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Surface Modification of Conducting Substrates. Existence of Azo Bonds in the Structure of Organic Layers Obtained from Diazonium Salts

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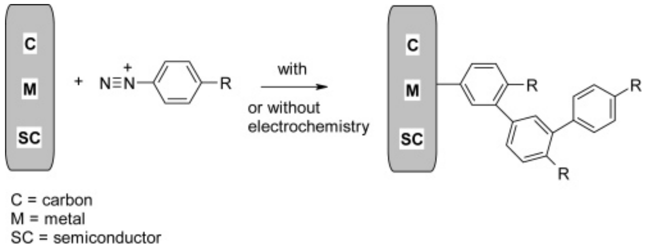
This paper analyzes the structures of organic layers that are obtained on metals or carbon by electrochemical reduction of diazonium salts or by simple dipping of the substrate in a diazonium solution. There is a general agreement in the literature on the polyphenylene structure of these layers. But, previous results based on XPS data have indicated the possible presence of azo groups in these layers. IR and TOF-SIMS experiments demonstrate the existence of these azo groups included in the polyphenylene chains. A mechanism is presented that accounts both for the growth of polyphenylene chains and the inclusion of azo bonds in these chains.

Introduction

Scheme 1



The electrochemical reduction of diazonium salts[1,2] on carbon, metal,[1c] or semiconductor electrodes leads to the formation of polyphenylene[3] layers covalently bonded[4] to the surface. The formation of similar layers can also be obtained without electrochemistry[5−7] by simple dipping of the substrate in the solution of the diazonium salt but also in a solution of the parent amine in the presence of sodium nitrite[5,8,9] or iso-amyl nitrite.[10] A structure has been proposed[11] for these polyphenylene layers; it is shown in Scheme 1. A mechanism has been published to account for their formation.[12] The large number of spectroscopic investigations performed on these layers has generally confirmed this structure. However, Bélanger[13] was the first to advocate the presence of azo (−N═N−) groups in the layer to account for the presence of XPS (X-ray photoelectron spectroscopy) signals at 400 eV. It is the purpose of the present paper to examine the possible presence of such groups and to propose a mechanism for their formation.

As indicated previously, the main support for the possible presence of azo groups in the polymeric layer produced by

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the reduction of diazonium salts is the observation of a 400 eV peak in the XPS spectra. This peak has been observed on carbon during the reduction of the 4-nitrobenzene diazonium on carbon,[1b,13] on platinum,[14] and on copper.[15] But, the 4-nitrobenzene diazonium is not a very good surface modifier to demonstrate the presence of azo groups; the nitro group (observed at 406 eV) can be reduced electrochemically, in particular, if the potential is swept to very negative potentials (−2.9V/Ag/Ag+ in ref 14). The electrochemical reduction of the nitro groups leads to hydroxylamino or amino groups,[16] the XPS signals of which are close to 400 eV. In addition, it has been demonstrated that nitro groups can be reduced under the XPS beam to produce signals at 400 eV.[7,17,18] The results obtained from diazonium salts not substituted by nitro groups are more convincing. The 400 eV XPS peaks have been observed from the electrochemical reduction of 4-carboxybenzene diazonium on carbon[13] and iron,[19] of 4-perfluorohexylbenzene diazonium on iron,[20] and of 4-iodobenzene diazonium on gold.[21] This 400 eV signal has also been observed by spontaneous grafting or electrografting of 4-bromobenzene diazonium on iron;[22] the peaks were of similar intensity with both procedures. After spontaneous grafting (without electrochemistry) of the benzene diazonium on copper,[15] the presence of the 400 eV peak was observed both on bare (deoxidized) Cu and on the native oxide Cu surface. Assigning the presence of the 400 eV peak to the azo groups, it was deduced that the film on bare Cu contained one azo group for the 5.9 phenyl ring, while the film on the native oxide Cu contained one azo group for every 17.4 phenyl ring. Very recently, Bélanger and Toupin[23] examined the XPS spectra of polyphenylene grafted carbon black by an in situ generated benzenediazonium salt. In this case, a 400 eV N1s signal was not detected on the untreated substrate, but a small signal was observed after the surface had been modified. This signal was observed up to 300 °C, indicating a strong covalent bond.[23] The attached polyphenylene layers will be referred to, for example, as ***Fe*CF$_3$** by the symbol of the substrate and the substituent of the diazonium salt.

Results and Discussion

We have analyzed the layers obtained from different diazonium salts (excluding 4-nitro for the reasons given previously) on different substrates in search of spectroscopic evidence for the —N═N— bond in the polyphenylene. Two spectroscopic techniques have been used: FTIR-ATR (Fourier transform infrared attenuated total reflection) and TOF-SIMS (time-of-flight secondary ion mass spectroscopy). The samples were prepared to limit the thickness (typically a few tenths of a nanometer) of the organic layers so that the IR beam probed the total thickness of the layer. Conversely, the ionic beam (Au$^+$ ions) of the TOF-SIMS only analyzed the extreme surface of the layer. Therefore, the two methods are complementary. To explore the depth of the layer by TOF-SIMS, the intensity of the characteristic fragments was recorded while a beam of Cs$^+$ ions etched the layer.

Table 1. IR (ATR) Spectra of Polyphenylene Layers

sample	preparation	position of the band[a] (cm^{-1})
Azobenzene	neat	1456 (s)
4-aminoazobenzene	neat	1461 (m)
4-phenylazobenzene-diazonium	neat	1458 (w)
***Cu*N═NC$_6$H$_5$**	electrochemical reduction (ACN)[b]	1458
***Fe*H**[1c,12b]	electrochemical reduction (ACN)[b]	1449
***Cu*H$_1$**	electrochemical reduction (ACN)[b]	1450
***Cu*H$_{2-4}$**[c]	chemical grafting[c]	1456−1457
***Cu*Br**	electrochemical reduction (ACN)[b]	1457
***Au*I**	electrochemical reduction (ACN)[b]	not detected

[a] We have checked that these bands do not appear in the corresponding diazonium salt and therefore that they pertain specifically to the polyphenylene layer. [b] See Experimental Section. [c] ***Cu*H$_2$**: Bare Cu, dipping in the diazonium solution (ACN), or ***Cu*H$_3$**: native Cu, dipping in the diazonium solution (ACN), or ***Cu*H$_4$**: native Cu, dipping in the diazonium solution (0.1 N H$_2$SO$_4$).

We have examined samples both electrografted and chemically grafted. Cu samples were prepared with and without previous deoxidation of the surface and both in ACN (acetonitrile) and in dilute sulfuric acid to test whether the preparation of the surface had any influence on the formation of azo groups (see Experimental Procedures for the preparation of the surfaces).

Table 1 reports the position of the IR azo bands observed on different substrates altogether with the spectrum[24] of azobenzene, of its 4-amino derivative, of 4-phenylazo benzenediazonium, and that of 4-phenylazo phenyl groups attached to a copper surface. Figures S4−S8 in the Supporting Information present the spectra of azobenzene, 4-aminoazobenzene, ***Cu*N═NC$_6$H$_5$**, ***Cu*H$_2$**, and ***Cu*Br**.

We also examined different samples by TOF-SIMS. After a careful mass calibration of the spectrum, it is possible to obtain an exact mass for the different peaks that are observed. This permits an unambiguous assignment of the fragments. We have included in Table 2 the fragments observed on the TOF-SIMS spectrum of 4-phenylazo polyphenylene layers as a reference (obtained by electrochemical reduction of the 4-phenylazo benzenediazonium $^{+}{}_{2}$**NC$_6$H$_4$—N═N—C$_6$H$_5$**). A more detailed table (Table S3 in the Supporting Information) gathers all the significant fragments and the area of the peaks. Figure 1 presents an example of the fragments (obtained from a very thin layer on carbon).

We have also measured the relative intensities of the fragment **C$_6$H$_5$N═N$^+$** in the spectra of ***Cu*H** prepared in

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Table 2. TOF-SIMS Spectra of Polyphenylene Layers

sample	fragment	structure of the fragments
CuN=NC$_6$H$_5$[a]	A and B	fragment A, $m/z = 105.045$
FeH[a]	A and B	**$C_6H_5{-}N{=}N^+$**
CuH$_1$[a]	A and B	fragment B, $m/z = 182.084$
CuH$_{2-4}$[b]	A	**$C_6H_5{-}N{=}N{-}C_6H_5^+$**
CH[a]	A and B	
CCOOH[a]	A	
CuBr[a]	C and D	fragments C and D, $m/z = 182.956$, 184.954[c] **$Br{-}C_6H_4{-}N{=}N^+$**
FeCF$_3$[a]	E and F	fragment E, $m/z = 173.032$ **$CF_3{-}C_6H_4{-}N{=}N^+$** fragment F, $m/z = 251.079$ **$CF_3{-}C_6H_4{-}N{=}N{-}C_6H_5^+$**
AuI[a]	G and H	fragment G, $m/z = 216.939$ **$IC_6H_4N^-$** Fragment H, m/z = 231.950 **$IC_6H_5N_2+$**

[a] Prepared by electrochemical reduction in ACN. [b] Prepared as follows: **CuH$_2$**: bare Cu, dipping in the diazonium solution (ACN), or **CuH$_3$**: native Cu, dipping in the diazonium solution (ACN), or **CuH$_4$**: native Cu, dipping in the diazonium solution (0.1 N H_2SO_4). [c] Corresponds to the two isotopes of bromine.

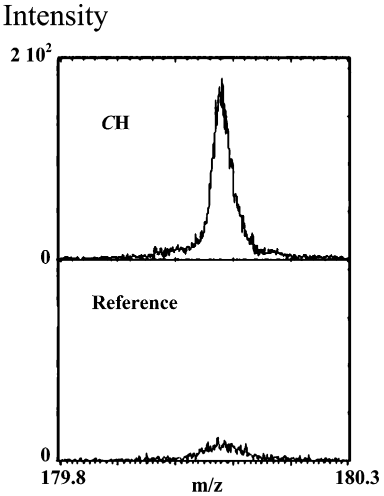


Figure 1. Fragment **$C_6H_4N{=}NC_6H_4^+$** from **CH** (prepared by electrochemical reduction of benzenediazonium on glassy carbon) (top) and untreated glassy carbon as reference.

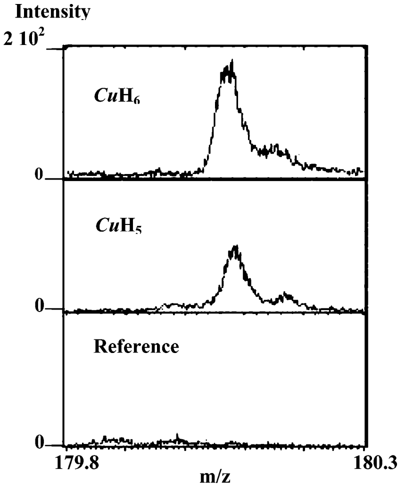


Figure 2. Fragment **$C_6H_4N{=}NC_6H_4^+$** from a thin (5.4 nm, **CuH$_5$**) and a thick (80 nm, **CuH$_6$**) **CuH** layer (see text) obtained by electrochemical reduction of bezenediazonium on copper.

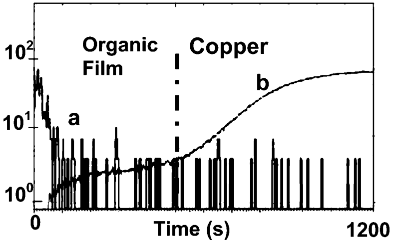


Figure 3. Etching of the organic layer with Cs^+ ions. Profile through a 80 nm thick **CuH$_6$** layer. Increasing etching time corresponds to the analysis of a deeper and deeper position inside the organic layer. Polyphenylene−copper interface at the crossing of the two signals is attained after ~550 s of etching. (a) Fragment **$C_6H_5N_2^+$** and (b) copper.

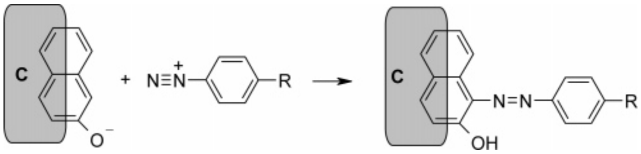
different ways (see Experimental Procedures). TOF-SIMS is not a quantitative method, and the peak intensity depends on the environment of the fragment that is extracted, but for very similar layers and under identical experimental conditions, the comparison of peak intensities gives a good idea of the relative concentration of azo groups in the organic layer. The intensity of the peak due to the **$C_6H_5N{=}N^+$** fragment depends on whether the samples are prepared chemically or electrochemically and varies by a factor not larger than 3. The relative concentration of N=N groups calculated from the IR spectra lies in a similar range. Therefore, the amount of azo groups at the surface of the layer does not depend significantly on the sample preparation whether by electrochemistry or by simple dipping in a diazonium solution (in ACN or in aqueous medium). The range of variations is the same as that observed by McCreery and Hurley.[15]

We also tried to find whether the concentration of azo groups varied within the layer. We therefore examined two layers of polyphenylene on copper; the first one (**CuH$_5$**) was obtained in a single scan (50 mV s^{-1}) from the open circuit potential (−0.26 V/SCE) to −1.10 V/SCE in a 1 mM solution of benzenediazonium, the second one (**CuH$_6$**) was obtained by chronoamperometry (−1.10 V/SCE for 30 s) from a 10 mM solution. The height (d) of the two layers was measured by ellipsometry: **CuH$_5$**: $d = 5.4 \pm 0.9$ nm and **CuH$_6$**: $d = 80 \pm 1.6$ nm. Figure 2 presents the fragment **$C_6H_4N{=}NC_6H_4^+$** observed on these layers. The intensity of **CuH$_6$** is less than twice that of the same peak obtained from **CuH$_5$**. A similar ratio is observed for the peaks $C_6H_4N_2^+$, $C_6H_5N_2^+$, $C_6H_4N_2C_6H_6^+$, and $C_6H_5N_2C_6H_5^+$ (not shown).

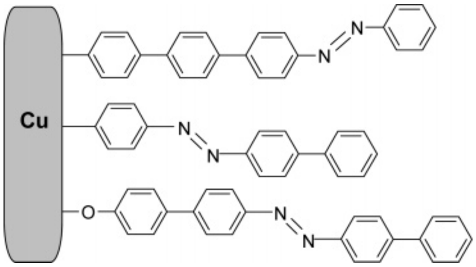
The concentration of azo groups through the **CuH$_6$** layer was also determined by etching the polymeric layer with a Cs^+ ion beam. The intensity of $C_6H_5N_2^+$ (Figure 3) was measured as a function of time during etching. Its intensity remains approximately constant through the layer, but a 10-fold increase is observed close to the outer surface of the layer. This is in agreement with the previous observation of a somewhat larger signal for a thick layer as compared to a thin layer. This corresponds to an increased concentration of azo groups at the outer surface of the layer, and we speculate that it is related to steric effects. As we shall see next, the structure of the layer becomes more and more sterically crowded as the number of azo groups increases (structure **9** in Scheme 6). As the thickness of the layer increases, it becomes rougher and rougher,[7a] and this would favor the presence of a larger amount of azo groups.

We also tried to confirm the presence of azo bonds directly on the surface of carbon (Scheme 2) as proposed by Bélanger

Scheme 2



Scheme 3

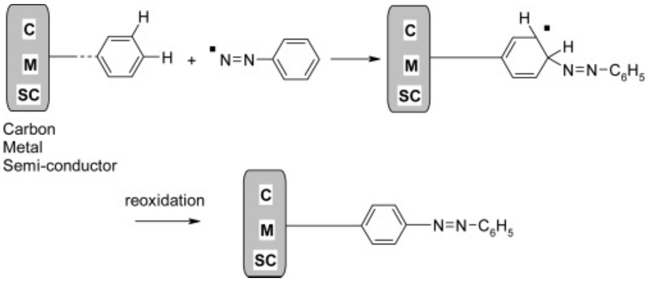


et al.[13,23] For this purpose, we prepared a very thin layer (***C*H**) of polyphenylene on a carefully polished glassy carbon by reduction of a 1 mM solution of benzenediazonium. A single scan cyclic voltammogram was recorded from +0.2 to −0.2 V/SCE at 50 mV s^{-1}. Under similar conditions, McCreery et al.[25] obtained a monolayer of biphenyl on an atomically flat carbon (pyrolized photoresist). Under these conditions, peaks were observed by TOF-SIMS that correspond to $C_6H_5N_2^+$ (A) and $C_6H_5N_2C_6H_5^+$ (B) but also $C_6H_4N_2^+$, $C_6H_4N_2C_6H_5^+$, $C_6H_5N_2^+$, and $C_6H_4N_2C_6H_4^+$. Very interestingly, a small peak can be assigned to $\mathbf{C(OH){-}C{-}N{=}N{-}C_6H_5^+}$, and this fragment can be assigned to the structure shown in Scheme 2. A large peak is also observed that can be tentitatively assigned to $\mathbf{CH_3{-}C_{13}H_{26}{-}CH(OH){-}NH{-}NH_2^+}$, and it would correspond to part of the carbon of the electrode with a hydrazine group resulting from the hydrogenation of an azo group. This gives confidence in the existence of this structure proposed by Bélanger et al.[13,23] Altogether, with the XPS data reported in the Introduction, the previous IR and TOF-SIMS data indicate the presence of azo bonds in the polymeric layer formed upon the reduction of aromatic diazonium salts on carbon, copper iron, and gold.

What can be the mechanism leading to the formation of these azo bonds? Bélanger et al.[13,23]assigned their formation to the reaction of diazonium salts with the phenoxy functions located on the carbon surface as shown in Scheme 2. This reaction is well-known and is used for the synthesis of many coloring matters.[26] From the ratio of the NO_2 (406 eV)/N (400 eV peak), it was concluded that 75% of the aryl groups was bonded to the carbon by N=N− bonds.

McCreery and Hurley[15] proposed the formation of azo bonds inside the layer as shown in Scheme 3. In this case, a diazonium ion would attack the outer aromatic ring. This outer phenyl ring would be electron-rich, with copper acting as an electron donor substituent. However, polyphenylene layers several nanometers thick can be obtained with and without electrochemical induction, and it is unlikely that an electron donating inductive effect could be operative through so many aryl groups (0.6 nm ≈ 1 monolayer). These authors judge the presence of azo bonds directly bonded to the surface of copper unlikely for two reasons: (i) copper is a promoter of the dediazonation reaction (Sandmeyer and Gatterman reaction)[27] and (ii) a Cu−N=N−aryl structure would give two signals in XPS.

Scheme 4



Let us try to rationalize the formation mechanism of these azo bonds. First of all, are there azo bonds directly on the surface? The mechanism proposed by Bélanger et al.[13,23] on carbon (Scheme 2) seems very likely. Oxygen functions are present on the surface of carbons, they can be chemically modified[28] in many ways, and the reaction of diazonium salts with, for example, β-naphtol is a classical method for the qualitative detection of diazonium salts.[29] Our experiments with a close to monolayer surface of polyphenylene on carbon indicate the presence of several fragments that can be assigned to the presence of an azo bond. In addition, the existence of a fragment $\mathbf{C(OH){-}C{-}N{=}N{-}C_6H_5^+}$ is in good agreement with Scheme 2. On metals, the reaction of diazonium salts with surface oxide is not known, and therefore, the reaction with the surface should be restricted to carbon. We can now discuss the mechanism responsible for the formation of azo bonds in the middle or at the extremity of polyphenylene chains.

The first reaction that could be considered is the reaction of a diazenyl radical with an aromatic ring attached to the surface as in Scheme 4.

This mechanism implies the existence of a diazenyl radical, and it has been demonstrated that such radicals are not intermediates in the electrochemical reduction of diazonium salts[30] at a low driving force (i.e., at potentials that are not very negative). These diazenyl radicals can, however, be produced at a high driving force[31] (by pulse radiolysis) or at very negative potentials. Very negative potentials (to −2.9 V/Ag/Ag^+) were used by Bureau et al.,[14] and in this case, it may be that the 400 eV XPS peak is partly due to azo bonds, but most of the signals should correspond to amino groups obtained by the reduction of nitro groups. Another possibility would imply the reaction of the diazonium cation itself with

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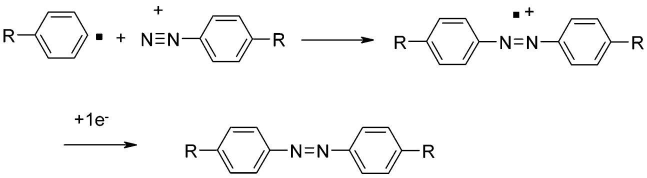
Scheme 5



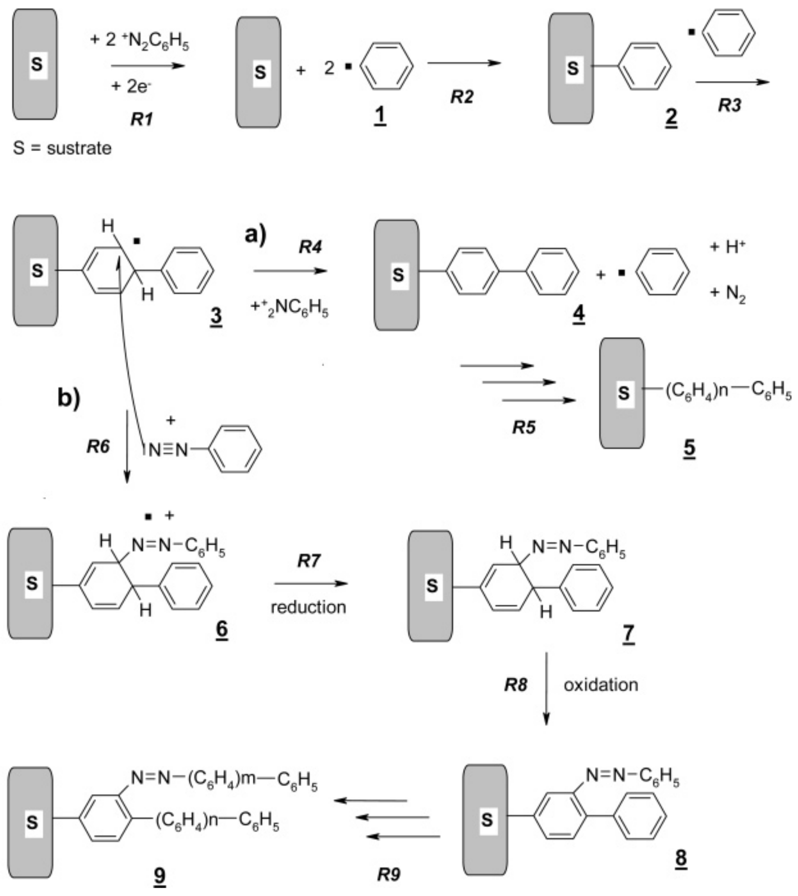
an aromatic ring at the end of the chain, but such a reaction only occurs if the aromatic ring is activated by OH or NH_2 groups as discussed previously.[26]

One could also consider the reaction of a diazonium salt with an aryl radical in solution, but such a reaction would produce an azobenzene in solution after reduction of the radical cation (Scheme 5). Diazenes (**Ar—N═N—Ar′**) are indeed formed, as side products, during the dediazonation reaction in the presence of aromatics.[32−34] This dediazonation reaction is realized in aqueous media in the presence of a base along the Gomberg−Bachmann procedure,[32,33] and it produces aryl radicals in a solution containing diazonium ions. This situation is not so different from that taking place during electrografting. The reaction shown in Scheme 5 also has been confirmed by ESR[35] (electronic spin resonance). But, if an azobenzene was obtained through this reaction, it would be formed in solution. If, for some reason, it were entrapped in the organic layer, it would be rinsed away as most of the groups working on the subject have carefully rinsed their samples, often under ultrasonication. Therefore, even if the formation of azobenzene could be possible in solution, it should not be found in the organic layer under the experimental conditions commonly used.

In our opinion, the most likely mechanism for the formation of azo bonds in the organic layer is summarized in Scheme 6 (for an unsubtituted benzene diazonium for sake of simplicity). It is derived from the mechanism that has been previously published for the growth of polyphenylene layers.[12] Reaction **R1** involves the monoelectronic reduction of two diazonium salts to give two aryl radicals. One of these two radicals binds to the substrate (**R2**), while the second one attacks the already grafted phenyl group **2** to give a cyclohexadienyl radical **3**, through reaction **R3**. At this point, two ways are opened: the first one (i) through reactions **R4** and **R5** leads to a pure polyphenylene layer **5**. Reaction **R4** is an electron exchange leading to the reoxidation of the cyclohexadienyl radical and reduction of a benzenediazonium. These reactions have been previously discussed and supported by literature data.[12]

The formation of azo bonds (path b) in the polymeric chains begins by an attack of a diazonium on the cyclohexadienyl radical **3**; this reaction is similar to that shown in Scheme 5, the aryl radical being replaced by a cyclohexadienyl radical. The addition of a cyclohexyl radical with a diazonium salt previously has been observed[36,37] to give a diazene. Reaction **R6** gives rise to a radial cation **6** that should be readily reduced (**R7**) to give **7**. This reduction can take place through an electron exchange with the metal either connected or not (electron transfer can occur through the layer[25]). Alternatively, an electron exchange with an aryl radical is possible. Reaction **R8** involves the reoxidation of a cyclohexadiene; the driving force for this reaction being the restoration of the aromaticity and of the conjugation of

Scheme 6



Scheme 7

$$\mathbf{6} + C_6H_5N_2^+ \rightarrow \mathbf{8} + C_6H_5^{\bullet} + N_2 + H^{\bullet}$$

the two substituants. Alternatively, if one considers the sum of reactions **R7** + **R8** leading from **6** to **8**, it amounts to the addition of one electron and the loss of two hydrogen atoms. This is equivalent to the reaction shown in Scheme 7 (i.e., to the reaction of a diazonium salt with **6** and to the formation of **8**, a phenyl radical, nitrogen, and a proton).

The aryl radicals formed in reaction **R4** and possibly **R7** + **R8** could now attack the phenyl groups as in reaction **R3** leading to the growth of the chain through reactions **R2** + **R3** + **R4** + **R5** or **R2** + **R3** + **R6** + **R7** + **R8** + **R9.** Reactions **R4** and **R7** + **R8** are responsible for the (at least) partly catalytic mechanism. This explains the growth of polyphenylene layers even without electrochemistry, but also the presence of azo bonds in these layers.

Conclusion

The presence of azo bonds in the covalently bonded layers obtained by reduction of diazonium salts has been previously advocated. These previous investigations were based on the observation of N_{1s} 400 eV peaks. But, such XPS peaks may as well correspond to amines or other nitrogen functions. The present study brings a strong support to the existence of azo bonds. TOF-SIMS experiments clearly evidence fragments such as **Ar−N═N** or **Ar−N═N−Ar**, where Ar is a substituted or unsubstituted aryl group. A mechanism is presented that rationalizes, at the same time, the formation of polyphenylene chains and the presence of azo bonds included in these chains.

Experimental Procedures

The diazonium salts were prepared[29] from a cold (in ice) solution of the corresponding amines (1 mM) in HBF_4 by the slow addition of $NaNO_2$ (1.1 mM) dissolved in the minimum amount of water. The precipitate was filtered, washed with ether, and dried in vacuum.

The iron substrate was a coupon of mild steel of 99% purity polished with a polishing cloth (DP-Nap, Struers) using 1 μm diamond paste. The copper substrate was a coupon of copper deposited (by physical vapor deposition, −PVD) on Si wafers. The gold substrate is deposited by PVD on a chromium layer on top of glass. The carbon substrate is a piece of glassy carbon (Tokai) polished with 1 μm diamond paste. All the samples were rinsed in acetone under sonication (10 min) before use.

Films thicknesses were measured by ellipsometry with a Sopra GES5 spectroscopic analyzer equipped with a microspot. The angle of the incident beam was 75° and that of the analyzer was 20°. A model for polymers on copper was used.

TOF-SIMS spectra were obtained with an ION-TOF IV with Au^+ primary ions at 25 keV. The analyzed zone was 150 μm^2, and the acquisition time was 75 s. Blank samples were analyzed in the same run as the modified samples. Etching of the polymeric layer on a 500 μm^2 surface was obtained with a Cs^+ ion beam. Analysis of the etched surface was performed in between the etching periods. The peak intensity refers to the area of the peak normalized to the total intensity of the spectrum.

The IR spectra are recorded on a Bruker Tensor 27 used in the total infrared reflection mode. The spectrometer was equipped with a Durascope accessory (from Sens IR Technology), where the sample was pressed against a diamond window. This accessory is a micro-ATR system that makes use of a diamond base sampling platform. The same Au, Pt, Cu, and Fe plates are used for recording the background and the spectra. In every sample, the absence of the IR diazonium band was ascertained, indicating a proper rinsing of the sample.

The potentiostat was a VPM from Princeton Applied research with BioLogic software. The electrochemical cell was equipped with a saturated calomel electrode (SCE) reference. A carbon counter electrode and the sample to be electrografted were the working electrode, and the solutions were deoxygenated.

***Cu*N═NC$_6$H$_5$**, ***Fe*H**, ***Cu*H$_1$**, ***C*COOH**, ***Cu*Br**, ***Fe*CF$_3$**, and ***Au*I** were obtained by electrochemical reduction of a 10 mM solution of the corresponding diazonium in ACN + 0.1 M NBu_4BF4. Electrografting was achieved in the potentiostatic mode at −1.1 V/SCE for 300 s.[12b] After electrolysis, the sample was carefully rinsed with acetone.

Chemically grafted samples of ***Cu*H** were obtained in the following way: (i) ***Cu*H$_2$** bare Cu, dipped in the diazonium solution (ACN). The sample was rinsed with acetone, dipped for 30 s in 2.5% citric acid, rinsed with deoxygenated acetone, dried under nitrogen, and immediately immersed in a deoxygenated 10 mM solution of benzene diazonium in ACN for 10 min and finally rinsed with acetone. (ii) ***Cu*H$_3$** native Cu was dipped in the diazonium solution (ACN). The same procedure as stated previously without deoxidation of the surface with citric acid was performed. (iii) ***Cu*H$_4$** native Cu was dipped in the diazonium solution (H_2SO_4 0.1 N). The same procedure as stated previously replacing ACN by H_2SO_4 0.1 N was performed. In this case, the surface was deoxidized by the solution itself.

In addition, samples were prepared to investigate the effect of the thickness layer: (iv) ***Cu*H$_5$**, was prepared on copper in a 1 mM solution by a single scan (scan rate: 50 mV s^{-1}) from the open circuit potential (−0.26 V/SCE) to 1.1 V/SCE to obtain thin layers. (v) ***Cu*H$_6$** was prepared in the same way as ***Cu*H$_1$** for comparison with ***Cu*H$_5$**. (vii) ***C*H** was prepared from a 1 mM solution of benzenediazonium by a single scan of the glassy carbon electrode from + 0.2 to −0.2 V/SCE at 50 mV s^{-1}.

Supporting Information Available: Table S3 and Figures S4−S8. This material is available free of charge via the Internet at http://pubs.acs.org.

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