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ORIGINAL PAPER

Agarose-based hydrogel as an electrografting cell

Brigitte Mouanda · Veronique Eyeffa · Serge Palacin

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Abstract An agarose gel was used as an electrochemical cell to graft vinylic polymer layers on conductive surfaces by electro-initiated radical electrografting of various water-soluble and hydrophobic vinylic monomers in the presence of diazonium ions. The process was followed by in situ electrochemical measurements and the resulting grafted layer was characterized by infrared (IRRAS) and photoelectron (XPS) spectroscopy.

Keywords Hydrogel · Cathodic electrochemical polymerization · Grafted surface

1 Introduction

Hydrogels are hydrophilic materials based on three-dimensional networks held together by crosslinks of covalent bonds and weak cohesive forces such as hydrogen or ionic bonds. These crosslinked macromolecular structures are able to take up large quantities of water and biological fluids without dissolution. Hydrogels are used in the biomedical field for contact lenses, artificial corneas, wound dressing, coating for sutures and catheters [1]. Thanks to their ability to swell and to release trapped particles into the surrounding medium, hydrogels are also used as drug delivery systems. For the latter application, Wallace et al. [2] synthesized composite materials comprising conducting polymers and hydrogels to drive the delivery electrochemically, although high porosity and efficient ion-transport generally provide good conducting properties to hydrogels. New and wide applications of hydrogels were recently proposed, such as chemical reactors, microreactors, electrochemical/photochemical sensors, microanalysis and combinatory chemistry [3–6]. For example, agarose, which is a linear polymer consisting of alternating D-galactose and 3,6-anhydro-L-galactose units (Scheme 1) finds applications in the biochemical field for the separation of nucleic acids by electrophoresis [7].

Our laboratory is mainly concerned with cathodic electrografting [8]. Cathodic electrografting is a powerful technique for modifying and decorating conducting surfaces with organic matter. It finds application in various fields including biocompatibility, sensors, protection again corrosion, lubrication, soldering, functionalization, adhesion, template chemistry [9] and industrial effluent clean-up [10]. Cathodic electrografting of polymers [8] is based on the initiation, then polymerization, of electroactive monomers on the electrode, either conducting or semi-conducting. The adherence of the electrografted films, which can be considered as disordered polymer brushes [11], is ensured by a carbon-metal covalent bond [12]. Cathodic electrografting may proceed via a purely anionic mechanism, under drastic anhydrous conditions, but also via electro-induced radical polymerization (EIRP). Indeed, using diazonium salts as initiators, it is possible to graft vinylic polymer chains to various conducting surfaces in aqueous solutions [13] or micellar suspensions [14]. In the present study, we apply for the first time electro-induced radical polymerization in aqueous medium using a hydrogel as electrochemical cell. This method avoids the use of a liquid electrolytic for the electrografting step, allowing both liquid-free and localized modification of the electrode surface.

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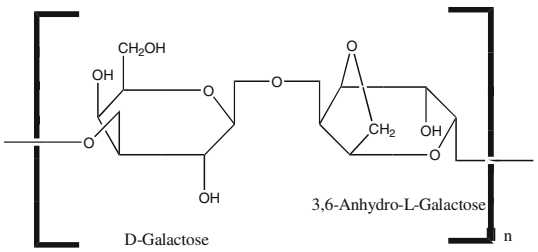
B. Mouanda (✉) · V. Eyeffa · S. Palacin
Chemistry of Surfaces and Interfaces, CEA, IRAMIS, SPCSI, 91191 Gif-sur-Yvette Cedex, France
e-mail: brigitte.mouanda@cea.fr



Scheme 1 Formula of agarose

2 Experimental

2.1 Reagents

We used Agarose Type I-B with a sulphate content lower or equal to 0.12% and a gel strength higher or equal than 1,800 g cm^{-2} (for an agarose concentration of 1.0% (w/v)) and higher or equal than 3,200 g cm^{-2} (for an agarose concentration of 1.5% (w/v)).

4-Nitrobenzenediazonium tetrafluoroborate (NBDT, $O_2NC_6H_4N_2^+BF_4^-$, 97%), acrylic acid (AA, H_2C=CHCOOH, 99%), 2-hydroxyethylmethacrylate (HEMA, H_2C=$C(CH_3)COOCH_2CH_2OH$, 99%), butyl methacrylate (BuMA, H_2C=$C(CH_3)COO(CH_2)_3CH_3$, 99%), sodium dodecyl sulphate (SDS, $CH_3(CH_2)_{11}OSO_3Na$, 98.5%) were used as received from Aldrich except the vinylic monomers that were distilled under vacuum. H_2SO_4 (95%) was from Labosi. Tetraethylammonium perchlorate (TEAP) was from Acros.

2.2 Gel preparation

An aliquot of agarose powder (0.3 g (1.5 wt%)) were slowly sprinkled in 20 mL of de-ionized water while stirring to prevent clumping. Water evaporation was prevented by a paraffin paper. The beaker was then heated with a boiling water bath for 5–10 min under continuous stirring, until the agarose dissolved completely. Heating was stopped at 93 °C and the mixture was allowed to cool. When the temperature had fallen to 65 °C, the solution was poured into a pre-warmed beaker. A tight and elastic gel was then obtained.

2.2.1 Patterned agarose gel

When patterned hydrogel-cells were used, the preparation was slightly modified, as follows: A master exhibiting parallel lines 120 μm wide with a 120 μm pitch was prepared on a silicon wafer by photolithography using Az9260 as photoresist. This master was used as a mold for the formation of hydrogel patterned cells. The gel (4%) was synthesized in the presence of the HEMA monomer (1.9 M) as described in the supporting information. Indeed, the method gives higher monomer concentrations within the hydrogel-cell and thicker grafted films after electrodeposition, which makes characterization of the final pattern easier. When the temperature reached 65 °C, the solution was poured onto the pre-warmed master. After cooling, the gel was gently removed from the master, sliced and immersed in the electrochemical solution containing the diazonium salt as described below.

2.3 Hydrogel-cell electrografting

2.3.1 Hydrogel-cells preparation

(a) Hydrogel-cell electrografting with NBDT: 75 mg (3×10^{-2} M) of NBDT were dissolved in 10 mL of de-ionized water, under agitation. H_2SO_4 was added to lower the pH to 2 (diazonium salts are not stable in neutral or basic conditions). The hydrogels were then dipped into the resulting solution under argon bubbling for 30 min (changing the time of diffusion between 30 min and 3 h has no effect on the final result). The gels were quickly dried under absorbent paper before the electrografting process.

(b) Hydrogel-cell electrografting with water-soluble monomers (AA as example): The electrochemical solutions were prepared by mixing 3.5 mL (3.7 M) of AA, 70 mg of NBDT in 10 mL of de-ionized water. No H_2SO_4 addition was necessary with AA, which is acidic enough. The diffusion in the hydrogel was performed as above.

(c) Hydrogel-cell electrografting with hydrophobic monomers in emulsion (BuMA as example): The emulsions were prepared by mixing 50 mg of SDS with 20 mL of de-ionized water under strong agitation, for 15 min. Then 14 mL (2.6 M) of BuMA were added. The agitation was continued for 15 min. Then 76 mg (9.4×10^{-3} M) of NBDT and a drop of H_2SO_4 were added to the electrochemical solution. The diffusion in the hydrogel was performed as described above.

(d) Hydrogel-cell electrografting for localized electrografting: As for patterned hydrogel-cells, the monomers were added during the gel formation; the electrochemical solution was prepared with only 20 mL of water containing 140 mg (3×10^{-2} M) of NBDT and a drop of H_2SO_4. The diffusion in the hydrogel was performed as described above.

2.3.2 Electrografting process

The electrografting process was carried out with the hydrogel as electrochemical cell. The gel (1 in Fig. 1) was supported by the working electrode (2 in Fig. 1). The

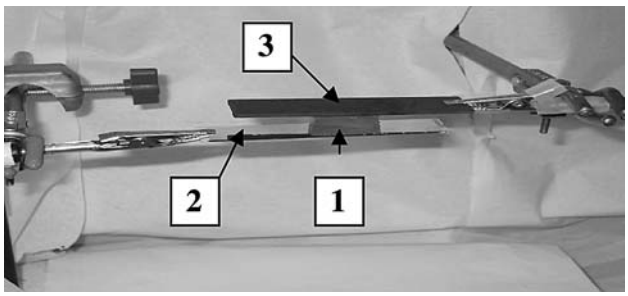


Fig. 1 A picture of the agarose gel between the two electrodes. For the purpose of the picture, the agarose gel was intentionally stained with a red dye. 1 is the hydrogel-cell, 2 the gold working electrode, 3 the graphite counter-electrode

working electrodes were Pyrex glass slides coated with 2 nm of chromium and 100 nm of gold (99.99%) by vacuum evaporation. The auxiliary electrode (3 in Fig. 1) was a graphite foil of large surface area. The reference electrode was shorted with the anode. The potential indicated by the potentiostat was thus the potential difference between the working and counter-electrodes. It did not reflect the absolute potential value experienced by the cathode.

Cyclic voltammetry was used to perform and follow the hydrogel-cell cathodic electrografting. Electrochemical analysis was done using an EG&G potentiostat, model 273A with automatic correction for ohmic drop. The experimental set-up is shown in Fig. 1. In the following voltammograms, only two voltammetric cycles are represented for sake of clarity.

After cathodic grafting the gold slides were rinsed in water for PAA (polyacrylic acid) films or DMF for PBuMA (polybutyl methacrylate) films, submitted to ultrasonic treatment in water, or DMF, rinsed with acetone, dried under a nitrogen flux, before IRRAS and XPS analysis.

2.4 Characterization

IRRAS spectra were obtained with a Bruker VERTEX 70 spectrometer with a mono reflection ATR Pike-Miracle™ device. Acquisitions were done with a DTGS detector with 32 scans at resolution of 2 cm^{-1}. IRRAS was used both to confirm the composition of the grafted films and to estimate their thickness. Thickness variations of the films were correlated with transmittance variations of the characteristic peaks (NO_2 group at 1,350 cm^{-1} for PNP (polynitrophenylene), the acid group at 1,727 cm^{-1} for PAA and the ester group at 1,732 cm^{-1} for PBuMA). A lower transmittance value obviously corresponds to a thicker film.

Photoemission studies were performed with a Vacuum Generator Escalab 210 spectrometer, using the monochromatized Al-$K\alpha$ line at 1486.6 eV for XPS. A fixed analyser pass energy of 20 eV was used for C1s core level scans. The photoelectron take-off angle was 90° with respect to the sample plane, which provides an integrated sampling depth of approximately 15 nm for XPS. The energy scale of the instrument was calibrated by setting Au $4f_{7/2} = 84.00$ eV, $Ag3d_{5/2} = 368.70$ eV, $CuL_3M_{4,5}$-$M_{4,5} = 567.90$ eV and $Cu2p_{3/2} = 932.65$ eV. During XPS measurements, these levels were not shifted in energy, thus suggesting that no charging phenomena occurred in the films.

No direct measurement of the molar masses (Mw or Mn) of the grafted polymers was possible since the grafted films could not be separated from their substrate under mild and controlled conditions.

3 Results and discussion

All the experiments reported here were performed with agarose gel as a cell. Only three examples are detailed here, to illustrate the versatility of the process: (i) grafting a diazonium salt (NBDT); (ii) grafting a water-soluble vinylic monomer (AA); (iii) grafting a hydrophobic monomer in emulsion conditions (BuMA). Supplementary material gathers other examples of both cases, together with studies of experimental parameter variations. Agarose could also be replaced by polyacrylamide, as shown in the supplementary material.

As the gel preparation requires heating to disperse the dextran macromolecules, the thermal stability of the radical polymerization precursors was an issue to be considered for choosing between free diffusion of the reactants in the preformed gel and dissolution of the reactants in the starting agarose solution. Our comparison tests indicated that it was actually possible to add the vinylic monomer to the starting agarose solution before the heating step (see supplementary material with HEMA as monomer). IRRAS analysis of the final gel showed that HEMA was not significantly damaged by the heating step. Moreover, the HEMA final concentration within the gel was estimated three times higher than obtained by the free diffusion route, which eventually led to thicker grafted films. However that method could not be applied to the diazonium salts, which are much more fragile, and to hydrophobic monomers. Hence, unless stated otherwise, we only used free diffusion of the vinylic + diazonium salt mixture into the preformed hydrogel to prepare the solid electrolyte.

3.1 Hydrogel-cell electrografting of pure diazonium salts

Electrografting was performed by cycling ten times between the equilibrium potential (+0.04 V) and the final

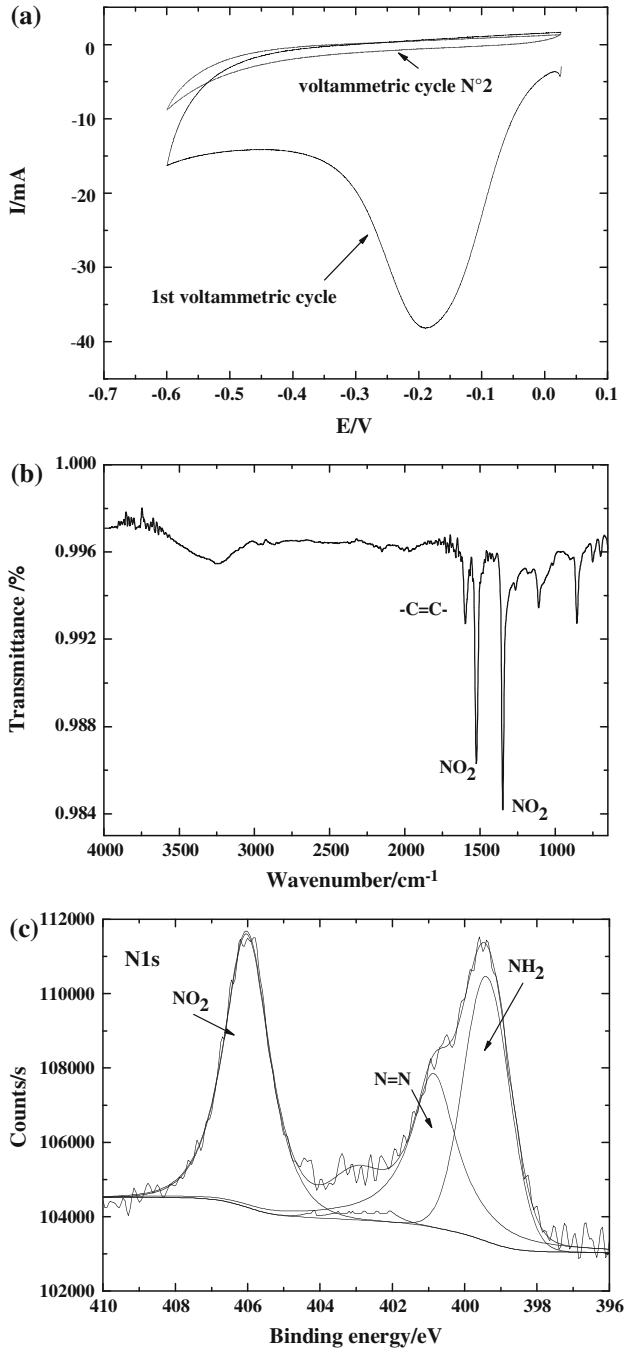


Fig. 2 **a** Voltammogram of an aqueous agarose gel containing NBDT in contact with the gold surface. **b** IRRAS spectrum of the gold slide surface obtained after cathodic electrografting of NBDT from a hydrogel-cell. **c** XPS spectrum of the core level N1s of electrografted PNP thin film on gold surface from a hydrogel-cell

potential (−0.6 V) at 20 mV s^{-1} scan rate. The resulting voltammogram is shown in Fig. 2a (only the first and second cycles are represented) and the IRRAS spectrum of the grafted film is represented in Fig. 2b. In Fig. 2a, the reduction peak of the N_2^+ groups appears at −0.19 V. The slight difference observed from classical conditions (−0.1 V when reducing NBDT in aqueous solution) is assumed to arise from a lack of conductivity within the hydrogel-cell or the peculiar solvation environment provided by the gel that could stabilize the diazonium cation. Electroreduction of aryl diazonium salts has been extensively studied. The first reduction process involves the transfer of one electron, yielding the unstable aryldiazonium radical $ArN_2^{\cdot}$ at low reduction potential [13]. This radical further decomposes yielding N_2 and aryl radical $Ar^{\cdot}$. The generated aryl radicals, binding to the surface via covalent bonds, give a polyphenylene-like grafted film. Thus, the reduction peak decreases in intensity with the number of cycles, as shown by Fig. 2a. This behaviour is characteristic of an electrode passivation resulting from the progressive coating by a polymer film [15, 16]. The IRRAS spectrum (Fig. 2b) exhibits the characteristic NO_2 bands of the expected polynitrophenylene-like film at 1,524 and 1,350 cm^{-1} attributed to the stretching vibration of this group. The absorption band at 1,600 cm^{-1} indicates the presence of the phenyl groups. XPS analysis (Fig. 2c for N1s, Fig. Sup. Mat. a2 for C1s and Fig. Sup. Mat. a3 for O1s) confirmed the IRRAS results. The N1s peak centred at 406 eV is characteristic of the NO_2 group, together with the O1s peak centred at 533 eV. The second peak around 399 eV can be assigned to various forms of nitrogen derivatives, including amino groups arising from electroreduction of the nitro group. The deconvolution of the peak at 399 eV also reveals a shoulder peak centred at 401 eV, which is attributed to azo groups (–N=N–) coming either from incomplete electro-reduction of the diazonium group (as already shown by Belanger [17]) or from a direct coupling reaction between the diazonium salt and any grafted aromatic ring in the polynitrophenylene-like film (PNP). Finally, the C1s peak centred at 284.8 eV is attributed to the carbon double bond of the aromatic nucleus. The deconvolution of this peak shows the carbon directly bonded with the nitrogen atom. In Fig. Sup. Mat. a1, the presence of the Au 4f peak centred at 84 eV indicates that the thickness of that PNP grafted film is less than 5 nm.

In order to estimate the surface coverage of the PNP films, we investigated the electrochemical properties of the grafted nitrophenyl groups using TEAP (5×10^{-2} M) as supporting electrolyte in acetonitrile. Nitrophenyl groups grafted on a gold surface show two electron transfer steps, as shown by Uetsuka [18] at *ca.* −1.2 V and −1.5 V. From the experimental transferred charge we could estimate the surface coverage as 8×10^{-10} mole cm^{-2} for 10 min of electrografting (ten cycles at 20 mV s^{-1} with a final potential at −0.6 V) and 13×10^{-10} mole cm^{-2} for 30 min of electrografting (ten cycles at 20 mV s^{-1} with a final potential at −1.6 V). These values are in agreement with those obtained with films synthesized in homogeneous conditions (without the presence of the gel) on gold [19].

These figures are lower than those reported for spontaneous PNP grafting on glassy carbon from PDMS stamps by Downard, but comparable to spontaneous grafting observed from the same PDMS stamps on pyrolyzed photoresist film (PPF) [20]. Both carbon-based surfaces are prone to spontaneous reactions with diazonium salts, as already shown with carbon nanotubes [21]. However, we did not observe any spontaneous grafting from our agarose hydrogel-cells when put in contact with gold, which is consistent with the very few reports on spontaneous diazonium grafting on gold.

3.2 Hydrogel-cell EIRP from water-soluble vinylic monomers: NBDT/acrylic acid couple

As already described [14], the diazonium salt plays a double role in EIRP: it forms a primer PNP-like grafted film under cathodic conditions, as demonstrated in the previous section; it also acts as a radical initiator of the polymerisation of the vinylic monomer that diffuses out of the hydrogel. As already demonstrated in classical electrochemical conditions [14], the growing radical oligomers may react with the PNP primer film and eventually form a vinylic polymer layer chemically grafted to the electrode surface. The following experiments show that this process is also efficient when using a hydrogel as reservoir instead of a liquid electrolytic. Various couples involving NBDT as radical initiator and different vinylic monomers were studied.

Acrylic acid (AA) is a vinylic monomer totally miscible in water. The electrochemical medium was prepared as previously described. The electrografting conditions were: ten voltammetric cycles from the equilibrium to the final potential (−1.8 V) at 10 mV s^{-1} scan rate. An experiment was also performed without NBDT in the electrografting solution. It resulted in no grafted film on the gold plate. This test shows that the presence of the NBDT is essential for the grafting of the vinylic film.

The voltammogram recorded during the electrografting experiment with the NBDT/AA couple is represented in Fig. 3a (first and last cycles only). The reduction peak of the diazonium salt at −0.5 V is only visible during the first scan, at a reduction potential significantly more cathodic than in previous experiments with NBDT alone. This potential shift is attributed to the conductivity decrease arising within the gel from hydrogen bonds between dextran and acrylic acid molecules that modify the gel texture. The IRRAS spectrum recorded on the resulting grafted film (see Fig. Sup. Mat. f) shows the characteristic acid group of PAA at 1,727 cm^{-1} (stretching vibration of C=O group) and the NO_2 group of PNP at 1,530 and 1,350 cm^{-1}. The XPS analysis (Fig. 3b) also confirms the presence of both polymers. Indeed, the C1s peak shows PNP, with the peak centred at 284.8 eV attributed to the carbon double bond of

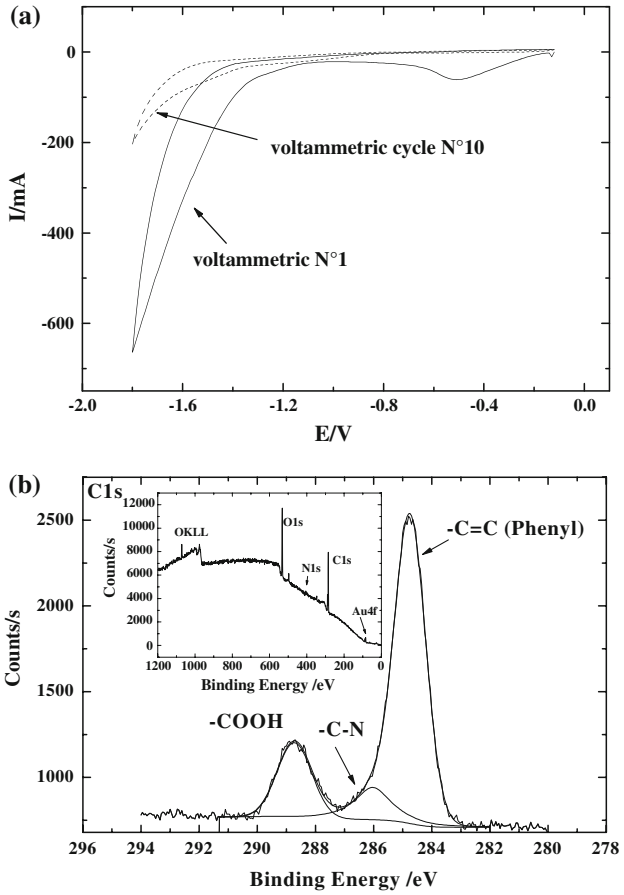


Fig. 3 **a** Voltammogram of an aqueous agarose gel containing AA and NBDT in contact with the gold surface. **b** XPS spectra of the survey (insert) and the core level C1s of electrografted PNP-PAA on gold surface from a hydrogel-cell. The global spectrum shows a very thin Au4f peak at 84 eV that indicates that the thickness of the grafted layer is around 15 nm

phenyl groups, and PAA with the peak centred at 289 eV, assigned to acid groups (–COOH). Nitrogen peaks (not shown) attributed as above are visible (even though weak) in the N1s region. The global spectrum represented in Fig. 3b shows a very small Au4f peak at 84 eV indicating an overall film thickness between 10 and 15 nm, XPS is only sensitive to the outer 15 nm of the coating (mean escape depth of electrons in polymeric material).

The influence of several experimental parameters was studied with this system: final potential, monomer concentration and the relationship between the thickness of the gel and the thickness of the final grafted film. Details on these studies are gathered in the supplementary material. The main conclusions are the following:

- The thickness of the grafted film logically increases with the final potential applied to the gel. At highly cathodic potentials (below −1.5 V) it is likely that the radical polymerization of acrylic acid is initiated not

only by the aryl radicals produced by the reduction of the NBDT molecules but also by hydrogen radicals resulting from the reduction of protons [14]. The lack of grafting observed in the absence of NBDT, however, shows that the initiation by hydrogen radicals alone is not sufficient to ensure the grafting of the vinylic polymers onto the substrate.

- Thicker films are also obtained when the concentration of the source solution is increased, directly correlated with the actual concentration of AA within the agarose gel after diffusion of the source solution (IRRAS measurements at 1,693 cm^{-1}, carboxylic acids conjugated with the C=C double bonds: 3% (3.7 M), 7% (5.2 M), 9% (7.4 M)).
- The thickness of the hydrogel-cell in the 0.8–2.2 cm range has no effect on the thickness of the final grafted film. Actually, the planarity of the gel surface seems to be the most important parameter, because it directly acts on the contact area of the gel with the two electrodes. Although we tried to keep the actual pressure applied to the hydrogel-cell at the same value (around 2 g cm^{-2}), this parameter could explain the weak variation observed on the IRRAS spectra recorded on similar samples.
- Finally, the repetitiveness of the process was studied. For this purpose, the agarose gel was immersed only once in the electrolytic seeding solution under argon bubbling and then used several times for hydrogel-cell electro-induced radical grafting. The IRRAS spectra recorded on the successive gold samples were collected. The results indicate that agarose gel can be used *ca.* ten times consecutively without refilling and with no significant decrease in the thickness of the resulting grafted film.

Supplementary material also gives the results obtained with another water-soluble monomer, HEMA, which was shown to be grafted as AA by hydrogel-cell EIRP.

3.3 Hydrogel-cell EIRP with hydrophobic monomers: NBDT/BuMA couple in emulsion

The conditions described above cannot be directly applied to vinylic monomers that exhibit very poor water solubility. Indeed, the diffusion of the seeding solution within the gel requires good dispersion of the reactants in the seeding electrolytic solution.

Following our recent study of cathodic electrografting from emulsions [14], we demonstrated that emulsions of hydrophobic monomers in water can be successfully diffused within hydrogels to be used as electrolytic reservoirs for EIRP.

We selected butyl methacrylate (BuMA, whose solubility in water is only 0.6 wt%) as hydrophobic vinylic monomer to demonstrate hydrogel-cell EIRP. The anionic surfactant was sodium dodecyl sulfate (SDS). The surfactant concentration was close to the critical micellar concentration 3×10^{-3} M (the cmc was estimated by recording the

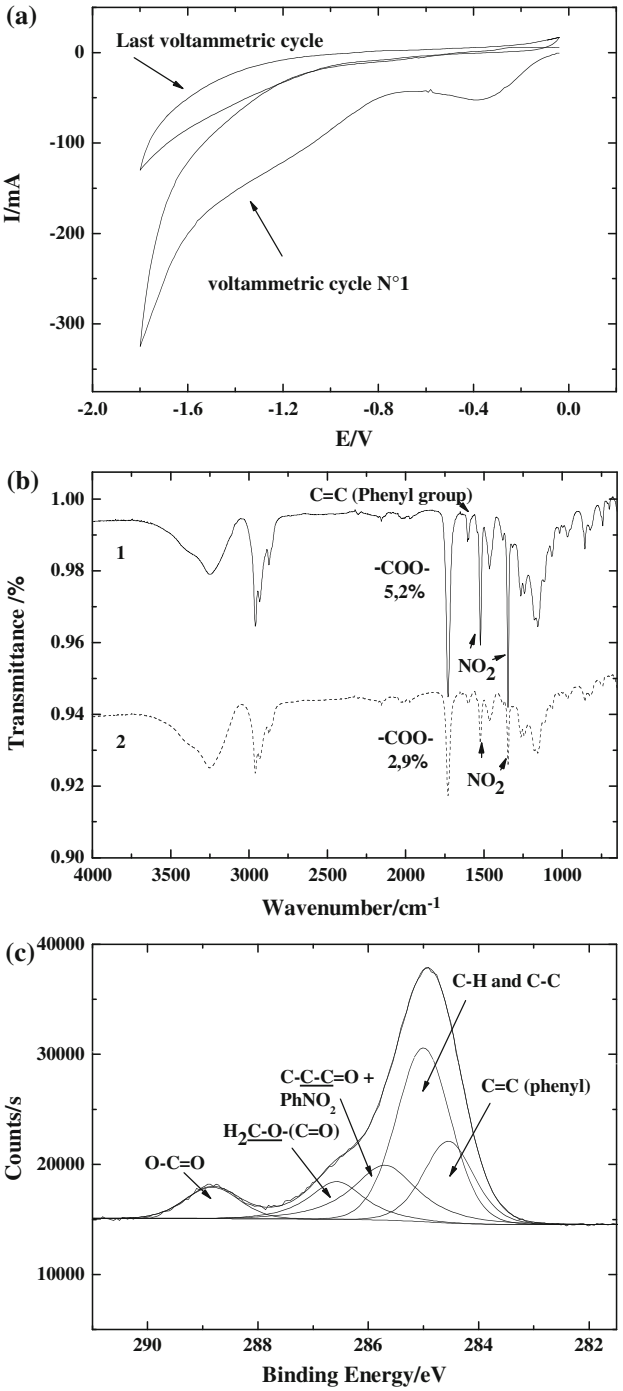


Fig. 4 **a** Voltammogram of an aqueous agarose gel containing NBDT and BuMA in emulsion in contact with gold surface. **b** IRRAS spectra of the gold slide surface after cathodic electrografting of NBDT and BuMA in emulsion from a hydrogel-cell, before and after ultrasonic treatment. **c** XPS spectrum of the core level C1s of electrografted PNP-PBuMA on gold from a hydrogel-cell

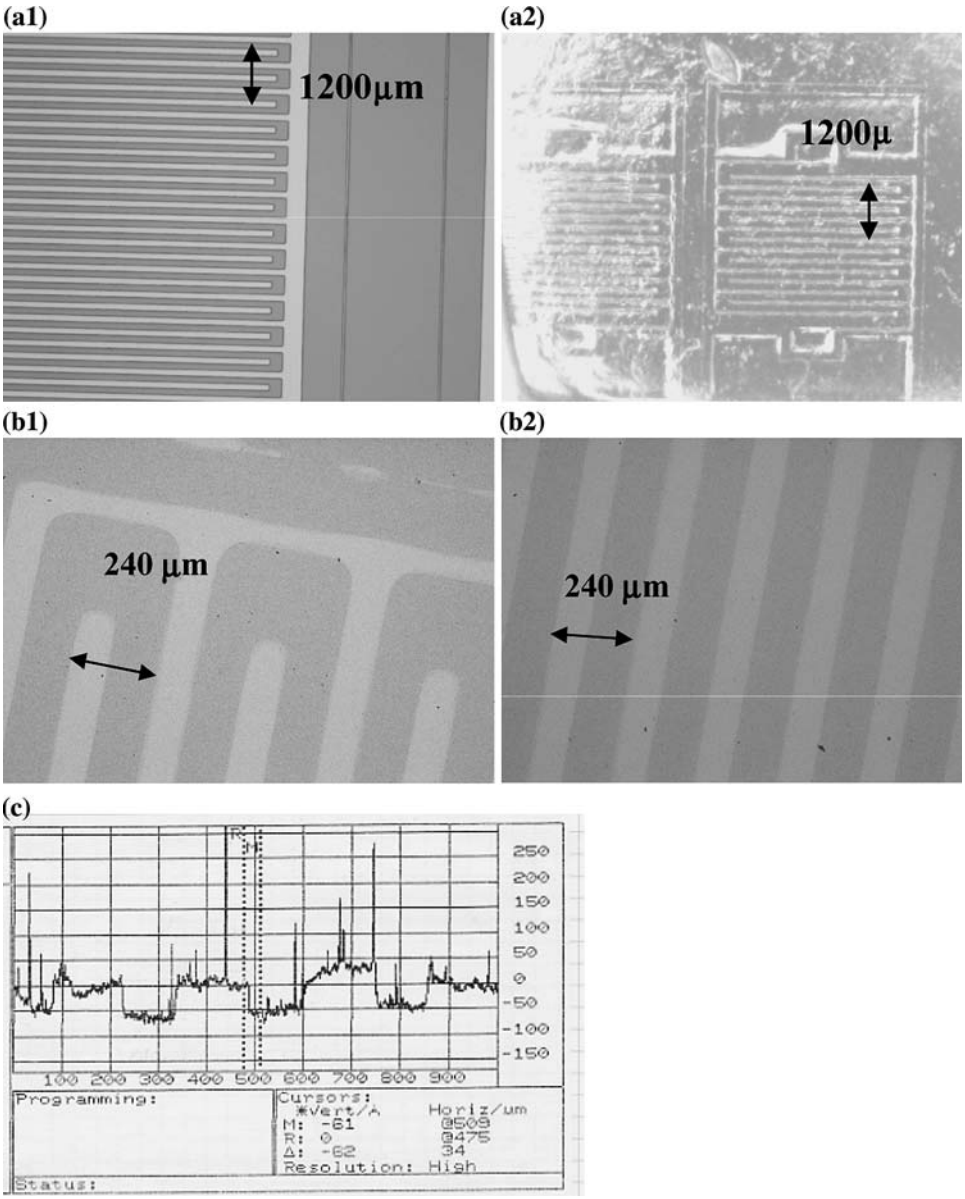


Fig. 5 Optical micrographs of a patterned silicon wafer (**a1**), of the agarose gel (**a2**) and the lines transferred by EIRP on the gold slide surface (**b1**, **b2**) with an agarose gel containing HEMA. **c** The profile of the surface measured by profilometry

conductivity of our system [BuMA + SDS + NBDT + H_2SO_4] as a function of SDS concentration [22]; our value is close to published ones for a similar system: $\sim 5 \times 10^{-3}$ M for SDS + NBDT [23]).

The electrolytic seeding emulsion was prepared as described above and the gel of agarose was left in contact with the monomer emulsion for 3 h. The electrografting conditions were: ten voltammetric cycles from the equilibrium to the final potential (−1.8 V) at 10 mV s^{-1} scan rate. Figure 4a shows the voltammogram recorded during the electrografting and the reduction potential of the diazonium molecules appears at −0.38 V. The IRRAS spectra recorded before (1) and after ultrasonic treatment (2) in DMF, are represented in Fig. 4b. As observed with water-soluble monomers, the ultrasonic treatment discarded a significant amount of ungrafted polymer. The XPS analysis (Fig. 4c) confirms that the layer has a thickness around 10–15 nm (in the global spectrum (not shown) the Au4f peak is very small). The decomposition of the C1s peak shows the carbon double bond of phenyl groups centred at 284.5 eV and the aliphatic carbon of the PBuMA centred at 285 eV. The carbon of the PBuMA ester groups appears at 288.8 eV.

We have shown that the SEEP (surface electroinitiated emulsion polymerization) process can be applied with an agarose gel and it leads to grafted thin layers onto the gold surface.

3.4 Hydrogel-cell EIRP for localized grafting

In this section we describe how hydrogel-cell electrografting can be used to transfer a pattern from the gel onto the substrate. The process actually derives from the

well-known microcontact printing technique (μCP) originally described by Whitesides [24] and more recently applied to diazonium salts by Downard [20]. Indeed, the transfer of matter from the patterned gel to the substrate occurs only in the areas actually in contact. The main difference with μCP is that a potential is applied through the patterned gel to improve the transfer of material and its actual grafting to the substrate.

For these experiments, the hydrogel stiffness was increased by using a higher agarose concentration during preparation (4 wt%). Hence, the patterned gel was expected to withstand more easily the stress experienced during the EIRP step, both from mechanical and electrodynamic origins. The hydrophilic monomer HEMA was used and incorporated during the preparation of the gel as described in the experimental section. The patterned silicon wafer, the patterned gel and the modified gold plate are therefore shown in Fig. 5. The transferred pattern can be clearly seen on the optical micrographs. The grafted lines are 130 μm wide, spaced by 110 μm and ~6 nm thick, as measured by profilometry. This first result is promising. Experiments are currently in progress to decrease the size of the transferred pattern and check the resolution limit of this "electroprinting" technique.

4 Conclusion

We demonstrated that hydrogels such as agarose or polyacrylamide can be used as electrolytic reservoirs for electrografting polyphenylene-like or vinylic polymer films through the electro-induced radical polymerisation mechanism. The resulting grafted films are comparable in thickness and composition to similar films obtained from fluid electrolytic solutions in a classical electrochemical cell. A pattern carved in the hydrogel can even be transferred and "electroprinted" on the electrode surface, opening the way to efficient one-step localized polymer grafting on any conducting substrate. This novel method, which avoids dipping the substrate in a solution, could be applied to locally modify very large pieces of conducting material which cannot be easily dipped in an electrolytic solution, is also significantly less solvent-consuming, since the same soaked-hydrogel can be used several times with similar results.

References

1. Pal K, Banthia AK, Majumdar DK (2007) AAPS Pharm Sci Technol 8:21
2. Small CJ, Too CO, Wallace GG (1997) Polym Gels Netw 5:251
3. Hazra A, Sen P, Basumallick IN (2001) J New Mater Electrochem Syst 4:89
4. Kaneko M, Mochizuki N, Suzuki K, Shiroishi H, Ishikawa K (2002) Chem Lett 31:530
5. Suzuki K, Shiroishi H, Hoshino M, Kaneko M (2003) J Phys Chem A 107:5523
6. Akmal N, Usmani AM (2003) Polym News 28:143
7. Andrews AT (1993) Electrophoresis: theory, techniques and biochemical and clinical application. Oxford Science Publications, Oxford
8. Palacin S, Bureau C, Charlier J, Deniau G, Mouanda B, Viel P (2004) Chem Phys Chem 10:1468
9. Burrell MC, Codela PJ, Fontana JA, Chera JJ, McConnell MD (1989) J Vac Sci Technol A 7:55
10. Viel P, Dubois L, Lyskawa J, Sallé M, Palacin S (2007) Appl Surf Sci 253:3263. Viel P, Palacin S, Descours F, Le Derf F, Lyskawa J, Sallé M (2003) Appl Surf Sci 212:792. Lyskawa J, Le Derf F, Levillain E, Mazari M, Sallé M, Dubois L, Viel P, Bureau C, Palacin S (2004) J Am Chem Soc 126:12194
11. Tourillon G, Garrett R, Lazarz N, Raynaud M, Reynaud C, Lecayon G, Viel P (1990) J Electroanal Chem 137:2499
12. Deniau G, Azoulay L, Jegou P, Le Chevallier G, Palacin S (2006) Surf Sci 600:675
13. Zhang X, Bell JP (1999) J App Polym Sci 73:2265
14. Deniau G, Azoulay L, Bourgerolles L, Palacin S (2006) Chem Mater 18:5421
15. Tanguy J, Deniau G, Auge C, Zalczer G, Lecayon G (1994) J Electroanal Chem 377:115
16. Pinson J, Podvorica F (2005) Chem Soc Rev 34:429
17. Laforgue A, Addou T, Bélanger D (2005) Langmuir 21:6855
18. Uetsuka H, Shin D, Tokuda N, Saeki K, Nebel CE (2007) Langmuir 23:3466
19. Paulick MC, Brooksby PA, Abell AD, Downard AJ (2007) J Phys Chem C 111:7808
20. Garett DJ, Lehr J, Miskelly GM, Downard AJ (2007) J Am Chem Soc 129:15456
21. Bahr JL, Tour JM (2001) Chem Mater 13:3823
22. Chang HC, Lin YY, Chern CS, Lin SY (1998) Langmuir 14:6632
23. González-Romero E, Fernández-Calvar B, Bravo-Díaz C (2002) Langmuir 18:10311
24. Gates BD, Xu Q, Stewart M, Ryan D, Willson CG, Whitesides GM (2005) Chem Rev 105:1171