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Connector Ability To Design Superhydrophobic and Oleophobic Surfaces from Conducting Polymers

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In the aim of creating superoleophobic surfaces using monomers with short perfluorinated chains, to avoid drawbacks associated with PFOA, original semifluorinated (C_4F_9, C_6F_{13}) 3,4-ethylenedioxypyrrole derivatives were synthesized. These monomers were obtained using the faster synthetic method than previously described with some analogues, characterized and electrochemically polymerized on gold plates. The obtained surfaces exhibited superhydrophobic (contact angle with water of 157° and 158°, respectively) and oleophobic properties (contact angle with hexadecane: 88° and 108°, respectively). The comparison between these new monomers and already published analogue EDOP6 confirms the importance of the bipolaronic form of conductive polymer for obtaining surface nanoporosity and as a consequence improving surface oleophobicity. Thus, little change in the molecule design of the connector and the spacer of the monomer can have a significant influence on the surface oleophobicity.

Introduction

The control of surface wettability and in particular of surface hydrophobicity is of great significance in many application domains.[1−6] Since the discovery in nature of self-cleaning leaves, by Barthlott and Neinhuis,[7,8] extensive studies of such superhydrophobic surfaces[9−12] have revealed the importance of roughness and morphology as well as the chemical nature of the surface on the wettability based on Wenzel's[13] and Cassie−Baxter's theories.[14,15] The development of artificial approaches has been used to create rough surfaces, such as lithographic methods,[16,17] acid treatment,[18] layer-by-layer assemblies,[19−21] template-based extrusion methods,[22,23] and electrospinning.[24,25] Among these methods, the electrochemical surface modifications are inexpensive, fast, and easy to use,[26−31] and the electrochemical deposition of substituted organic conducting polymers can be used to generate structured films.[29−32] The introduction of a hydrophobic substituent in the chemical structure of the monomer allows to have the hydrophobic part necessary to the elaboration of liquid-repellent surfaces. This process which allows a fast deposition of superhydrophobic conductive polymer films is one-pot (no post-treatment) and using soft conditions as was previously reported by Tsujii et al.[29a,b] They reported the electrodeposition of poly(1-*n*-octadecylpyrrole) films, consisting of "needlelike microstructures" and showing super-water-repellent properties and excellent stability to organic solvents and temperature. Their coating using fluorinated alkylsilane increased the contact angle of salad oil from 0° to 136°.[29c] Very recently, the group of Tsujii also reported the water and oil-repellent properties of electrodeposited semifluorinated polypyrroles.[29d] Our group was the first to demonstrate the impact of the introduction of a fluorinated moiety in the monomers structure before the electrochemical polymerization step. The surfaces obtained exhibited incomparable superhydrophobic as well as oleophobic or superoleophobic behavior.[30−32] Furthermore, in the course of our

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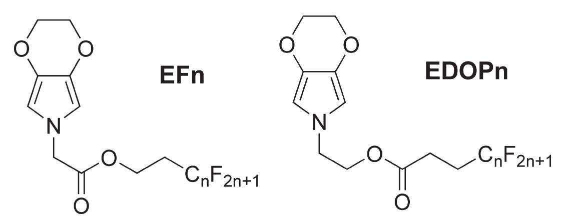
Scheme 1. Synthesized Monomers (EF*n*, with *n* = 4 and 6) and Previously Reported Monomers (EDOP*n*, with *n* = 6 and 8)



work, we demonstrated the possibility to tune surface morphology as well as its wettability by properly choosing the molecular design of the monomer.[32] Thus, electrodeposited polymer films with various morphology and oil-repellency properties were realized from semifluorinated thiophenes, 3,4-ethylenedioxythiophenes (EDOT), pyrrole, 3,4-ethylenedioxypyrroles (EDOP), and 3,4-propylenedioxypyrroles (ProDOP). Among all these series, 3,4-ethylenedioxypyrrole derivatives (Scheme 1, EDOP*n*) exhibited exceptional oil-repellent properties due to surface nanoporosity created during the electropolymerization.

Recently, new fluorinated polymers (C4 polymers) containing perfluorobutyl side chains were studied in the literature in order to avoid the problems associated with PFOA.[33] Our challenge is now to synthesize original monomers with short perfluorinated chains and with less time-consuming synthesis step with the intention of finding environmentally friendly and to give a nontoxic alternative. Another challenge is to determine the influence of other chemical elements present in the monomer structure (for example, the connector and the spacer between the heterocycle and the fluorinated chain) on the surface properties of the electrodeposited polymers. Hence, 3,4-ethylenedioxypyrrole derivatives (Scheme 1, EF*n*) were produced in this work containing respectively 4 and 6 perfluoromethylene units (EF4 and EF6) (Scheme 2), following a shorter synthetic method than that one used in previous studies (6 steps against 11). The monomers EF*n* differ from the monomers EDOP*n* by the spacer (ethyl → methyl) and the connector (oxy−carbonyl → carbonyl−oxy), which corresponds to the chemical function connecting the polymerizable cycle and the fluorinated chain.

After the electropolymerization step, the surface properties, especially surface wettability and morphology, were analyzed using static and dynamic contact angle measurements and scanning electron microscopy. All the results were compared to the previously studied monomers in order to evaluate the molecular design impact on the surface properties.

Experimental Section

Synthesis of the Monomers. All reagents were obtained from Sigma-Aldrich. The synthesis of EF*n* was performed using a six-step synthetic route (Scheme 2). The five steps to synthesize 2-(2,3-dihydro-1,4-dioxino[2,3-*c*]pyrrol-7(2*H*)-yl)acetic acid (**5**) were inspired by the synthetic way of Walczak et al.[34] with a difference in the third step where 1,3-dibromopropane was changed by 1,2-dibromoethane.

Synthesis of Triethyl Nitrilotriacetate. Nitrilotriacetic acid (50.00 g, 262 mmol), ethanol (absolute, 500 mL), and sulfuric acid (concentrated, 15 mL) were added to a round-bottom flask containing a stir bar and an argon atmosphere and outfitted with a reflux condenser. The mixture was refluxed for 3 h, cooled to room temperature, and concentrated in vacuum. The concentrate was immediately dissolved into 300 mL of dichloromethane and washed with small portions of saturated sodium bicarbonate until the evolution of gas ceased. The solvent was removed, and the resulting concentrated liquid was distilled by a Kugelrohr (bp 120 °C at 0.1 mbar) to yield 50.4 g (70%) of clear oil. Yield 70%; tr: 12.71 min. δ_H ($CDCl_3$): 4.11−4.21 (q, *J* = 7 Hz, 6H), 3.65 (s, 6H), 1.22−1.29 (t, *J* = 7 Hz, 9H). δ_C ($CDCl_3$): 170.79, 60.66, 55.11, 14.17. MS (70 eV): *m*/*z* (%): 275 (3) [M^+], 202 (100) [$C_9H_{16}O_4N^+$], 130 (76) [$C_6H_{12}O_2N^+$], 59 (100) [$C_3H_9N^+$]. IR (main vibration): υ = 1747 cm^{-1}.

Synthesis of 2. Ethanol (absolute, 402 mL) and sodium metal (17.14 g, 745 mmol) were added to a round-bottom flask containing a stir bar and an argon atmosphere and outfitted with a reflux condenser. 45.21 g of triethyl nitrilotriacetate (137.42 mmol) and 23.68 g of diethyl oxalate (137.42 mmol) were added after complete dissolution of the sodium. The mixture was refluxed overnight and became gelatinous. After cooling to room temperature, the mixture was poured into 965 mL of deionized water, chilled in an ice bath, and acidified with 160 mL of glacial acetic acid. The precipitate was isolated via vacuum filtration and washed with several portions of deionized water to yield 34.15 g (70%) of a white solid.

2: Diethyl 1-(2-Ethoxy-2-oxoethyl)3,4-dihydroxy-1*H*-pyrrole-2,5-dicarboxylate. Yield 70%; mp: 120−121 °C. δ_H ($CDCl_3$): 7.52 (s, 2H), 5.32 (s, 2H), 4.33−4.43 (q, *J* = 7 Hz, 4H), 4.15−4.25 (q, *J* = 7 Hz, 2H), 1.34−1.41 (t, *J* = 7 Hz, 6H), 1.23−1.30 (t, *J* = 7 Hz, 3H). δ_C ($CDCl_3$): 169.27, 162.11, 139.32, 110.83, 61.32, 47.61, 14.22. IR (main vibrations): υ = 3344, 1752, 1689, 1658 cm^{-1}.

Synthesis of 3. 2 (8 g, 24.3 mmol), 1,2-dibromoethane (4.62 g, 24.3 mmol), anhydrous potassium carbonate (8.39 g, 60.8 mmol), and 80 mL of DMF were added to a round-bottom flask containing a stir bar and an argon atmosphere and outfitted with a reflux condenser, The mixture was heated to 105 °C for 3 days. The initial yellow color was attributed to the formation of alcoolate dianion. The solution color changes until becoming black after 3 days. After being cooled to room temperature, the mixture was poured into deionized water (80 mL). The solids were collected via vacuum filtration and washed with several portions of deionized water. The solids were recrystallized from hot methanol to yield 4.57 g (53%) of a yellow solid, in agreement with the works of Dallacker et al.[35]

3: Diethyl 7-(2-Oxoethyl)-2,3,4,7-tetrahydro-1,4-dioxino-[2,3-*c*]pyrrole-6,8-dicarboxylate. Yield 53%; tr: 20.44 min; mp: 109−110 °C. δ_H ($CDCl_3$): 5.51 (s, 2H), 4.15−4.37 (m, 10H), 1.23−1.38 (m, 9H). δ_C ($CDCl_3$): 169.42, 160.46, 136.29, 110.82, 65.48, 61.22, 60.68, 47.31, 14.32, 14.14. MS (70 eV): *m*/*z* (%): 355 (6) [M^+], 282 (14) [$C_{13}H_{16}NO_6{}^+$], 196 (38) [$C_9H_{10}NO_4{}^+$]. IR (main vibrations): υ = 1753, 1713, 1658 cm^{-1}.

Synthesis of 4. 3 (3.40 g, 9.6 mmol), deionized water (8.71 mL), acetone (4.84 mL), and potassium hydroxide (2.69 g, 48 mmol) were added to a round-bottom flask. The mixture was bubbled with argon for 20 min and then refluxed for 3 h, resulting in a deep brown solution. The organic volatiles were removed in vacuum, and the resulting aqueous mixture was chilled in an ice bath. To the mixture was added concentrated sulfuric acid until pH of 5−6 and the precipitation of a white solid. This precipitate was filtered and washed with several portions of deionized water and dried. 1.46 g (56%) of the product **4** was obtained. The temperature of decarboxylation (≈170 °C) was determined by differential scanning calorimetry and thermogravimetry.

Synthesis of 5. 44 mL of heavy mineral oil was added to a round-bottom flask containing a stir bar and an argon atmosphere. The solution was heated to 80−100 °C, deoxygenated with three vacuum/argon purges, and then heated to 160 °C. Under argon, **4** (5.94 g, 21.9 mmol) was added in small portions. The resulting slurry was stirred for an additional 10 min and then

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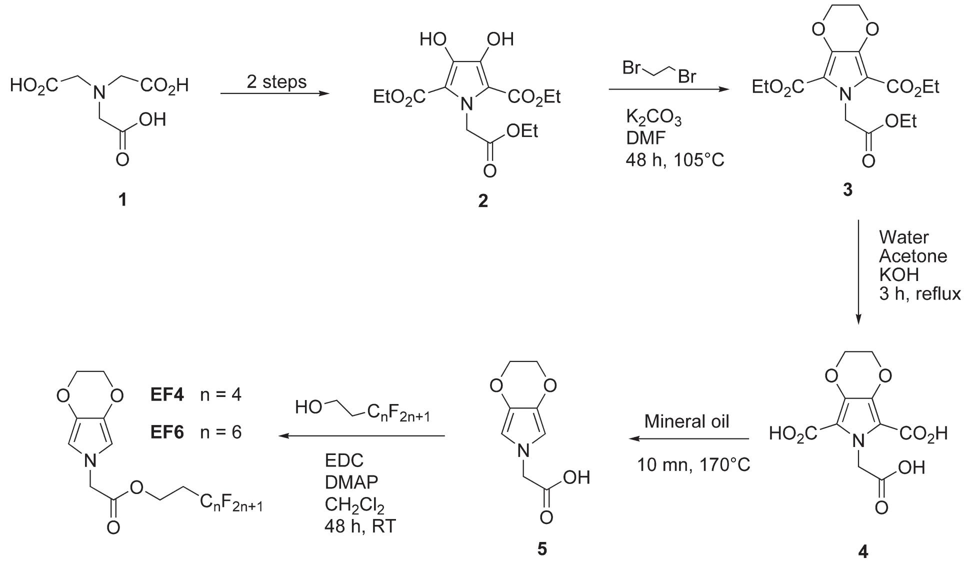
Scheme 2. Synthetic Route of Highly Fluorinated Monomers



cooled to room temperature. After 150 mL of hexane was added, the solution was filtrated. The remaining solids were dissolved in methanol (150 mL), the solution was filtrated, and the solvent was removed to give 521 mg (13%) of a black solid.

5: 2-(2,3-Dihydro-1,4-dioxino[2,3-*c*]pyrrol-7(2H)-yl)acetic Acid. δ_H (DMSO-d_6): 5.97 (s, 2H), 4.02 (s, 4H), 3.80 (s, 2H). δ_C (DMSO-d_6): 101.68, 79.10, 65.10, 54.73. MS (ESI): 182.1 [M − H].

Synthesis of EF4 and EF6. 4-(Dimethylamino)pyridine (DMAP) (10 mg) and *N*-(3-(dimethylamino)propyl)-*N*′-ethylcarbodiimide hydrochloride (EDC) (180.37 mg, 1.2 mmol) were added to a solution of **5** in anhydrous dichloromethane. The reaction was stirring for 30 mn at room temperature, and then 3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol (*F*-butyl length) or 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecanfluorooctan-1-ol (*F*-hexyl length) (1 mmol) was added. After 2 days, the solvent was removed and the product purified two times by column chromatography (silica gel; eluent for first column: ethyl acetate and for second column: dichloromethane then dichloromethane/ethyl acetate (5/5)). The retention time of the monomers is 13.347 mn for EF4 and 14.373 mn for EF6.

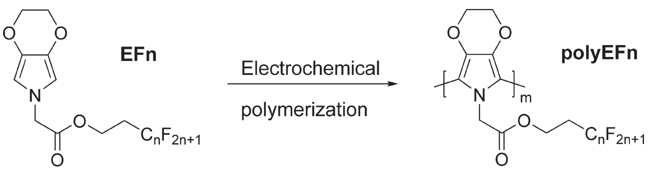
EF4: 3,3,4,4,5,5,6,6,6-Nonafluorohexyl 2-(2,3-dihydro-[1,4]-dioxino[2,3-*c*]pyrrol-6-yl)acetate. Yield 10%; tr: 13.37 min. δ_H ($CDCl_3$): 6.07 (s, 2H), 4.39−4.48 (m, 4H), 4.19 (s, 4H), 2.36−2.62 (m, 2H). δ_C ($CDCl_3$): 157.64, 121.10, 102.38, 65.72, 57.27, 51.17, 30.34. δ_F ($CDCl_3$): −81.44; −114.38; −124.92; −126.38. MS (70 eV): *m*/*z* (%): 429 (12) [M^+], 138 (100) [$C_7H_8NO_2^+$].

EF6: 3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl 2-(2,3-dihydro-[1,4]dioxino[2,3-*c*]pyrrol-6-yl)acetate . Yield 10%; tr: 14.23 mn. δ_H ($CDCl_3$): 6.07 (s, 2H), 4.31−4.55 (m, 4H), 4.18 (s, 4H), 2.37−2.61 (m, 2H). δ_C ($CDCl_3$): 157.64, 121.10, 102.38, 65.72, 57.27, 51.17, 30.40. δ_F ($CDCl_3$): −81.21; −115.22; −122.36; −123.34; −123.92; −126.54. MS (70 eV): *m*/*z* (%): 529 (8) [M^+], 138 (100) [$C_7H_8NO_2^+$].

Results and Discussion

Synthesis. The monomers in highly fluorinated series represented in Scheme 2 were synthesized in six steps. The two first steps (esterification of nitrilotriacetic acid and preparation of 3,4-dihydroxypyrrole triester **2** according to Hinsberg condensation) were realized in the same conditions as previously reported by Walzcak et al.[34] In the third step, 1,3-dibromopropane was replaced by 1,2-dibromoethane to obtain **3**. This compound was obtained by double nucleophilic substitution according to synthesis of Williamson, in anhydrous DMF and with potassium carbonate. During the reaction the mixture became yellow, which is typical color of the alcoholate dianion.[36] This product was purified by precipitation in water followed by filtration. The recrystallization in methanol led to **3** with a high degree of purity. The saponification of the three esters was realized in water/acetone cosolvent system. After acid work-up, **4** was obtained in good yield. The fourth step was the thermal decarboxylation of the two carboxylic groups in position 2 and 5 of **4** using mineral oil as heat transfer agent. The decarboxylation temperature was determined by differential scanning calorimetric analysis (DSC) and thermogravimetric analyses (TGA) under an inert atmosphere. The degradation onset was observed at 170 °C using a temperature ramp of 10 °C/min by DSC and 5 °C/min by TGA. After removing the mineral oil by washing with hexane and extraction with methanol, **5** was successfully obtained. Afterward, the highly fluorinated monomers, coded respectively EF4 and EF6, were obtained by an esterification reaction in dichloromethane, between **5** and a semifluorinated (*F*-hexyl or *F*-butyl) alcohol with *N*-(3-(dimethylamino)propyl)-*N*′-ethylcarbodiimide hydrochloride (EDC) and 4-(dimethylamino)pyridine (DMAP) as coupling agents. The products were obtained in 10% isolated yields.

Scheme 3. Representation of the Monomer Electropolymerization



Electrochemistry and Polymer Characterization. The electropolymerization of monomers EF*n* was studied using solutions of tetrabutylammonium hexafluorophosphate ($TBAPF_6$, 0.1 M) in anhydrous acetonitrile as represented in Scheme 3. Monomer oxidation potentials were determined by single potential scan using cyclic voltammetry between 0 and 2 V versus saturated calomel electrode (SCE) and using platinum disk as working electrode. The oxidation potential of EF4 and EF6 was about 0.97 V vs SCE, in agreement with the literature.[34,37,38] To show

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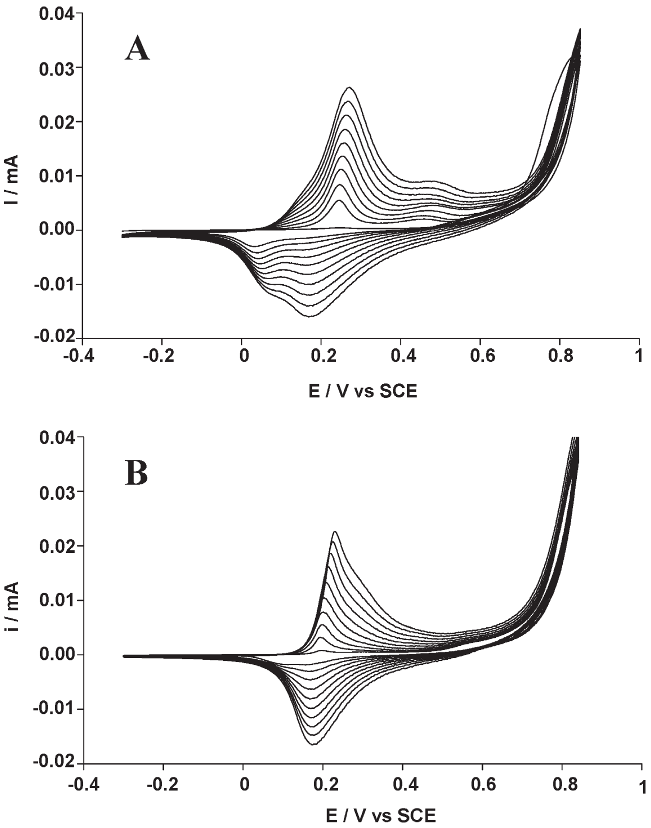

Figure 1. Cyclic voltammogram for (A) EF6 and (B) EF4 (0.01 M) on Pt electrode recorded in 0.1 M TBAPF$_6$/acetonitrile (10 scans).

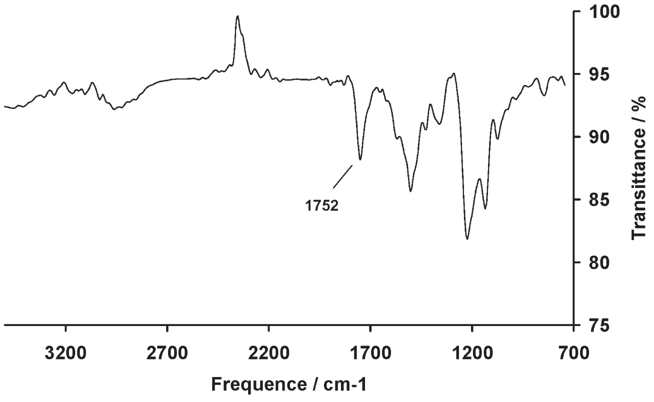

Figure 2. IR spectrum of polyEF4.

the monomer polymerizability and determine the polymer oxidation and reduction potentials, multiple potential scans between −0.3 and 0.85 V were performed as illustrated in Figure 1. These cyclic voltammograms exhibit homogeneous growth of the polymer films with a half-wave potential $E_{1/2}$ of about 0.20 V for EF4 and 0.22 V for EF6. A second peak was also observed, especially in the case of EF6, at ~0.49 V during the doping and 0.05 V during the dedoping. This peak was previously attributed to the formation of bipolaronic forms, which may have an influence on the surface morphology.[31]

For surface analyses, polymer films were electrodeposited on gold plate by chronoamperometry using constant potential of 0.85 V and a deposition charge of 225 mC/cm^2. The polymer films, electrodeposited on gold surfaces, were characterized by infrared using imaging infrared in reflection mode (Figure 2). The presence of the polymers is confirmed by the ester band at 1752 cm^{-1} and the C−F band at 1136 cm^{-1}.

Wettability. First, the surface wettability was measured by static contact angle measurements with three liquids of different superficial tension: water ($\gamma = 72.8$ mN/m) to determine surface hydrophobicity, diiodomethane ($\gamma = 50.0$ mN/m), and hexadecane ($\gamma = 27.6$ mN/m) to explore surface oleophobicity. The drop volume used for the measurements is 2 μL. Table 1 gathers the mean static contact angles. The electrodeposited films exhibited superhydrophobic properties with static water contact angle of about 160° for the two polymer films. These films also exhibited oil-repellency properties with static hexadecane contact angles of about 108° for polyEF6 and 88° for polyEF4. These monomers did not allow reaching superoleophobicity as compared to previous works from homologue series (EDOP*n*, Scheme 1).[32] This very high difference in surface oleophobicity between polyEF6 and polyEDOP6 cannot be explained only by the surface chemistry. Dynamic contact angles were measured (hysteresis) by the tilted-drop method[39] using 6 μL droplets. Different behaviors have been observed on these two films. Indeed, water and diiodomethane droplets could roll off polyEF6 films with small sliding angles (7° for water and 10° for diiodomethane), whereas hexadecane remain stuck on the films. The hysteresis, determined just before the liquid droplets roll off the surface, is 9° for water ($\theta_a = 160°$ and $\theta_r = 151°$) and 20° for diiodomethane ($\theta_a = 149°$ and $\theta_r = 129°$). On the contrary, in the case of polyEF4, water, diiodomethane, and hexadecane droplets remained stuck on the surface even with sliding angle of 90°. To understand theses results, the surface morphology has been examined by SEM.

Morphology and Roughness. SEM images obtained are showed in Figure 3A for polyEF4 and Figure 3B for polyEF6. The two polymer films were microstructured with spherical and cauliflower microstructures, already observed in electrodeposited fluorinated polythiophene or poly(3,4-propylenedioxypyrrole) films.[30c,32a] The films obtained from EF6 were rougher than that obtained from EF4, as shown also using optical profilometry ($R_a \approx 724$ nm and $R_q \approx 2520$ nm for polyEF6 whereas $R_a \approx 514$ nm and $R_q \approx 1440$ nm for polyEF4). The lengths of the microstructures are also very different and seem equal to 2−5 μm and 100−500 nm for polyEF4 and polyEF6, respectively. The differences in the lengths of the microstructures, the roughness, and the fluorinated chain length allow to understand the differences observed in the wettability of these two films. In the case of polyEF6, water and diiodomethane cannot penetrate in the spaces between the microstructures because the volume of the spaces is very small, and as a consequence the adhesion of these liquids on the surface is extremely low. However, hexadecane can penetrate because of its extremely low surface tension. These surfaces are very different of polyEDOP6 films, which are micro- and nanostructured as shown in Figure 3C. This double surface structuration highly decreases the adhesion of liquids, as already reported in a large number of articles,[40−44] and even repels liquids of very low surface tension such as hexadecane.

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Table 1. Static and Dynamic Contact Angle Data ($Q_s \approx 225$ mC/cm^2)

	static contact angles [deg]			dynamic contact angles for water [deg]	
monomer	water	diiodomethane	hexadecane	H	α
EF4	157	145	88		sticking behavior
EF6	158	152	108	9	7
EDOP6 [ref 31]	160	150	141	2	3

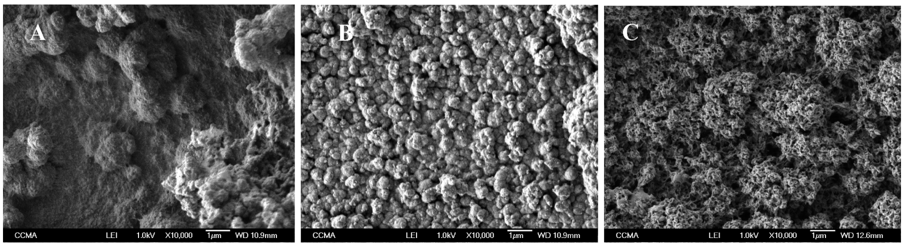

Figure 3. SEM images of (A) polyEF4, (B) polyEF6, and (C) polyEDOP6. The scale bar represents 1 μm.

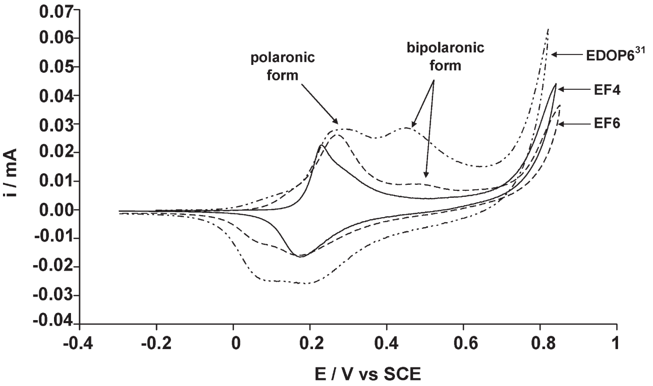

Figure 4. Cyclic voltammograms of EF4, EF6, and EDOP6 (0.01 M) on Pt electrode recorded in 0.1 M TBAPF$_6$/acetonitrile.

Previously, it has been demonstrated by studying the electropolymerization of the previously reported EDOP and ProDOP derivatives, which differ by one methylene unit on the 3,4-alkylenedioxy bridge, that surface nanoporosity was only observed in polyEDOP derivatives.[32a] The surface nanoporosity may be due to the presence of bipolaronic forms (second peak in the cyclic voltammetry curves), which induce a supplementary anion diffusion inside the polymer to neutralize it and change the surface morphology of the resulting polymer films. Although a second peak was present in the cyclic voltammetry curves of EF6, its intensity, in comparison with the first one, was much lower than in the case of the previously synthesized EDOP derivatives (Figure 4). As illustrated in Scheme 1, EF6 differs from EDOP6 by the spacer and the connector between the EDOP heterocycle and the fluorinated chain. Thus, the replacement of the oxy−carbonyl group by a carbonyl−oxy group can also impede π-stacking interactions and hence the interchain dimerization of polarons. Indeed, to have π-stacking interactions, the polymer should be as planar as possible, and this planarity can be modified by the spacer or connector. Thus, if the length of the 3,4-alkylenedioxy bridge can have a dramatic influence on the surface morphology,[32] it is also the case of the spacer and the connector between the heterocycle and the fluorinated chain. These differences in the cyclic voltammetry curves explain the high differences observed in the surface morphology of polyEF6 and polyEDOP6 films and as a consequence in their wettability. This work shows the modification of one element of the chemical structure of the monomer; even the spacer or the connector can have a high influence on the surface morphology and as a consequence on the surface wettability (especially oleophobicity).

Conclusions

In this study, we have reported the synthesis and characterization of original fluorinated (*F*-hexyl and *F*-butyl) EDOP derivatives, named EF4 and EF6, differing from the already known EDOP6[31] by the spacer and the connector. The electropolymerization of these monomers was studied by electrochemical methods, and the surface properties of the corresponding conductive polymer films were evaluated in terms of static and dynamic contact angle measurements and surface morphologies. The polymers films exhibit superhydrophobic and oleophobic properties. The films are microstructured but do not contain nanoporosity such as polyEDOP6. We established though the possible use of a *F*-butyl EDOP derivative to reach superhydrophobic as well as oleophobic surface properties. And as it has been demonstrated that compounds containing perfluorinated chains of four carbon atoms do not bioaccumulate,[45] this work represents a new insight into the construction of supersurfaces avoiding problems associated with long fluorinated tails. This work confirms the importance of surface nanoporosity for obtaining highly oleophobic properties. The presence of surface nanoporosity seems to be related to the monomer structure and the shape of the electrochemical curves. The molecular design is, therefore, a choice tool to modulate surface morphology and wettability.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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