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Surface nanostructure control with poly(ethylene glycol) (PEG) spacer by templateless electropolymerization

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Abstract

Controlling the shape of surface nanostructures is fundamental for various potential applications for example, in water harvesting systems, liquid transportation or oil/water separation membranes. Here, the creation of porous surface structures is made by a process called templateless electropolymerization, in which water (H₂O) is oxidized/reduced to form gas (O₂/H₂) bubbles onto the surfaces and acting as soft template for the polymer growth. Keeping the monomer (thieno[3,4-*b*]thiophene) and the substituent (pyrene) constant, we demonstrate how a flexible PEG spacer can affect the structure shape. Here, when the PEG spacer increases, the structures change from nanotubes (1D growth), to nanoribbons (2D) and after to hollow nanospheres (3D), which also affects the wetting properties.

Keywords: Nanostructures, Wettability, Hydrophobicity, Electrochemistry, Bioinspiration.

1 Introduction

Due to their large surface area, nanotube arrays have gathered significant interest over recent years for their potential applications in electronic and optical devices, sensors, and for the control surface wetting properties [1–8]. Beyond these applications, well-controlled surface structures are also observed and studied in natural surfaces (gecko pads, plants or wings) [9–12]. In order to develop well-ordered surface structures, many researches in the literature were performed but their preparation often required long and difficult processes such as the use of hard templates, with anodized aluminum oxide (AAO) membranes for example [13,14]. For each desired in the nanotube parameter (diameter, height...) it is necessary to employ another membrane.

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To avoid the need of templates, researchers have recently become interested in using templateless electropolymerization as an alternative and rapid approach to obtain easily and quicker controllable porous nanostructures [15–20]. In this alternative method, gas bubbles released *in-situ* directly on the surface as soft templates for the polymer growth and are responsible of their porosity. In the literature, the electropolymerization of pyrrole in water (H₂O) has been extensively studied [21–29]. H₂O is necessary for the released of gas bubbles (O₂ and/or H₂ depending on experimental parameters) but a surfactant is necessary to stabilize the gas bubbles.

In organic solvent such as dichloromethane (CH₂Cl₂), recent studies have identified approaches that eliminate the need for surfactants and thus permit the formation of tubular features by electropolymerization such as vertically aligned nanotubes with even extremely strong water adhesion. Exceptional results were obtained for example with very aromatic and rigid monomers favoring π -stacking interactions such as 3,4-phenylenedioxythiophene (PheDOT), 3,4-naphthlenedioxythiophene (NaphDOT) and thienothiophene derivative [30–33]. However, in organic solvent it is important to study the influence of H₂O content because it has often a high influence for example on the number of nanotubes [34].

Among the available monomers, thieno[3,4-*b*]thiophene not only has exceptional polymerization capacity but it can lead also to various porous structures and is easy to functionalize [35–37]. More precisely, unique results were reported when both thieno[3,4-*b*]thiophene is used as the monomer and pyrene because the last one participates to electropolymerization and also induces high π -sticking interactions [38–41]. In this work, we study how the presence of a poly(ethylene glycol) (PEG) spacer between thieno[3,4-*b*]thiophene and pyrene can affect the polymer growth by templateless electropolymerization. Moreover, for future works it was reported in the literature [42–45] that the PEG can be used as an inert spacer in a wide range of biotechnological applications such as to display peptides and proteins on surfaces for diagnostic purposes, to adsorb or link to various biomolecules, or to immobilize

bacteria and antibodies. Here monomers with various PEG spacers from 1 to 4 as shown in Figure 1. In order to better characterize the influence of H₂O in the templateless electropolymerization process, we compare results obtained in CH₂Cl₂ and CH₂Cl₂ saturated with H₂O (called here CH₂Cl₂ + H₂O).

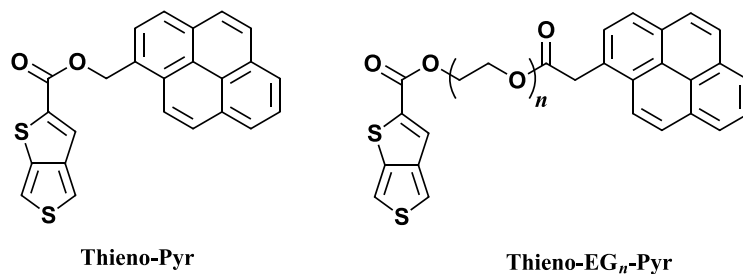


Fig. 1. Monomers investigated in this work (*n* = 1, 2, 3 and 4).

2 Materials and methods

2.1 Monomer synthesis

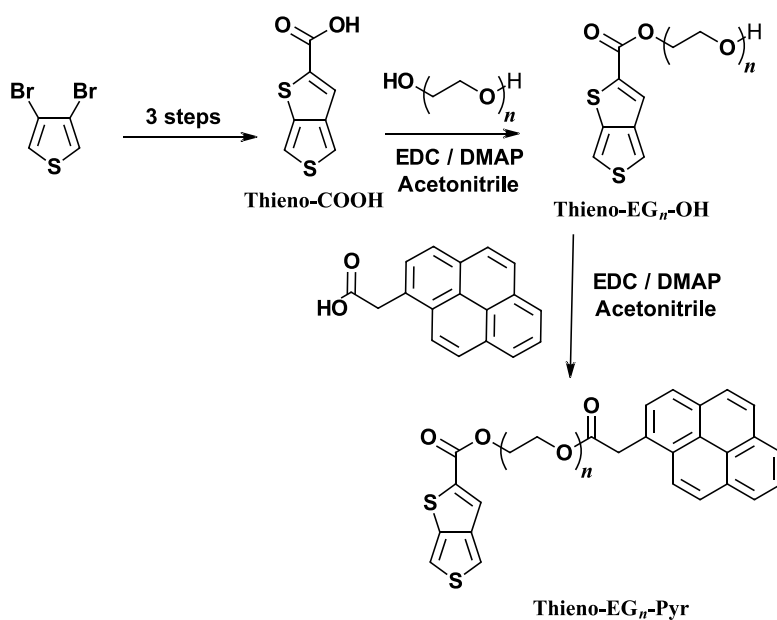


Fig. 2. Synthesis way to the monomers.

Pyren-1-ylmethyl thieno[3,4-*b*]thiophene-2-carboxylate (**Thieno-Pyr**) was synthesized using a previously reported procedure [35–37]. For the original monomers (Figure 2), thieno[3,4-*b*]thiophene-2-carboxylic acid (**Thieno-COOH**) was synthesized in three steps from 3,4-dibromothiophene [46–48]. Then, 1 eq of **Thieno-COOH** was dissolved in 20 mL of anhydrous acetonitrile and mixed with 1 eq of *N*-(3-dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDC) and 20 mg of 4-(dimethylamino)pyridine (DMAP). After stirring for 30 min, 1.2 eq of the corresponding diol (spacer) dissolved in acetonitrile was added to the mixture. After one day, the products were purified by column chromatography on silica gel (eluent: diethyl ether / petroleum 70:30) to obtain **Thieno-EG_n-OH**.

Thieno-EG₁-OH: 2-hydroxyethyl thieno[3,4-*b*]thiophene-2-carboxylate. Yield 58%; Yellow oil; δ_{H} (400 MHz, CDCl₃): 7.74 (s, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.30 (dd, *J* = 2.7 Hz, *J* = 0.8 Hz, 1H), 4.47 (t, *J* = 4.4 Hz, 2H), 3.95 (m, 2H), 2.05 (s, 1H); δ_{C} (400 MHz, CDCl₃): 163.36, 145.77, 139.72, 138.92, 124.08, 116.96, 111.47, 65.14, 61.21; MS (70 eV): *m/z* 228 (M⁺, 50), 184 (C₇H₄O₂S₂⁺, 100), 167 (C₇H₃OS₂⁺, 70).

Thieno-EG₂-OH: 2-(2-hydroxyethoxy)ethyl thieno[3,4-*b*]thiophene-2-carboxylate. Yield 37%; Yellow oil; δ_{H} (400 MHz, CDCl₃): 7.73 (s, 1H), 7.61 (d, *J* = 2.7 Hz, 1H), 7.29 (dd, *J* = 2.7 Hz, *J* = 0.8 Hz, 1H), 4.48 (t, *J* = 4.7 Hz, 2H), 3.83 (t, *J* = 4.7 Hz, 2H), 3.76 (t, *J* = 4.1 Hz, 2H), 3.66 (t, *J* = 4.9 Hz, 2H); δ_{C} (400 MHz, CDCl₃): 163.07, 145.85, 139.76, 139.13, 123.96, 116.90, 111.45, 72.46, 69.03, 65.86, 64.58, 31.79.

Thieno-EG₃-OH: 2-(2-(2-hydroxyethoxy)-ethoxy)ethyl thieno[3,4-*b*]thiophene-2-carboxylate. Yield 22%; Yellow oil; δ_{H} (400 MHz, CDCl₃): 7.77 (s, 1H), 7.64 (d, *J* = 2.7 Hz, 1H), 7.32 (dd, *J* = 2.7 Hz, *J* = 0.8 Hz, 1H), 4.5 (t, *J* = 4.7 Hz, 2H), 3.86 (t, *J* = 4.8 Hz, 2H), 3.73 (m, 6H), 3.64 (t, *J* = 4.9 Hz, 2H);

δ_{C} (400 MHz, CDCl_3): 135.78, 125.52, 116.85, 72.51, 70.82, 70.45, 69.09, 61.85, 49.18, 34.23, 33.95, 30.33, 25.62, 24.94.

Thieno-EG₄-OH: 2-(2-(2-(2-hydroxyethoxy)-ethoxy)ethyl thieno[3,4-*b*]thiophene-2-carboxylate. Yield 30%; Yellow oil; δ_{H} (400 MHz, CDCl_3): 7.73 (s, 1H), 7.61 (d, $J = 2.7$ Hz, 1H), 7.29 (dd, $J = 2.7$ Hz, $J = 0.8$ Hz, 1H), 4.47 (t, $J = 4.7$ Hz, 2H), 3.82 (t, $J = 4.9$ Hz, 2H), 3.66 (m, 10H), 3.59 (t, $J = 2.7$ Hz, 2H); δ_{C} (400 MHz, CDCl_3): 134.91, 135.78, 125.52, 123.90, 116.83, 111.40, 72.52, 69.08, 67.97, 64.69, 61.76, 33.96, 30.32, 25.62, 24.95.

The investigated monomers were synthesized *via* a simple esterification reaction (scheme 2). 1.3 eq of 1-pyreneacetic acid was dissolved in 20 mL of anhydrous acetonitrile in the presence of 1.2 eq of (EDC) and 20 mg of DMAP. After stirring for 30 min, **Thieno-EG_n-OH** dissolved in acetonitrile was added. After one day, the products were purified by chromatography on silica gel (eluent: diethyl ether / petroleum 70:30).

Thieno-EG₁-Pyr: 2-(2-(5,9-dihydropyren-1-yl)acetoxy)ethyl thieno[3,4-*b*]thiophene-2-carboxylate. Yield 58%; Orange oil; δ_{H} (400 MHz, CDCl_3): 8.25 (d, $J = 9.2$ Hz, 1H), 8.09 (m, 4H), 7.95 (m, 4H), 7.28 (d, $J = 2.7$ Hz, 1H), 7.22 (s, 1H), 7.12 (dd, $J = 2.7$ Hz, $J = 0.7$ Hz, 1H), 4.49 (m, 4H), 4.41 (s, 2H); δ_{C} (400 MHz, CDCl_3): 171.28, 162.62, 145.57, 139.60, 138.52, 131.15, 130.79, 130.65, 129.37, 128.38, 127.94, 127.24, 125.85, 125.18, 125.05, 124.94, 124.81, 124.58, 123.68, 123.09, 116.73, 111.10, 62.92, 62.21, 39.43.

Thieno-EG₂-Pyr: 2-(2-(2-(5,9-dihydropyren-1-yl)acetoxy)ethoxy)ethyl thieno[3,4-*b*]thiophene-2-carboxylate. Yield 40%; Orange oil; δ_{H} (400 MHz, CDCl_3): 8.02 (m, 9H), 7.64 (s, 1H), 7.53 (d, $J = 2.7$ Hz, 1H), 7.24 (dd, $J = 2.7$ Hz, $J = 0.8$ Hz, 1H), 4.37 (s, 2H), 4.29 (m, 4H), 3.69 (t, $J = 4.7$ Hz, 2H), 3.61 (t, $J = 4.8$ Hz, 2H); δ_{C} (400 MHz, CDCl_3): 171.53, 162.94, 145.83, 131.27,

⁶ 128.37, 128.08, 127.94, 127.36, 127.31, 126, 125.03, 124.99, 124.84, 124.68, 123.85, 123.24, 123.03, 116.83, 111.39, 69.11, 68.87, 64.55, 64.26, 39.38.

Thieno-EG₃-Pyr: 2-(2-(2-(2-(6,10-dihydropyren-1-yl)acetoxo)ethoxy)ethoxy)ethyl thieno[3,4-*b*]thiophene-2-carboxylate. Yield 30%; Orange oil; δ_{H} (400 MHz, CDCl₃): 8.03 (m, 9H), 7.66 (s, 1H), 7.53 (d, *J* = 2.7 Hz, 1H), 7.23 (dd, *J* = 2.7 Hz, *J* = 0.6 Hz, 1H), 4.36 (m, 4H), 4.27 (t, *J* = 4.6 Hz, 2H), 3.63 (m, 4H), 3.43 (s, 4H); δ_{C} (400 MHz, CDCl₃): 169.63, 137.84, 137.37, 133.89, 128.92, 126.53, 126.18, 126.03, 125.50, 125.41, 124.12, 123.63, 123.39, 123.24, 122.95, 121.94, 121.42, 114.90, 109.49, 68.72, 68.58, 67.19, 62.69, 62.41, 47.27, 45.81, 37.55, 32.06, 29.09, 28.43.

Thieno-EG₄-Pyr: 2-(2-(3-(2-(2-(6,10-dihydropyren-1-yl)acetoxo)ethoxy)propoxy)ethoxy)ethyl thieno[3,4-*b*]thiophene-2-carboxylate. Yield 17%; Orange oil; δ_{H} (400 MHz, CDCl₃): 8.04 (m, 9H), 7.67 (s, 1H), 7.54 (d, *J* = 2.7 Hz, 1H), 7.24 (dd, *J* = 2.7 Hz, *J* = 0.8 Hz, 1H), 4.43 (t, *J* = 4.7 Hz, 2H), 4.37 (s, 2H), 4.25 (t, *J* = 4.6 Hz, 2H), 3.75 (t, *J* = 4.9 Hz, 2H), 3.61 (m, 4H), 3.51 (t, *J* = 2.9 Hz, 2H), 3.43 (s, 4H); δ_{C} (400 MHz, CDCl₃): 171.52, 163.03, 145.85, 131.30, 130.82, 130.79, 128.42, 128.08, 127.93, 127.41, 127.30, 126.01, 125.53, 125.28, 125.13, 124.86, 123.32, 116.77, 111.38, 70.70, 70.50, 69.00, 64.69, 64.27, 39.43, 34.24, 30.33.

2.2 Electropolymerization

All electropolymerisation experiments were performed with an Autolab potentiostat (from Metrohm). Three electrodes were used: a 2 cm² gold-coated silicon wafer as working electrode (from Neyco), a carbon rod as a counter-electrode (from Metrohm) and a saturated calomel electrode (SCE) as a reference electrode (from Hach Lange). The electrolyte used was tetrabutylammonium perchlorate (Bu₄NCl₄) (0.1 M). Two different solvents were used: either dichloromethane (CH₂Cl₂) or dichloromethane saturated with water (CH₂Cl₂ + H₂O). The latter was prepared by mixing CH₂Cl₂ with a high amount of H₂O and removing any excess H₂O by extraction after decantation.

For each synthesized monomer, the oxidation potential (E^{ox}) was first determined and the templateless electrodepositions were performed by cyclic voltammetry from -1 V to E^{ox} at a scan rate of 20 mVs⁻¹ and using different number of scans (1, 3 and 5). After each deposition, the substrates were washed three times in dichloromethane to remove any unreacted monomer or residual electrolyte.

2.3 Surface characterization

The surface structures were characterized by scanning electron microscopy (SEM) with a 6700F microscope of JEOL. For the surface wettability, a DSA30 goniometer (from Bruker) was used with 2 μ L water droplets and the apparent contact angles with water (θ_w) were taken at the triple point ($n = 5$).

3 Results and discussion

3.1 Formation of porous structures by templateless electropolymerization

In agreement with previous works [34], in order to determine the influence of H₂O content on the release of O₂/H₂ bubble and the resulting surface structures, templateless electropolymerizations were performed with two solvents; first, CH₂Cl₂ because this solvent show that porous structures can be formed with this solvent that means at very low H₂O content. Then, CH₂Cl₂ was also saturated with water solvent called here CH₂Cl₂ + H₂O) in order to release a much higher amount of O₂/H₂ bubbles. The cyclic voltammogram of the two solvents with 0.1 M of Bu₄NClO₄ and without any monomer are clearly different (Figure 3). A large peak at ≈ -0.5 V vs SCE is present during the back scan in CH₂Cl₂ + H₂O, confirming the reaction $2 \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 \text{ (bubbles)} + 2 \text{OH}^-$. The peak starts at ≈ 0.0 V extends to ≈ -0.85 V. For the reaction $2 \text{H}_2\text{O} \rightarrow \text{O}_2 \text{ (bubbles)} + 4\text{H}^+ + 4\text{e}^-$, a peak is present during the forward scan but starts rather from roughly 2.0 V vs SCE.

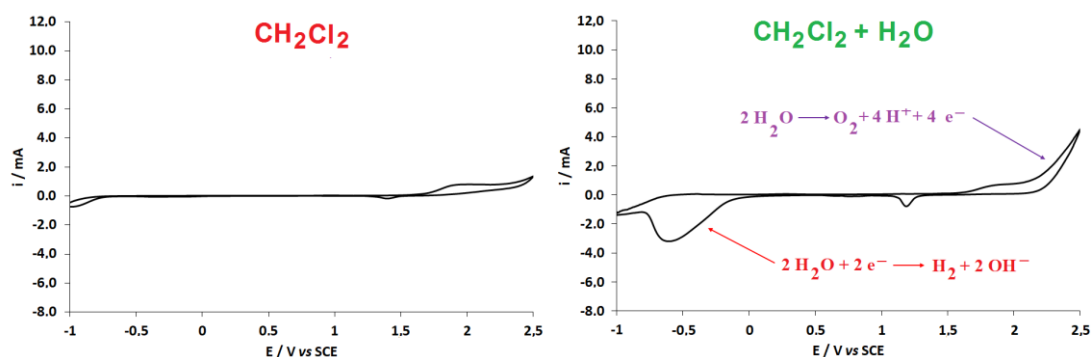


Fig. 3. Cyclic voltammograms (1 scan) of the two solvents (CH_2Cl_2 (on the left) and $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$ (on the right)) with Bu_4NClO_4 as supporting electrolyte. Scan rate: 20 mVs^{-1} . The curves are given in intensity (i in mA) vs potential (E in V).

After adding the monomers to the electrochemical cell, their oxidation potential was found to be $E^{\text{ox}} = 1.55 - 1.75 \text{ V vs SCE}$ that means lower than the potential of water oxidation. Then, electrodepositions were performed from -1 V to E^{ox} at scan rate of 20 mV s^{-1} . In this potential range, it is especially expected the released of H_2 bubbles during the back scans. In order to observe the polymer growth, the number of scans was varied (1, 3 and 5).

Representative cyclic voltammograms after 5 scans for all the monomers are presented in Figure 4. In CH_2Cl_2 , the presence of the polymer oxidation and reduction peaks are clearly present at roughly $0.5 - 1.0 \text{ V}$. The peak intensity is important for all the monomers. In $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$, a large peak at $\approx -0.5 \text{ V}$ is observed corresponding to water reduction as explained above. The presence of H_2O also clearly affects the polymer growth because the polymer oxidation and reduction peaks change. These changes are dependent on the monomers that means here on the PEG spacer.

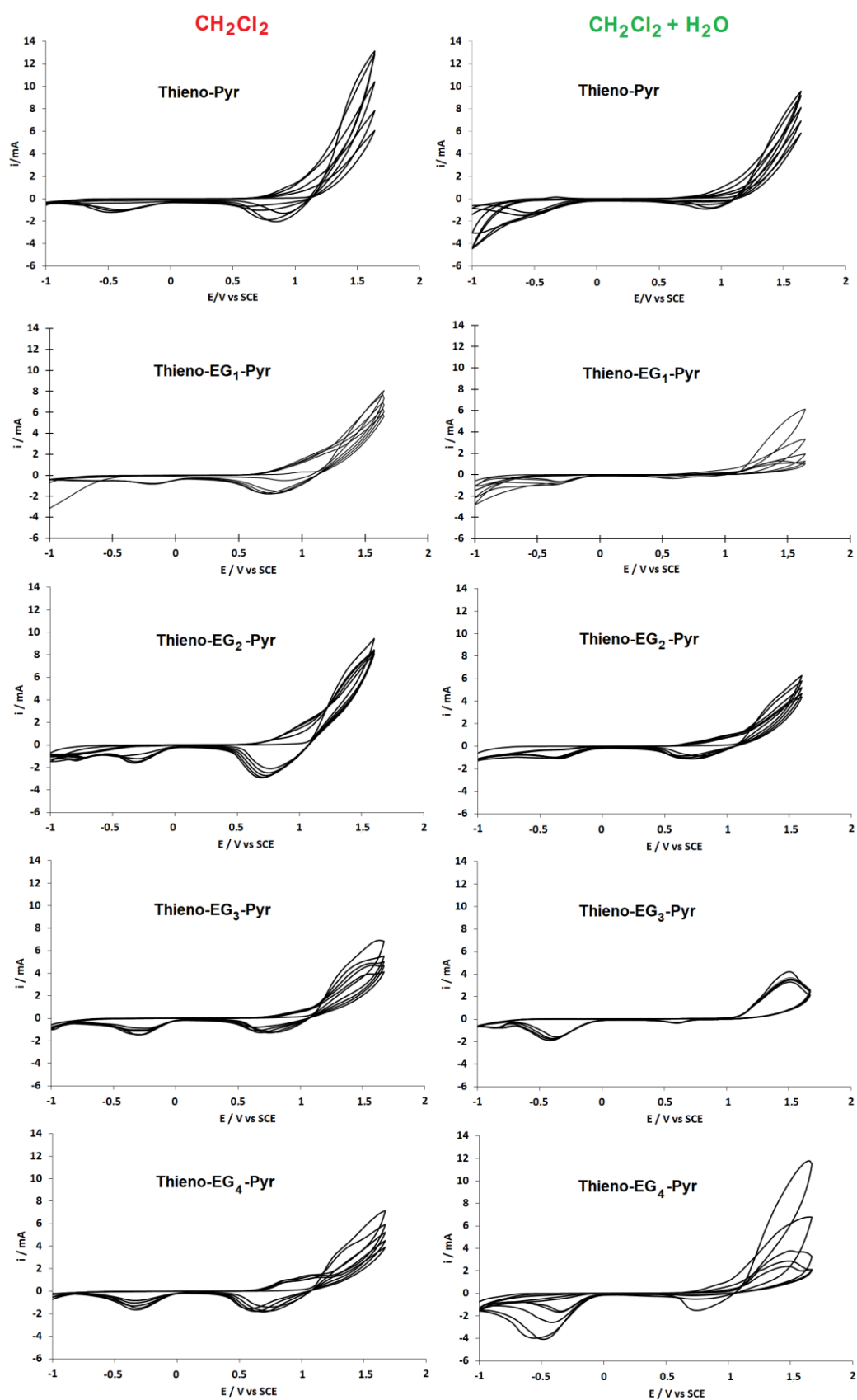


Fig. 4. Cyclic voltammograms (5 scans) of monomers in CH_2Cl_2 and $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$ with 0.1 M of Bu_4NClO_4 as electrolyte. Scan rate: 20

3.2 Morphological study of the surface structures

The surface morphologies after electrodeposition by cyclic voltammetry (3 scans) of all monomers in the two solvents CH₂Cl₂ and CH₂Cl₂ + H₂O are highlighted in Figure 5 and 6. From these images, it is clear that the presence of H₂O has a huge influence of the surface structures. In CH₂Cl₂, expected with Thieno-Pyr, the surfaces are not porous and only spherical structures or cauliflower-like structures are observed. Some huge porous structures are observed with Thieno-Pyr indicating its higher capacity to form porous structures. This is expected because it was shown that the polymer rigidity seems to be a very significant parameter on the formation of porous structures by templateless electropolymerization.

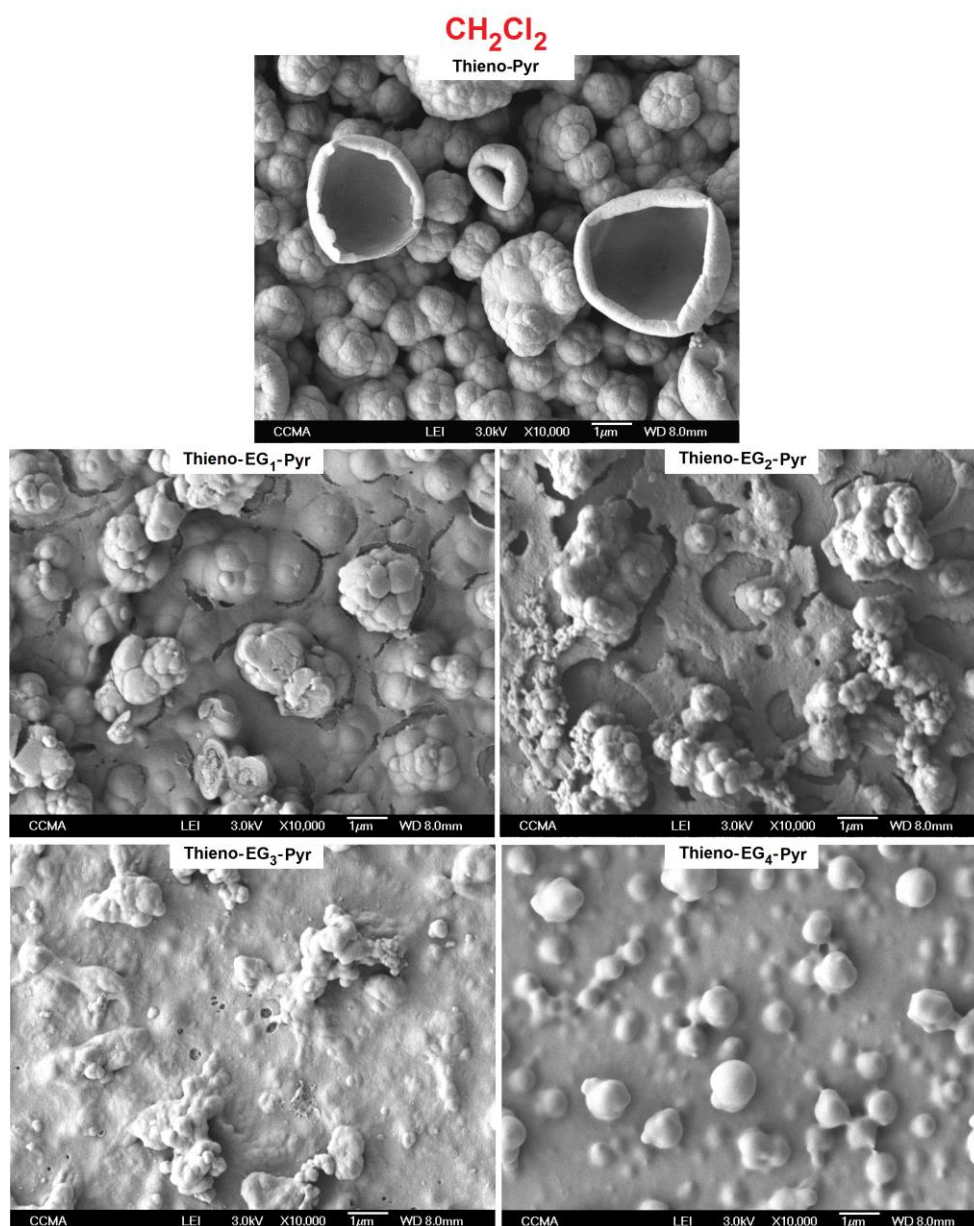


Fig. 5. SEM images of polymer surfaces obtained from different monomers in CH_2Cl_2 by cyclic voltammetry. Number of scans 3.

The SEM images of the polymer surfaces electrodeposited in $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$ are gathered in Figure 6. SEM images were also done after substrate inclination in order to better see the structures (Figure 7). In this solvent, a very nice change in surface structures is observed. Without spacer (**Thieno-Pyr**), a huge number of tubular structures is formed. The polymer growth is mainly mono-dimensional (1D). Then, when the length of the PEG spacer increases, the polymer growth become two-dimensional (2D) with nano-ribbons and then three-dimensional (3D) with hollow spheres. These results are in agreement with

¹² the literature data [46]. Thieno-Pyr is highly rigid and highly favors π -stacking interactions. As a consequence, the polymer growth is induced especially in one direction and nanotubes are formed. When a PEG spacer is used, the polymer becomes more flexible, which decreases the preferential interactions. The polymer films become even completely smooth when the PEG spacer is long because the polymer solubility also increases.

Finally, in order to better measure the polymer thickness and to better see the changes in surface morphology, cross-sectional SEM images were also performed with each surface (Figure 8). Only with Thieno-Pyr, it is clearly observed the presence of vertically aligned nanotubes of $\approx 2\ \mu\text{m}$ in height and $0.3\ \mu\text{m}$ in diameter. Indeed, we have previously demonstrated the importance to saturate CH_2Cl_2 with H_2O to form a huge number of nanotubes [34]. Moreover, the vertically aligned nanotubes are capped by other tubular structures of slightly larger diameter and $\approx 0.6\ \mu\text{m}$ in height. It is also confirmed the presence of nano-ribbons with Thieno-EG₁-Pyr, hollow spheres with Thieno-EG₂-Pyr and relatively smooth surfaces with Thieno-EG₄-Pyr. The polymer thickness remains relatively the same ($\approx 1\ \mu\text{m}$) excepted with Thieno-EG₃-Pyr, which leads to much lower thickness ($\approx 0.1\ \mu\text{m}$).

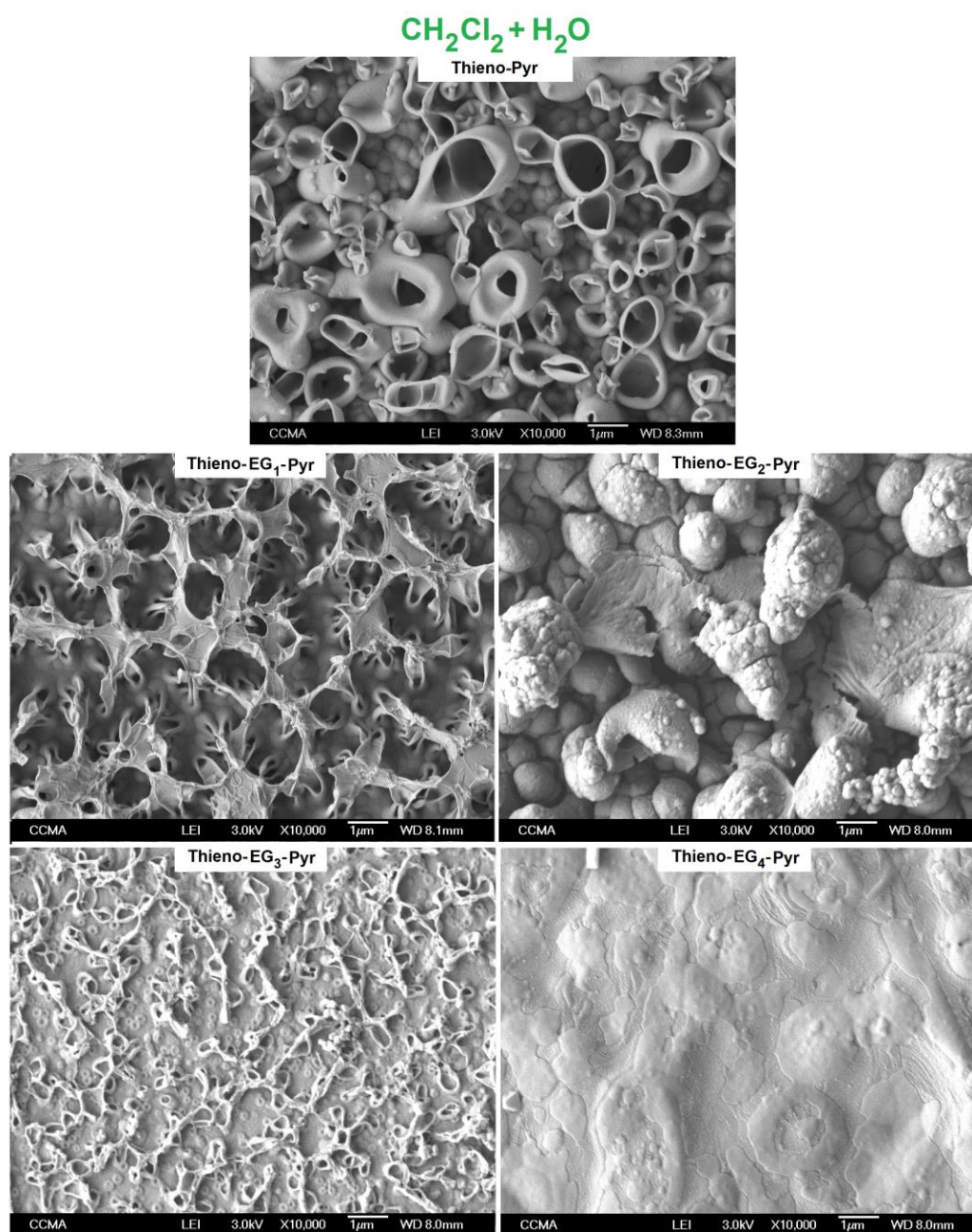


Fig. 6. SEM images of polymer surfaces obtained from different monomers in $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$ by cyclic voltammetry. Number of scans 3.

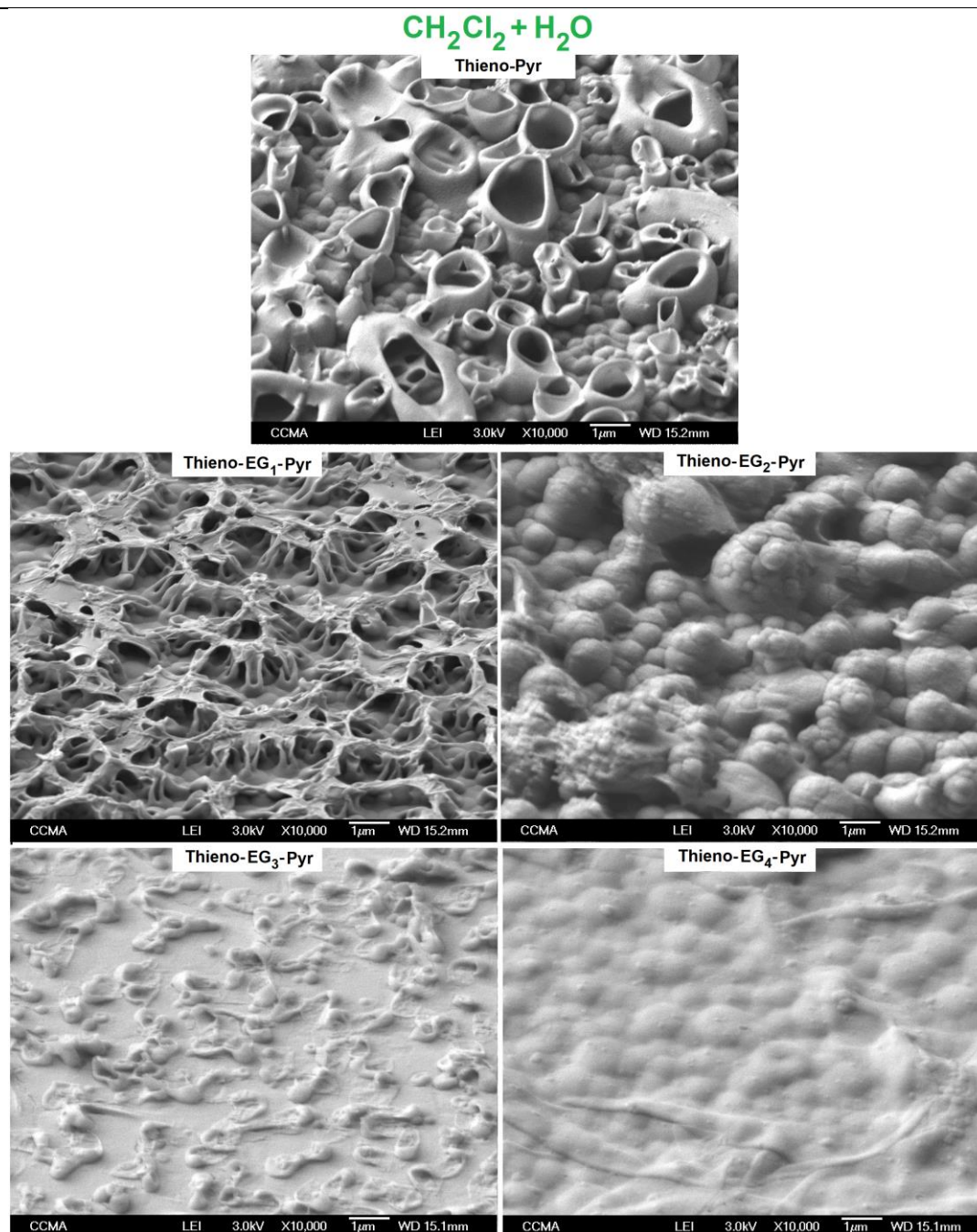


Fig. 7. SEM images of polymer surfaces obtained from different monomers in $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$ by cyclic voltammetry. Number of scans 3.

The substrates are inclined at 45° .

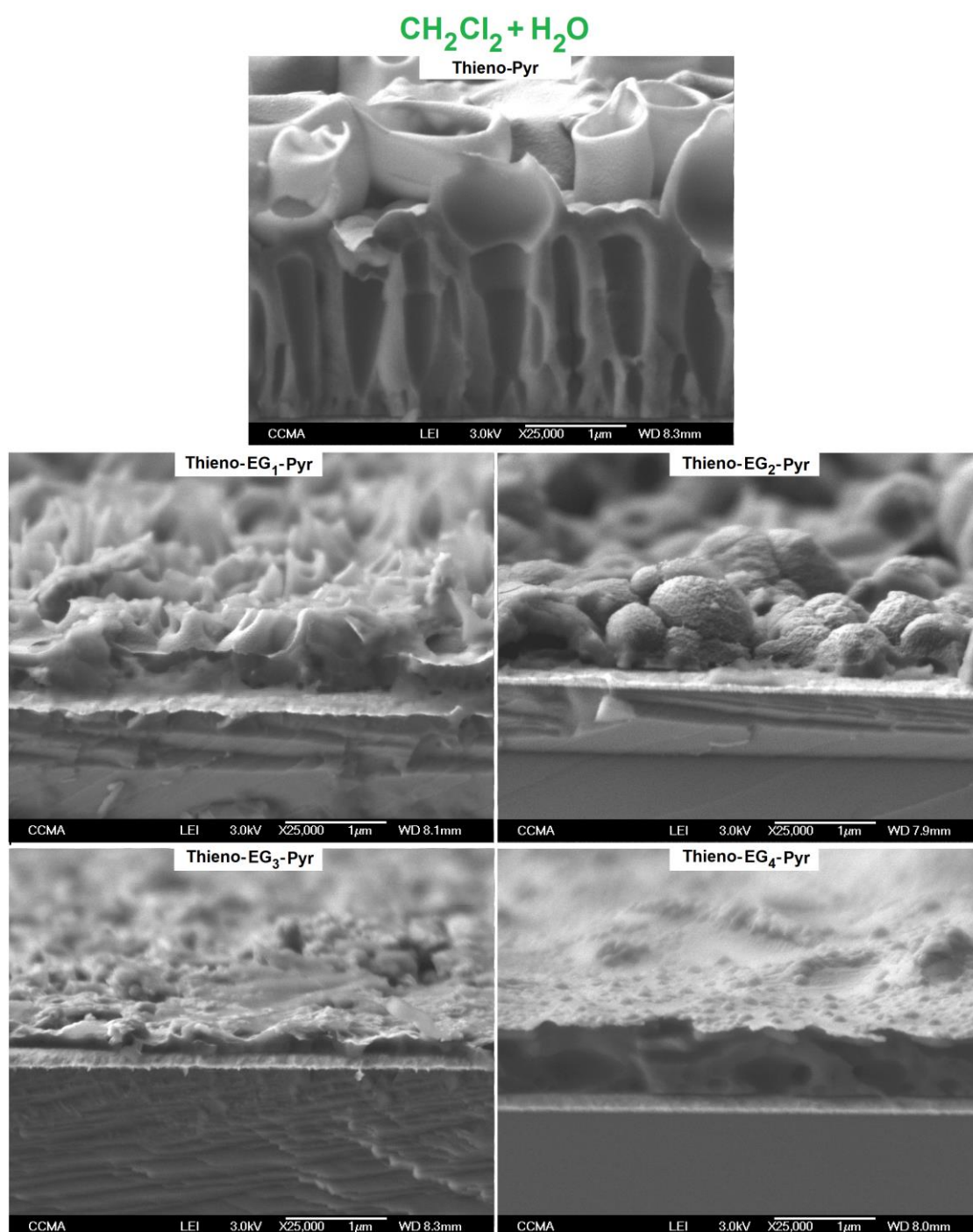


Fig. 8. Cross-sectional SEM images of polymer surfaces obtained from different monomers in $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$ by cyclic voltammetry. Number of scans 3.

3.3 Wetting properties of the resulting surfaces

Surface hydrophobicity of all surfaces after electrodeposition has also been investigated by measuring water contact angles (Table 1 and 2). In CH_2Cl_2 , the water contact angle is around 90° because these surfaces are not very structured even if the contact angle can increase or decrease as a function of the number of deposition scans (Table 1).

In $\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O}$, the surfaces with hollow spheres are relatively hydrophilic but the structures are not very porous (Table 2). As a consequence, water droplets enter in almost all the surface structures (Wenzel equation), as schematized in Figure 9 [47]. By contrast, the surfaces with nanotubes and especially nano-ribbons are highly hydrophobic because a certain amount of air can be trapped inside the surface structures (Cassie-Baxter equation) [48]. More precisely, here this is an intermediate state between the Wenzel and the Cassie-Baxter state [11,49,50]. Indeed, here the water adhesion is extremely high and water droplets do not move even if the substrate inclination is above 90° .

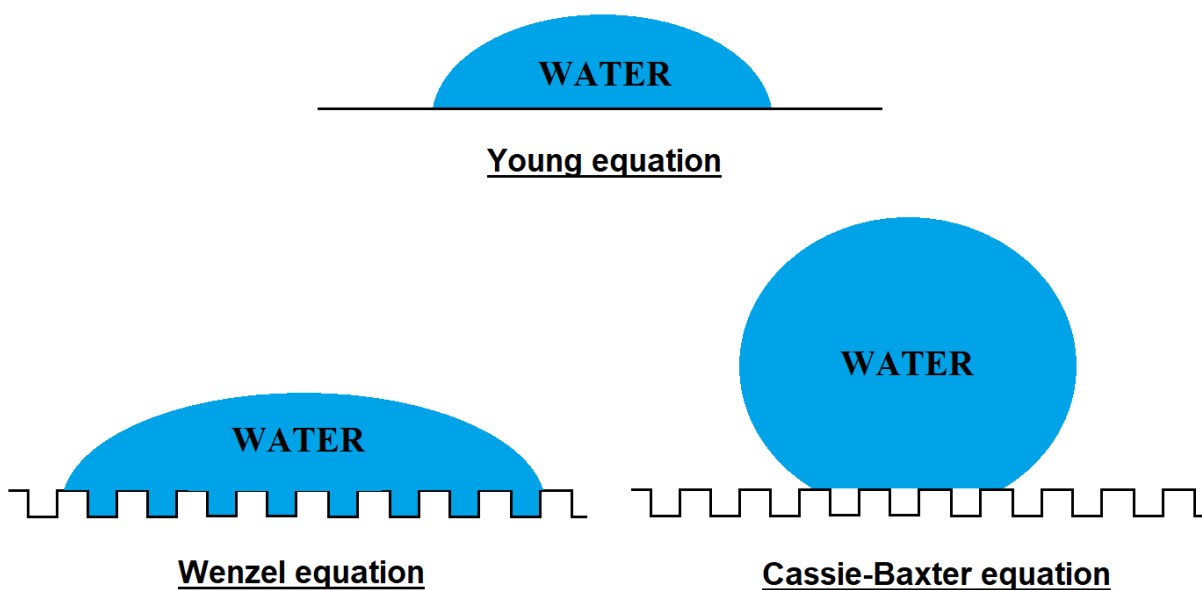


Fig. 9. Schematic representation of a water droplet on a smooth surface following the Young equation, on a rough surface following the Wenzel and the Cassie-Baxter equation, for an intrinsically hydrophilic material (Young angle $< 90^\circ$).

Table 1. Wettability data for the polymer films obtained by cyclic voltammetry in CH₂Cl₂.

Polymer	Number of deposition scan	θ_w [deg]
Thieno-Pyr	1	82.3 ± 7.8
	3	79.7 ± 8.7
	5	82.0 ± 10.1
Thieno-EG₁-Pyr	1	89.2 ± 2.4
	3	98.4 ± 5.1
	5	95.9 ± 4.6
Thieno-EG₂-Pyr	1	78.7 ± 1.9
	3	93.0 ± 6.4
	5	18.3 ± 6.4
Thieno-EG₃-Pyr	1	42.4 ± 3.8
	3	99.3 ± 4.4
	5	121.8 ± 6.4
Thieno-EG₄-Pyr	1	78.7 ± 4.1
	3	90.8 ± 4.8
	5	106.2 ± 5.0

Table 2. Wettability data for the polymer films obtained by cyclic voltammetry in CH₂Cl₂ + H₂O.

Polymer	Number of deposition scan	θ_w [deg]
Thieno-Pyr	1	96.2 ± 5.8
	3	80.2 ± 4.5
	5	104.2 ± 8.1
Thieno-EG₁-Pyr	1	82.1 ± 4.9
	3	115.1 ± 1.9
	5	131.0 ± 4.5
Thieno-EG₂-Pyr	1	43.4 ± 5.9
	3	35.0 ± 17.9
	5	36.9 ± 5.9
Thieno-EG₃-Pyr	1	64.2 ± 10.7
	3	55.9 ± 1.9
	5	75.4 ± 2.1
Thieno-EG₄-Pyr	1	58.9 ± 6.6
	3	60.3 ± 7.6
	5	73.2 ± 8.5

4 Conclusions

In this original work, using a model approach, we wanted to demonstrate how it is possible to tune the shape of porous nanostructures, created by templateless electropolymerization then gas bubbles are formed from H₂O onto the substrate. Here, thieno[3,4-*b*]thiophene and pyrene were chosen as the monomer and the substituent, respectively, for their strong capacity to form nanotubular structures, while PEG spacers of different length were used to give some flexibility. Here, for example, we observed that when the PEG spacer increases, the structures change from nanotubes (1D), to nanoribbons (2D) and after to hollow nanospheres (3D), affecting also the wetting properties. This work has huge potentials applications for example as in water harvesting systems, liquid transportation or oil/water separation membranes.

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References

- [1] Yu S, Guo Z G, Liu W M. Biomimetic transparent and superhydrophobic coatings: From nature and beyond nature. **Chemical Communications**, 2015, 51, 1775–1794.
- [2] Kwon O S, Park S J, Lee J S, Park E, Kim T, Park H W, You S A, Yoon H, Jang J. Multidimensional conducting polymer nanotubes for ultrasensitive chemical nerve agent sensing. **Nano Letters**, 2012, 12, 2797–2802.
- [3] Cheng Z J, Gao J, Jiang L. Tip geometry controls adhesive states of superhydrophobic surfaces. **Langmuir**, 2010, 26, 8233–8238.
- [4] Ge L, Sethi S, Ci L, Ajayan P M, Dhinojwala A. Carbon nanotube-based synthetic gecko tapes. **Proceedings of the National Academy of Sciences of the United States of America**, 2007, 104, 10792–10795.

-
- [5] Xu M, Du F, Ganguli S, Roy A, Dai L. Carbon nanotube dry adhesives with temperature-enhanced adhesion over a large temperature range. **Nature Communications**, 2016, 7, 13450.
- [6] Aslanidou D, Karapanagiotis I. Superhydrophobic, superoleophobic and antimicrobial coatings for the protection of silk textiles. **Coatings**, 2018, 8, 101.
- [7] Al-Azawi A, Latikka M, Jokinen V, Franssila S, Ras R H A. Friction and wetting transitions of magnetic droplets on micropillared superhydrophobic surfaces. **Small**, 2017, 13, 1700860.
- [8] Cheng Y, Yang H, Yang Y, Huang J Y, Wu K, Chen Z, Wang X Q, Lin C J, Yuekun Lai Y K. Progress in TiO₂ nanotube coatings for biomedical applications: A review. **Journal of Materials Chemistry B**, 2018, 6, 1862–1886.
- [9] Sun Z, Liao T, Liu K, Jiang L, Kim J H, Dou S X. Fly-eye inspired superhydrophobic anti-fogging inorganic nanostructures. **Small**, 2014, 10, 3001–3006.
- [10] Liu K S, Du J X, Wu J T, Jiang L. Superhydrophobic gecko feet with high adhesive forces towards water and their bio-inspired materials. **Nanoscale**, 2012, 4, 768–772.
- [11] Szczepanski C R, Darmanin T, Guittard F. Recent advances in the study and design of parahydrophobic surfaces: From natural examples to synthetic approaches. **Advances in Colloid and Interface Science**, 2017, 241, 37– 61.
- [12] Barthlott W, Mail M, Bhushan B, Koch K. Plant surfaces: Structures and functions for biomimetic innovations. **Nano-Micro Letters**, 2017, 9, 23.
- [13] Lin H A, Luo S C, Zhu B, Chen C, Yamashita Y, Yu H h. Molecular or nanoscale structures? The deciding factor of surface properties on functionalized poly(3,4-ethylenedioxythiophene) nanorod arrays. **Advanced Functional Materials**, 2013, 23, 3212–3219.
- [14] Lee L, Park S J. 2014 Porous anodic aluminum oxide: anodization and templated synthesis of functional nanostructures. **Chemical Reviews**, 2014, 114, 7487–7556.
- [15] Yuan J Y, Qu L T, Zhang D Q, Shi G Q. 2004 Linear arrangements of polypyrrole microcontainers. **Chemical Communications**, 2004, 0, 994–995.
- [16] Parakhonskiy B, Andreeva D, Möhwald H, Shchukin D G. Hollow polypyrrole containers with regulated uptake/release properties. **Langmuir**, 2009, 25, 4780–4786.
- [17] Szczepanski C R, M'Jid I, Darmanin T, Godeau G, Guittard F. A template-free approach to nanotube-decorated polymer surfaces using 3,4-phenylenedioxythiophene (PhEDOT) monomers. **Journal of Materials Chemistry A**, 2016, 4, 17308–17323.

- [18] Darmanin T, Guittard F. A one-step electrodeposition of homogeneous and vertically aligned nanotubes with parahydrophobic properties (high water adhesion). **Journal of Materials Chemistry A**, 4, 3197–3203.
- [19] Darmanin T, Godeau G, Guittard F, Klimarevav E L, Schewtschenko I, Perepichka I F. A templateless electropolymerization approach to porous hydrophobic nanostructures using PheDOT monomers with electron-withdrawing groups. **ChemNanoMat**, 2018, 4, 656–662.
- [20] Gbilimou A, Darmanin T, Godeau G, Guittard F. A templateless electropolymerization approach to nanorings using substituted 3,4-naphthalenedioxythiophene (NaPhDOT) monomers. **ChemNanoMat**, 2018, 4, 140–147.
- [21] Qu L T, Shi G Q, Chen F, Zhang J X. Electrochemical growth of polypyrrole microcontainers. **Macromolecules**, 2003, 36, 1063–1067.
- [22] Qu L T, Shi G Q, Yuan J Y, Han G Y, Chen F. Preparation of polypyrrole microstructures by direct electrochemical oxidation of pyrrole in an aqueous solution of camphorsulfonic acid. **Journal of Electroanalytical Chemistry**, 2004, 561, 149–156.
- [23] Kim J T, Seol S K, Je J H, Hwu Y, Margaritondo G. The microcontainer shape in electropolymerization on bubbles. **Applied Physics Letters**, 2009, 94, 034103.
- [24] Parakhonskiy B, Shchukin D. Polypyrrole microcontainers: Electrochemical synthesis and characterization. **Langmuir**, 2015, 31, 9214–9218.
- [25] Debiemme-Chouvy C. One-step electrochemical synthesis of a very thin overoxidized polypyrrole. **Electrochemical and Solid State Letters**, 2007, 10, E24–E26.
- [26] Debiemme-Chouvy C, Fakhry A, Pillier F. Electrosynthesis of polypyrrole nano/micro structures using an electrogenerated oriented polypyrrole nanowire array as framework. **Electrochimica Acta**, 2018, 268, 66–72.
- [27] Fakhry A, Cachet H, Debiemme-Chouvy C. Mechanism of formation of templateless electrogenerated polypyrrole nanostructures. **Electrochimica Acta**, 2015, 179, 297–303.
- [28] Fakhry A, Pillier F, Debiemme-Chouvy C. Templateless electrogeneration of polypyrrole nanostructures: impact of the anionic composition and pH of the monomer solution. **Journal of Materials Chemistry A**, 2014, 2, 9859–9865.
- [29] Debiemme-Chouvy C. Template-free one-step electrochemical formation of polypyrrole nanowire array. **Electrochemical Communications**, 2009, 11, 298–301.
- [30] Ramos Chagas G, Darmanin T, Godeau G, Guittard F. Nanocups and hollow microspheres formed by a one-step and templateless electropolymerization of thieno[3,4-b]thiophene derivatives as a function of the substituent. **Electrochimica Acta**, 2018, 269, 462–478.

- [31] Ramos Chagas G, Darmanin T, Guittard F. One-step and templateless electropolymerization process using thienothiophene derivatives to develop arrays of nanotubes and tree-like structures with high water adhesion. **ACS Applied Materials and Interfaces**, 2016, 8, 22732–22743.
- [32] Ramos Chagas G, Akbari R, Godeau G, Mohammadizadeh M, Guittard F, Darmanin T. Electrodeposited poly(thieno[3,2-b]thiophene) films for the templateless formation of porous structures by galvanostatic and pulse deposition. **ChemPlusChem**, 2017, 82, 1351–1358.
- [33] Bai S, Hu Q, Zeng Q, Wang M, Wang L. Variations in surface morphologies, properties, and electrochemical responses to nitro-analyte by controlled electropolymerization of thiophene derivatives. **ACS Applied Materials and Interfaces**, 2018, 10, 11319–11327.
- [34] Thiam E h Y, Dramé A, Sow S, Sene A, Szczepanski C R, Dieng S Y, Guittard F, Darmanin T. Designing nanoporous membranes through templateless electropolymerization of thieno[3,4-b]thiophene derivatives with high water content. **ACS Omega**, 2019, 4, 13080–13085.
- [35] Wynberg H, Zwanenburg D J. Thieno[3,4-b]thiophene. The third thiophthene. **Tetrahedron Letters**, 1967, 8, 761–764.
- [36] Wang P F, Fan H J, Zhu X Z. A 2-(trifluoromethyl)thieno[3,4-b]thiophene-based small-molecule electron acceptor for polymer solar cell application. **Dyes and Pigments**, 2018, 155, 179–185.
- [37] Wada Y, Asada Y, Ikai T, Maeda K, Kuwabara T, Takahashi K, Kanoh S. Synthesis of thieno[3,4-b]thiophene-based donor molecules with phenyl ester pendants for organic solar cells: Control of photovoltaic properties via single substituent replacement. **ChemistrySelect**, 2016, 1, 703–709.
- [38] Khodja M, El Kateb M, Beji M, Guittard F, Darmanin T. Tuning nanotubular structures by templateless electropolymerization with thieno[3,4-b]thiophene-based monomers with different substituents and water content. **Journal of Colloid and Interface Science**, 2020, 564, 19–27.
- [39] Sow S, Dramé A, Thiam E h Y, Orange F, Sene A, Dieng S Y, Guittard F, Darmanin T. Nanotubular structures via templateless electropolymerization using thieno[3,4-b]thiophene monomers with various substituents and polar linkers. **Progress in Organic Coatings**, 2020, 138, 105382.
- [40] Sane O, Diouf A, Morán Cruz G, Savina F, Méallet-Renault R, Amigoni S, Dieng S Y, Guittard F, Darmanin T. Coral-like nanostructures. **Materials Today**, 2019, 31, 119–120.
- [41] Bousrih I, El Kateb M, Szczepanski C R, Beji M, Guittard F, Darmanin T. A bioinspired strategy for designing well-ordered nanotubular structures by templateless electropolymerization of thieno[3,4-b]thiophene-based monomers. **Philosophical Transactions of the Royal Society A**, 2020, 378, 20190450.

- [42] Xue Y, O'Mara M L, Surawski P P T, Trau M, Mark A E. Effect of poly(ethylene glycol) (PEG) spacers on the conformational properties of small peptides: A molecular dynamics study. **Langmuir**, 2011, 27, 296–303.
- [43] González-Fernández E, Staderini M, Avlonitis N, Murray A F, Mount A R, Bradley M. Effect of spacer length on the performance of peptide-based electrochemical biosensors for protease detection. **Sensors and Actuators B: Chemical**, 2018, 255, 3040–3046.
- [44] Wang S Q, Guo X J, Wang L Y, Wang W C, Yu Y T. Effect of PEG spacer on cellulose adsorbent for the removal of low density lipoprotein cholesterol. **Artificial Cells, Blood Substitutes, and Biotechnology**, 2006, 34, 101–112.
- [45] Liese S, Netz R R. Influence of length and flexibility of spacers on the binding affinity of divalent ligands. **Beilstein Journal of Organic Chemistry**, 2015, 11, 804–816.
- [46] Zhao Y C, Stejskal J, Wang J X. Towards directional assembly of hierarchical structures: aniline oligomers as the model precursors. **Nanoscale**, 2013, 5, 2620–2626.
- [47] Wenzel R N. Resistance of solid surfaces to wetting by water. **Industrial and Engineering Chemistry**, 1936, 28, 988–994.
- [48] Cassie A B D, Baxter S. Wettability of porous surfaces. **Transactions of the Faraday Society**, 1944, 40, 546–551.
- [49] Marmur A. Hydro- hygro- oleo- omni-phobic? Terminology of wettability classification. **Soft Matter**, 2012, 8, 6867–6870.
- [50] Feng L, Zhang Y N, Xi J M, Zhu Y, Wang N, Xia F, Jiang L. Petal effect: A superhydrophobic state with high adhesive Force. **Langmuir**, 2008, 24, 4114–4119.