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Interfacial polymerization of a 3,4-ethylenedioxythiophene derivative using Langmuir–Blodgett technique. Spectroscopic and electrochemical characterizations

Odile Fichet, François Tran-Van, Dominique Teyssie, Claude Chevrot*

*Laboratoire sur les Polymères et les Matériaux Electroactifs (LPME)—E.A.2528—Université de Cergy-Pontoise
5, mail Gay Lussac—Neuville-sur-Oise, 95031 Cergy-Pontoise Cedex, France*

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Abstract

In this study, we have used an EDT derivative with a tetradecyloxy chain (EDTMC14) that renders the monomer soluble in organic solvents as well as suitable for Langmuir–Blodgett (LB) experiments. EDTMC14 monomer was investigated regarding its spreading and polymerization behavior at the air–water interface. The polymerization at the interface depends on the CAN concentration and pH in the subphase. For comparison, we have studied the behavior of the corresponding polymer (PEDTMC14) obtained by chemical polymerization. The different LB films showed the same characteristics in FTIR spectroscopy and electrochemistry and conductivity measurements. These results may indicate that both polymers have essentially the same molecular structure in the p-doped state, and that the pre-organization of the monomers in the Langmuir films seems to have no dramatic influence on the polymer properties. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Langmuir–Blodgett films; IR spectroscopy; Polymers; Electrochemistry

1. Introduction

The preparation of high quality ultrathin films of conducting polymers has great relevance to technological applications such as sensors and molecular electronics [1,2]. Among the most interesting molecules from this point of view are conjugated polyheterocycles, which are electrically conductive in oxidized forms mainly. One of the most adequate techniques, which allows the ordered build-up, layer-by-layer, of molecular controlled architectures is the Langmuir–Blodgett (LB) deposition technique [3,4]. Nevertheless, the use of the LB technique requires electroactive monomers or polymers whose structures have been modified in order to show amphiphilic properties.

Electroactive polymers can be spread in the same way as used for small molecules. Amphiphilic derivatives of polypyrrole, polythiophene and polyaniline have been studied as monolayers at the air–water interface and in

LB films. For example, monolayers of poly(3-decyl pyrrole) show both poor stability and poor homogeneity [5]. Recently, Sigmund et al. [6] have reported the study of new polar substituted polypyrrole, poly(5-acetamido-4,5,6,7-tetrahydro-2H-benzo[c]pyrrole) but the polymer forms a complex thin film structure at the interface rather than a simple floating monolayer. Stable monolayers of poly(2-decyloxyaniline) have been obtained at an air–water interface and could be transferred onto solid substrates [7]. However, poly(3-alkylthiophenes) are not able to give stable and transferable monolayers on the water surface [8]. Indeed the thiophene rings are not hydrophilic enough to render the polymer molecules surface active. However, the introduction of an oxygen atom between the thiophene ring and the alkyl side chain enhances the polarity of the macromolecule and allows the use of LB technique [9,10]. Recently, we have reported the first experiments on LB films of an alkoxy derivative of poly(3,4-ethylenedioxythiophene) [11]. Due to its interesting hydrophobic/hydrophilic balance, this polymer forms stable and reproducible monolayer at the air–water interface which can be easily

*Corresponding author. Tel.: +33-1-34-25-70-42; fax: +33-1-34-25-70-71.

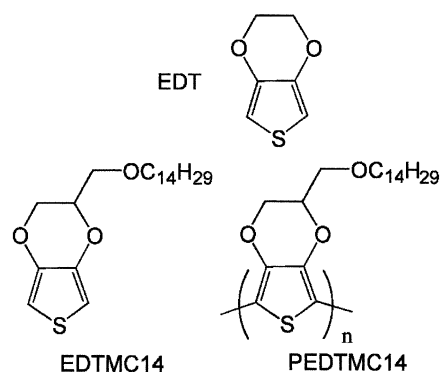
E-mail address: claudette.chevrot@chim.u-cergy.fr (C. Chevrot).

transferred by LB technique without mixing it with fatty acid.

Another approach to prepare a polymer monolayer involves spreading a monolayer of amphiphilic monomer molecules on a subphase containing the oxidizing agent. The monomer can then be polymerized at the interface and transferred onto various substrates. One primordial difference between LB polymerizations and their solution counterparts is that the monomers are essentially ‘pre-oriented’ by the surface and through the use of different applied surface pressures, the distance between reacting monomers can be changed. For instance, 3-octadecylpyrrole forms a stable monolayer at the air–water interface using iron(III) chloride solution as a subphase; however, no polymerization occurred [12]. When a large excess of unsubstituted pyrrole was added in the spreading solution, copolymerization occurred at the air–water interface. The resulting copolymer was largely unsubstituted polypyrrole. Surprisingly, the 3-hexadecylpyrrole monolayer has been polymerized at the air–water interface without additional pyrrole and using iron(III) chloride [13,14] or ammonium peroxodisulfate [15] as oxidative agent in the subphase. The alkyylaniline polymerization was carried out on an acidic subphase and ammonium peroxodisulfate [14]. Sagisaka et al. [16] have reported that 2-octadecyloxyaniline spontaneously oligomerized in monolayer at the air–water interface by oxygen contained in the air and/or water. In contrast to polypyrrole and polyaniline, which can be synthesized at the air–solution interface, thiophene did not polymerize. Indeed, its redox potential is higher than the potential of water and the thiophene cation radical probably presents a too high reactivity in neutral water.

In the field of polythiophene derivatives, poly(3,4-ethylenedioxythiophene) (PEDT) has attracted significant attention in recent years. The alkyldioxy substituent in the 3 and 4 positions prevents the occurrence of the $\alpha\beta$ coupling. Moreover, the electron donating oxygen atoms decrease the oxidation potential compared to other thiophene derivatives and stabilize the oxidized polymer. Furthermore, the presence of the ethylenedioxy group on the thiophene ring increases the hydrophilicity of the molecule.

In this study, we have used an EDT derivative with a tetradecyloxy chain (EDTMC14) that renders the monomer soluble in organic solvents as well as suitable for LB experiments. EDTMC14 monomer was investigated regarding its spreading and polymerization behavior at the air–water interface. For comparison, we have studied the behavior of the corresponding polymer (PEDTMC14) obtained by chemical polymerization. The different LB films were characterized by FTIR spectroscopy, electrochemical and conductivity measurements. The chemical structures are presented in Scheme 1.



Scheme 1. Chemical structure of EDT, EDTMC14 and PEDTMC14.

2. Experimental

The EDTMC14 monomer and PEDTMC14 polymer were synthesized chemically using a procedure described elsewhere [17]. The polymerization degree and the PEDTMC14 solubility are closely correlated to the initial molar ratio of the oxidizing agent to the monomer. As already published [18], an increase of this ratio leads to an increase in the length of the macromolecular chain but decreases drastically the proportion of the soluble fraction after dedoping in ammonia (10% w/w). In order to optimize the PEDTMC14 solubility, we have used only one equivalent of oxidizing agent, which leads to a solution without insoluble fraction after dedoping by ammonia solution. As expected, we obtained a material with a low molecular weight ($M_n=2900$ g mol⁻¹; $I_p=1.44$; evaluated by SEC using polystyrene standards).

Iron(III) chloride hexahydrate (99%), and ammonium cerium(IV) nitrate (CAN) (99.99%) were purchased from Acros and Aldrich, respectively. Perchloric acid (HClO₄) and acetonitrile (RS per polarografia) (Carlo Erba), hydrochloric acid (HCl) and lithium perchlorate (LiClO₄) (Acros) were used as received.

The LB experiments were carried out with a Nima (611D system) or an Atemeta trough. The subphase is Millipore Q-grade water system with a resistivity higher than 18 MΩ cm. Isotherms of surface pressure vs. mean molecular area (π -A) were measured at 20 ± 1 °C. The balance was zeroed before each experiment. Spreading solutions are prepared from HPLC grade chloroform (Aldrich). The spreading solvent is allowed to evaporate for 10 min prior to compression. The molecular weight per repeat unit is 368 g mol⁻¹. Typical values of the continuous barrier rates used to compress the monolayer were of the order of 4 Å² min⁻¹ molecule⁻¹. At least two measurements are done for each set of experimental conditions.

Infrared spectra were recorded on Bruker FTIR spectrometer (Equinox 55). The IR spectra were measured from pressed pellets in KBr matrix or from CaF₂

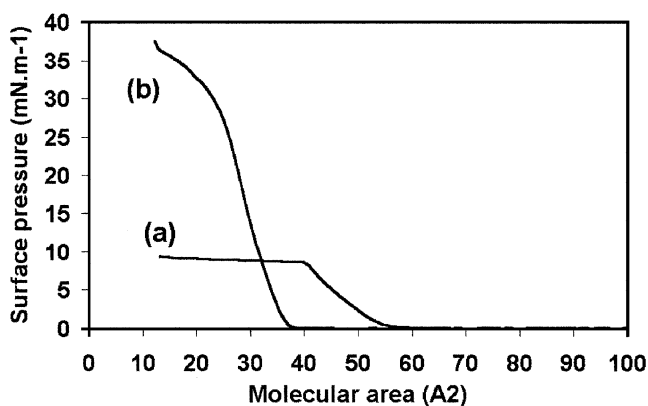


Fig. 1. Pressure–area isotherms of (a) EDTMC14 and (b) PEDTMC14 at an air–water interface. $T=20\text{ }^{\circ}\text{C}$. Subphase: pure water. Compression rate: $4\text{ }\text{\AA}^2\text{ molecule}^{-1}\text{ min}^{-1}$. Isotherm of PEDTMC14 is reported in molecular area per repeat unit.

substrates for the LB films. Electrochemical experiments are carried out with a one-compartment three-electrode glass cell. The working electrode is an ITO glass onto which the polymer was deposited by Langmuir–Blodgett technique. A saturated calomel electrode (SCE) was used as a reference electrode for all the electrochemical experiments with a salt bridge containing the supporting electrolyte. The SCE electrode potential was measured against the ferrocene/ferricinium (Fc/Fc^+) couple in acetonitrile ($E=0.305\text{ V}/\text{SCE}$) and electrochemical measurements in this media have been reported vs. this couple. The counter-electrode is a platinum wire. Voltammetry is performed on an EGG Princeton Applied Research model 273 potentiostat/galvanostat controlled by a personal computer via EGG Princeton Applied Research model 270 electrochemical software. Conductivity measurements were performed with a Keithley on the LB films deposited on a network of interdigitated electrodes (width: $20\text{ }\mu\text{m}$, spacing: $20\text{ }\mu\text{m}$, length: $3.16\text{ }\mu\text{m}$). All experiments were carried out at room temperature. All substrates were soaked in chromo-sulfuric acid and rinsed thoroughly with purified water before use.

3. Results and discussion

3.1. Monolayer experiments

Fig. 1 shows the pressure–area (π – A) isotherm for EDTMC14 on purified water. Upon compression, the pressure was observed to increase monotonically to a 10 mN m^{-1} plateau pressure. The area per monomer is found to be $54\text{ }\text{\AA}^2$ by extrapolation of the linear section of π – A curve to zero pressure. The plateau pressure is independent of the compression rate. No collapse is detectable on the isotherm. This low-pressure plateau corresponds to a relative large limiting area per monomer ($A=40\text{ }\text{\AA}^2$) compared with a dense arrangement of one

alkyl chain approximately $20\text{ }\text{\AA}^2$ [19]. It is possible that at low pressures, the head groups are lying nearly flat on the water surface but are forced to align vertically at 10 mN m^{-1} surface pressure in order to accommodate for the packing of the hydrocarbon tail groups. However, it is worth noting that stable monolayers have been prepared with EDTMC14 whereas alkylthiophene does not form stable monolayers [7]. The presence of an ethylenedioxy group on the thiophene ring increases the hydrophilicity of the molecule. However, just before the plateau at 8 mN m^{-1} surface pressure, all attempts to transfer the monolayer of EDTMC14 from the air–water interface onto the solid substrate failed.

Stable monolayers were also obtained from chemically synthesized PEDTMC14 with a pressure collapse at approximately 30 mN m^{-1} (Fig. 1). The condensed phase forms a rigid film at the air–water interface when the pressure is higher than 25 mN m^{-1} . Extrapolation to zero pressure gives an area of $37\text{ }\text{\AA}^2$ per repeat unit. This lower area per unit compared to monomer ($A=54\text{ }\text{\AA}^2$) can be explained by the presence of covalent bonds between the EDTMC14 units. However, this limiting area per monomer unit is higher than previously reported for alkylthiophene polymers ($A_0=5\text{--}10\text{ }\text{\AA}^2$), which form aggregates at the air–water interface [20].

Thus, it can be concluded that in the case of EDTMC14 the molecular area is not determined by the alkyl chain but also that the PEDTMC14 molecules do not form aggregates at the interface.

3.2. Polymerization at the interface

Iron(III) chloride and CAN are well known oxidative agents and have been successfully used to polymerize EDT derivatives in solution [21,22]. Direct polymerization of the EDTMC14 monolayers at the air–water interface via the introduction of an oxidative agent (FeCl_3 and CAN) into the aqueous subphase has been studied. The reaction at the interface is monitored by following the π – A isotherms changes. When FeCl_3 or CAN are introduced in the aqueous subphase at $\text{pH}=6.5$, the π – A isotherms are not changed whatever the salt concentration and the polymerization does not occur. Bazzoui et al. [23] have shown that a strongly acidic medium favors electropolymerization at low potentials. For this reason, we have studied the EDTMC14 monolayer polymerization on acidic subphase.

The π – A isotherms of a EDTMC14 monolayer were recorded onto a subphase containing different concentrations of FeCl_3 and perchloric acid ($\text{pH}=2.4$). The isotherms were not changed compared with water as subphase and polymerization did not occur.

The same experiments were carried out with CAN in the subphase in similar conditions (perchloric acid, $\text{pH}=2.4$). Fig. 2 displays the pressure–area isotherms obtained with CAN concentrations from 10^{-4} to 10^{-3}

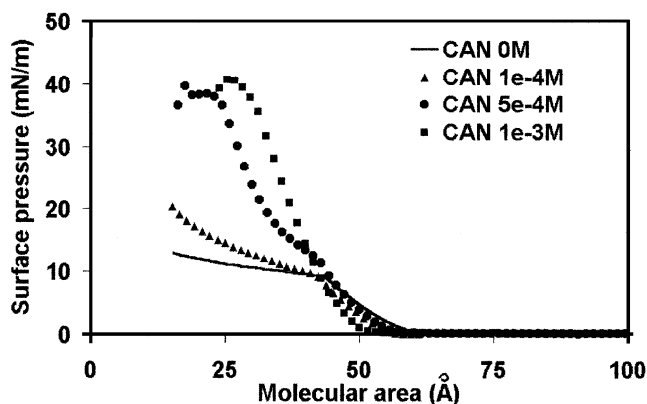


Fig. 2. Pressure–area isotherms of EDTMC14 on different CAN concentrations in the subphase. pH=2.4. Compression rate : $4 \text{ Å}^2 \text{ molecule}^{-1} \text{ min}^{-1}$. Temperature: 20°C .

mol l^{-1} . The plateau disappears when the CAN concentration in the subphase is higher than $5 \times 10^{-4} \text{ mol l}^{-1}$. These measurements indicate that CAN concentrations higher than $10^{-4} \text{ mol l}^{-1}$ are necessary to observe polymerization. On the acid subphase containing CAN ($10^{-3} \text{ mol l}^{-1}$), the isotherm does not show any plateau. The condensed phase forms a rigid film at the air–water interface if the pressure is higher than 30 mN m^{-1} and the collapse is observed at 40 mN m^{-1} corresponding to a molecular area of $28 \text{ Å}^2 \text{ molecule}^{-1}$. Extrapolated molecular area at zero pressure is obtained at $46 \text{ Å}^2 \text{ molecule}^{-1}$. Taking into account the molecular dimensions of 3,4-ethylenedioxythiophene-methanol (EDTM) ($7.2 \text{ Å} \times 4.6 \text{ Å}$) from CPK model, it can be deduced that the EDT ring in the monolayer is nearly flat on the surface. This behavior is independent of the nature of the acid (HCl or HClO_4) at pH=2.4. This indicates that the nature of the counter-ion of the acid has no influence on the polymerization process. However, the subphase pH has a marked effect on the π –A isotherms of the monolayer. The disappearance of the plateau and the increase of the collapse surface pressure are observed only when the subphase pH is lower than approximately 2.7.

The π –A isotherms of chemically synthesized PEDTMC14 (Fig. 1) and EDTMC14 polymerized at the interface on CAN ($10^{-3} \text{ mol l}^{-1}$) acidic subphase (Fig. 2) have the same shape but the interface polymerized EDTMC14 isotherm is shifted toward larger areas. So the two polymers might adopt a different organization at the air–solution interface.

In order to understand the influence of the pH on the polymerization of EDTMC14 in Langmuir films, we have studied the evolution of oxidation potential of EDT as a model compound soluble in aqueous solution in different acidic aqueous solutions. Fig. 3 shows cyclic voltamperograms between 0.30 V and 1.10 V/SCE of EDT $10^{-2} \text{ mol l}^{-1}$ in LiClO_4 0.1 mol l^{-1} with different

acidic electrolytes. We clearly observe a decrease of the oxidation potential of the monomer as the concentration of acid increase which would indicate a stabilization of the cation radical. Similar results have been already observed by Bazzouai et al. for thiophene [23]. Thus, polymerization of EDT in aqueous phase would be more efficient when the acidity increases. Indeed, Seo and Chung have shown that chemical polymerization rate of the EDT in aqueous solution increases with the initiator concentration and this rate is maximum when pH is equal to 2.7 [21]. A similar behavior might explain the influence of the pH on the polymerization of EDTMC14 at the interface.

The above results from π –A measurements suggest that a polymerization occurs at the air–water interface. The fact that the polymerization with CAN happens and not with FeCl_3 for the same acidic subphase composition is probably due to a thermodynamic effect. Indeed, CAN is a stronger oxidant than iron (III) chloride. The standard potentials defined by cyclic voltammogram as $(E_{\text{pa}} + E_{\text{pc}})/2$ (where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively) is approximately 300 mV higher for CAN than for FeCl_3 . The polymerization at the interface depends on the CAN concentration and pH in the subphase. In order to confirm this assumption, the monolayer has been transferred onto solid substrates and characterized with different techniques. The CAN concentration is kept at $10^{-3} \text{ mol l}^{-1}$ and the pH subphase at 2.4 for all experiments carried out on EDTMC14 monomer. The LB films of EDTMC14 fabricated from the subphase containing CAN will be referred to as EDTMC14/CAN LB films hereafter.

3.3. Transfer

Built-up films of chemically synthesized PEDTMC14 and of EDTMC14/CAN LB films are obtained by vertical lifting method with a dipping speed of 10 mm min^{-1} . After each cycle, the substrate is dried for 10

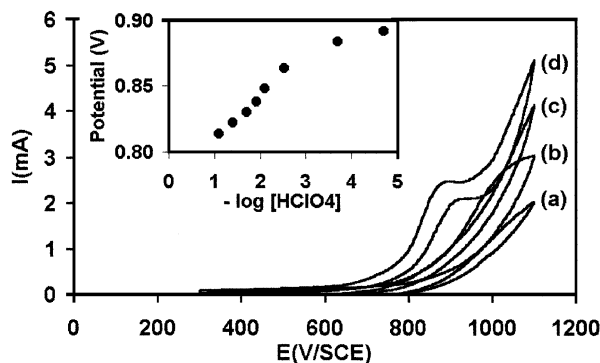


Fig. 3. Cyclic voltamperograms of EDT $10^{-2} \text{ mol l}^{-1}$ in water with different acid (HClO_4) concentrations. (a) $2.10^{-5} \text{ mol l}^{-1}$, (b) $2.10^{-2} \text{ mol l}^{-1}$, (c) $5.10^{-1} \text{ mol l}^{-1}$, (d) 1 mol l^{-1} . Scan rate = 0.1 V s^{-1} . Electrolyte: $0.1 \text{ mol l}^{-1} \text{ LiClO}_4$. Ref.: SCE.

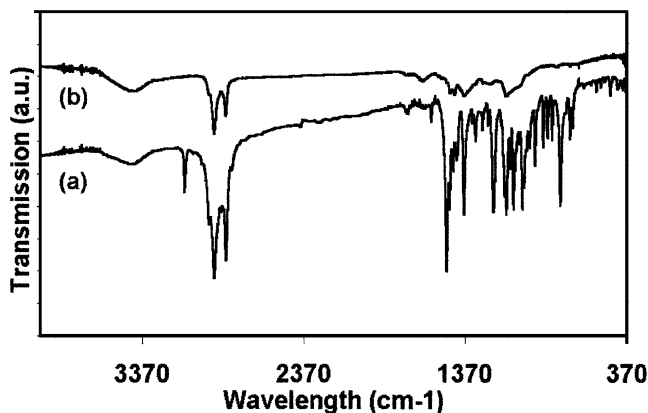


Fig. 4. Infrared spectra of (a) EDTMC14 and PEDTMC14 in KBr pellet.

min in air. Furthermore, all monolayers are transferred at a 20 mN m^{-1} pressure. All depositions are done for downstroke and upstroke of the substrate, leading to a Y-type structure. Deposition ratios close to unity are obtained.

3.4. Spectroscopic FTIR characterizations

The FTIR characterization of EDTMC14 and PEDTMC14 obtained by chemical polymerization has been carried out. Fig. 4 shows the FTIR spectra of monomer and polymer in KBr pellet. The symmetric and asymmetric CH_2 stretching vibrations and the stretching in the C–O–C bond of the hydrocarbon tail group are found in the $3000\text{--}2800 \text{ cm}^{-1}$ and 1190 cm^{-1} region, respectively. Absorption peaks occurring at 1115 and 1070 cm^{-1} are assigned to C–C and C–O stretching of oxyethylene ring respectively [24]. All these bands are present in the monomer and polymer spectra. In the monomer spectrum, vibration at 1486 cm^{-1} due to C=C stretch originates from the thiophene ring [25,26] and the absorption band at 3108 cm^{-1} is assigned to =C–H vibration of the thiophene ring. The

Table 1
Position of vibrational modes of C=C and C–H bonds in different samples

Molecule/subphase	State	$\nu(\text{C–H})$	$\nu(\text{C=C})$	$\nu(\text{C–C})$
<i>Powder</i>				
EDTMC14	–	3108	–	1486 1376
PEDTMC14	Dedoped	–	–	– 1364
<i>LB films</i>				
EDTMC14/CAN	Doped	–	1645	1515 –
EDTMC14/CAN + ammonia	Partially doped	–	–	1527 1351
EDTMC14/CAN + hydrazine	Partially doped	–	1633	1573 1356
PEDTMC14/water	Dedoped	–	–	1527 1369
PEDTMC14/CAN	Doped	–	1639	1510 –

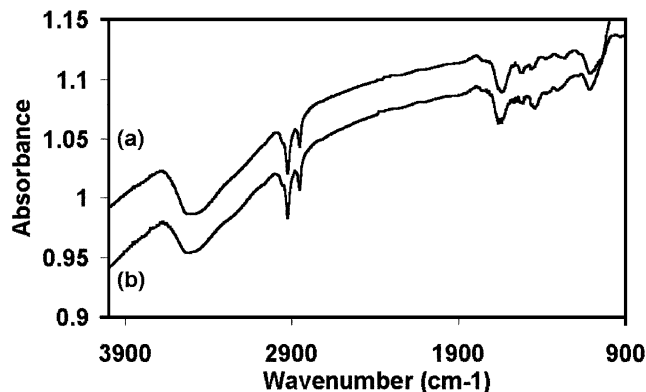


Fig. 5. Infrared spectra of 30 layers LB films on CaF_2 of (a) EDTMC14/CAN LB films, (b) PEDTMC14 obtained on $10^{-3} \text{ mol} \cdot \text{l}^{-1}$ CAN ($\text{pH}=2.4$) solution subphase.

disappearance of this last band can be considered as a proof that polymerization occurred.

In order to confirm the interfacial polymerization, infrared spectra of monolayers transferred onto CaF_2 substrates were measured. The results are reported in the Table 1. The IR spectra of EDTMC14/CAN LB films (Fig. 5a) show the disappearance of the C–H peak (3108 cm^{-1}), which confirms the polymerization the EDTMC14 monomer at the air–water interface. In order to obtain doped PEDTMC14 LB films, 30 layers of PEDTMC14 on $10^{-3} \text{ mol l}^{-1}$ CAN ($\text{pH}=2.4$) subphase are transferred onto CaF_2 substrate. The IR spectrum is shown on Fig. 5b. This spectrum is identical to the one obtained from the EDTMC14 (which is believed to polymerize) on the same subphase. This result clearly indicates that both polymers prepared in bulk and at the air–water interface have essentially the same chemical structure in the p-doped state.

Fig. 6 shows the IR spectra of the samples in the range $1800\text{--}1300 \text{ cm}^{-1}$. For EDTMC14/CAN LB films

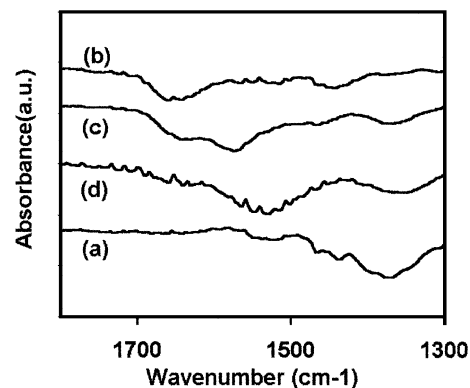


Fig. 6. Infrared spectra of 30 layers LB films on calcium fluoride of (a) PEDTMC14 LB films, (b) EDTMC14/CAN LB films, (c) EDTMC14/CAN LB films treated with hydrazine vapors, and (d) EDTMC14/CAN LB films treated with ammonia solution.

(Fig. 6b), the spectrum exhibits a large absorption band at 1645 cm^{-1} , which is missing for the dedoped PEDTMC14 LB films obtained on pure water subphase (Fig. 6a). On the contrary, absorption band at 1369 cm^{-1} is missing in the spectrum recorded on the EDTMC14/CAN LB films.

The absorption band occurring at approximately 1640 cm^{-1} has been already observed in unsubstituted PEDT by Seo and Chung [21]. They have assigned it to the presence of carbonyl group in the polymer obtained with potassium persulfate as initiator. According to these authors, the carbonyl group would be due to an over-oxidation of the polymer in water by analogy to what is observed in the thiophene and pyrrole polymerization. The overoxidation of the polymer is usually observed during electrochemical study [27] but is probably more difficult to achieve in solution during chemical synthesis. In any case, the formation of a carbonyl group is possible during the polymerization of thiophene and pyrrole because of the free β -position of the ring but it is not the case in the EDT.

So, we think that this band at 1640 cm^{-1} could be rather assigned to a C=C bond whose position depends on the doping level of polymer. In order to better understand the origin of the absorption band in this region, we have recorded the IR spectrum of the EDTMC14/CAN LB films before and after dedoping i.e. soaking 2 h in a 1 mol l^{-1} ammonia solution (Fig. 6b,d). The absorption band at 1645 cm^{-1} decreases and simultaneously bands centered at 1527 and 1351 cm^{-1} appear. The same dedoping experiment carried out during 1 min in hydrazine vapor leads to a decrease in the absorption band at 1645 , which is shifted to 1633 cm^{-1} . Moreover, other bands appear at 1573 and 1356 cm^{-1} (Fig. 6c). Vibrations in the region 1550 – 1500 cm^{-1} and 1400 – 1350 cm^{-1} have been ascribed to the stretching of the C=C and C–C bonds, respectively in the thiophene ring [25,26]. So we suggest that the shifts of these two bands are strongly dependent on the doping level of the conducting polymer in which the p-doped state is well known to be highly stabilized by electron-donating ethylenedioxy group and/or by the lamellar structure of the LB films [28]. Indeed, all the C=C bands in the range 1650 – 1350 cm^{-1} can be modified by exposition of the samples at an oxidative or reductive agent.

3.5. Electrochemical measurements

We have first used chemically and electrochemically synthesized PEDTMC14 in order to compare the electroactivity of thin films with the one deposited by the LB technique or obtained by polymerization at the air–water interface. All thin films were characterized in $0.1\text{ mol l}^{-1}\text{ LiClO}_4/\text{CH}_3\text{CN}$ medium and all potentials are given vs. Fc/Fc^+ .

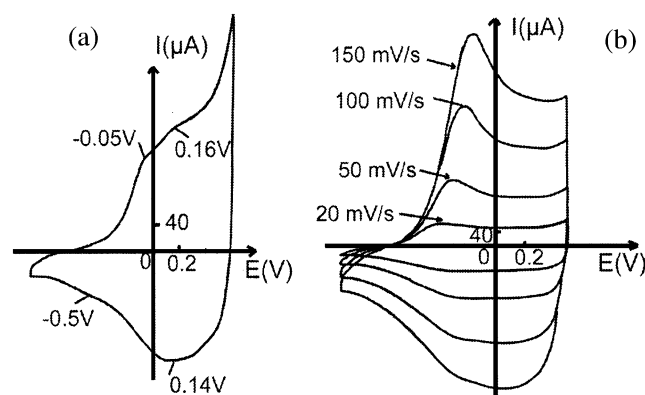


Fig. 7. Cyclic voltammetry of PEDTMC14 thin film obtained by (a) evaporation of a PEDTMC14 solution. Scan rate = 0.1 V s^{-1} . (b) Electrodeposition of EDTMC14 at different scan rates. Solution: $0.1\text{ mol l}^{-1}\text{ LiClO}_4/\text{CH}_3\text{CN}$. Ref.: Fc/Fc^+ .

The chemically synthesized polymer was cast in thin film by evaporation of a PEDTMC14 solution. Cyclic voltammetry was carried out between -0.95 and 0.60 V vs. Fc/Fc^+ . PEDTMC14 is oxidized (Fig. 7a) with peaks at -0.05 and 0.16 V at a scan rate of 0.10 V s^{-1} . On the cathodic scan, only one broad reduction peak at 0.14 V is observed with a shoulder at approximately -0.50 V . During successive scans we clearly observe a reversible optical modification of the film which changes from purple to light blue when oxidized as it is usually observed for the PEDT derivatives [29].

PEDTMC14 is easily electrodeposited as a film on ITO electrodes. The repeated scan electropolymerization behavior of a $10^{-3}\text{ mol l}^{-1}$ solution of EDTMC14 in acetonitrile was examined under argon atmosphere. The electrochemical growth is shown in Fig. 8. The monomer is oxidized from 0.75 V through an irreversible process due to the formation of unstable cation radicals. With repeated scanning, a redox current quickly increases indicating the growth of a film of an electroactive polymer. Indeed, after washing the polymer film with monomer-free electrolyte solution, the redox behavior of the film was studied (Fig. 7b). At a scan rate of 0.10 V s^{-1} , the oxidation peak of the electrodeposited film occurs at -0.22 V . On the reverse scan, two reductive peaks are observed at 0.08 and -0.24 V . This electrochemical behavior is in good agreement with that described by Reynolds et al. [30] for an alkylated PEDT with a close chemical structure. As already suggested by these authors, we think that multiple reductions may be due to the sequential reduction of dicationic bipolaronic charge carrier to cation radical then to neutral polymer. Between 0.02 and 0.15 V s^{-1} , the anodic peak current increases linearly with the scan rate, which indicates a no diffusion limited redox process. Compared to the chemically synthesized polymer, the electrosynthesized film is oxidized at a lower potential, which

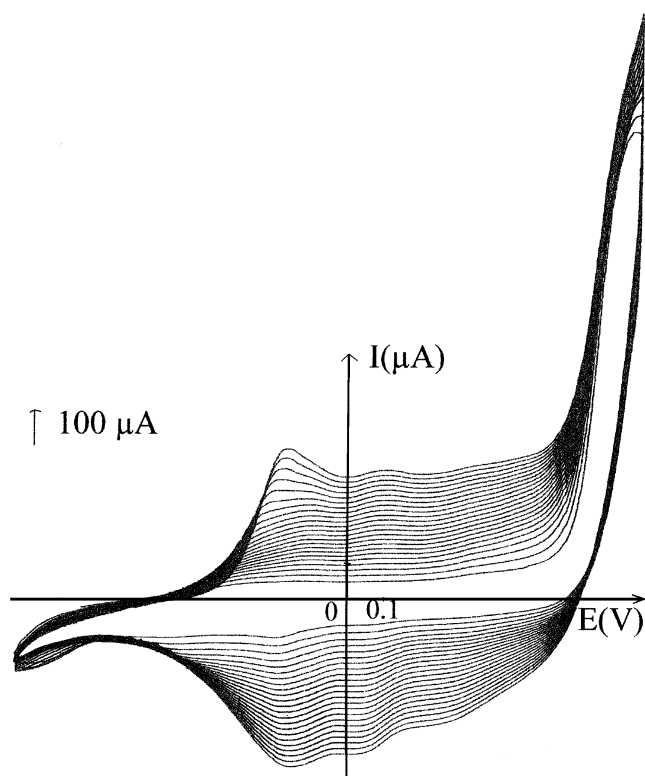


Fig. 8. Electropolymerization of a 10^{-3} mol l^{-1} solution of EDTMC14 in acetonitrile in an argon atmosphere on ITO electrodes. Scan rate = 0.1 V s^{-1} . Ref.: Fc/Fc^{+} .

may indicate an increase of the electronic delocalisation leading to a stabilization of the oxidized species probably due to an increase of the macromolecular chain length.

In contrast to the electrodeposited or evaporated thin layers, the LB deposited films are well ordered. In order to examine the influence of the macromolecular organization on the electrochemical behavior of the film, we have studied, at first, the electroactivity of the PEDTMC14-deposited LB films. In studying the electroactivity of some LB films with a variable number of layers in different electrolyte compositions (0.1 mol l^{-1} $LiClO_4/CH_3CN$ or 0.1 mol l^{-1} $LiClO_4/H_2O$) we never observed any electrochemical responses. Such a behavior suggests that the organization of the LB films may lead to a lamellar structure with alternated conducting (heterocycles) and insulating (alkyl chains) planes. In this configuration, the diffusion of the counter ion—which ensures the electroneutrality of the film during the redox process—may be limited by its specific hydrophobic interactions or compactness, which inhibits the electrochemical response. From these electrochemical results, it seems that the quality and compactness of the film is high enough to prevent anions to penetrate into the film. Similar electrochemical results have been observed with other molecules in LB films and SAM

[30–33]. Indeed, Majda et al. have shown that long alkyl chain molecules (octadecanethiol and octadecylalcohol) SAM are able to block access to the surface, which leads to a passivation of the electrode.

In order to determine the effect of the doping in the LB films before the electrochemical characterization, we have also studied the electrochemical behavior of EDTMC14/CAN LB films. In this case, the polymer is doped. Ten layers of EDTMC14/CAN LB films have been transferred onto ITO electrode, then washed and placed into a 0.1 mol l^{-1} $LiClO_4/CH_3CN$ electrolyte. In contrast to undoped PEDTMC14 LB films, one can observe a redox system with anodic peak at 0.18 V and cathodic peak at -0.19 V at a scan rate of 0.2 V s^{-1} (Fig. 9). Cyclic voltammograms of the modified electrode were obtained as a function of the scan rate between 0.2 and 0.8 V s^{-1} . The anodic peak intensity variation vs. scan rate indicates a thin layer behavior with a current not limited by the diffusion of counterions. The prior doping of the Langmuir–Blodgett films would allow the redox process to be effective and seems to be an important parameter for this kind of well-ordered film.

These results are confirmed in studying the electrochemical behavior in the same electrolyte of PEDTMC14 deposited by LB technique with the presence of CAN in the subphase. In this case, CAN acts as a doping agent of the polymer during the formation of the LB films, which ensures the presence of counterions in the films. Thus, the process of insertion of anions is not a limiting factor. As expected, the films are electroactive during the potentiodynamic scans and voltammograms are very close to that obtained from

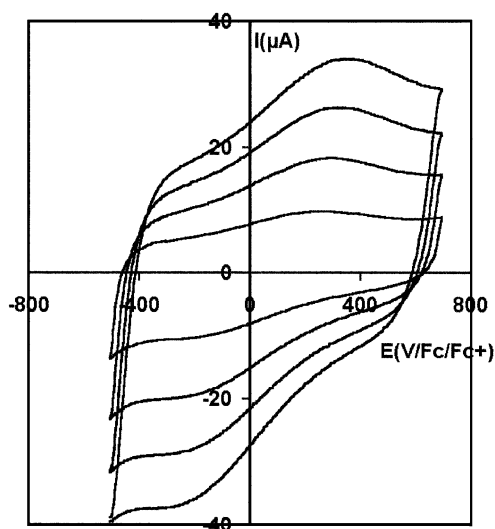


Fig. 9. Cyclic voltammetry of EDTMC14/CAN Langmuir–Blodgett films (10 layers) at different scan rates: (a) 0.2 V s^{-1} , (b) 0.4 V s^{-1} , (c) 0.6 V s^{-1} , (d) 0.8 V s^{-1} . Solution: 0.1 mol l^{-1} $LiClO_4/CH_3CN$. Ref.: Fc/Fc^{+} .

EDTMC14 Langmuir–Blodgett films. Compared with the electropolymerized polymer or to polymers which have been chemically synthesized and deposited by evaporation, the electrochemical response of LB films is less well defined with a large increase of the ΔE_p . This difference could be explained by the introduction of the counter-ion during the elaboration and subsequent doping of the LB films which would limit the mobility of the counter ions.

3.6. Conductivity measurements

It was reported that the conductivity of dedoped PEDTMC14 LB films at room temperature was of the order of $10^{-7} \text{ S cm}^{-1}$ [11]. However, the plane conductivity measured on PEDTMC14 LB films transferred from the CAN 10^{-3} M subphase is approximately $2 \times 10^{-2} \text{ S cm}^{-1}$, the PEDTMC14 are thus in a doped state. These results are in agreement with the IR and electrochemical studies.

Moreover, conductivity measurements of EDTMC14/CAN LB films revealed similar conductivities (approx. $2 \times 10^{-2} \text{ S cm}^{-1}$) to those obtained for the PEDTMC14 doped LB films. This result is also a very strong proof that the EDTMC14 monomer was simultaneously polymerized and doped at the air–solution interface on the CAN subphase otherwise the deposit would be insulating. Moreover the conductivity value of this film is of the same order of magnitude as observed for other conducting polymers in LB films [2] which suggests that the quality of the films built on the CAN subphase is satisfactory.

4. Conclusion

EDTMC14 is an EDT derivative with a tetradecyloxy chain that renders the monomer and the corresponding polymer (PEDTMC14) soluble in organic solvents and amphiphilic enough for LB experiments. EDTMC14 monomer and PEDTMC14 polymer form stable monolayer at the air–water interface. By contrast to the polymer, all attempts to transfer the EDTMC14 monolayer from pure water interface onto solid substrate failed.

The EDTMC14 polymerization at the air–water interface was studied. It was accomplished by spreading a EDTMC14 solution onto a concentrated oxidizing (CAN) and perchloric acid subphase.

The different LB films obtained from EDTMC14 (polymerized at the air–solution interface) or PEDTMC14 (obtained by chemical polymerization and subsequently spread at the air–water interface) showed the same characteristics in FTIR spectroscopy and electrochemistry and conductivity measurements. These results may indicate that both polymers have essentially

the same molecular structure in the p-doped state, and that the pre-organization of the monomers in the Langmuir films seems to have no dramatic influence on the polymer properties.

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