Understanding the Redox-Induced Polymer Grafting Process: A Dual Surface-Solution Analysis

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As recently reported, the Graftfast process is a grafting method that provides covalently grafted polymer films. It relies on the chemical reduction of diazonium salts by reducing agents in absence or presence of a vinylic monomer. Contrary to electroinduced methods delivering strongly grafted and stable polymer films such as cathodic electrografting (CE) of vinylic monomers (which requires drastic experimental conditions) or surface electroinitiated emulsion polymerization (SEEP), the Graftfast process provides strongly grafted polymer films on any type of materials (conductors, semiconductors, and insulators). Moreover, it is a fast one-step reaction occurring at atmospheric pressure, ambient air and room temperature in water, which makes it more suitable for applications than the slower ATRP-based methods. This article aims to complete the first paper on this process by giving preliminary answers to the question: How does the Graftfast process work? To achieve this mechanistic study, dual surface-solution analyses were performed. Both spontaneous and redox-induced grafting of polynitrophenylene-like (PNP) films and poly(hydroxyethyl) methacrylate (PHEMA) films were analyzed by infrared-attenuated total reflection (IR-ATR) and X-ray photoelectron spectroscopy (XPS) while the corresponding reactive solutions were studied by electronic paramagnetic resonance, EPR (spin-trapping method using 2-methyl-2-nitrosopropane MNP as spin-trapping agent). The EPR spectra and hyperfine structure of MNP adducts provide evidence of aryl radicals production, growing polymer chains radicals formation, and the existence of critical concentration values, leading to favorable grafting kinetics.

1. Introduction

Surface modification of materials via the grafting of polymer films with specific chemical functionalities has become a crucial issue in the last two decades. Indeed, various fields of application such as depollution, microelectronics, automobile, biomedical, and lubrication are interested in giving surfaces new properties (adhesion, wettability, biocompatibilization, etc.). To induce new properties to materials, researchers have explored the synthesis of organic, mineral, or composite layers through "physisorption" or "chemisorption" methods. The former includes, for example, painting, spin coating, vacuum evaporation, or the Langmuir−Blodgett technique but leads to quite fragile coatings. On the contrary, the latter creates a true chemical bonding between the organic film and the substrate and groups together

techniques such as plasma polymerization,[1,2] self-assembly of mono- and multilayers,[3−5] atom-transfer radical polymerization (ATRP),[6,7] ring-opening metathesis (ROMP),[8] and anodic[9] or cathodic electropolymerization[10] (including the latest electrochemical grafting technique developed in our lab called SEEP for surface electroinitiated emulsion polymerization[11,12]). However, vacuum coating techniques are complex, expensive, and appropriate only for small substrates; self-assembled monolayers are fragile (except in the case of silanes on oxides) and limited to a few substrate-molecule couples; ATRP and ROMP allow to control the thickness and the molecular weight of the grafted polymer but involve high temperature and long reaction time;[13]

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finally, cathodic electrografting leads to strongly adherent films but is restricted to (meth)acrylic derivatives and conductive or semiconductive surfaces.[13,14]

To overcome these limitations, an innovative chemical synthesis method called Graftfast, described for the first time by Mévellec et al.,[15] has been recently developed to graft organic polymer films onto any type of surface. Indeed, this coating technology applies to insulators or conductors, materials from glass to metal including Teflon (PTFE), natural plastics like latex or rubber, cellulose (wood, paper), artificial or natural fibers, ceramics, nanoparticles, carbon nanotubes, etc. This process leads to stable, homogeneous, and covalently grafted polymer films with controlled thickness. It is an extremely simple process that consists of a short one-step reaction occurring at atmospheric pressure, ambient air, and room temperature in water (green chemistry). The Graftfast reaction takes inspiration from the electrochemical reduction of diazonium salts,[16,17] an attractive method for easy surface modification on carbon,[18] metals,[19] and semiconductors[20-22] widely investigated for the past 10 years. Instead of an electrochemical reduction (responsible for most of the limitations of this process), Graftfast is based on a simple redox activation of aryl diazonium salts (strong oxidizing agents) with a reducing agent as, for instance, iron powder, hypophosphorous acid or L-ascorbic acid in absence or presence of a vinylic monomer. The Graftfast process leads to the formation of a grafted polyphenylene-like (PP) layer when no vinylic monomer is present or to thin grafted polymer films, when a vinylic monomer is present in the starting mixture (in this paper, "polymer" exclusively refers to chains obtained from the polymerization of vinylic monomers, whereas aryl radicals (from the diazonium salt reduction) form what we call polyphenylene-like layers).

If the mechanism of the electroreduction of aryl diazonium salts with or without vinylic monomer has been widely reported in the literature[18,23,24] and more recently by Tessier et al.,[12] the mechanism originally proposed by Mévellec et al. for the Graftfast process[15] has not yet been experimentally evidenced, although both rely on the reduction of the diazonium salt into aryl radicals, which

are then able to (i) form a grafted polyphenylene-like film on the substrate[25-27] and (ii) initiate the radical polymerization of the monomers if present. Recent works by Adenier et al. have also demonstrated the spontaneous grafting of a PP layer at reducing metals surface such as iron, copper or zinc[28] and surprisingly also on gold.[29]

Thus, the objective of the present work is the better understanding of the Graftfast mechanism. We will first concentrate on the spontaneous grafting from pure diazonium salts, which acts as an "interfering process" both for chemical and electrochemical grafting from diazonium salts. We will focus on the spontaneous grafting from pure diazonium salts on gold, since gold is normally unable to reduce the diazonium salts. We will then demonstrate, using IR-ATR and XPS analyses, that a reducing agent is essential in the Graftfast process in order to graft polymers. In parallel, we will follow the reaction from the solution-side by Electronic Paramagnetic Resonance EPR using the spin-trapping method. Thanks to those dual surface and solution analyses, we will demonstrate, for the first time, that aryl radicals are indeed involved in the redox-induced grafting of the PP layer but also in the grafting of polymer films.

For simplicity's sake, the study is restricted to the reduction of 4-nitrobenzenediazonium tetrafluoroborate with L-ascorbic acid using 2-hydroxyethyl methacrylate as a monomer, gold plates as substrates (in the part concerning surfaces) and 2-methyl-2-nitrosopropane as spin-trap (in the EPR study).

2. Experimental Section

2.1. Chemicals. All the experiments were conducted in deionized water (DI water). All standard chemicals were purchased from Sigma Aldrich. In this study, the vinylic monomer was 2-hydroxyethyl methacrylate (HEMA, 97%), the reducing agent L-ascorbic acid or Vitamin C (VC, >99%), the compound used to generate the spin-trap (cf 2.4.) was the 2-methyl-2-nitrosopropane dimer (MNP dimer) and the standard for EPR quantitative study was 4-hydroxy-TEMPO (97%). Those reactants were used as received; in particular, the vinylic monomer was not distilled to remove commercial inhibitors. Prior to use, 4-nitrobenzenediazonium tetrafluoroborate (NBD, 97%) was purified by precipitation in diethyl ether.

Photochemistry,[30,31] polymer chemistry,[32] biology and medicine[33,34] are current application fields for spin-trapping.

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2-Methyl-2-nitrosopropane (MNP) is a spin-trap of interest because, as other nitroso traps, the EPR spectrum hyperfine splitting of the formed spin-adducts allows to determine unambiguously the structure of the trapped radical.[35−37] As many nitroso compounds, MNP is a dimer in the solid state. To act as spin-trap, its dissociation into monomer is required. That step may lead to some experimental difficulties, detailed in section 2.4.[38,39]

L-Ascorbic acid (VC) was chosen as reducing agent in this study for its ability to reduce 4-nitrobenzenediazonium tetrafluoroborate (NBD).[40] Moreover, unlike iron powder,[15] VC acts as a reducer in homogeneous phase, which is essential for a quantitative study. VC is also unable to reduce protons from the solvent which will ease our interpretations by avoiding any potential hydrogen radical formation from the reactive mixture. Ascorbic acid has already been used as a reducer, for instance, in Sandmeyer reaction[41] or for the reduction of metal ions in solution,[42,43] particularly in the case of gold[44,45] or silver[46,47] nano-object formation.

2.2. Preparation of Gold Substrates. Gold substrates were obtained by vacuum evaporation of pure gold (99.99% from Williams Advanced Materials) at room temperature on 37 × 6 mm^2 glass plates supplied by RS France (homemade cut from 76 × 26 mm^2 glass plates). Prior to evaporation, the glass plates were rinsed 10 min under ultrasonication in water, ethanol and acetone successively. Then, in a Balzers BAK 600 evaporator, a 3−10 nm chromium sublayer was first deposited to enhance gold adhesion on glass and then 50−150 nm of gold were evaporated under a residual pressure of 1×10^{-7} bar, at room temperature. Gold plates were used without further cleaning treatment.

2.3. Grafting of Polyphenylene (PP) Films and Vinylic Polymers. Typical Graftfast experiments were carried out in open air, at room temperature, atmospheric pressure, in one step and with magnetic stirring. In this work, three studies were carried out: the spontaneous grafting (as a reference) and the reduction of the NBD salt by ascorbic acid in the (i) absence and (ii) presence of the HEMA monomer (Graftfast process).

In the case of the study of the spontaneous grafting of PP layers or PHEMA films, the gold plates were simply immersed in a 0.05 M NBD solution, respectively, in the absence or presence of HEMA (5 equiv. vs NBD).

In the case of the study of the reduction of the diazonium salt by L-ascorbic acid in absence of a vinylic monomer, the NBD

aryl diazonium salt was dissolved in 50 mL of DI water to reach the typical final concentration of 0.05 M. Gold plates were introduced in the solution and, in order to start the reaction, various amounts of L-ascorbic acid (VC) were added. The final concentration of VC used during this study was running from 0.005 M (1/10 equiv vs NBD) to 0.05 M (1 equiv). Instantaneously, the pale yellow solution turned into a lemon yellow mixture (cf 3.2.) and a few small bubbles were observed, corresponding to dinitrogen evolution from the reduction of NBD by VC.

In the case of the study of the reduction of the diazonium salt by L-ascorbic acid in the presence of a vinylic monomer, we proceeded as above, but the concentration of VC was fixed at 0.005 M (1/10 equiv vs NBD), as a ratio of 1/10 of VC/NBD appeared to give the best results on surfaces (see the Supporting Information, Table S1). The vinylic monomer (HEMA) was then rapidly added for a final concentration of either 1.25, 5, 15, 25, or 50 equiv vs NBD.

After the reaction time (arbitrarily 60 min in this study), the gold substrates were rinsed according to the following rinsing procedure: water, ethanol and acetone, and sonication in dimethyl formamide (DMF) or dimethyl acetamide (DMA) for 5 min (the applied ultrasonic power was ca. 60 W). They were then studied ex situ by IR-ATR, XPS, and the thickness of the resulting films was measured with a mechanical profilometer.

2.4. EPR Protocol. The spin-trapping technique,[35] widely applied in chemistry, biology and medicine, is used for the detection and identification of short lifetime free radicals. It consists in the addition of, commonly, nitroso or nitrone compounds, which give rise to nitroxide radicals as a result of spin-trapping. This technique can also be applied in polymer research to study living anionic polymerization, alternating copolymerization or radical polymerization (herein ref[35]). Kunitake et al.[48] have examined the radical polymerization of several monomers including methyl methacrylate initiated by the thermal decomposition of, in particular, azobis-isobutyronitrile (AIBN) with 2-methyl-2-nitrosopropane or N-tert-butyl-α-phenylnitrone (PBN) as spin-trap. Moreover, a few teams investigated the spin-trapping of hydroxyl radicals[49] or aryl radicals[37,50] aiming to define the role of such species in genetic damaging such as in DNA, RNA, and their components.

In this study, the compound of interest as a spin-trap is the monomer of the 2-methyl-2-nitrosopropane dimer. The spin-trap solution was prepared, at room temperature, in a nitrogen flow glovebox (oxygen free atmosphere) by dissolving about 0.2 g of the MNP dimer in 50 mL of DI water previously bubbled 10 min with argon gas. Then, the solution was stirred overnight in a closed vial at room temperature in the dark to dissolve as much MNP dimer powder as possible and to reach stable monomer−dimer equilibrium (approximately 10 h after dissolution[38]). This solution is very sensitive to temperature, light, and oxygen and is stable for a limited period of time.[38] Thus, it is easily understandable that the spin-trap solution was prepared just before its use, stored for no more than a day in an adequate location and divided into typically 12 flasks of 4 mL. The equilibrium of the MNP dimer (colorless liquid) and monomer (blue liquid)[51] in aqueous solution imposes to measure the

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monomer concentration in solution. A simple method using UV/vis spectrometry adapted from literature[39] was used to find out the MNP monomer concentration in solution. Kuwabara et al.[38] have determined a molar absorbance coefficient of $\varepsilon_{662\,nm} = 10 \pm 5\,M^{-1}\,cm^{-1}$ for the MNP monomer. The concentration of MNP solutions based on the absorbance values at 662 nm (obtained with a Lambda 650 Perkin-Elmer UV/vis spectrometer) was 1.5 mM in average (and always within the 1−3 mM range).

2.4.1. Spontaneous Grafting of PP Films on Gold. An initial solution (0.021 M) of the diazonium salt (NBD) was prepared. 200 μL of this solution were added to the spin-trap solution (4 mL) to obtain a NBD final concentration of 1 mM. The NBD concentration was chosen in order to always work with an excess (at least a slight one) of MNP spin-trap compared to the diazonium salt. Hence, we can assume that the reached concentration of MNP in its monomer form is sufficient to spin-trap all the radicals created from the reduction of the diazonium salt.

2.4.2. Grafting PP Films from the Reduction of NBD. In the case of the study of the reduction of the diazonium salt by L-ascorbic acid in absence of a vinylic monomer, the variation of the reducing agent concentration was examined. The NBD-MNP mixture was prepared as described in the previous section, and L-ascorbic acid (reducing agent) in aqueous solution was added in order to reach the desired concentrations (identical to those tested in the surface study) that is to say 0.1 mM (1/10 equiv vs NBD), 0.2 mM (1/5 equiv), 0.5 mM (1/2 equiv), 0.75 mM (3/4 equiv), or 1 mM (1 equiv) in solution.

2.4.3. Grafting Polymer Films from the Reduction of NBD/ HEMA Mixtures. In the case of the study of the reduction of the diazonium salt by L-ascorbic acid in presence of a vinylic monomer, 200 μL of an initial solution of L-ascorbic acid (VC) and from 3 to 9 μL of HEMA monomer were added to the above-described NBD-MNP mixture so as to reach final concentrations of respectively 0.1 mM (1/10 equiv vs NBD) (the ratio between VC and NBD was kept constant and its value is explained in 2.3.) and either 1.25 mM (1.25 equiv vs NBD), 5 mM (5 equiv) or 15 mM (15 equiv) as a parallel to the surface study.

The addition of all the reactants together was made as fast as possible and the solution was introduced directly in the EPR liquid cell.

2.5. Spectroscopic and EPR Analyses. Infrared spectra were obtained on a Bruker VERTEX 70 spectrometer equipped with ATR (Attenuated Total Reflection) Pike-Miracle device. The detector was a MCT working at liquid nitrogen temperature. The spectra were obtained after 256 scans at 2 cm^{-1} resolution and contributions from H_2O and CO_2 (gas) were subtracted.

X-ray photoemission spectroscopy (XPS) analyses were performed with a Kratos Axis Ultra DLD using a high-resolution monochromatic Al−Kα line X-ray source at 1486.6 eV. Fixed analyzer pass energy of 20 eV was used for core level scans. The photoelectron takeoff angle was always normal to the surface, which provided an integrated sampling depth of approximately 15 nm. A survey spectrum and core-level spectra of C1s (280 - 290 eV), O1s (526−538 eV) and N1s (396−410 eV) regions were systematically recorded. The energy scale of the instrument was calibrated by setting Au 4f$_{7/2}$ = 84.00 eV, Ag3d$_{5/2}$ = 368.70 eV, CuL$_3$M$_{4,5}$M$_{4,5}$ = 567.90 eV, and Cu 2p$_{3/2}$ = 932.65 eV. When charging phenomena occurred, the charge was counterbalanced by adjusting the Au 4f$_{7/2}$ level of the pristine gold substrate (reference sample always analyzed if the charge neutralizer was employed) at 84.00 eV and by applying this shift to all the

samples studied in the same batch. Spectra were treated with Avantage software.

Thickness measurements were carried out with a mechanical profilometer Dektak 30 ST using a lateral resolution of 50 μm.

EPR spectra were recorded at the X band (9.4 GHz) on a Bruker ER-200D EPR spectrometer equipped with a high sensibility cavity. EPR measurements were performed at room temperature using a flat quartz aqueous cell. The typical instrument settings were: microwave power 2 mW, gain 1×10^5, modulation amplitude 0.1 G, time constant 81.92 ms. Hyperfine splitting constants and spectra deconvolution were determined by means of an automated simulation program using the Levenberg−Marquardt method. For all the spectra Lorentz line shapes were assumed. Radical concentrations were calculated from a 5 mM 4-hydroxyTEMPO water solution.[52]

3. Results and Discussion

As mentioned above, spontaneous grafting of PP films from diazonium salts was observed not only on reducing metals (such as iron, zinc, or copper) but also on gold, which is quite surprising because of the known redox properties of diazonium moieties. In order to estimate the actual role of the reducer in the Graftfast process, we studied the spontaneous grafting (i.e., without any reducer in solution) of polyphenylene-like layers and also of poly(hydroxyethyl) methacrylate PHEMA on gold substrates. Then, the redox activation of NBD by ascorbic acid (VC) and the subsequent formation of grafted polyphenylene-like primer layer on gold substrate were studied for various VC/NBD ratios. Finally, the same redox activation in presence of HEMA vinyl monomer and the resulting grafted polymer film were studied for several HEMA concentrations. In both cases, EPR experiments were carried out to characterize the radical moieties.

3.1. Spontaneous Grafting. Gold substrates immersed (60 min) in a solution containing only the diazonium salt were analyzed, after the rinsing procedure (cf 2.1.), by IR-ATR and XPS. The resulting IR spectrum (Figure 1) exhibits two weak absorption bands at 1525 and 1350 cm^{-1} attributed to, respectively, the asymmetric and symmetric stretching of aryl-NO$_2$ group which are characteristic of a polynitrophenylene-like (PNP) layer. The N 1s core level XPS analysis (Figure 2) reveals three main peaks. The peak centered at 405.8 eV corresponds to nitro groups; NH$_2$ or N=N appears in a broad peak at 399.9 eV, as widely described in the literature[12,19,53,54] and discussed by Mévellec et al.[15] Those peaks confirm the presence of the PNP layer on the gold substrates. Finally, the peak at a lower binding energy (397.5 eV) is assumed to correspond to Au−N bonds because a similar binding energy peak was found when studying gold nitrite[55] or electrochemical oxidation of aliphatic amines.[56] The C 1s core level analysis (not presented here)

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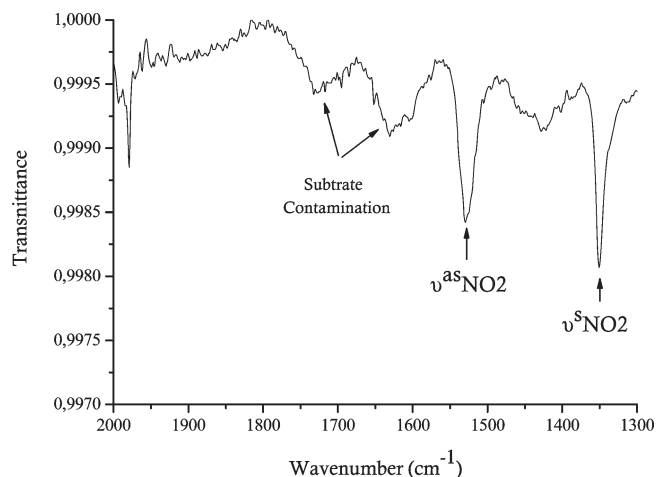
Figure 1. IR-ATR spectra of PNP layer spontaneously grafted on gold plates obtained by immersion of the substrates in a 0.05 M NBD solution for 60 min.
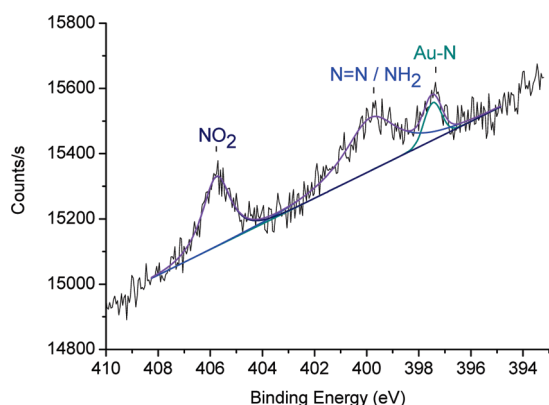

Figure 2. Typical XPS N 1s core level spectrum of PNP layer spontaneously grafted on gold plates obtained by immersion of the substrates in a 0.05 M NBD solution for 60 min.

also confirms the presence of a PNP layer on the gold substrate. Because of the more similar IR intensities and XPS spectrum than in thiol-derivated nitrobenzene mono-layers on gold (the total N 1s peak area is 350 a.u. in case of diazonium salt derived nitrobenzene layers and 460 a.u. in case of thiol derived nitrobenzene monolayers), we assume that this polynitrophenylene-like layer is very thin.

This so-called spontaneous or open-circuit potential reaction of arenediazonium salt has also been reported for a range of metals and carbon materials.[28,53] The spontaneous grafting of PNP layer on gold has already been observed on the one hand by Podvorica et al.[29] both in acidic and basic media and on the other hand by Lehr and co-workers in acetonitrile and aqueous acid solutions.[57] Contrarily to other metals such as copper ($E^{\circ}_{Cu^{2+}/Cu} = 0.34$ V), iron ($E^{\circ}_{Fe^{2+}/Fe} = -0.45$ V) or nickel ($E^{\circ}_{Ni^{2+}/Ni} = -0.26$ V), gold ($E^{\circ}_{Au^{3+}/Au} = 1.5$ V) should, a priori, not be able to reduce diazonium salts into the corresponding aryl radicals as NBD redox potential was measured by cyclic voltammetry at 0.45−0.55 V/ENH. Hence, the mechanism involved in this phenomenon remains unclear.

The EPR study of the NBD solution containing MNP spin-trap revealed no radicals, which could prove that no spontaneous homolytic dediazoniation of the diazonium salt has occurred. However, this result has to be carefully considered. Indeed, Lehr et al.[57] calculated a packing density of 12×10^{-10} mol cm^{-2} for a close-packed layer of NP groups on a flat surface. In our experiments, the gold plates have a surface area of 2.1 cm^2 and the concentration detection limit of the EPR in our experimental conditions has been estimated at 4×10^{-7} mol. Thus, it seems that the very low concentration of aryl radicals needed to ensure the grafting of a packed monolayer of PNP cannot be detected by EPR. Therefore, it is difficult to conclude on the involving of aryl radicals in the spontaneous grafting mechanism.

According to Lehr et al.,[57] the spontaneous reaction on gold substrates in aqueous acid solution could be explained measuring the open-circuit potential (OCP) of the working electrode. When the OCP is low enough, electrons can be transferred at a significant rate to the diazonium cation creating an aryl radical and the film growth. When the OCP becomes too positive, the rate of the electron transfer is negligible and the growth slows to a stop or does not occur at all. However, we did not observe any grafted PHEMA on the gold surface when gold substrates were left in contact with a NBD/HEMA mixture without any reducing agent meaning that no aryl radicals have initiated the radical polymerization of the vinylic monomer. Hence, it tends to prove that no spontaneous homolytic dediazoniation occurred when gold substrates are in direct contact with diazonium salts and a homolytic dediazoniation activated by the gold surface is highly unlikely, owing to the redox potentials given above. As our XPS spectra exhibit N peaks that can be attributed to Au−N and to N=N moieties, we assume that either the diazonium salt cations themselves or the nitrobenzene cations resulting from an heterolytic dediazoniation, which are known to be intermediate species in the degradation of the diazonium salt into nitrophenol,[58] are able to graft spontaneously on electron rich surfaces such as metals. Nevertheless, this mechanism involving cationic species is not consistent with the grafting in basic solution observed by Podvorica et al.[29] assumed to occur at pH 10 via the spontaneous homolytic dediazoniation of diazoates producing aryl radicals. This is therefore in good agreement with the study of Pazo-Llorente and co-workers[59] which suggests a variation of the grafting mechanism according to the solvent. Additional work is currently in progress to confirm or invalidate the hypothesis of a cationic mechanism in aqueous solution.

As mentioned above, no PHEMA could be observed after immersion of gold substrates in solutions containing NBD and HEMA: only grafted PNP thin films were observed in that case (the grafting mechanism remains unclear). Therefore, it seems that the reducing agent is

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(58) Zollinger, H., *Diazo Chemistry I: Aromatic and Heteroaromatic Coumponds*; VCH: Weinheim, Germany, 1994.
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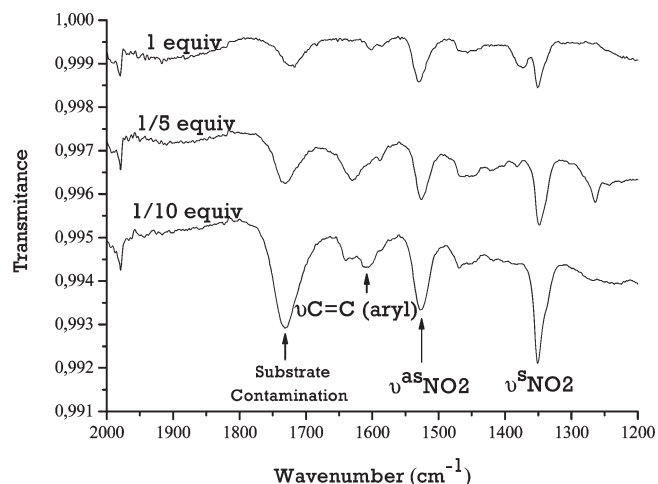
Figure 3. IR-ATR spectra of PNP layers grafted on gold plates by Graftfast (NBD 0.05 M and different ratio VC/NBD: 1, 1/5, 1/10).

essential in the Graftfast process in order to graft vinylic polymers.

3.2. Reduction of the Diazonium Salt by L-Ascorbic Acid. *Redox-Activated Grafting of PP Films on Gold.* Gold plates were introduced in a solution containing NBD and ascorbic acid (1, 1/5 or 1/10 equiv vs NBD), as described in section 2.3. The resulting polynitrophenylene-like (PNP) films were analyzed after the rinsing procedure (cf 2.1.) by IR-ATR (Figure 3). All spectra exhibit two major absorption bands at 1525 and 1350 cm^{-1} attributed, as above, to aryl-NO$_2$ groups. The weak peak at 1600 cm^{-1} is typical of the presence of phenyl groups. Thus, those spectra are characteristic of a polynitrophenylene-like film.

XPS analyses were undertaken to confirm the presence of the PNP film. The N 1s core level analysis (see the Supporting Information, Figure S2) shows a high binding energy peak (406 eV) corresponding to nitro groups and a broad peak centered at 400 eV from a mixture of amino and azo groups, as previously indicated. As those IR and XPS spectra were obtained on PNP films thoroughly rinsed under sonication in appropriate solvents, they confirm a strong chemical bonding between the PNP layer and the gold substrate.

Various VC/NBD ratios were studied and a tendency seems to come out of our IR-ATR spectra. Indeed, it appears that a slightly higher absorbance value was observed at 1525 and 1350 cm^{-1} for the 1/10 ratio (i.e., ten times less ascorbic acid than NBD). Nevertheless, it is difficult to conclude on any "best" PNP grafting conditions from those experiments, for two main reasons. First, the observed differences in IR absorption intensity are close to the sensitivity threshold of the IR-ATR equipment (0.05%). Second, those absorption values are also close to those observed for a spontaneous grafting of NBD, previously described in section 3.1. Therefore, it is likely that the grafting of polyphenylene-like layers in presence of a reducing agent is actually a combination of the spontaneous process and the redox-activated process.

EPR Investigation. Solutions of NBD, ascorbic acid, and MNP as spin-trap were prepared as described in 2.4. and EPR spectra were recorded every 10 min for 60 min.
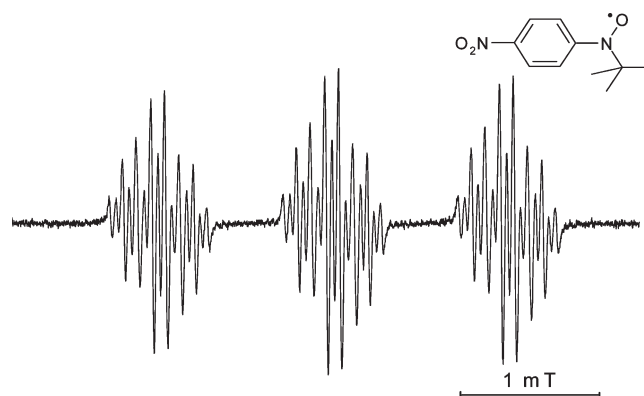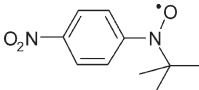
Figure 4. Typical EPR spectrum of MNP adducts of nitro aryl radicals obtained in the case of NBD (1 mM) reduction by VC (0.1 mM) in the presence of MNP (excess) and recorded 2 min after the addition of VC.

Table 1. Hyperfine Coupling Constants of Nitro Aryl Radicals MNP Adducts

	HFSCs (mT)	
	aN	others
	1.284	0.21 (2H); 0.097 (2H); 0.050 (a$_N$NO$_2$)

A typical EPR spectrum of the MNP adduct is shown in Figure 4. The simulation reveals that the spin-adduct is coupled to a nitrogen atom and two pairs of equivalent hydrogens atoms (identified as the ortho- and meta-protons in the aromatic ring). It is also possible to resolve an additional splitting due to paramagnetic nuclei in the para-position in the aromatic ring. Nitrogen and proton hyperfine splittings of the spin adducts are diagnostic parameters for the identification of the trapped-radicals. The hyperfine splitting constants (HFSCs) of these spin-adducts are given in Table 1. They are in accordance with MNP adducts of nitrophenyl radicals reported in the literature.[37] Thus, for the first time, the presence of aryl radicals in the Graftfast process is demonstrated.

To establish a connection between the grafting of PNP layers on surfaces and the quantity of radicals formed with time, various ratios of VC/NBD were tested and the reactions followed by EPR (Figure 5).

It is important to point out that the concentration reported in Figure 5 is the concentration of the spin-adduct, a time-stable compound in the time scale of our experiments. Thus, each measurement corresponds to the sum of all the radicals spin-trapped from the beginning of the experiment.

All the kinetic curves in Figure 5 can be decomposed in three steps: an initial rapid increase (the extrapolated curve at $t = 0$ is clearly not null), after 2 min the reaction proceeds at a slower rate and finally a saturation of the amplitude of the EPR signal is observed that can be attributed to the consumption of the reducing agent. We assume that this nitrophenyl radical creation as the reaction goes along is essential in the Graftfast process and occurs thanks to a slow reduction rate. Another striking result from Figure 5 is that the amount of trapped

Figure 5. Evolution of nitrophenyl radical MNP adduct concentration with time in case of the reaction of MNP (excess), NBD (1 mM), and VC in the following ratios VC/NBD 1/10(green square), 1/5(blue circle), 1/2(purple triangle), 3/4(red rhombus), 1(black inverse triangle).

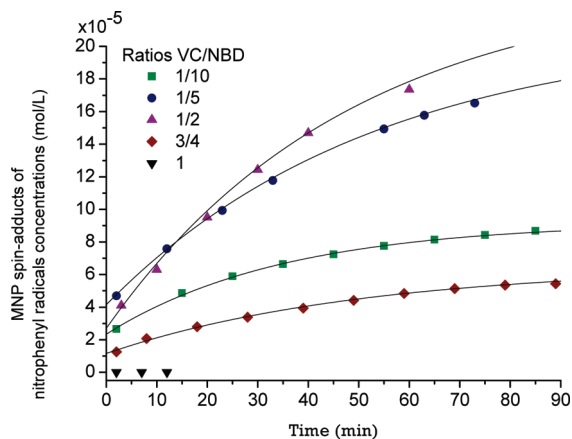radicals does not follow the original amount of VC: indeed, the concentration of observed spin-trapped radicals is significantly lower for 1/2, 3/4, and 1 VC/NBD ratios than for lower ones. That trend appears quite obviously when plotting the concentration of nitrophenyl radicals divided by the VC initial concentration versus time (see the Supporting Information S3).

Let us first consider the lower VC/NBD ratios. When VC/NBD = 1/10 (or 1/5), the total concentration of aryl radicals formed at the end of the experiment (i.e., the asymptotic value of those two curves in Figure 3) is found to be close to 0.1 mM (or respectively 0.2 mM), which corresponds to the VC initial concentration: all the ascorbic acid has reacted with the diazonium salt in those cases. In other terms, the only consumption route for VC was the reduction of NBD and we almost formed and trapped as many aryl radicals as possible (in water, ascorbate is considered to be the reducing agent so it can only activate an one-electron reduction[60]). Those figures also prove that the MNP spin-trap was verily introduced in excess and that the stability of the MNP adducts is sufficient for the period of time studied.

Let us now discuss the spin-trapped concentrations recorded for the higher VC/NBD ratios. Surprisingly, no MNP adducts was detected with VC/NBD = 1 and the amount of spin-trapped species was significantly lower than expected for VC/NBD = 1/2 or 3/4. A competition between the spin-trapping reaction and at least another reaction seems to occur.

Several hypotheses can be proposed to explain the low amounts of MNP-adducts at high concentrations of VC.

First, the spin-adducts may be reduced directly by excess VC into the corresponding EPR-silent hydroxylamines, as already observed by Reszka et al.[37]

Second, dimerization of the aryl radicals may occur. Indeed, with higher VC/NBD ratios, excess aryl radicals are formed in solution and the dimerization (an order 2 reaction with respect to NBD) may become predominant compared to the spin-trapping reaction (order 1). According to some recent gas chromatography–mass

spectrometry (GCMS) experiments (not presented here), this hypothesis is however to be discarded. Indeed, no dimers from the reaction between two nitrophenyl radicals were identified for a VC/NBD ratio of 1, whereas for lower ratios at the same reaction time, this dimer was detected.

Third, ascorbic acid may react with the diazonium salt in a nonredox way.[61,62] According to the literature, this reaction leads to the 3-O-arenediazoascorbic acid (diazo ether) formation, displaying an absorbance maximum at λ_{max} = 358 nm (yellow color). As mentioned in section 2.3, in our experiments, a NBD solution (pale yellow) turns immediately into an intense yellow by addition of ascorbic acid (whatever the VC/NBD ratio). The UV/vis spectrum of such a mixture (see the Supporting Information, Figure S4) exhibits a maximum of absorbance at 356 nm which speaks for the diazo ether formation. Thus, it seems likely that the reaction that competes with the reduction of the diazonium salt by ascorbic acid is the formation of a diazo ether by direct reaction of those two reactants. This is consistent with the observed decrease of aryl radicals in solution when the concentration of ascorbic acid is increased.

Surface-Solution Comparison. EPR experiments demonstrated, for the lower range of VC/NBD ratios, the presence of nitrophenyl radicals during the diazonium salt reduction by ascorbic acid and allowed to determine the evolution of their concentration with time. For lower VC/NBD ratios, we detected as many aryl radicals as expected (corresponding to the initial VC concentration). In all cases, IR-ATR measurements seem in accordance with those EPR results. Indeed, aryl radicals were formed (since they were observed after spin-trapping) and a PNP layer was observed on gold surfaces. However, we could not find a monotonous relationship between the observed radical concentration (as estimated from the spin-trapping experiment) and the thickness of the final PNP film. Indeed, varying the VC/NBD ratio allowed us to demonstrate that NBD and the corresponding aryl radicals actually experienced many termination chemical routes, including dimerization and formation of diazo-ethers, in addition to their grafting on the gold surface. It is thus quite difficult to conclude on any "best" conditions leading to the thickest PNP film, although we observed thicker PNP grafted films for VC/NBD = 1/10 than for higher ratios (Figure 3). When stoichiometric VC/NBD ratio was used, no aryl radicals were detected by EPR whereas gold surfaces showed a very weak IR-ATR absorption at 1600, 1525, and 1350 cm^{-1}, characteristic of a PNP layer. Those signals may be attributed to the spontaneous grafting of diazonium salts on gold,[29] as already described in section 3.1.

3.3. Redox-Activated Grafting from the NBD/HEMA Mixtures. *Grafting of Polymers on Gold.* Gold plates were introduced in a solution containing NBD diazonium salt, ascorbic acid (1/10 equiv vs NBD) and HEMA

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(61) Costas-Costas, U.; Gonzalez-Romero, E.; Bravo-Diaz, C. *Helv. Chim. Acta* **2001**, *84*, 632–648.
(62) Doyle, M. P.; Nesloney, C. L.; Shanklin, M. S.; Marsh, C. A.; Brown, K. C. *J. Org. Chem.* **1989**, *54*, 3785–3789.

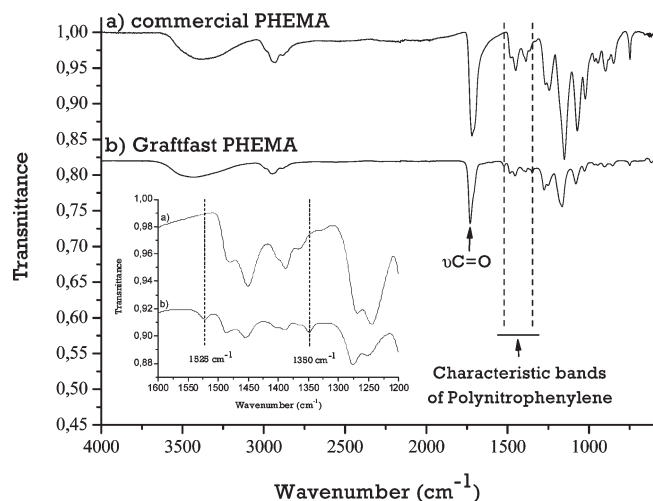6236 *Chem. Mater., Vol. 22, No. 23, 2010*

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Figure 6. IR-ATR spectra of (a) spin-coated PHEMA (20000 g/mol) film and (b) PHEMA grafted film obtained by Graftfast (NBD 0.05 M, VC 0.005 M, and HEMA 15 equiv vs NBD) on gold plates. Inset: zoom of the characteristic polynitrophenylene-like layer absorption bands signature.

Table 2. IR Absorption C=O Band Intensity and Thickness of the Corresponding Graftfast Films Obtained with NBD 0.05 M, VC (1/10 equiv vs NBD), and Various HEMA Ratios

	HEMA equiv. versus NBD				
	1.25	5	15	25	50
IR $\nu_{C=O}$ band (1730 cm^{-1}) (%)		0.30	8.05	7.0	6.9
profilometer thickness $\pm$ 5 (nm)	10	18	38	34	31

vinylic monomer (1.25, 5, 15, 25, or 50 equiv vs NBD), as described in section 2.3.

A typical resulting poly(hydroxyethyl) methacrylate (PHEMA) film was analyzed after the rinsing procedure by IR-ATR and compared to a commercial PHEMA spectrum (Figure 6). The two spectra are identical (particularly the 1730 cm^{-1} absorption band (stretching vibration of C=O groups)) meaning we actually grafted PHEMA on gold substrates. However, additional peaks in grafted PHEMA films are observed and, as in section 3.2, are attributed to NO$_2$ groups (1525 and 1350 cm^{-1}) and phenyl groups (1600 cm^{-1}), meaning that nitrophenyl groups are also present in the film. The intensity of the 1730 cm^{-1} absorption band (characteristic of the PHEMA grafting) (Table 2a) and the film thickness (Table 2b) were followed to investigate the evolution of the grafting when varying the starting HEMA concentration. The variations of those two parameters with HEMA starting concentration are parallel indicating that an increase in the IR absorption intensity is mainly related to an increase in the film thickness and not in the film density. A 1.25-fold molar excess of HEMA over the diazonium salt did not lead to any PHEMA grafting but only to a PNP layer. However, a 15-fold HEMA/NBD molar excess seems to be a critical value from which the PHEMA film reaches a maximum thickness of around 35 nm. This critical value can be explained in terms of polymer solubility in the aqueous medium. Indeed, at low concentration of monomer, physisorption of nongrafted polymer chains precipitating on the substrates was observed preventing growing radical chains from grafting. But in the case of
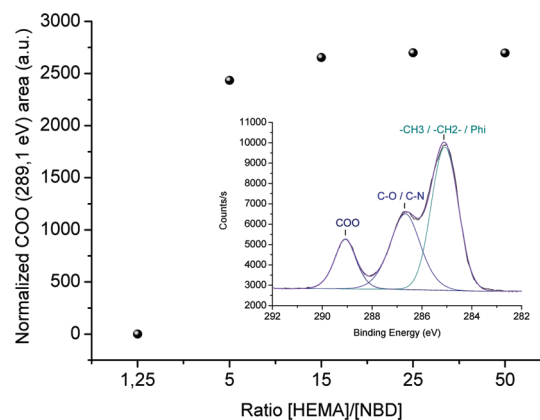
Figure 7. Evolution of COO area calculated from XPS spectra in the case of PHEMA films obtained with NBD 0.05 M, VC (1/10 equiv vs NBD) and various HEMA ratios (1.25, 5, 15, 25, 50 equiv vs NBD). Inset: typical XPS C 1s core level spectrum of a Graftfast PHEMA films (ratio 25).

high monomer concentration, the phenomenon was attenuated, because the solubility of the polymer in this monomer-rich aqueous solution was increased.

XPS analyses were also carried out in order to study the PHEMA grafted films. A typical C1s core level spectrum (insert in Figure 7) is composed of three main peaks. The peak centered at 285.08 eV corresponds to alkyl groups (−CH$_2$−, −CH$_3$), −C−O− or −C−N− simple bonds appear at 286.67 eV and the peak at a higher binding energy (289.08 eV) is assigned to the carbonyl ester group COO, confirming the grafting of PHEMA on the gold substrates. In order to compare the different graftings, the area of the carbonyl peak was plotted function of the different reaction conditions. The resulting graph (Figure 7) corroborates the IR-ATR measurements, i.e., the presence of PHEMA films on the substrates is confirmed and thicker films are obtained for higher monomer concentrations. In the N 1s core level analysis (not shown here), we obtained a complex spectrum including the nitro groups (-NO$_2$) at 406 eV but also azo and amino groups in a broad peak centered at 400.2 eV.[12,23,24] The area of nitro plus amino peaks has been found to be three times higher for a 1.25-fold molar excess of HEMA over NBD ($\sim$10 nm PNP layer) than for a 15-fold molar excess (35 nm thick PHEMA film). As XPS is sensitive only to the outer 10−15 nm of the coating, we believe that nitro-phenyl groups are found in the PHEMA films structure because they initiate the polymerization of the monomer and thus are located at the PHEMA chains ends.[12] The amount of detected nitrogen is, however, much higher in the case of a pure PNP layer since the latter is entirely formed of nitrophenyl groups. The presence of nitrophenyl moieties in the PHEMA structure is also confirmed by IR-ATR because increasing the PHEMA film thickness increases the absorption intensity of the characteristic bands of nitro and phenyl groups. Moreover, a thin polymer film (as the film obtained with 5 equiv HEMA vs NBD) showed an absorption intensity of the nitro and phenyl bands slightly higher than in the case of pure PNP films. That result validates the hypothesis originally given by Mevellec,[15] i.e., the presence of a PNP sublayer allowing the grafting of the PHEMA chains.[12]

Figure 8. (a) Typical EPR spectrum of MNP adducts obtained in the case of NBD (1 mM) reduction by VC (0.1 mM) in the presence of MNP (excess) and HEMA (1.25 equiv vs NBD) and recorded 2 min after the addition of VC; (b, c) decomposed spectra of MNP adducts of respectively aryl radicals and growing PHEMA chains. The corresponding spin-adducts formula are given on the right.

The observed XPS carbon–nitrogen ratio allows us to estimate the grafted PHEMA degree of polymerization (DP). Indeed, assuming that the film is thick enough (> 25 nm) so that the PNP sublayer is not probed and that only one nitrophenyl moiety is grafted at each polymer chain end, grafted PHEMA chains DP was estimated to range between 20 and 80 depending on the HEMA/NBD ratio used.

EPR Investigation. Solutions of NBD, ascorbic acid (1/10 equiv vs NBD), HEMA (1.25, 5, and 15 equiv vs NBD) and MNP as spin-trap were prepared as described in section 2.4, and EPR spectra were recorded every 10 min for 60 min. A typical EPR spectrum is shown in Figure 8a. As previously illustrated, the interpretation of the hyperfine splittings is a powerful tool to determine the structure of the trapped radicals. The EPR spectrum is analogous to the one obtained in section 3.2. (case of the simple reduction of NBD alone) but shows an additional component.

The simulation reveals that the spectrum is composed of a composite pattern: the main component is attributed to aryl radical adducts (Figure 8b); superimposed on this signal, a spectrum corresponding to a spin-adduct coupled with only one nitrogen with a hyperfine splitting constant of $a_N = 1.62$ mT was observed. This latter is attributed to the spin adduct formed by the reaction of PHEMA chain propagation radical with MNP (Figure 8c).

The spin-trapping technique cannot give any information on the polymer degree of polymerization (DP). Indeed, whatever its value, the signal of the spin adduct remains identical because only a nitrogen coupling is involved. Moreover, as we believe that the radical polymer chains formed in solution react very quickly with the MNP spin-trap preventing them to react with HEMA moieties and so to grow, DP are probably smaller than in a solution free of MNP spin-trap (conditions of normal Graftfast reaction). Nevertheless, the existence of aryl radicals and growing polymer chains, during the reduction of diazonium salt by ascorbic acid in presence of HEMA, is demonstrated.

Various HEMA concentrations were tested and the reactions followed by EPR. As two different spin adducts were identified, we studied the evolution of their concentrations separately. Numerical simulations were employed for all spectra in order to determine the concentration of each spin adduct, MNP adducts of nitrophenyl radicals and of radical polymer chains. The results are presented in Figure 9. For spectra shown in panels a and b in Figure 9 (ratio HEMA/NBD = 1.25), we observed a decrease in the concentration of the spin-adducts. As explained in section 3.2, this can only be relevant to the spin-adduct reactivity so, in this part, we will not go into quantitative interpretations. Indeed, nitroxide compounds are sensitive to carbonated radicals, which in this case could be the growing polymer chains or aryl radicals, to form alkoxyamines.[52,63] All the reactions identified as likely to occur in this case are represented in Scheme 1.

First of all, the more HEMA in the starting solution, the less MNP adducts of aryl radicals were formed (degradation due to the reaction with growing polymer chains, see Scheme 1) and the more MNP adducts of polymer growing chains were detected (degradation could also occur but globally there is an increase). This is in accordance with the presumed initiation of the HEMA polymerization by aryl radicals and an increase of the polymerization speed with the HEMA concentration. Indeed, the aryl radicals participating in the HEMA polymerization initiation cannot be spin-trapped (they do not contribute to the aryl radicals MNP adducts signal whereas the growing polymer chains initiated by those radicals can be spin-trapped and detected).

Over 40 min, the spin adducts concentrations seemed to reach constant values meaning either that they became stable and no more species are formed, or that their degradation exactly compensates their production. This phenomenon could be due to the fact that after 40 min, a lot less diazonium salt is reduced by ascorbic acid, leading

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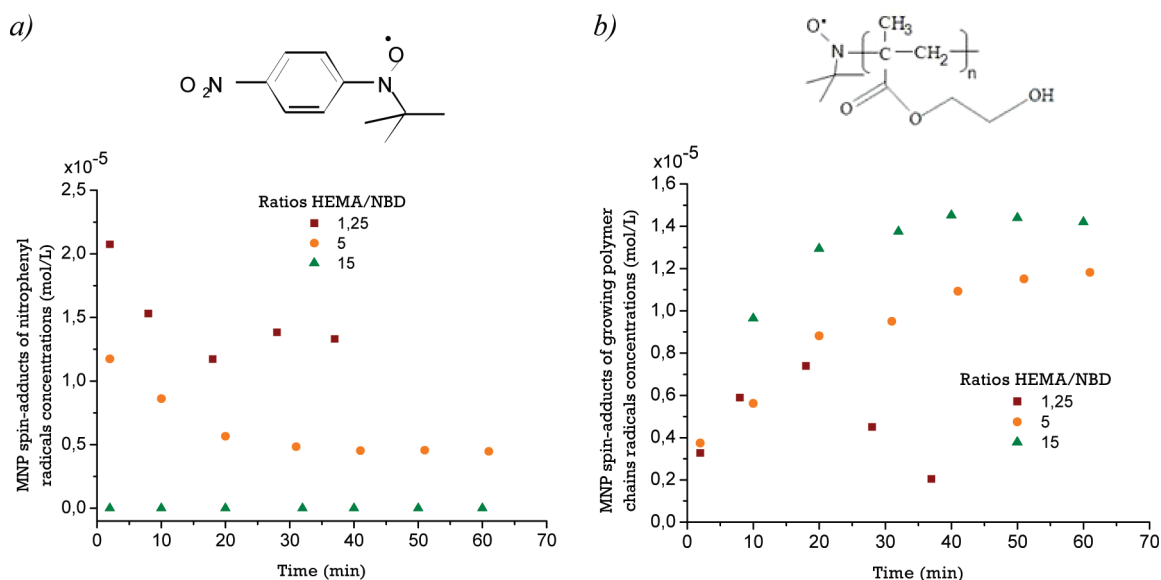
a)

b)

Figure 9. Evolution of (a) nitrophenyl radical and (b) growing polymer chains radicals MNP adduct concentration with time in case of the reaction of MNP (excess), NBD (1 mM) and VC (0.1 mM) and the following ratios HEMA/NBD 1.25(red square), 5(orange circle), 15(green triangle).

Scheme 1. Representation of All the Reactions Identified As Likely to Occur during the Graftfast Reaction in Presence of a MNP Spin-Trap[a]
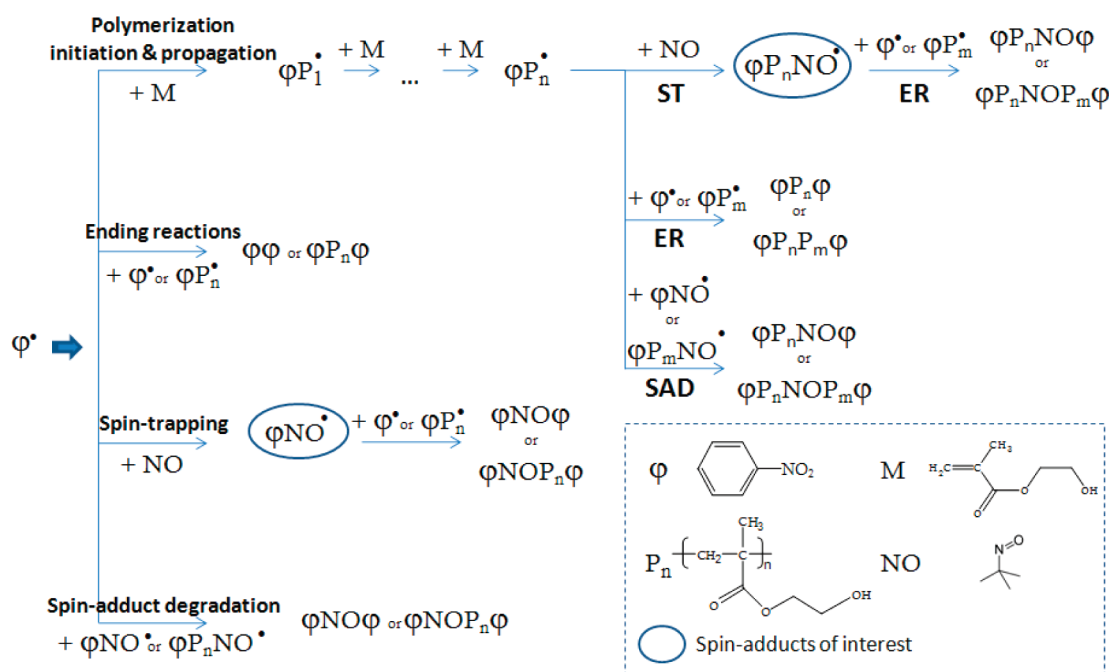
[a] ER is an abbreviation for ending reactions, ST for spin-trapping, and SAD for spin-adduct degradation.

to fewer growing polymer chains being created, that is to say, fewer species able to damage the spin adducts.

Finally, the whole behavior of the curves obtained for HEMA/NBD = 1.25 is difficult to explain. We assumed this is strongly related to the quantity of reactions involved in the process described in Scheme 1 and to the rates of the reactions against one another. However, the reasons why fewer and fewer MNP adducts of growing polymer chains are observed after 20 min while more MNP adducts of aryl radicals are detected remain unclear.

Surface-Solution Comparison. The surface analyses of the grafting of PHEMA films on gold substrates

through the chemical reduction of a diazonium salt by acid ascorbic revealed the existence of a critical HEMA concentration value from which the PHEMA film thickness reaches a maximum. This tendency is confirmed and finds an explanation in the EPR study. Indeed, the more HEMA introduced in solution, the more growing polymer chains were formed. No surface grafting studies in time were performed; however, it is likely that the highest film thickness will be obtained for approximately 40 min, because for longer times, only negligible amounts of growing polymer chains are formed.

4. Conclusions

The grafting of diazonium salts or polymers on gold surface was achieved by the Graftfast process. To simplify the mechanism investigation, we used a unique set of reactants but varied their concentrations in solution. Graftfast is a "grafting to" technique, allowing to synthesize strongly grafted polymer films on any type of materials with a thickness controlled by reaction time. The principle of the process is based on the chemical reduction of diazonium salts by reducing agents in absence or presence of a vinylic monomer.

The study of substrates immersed in solutions containing only the diazonium salt showed a weak grafting of PNP layer similar to the one observed while using VC as reducer. This spontaneous grafting mechanism remains unclear but it might involve cationic degradation species different from ones resulting from the redox activation of aryl diazonium salts. Moreover, the study of substrates immersed in solutions containing only the diazonium salt and the vinylic monomer proved that the reducing agent is essential to force the diazonium salt to form aryl radicals and, eventually, graft polymers in the Graftfast process.

When only the diazonium salt is present with the reducing agent, we demonstrated the formation of aryl radicals able to graft on the surface. We revealed that the highest concentration of those radicals does not necessarily give the thickest PNP film and that according to synthesis parameters it was ranging from no grafting (because of the promotion of side-reactions) to thin PNP films grafted on gold substrates. In the case of redox-activated polymer grafting from monomer/diazonium salt mixtures, we confirmed the initiation of polymerization by aryl radicals and we detected the so formed growing polymer chains able to graft on the PNP sublayer. A close relationship between the monomer initial concentration and the number of growing polymer chains formed was established and we extracted the monomer concentration critical value leading to thickest films.

Additional work is in progress to go even further into the understanding of the Graftfast grafting mechanism including, for instance, GCMS (for solution-side) and TOF-SIMS (for surface-side) experiments. The localization of the grafting (Mesnage et al.) as well as applications of the process in polymer metallization (Garcia et al.) and for biochips (Berthelot et al.) are also currently being investigated and are about to be published.