

Radical Scavenger Properties of Some 1,2-Dithiol Compounds Against Electropolymerization of Aniline

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The kinetics of aniline electropolymerization was investigated in acidic H₂O/CH₃CN solutions and in presence of some 1,2-dithiol compounds. The reactions were studied under cyclic potential scanning to measure the electric charge involved between the redox states of the electrodeposited polymers. The electrochemical growth of electrodeposits was kinetically dependent upon the dithiol. Generally, in presence of 1,2-dithiol compounds the growth of electropolymer was slower than observed for aniline alone. In the presence of 3-aminophenyl-5-(4-methoxyphenyl)-1,2-dithiol the aniline electropolymerization was accelerated and led to an improvement in the conductivity of polymer films. In order to establish the nature of the process, aniline electropolymerization or co-polymerization with the 1,2-dithiol compounds, electrodeposits were prepared on vitreous carbon plates and then analyzed by scanning electron microscopy. The morphology was a fibrillar one and the analysis showed that sulfur element was inside the electrodeposits.

Key Words: 1,2-Dithiol, Polyaniline, Copolymerization, Inhibition, Cyclic voltammetry.

INTRODUCTION

Organosulfur derivatives are exogenic compounds known as antioxidants in various therapeutic applications. Among these sulfur compounds, 1,2-dithiol-3-thiones (dithiolethiones) **1** are extensively investigated owing to their chemopreventive effects in numerous conditions *i.e.*, prevention of hepato-, nephro-, tenotoxicity, neuroprotection, effect in inflammation, cerebral and cardiac ischemia and cancer chemoprevention¹⁻³. Among others, anethole dithiolethione (Sulfarlem®) **1b**, widely used in human therapy for its choleric and sialogogic properties, has been described recently as a potential efficient chemopreventive agent for lung cancer in human^{4,5}.

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So far, cancer preventive efficiency of dithiolethiones was mainly regarded through modulation of detoxification enzymes. Indeed the phase 1 and phase 2 enzymes induction properties of these molecules are well documented⁶⁻⁹. Nevertheless, the molecular mechanism by which these molecules manifest the increase in levels of detoxification enzymes is not clarified. It has been noted that many inducers of phase II enzymes possess electrophilic centers and that the anticarcinogens may also induce the signalling process by production of reactive oxygen species, both criteria suggested for dithiolethiones^{10,11}. It has also been suggested that the dithiolethiones could also inhibit carcinogenesis by a free radical scavenging mechanism¹²⁻¹⁷.

Redox properties of the dithiolethiones were also studied through electrochemical studies¹⁸⁻³². Fleury *et al.*^{22,23} suggest the intermediary one-electron reduction but without structural evidence. The measurements of cathodic current show the occurrence of a dimerization in competition a two-electron opening of the dithiol ring^{18,26}. From these electrochemical studies it emerges that radicals arising from a one-electron reduction are key intermediates in the reductive process pathway of these molecules. Nevertheless the reactivity of these radicals has not been discussed so far.

In present study, we used electropolymerization of aniline as a test reaction for checking the ability of some dithiolethione compounds as antioxidant substrates. Polyaniline (PANI) is easily prepared by chemical or electrochemical oxidation of aniline leading to powder or thin layer deposited film, respectively. The chemical oxidation of aniline with suitable oxidant, or its electrochemical oxidation generates radical cations. Once these primary radical cations are formed, they react with aniline molecules. It has been concluded that the radical cations of aniline in the form of the pernigraniline oxidation state are first formed and adsorbed, with subsequently polymerize leading to the growing polymer chains³³. The electrochemical process may be carried out in acidic aqueous media³⁴ or non aqueous media³⁵. When water is present the polymerization medium deactivation or degradation of the polymers occurs, especially for polyaniline. Despite this radical process the electropolymerization has not been investigated in the presence of additional radical scavengers. Polymerization of aniline in presence of phenols known as antioxidant was recently studied.

Recently, the incorporation of organic compounds into conducting polymer films made from aniline and leading to copolymers has attracted considerable attention due to the possibility to design organic/polymer composite materials with various properties³⁶⁻⁴⁰. In this field, sulfur containing compounds had been scarcely investigated³⁹⁻⁴³. At the present time 1,2-dithiol derivatives have been the subject of several electrochemical studies aiming the understanding of their antioxidant properties^{3,44-46}. We were mainly interested in studying the antiradical effect of some derivatives towards the radical electropolymerization of aniline. In this paper, the results of aniline electropolymerization carried out in the presence of the 1,2-dithiol compounds **1-4** (Fig. 1) in aqueous-organic solution.

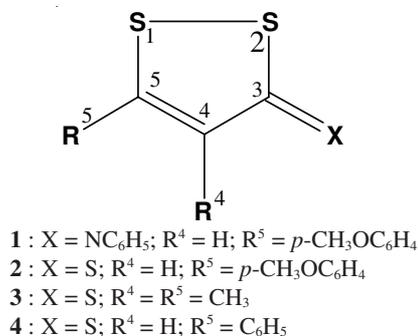


Fig. 1. Structures of the 1,2-dithiol derivatives investigated

EXPERIMENTAL

Electrochemical procedures: All electrochemical experiments were performed in a three-electrode cell. In the voltammetry studies the working electrode was a platinum disc or a vitreous carbon disc, of 2 or 3 mm in diameter, respectively. In the electropolymerization experiments the working electrode was a vitreous carbon plate of 2 mm × 10 mm × 100 mm. The reference electrode was an aqueous calomel electrode (SCE) and the counter electrode was a graphite carbon rod. All electrode potentials are referred to the SCE. For cyclic voltammetry and electropolymerization potentiostat EGG/PAR model 273 and scanning electron microscopy were used. Voltammetry and electropolymerization were performed at room temperature under nitrogen atmosphere, in aqua-organic solutions.

Aniline (99.8 %; acros-organics) was used as purchased from the manufacturer. Sulphuric acid (99 %; Carlo-Erba) and all other used chemicals were of analytical grade. Electrolytic solutions were made from the sulphuric acid with acetonitrile (99.9 %; Carlo-Erba) and double distilled water. The 1,2-dithiol derivatives were prepared by reported method. The identity and purity of the synthesized compounds were confirmed by melting point measurement and by high resolution mass spectrometry.

Electropolymerization: Polyaniline and copolymers of aniline and 1,2-dithiol compounds were prepared from solution made of water and acetonitrile containing 0.1 M aniline and 0.5 M sulphuric acid. To fabricate polyaniline a glassy carbon or platinum rotating or stationary disc as a working electrode was subjected to a cyclic potential ranging from -0.2 to 0.9 V vs. SCE at scan rate of 50 mV/s. The quantity of the polyaniline was determined by the total charge consumed.

RESULTS AND DISCUSSION

Polymer characterizations: Fig. 2 shows voltammograms obtained from the electrochemical deposition of polyaniline in sulphuric acid using a potential range of -0.1 to 0.9 V vs. SCE at scan rate of 50 mV/s. The prepared polyaniline exhibits

a typical redox behaviour characterized by two predominant peak couples, which correspond to leucoemeraldine/emeraldine (A1/C1) and emeraldine/pernigraniline (A2/C2) transformations, respectively. Polyaniline has three distinguished oxidation states: leucoemeraldine base, emeraldine base and pernigraniline base. The inter-transformation^{47,48} among these oxidation states is shown in Fig. 3.

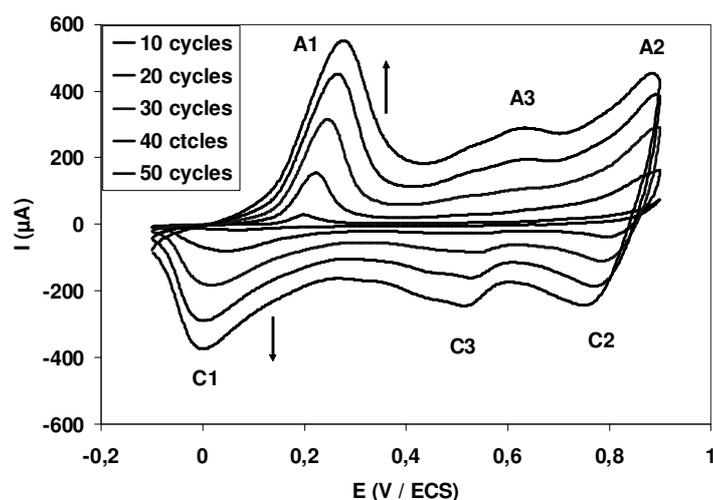


Fig. 2. Cyclic voltammograms of the electrolysis of a solution consisting of 0.1 M aniline and 0.5 M H₂SO₄, Scan rate of 50 mV s⁻¹

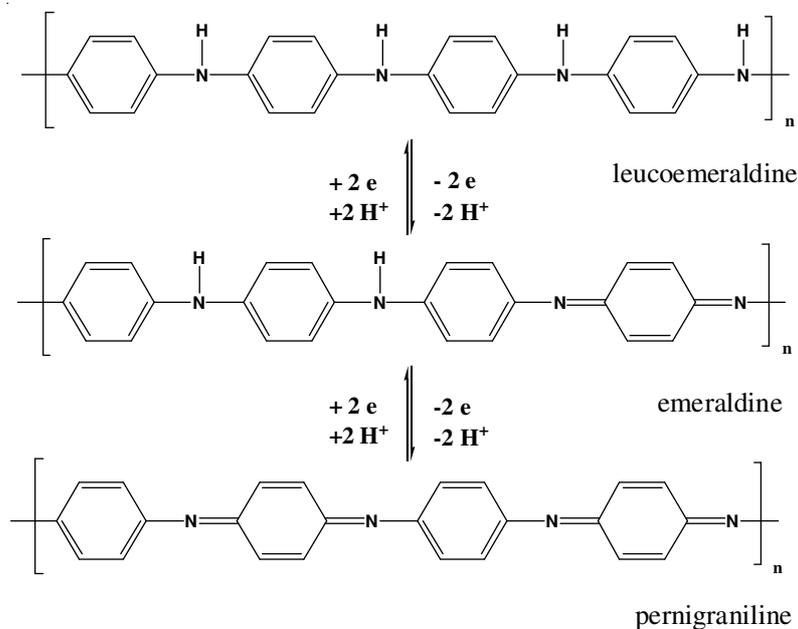
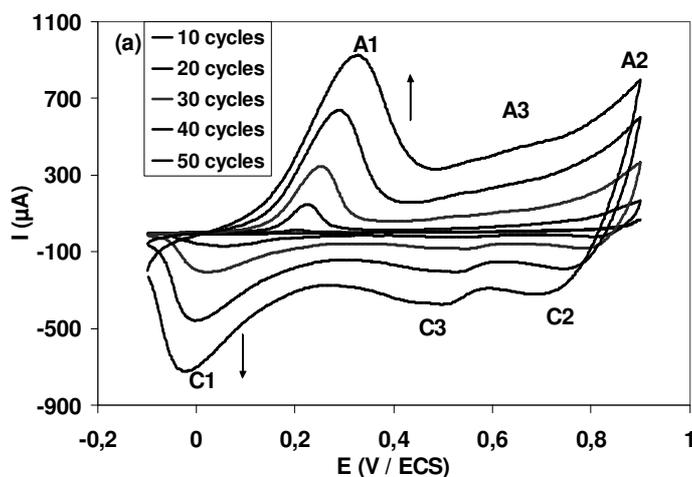


Fig. 3. Transformation of different forms of polyaniline

The minor set of peaks (A3/C3) is assigned to imperfectness in the linear structure of the polymer and/or polymer degradation products, presumably benzoquinone and the related compounds^{49,50}. The quality of the polymer can be remarkably influenced by parameters such as the counter ions and reaction medium. Considering the results from other works^{49,51} sulphuric acid in aqueous-organic is the most suitable medium to produce polyaniline. Of course, cyclic voltametry was employed, as it was more convenient an electrode and eventually prepare the suitable fibre in a highly reproducible manner. The thickness of this new fibre can be controlled by the number of cyclic voltametry cycles. The SEM studies on the polyaniline film revealed that the polymer has a porous and relatively homogeneous structure, which is shown in Fig. 7.

Electrochemical of polyaniline and polyaniline + dithiol: A series of cyclic voltammograms of dithiol-aniline polymerization on a platinum electrode rotating in a mixed solution with volume ratio of water to acetonitrile of 1:4 containing constant concentration of $C_6H_5NH_2$ (0.1 M), dithiol (2.5 mM) and H_2SO_4 (0.5 M) are shown in Fig. 1, at a ambient temperature (25 °C) and under nitrogen. The experimental results, in absence or in the presence of the dithiols, show that upon the oxidation of its monomer the polyaniline film starts to form and develop on the electrode surface according to numbers cycles as seen from its cyclic voltammogram (Figs. 2 and 4). The oxidation and reduction peaks of the polyaniline film increase in intensity as the film grows in absence or in presence of the dithiols. Fig. 4a the presence of **1** in the solution of aniline accelerates the formation and causes an improvement in the conductivity of polyaniline films. In comparison to the Fig. 4a, it is noted that the peaks of oxidation and reduction broader follow-up by one move potential towards more positive values in oxidation and reducible in reduction, after 50 cycles the anodic potential of couple A1/A2 without dithiol is 277.6 mV vs. ECS and in the presence of **1** is 316.2 mV vs. ECS, with a decreasing in the anodic intensity of the degradation products (A3).



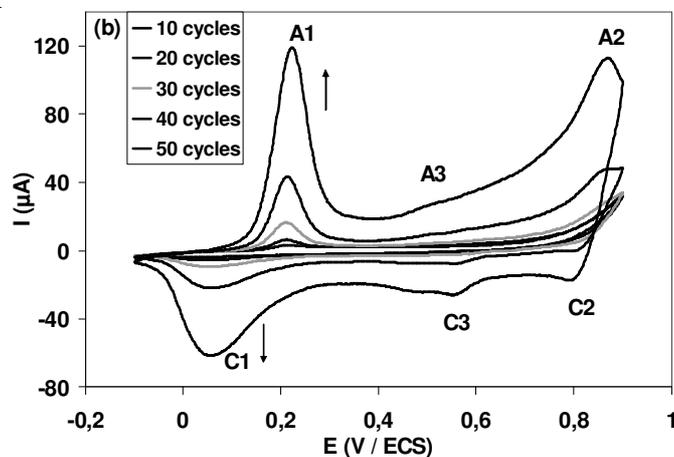


Fig. 4. Cyclic voltammograms of the electrolysis of a solution consisting of 0.1 M aniline and 0.5 M H₂SO₄. (a) in the presence of 0.25 mM **1**; (b) in the presence of 0.25 mM **2**, Scan rate of 50 mV s⁻¹

The augmentation in the peak intensity of the film in presence of **1** is much faster than the others compounds due to the catalytic effect (Fig. 5).

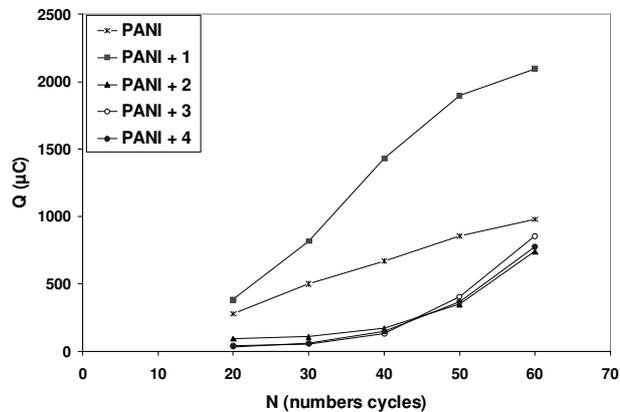


Fig. 5. Relationship between Q (μC) of the polyaniline film deposited according to numbers cycles of the different dithiols

Fig. 4b shows that the presence of **2** (Sulfarlem[®]) in the solution contains aniline causes a decreasing in the intensity of peaks (the peaks are smaller) and that the peaks become less broad. A comparison of Figs. 2 and 4b reveals that **2** acts as an inhibitor for aniline polymerization (antiradical activity) and the oxidation of leucoemeraldine and emeraldine is done with less low potentials. In recent years many reports have been devoted to the use of **2** is well known as Sulfarlem[®] and 4-methyl-5-(2-pyrazinyl)-1,2-dithiol-3-thione (Oltipraz) as cancer chemopreventive

or antioxidant drugs^{1,3}. The main hypothesis of this effect is based on the antioxidant activities or the free radical scavenger and glutathione inducer properties of the 1,2-dithiol-3-thiones^{11,17}. Moreover, it is observed the same evolution in the presence of **3** and **4** during the electropolymerization of aniline.

The charge passed during the electropolymerization of these films in the neutral blank solution (0.1 M aniline + 0.5 M H₂SO₄) and in presence 0.25 mM of the dithiols was measured. The charge, which is proportional to the thickness of the deposit, varies according to the compound added in the solution. Fig. 5 shows the results of these measurements. It is noted that a very significant evolution of the quantity electricity after of the dithiols consumption in the solution of the polymerization. The rate deposition (R) of polyaniline film in the electrode work in absence and in presence of dithiols ($\mu\text{C}/\text{N}$) is calculated from the slope of the Q-N relation in Fig. 5. This slope represents the growth rate at a given concentration of aniline and dithiols (Table-1). The results from the experiments of cyclic voltammetry rotating disk electrode show that the polymerization rate of aniline in presence of **2**, **3** and **4** inhibit the polymerization. A possible explanation for the inhibition is that the aniline radical cations generated during the oxidation of aniline are captured by **2**, **3** and **4**.

TABLE-1
CHARACTERISTIC ELECTROCHEMICAL OF THE VARIOUS COMPOUNDS
STUDIED OBTAINED FROM CV AT A Pt WORKING ELECTRODE
AFTER 50 CYCLES AT A SCAN RATE 50 mV s⁻¹

| Compounds | Q _{ox} (mC) | R ($\mu\text{C}/\text{N}$) | Peak A1 | |
|-----------------|----------------------|------------------------------|--------------------------|-----------------------------------|
| | | | E _{pa} (mV/ECS) | I _{pa} (μA) |
| PANI | 4.4 | 17.5 | 277.6 | 426.4 |
| PANI + 1 | 8.7 | 45.1 | 316.2 | 713.5 |
| PANI + 2 | 0.8 | 4.3 | 223.3 | 110.2 |
| PANI + 3 | 0.9 | 7.3 | 226.4 | 123.4 |
| PANI + 4 | 1.0 | 6.5 | 225.0 | 138.9 |

Electrocatalytic properties of polyaniline-dithiols composite: Fig. 6 show the evolution of the quantity consumed electricity (Q) during the electropolymerization of aniline in the neutral blank solution according to the number cycles is linear. The addition of the **1**, **2** and **4** in the neutral blank solution (0.1 M aniline + 0.5 M sulphuric acid + 2.5 mM dithiol) on an electrode modified before hand by the polyaniline increase the production rate of polymer (Table-2). This increase can be due to the oxidation of the dithiols on the new electrode of polyaniline. Contrary of the experimental results (Table-2), this catalytic effect can be due to the oxidation of these compounds in the presence of the aniline radical cations generated during the oxidation of aniline on this electrode.

The catalytic mechanism related to the role of dithiol is presumed as follows:

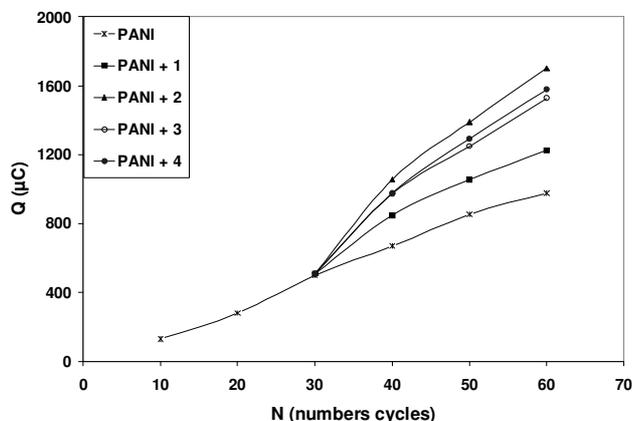
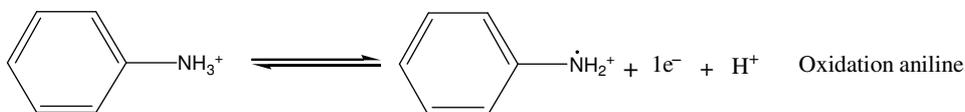
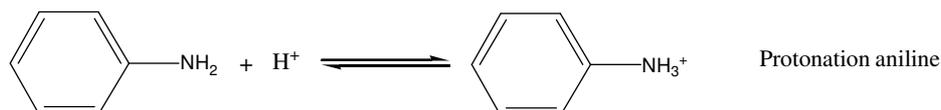


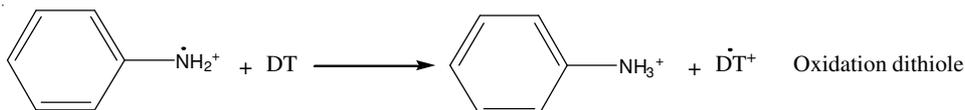
Fig. 6. Evolution of the quantity formed to express in μC (Q) on a Pt electrode working modified according to numbers of cycles in the presence of derived the dithiols

TABLE-2
CHARACTERISTIC ELECTROCHEMICAL OF THE VARIOUS COMPOUNDS
STUDIED OBTAINED FROM CV AT A Pt WORKING ELECTRODE
MODIFIED AFTER 50 CYCLES AT A SCAN RATE 50 mV s^{-1}

| Compounds | Q_{ox} (mC) | R ($\mu\text{C/N}$) | Peak A1 | |
|-----------|----------------------|-------------------------|--------------------------|-----------------------------------|
| | | | E_{pa} (mV/ECS) | I_{pa} (μA) |
| PANI | 4.4 | 17.5 | 277.6 | 426.4 |
| PANI + 1 | 5.2 | 23.5 | 280.1 | 456.2 |
| PANI + 2 | 6.5 | 39.1 | 284.9 | 528.9 |
| PANI + 3 | - | 34.7 | 285.2 | 531.6 |
| PANI + 4 | 6.1 | 35.2 | 283.1 | 535.7 |



The aniline radical cation will oxidize the dithiol (DT)



The oxidation reaction of dithiol has like consequence an increase in the rate deposition.

Morphology of the polymers and copolymerization: The synthesis a polymer electrochemically on an electrode surface, formation of conductive and in soluble product is highly required. It causes the polymer to deposit on the vitreous carbon surface as a cohesive film that does not passivate the surface but allows further electropolymerization. The quality of the polymer can be greatly influenced by parameters such as the reaction medium. The electrochemical deposition of polyaniline, in vitreous carbon plate of 2 mm × 10 mm × 100 mm, was performed in sulphuric acid an aqueous-organic using a potential range of -0.3 to 1 V vs. ECS at scan rate of 50 mV s⁻¹. The images of polymers in the presence of dithiol B, C and polyaniline A are shown in Fig. 7. The unmodified polyaniline film (Fig. 7A) show a porous morphology with the presence of fibrils throughout the polymer surface, as is common in polyaniline films prepared in an H₂SO₄ medium^{52,53}. The films morphology of polyaniline in the presence of 3-phenylamine-5-*p*-methoxyphenyl-1,2-dithiol did not alter but led to a visibly higher amount of fibrils with more

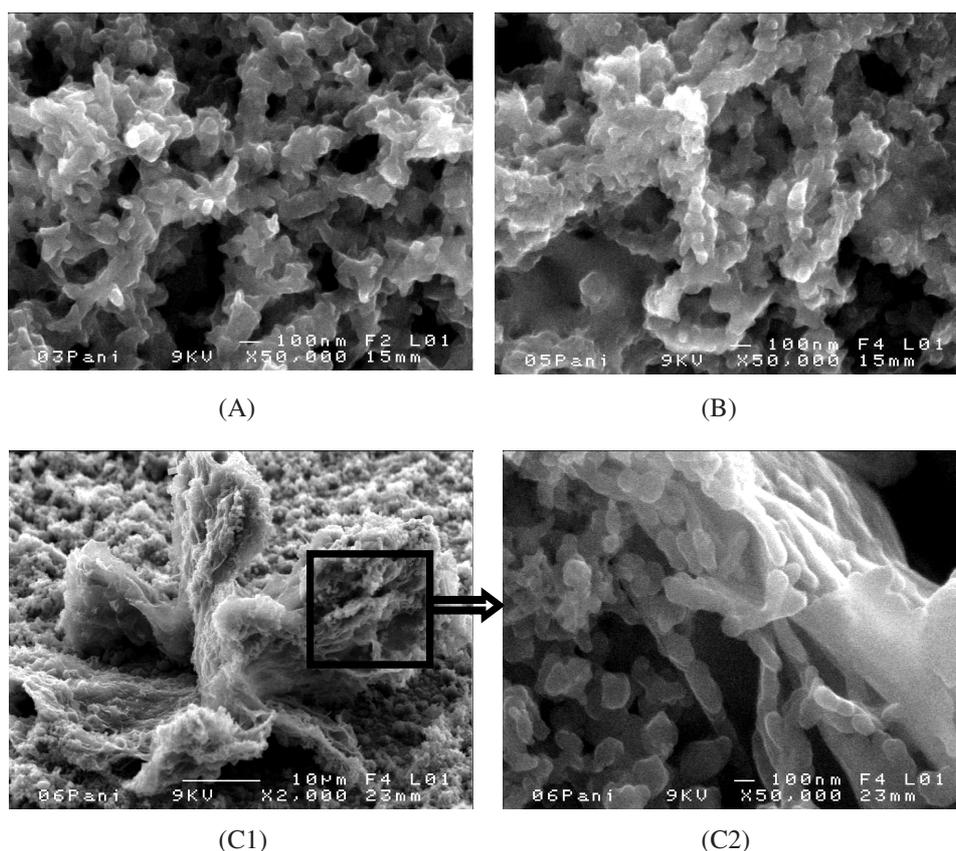


Fig. 7. Scanning electron micrographs of (A) polyaniline, (B) polyaniline + 3-phenylamine-5-(4-methoxyphenyl)-1,2-dithiol and (C) polyaniline + 5-(4-methoxyphenyl)-1,2-dithiol-3-thione (Sulfarlem[®]), coated on a vitreous carbon plate of 2 mm × 10 mm × 100 mm

significant diameters (Fig. 7B). The resulting film thickness of polyaniline coating was roughly 20 μm after 10 cycles. The polyaniline/5-*p*-methoxyphenyl-1,2-dithiol-3-thione film shows a morphology fibre of low diameter with sheets contains fibres under the condition indicated above (Fig. 7C). This modification of the morphology film may be due to copolymerization. The formation rate of polymers depends significantly with the nature dithiol. The rate formation of the polyaniline/3-phenylamine-5-*p*-methoxyphenyl-1,2-dithiol and the pure polyaniline is fastest than in the presence of others dithiols. The change of the morphology of polyaniline was caused by the polymerization rate and the presence of the dithiol.

Conclusion

The electropolymerization of aniline in absence and in the presence of the dithiols has been studied. The cyclic voltammograms recorded during the electropolymerization of aniline on a platinum electrode rotating indicate that the presence of 5-*p*-methoxyphenyl-1,2-dithiol-3-thione is well known as Sulfarlem[®], 4,5-dimethyl-1,2-dithiol-3-thione and the benzo-1,2-dithiol-3-thione inhibits polymerization (anti-radical) on the other hand the presence of 3-phenylamine-5-*p*-methoxyphenyl-1,2-dithiol increases the rate deposition (R). On an electrode modified before hand by polyaniline the presences of the dithiols increase the rate of electropolymerization. This catalytic effect can be attributed to the oxidation of the dithiols in the presence of the aniline radical cations generated during the oxidation of aniline. Polyaniline modified electrodes can find applications in the development of chemically modified electrodes for chemical and biochemical sensing purposes.

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