Surface Modification of Halogenated Polymers. 10. Redox Catalysis Induction of the Polymerization of Vinylic Monomers. Application to the Localized Graft Copolymerization of Poly(tetrafluoroethylene) Surfaces by Vinylic Monomers

Catherine Combellas,* Frédéric Kanoufi, and Sandra Nunige

Laboratoire Environnement et Chimie Analytique, CNRS-ESPCI, 10 rue Vauquelin,
75231 Paris Cedex 05, France

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The polymerization of vinylic monomers such as DMAEMA (2-dimethyaminoethyl methacrylate) can be triggered electrochemically by an electrode and/or a solution electrogenerated reducer (redox catalysis). The electrochemical mechanism is similar to that of other vinylic monomers. As the polymerization can be induced by redox catalysis, the DMAEMA polymerization can be transposed onto the *n*-doped poly(tetrafluoroethylene) (PTFE) surfaces obtained by local scanning electrochemical microscopy reduction of PTFE. The copolymerization is evidenced by the ion-exchange properties of the obtained material. The amount of deposited polymeric material, of estimated width 50−150 nm, is related to the different experimental conditions. The mechanistic observations about the DMAEMA reduction allow a better insight into the PTFE reduction and subsequent DMAEMA copolymerization. It also nicely demonstrates that higher current densities are supported by microelectrode edges.

Introduction

Surface treatments of polymers have many uses, such as the enhancement of aesthetic properties, the increase of wear resistance, the decrease of friction coefficient, or, on the contrary, the increase of adhesion when bonding the polymer to another substrate. Fluoropolymers, in particular, have innately low surface tensions, which are a useful feature when low friction is required but prevent bonding or any application in a hydrophilic or polar environment.

Different types of modifications of fluoropolymers are available, which proceed either (i) in solution by photochemistry or reduction and result in the reduction of the polymeric surface and generally in its carbonization[1−5] or (ii) in the gas phase by X-ray or laser irradiation, ion or electron bombardment, or plasma treatment.[6] Functionalization of carbonized fluoropolymers by hydrophilic polymers has been studied extensively when the fluoropolymer surface has been modified by high-energy radiation,[7] plasma,[8−15] ozone,[16] or UV treatment[17] and to a lesser extent by chemical treatment.[18] Most of the examples deal with poly(tetrafluoroethylene) (PTFE) for biomedical and microelectronic applications.

The usual method consists of (i) grafting a monomer onto the PTFE modified surface and (ii) performing radical-initiated polymerization using UV in an aqueous solution. Classical monomers are hydrophilic, such as acrylic acid, acrylamide, *N*,*N*-dimethylacrylamide, sodium 4-styrenesulfonate, and 2-dimethyaminoethyl methacrylate (DMAEMA).[8,16] This method yields covalent bonds between the polymer and the modified PTFE surface. Defluorination of the PTFE surface and grafting by the hydrophilic monomer can also be performed simultaneously by γ[19,20] or laser[21] irradiation. Copolymerization results in a hydrophilic character of the surface and causes an enhancement in its adhesive properties.

We have already shown that localized functionalization of PTFE can be achieved once PTFE has been reduced locally. The ability to functionalize the surface on a local

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scale is important if one wants to take advantage of both a fluoropolymer inert environment and chosen chemical properties of the surface resulting from the functionalization.[22−25] Localized PTFE reduction was performed either in contact with or in the vicinity of an electrode; in the latter case, either (i) a band microelectrode separated from the polymer by an insulating gap[26] or (ii) a scanning electrochemical microscope (SECM)[27,28] with disk or band microelectrodes[23] was used to generate, in the vicinity of the PTFE, the radical anion $M^{\bullet-}$ of a redox mediator M, which in turn reduces locally the PTFE. It gives *n*-doped polymeric carbon that is able to reduce aryldiazonium or metallic salts, leading to the grafting of the corresponding organic synthons[29] or metals to the polymeric surface.[30] The mechanism proposed for the PTFE reductive transformation into *n*-doped material is represented by the following set of equations:

$$2nM^{\bullet-} + (CF_2)_n \rightarrow 2nM + (C)_n + 2nF^- \qquad (1)$$

$$\delta nM^{\bullet-} + \delta n\mathrm{Cat}^+ + (C)_n \rightarrow \delta nM + (C^{\delta-}, \delta\mathrm{Cat}^+)_n \qquad (2)$$

where $(C)_n$ corresponds to polymeric carbon, which is *n*-doped into $(C^{\delta-}, \delta\ \mathrm{Cat}^+)_n$ after injection of an extra charge δe^- per C atom and an equivalent incorporation of the electrolyte cation (generally Cat^+), to maintain the material electroneutrality.

Besides, deactivation of reduced PTFE zones by air or oxidant exposure yields unsaturations on the polymeric surface that are prone to graft copolymerization; this allowed us to graft a cation exchanger such as poly(acrylic acid) onto PTFE.[31]

Here, we have tried to take advantage of the *n*-doped character of polymeric carbon obtained by electrochemical reduction to initiate an anionic copolymerization without photochemical induction. A vinylic monomer was chosen because the electroreduction of vinylic monomers on conducting or semiconducting electrodes is well described in the literature.[32−40] Generally, the process gives electrografted polymer on the electrode and also some ungrafted polymer in solution. The electrografting reaction has been thoroughly described for methacrylonitrile, acrylonitrile, and various other vinylic nitriles and also for acrylates such as ethylacrylate and methylmethacrylate. We have assumed that such electro-induced copolymerization should also take place on a doped polymeric carbon surface facing the electrode. DMAEMA was chosen as the monomer, although its electrochemically initiated polymerization has not been mentioned in the literature, because grafted poly-DMAEMA should be easy to characterize in solution from its anion exchange properties. Moreover, poly-DMAEMA is a polyelectrolyte particularly interesting in drug delivery applications.[41] Copolymerization was performed either after or at the same time as reduction.

Experimental Section

Materials and Apparatus. The PTFE samples used were PTFE plaques (diameter, 2 cm; thickness, 3 mm) supplied by Goodfellow (U.K.). Before treatment, they were polished (abrasive paper P4000, Presi, Grenoble, France), rinsed in ethanol under sonication for 5 min, and dried in an oven (80 °C overnight).

For the PTFE reduction in dimethylformamide (DMF) solution, tetrabutylammonium tetrafluoroborate was used as the electrolyte; it was synthesized from ammonium tetrafluoroborate and tetrabutylammonium chloride (Fluka, France) and recrystallized in petroleum ether.[42] DMF (puriss, Fluka) was used as received.

Ultrapure water was obtained in the laboratory (Milli-Q grade).

The other chemical reagents were purchased from Aldrich (Saint-Quentin Fallavier, France) and used as received, except DMAEMA which was purified in some cases on an activated basic aluminum oxide column (Brockmann I, Aldrich).

Platinum wires used in the ultramicroelectrodes (diameter of the wire, $\Phi = 25$, 50, 100, and 250 μm) were of 99.9% purity (Goodfellow, U.K.). Ultramicroelectrode tips were obtained according to the literature.[43]

UV spectra were recorded on a Uvikon 860 spectrophotometer (Kontron Instruments), and fluorescence spectra were recorded on a Fluoro Max-2 spectrofluorimeter (Jobin Yvon/Spex).

PTFE Electrochemical Reduction. Reduction of PTFE was achieved in a solution of DMF containing 0.1 M NBu_4BF_4 and 50 mM 2,2′-dipyridyl by applying a reductive potential of −2.4 V/Ag/AgCl to a gold or platinum working electrode for 400 s, as previously reported.[27,28] The counter electrode was a platinum wire, and the reference electrode was Ag/AgCl; their diameters were $\Phi = 1$ mm when a millimetric tip was used and $\Phi = 250$ μm with microelectrodes.

Two different types of electrode systems were used: (i) a millimetric platinum tip ($\Phi = 1$ mm) in contact with a PTFE plaque and (ii) a platinum microelectrode ($\Phi = 25$, 50, 100, and 250 μm) in the vicinity of a PTFE plaque. In case (ii) the tip was moved by a home-built SECM, and the solution contained also 5 mM

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phthalonitrile. The latter did not interfere with PTFE reduction; it allowed the distance between the PTFE and the electrode surfaces to be adjusted according to an already described procedure. The whole device was kept under nitrogen in a polyethylene bag (glovebag, Aldrich) during the experiment. The humidity in the plastic bag was maintained as low as possible, RH < 0.3, with molecular sieves; this was checked by a hair hygrometer.

Electrochemical procedures were performed either in a droplet of ~50 μL of solution or in a 5 mL bath. Reduction resulted in carbonaceous ellipsoids[28] with a thickness of some 0.1 μm and a diameter of 1−2 mm in case (i) and 100−400 μm in case (ii). The solution was degassed with nitrogen for 10 min before use and maintained under nitrogen during the whole experiment.

In all electrochemical procedures (PTFE reduction and monomers cyclic voltammetry), potentials were imposed and currents measured by a potentiostat/galvanostat (PAR 263A model, EGG, U.S.A., or CH720A, CH Instruments).

Photochemical Graft Copolymerization. Once carbonized, the PTFE sample was rinsed in acetone and left to react with air, water, or a $H_2O/H_2O_2/NH_3$ mixture (1:1:1, v/v/v) to oxidize the modified zone and obtain peroxide and hydroperoxide functionalities. No incidence of the reactant used to oxidize carbonized PTFE was observed on the copolymerization yields.

Copolymerization was performed under conditions similar to those used for acrylamide acid copolymerization with polyethylene terephthalate.[44]

The reactant mixture consisted of an aqueous solution containing DMAEMA (30 wt %) and 5×10^{-3} M $NaIO_4$. The PTFE plaque was inserted into a flask and covered with 5 mL of the latter solution. Photopolymerization was started by irradiating the flask by a 4.4 mW cm^{-2} low-pressure mercury lamp (Oriel) for about 1 day. Once polymerization was over, the solution had turned viscous. Then, the plaque was removed from the flask and rinsed thoroughly (i) in distilled water at room temperature, (ii) two times for 2 h in distilled water at 50 °C, (iii) in 11 M hydrochloric acid for 30 min, (iv) in a sodium hydroxide bath (pH = 11) for 30 min and (v) in distilled water.

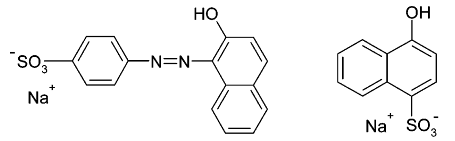
Electrochemical Graft Copolymerization. Two procedures for the electrochemical graft copolymerization were used depending on whether the monomer was introduced (i) after or (ii) during PTFE reduction. Before use, the DMAEMA solution was deaerated by a nitrogen flow for 20 min. In case (i), immediately after PTFE reduction, if reduction had been performed in a bath, the monomer was added to the reductive bath, or if reduction had been carried out in a droplet, the latter was removed and replaced by a droplet of the DMAEMA solution. In case (ii) PTFE reduction was performed in the presence of DMAEMA. After copolymerization, the plaque was successively rinsed in acetone, ethanol, and water and then left for one night in water.

Passivation of the electrode may be observed at high DMAEMA concentrations; this results from electropolymerization at the electrode and could be partly responsible for the moderate amount of grafted polymer obtained.

Characterization of the Grafted Film. The amount of grafted copolymer was determined indirectly by complexing the copolymer acidic form by an anion possessing spectroscopic properties. According to the literature, the pK_a of the copolymer was ~7, and therefore in acidic media, the copolymer was of cationic nature and prone to complexation with anions.[45]

For that, the grafted plaque was first left in an acidic solution (HCl, pH = 3.5) in the presence of 5 mM of the anion for one night. Both anions represented in Scheme 1 were used. The acid orange 7 (AO^-) can be characterized by visible absorption spectroscopy (λ_{max} = 480 nm) while sodium naphthol sulfonate (NS^-) exhibits fluorescent properties (λ_{max} = 430 nm for the emission with λ_{ex} = 330 nm for the excitation). The former was used for millimetric reduced zones and the latter, which can be detected with a higher sensitivity, for smaller modifications.

Scheme 1



acid orange 7, AO^- 1,4-napthol sodium sulfonate, NS^-

After complexation, the excess of unreacted anion was eliminated by contact with an acidic solution. For AO^-, a droplet of an acidic solution (HCl, pH = 3) was deposited three times for 10 min on the reduced zone. For NS^- the plaque was immersed into a (HCl, pH = 5) bath for 10 min.

To extract the anion from the film, the exchange reaction was performed in a 10 μL droplet of a basic or neutral solution deposited on the modified zone. For AO^-, a droplet of a NaOH solution (pH = 11) was reacted for 30 min. Such a droplet was then removed, the copolymer was rinsed in a known volume of the basic solution, and an excess of basic solution was added to the two latter volumes so that the total volume was 200 μL. The amount of anions extracted from the film was deduced from the 250−600 nm spectrum of the solution and the calibration curve at the absorption maximum. For NS^-, a droplet of a KH_2PO_4/K_2HPO_4 (0.026 M/0.091 M) buffer solution (pH = 7.5) was reacted for 30 min. The NS^- containing droplet was then completed to 300 μL before spectroscopic analysis by fluorescence (λ_{ex} = 330 nm, emission registered between 350 and 500 nm and measured at the maximum).

An average thickness of the grafted film could be estimated, if one assumes that the copolymer film was cylindrical with a constant thickness. The latter could be related to the cationic amino sites surface concentration, Γ, by the following relationship:

$$e = (\Gamma_f - \Gamma_i)M/\rho \qquad (3)$$

where Γ_f and Γ_i are the N surface concentrations respectively in the case of grafted and ungrafted PTFE, M is the molecular mass of the monomer (157 g mol^{-1} for DMAEMA), and ρ is the density of the monomer (0.93 g cm^{-3} for DMAEMA). In all cases, Γ_i was lower than the residual signal from the spectrophotometer.

Results and Discussion

As expected, PTFE activation was necessary to graft the surface (see entry 0 in Table 1).

DMAEMA photochemical copolymerization following reduction was tested with a contacting millimetric electrode used. Activation of the PTFE surface by a strong enough reducing species such as the 2,2′-dipyridyl radical anion was necessary to copolymerize the surface (compare entries 1 and 2 in Table 1).[27] UV analysis by acid orange 7 gave a poorly reproducible surface coverage (from 30 to 60 nmol cm^{-2} with a 1 M DMAEMA solution). Besides, we found that (i) it was difficult to sort the ungrafted polymer from that grafted at the electrode and (ii) the grafted film stability was poor because its capacity at the second use had decreased dramatically. Such results contrast with those obtained for the photochemical copolymerization of acrylic acid on PTFE,

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Table 1. Graft Copolymerization of PTFE with Poly-DMAEMA

entry	reactants	PTFE modification	N surface concentration Γ,[a] nmol cm^{-2}
	Blank (No Activation)		
0	DMAEMA	no	0
	Photochemical Polymerization (2) after Local Reduction (1)[b]		
1	(1) phthalonitrile (2) + DMAEMA	no	0
2	(1) 2,2′-dipyridyl (2) + DMAEMA	yes	30−60
	Electropolymerization (2) after Local Reduction (1)[b,c]		
3	(1) phthalonitrile (2) + DMAEMA	no	0
4	(1) 2,2′-dipyridyl (2) + DMAEMA	yes	10−100
	Simultaneous Local Electropolymerization and Reduction[b,d]		
5	phthalonitrile + DMAEMA	no	0
6	DMAEMA	no	0
7	2,2′-dipyridyl +DMAEMA	yes	5−70

[a] Depending on the experimental conditions (see text). [b] Local reduction of the PTFE surface is performed at the reduction potential of the redox mediator (phthalonitrile or 2,2′-dipyridyl) generated at the microelectrode, except for entry 6 where DMAEMA is reduced at the microelectrode to induce the local reduction of PTFE. [c] Steps 1 and 2 as sketched in Figure 3a. [d] Direct electropolymerization as sketched in Figure 3b.

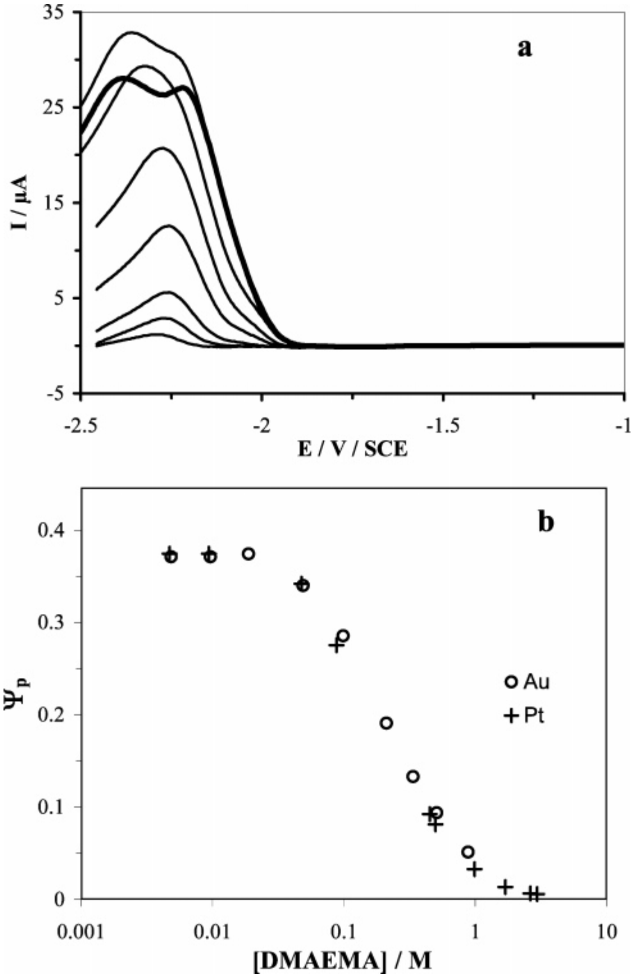

Figure 1. Cyclic voltammetry of DMAEMA in DMF + 0.1 M NBu_4BF_4. a: Au disk electrode, diameter, 1 mm. Background subtracted. Scan rate, 100 mV s^{-1}. [DMAEMA]: thin line, from bottom to top, 4.9, 9.7, 19, 47, 98, 216, and 551 and thick line, 1023 mM. b: ○, Au disk, diameter 1 mm; +, Pt disk, diameter 250 μm. DMAEMA reduction peak current adimensionalized by comparison to the reversible one-electron peak current of phthalonitrile (dimensionless current = 0.446) and corrected from the variation of diffusion coefficient with [DMAEMA].

which gives a highly stable film even after 1 year of air exposure.[31] A hypothesis is that the DMAEMA film is mainly adsorbed rather than grafted. In the following, we will only focus on electrochemical polymerization.

DMAEMA Reduction in DMF. The reducibility of the DMAEMA monomer at different concentrations ranging from 5×10^{-3} to 1 M was first studied. Figure 1a presents the reduction of a 5 mM DMAEMA solution on a millimetric Au electrode. DMAEMA is reduced at approximately −2.21 V versus saturated calomel electrode (SCE) with a peak current smaller than the one-electron reversible reduction peak for phthalonitrile at the same concentration. This indicates that the DMAEMA reduction consists of an exchange of one electron followed by an irreversible second-order chemical step that consumes the DMAEMA, likely a dimerization step. When increasing the concentration, the reduction occurs in the same potential region but a shoulder or a pre-wave or two reduction peaks appear, and the reduction corresponds to amounts of transferred electrons decreasing with [DMAEMA].

Figure 1b presents the evolution of the dimensionless DMAEMA peak current, corrected from changes in the diffusion coefficient due to viscosity changes at high concentrations, at both Au millimetric and Pt micrometric electrodes, with [DMAEMA]. For concentrations higher than 20 mM, the DMAEMA reduction requires an electron stoichiometry decreasing with [DMAEMA]. This confirms that the product generated by the first electron transfer to DMAEMA is engaged in a chemical reaction that consumes an abundant amount of DMAEMA. This behavior is identical to that observed during the reduction of other vinylic monomers, Vin, such as acrylonitrile and so forth[46,47] and whose reduction leads to the anionic polymerization of Vin. Briefly, the first electron transfer to Vin (eq 4) generates the radical anion of the vinylic monomer, Vin$^{\bullet-}$, which dimerizes, at a rate k_d, in solution thanks to a radical coupling initiation (eq 5). The formed dianionic species initiates and propagates the anionic polymerization of Vin in solution, with a rate of k_p (eq 6).

$$\text{Vin} + \text{e} \rightarrow \text{Vin}^{\bullet-} \qquad (4)$$

$$2\text{Vin}^{\bullet-} \xrightarrow{k_d} \text{Vin}_2^{\;2-} \qquad (5)$$

$$\text{Vin}_n^{\;2-} + \text{Vin} \xrightarrow{k_p} \text{Vin}_{n+1}^{\;2-} \quad \text{for} \quad n \geq 2 \qquad (6)$$

The propagation reaction (eq 6) clearly demonstrates that under proper conditions, the reduction of Vin leads to abundant consumption of Vin and could cause exchange currents of values much lower than one electron per mole of Vin. Simulation of such a reductive polymerization mechanism by numerical computation has been described.[47,48] It confirms the observation of the low electron stoichiometry

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but also of multiple-peak cyclic voltammetric features. Such behavior is representative of the peculiar polymer growth from the electrode surface through a uniformly moving polymer/solution boundary. Owing to the similarity of the DMAEMA and vinylic monomer cyclic voltammetry features, the DMAEMA reduction leads to its electrochemically initiated anionic polymerization according to the vinylic reduction mechanism presented by eqs 4−6. If the mechanism theoretical analysis allows the explanation of the experimental observations, it is not realistic to use it to extract the mechanism kinetic parameters since (i) too many reaction rates are unknown (k_d, k_p, but also the rates of the termination steps) and (ii) the proposed mechanism does not describe the polymerization on the electrode surface frequently observed experimentally.

Polymerization in solution could be triggered by using a solution electron donor to initiate the reduction/polymerization of Vin rather than an electrode. Generally such a strategy can be achieved by recoursing to redox catalysis. This electrochemical method is well documented[49−51] even though it has not been used, to our knowledge, to initiate vinylic monomer electropolymerization. Briefly, as sketched in eqs 7, 8, 5, and 6, a redox mediator, M, is reduced to the electrode into a radical anion, $M^{\bullet -}$, by a reversible one-electron transfer at a potential more positive than the reduction potential of Vin. The homogeneous electron-transfer reaction between $M^{\bullet -}$ and Vin, even though endothermic, is favored owing to the successive irreversible chemical transformation(s) of Vin $^{\bullet -}$.

$$M + e \rightarrow M^{\bullet -} \tag{7}$$

$$M^{\bullet -} + \text{Vin} \underset{k_{-0}}{\overset{k_0}{\rightleftharpoons}} M + \text{Vin}^{\bullet -} \tag{8}$$

$$2\text{Vin}^{\bullet -} \xrightarrow{k_d} \text{Vin}_2{}^{2-} \tag{5}$$

$$\text{Vin}_n{}^{2-} + \text{Vin} \xrightarrow{k_p} \text{Vin}_{n+1}{}^{2-} \quad \text{for} \quad n \geq 2 \tag{6}$$

The cyclic voltammograms in Figure 2 show examples of redox catalysis of the DMAEMA reduction at millimolar and molar DMAEMA concentrations. The phthalonitrile radical anion ($E^0 = -1.59$ V vs SCE) is not a strong enough reducer to allow the reduction of DMAEMA (see the first system in Figure 2b, it is unchanged after addition of DMAEMA). Besides, the 2,2′-dipyridyl radical anion ($E^0 = -2.10$ V vs SCE) can transfer its electron to the DMAEMA and then catalyze its reduction. For the catalytic polymerization to be effective, the rate constant of the mediated electron-transfer reaction (forward reaction 8, k_0) must be high enough, and it rises higher as the coupling reaction 5 becomes slower. Practically, this means that the mediator standard reduction potential, $E_M{}^0$, must be close to that of DMAEMA, $E_{DMAEMA}{}^0$, or when this value is not known, $E_M{}^0$ must be close to the reduction potential of DMAEMA, $E_{p,DMAEMA}$ (for example, one would choose M such that $E_M{}^0 - E_{p,DMAEMA}{}^0 < 200$ mV).[49]

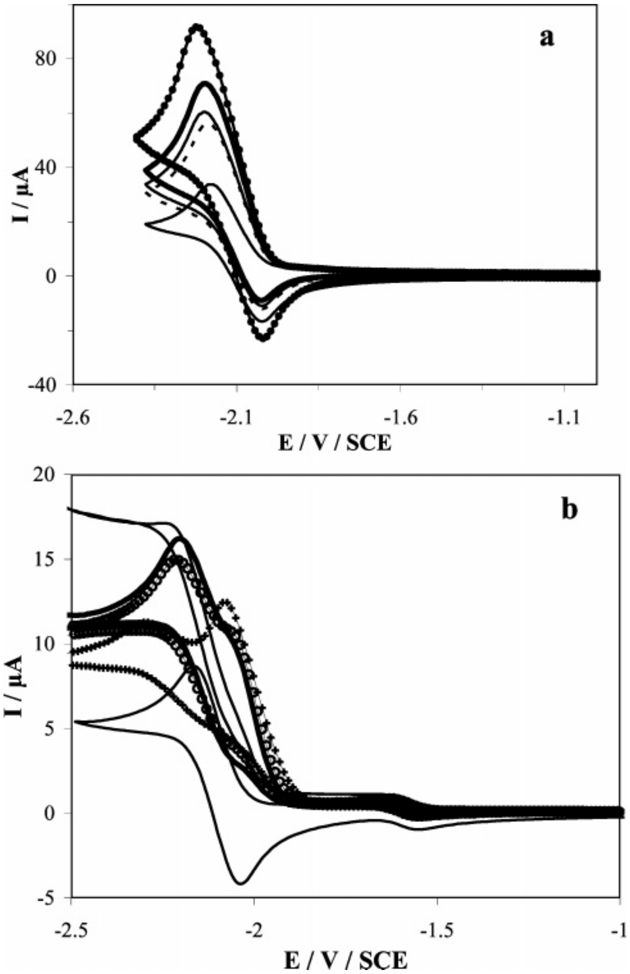

Figure 2. Cyclic voltammetry of redox catalysis of, a, low and, b, high concentration of DMAEMA by 2,2′-dipyridyl in DMF + 0.1 M NBu_4BF_4. Scan rate, 100 mV s^{-1}. a: Au electrode diameter, 1 mm. [DMAEMA] thin line (bottom), 0; dashed line, 5.3; thin line (top), 7.3; thick line, ○, 8.9 mM; [2,2′-dipyridyl] 4.3 mM except for, ○, 8.1 mM. b: Pt disk, diameter, 250 μm. [DMAEMA] dashed line, 0 (bottom) and 0.1 (top); thick line, 0.3; ○, 0.5; +, 1.7 M; [2,2′-dipyridyl] 50 mM. The first system at −1.6 V corresponds to [phthalonitrile] = 4.8 mM.

The catalyzed reduction is illustrated, in Figure 2a,b, by the increase of cathodic current and the loss of anodic reversibility of the 2,2′-dipyridyl system whether reduction is performed in the presence of <10 mM or >0.3 M of DMAEMA, respectively. As observed in Figure 1b, multiple reduction peaks appear at high [DMAEMA].

From a mechanistic point of view, kinetic rate constants could be extracted from such redox catalysis experiments. This could be achieved at low [DMAEMA] if one assumes that the DMAEMA reduction does not lead to polymerization and might be simplified to reactions 7, 8, and 5 only. However, such a situation is restrictive and does not apply when increasing the monomer concentration, as polymerization (step 6) becomes predominant. In the latter case, the reaction mechanism becomes likely too complex to be simply modeled. Indeed, the increase of [DMAEMA] leads to (i) an increase of the medium viscosity and thus to a decrease of the species diffusion coefficient and (ii) an increase of

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the number of unknown chemical steps and values of their rate constant. However, as observed during the direct DMAEMA reduction, when increasing [DMAEMA], the redox catalysis efficiency, revealed as the increase of the first reductive peak at approximately −2.2 V in Figure 2b, does not change much. Again, it shows that the electron stoichiometry of the homogeneous reduction of DMAEMA decreases with [DMAEMA]. This outlines the increasing importance of the polymerization propagation step 6 and confirms the polymer growth through a moving (propagating) polymer/solution boundary. We did not attempt to have a deeper and more questioning insight.

From the practical point of view of the SECM and PTFE reduction, as the phthalonitrile radical anion is inert toward DMAEMA and, therefore, does not induce any PTFE reduction, it will be a helpful redox probe for the SECM tip positioning. Besides, because it is well-known that the 2,2′-dipyridyl radical anion catalyzes PTFE reduction, such a redox mediator will be used to reduce both PTFE and also, under favorable conditions, DMAEMA and therefore to allow its polymerization.

The PTFE reduction carbonized product was demonstrated to possess, after reduction, a reductive character, as it allows diazonium and metallic salts reduction.[25,29] So far, it is unclear whether this carbonaceous material is a *n*-doped material, described by eq 2, or whether it encapsulates reducing species such as for example the 2,2′-dypiridyl radical anion. In the latter case, the doped carbonaceous material would rather be formed by eq 2′:

$$\delta n\mathrm{M}^{\bullet-} + \delta n\mathrm{Cat}^{+} + (\mathrm{C})_n \rightarrow \delta n\mathrm{M} + (\mathrm{C}, \delta(\mathrm{M}^{\bullet-}, \mathrm{Cat}^{+}))_n \quad (2')$$

where $(\mathrm{C}, \delta(\mathrm{M}^{\bullet-}, \mathrm{Cat}^{+}))_n$ corresponds to the carbonaceous material in which the 2,2′-dypiridyl radical anion is incorporated, as an ion pair, to maintain the material electroneutrality.

Within both hypotheses, one could then expect that the PTFE reduction product will likely catalyze the DMAEMA reduction and allow DMAEMA polymerization at its carbonaceous surface.

Copolymerization after Reduction. This section will demonstrate the latter proposition by putting in contact a reduced PTFE zone with a DMAEMA solution, as schematically sketched in Figure 3a, and observing how the reduced PTFE zone is affected. As mentioned with photochemical polymerization, activation of the PTFE surface by a strong enough reducing species is necessary to copolymerize the surface (compare entries 3 and 4 in Table 1).[27]

The reduced PTFE zones have been obtained by SECM with an electrode generating a reductive species during a constant time, held at a constant distance from the PTFE surface or in contact with it. It was shown, in a preceding work, that for a given reduction time, the amount of reduced PTFE is proportional not only to the charge flowing through the electrode, *Q*, but also to the extension of the lateral PTFE surface modification, *S*.[28] As presented in Table 2, every time a freshly reduced PTFE zone is left in contact with a DMAEMA solution, an ion-exchanging polymeric film is selectively grown on the reduced PTFE zone, while no polymerization occurs on either untreated PTFE or reduced PTFE deactivated by air, oxygen, or water traces. This indicates that the doped reduced PTFE is able to initiate the DMAEMA reduction, either (i) as an electrode would do, as sketched by the right part of Figure 3a and eq 9, or (ii) by heterogeneous mediated electron transfer (eq 9′) similar to its homogeneous counterpart (eq 8) from the 2,2-dipyridyl radical anion incorporated into the reduced PTFE:

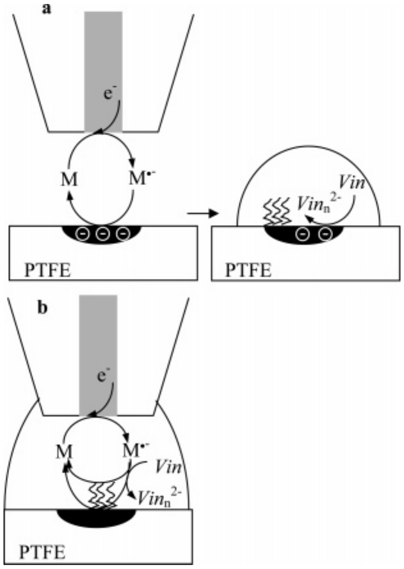

Figure 3. Schematic representation of the local PTFE reduction-copolymerization with a vinylic monomer, Vin. a: Copolymerization performed in a droplet of monomer, Vin, solution, after the PTFE reduction step by the radical anion of M electrogenerated at the microelectrode. b: Simultaneous copolymerization and reduction in a droplet of solution of a redox mediator M and monomer, Vin.

Table 2. Polymerization of DMAEMA after PTFE Reduction[a]

entry	Pt electrode Φ, μm	distance *d*, μm	bath/ droplet	reduced zone surface area *S*, 10^{-3} cm^2	N surface concentration Γ, nmol cm^{-2}
1	250	26	bath	7.5	47
2	250	30	bath	3.4	50
3	250	29	bath	3.6	30
4[b]	250	31	bath	3.2	39
5[b]	250	30	bath	4.0	77
6[b]	250	25	droplet	1.4	23
7[b]	250	25	droplet	1.8	22
8[b]	250	30	droplet	1.5	15
9	50	17	bath	0.93	61
10[b]	100	23	bath	2.2	59
11	1000	contact	bath	28	44

[a] 1 M DMAEMA, 17:100 (v/v). [b] Monomer purification.

$$(\mathrm{C}^{\delta-}, \delta\mathrm{Cat}^{+})_n + \delta n\mathrm{Vin} \rightarrow (\mathrm{C})_n + \delta n\mathrm{Vin}^{\bullet-} + \delta n\mathrm{Cat}^{+} \quad (9)$$

$$(\mathrm{C}, \delta(\mathrm{M}^{\bullet-}, \mathrm{Cat}^{+}))_n + \delta n\mathrm{Vin} \rightarrow (\mathrm{C})_n + \delta n\mathrm{Vin}^{\bullet-} + \delta n\mathrm{Cat}^{+} + \delta n\mathrm{M} \quad (9')$$

For a given electrode diameter, Φ, the influence of some experimental parameters on the reduced zone surface area, *S*, and on the surface concentration of the grafted amino groups, Γ, was then studied. The electrode−substrate distance, *d*, the experiment medium (bath or droplet), and the monomer purity (without and with purification on an activated basic alumina column) were varied. It is difficult to compare precisely the experiments performed in a bath because in such a case, each modification is completely independent from the others: each one was performed on a different PTFE plaque, with its own polishing conditions and so forth. Such difficulty is circumvented by performing the experiment in a droplet because it is then possible to use the same PTFE plaque with different experimental conditions corresponding to different droplets.

Entries 1−5 in Table 2 confirm that *S* decreases when *d* increases from 26 to 29−31 μm, as already observed. The highest Γ should be obtained for the lowest *d*; however, it is not reasonable to position reproducibly the electrode assembly, a 250 μm Pt diameter electrode embedded in a glass insulating sheath of approximately 400−500 μm external diameter, closer than 25 μm to the surface without any contact (between the glass or the Pt disk and the PTFE). That is why lower *d* values were not used. The electrode−substrate distance, *d*, has no effect on Γ, which is roughly 50 nmol cm^{-2} in all cases. Comparison of entries 1−3 to entries 4 and 5 shows that monomer purification does not modify Γ.

Comparison of entries 1−5 to entries 6−8 shows that performing the reduction and the copolymerization in a droplet decreases both *S* and Γ. This should result from the way the experiment is conducted in a droplet. The lower PTFE modification area, *S*, indicates that in a droplet, a smaller amount of reducer reaches the PTFE surface. This could be due, for example, to a higher sensitivity of the small droplet volume to scavenging pollutants such as oxygen or water. Such species may react chemically with the electrogenerated reducer, lower its concentration at the PTFE surface, which, in turn, focalizes the PTFE reduction on a smaller area. This focalization process is known as the chemical lens.[52,53] The effect on the surface coverage could also be related to the same chemical lens phenomenon. The lower the quantity of reducer, the lower the amount of *n*-doped reduced PTFE and the lower the amount of copolymerized DMAEMA. Moreover, when the reduction solution is removed and replaced by the copolymerization solution, some part of the reactive polymer surface may be exposed to the atmosphere inside the glove bag and get deactivated. This is avoided in a bath because in that case, at the end of the reduction, DMAEMA is added to the bath and the surface is never naked. The mean surface concentrations obtained are respectively ∼50 and ∼20 nmol cm^{-2} in a bath and a droplet for a 1 M DMAEMA concentration.

The electrode diameter has an influence on *S*, as already observed,[38] but not on Γ, which remains close to ∼50 nmol cm^{-2} (entries 9−11, bath).

The influence of the DMAEMA concentration used in the polymerization reaction on *S* and Γ was studied. The experiments were carried out with an electrode diameter of 250 μm either with the electrode contacting the PTFE surface or under an SECM configuration and a 25 μm electrode−substrate distance. Using a contacting electrode or under the SECM configuration, the DMAEMA concentration has no influence on *S*, as expected since copolymerization is performed after PTFE reduction (see Figure 4, + under SECM conditions).

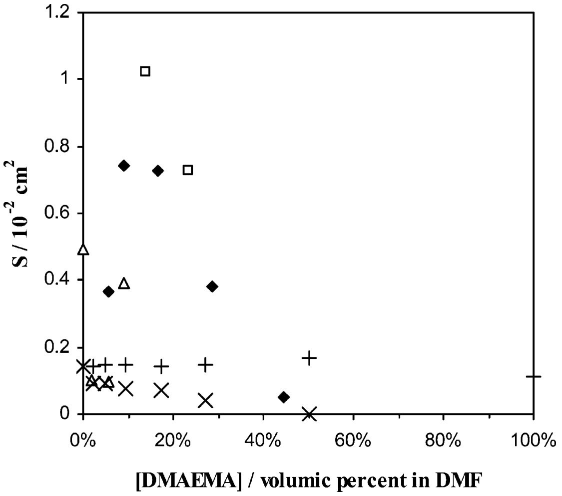

Figure 4. Reduced zone size as a function of DMAEMA volumic percent. Reduction in the presence of DMAEMA except for +. Purified DMAEMA except for ◆ and Δ. □ and ◆, bath and contact; ▲, bath, SECM, *d* = 25 μm; × and +, droplet, SECM, *d* = 25 μm; +, copolymerization with DMAEMA after reduction. 250 μm diameter Pt disk.

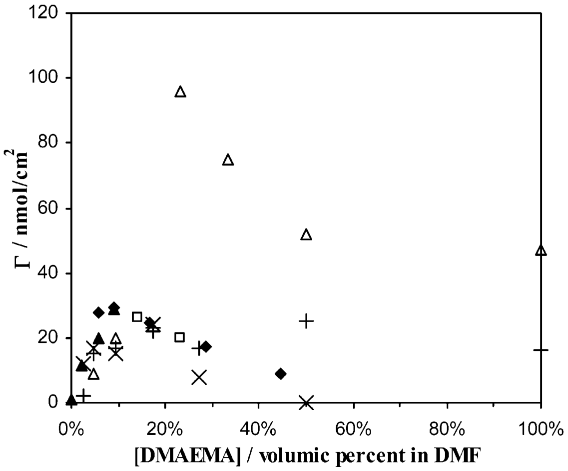

Figure 5. N surface concentration (Γ) as a function of DMAEMA volumic percent. Copolymerization after reduction in a droplet; Δ, contact; +, SECM, *d* = 25 μm. Reduction in the presence of DMAEMA; Purified DMAEMA except for ◆, ▲. □ and ◆, bath and contact; ▲, bath, SECM, *d* = 25 μm; ×, droplet, SECM, *d* = 25 μm. 250 μm diameter Pt disk.

For DMAEMA volume percents lower than 15%, Γ is about the same either with a contacting electrode or under a SECM configuration. Conversely, for higher DMAEMA concentrations, Γ is higher with a contacting electrode; in the latter case, it increases until ∼100 nmol cm^{-2} for a ∼ 20% concentration, then decreases gently until ∼50 nmol cm^{-2} for pure DMAEMA (see Figure 5, Δ). Under the SECM configuration, there is no such clear maximum and Γ does not exceed ∼25 nmol cm^{-2} even for pure DMAEMA (see Figure 5, +). The higher Γ obtained with a contacting electrode could result from the higher thickness of reduced polymer due to the contacting electrode entering slightly into the polymer. With a contacting electrode, the Γ decrease observed for DMAEMA concentration > 30% should be due to the increase of the medium viscosity as a result of the high monomer concentration. The latter would decrease the mobility of the reactive species in the bulk and decrease the growth of the polymeric chains at the material surface. The

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dependence of the grafting yield on the monomer concentration has already been observed in the case of the grafting of poly(acrylic acid) on a polypropylene[54] or a PTFE surface. In the latter case, the maximum grafting yield was obtained for 30% monomer.

Simultaneous Copolymerization and Reduction. Because the lifetime of the reactive species obtained upon PTFE reduction is low, it is not easy to perform reproducible experiments when the monomer is added at the end of PTFE reduction. Simultaneous reduction and copolymerization should avoid this disadvantage. The procedure employed is schematically represented in Figure 3b. Entries 5−7 of Table 1 confirm the usefulness of the activation of the PTFE surface by the 2,2′-dipyridyl radical anion to copolymerize the surface.[27]

First, a blank experiment was carried out, in which a droplet containing 0.1 M DMAEMA was deposited on a PTFE plaque in the vicinity of a microelectrode biased at −2.4 V/Ag/AgCl, a potential reductive enough to allow the DMAEMA reduction. No modification of PTFE occurred. Conversely, when 2,2′-dipyridyl is present, the characteristic black color of reduced PTFE can be observed by the naked eye, and ion exchange properties of the modified PTFE can be evidenced. This indicates that, even though the radical anion of the DMAEMA is a strong reducer, it is not long-lived enough to allow the PTFE reduction. Indeed, in the feedback mode of the SECM, the electrogenerated redox probe needs to be stable enough to reach the substrate and get regenerated at its surface.[55] The stability of the probe for possible regeneration depends on the tip−substrate distance but also on the rate of the electron transfer at the substrate.[56] The same condition on the lifetime of the electrogenerated probe must be fulfilled when it is used for surface modification; it depends on both the tip−substrate distance and the surface etching rate. Under our experimental conditions ($d > 20$ μm and $k_{\mathrm{PTFE}} \approx 0.1$ cm/s), the etching of PTFE would require, according to Figure 8 in ref 56, electrogenerated reducers having a lifetime longer than 0.1 s.

The influence of the presence of DMAEMA during PTFE reduction on the reduced zone area, S, was studied. With a contacting electrode, the reproducibility of S is poor because the electrode may contact the surface to different extents. When the experiment is carried out in a bath with a 25 μm diameter microelectrode positioned at 8 μm from the PTFE surface before DMAEMA addition, S is slightly lower in the presence of DMAEMA (3.0 instead of 3.6×10^{-4} cm^2). This should result from the lower lifetime of the 2,2′-dipyridyl radical anion that is prone to reduce homogeneously DMAEMA as shown in Figure 2. Besides, DMAEMA polymerization at the electrode must also be taken into account.

The experiments carried out in a bath under SECM conditions with different DMAEMA concentrations, c, and the same PTFE plaque are difficult to interpret because for a given d, the electrode current, i, depends on DMAEMA concentration. This means that our procedure, which consists of controlling d by i, requires that approach curves are known for the DMAEMA concentration used. This was out of the scope of this paper. Only the approach curve for a 1 M DMAEMA concentration (17%) was determined, and the distance for all concentrations was roughly adjusted with that curve. This drawback is circumvented by performing the experiment in a droplet; d is then adjusted for each droplet before DMAEMA addition, and the distance is known precisely.

Figure 4 shows that for experiments performed in a droplet, for a given c, S is smaller when reduction has been performed in the presence of DMAEMA (compare + and × for, respectively, reduction in the absence and presence of DMAEMA). This had been noticed in a bath (see above) and can be explained in the same way. When DMAEMA is present, the 2,2′-dipyridyl radical anion is engaged in the homogeneous reduction of DMAEMA, eq 8, as observed in Figure 2b. Its lifetime decreases, and the PTFE reduction is confined in a smaller region. As long as the PTFE surface is reduced into a carbonaceous material, the homogeneous reduction of DMAEMA by the 2,2′-dipyridyl radical anion is kinetically controlled by a smaller than 10 s^{-1} apparent rate constant. The tendency observed for the influence of the presence of DMAEMA in a bath is the same (not shown because d is poorly controlled from one sample to another).

In the experiments represented by the ◆, ▲, and □ symbols in Figure 4 (bath), S increases with [DMAEMA] until [DMAEMA] ∼ 1 M (17% volumic percent), and then it decreases. In the 0.1−1 M range, it is in agreement with the inspection of the cyclic voltammogram of a DMAEMA + 2,2′-dipyridyl solution, presented in Figure 2b. Indeed, the catalytic efficiency for DMAEMA reduction, i_{cat}, follows the same trends: $i_{\mathrm{cat,0.1M}} > i_{\mathrm{cat,0.3M}} \approx i_{\mathrm{cat,0.5M}} \approx i_{\mathrm{cat,1M}} > i_{\mathrm{cat,1.7M}}$, which explains that the 2,2′-dipyridyl radical anion lifetime is smaller in 0.1 M solution than in the 0.3−1 M range, itself smaller than for 1.7 M solution. However, for 1.7 M DMAEMA solution a smaller surface area is observed; therefore, the only inspection of the cyclic voltammetry is not enough to explain the experimental behavior. As reported previously,[28] the observation of the reduction current flowing through the electrode is more pertinent. Figure 6a presents the chronoamperograms recorded at the tip during the reduction of PTFE in a droplet of solution, in the absence or presence of DMAEMA (respectively + and × symbols in Figure 4). When DMAEMA is present, the tip current is smaller, the 2,2′-dipyridyl regeneration at the PTFE surface, eqs 1 and 2, is lower because the 2,2′-dipyridyl radical anion is consumed by the DMAEMA reduction, eq 8. As presented in Figure 6b, there is a good correlation, for a given tip−substrate distance, between S and Q, the charge flowing at the tip for the 2,2′-dipyridyl reduction. For [DMAEMA] < 1 M the chronoamperometric experiments (see Figure 6a,b) reflect the trends on the efficiency of the redox catalysis (the higher [DMAEMA], the lower the DMAEMA redox catalysis efficiency, the more stable the 2,2′-dipyridyl radical anion, the higher the PTFE reduction and Q), while for molar DMAEMA concentrations, both the catalytic efficiency and

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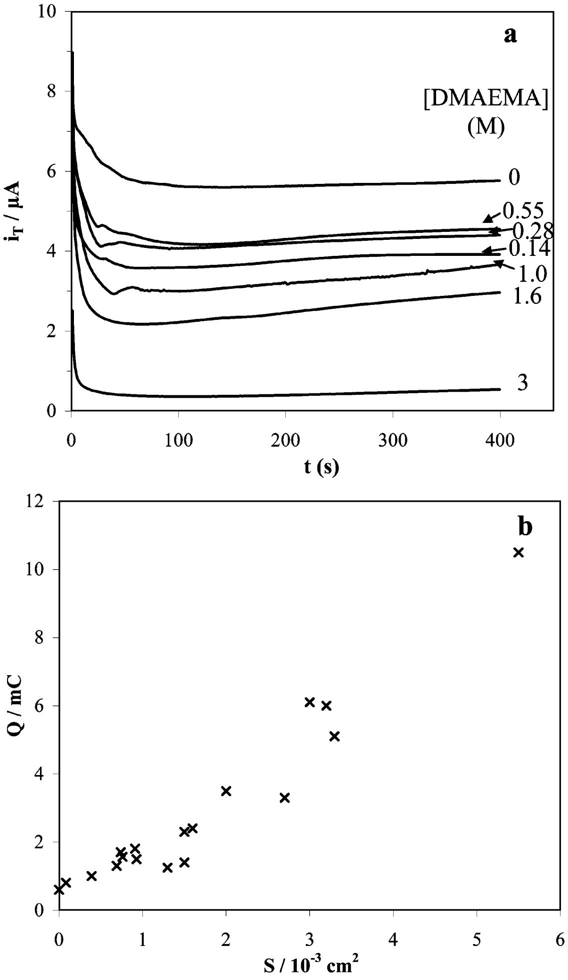

Figure 6. PTFE reduction by electrogenerated 2,2′-dipyridyl radical anion in the presence of DMAEMA at a Pt disk electrode, diameter 250 μm, held at $d = 25$ μm from the PTFE surface. DMF + 0.1 M NBu_4BF_4, [2,2′-dipyridyl] = 50 mM. a: chronoamperograms ($i-t$ curves) of the reduction of 2,2′-dipyridyl at the Pt disk. [DMAEMA]: 0, 0.14, 0.28, 0.55, 1.0, 1.6, and 3 M. b: Evolution of the charge, *Q*, injected for 2,2′-dipyridyl reduction with the surface *S* of the reduced PTFE zone. 0 < [DMAEMA] < 3 M.

Q decrease when [DMAEMA] increases. In this concentration domain, the polymerization is likely so efficient in the solution and at the electrode that it blocks the 2,2′-dipyridyl radical anion propagation in solution and consequently the PTFE reduction.

The lifetime of the 2,2′-dipyridyl radical anion influences not only the surface area, *S*, of the PTFE reduction zone but also its shape. Indeed, in the presence of DMAEMA, one can observe, as shown in Figure 7, that the coloration of the reduced PTFE zone and thus the extent of PTFE reduction are lower in the presence of DMAEMA, which confirms the results observed in Figure 4; moreover, the coloration is exalted on a circle representative of the microelectrode edge (see Figure 7b). Under certain conditions of distance between the electrode and the PTFE surface, one might even observe that the PTFE modification is confined along a circle (see Figure 7c). The latter phenomenon is observed when the 2,2′-dipyridyl radical anion has the lowest probability to reach the PTFE surface, as discussed above. Theoretically,[57] the highest flux of matter (here of the 2,2′-dipyridyl radical anion) is present at the microelectrode edge where the current density is maximum. It is then expected, when the electrogenerated radical anion is unstable, that its concentration is high at the electrode edge and it does not escape much from the edge. One expects the expansion of the radical anion within a crown encircling the microelectrode edge. If this lifetime is high enough, the radical anion will reach the surface and react with it along a circle that is the image of the microelectrode edge, as observed experimentally. This behavior nicely illustrates the edge effect of microelectrodes (high current density flow at the microelectrode edges), which was often demonstrated theoretically[57] but, more rarely, illustrated experimentally during ElectroChemiLuminescence generation at disk microelectrodes,[58] during electrodeposition processes,[59] or during interferometric observation of micro-cantilever double-layer charging.[60]

Concerning the surface concentration of the amino groups, Γ, many features observed for successive reduction and polymerization remain true. Indeed, the highest Γ are obtained (i) with a contacting electrode or under SECM conditions when the electrode is as close as possible to the PTFE plaque, that is, for example, when $\Phi = 250$ μm for $d = 25$ μm and (ii) when the experiment is performed in a bath rather than in a droplet (see Figure 5). There is no influence of the monomer purification on Γ (compare □ and ◆ for respectively monomer purification or without it). There is a maximum for Γ as a function of DMAEMA concentration when copolymerization is carried out during reduction. It corresponds to a 1 M DMAEMA concentration (17%); it is ~ 30 nmol cm^{-2} when the reaction is performed in a bath with a contacting electrode (□, ◆) or an electrode close to the surface in a bath (▲) and $\sim$15 nmol cm^{-2} in a droplet (×).

The main difference in Γ between the two methods is that Γ is lower when performing PTFE reduction in the presence of DMAEMA than when copolymerization is carried out after reduction. This can be seen in Figure 5 either for a contacting electrode (compare Δ and (□, ◆) for respectively reduction in the absence and presence of DMAEMA) or for the microelectrode of a SECM (compare + and × for respectively reduction in the absence and presence of DMAEMA).

Extension to Other Vinylic Monomers: 4-Vinylpyridine. 4-Vinylic pyridine is described in the literature as prone to electroreduction in the same way as other vinylic monomers;[61,62] it also leads to films deposition on the electrode.

Similar electropolymerization experiments were performed in the presence of 4-vinylpyridine instead of DMAEMA. Figure 8 exhibits the voltammogram of phthalonitrile and

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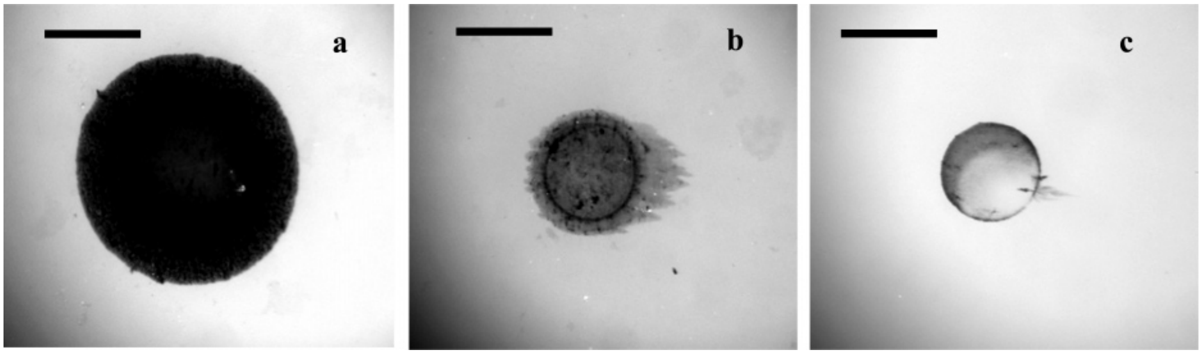

Figure 7. PTFE surfaces locally reduced (black area) in DMF + 0.1 M NBu_4BF_4 + 6 mM phthalonitrile and 47 mM 2,2′-dipyridyl. Pt disk microelectrode, diameter 250 μm (scale bar), held at $d = 25$ μm (a, b) or 30 μm (c) from the PTFE surface. Reduction time: 400 s. a, in the absence of DMAEMA; b, c, in the presence of 1 M DMAEMA.

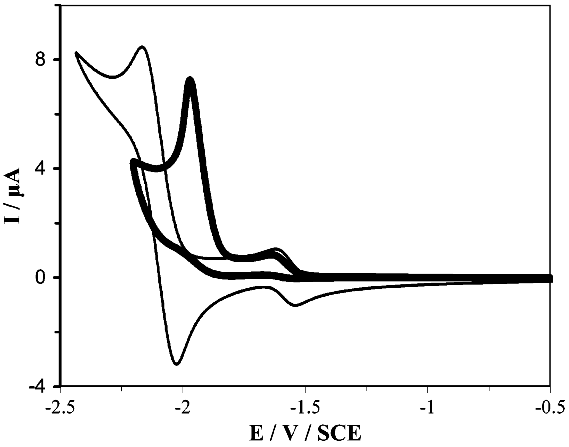

Figure 8. Cyclic voltammetry of 4-vinylpyridine in DMF + 0.1 M NBu_4BF_4 + 6 mM phthalonitrile and 47 mM 2,2′-dipyridyl. Pt electrode diameter, 250 μm. Scan rate, 100 mV s^{-1}. [4-Vinylpyridine]: thin line, 0; thick line, 1.5 M.

2,2′-dipyridyl in the absence and presence of 4-vinylpyridine. It shows that the 2,2′-dipyridyl radical anion is also able to reduce homogeneously 4-vinylpyridine. The obtained N surface concentrations with both electrochemical procedures are of the same order of magnitude as with DMAEMA, that is, ~30 nmol cm^{-2} for a 250 μm diameter electrode held at 26 μm from the substrate.

Conclusion

PTFE can be copolymerized with DMAEMA electrochemically after or during reduction. The DMAEMA polymerization can be triggered electrochemically. The electrochemical mechanism is similar to that of other vinylic monomers. The polymerization can also be initiated homogeneously by electrogenerated redox catalysts, such as the 2,2′-dypiridyl radical anion. This then allowed us to transpose the DMAEMA copolymerization to the *n*-doped, locally reduced PTFE surfaces.

For electrochemical copolymerization, whether the monomer is added after reduction or present during reduction, the highest modified zones surfaces, *S*, and surface coverages, Γ, are obtained with a microelectrode contacting the PTFE surface. Nevertheless, such a method with a contacting electrode suffers from a poor reproducibility. To circumvent such a drawback, reduction can be achieved in the vicinity of the electrode of an SECM. *S* and Γ are then lower but reproducible; the highest *S* and Γ are obtained with an as small as possible distance between the electrode and the PTFE surface.

The results are more reproducible when copolymerization is performed during reduction. Moreover, the reactions can be carried out in a bath or in a droplet of solution. The disadvantage of the latter method is that the size of the modified zone is lower because the surface exposed to the surrounding atmosphere is greater. The main advantage of using droplets is that modifications of different types can be obtained on the same substrate surface.

When copolymerization is performed after reduction, DMAEMA is reduced by the *n*-doped reduced PTFE surface. When the monomer is present during the PTFE reduction, the lifetime of the electrogenerated reducing reagent decreases because it is partly consumed in the homogeneous monomer reductive polymerization. This leads to smaller modified PTFE zones, which could even, under certain circumstances, confine to a circle image of the microelectrode edge. This illustrates nicely the nonuniformity of the current density at microelectrodes.

Finally, the PTFE copolymerization was extended to other vinylic monomers such as vinylpyridine.

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