilute aqueous acidic solution.⁴ The organic groups are strongly attached as they cannot be removed by a vigorous ultrasonic rinsing. The organic layers thus formed have been thoroughly characterized by cyclic voltammetry,^{1–15} XPS,^{1,5,9} IR,^{1,8} Raman,^{7a,b,8} and RBS³ spectroscopy and by scanning probe microscopy.^{10,11} The organic layer which is attached to the surface can be used for the immobilization of enzymes^{3,12} and catalysts,¹¹ the improvement of carbon–epoxy composites,⁴ the preparation of selective electrodes,^{9a,12,14,15} the preparation of chromatographic stationary phase,^{9b} and the derivatization of nanotubes.⁸ More recently, we have shown that reduction of diazonium salts on an iron electrode leads to the attachment of aryl groups to the surface of the iron electrode.¹⁶ This was demonstrated by transfer experiments where the cyclic voltammogram of reporting groups could be observed after thorough rinsing of the electrode and by IR, XPS, and RBS spectroscopy. It was possible to observe a signature of the Fe–C bond by XPS spectroscopy. The grafting process on carbon or iron can be assigned to the very reactive aryl radicals obtained upon reduction (at potentials close to zero volt vs saturated calomel electrode (SCE)) of the diazonium salts. This reaction is not unprecedented as the electrochemical reduction of aryl diazonium salts in aprotic solvents (sulfolane and acetonitrile) on mercury electrodes has been investigated by Elofson and Gadallah.^{17–22} The aryl radicals which are formed through a one-electron

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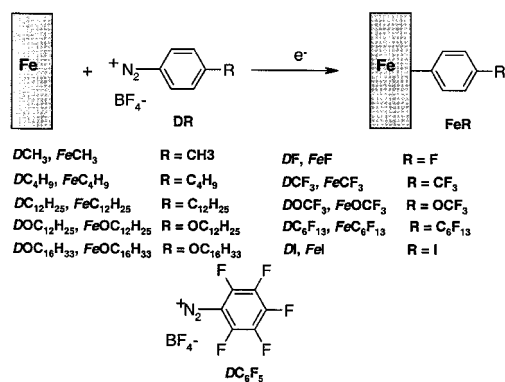
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Scheme 1



reduction give rise to arylation reactions^{19,20} or Pschorr cyclizations.²² Besides biphenyl¹⁹ and fluorenone,²² these authors found organomercuric products²² (4'-substituted benzophenonemercury upon reduction of the diazonium salt of 2-amino 4'-substituted benzophenone) in up to 65% yield, clearly indicating the reaction of aryl radicals with the metal of the electrode. This paper will describe the electrochemical reduction of diazonium salts (**DR**, Scheme 1) leading to the attachment of aryl groups to the iron surface (**FeR**, Scheme 1). These aryl groups are substituted on the 4-position by alkyl chains of variable length, fluoro substituents, an iodine atom, or five fluorine atoms (pentafluorophenyl group). As these groups should provide hydrophobic layers and limit the diffusion of oxygen and protons, the protection of the iron surface against corrosion could be a possible application of these strongly attached organic layers. The effect of the layers obtained in this way on the corrosion of iron will be estimated.

Experimental Section

Chemicals and Electrodes. ACN was obtained from Merck (Uvasol), H₂SO₄ from Prolabo (Tritrinorm), and NBu₄BF₄ from Fluka (Puriss.). Diazonium salts were obtained by standard methods²³ from the corresponding amines. The amines were commercially obtained except for 4-dodecyloxyaniline, 4-hexadecyloxyaniline, and 4-perfluorohexylaniline which were prepared as described below. The diazonium salts were kept in a freezer before use. All aromatic amines should be treated as potentially carcinogenic, and diazonium salts are very sensitive to shock when perfectly dry and detonate violently upon gentle heating. However, tetrafluoroborates which are used in this study are unusually stable as they can be heated in the dry state to give the Balz–Schiemann reaction.²⁴

4-Methylbenzene Diazonium Tetrafluoroborate (DCH₃).²⁴ White solid, mp = 110 °C dec (lit. 110 °C dec). ¹H NMR (200 MHz, DMSO): δ (ppm) = 2.5 (q, 3H, CH₃), 7.8, 8.5 (two d, J = 8.5 Hz, 4H, aromatics).

4-n-Butylbenzene Diazonium Tetrafluoroborate (DC₄H₉).²⁵ In an Erlenmeyer flask placed in an ice bath, 4-n-

butyl aniline (149 mg, 1 mmol) is dissolved in HBF₄ (34%, d = 1.23, 30 mL) and stirred for 15 min, then NaNO₂ (1.5 mmol, 103 mg) is added. The mixture is stirred for 20 min. CH₂Cl₂ (30 mL) is then added, and the organic and aqueous layers are separated in a separatory funnel. The organic phase is dried over MgSO₄ and evaporated to give a pale yellow solid. No melting point could be measured as described in the literature.²⁵ ¹H NMR (200 MHz, DMSO): δ (ppm) = 0.9 (t, ³J = 6 Hz, 3H, CH₃), 0.8–2.8 (m, 4H, CH₂), 2.8 (t, ³J = 8 Hz, 2H, CH₂ benzylic), 7.6, 8.5 (two d, ³J = 8 Hz, 4H, aromatics).

4-n-Dodecylbenzene Diazonium Tetrafluoroborate (DC₁₂H₂₅).²⁶ White solid, mp = 70 °C dec. ¹H NMR (200 MHz, DMSO): δ (ppm) = 0.85 (t, ³J = 6 Hz, 3H, CH₃), 1.1–2.8 (m, 20 H, CH₂), 2.5 (t, ³J = 8 Hz, 2H, CH₂ benzylic), 7.8–8.5 (two d, ³J = 8 Hz, 4H, aromatics).

4-n-Dodecyloxybenzene Diazonium Tetrafluoroborate (DOC₁₂H₂₅). This was prepared from 4-dodecyloxyaniline²⁷ as described before: white solid, mp = 73 °C dec. ¹H NMR (200 MHz, DMSO): δ (ppm) = 0.8–1.8 (m, 23H, aliphatic protons), 4.3 (t, 2H, O–CH₂), 7.5, 8.5 (two d, ³J = 8 Hz, 4H, aromatics).

4-n-Hexacyloxybenzene Diazonium Tetrafluoroborate (DOC₁₆H₃₃). This was prepared in the same way from hexadecyloxyaniline, but the diazonium salt still contained some amine: white solid. ¹H NMR (200 MHz, DMSO): δ (ppm) = 0.8–1.8 (m, 33H, aliphatic protons), 4.2 (t, 2H, O–CH₂), 7.2–8.5 (two d, ³J = 8 Hz, 4H, aromatics).

4-Fluorobenzene Diazonium Tetrafluoroborate (DF). White solid, mp = 158 °C dec (lit. 154.5 °C dec). ¹H NMR (200 MHz, DMSO): δ (ppm) = 7.9–8.8 (two d, ³J = 8.5 Hz, 4H, aromatics). ¹⁹F NMR (400 MHz, DMSO) δ = 79.3 (s).

4-Trifluoromethylbenzene Diazonium Tetrafluoroborate (DCF₃). White solid, mp = 77 °C dec. ¹H NMR (200 MHz, DMSO): δ (ppm) = 8.2–8.6 (two d, ³J = 8.7 Hz, 4H, aromatics). ¹⁹F NMR (400 MHz, DMSO) δ = 63.1 (s).

4-Trifluoromethoxybenzene Diazonium Tetrafluoroborate (DOCF₃). White solid, mp = 71 °C dec. ¹H NMR (200 MHz, DMSO): δ (ppm) = 8.1–8.8 (two d, ³J = 8.5 Hz, 4H, aromatics). ¹⁹F NMR (400 MHz, DMSO) δ = 57.1 (m).

4-Perfluorohexylbenzene Diazonium Tetrafluoroborate (DC₆F₁₃).²⁸ This was obtained from 4-perfluorohexylaniline²⁸ (synthesized according to Crich). White solid, mp = 162 °C (lit. 165 °C dec²⁸). ¹H NMR (200 MHz, DMSO): δ (ppm) = 8.4–8.9 (two d, ³J = 8.7 Hz, 4H, aromatics). ¹⁹F NMR (400 MHz, DMSO): δ = 80.7 (t, 3F, CF₃), 111.5 (m, 2F, CF₂), 121.6 (m, 4F, 2 CF₂), 123.0 (m, 2F, CF₂), 126.3 (m, 2F, CF₂).

Pentafluorobenzene Diazonium Tetrafluoroborate (DC₆F₅). White solid, mp = 80 °C. ¹⁹F NMR (200 MHz, DMSO): δ (ppm) = 141–146 (m, 1F), 150–155 (m, 2F), 162–165 (m, 2F).

4-Iodobenzene Diazonium Tetrafluoroborate (DI).²⁴ White solid, mp = 126 °C (lit.²⁴ 123–124 °C). ¹H NMR (200 MHz, DMSO): δ (ppm) = 8.4 (two d, J = 8 Hz, 4H, aromatics).

Electrodes were prepared either from 1 mm diameter iron wire (Johnson–Matthey 99.99%) embedded in epoxy resin, from 15 mm diameter 99.5% iron disks, or from 3 mm diameter mild steel buttons maintained in a Teflon holder. Mild steel plates (containing Fe: 95.68%; C: 0.31%; Mn: 2.03%; P: 0.05%; S: 0.13%; N: 0.56%; Si: 0.10%; Cu: 0.07%; Ni: 0.18%; Cr: 0.30%; Sn: 0.01%; Al: 0.58%) were kindly given by the Société Sollac.

Electrochemical Equipment. Electrochemical curves were obtained either with a homemade potentiostat or a Versastat II from EGG (Priceton Applied Research). Impedance measurements were obtained with an EGG potentiostat 263A and a lock-in amplifier 5210 or with a 1255 Solartron frequency analyzer (Schlumberger) coupled to an EGG PAR273 potentiostat. The frequencies that were investigated ranged from 10^{–3} Hz to 100 kHz; the amplitude of the alternative potential was 5 or 10 mV, and 5 points were measured per decade of

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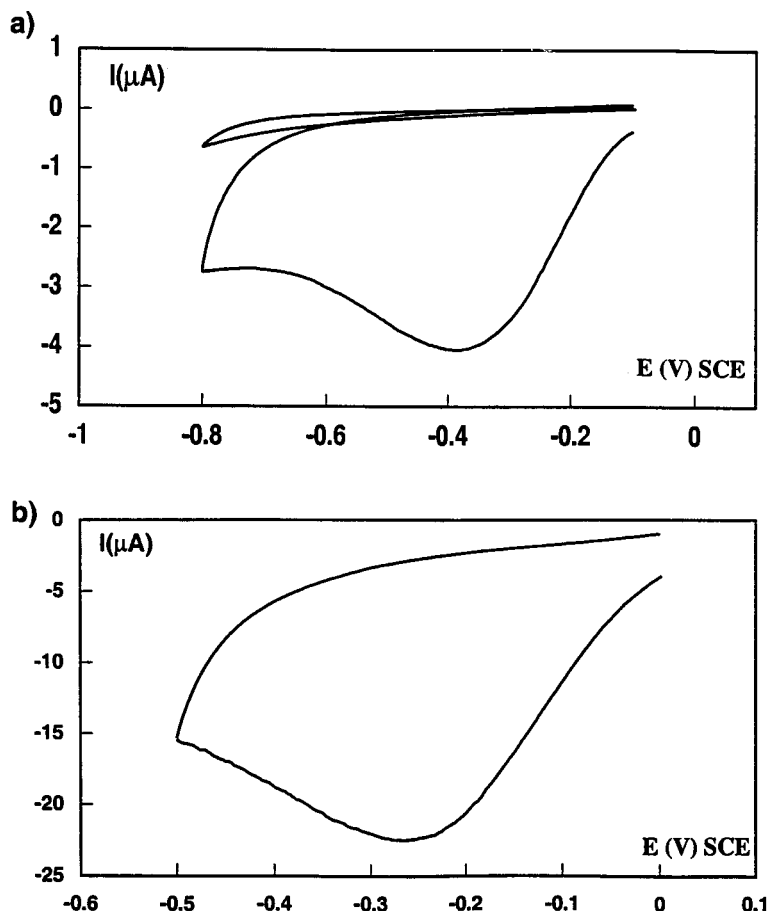


Figure 1. Cyclic voltammogram of a 2 mM solution of (a) 4-methylbenzene diazonium DCH_3 (first and fourth cycle) and (b) 4-perfluorohexylbenzene diazonium tetrafluoroborate DC_6F_{13} on an iron electrode in ACN + 0.1 M NBu_4BF_4 , $\nu = 0.2$ V/SCE. Reference SCE.

frequency. Corrosion currents were obtained from the Tafel plots with the EGG corrosion software.

The electrodes were grafted from 2 mM solutions of the diazonium in ACN + 0.1 M NBu_4BF_4 ; the potential was set at a value that was 300 mV negative to the voltammetric peak for 30 s in the case of DCH_3 - $\text{DOC}_{16}\text{H}_{33}$, DC_6F_5 , and DI and 30 min for DF - DC_6F_5 . After the electrolysis, the electrodes are thoroughly rinsed in an ultrasonic cleaner in ACN for 10 min.

FTIR spectra were obtained with a Bruker IFS 28 spectrometer. The grafted disks were analyzed by reflection with a 60° incident angle. The spectra of diazonium salts were recorded in the ATR (attenuated total reflection) mode with a zinc selenide prism.

XPS spectra were recorded with a Surface Science Instrument with a micro 300 μm diameter X-ray monochromatic beam Al $\text{K}\alpha$ ($h\nu = 1486.6$ eV). The energy bandwidth is 150 eV for large-scan spectra and 100 eV for the regions specific for the different elements. The sampling is 1.12 and 0.116 eV for large-scan and high-resolution spectra, respectively. The analyses were performed with an emission angle of 35° with reference to the surface.

Results

On a carbon electrode,¹ diazonium salts in ACN + 0.1 M NBu_4BF_4 present a one-electron irreversible wave at a potential close to 0 V/ECS. The height of the wave decreases to zero upon repetitive scanning. This blocking of the electrode corresponds to the reaction of the very reactive aryl radicals, formed upon one-electron reduction of the diazonium salt, with the carbon surface. The main difference between a carbon electrode and an

iron electrode is the available potential range. While electrochemical processes can be investigated between -2.8 and $+2.6$ V/ECS in ACN on a carbon electrode, the range is restricted to $-2.3/0$ V/ECS on an easily oxidized iron electrode in the same medium. Between these limits, a clean background current of the same order of magnitude as on carbon is observed. In ACN, it is therefore possible to observe,¹⁶ at negative potentials, the reduction of diazonium salts substituted with electron-donating groups; this reduction cannot be properly observed for diazonium salts bearing electron-withdrawing substituents (such as nitro groups) which are reduced at more positive potentials. For example, Figure 1 shows the voltammogram of 4-methyl benzenediazonium DCH_3 and 4-perfluorohexylbenzene diazonium tetrafluoroborate DC_6F_{13} in ACN + 0.1 M NBu_4BF_4 . In every case, the irreversible wave disappears upon the performance of successive scans as was previously observed on carbon; this blocking of both carbon and iron electrodes has been assigned^{1,16} to the attachment of aryl groups to the iron surface. Table 1 reports the voltammetric peak potentials of the different diazonium salts on carbon (for comparison) and on iron. Similar potentials are observed on carbon and iron electrodes. Relatively negative potentials are observed for alkyl substituents and relatively positive potentials are observed for DCF_3 and DOCF_3 , in agreement with the electron-releasing and -withdrawing character of the substituent. DF is reduced at -470 and -450 mV on

Table 1. Peak Potentials in Cyclic Voltammetry of the Diazonium Salts^a

diazonium	E_p (mV) glassy carbon electrode	E_p (mV) iron electrode
DCH₃	-450	-460
DC₄H₉	-410	-410
DC₁₂H₂₅	-350	-400
DOC₁₂H₂₅	-350	-360
DOC₁₆H₃₃	-270	-320
DF	-470	-450
DCF₃	-50	<i>b</i>
DOCF₃	-28	<i>b</i>
DC₆F₁₃	-230	-270
DC₆F₅	-390	<i>c</i>
DI	-390	-300

^a In ACN + 0.1 M NBu₄BF₄, reference SCE, scan rate 0.2 V s⁻¹, concentration of the diazonium 2 mM. ^b Too positive to be measured reliably. ^c Drawn out voltammogram. The peak cannot be measured.

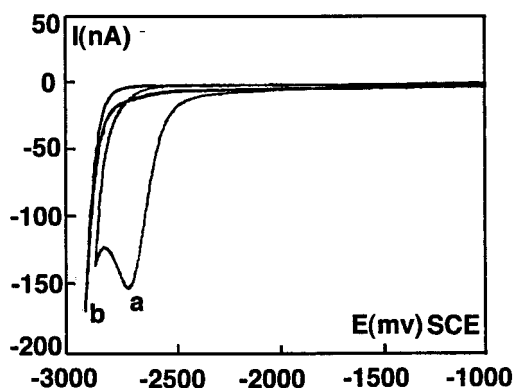


Figure 2. Cyclic voltammogram of a carbon electrode grafted with 4-fluorophenyl groups in ACN + 0.1 M NBu₄BF₄: (a) first and (b) second cycle, $\nu = 0.2$ V s⁻¹. Reference SCE.

iron and carbon, respectively; this is in line with the low electron-withdrawing character of a *p*-fluorine. It is more surprising to observe **DC₆F₁₃** and **DC₆F₅** with strongly withdrawing *p*-C₆F₁₃ or *m*-fluoro substituents at -230 and -390 mV, respectively, on carbon. These relatively negative reduction potentials may be due to the adsorption of the diazonium before the grafting reduction.

The grafting of the organic groups was achieved by reduction in ACN, as indicated in the Experimental Section. After the grafting electrolysis, the electrodes were thoroughly rinsed in an ultrasonic cleaner to ascertain that any organic material only deposited on the surface would be removed.

If the aryl group that is attached to an iron electrode is substituted with an electroactive group (for example, NO₂), it is possible to characterize its attachment through its voltammetric signal after transfer in a solution containing only ACN + 0.1 M NBu₄BF₄.¹⁶ This is not possible with alkyl or fluoro substituents of Scheme 1 on an iron electrode. In the case of alkyl substituents, alkyl groups are not reducible (nor are they on carbon), and in the case of fluoro substituents, the reduction takes place at a potential negative to the background (-2.3 vs -2.8 V/SCE on carbon). It was possible only on carbon to observe (after a thorough rinsing of the grafted electrode; see Experimental Section) the irreversible wave of **CF** (Figure 2) and **CCF₃** close to the values reported in the literature for C₆H₅F

and C₆H₅CF₃ (-2.82 and -2.49²⁹ V/SCE). This wave completely disappears on the second scan indicating complete reduction of the minute amount of aromatic groups attached to the surface.

Characterization of the attached layer was also achieved by IR spectroscopy. Parts a and b of Figure 3 show the FTIR spectra of 4-trifluoromethylbenzene diazonium **DCF₃** and pentafluorobenzene diazonium **DC₆F₅** tetrafluoroborate and of iron disks modified with 4-trifluorophenyl **FeCF₃** and pentafluorophenyl **FeC₆F₅** groups, respectively. Some characteristic bands of these spectra are summarized in Table 2. They confirm the presence of both the fluorine atoms (through CF stretching vibrations) and the aromatic rings (through C=C stretching and CH out-of-plane deformations) on the iron surface. The attachment to the iron surface of fluorinated moieties can also be characterized by XPS. Figure 4 shows the large energy range spectra of an untreated iron plate and of **FeC₆F₅** and **FeC₆F₁₃**. The presence of a peak at 688 eV, an energy characteristic of fluorine, the height of which increases with the number of fluorine atoms, is a clear indication of the attachment of the aryl groups. The peak of iron is always detected either because the organic layer is very thin or because it is incomplete. Other peaks are that of carbon, stemming from the organic layer but also from contamination, and of oxygen related to surface oxides.

Figure 5 shows the C_{1s} spectra of the same organic groups. A main component is centered at 285 eV and is related to C-C and CH carbons; it is partly due to contamination (several XPS spectra of untreated iron plates were recorded, and the carbon peak amounted at most to 13% of the value obtained after derivatization). A component at 288.3 eV on the spectrum of **FeC₆F₅** (Figure 5a) can be assigned to a C-F carbon; a more complex spectrum is obtained with **FeC₆F₁₃** (Figure 5b) with two high-energy peaks centered at 292 and 293.5 eV and related to CF₂ and CF₃. The F_{1s} spectra of **FeC₆F₁₃**, **FeC₆F₅**, and **FeOCF₃** are shown in parts a, b, and c of Figure 6, respectively. The spectrum of **FeC₆F₁₃** presents a peak at 688.4 eV in very good agreement with the literature data³² for CF₂ and CF₃. The spectrum of **FeC₆F₅** presents a peak centered at 685 eV corresponding to -C₆F₅ altogether with a minor peak of unknown origin. A decomposition occurs in the case of **FeOCF₃**, as only a minor peak at 688.8 eV corresponds to OCF₃ while the major peak could possibly be assigned to fluorine ions. This decomposition is likely due to the X-ray beam, as the product by itself is relatively stable. The Fe spectrum of **FeF** clearly shows the presence of metallic iron (Fe_{2p3/2} centered at 706.8 eV) and Fe(II) (Fe_{2p3/2} centered at 710.0 eV); this second component is asymmetric and accompanied by a shake-up satellite at 712.2 eV that is characteristic of a charge transfer of ligand → metal. These XPS spectra confirm the presence of fluorine on the surface and therefore the attachment of the aryl groups.

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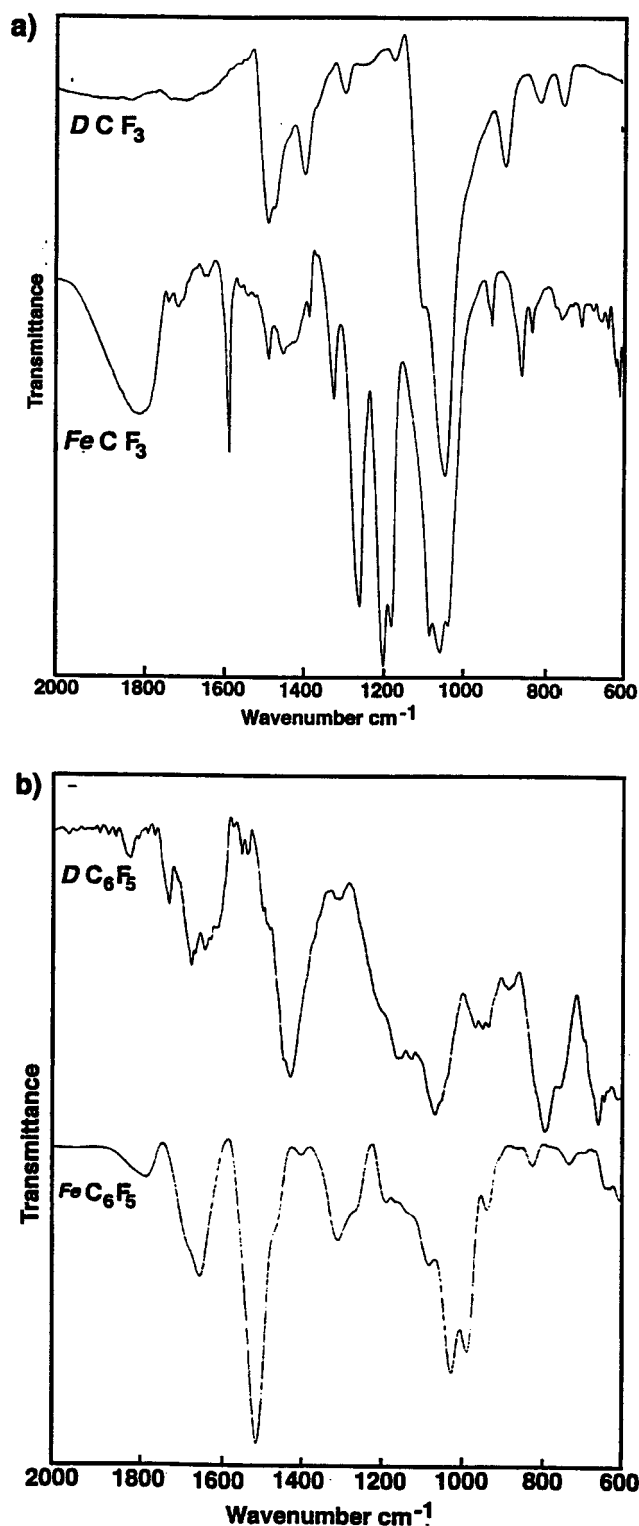


Figure 3. FTIR spectra of (a) trifluoromethylbenzene diazonium DCF_3 and of an iron electrode modified with trifluoromethylphenyl groups FeCF_3 and (b) pentafluorobenzene diazonium DC_6F_5 and of an iron electrode modified with pentafluorophenyl groups FeC_6F_5 .

The protective effect of the organic layer was assessed by measuring the extent to which it prevents the corrosion of iron. Two different parameters have been measured: the polarization resistance R_p and the corrosion current i_{corr} . Before any measurement, the modified iron or mild steel electrodes were left to stabilize in the measurement medium at the open potential until

its value had stabilized.³³ Polarization resistances R_p were measured either by sweeping the potential cathodically and anodically at 0.1 or 1 mV s⁻¹ (Figure 7 shows the example of $\text{FeC}_{12}\text{H}_{25}$) and obtained from the slope of the curve by the Stern and Geary method^{34–36} or from impedances measurements.³⁷ Both the real and imaginary parts of the impedances were obtained from the Nyquist diagrams (Z_{Im} vs Z_{Re} as a function of the frequency of the signal). From these plots, one can obtain the polarization resistance at low frequency and the capacity ($C = 1/\omega_{\text{max}}R_p$) from ω_{max} measured at the maximum of Z_{Im} .^{38,39} (Parts A and B of Figure 8 show examples of alkyl chains as substituents and fluoro substituents, respectively.) Finally, the corrosion current was measured from the intersection of Tafel slopes.^{40,41} (Parts A and B of Figure 9 show the example of $\text{FeOC}_{16}\text{H}_{33}$ and of FeCF_3 and $\text{FeC}_6\text{F}_{13}$, respectively.) Table 3 summarizes these results in different media.

For all the modified metallic surfaces and in the different media of Table 3, the polarization resistances are larger than those for the untreated surfaces and the corrosion currents are lower clearly indicating the presence of the organic layer. There is also a good correlation between the results obtained for the polarization resistance measured through two different methods. The increase of R_p can be observed in Figure 7, which shows a larger slope (and therefore a larger R_p) for the polarization curve of an iron electrode grafted with dodecylphenyl groups than for that of an untreated electrode. This same resistance has also been measured by impedance measurements both on iron and mild steel (under a stationary state at E_{corr}). Figure 8A shows the impedance diagram for an iron electrode grafted by methylphenyl, butylphenyl, and dodecylphenyl groups, and Figure 8B shows the diagram with fluorophenyl substituents; in every case, one observes larger values of R_p ($R_p = \lim_{\omega \rightarrow 0} Z(\omega)$) for the modified surfaces. With alkyl chains, the polarization resistance increases when the length of the alkyl chain increases and one observes, as shown in Figure 10, a linear relation between the polarization resistance and the number of carbons on the chain. This linear relation strongly suggests that the alkyl chains are standing up on the iron surface. When the electrode is derivatized, a large difference is also observed in the capacitive part of the diagram; ω_{max} is larger than that for the bare electrode which indicates a lower value of the capacitance of the electrode ($C = 1/\omega_{\text{max}}R_p$). This lower capacitance is obviously due to the attachment of the organic layer on the electrode which creates a capacitance in series with the double layer. This same observation can also be made in 5% aqueous KCl.

Parts A and B of Figure 9 show the semilogarithmic plots $\log I = f(E)$ in 0.1 N H_2SO_4 for bare iron and for

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Table 2. FTIR Spectra of Phenyl Groups Attached to the Iron Surface

	CF stretching (cm ⁻¹)	C=C stretching (cm ⁻¹)	CH out-of-plane deformation (cm ⁻¹)
FeF	1300	1490, 1570	840
DF	1250	1480, 1575	840
fluorobenzene	1220	1500, 1600	805
FeCF₃^a	1280	1470	800, 875
DCF₃^a	1195, 1255, 1315	1480	840
α,α,α -trifluorotoluene ^{30,31}	1135, 1180, 1320	1460	770
FeOCF₃	1165, 1225	1410	670
DOCF₃	1205, 1260	1440	745
trifluoromethoxybenzene	1265	1395	695
FeC₆F₅	1020	1410, 1670	
DC₆F₅	1050	1550, 1650	
pentafluorobenzene ^{30,31}	1070	1410, 1535, 1645	

^a **FeCF₃** and **DCF₃** each also show a very strong band at 1045 and 1065 cm⁻¹, respectively.

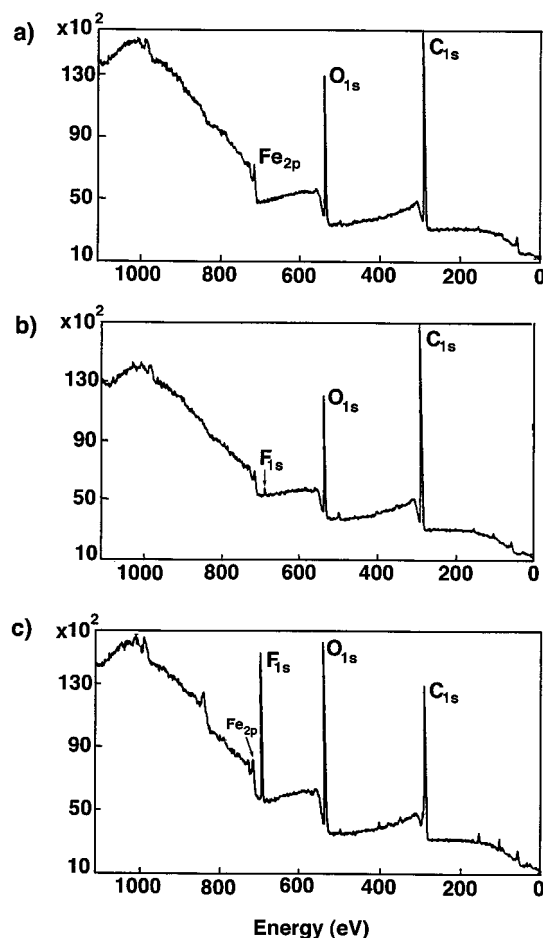


Figure 4. General XPS spectra of (a) an untreated iron plate, (b) **FeC₆F₅**, and (c) **FeC₆F₁₃**.

electrodes derivatized, respectively, with hexadecyloxy-phenyl groups **FeOC₁₆H₃₃** and fluoro phenyl groups **FeCF₃** and **FeC₆F₁₃**. The corrosion currents i_{corr} , which are obtained from these curves, are about 5–10 times lower than those obtained when an organic layer is attached to the iron surface. The corrosion potential shifts in an anodic manner (10–25 mV) for these groups. We have included in Table 3 the inhibition efficiency measured as $\text{I.E.} = 100(1 - i_{\text{corr}}^{\text{graft}}/i_{\text{corr}})$. The corrosion rate is inhibited both in acidic medium, where protons are the main oxidizing agents, and in neutral medium, where oxygen is responsible for the corrosion. In acidic medium, the corrosion potential is shifted toward anodic

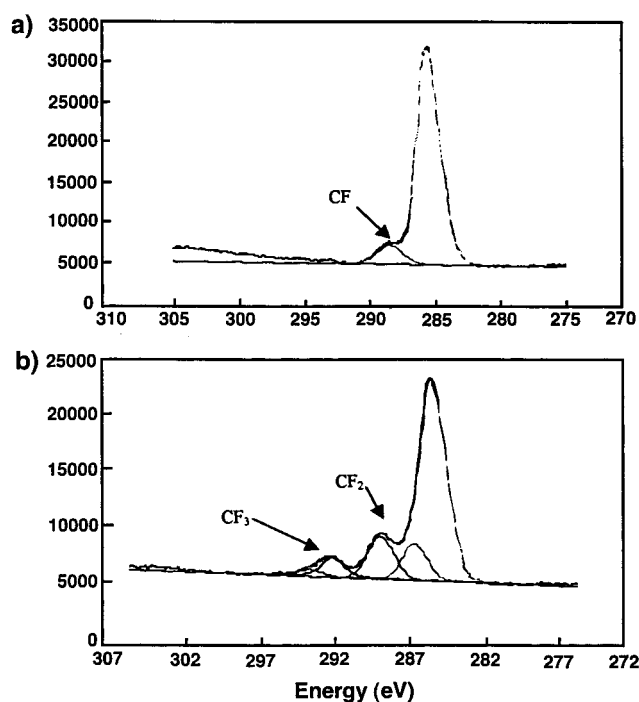


Figure 5. XPS spectra: C_{1s} region of (a) **FeC₆F₅** and (b) **FeC₆F₁₃**. Vertical scale is the intensity in arbitrary units.

potentials, indicating that the oxidation of iron is made more difficult.

We have measured the stability of the grafted layer as a function of the potential of the electrode. We prepared a steel electrode modified with iodophenyl groups **FeI** (by reduction of **DI** in an ACN + 0.1 M NBu₄⁺BF₄⁻ solution), as the iodine atom can be easily characterized on an iron surface both by XPS and Rutherford backscattering (RBS). This electrode was swept anodically from the corrosion potential in 0.1 N H₂SO₄ by the use of 75 and 150 mV at 1 mV s⁻¹. Then, the surface was examined by XPS and RBS; no significant variation of the surface concentration of iodine was observed for a 75 mV shift, but for a 150 mV shift, the iodine signal disappeared. On a 0.07 cm² mild steel electrode that was protected with iodophenyl groups, 9.8 mC were consumed for a 75 mV anodic shift from the corrosion potential; this charge corresponds to 5×10^{-8} moles of iron being dissolved (as also checked by titration of the solution by atomic absorption spectroscopy). This indicates that at more anodic potentials, the organic groups

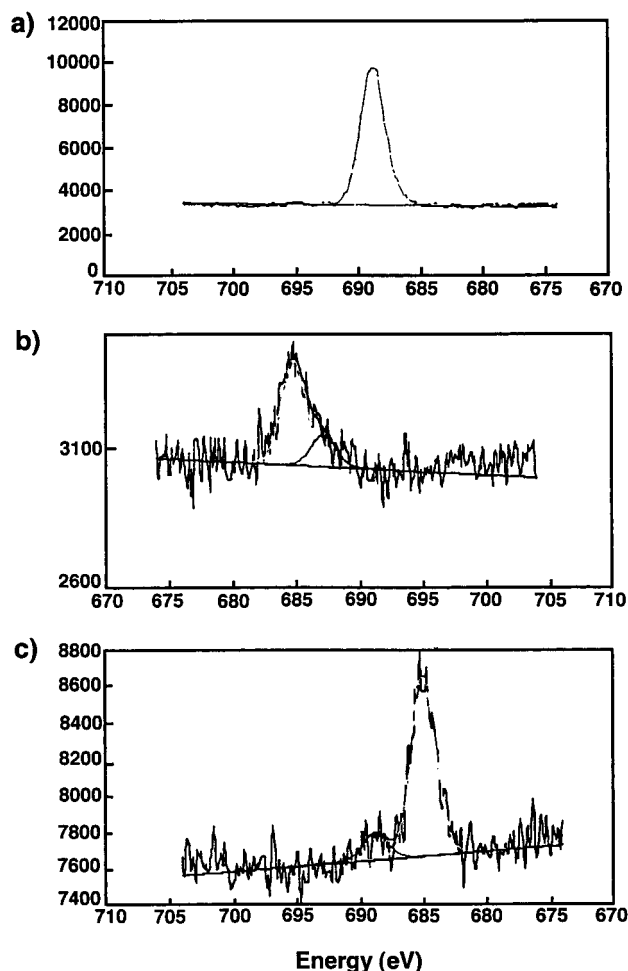


Figure 6. XPS spectra: F_{1s} region of (a) FeC_6F_{13} , (b) FeC_6F_5 , and (c) $FeOCF_3$. Vertical scale is the intensity in arbitrary units.

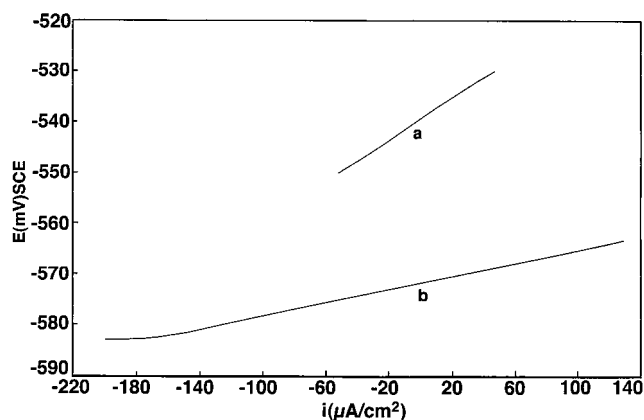


Figure 7. Polarization curve of 3 mm diameter iron electrode in a 0.1 N H_2SO_4 solution: (a) grafted with dodecylphenyl groups $FeC_{12}H_{25}$ and (b) untreated.

are cleaved from the surface simultaneously with the iron atoms. One can wonder how these organic groups cleave from the surface during the anodic corrosion process; do they cleave from the iron atom to which they are bonded or do they cleave as an organometallic species where the aryl group is still bonded to an iron atom? Therefore, the organic layers obtained by the reduction of diazonium salts reduce the corrosion rate of iron and steel although they do not completely block either the reduction of protons or oxygen or the oxida-

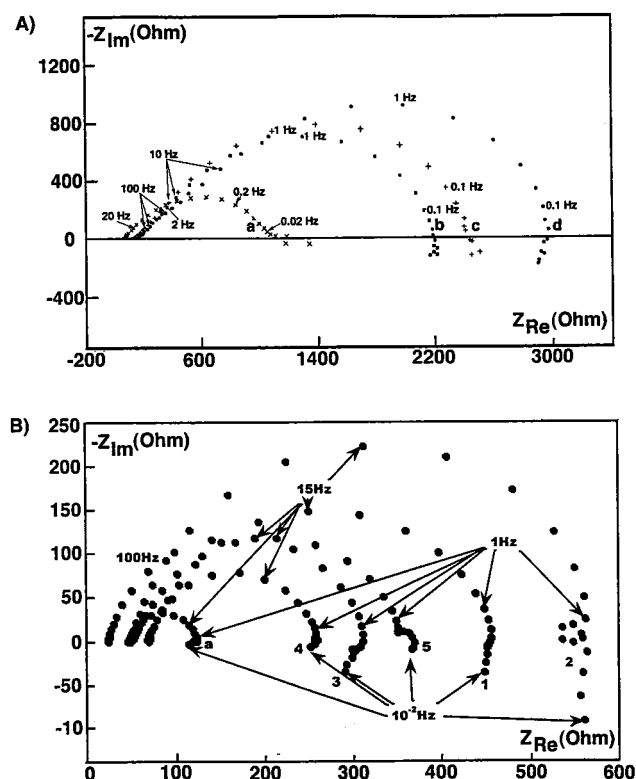


Figure 8. Impedance diagram of an iron electrode in 0.1 N H_2SO_4 . Upper curves A: (a) untreated, (b) grafted with methylphenyl groups $FeCH_3$, (c) grafted with butylphenyl groups FeC_4H_9 , and (d) dodecylphenyl groups $FeC_{12}H_{25}$. Lower curves B: (a) untreated; (1) FeF , (2) $FeCF_3$, (3) $FeOCF_3$, (4) FeC_6F_5 , and (5) FeC_6F_{13} .

tion of iron. They are, however, quite stable as they resist an anodic shift of potential of 75 mV.

Discussion

The inhibition efficiencies of Table 3 suggest the following comments. The electrolysis time of the grafting reaction does not seem to influence the structure of the organic layer very much; FeC_6F_5 was grafted during 30 s or 30 min, and the measured I.E. changed only from 66 to 78%. With alkyl substituents, the increase of the chain length from 4 to 16 carbons does not bring about much change in the I.E.; the resistance polarization indicates that the alkyl chains stand up on the surface, and the protective layer should therefore be thicker but the thicker layers may be less compact giving, altogether, the same order of protection as the shorter chains. As for the fluoro compounds, the I.E. does not seem to depend on the structure of the substituent, with a single fluorine atom affording the same protection as a six-carbon perfluorinated chain.

The inhibition efficiencies which are obtained with the above method and reported in Table 3 can be compared with those obtained, for example, by adsorbing propargylic alcohol ($c = 0.5$ mM). In this last case, it reaches, approximately, 90% in 0.5 M H_2SO_4 . The inhibition which is observed in Table 3 is therefore equivalent to that which is obtained with alkynols;^{33,37} however, in this last case, the inhibitor is in solution and a constant equilibrium is maintained between the molecules in solution and those on the surface. This is not the case

Table 3. Polarization Resistance and Corrosion Currents of Modified Iron and Steel Surfaces

sample	diazonium salt ^a	corrosive medium	R_p^b ($\Omega \text{ cm}^2$)	R_p^c ($\Omega \text{ cm}^2$)	i_{corr}^d ($\mu\text{A cm}^{-2}$)	E_{corr}^e (mV)	I.E. ^f
iron ^g	none	H ₂ SO ₄ , 0.1 N	78	71	570	-551	
iron	DC₄H₉	H ₂ SO ₄ , 0.1 N	154	162	117	-520	79
iron	DC₁₂H₂₅	H ₂ SO ₄ , 0.1 N	207	190	101	-523	82
iron	DOC₁₂H₂₅	H ₂ SO ₄ , 0.1 N	142	182	84	-541	85
iron	DF	H ₂ SO ₄ , 0.1 N	193	241	55	-545	90
iron	DCF₃	H ₂ SO ₄ , 0.1 N	276	293	47	-527	92
iron	DOCF₃	H ₂ SO ₄ , 0.1 N	293	168	60	-537	89
iron ^h	DC₆F₅	H ₂ SO ₄ , 0.1 N	188	175	125	-527	78
iron ⁱ	DC₆F₅	H ₂ SO ₄ , 0.1 N	182	164	122	-523	78
iron	DC₆F₁₃	H ₂ SO ₄ , 0.1 N	192	232	58	-520	90
steel	none	H ₂ SO ₄ , 0.1 N	95	106	168	-546	
steel	DC₁₂H₂₅	H ₂ SO ₄ , 0.1 N	224	337	48	-515	71
steel	DOC₁₂H₂₅	H ₂ SO ₄ , 0.1 N	219	254	43	-530	74
iron	none	NaClO ₄ , 5%	302	322	37	-690	
iron	DC₄H₉	NaClO ₄ , 5%	575	648	13	-637	64
iron	DOC₁₂H₂₅	NaClO ₄ , 5%	502	547	13	-636	64
iron	none	KCl, 5%	235	302	34	-692	
iron	DC₄H₉	KCl, 5%	630	658	6	-738	82

^a Used for the derivatization. ^b Obtained from the $i = f(E)$ curves. ^c Obtained from impedance measurements. ^d Obtained from Tafel slopes at E_{corr} . ^e In mV/SCE. ^f Inhibition efficiency. ^g Similar values are obtained for $i_{\text{corr}} = 497 \mu\text{A cm}^{-2}$, $R_p = 85 \Omega \text{ cm}^2$, and $E_{\text{corr}} = -500$ mV if the iron is first electrolyzed in ACN + 0.1 M NBu₄BF₄ in the absence of diazonium salt. ^h Electrolysis time of the diazonium is 30 s. ⁱ Electrolysis time of the diazonium is 30 min.

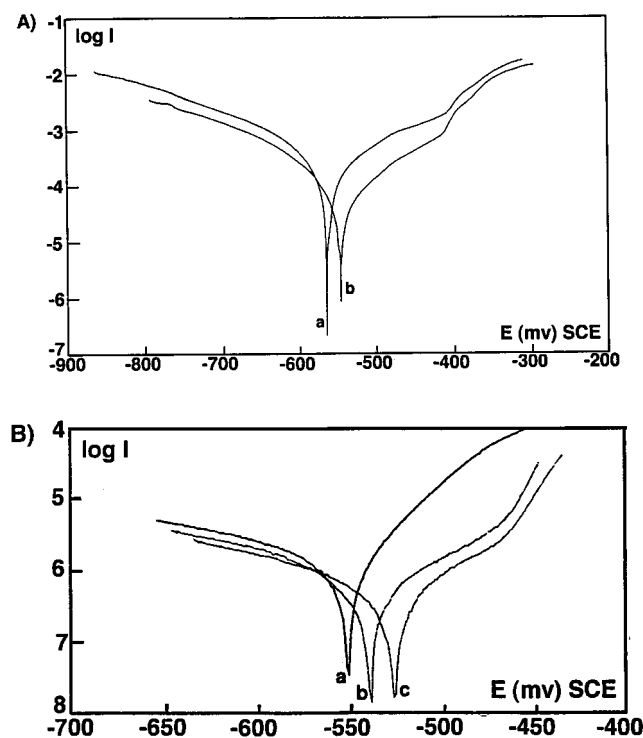


Figure 9. Semilogarithmic curves for the polarization of a 3 mm diameter iron electrode in 0.1 N H₂SO₄ solution. A: (a) untreated and (b) grafted with hexadecyloxy groups **FeOC₁₆H₃₃**. B: (a) untreated, (b) grafted with trifluoromethyl phenyl groups **FeCF₃**, and (c) grafted with perfluorohexyl phenyl groups **FeC₆F₁₃**. I in A.

considered here; once the organic group is cleaved, it cannot be replaced.

Comparison can also be made with hydroxyl terminated long chain (C₁₂, C₁₈) alkanethiols adsorbed on iron and further reacted with octyltriethoxysilane to both increase the chain length and provide lateral binding between the chains.⁴² With a C₁₈ alkanethiol in the weakly aggressive medium of 0.5 M NaCl, the transfer

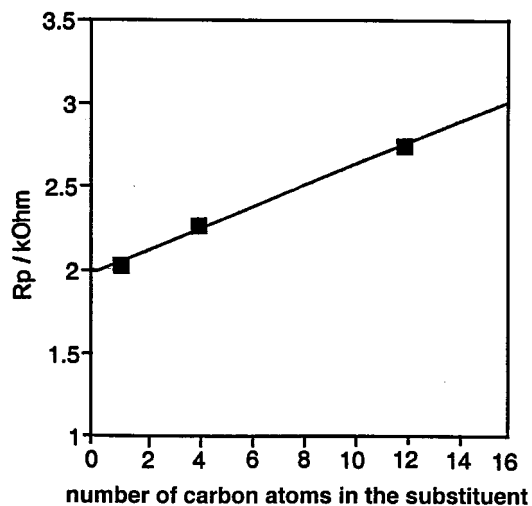


Figure 10. Polarization resistance R_p of an iron electrode derivatized with alkylphenyl chains as a function of the number of carbons in the alkyl chain.

resistance was increased about four times; after reaction with octyltriethoxysilane, the increase was about 4.5. However, the main drawback of this process is that the thiols desorb slowly from the iron surface. In a very interesting investigation, self-assembled monolayers of phosphonic acids have been used for the protection of engineering metals.⁴³ α,ω -Metal bisphosphonates self-assembled monolayers can be complexed by organic acids and acid-containing polymers such as fluoropolymers and ethylene-*co*-methacrylic acid. This property has been exploited in the construction of polymer/SAM/metal interfaces which can protect the metal from a hostile NaCl-water environment.

Metallic surfaces such as Fe, Ni, Pt, and Au have also been covalently modified by the electrochemical reduction of vinylic monomers such as acrylonitrile, methacrylonitrile, and butenenitrile. Thin polymeric layers (~ 10 – 50 nm) that are covalently bonded to the metal,

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the structures of which have been thoroughly investigated, are obtained.^{44–46} Protection of metal from corrosion by this process has been briefly investigated.⁴⁶ This process is somewhat similar to that described in this paper, as in both cases, a covalent bond is formed between the metal and the organic layer.

In a different way, conducting polymers such as polypyrrole or polyaniline can be deposited (but not covalently bonded) on mild steel or zinc by electro-oxidation.^{47–50} The electrosynthesis of polymer films on coinage metals is easy to carry out; it is much more difficult with oxidizable metals such as Fe, Zn, and Al,

as the oxidation potential of the metal is much more negative than that of the monomer and therefore dissolution of the metal will occur and stabilize the potential of the electrode at a negative value where monomer oxidation does not occur. Nevertheless, judicious choice of the electrolytic medium can reduce the dissolution rate of the metal without impeding monomer oxidation. The polymeric layers thus obtained evidence a protecting effect equivalent to the classical protective treatments used in the automotive industry.⁵⁰

As stated above, the strongly bonded organic layers obtained by reduction of diazonium salts on an iron surface provide a significant protection against corrosion. This protection could be improved by using these molecules for the further attachment of polymers; work is in progress to achieve this goal.

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