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Electrosynthesis of structured derivated polythiophenes: Application to electrodeposition of latex particles on these substrates

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Abstract

Synthesis of super-structured polymers is a great challenge because these entities could present a large choice of applications. Synthesis and electropolymerisation of thiophene derivatives are reported. Star-shaped 3D molecules are chosen because these structures ensure a high electronic conductivity. Three-dimensional structures could also assist the conductivity. 1,3,5-tris[5-(2,2′-dithienyl)]benzene **1**, tris(2,2′-dithienyl)methylcarbinol **2**, tris(5(2,2′:5′2″-terthienyl)methylcarbinol **3** are synthetised by different ways. UV and IR analysis are reported along with an AFM examination of the film. The first attempt of latex particle deposition on the film is also reported showing promising results in view of surface functionalisation.

Keywords: Conducting polymer; Electro-oxidation; Polythiophene; AFM; Particle electrodeposition

1. Introduction

Building super-structured conducting polymers is of great interest because of the original properties that could arise from such structures [1–4]. Among these types of polymer, polythiophene is one of the most promising candidate for future applications. Oligothiophenes have been shown to display interesting electrochemical properties [5–7], as well as very high charge carriers mobilities in field-effect transistors (FETs) [8,9] or interesting non-linear optical (NLO) properties like efficient two-photon absorption [10,11]. One promising application of such materials is the conception of light emitting devices (LED) [12,13] because of their intense fluorescence. Branched conducting polymers with electronically connected nodes are excellent candidates among the family of superstructured conducting polymers. With such polymers, there should be no need for interchain coupling or interchain electronic transfer to insure a high electronic conductivity [14,15]. Moreover, this type of material possesses a three dimensional structure which could also improve the conductivity. For these reasons, we have chosen to synthetise 3D star-shaped molecules with thiophenes branches and aromatic and non-aromatic connecting-up. These molecules are very promising since they have an unsubstituted α position and are easily polymerisable.

We report here the synthesis and the electrochemistry of such thiophene derivatives and we propose a new application for these polymer films to improve the adhesion of nanoparticles on a semi-conducting substrate. Indeed the controlled assembly of colloidal particles to form patterns in the nanometric range is an expanding area in materials processing. The fabrication of these materials is of interest for a large range of applications such as optical devices, photonic materials, magnetic data storage, biosensors... One of the methods to prepare patterned structures is the electrophoretic deposition of particles onto an electrode surface in aqueous medium. The particle adhesion on the substrate may be controlled by the presence of additives [16]. In this paper the effect of a functionalized polythiophene film on the particle electrodeposition is investigated. The film morphologies and adhesion of particles on an

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ITO electrode were imagined by means of atomic force microscopy (AFM).

2. Results and discussion

2.1. Synthesis and experimental procedures

The desired star-shaped molecules **1**, **2** and **3** (see Scheme 1) were synthetised following the procedure described in [17,18]. 1,3,5-tris[5-(2,2′-dithienyl)]benzene **1** was synthetised by a triple ketolisation and dehydration of three equivalents of acetyl-aromatic molecules with a tetrachlorosilane-ethanol reagent. Tris(2,2′-dithienyl)methylcarbinol **2** and tris(5(2,2′:5′2″-terthienyl)methylcarbinol **3** were synthesised by a classical nucleophilic addition of 5-(2,2′dithienyl)lithium on ethylchloroformiate. All the compounds were characterized by ^{1}H NMR and elemental analysis.

Electrosynthesis of the polymer was realised on an ITO electrode (glass blade covered with an ITO film). This electrode is very interesting because of its stainless and semiconducting properties. Before conducting the experiment, each electrode was cleaned by ultrasonication for 10 min in different solvents (acetone, dichloromethane, ether).

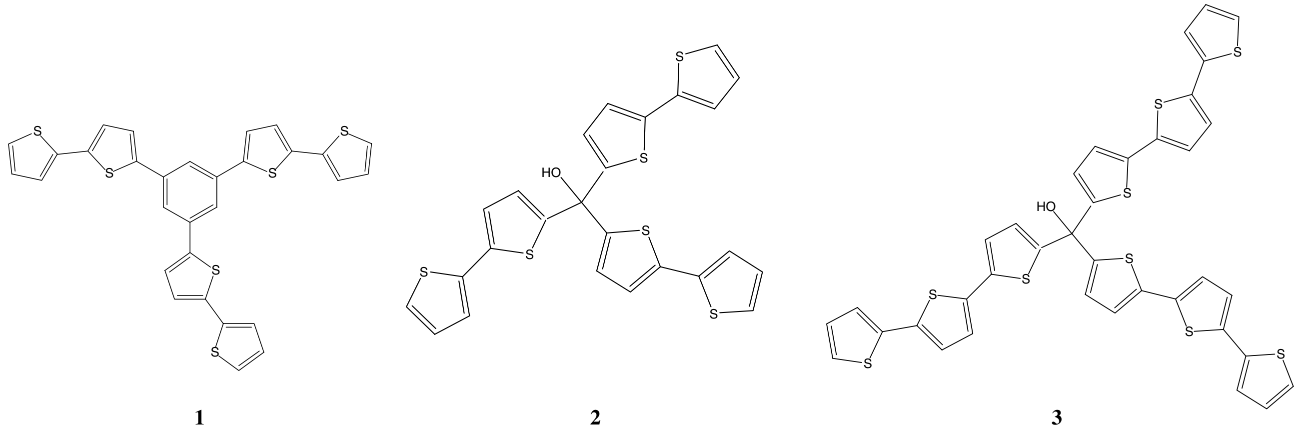
Electrochemical experiments were performed in a three compartments cell. The counter electrode was a Pt wire and the reference electrode was an aqueous saturated calomel electrode (E^0/SCE = E^0/NHE −0.2412 V) with a salt bridge containing the supporting electrode. The SCE electrode was checked against the ferrocene/ferricinium couple ($E^0 = +0.405$ V/SCE) before and after each experiment. The working electrode was the ITO electrode. Electrochemical deposits were made by cyclic voltammetry in dichloromethane with tetra-*n*-butylammoniumhexafluorophosphate electrolyte (0.1 M in dichloromethane) at a scan rate of 100 mV s^{-1} between 0 and 1500 mV/SCE. Concentration of monomers was around 1.3×10^{-3} M in dichloromethane. The electrochemical apparatus was an home made potentiostat (equipped with an ohmic drop compensation system), realized according to [19] and fitted with a PAR 173 Universal programmer, a Nicolet digital oscilloscope and a PC computer.

Using the same experimental set-up, electrodeposition of nanometric particles was realised on the ITO electrode covered with the electrosynthesized polymer. Monodisperse polystyrene latex particles (Alfa Aesar, mean diameter 50 nm) were cleaned by successive dilution/filtration in pure water (MilliQ, 18 MΩ cm) to eliminate residues formed during their synthesis. These negative particles were turned positive by adsorption of cethyltrimethylammonium bromide (CTAB) at 5×10^{-4} M. At this surfactant concentration the electrostatic repulsion was sufficient to prevent aggregation of the particles in the suspension [20]. According to previous experiments [21], electrodeposition experiments were carried out at pH 4, room temperature and at a particle concentration of 0.0012% in weight. A constant potential of −1 V versus the reference electrode was applied for 10 min. The electrode was then rinsed in pure water at pH 4 in order to remove unattached particles.

The ITO surface, the polymer film and the particle deposit were examined consecutively by AFM. The microscope (NT-MDT) with a SMENA measuring head is well fitted for the analysis of surface topography. The probe had a curvature about 10 nm, a tip 10–20 mm height, cone angle less than 22°. The resonant frequency of the cantilever was 255 kHz. The microscope was used in the tapping (semi contact) mode.

2.2. Monomer electrochemistry

Monomers **1**, **2** and **3** were all electro-oxidised in a solution of dichloromethane by cyclic voltammetry. The values of peak potentials of monomers, $\lambda_{\max}$ of UV–visible spectra and peak potentials of polymers are summarized in Table 1. In the case of **2**, the film obtained after electro-oxidation was characterized by cyclic voltammetry. A classical reversible voltammogram of conducting polymers was observed and the potential was about 1.0 V/ECS (see Fig. 1). The choice of the potential was explained in [17]. Oxidation of monomer **1** led to the formation of an elect-



1 **2** **3**

Scheme 1. Star-shaped molecules **1**, **2** and **3**.

Table 1
Peak potential values, λ_{max} of UV–visible spectra and peak potential values of polymers obtained with **1**, **2** and **3**

Monomers	Peak potentials (V/SCE)	λ_{max} (nm)	Peak potentials of the film (V/SCE)
1	1.05	370 and 448	0.90
2	1.26	474	1.00
3	1.06	X	X

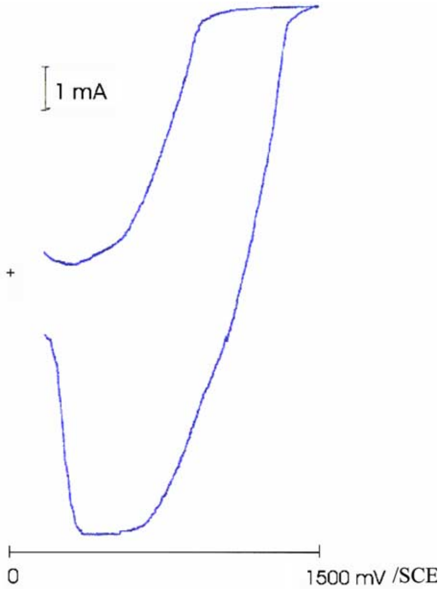


Fig. 1. Voltammogram of the film of polymer issued from 2.

roactive film on the electrode. This film was characterized electrochemically, showing a peak potential near 0.9 V/ECS. This value is in agreement with the value obtained in previous experiment [17]. The structure of the film was a star-shaped polymer. It was not possible that only one branch was involved in the polymerisation since the coupling of two units would have lead to the formation of a dimer. Therefore, at least two branches were oxidised. The thickness of the formed film can be estimated around 200 nm by measuring the consumed charge. Oxidation of **3** leads to an unexpected result. In fact, in a previous study [17], we have observed that **3** is irreversibly electrooxidized at 1.06 V/SCE. Unfortunately, no polymer formation was observed. **3** was oxidised again and formation of a film was observed. The film was not thick enough to be characterized electrochemically or by AFM. Some other attempts are in progress to improve the thickness and the quality of the film. The reactivity of cation radical of **3** is less important than the reactivity of cation radical of **2**. This result confirmed that reactivity of monomer decreased with the oligomer length. We observed formation of polymers with three monomers (**1**, **2** and **3**) but the quality of films obtained was better with monomer **2**. In this paper, we will present only results obtained with monomer **2**. Further analysis are in progress on monomers **1** and **3**.

Oxidation of **2** led to the formation of the polymer. We made several experiments with this compound. The polymer film was generated through 20 electrochemical cycles and the film was then rinsed with dichloromethane (*named first deposit*). The same experiment was also carried out but without rinsing the electrode. The resulting film was then dried in air without any other treatment (*named second deposit*). Eventually, we polymerised **2** with 30 electrochemical cycles without any rinsing (*named third deposit*).

2.3. Characterization of the film

UV analysis was carried out on the dried polymer film issued from **2**. The spectrum showed a broadened pic at a maximum wavelength of 474 nm (see Table 1). This broad pic is typical for a polymer. In fact, it could not be the starting monomer **2** because UV spectrum of **2** display a thin peak. Moreover, according to Fig. 2 we observed an increase of the absorbance with the number of electrochemical cycles (20 cycles or 30 cycles) which reveals an increase of the film thickness. This effect is not surprising since absorbance is directly proportional to the film thickness.

The IR spectrum of monomer **2** displays a large band at 3500 cm^{-1} due to the presence of an alcohol function in the molecule. This large peak should also be present in the polymer film (issued from **2**). However, the presence of this band is not very evident in the spectrum. It could be explained by the release of protons during the polymerisation process and subsequent protonation of the carbinol groups to produce a carbocation stabilized by delocalisation (Scheme 2).

At the end of the polymerisation experiment, the film consists of a mixture of dehydroxylated units and non-dehydroxylated units. This may explain why the characteristic band of alcohol function is not very well identified.

The polymer film was stable under mild acidic conditions. UV–visible and IR spectra performed before and after of immersion of the film in solutions at pH 4, proved

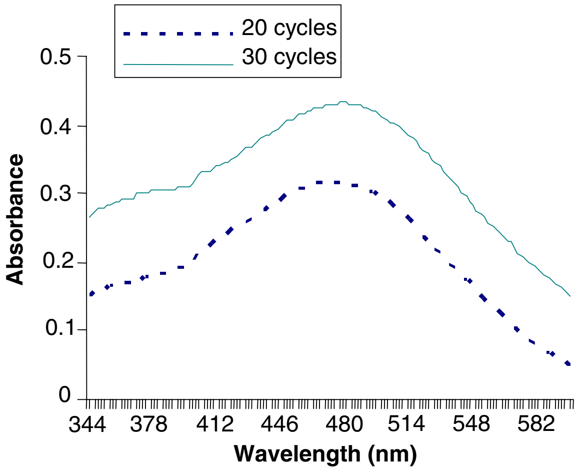
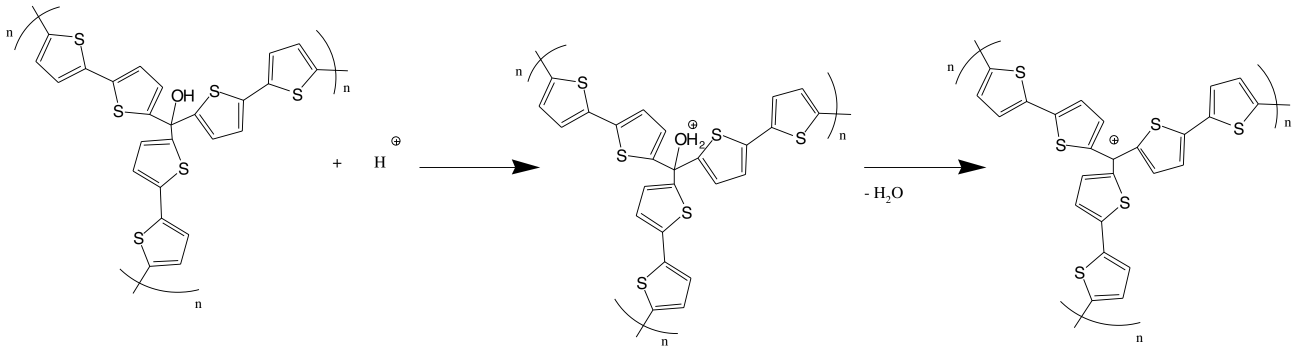


Fig. 2. UV–Visible spectrum of polymer issue from **2**.



Scheme 2. Formation of carbocation issued from **2.**

that the film was stable and could resist deposition experiments at this pH. The polymer film was also stable under wiping but was teared off with a polishing machine. Further chemical and mechanical studies of the stability of the film are under way. With regards to the particle deposition studies, the film was rinsed with water but not wiped prior to the experiments.

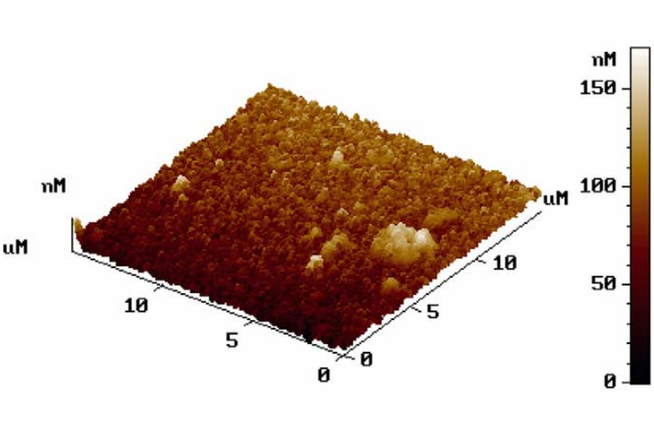


Fig. 3. AFM view of ITO electrode after cleaning.

The last characterisation of the dried polymer films was made with AFM. First the ITO surface was examined before the polymer electrosynthesis (see Fig. 3). The substrate appears quite homogeneous with a maximum roughness of 100 nm. The *first deposit* shown in Fig. 4 exhibits a structured grid of about 10 μm. These structure may be due to the crystallisation of the supporting electrolyte. This grid was no longer seen after rinsing the film with water or with dichloromethane. In the case of the *second deposit*, no structured grid but some rings were observed on the film surface (Fig. 5). The height of side rings was about 100 nm with a roughness of the same order than that of the substrate. It may be due to formation of bubbles or to entrapment of solvent drops which were released during the drying step. The film in the *third deposit* looked smoother than in the *first deposit*. The AFM view did not

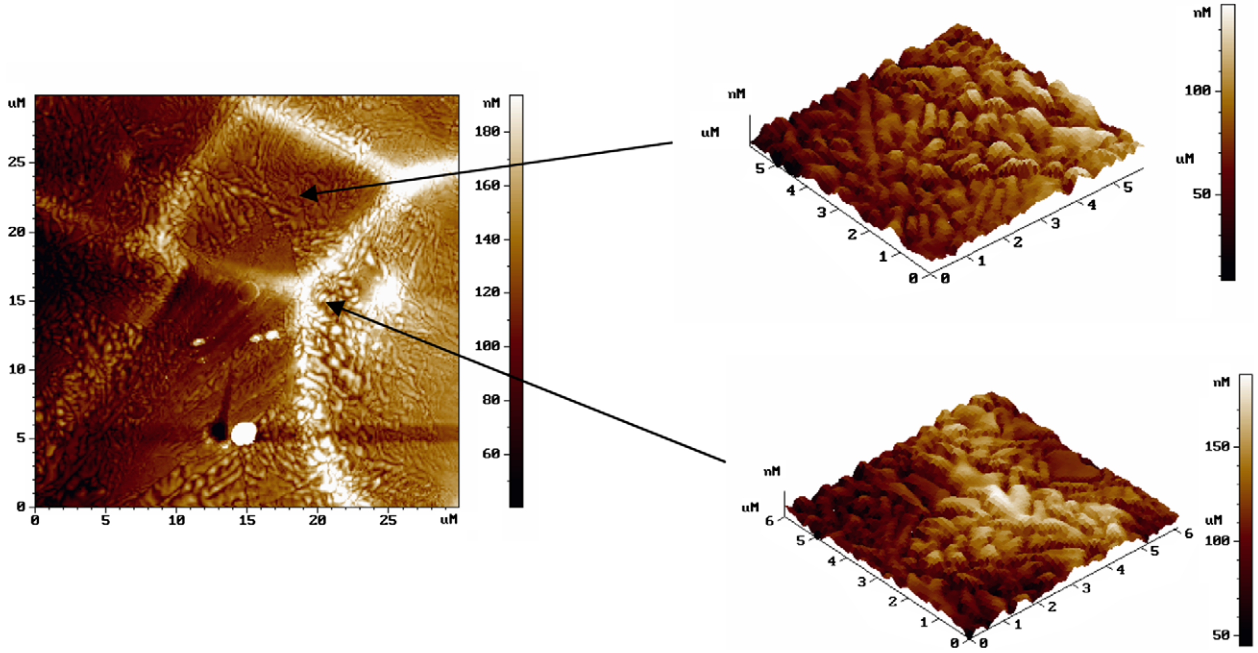


Fig. 4. AFM view of poly(tris[(2,2′-dithienyl)]methanol on ITO, obtained after 20 electrochemical cycles without rinsing.

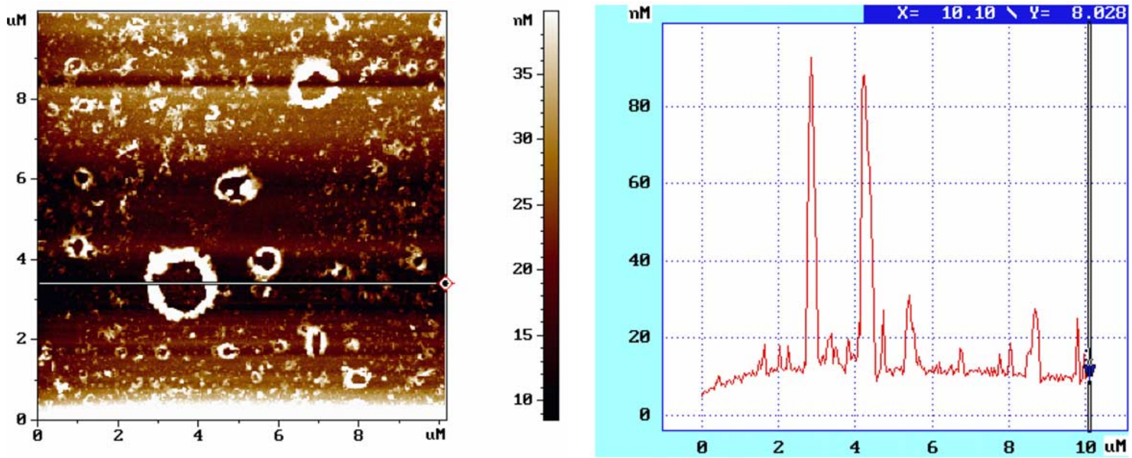


Fig. 5. AFM view of poly(tris[(2,2′-dithienyl)]methanol on ITO, obtained after 20 electrochemical cycles rinsing with dichloromethane. Profile of roughness of the electrode.

display any structured grid but some rings on many places of the film.

2.4. Deposit of latex particles

Preliminary experiments realised on the bare ITO (uncovered polymer substrates) revealed that latex particles do not attach onto the electrode. The same experiments were realised on the *first deposit* and characterized with AFM (Fig. 6). Mainly single particles and some aggregates were present on the surface. The grid present at the beginning of the experiment was no longer visible. It may have been destroyed during the adhesion experiment. Roughness analysis of the film exhibited blocks about 40 nm high. This

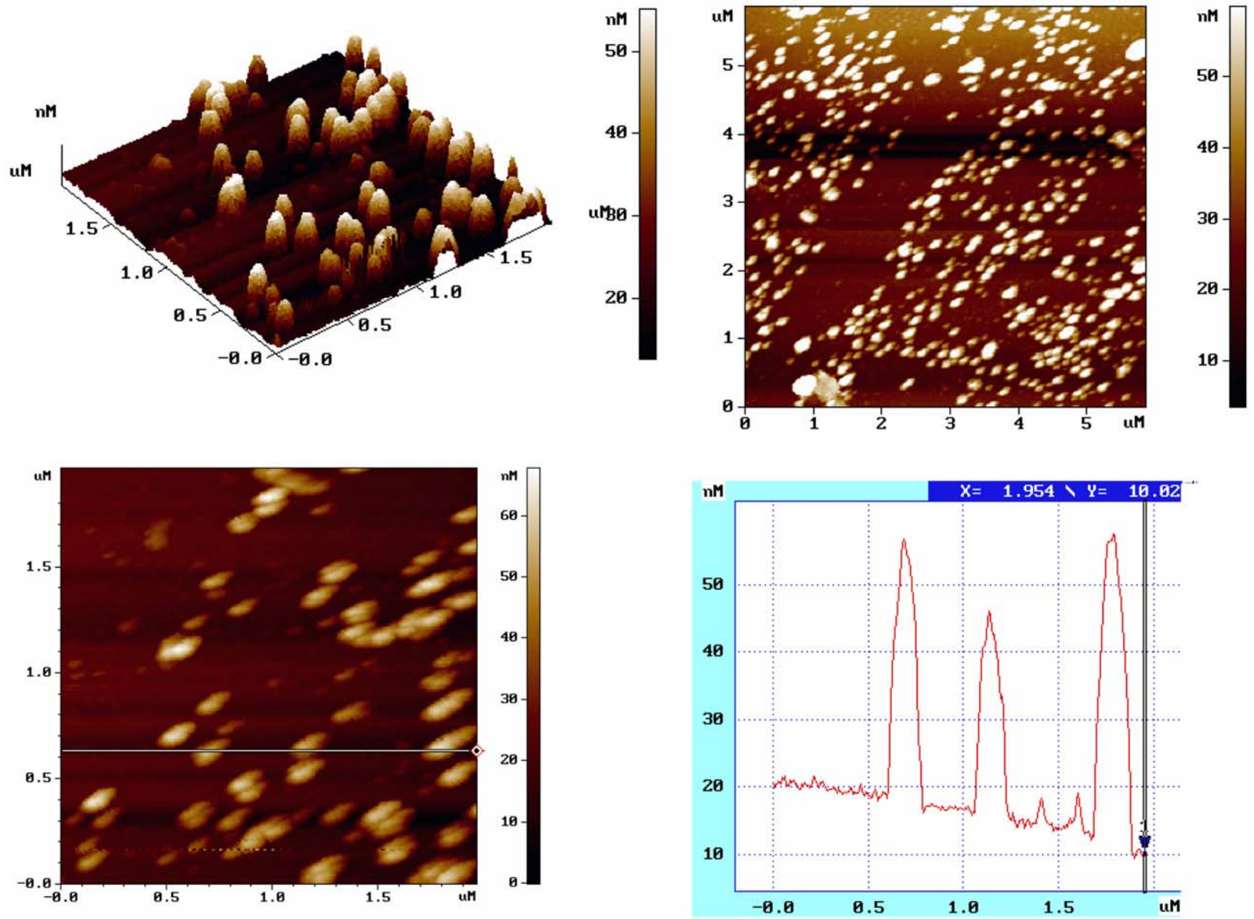


Fig. 6. AFM view of poly(tris[(2,2′-dithienyl)]methanol on ITO, obtained after 20 electrochemical cycles without rinsing and after deposit of 50 nm diameter latex particles. Profile of roughness of the electrode.

value is in the range of the latex particle diameter. Similar experiments were realised on the *second deposit*. No particles were observed on the film surface. These results showed that the polymer film was responsible for the adhesion of the particles. Moreover, the surfactant influences the particle electrodeposition by modifying the interfacial properties of both the particles and the electrode [20]. In case of *third deposit*, no latex particles were deposited onto the film. Further experiments are in progress to try to understand the influence of polymers and different surfactants in the deposition process.

3. Conclusion

Films of polythiophene derivative were formed and characterized (electrochemistry, IR, UV, AFM) with the purpose of surface functionalisation and more specifically latex particles adhesion. We report in this article, the first experiments realised with 1,3,5-tris[5-(2,2′-dithienyl)]benzene **1**. This work is very promising because latex particles could be indeed deposited on the polymer film as single units opening a route to surface micro or nano structuration. Further investigations are in progress to understand the mechanism of deposition and the influence of external parameters like surfactant, solvent… Some experiments are in progress with tris(2,2′-dithienyl)methylcarbinol **2** and with tris(5(2,2′:5′2″-terthienyl)methylcarbinol **3** to study the influence of the polymer film on the latex deposit.

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