

Molecular Design of Conductive Polymers To Modulate Superoleophobic Properties

Thierry Darmanin and Frédéric Guittard*

Université de Nice Sophia-Antipolis, Laboratoire de Chimie des Matériaux Organiques et Métalliques, EA 3155, Institut de Chimie de Nice, Equipe Chimie Organique aux Interfaces, Parc Valrose, 06108 Nice Cedex 2, France

Received February 23, 2009; E-mail: Frederic.GUITTARD@unice.fr

Ⓜ This paper contains enhanced objects available on the Internet at <http://pubs.acs.org/jacs>.

Abstract: Natural surfaces can be superhydrophobic, but on the other hand, superoleophobic properties are extremely rare. We demonstrate that modification of the 3,4-alkylenedioxy bridge length in pyrrole-derivative monomers can have a dramatic influence on the superoleophobic properties of electrodeposited conductive polymers. Here we report the synthesis and characterization of novel fluorinated 3,4-ethylenedioxy pyrrole (EDOP) and 3,4-propylenedioxy pyrrole (ProDOP) monomers and their corresponding electrodeposited polymers. The polymer surfaces were characterized by static and dynamic contact angle measurements, scanning electron microscopy, and cyclic voltammetry. Surprisingly, the antiwetting properties do not depend of the fluorocarbon chain length (*F*-octyl to *F*-hexyl) but are in fact governed by the nature of the electrochemically deposited core. Indeed, superhydrophobic and superoleophobic surfaces with extremely low hysteresis and sliding angles for water droplets were obtained by electrochemical polymerization of highly fluorinated EDOP, whereas highly fluorinated ProDOP gave only superhydrophobic surfaces with a sticky behavior. The difference in wettability is attributed to surface nanoporosity resulting from the doping process.

Introduction

Obtaining superphobic surfaces for dewetting of liquids such as water and oil is of both theoretical and practical interest,^{1–4} as has been reported in recent reviews.^{5–9} Although superhydrophobic properties are found naturally or with biomimetic approaches, there are only a few reports of superoleophobicity.^{10–21} As a general concept, because they possess oleophobic properties, fluorinated surface layers offer the potential for tuning between superhydrophobicity and superoleophobicity. In this work, we have demonstrated that highly fluorinated electrodeposited conductive polymers can be generated from a one-pot surface method. Lengthening of the 3,4-alkylenedioxy bridge present in the precursor monomers results in a dramatic on/off switch controlling the superoleophobic properties of these fluorinated surfaces.

The wettability of a solid surface is governed by the surface free energy, which may be calculated using Young's equation. Flat fluorinated materials exhibit the lowest known surface free energies, and on such substrates, the contact angle (CA, or θ) of a water droplet can rarely exceed 120°. ^{22–24} However, on some natural plant^{25–28} and insect^{29–33} surfaces, the CA for

- (1) Autumn, K.; Liang, Y. A.; Hsieh, S. T.; Zesch, W.; Chan, W. P.; Kenny, T. W.; Fearing, R.; Full, R. J. *Nature* **2000**, *405*, 681–685.
- (2) Ball, P. *Nature* **1999**, *400*, 507–508.
- (3) Feng, X.; Jiang, L. *Adv. Mater.* **2006**, *18*, 3063–3078.
- (4) Pugno, N. M. *J. Phys.: Condens. Matter* **2007**, *19*, 395001.
- (5) Zhang, X.; Shi, F.; Niu, J.; Jiang, Y.; Wang, Z. *J. Mater. Chem.* **2008**, *18*, 621–633.
- (6) Li, X.-M.; Reinhoudt, D.; Crego-Calama, M. *Chem. Soc. Rev.* **2007**, *36*, 1350–1368.
- (7) Roach, P.; Shirtcliffe, N. J.; Newton, M. I. *Soft Matter* **2008**, *4*, 224–240.
- (8) Ma, M.; Hill, R. M. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 193–202.
- (9) Xia, F.; Jiang, L. *Adv. Mater.* **2008**, *20*, 2842–2858.
- (10) Shibuichi, S.; Yamamoto, T.; Onda, T.; Tsujii, K. *J. Colloid Interface Sci.* **1998**, *208*, 287–294.
- (11) Tsujii, K.; Yamamoto, T.; Onda, T.; Shibuichi, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1011–1012.

- (12) Yan, H.; Kurogi, K.; Tsujii, K. *Colloids Surf., A* **2007**, *292*, 27–31.
- (13) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E. *Science* **2008**, *318*, 1618–1622.
- (14) Tian, Y.; Liu, H.; Deng, Z. *Chem. Mater.* **2006**, *18*, 5820–5822.
- (15) Xi, J.; Feng, L.; Jiang, L. *Appl. Phys. Lett.* **2008**, *92*, 053102.
- (16) Xie, Q.; Xu, J.; Feng, L.; Jiang, L.; Tang, W.; Luo, X.; Han, C. C. *Adv. Mater.* **2004**, *16*, 302–305.
- (17) Zimmermann, J.; Rabe, M.; Artus, G. R. J.; Seeger, S. *Soft Matter* **2008**, *4*, 450–452.
- (18) Cao, L.; Price, T. P.; Weiss, M.; Gao, D. *Langmuir* **2008**, *24*, 1640–1643.
- (19) Wang, C.-F.; Chiou, F.-H.; Ko, F.-H.; Chou, C.-T.; Lin, H.-C.; Huang, C.-F.; Chang, F.-C. *Macromol. Rapid Commun.* **2006**, *27*, 333–337.
- (20) Chen, W.; Fadeev, A. Y.; Hsieh, M. C.; Öner, D.; Youngblood, J.; McCarthy, T. J. *Langmuir* **1999**, *15*, 3395–3399.
- (21) Li, H.; Wang, X.; Song, Y.; Liu, Y.; Li, Q.; Jiang, L.; Zhu, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1743–1746.
- (22) Bertolucci, M.; Galli, G.; Chiellini, E. *Macromolecules* **2004**, *37*, 3666–3672.
- (23) Honda, K.; Morita, M.; Otsuka, H.; Takahara, A. *Macromolecules* **2005**, *38*, 5699–5705.
- (24) Katano, Y.; Tomono, H.; Nakajima, T. *Macromolecules* **1994**, *27*, 2342–2344.
- (25) Neinhuis, C.; Barthlott, W. *Ann. Bot.* **1997**, *79*, 667–677.
- (26) Barthlott, W.; Neinhuis, C. *Planta* **1997**, *202*, 1–8.
- (27) Gu, Z.-Z.; Wei, H.-M.; Zhang, R.-Q.; Han, G.-Z.; Pan, C.; Zhang, H.; Tian, X.-J.; Chen, Z.-M. *Appl. Phys. Lett.* **2005**, *86*, 201915.
- (28) Shirtcliffe, N. J.; Pyatt, F. B.; Newton, M. I.; McHale, G. *J. Plant Physiol.* **2006**, *163*, 1193–1197.

water can be greater than 150° . Extensive studies of such superhydrophobic surfaces have revealed the importance of surface roughness and morphology on wettability, and this work has guided the development of artificial superhydrophobic surfaces. Indeed, two models, based on the theories of Wenzel³⁴ and Cassie and Baxter,^{35,36} are often used to predict CAs on rough surfaces. In Wenzel theory, the water droplet follows the surface roughness, and a roughness parameter is introduced to account for superhydrophobic behavior; according to this theory, the CA and the hysteresis ($H = CA_{\text{advancing}} - CA_{\text{receding}}$) increase with roughness. On the other hand, Cassie–Baxter theory assumes that the water droplet does not penetrate inside the rough surface region but instead rests on top of the asperities. Thus, solid and air fractions are introduced to predict the superhydrophobicity. Because of the increase in air fraction, any change from the Wenzel to the Cassie–Baxter state causes a decrease in H .^{37,38} Thus, the Wenzel and Cassie–Baxter states are two stable states that can be applied as appropriate, depending on the surface morphology. For a particular surface topography, the droplet can also be in a metastable state, which explains, for example, the possibility of obtaining superhydrophobic surfaces from hydrophilic materials.³⁹ However, the validity of these theories is at present a subject of controversy.^{40,41} On the basis of the work of Pease,⁴² Bartell,⁴³ and Extrand,⁴⁴ Gao and McCarthy⁴⁰ demonstrated that the wettability depends on the solid–liquid interactions at the three-phase contact line and not on the interfacial area between the droplet and the surface. Thus, very large advancing/receding CAs, even $180^\circ/180^\circ$,^{40,45–47} can be obtained by forcing the three-phase contact line to adopt a very discontinuous form, which is not possible using the Cassie–Baxter theory.

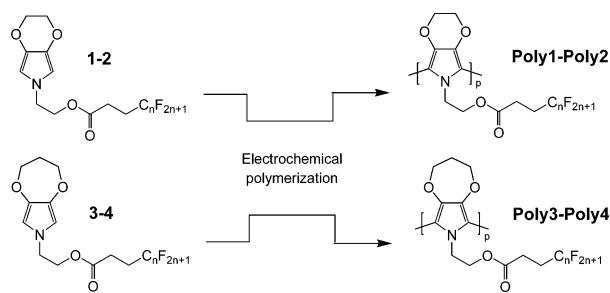
Numerous approaches that have been used to create rough surfaces, such as lithographic methods,^{47–50} template-based extrusion methods,^{51–54} layer-by-layer assembly,^{55–58} and

electrospinning,^{59–62} have been successfully applied to generate superhydrophobic surfaces. However, there are only a very few reports of both superhydrophobic and superoleophobic surfaces or of superlyophobic surfaces.^{10–21} This condition is not easy to achieve, since supporting droplets liquids with low surface tension (γ_L), such as oils, requires the surface tension of the solid (γ_S) to be extremely low ($\gamma_S < \gamma_L/4$).^{10,11} Moreover, Tuteja et al.¹³ demonstrated by fabrication of re-entrant surface curvature that although it is necessary to simultaneously have a hydrophobic substrate and surface roughness, other requirements must be met to generate truly superoleophobic surfaces. In particular, in the case of low-surface-energy liquids, such as oils, an additional force is needed prevent surface wetting. However, the fabrication of these re-entrant surface curvatures is expensive and laborious, necessitating numerous post-treatment steps.

In contrast, electrochemical methods are inexpensive, fast, and easy to use.^{14,15,63–68} Electrochemical deposition of substituted organic conducting polymers can be used to generate superhydrophobic surfaces very quickly and in one straightforward step. In this method, the resulting polymer is intrinsically hydrophobic because hydrophobic chains are pregrafted to the monomers. Furthermore, according to the electrochemical deposition conditions, the obtained films are sufficiently structured to exhibit superhydrophobic properties. Tsujii and co-workers^{63,64} formed superhydrophobic aligned needlelike poly(alkylpyrrole) structures that showed excellent stability with respect to both temperature and organic solvents. Other thiophene-based surfaces derived from pyrrole, poly(3,4-ethylenedioxythiophenes), displayed superhydrophobic properties.^{65–68} Unfortunately, these surfaces were not superoleophobic, but it was noted that the choice of polymerizable moiety in the conducting polymer seems to play an important role in the final surface morphology. Recently, the development of new synthetic approaches to poly(3,4-alkylenedioxy-pyrrole) derivatives has opened up the door to applications of this family of conjugated polymers. These new polypyrroles are commercially viable because of their extremely low oxidation potentials, very high stabilities in the doped state, and favorable electrochromic properties.^{69–77}

(29) Zheng, Y.; Gao, X.; Jiang, L. *Soft Matter* **2007**, *3*, 178–182.
 (30) Lee, W.; Jin, M.-K.; Yoo, W.-C.; Lee, J.-K. *Langmuir* **2004**, *20*, 7665–7669.
 (31) Wagner, T.; Neinhuis, C.; Barthlott, W. *Acta Zool.* **1996**, *77*, 213–225.
 (32) Gao, X.; Jiang, L. *Nature* **2004**, *432*, 36–36.
 (33) Parker, A. R.; Lawrence, C. R. *Nature* **2001**, *414*, 33–34.
 (34) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988–994.
 (35) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546–551.
 (36) Baxter, S.; Cassie, A. B. D. *J. Text. Inst.* **1945**, *36*, T67–T90.
 (37) Hyväluoma, J.; Timonen, J. *Europhys. Lett.* **2008**, *83*, 64002.
 (38) Yeh, K.-Y.; Chen, L.-J.; Chang, J.-Y. *Langmuir* **2008**, *24*, 245–251.
 (39) Cao, L.; Hu, H.-H.; Gao, D. *Langmuir* **2007**, *23*, 4310–4314.
 (40) Gao, L.; McCarthy, T. J. *Langmuir* **2007**, *23*, 3762–3765.
 (41) Panchagnula, M. V.; Vedantam, S. *Langmuir* **2007**, *23*, 13242.
 (42) Pease, D. C. *J. Phys. Chem.* **1945**, *49*, 107–110.
 (43) Bartell, F. E.; Shepard, J. W. *J. Phys. Chem.* **1953**, *57*, 455–458.
 (44) Extrand, C. W. *Langmuir* **2003**, *19*, 3793–3796.
 (45) Gao, L.; McCarthy, T. J. *Langmuir* **2007**, *23*, 9125–9127.
 (46) Gao, L.; McCarthy, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9052–9053.
 (47) Öner, D.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7777–7782.
 (48) Jopp, J.; Grüll, H.; Yerushalmi-Rozen, R. *Langmuir* **2004**, *20*, 10015–10019.
 (49) Gao, X.; Yan, X.; Yao, X.; Xu, L.; Zhang, K.; Zhang, J.; Yang, B.; Jiang, L. *Adv. Mater.* **2007**, *19*, 2213–2217.
 (50) Pacifico, J.; Endo, K.; Morgan, S.; Mulvaney, P. *Langmuir* **2006**, *22*, 11072–11076.
 (51) Feng, L.; Li, S.; Li, H.; Zhai, J.; Song, Y.; Jiang, L.; Zhu, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 1221–1223.
 (52) Sun, M.; Luo, C.; Xu, L.; Ji, H.; Ouyang, Q.; Yu, D.; Chen, Y. *Langmuir* **2005**, *21*, 8978–8981.
 (53) Yuan, Z.; Chen, H.; Tang, J.; Gong, H.; Liu, Y.; Wang, Z.; Shi, P.; Zhang, J.; Chen, X. *J. Phys. D: Appl. Phys.* **2007**, *40*, 3485–3489.
 (54) Che, G.; Lakshmi, B. B.; Martin, C. R.; Fisher, E. R.; Ruoff, R. *Chem. Mater.* **1998**, *10*, 260–267.

(55) Zhai, L.; Cebeci, F. C.; Cohen, R. E.; Rubner, M. F. *Nano Lett.* **2004**, *4*, 1349–1353.
 (56) Zhao, N.; Shi, F.; Wang, Z.; Zhang, X. *Langmuir* **2005**, *21*, 4713–4716.
 (57) Shi, F.; Wang, Z.; Zhang, X. *Adv. Mater.* **2005**, *17*, 1005–1009.
 (58) Zhang, X.; Shi, F.; Yu, X.; Liu, H.; Fu, Y.; Wang, Z.; Jiang, L.; Li, X. *J. Am. Chem. Soc.* **2004**, *126*, 3064–3065.
 (59) Jiang, L.; Zhao, Y.; Zhai, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 4338–4341.
 (60) Ma, M.; Mao, Y.; Gupta, M.; Gleason, K. K.; Rutledge, G. C. *Macromolecules* **2005**, *38*, 9742–9748.
 (61) Lim, J.-M.; Yi, G.-R.; Moon, J. H.; Heo, C.-J.; Yang, S.-M. *Langmuir* **2007**, *23*, 7981–7989.
 (62) Singh, A.; Steely, L.; Allcock, H. R. *Langmuir* **2005**, *21*, 11604–11607.
 (63) Yan, H.; Kurogi, K.; Mayama, H.; Tsujii, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 3453–3456.
 (64) Kurogi, K.; Yan, H.; Mayama, H.; Tsujii, K. *J. Colloid Interface Sci.* **2007**, *312*, 156–163.
 (65) Nicolas, M.; Guittard, F.; G ribaldi, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2251–2254.
 (66) Nicolas, M.; Guittard, F.; G ribaldi, S. *Langmuir* **2006**, *22*, 3081–3088.
 (67) Darmanin, T.; Nicolas, M.; Guittard, F. *Langmuir* **2008**, *24*, 9739–9746.
 (68) Darmanin, T.; Nicolas, M.; Guittard, F. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4322–4326.
 (69) Walczak, R. M.; Reynolds, J. R. *Adv. Mater.* **2006**, *18*, 1121–1131.

Scheme 1. Synthesized Monomers and Polymers ($n = 6$ and 8)

n	oxy bridge	code	
		monomer	polymer
6	ethylene	1	Poly1
8	ethylene	2	Poly2
6	propylene	3	Poly3
8	propylene	4	Poly4

The aim of this work was to synthesize and characterize highly fluorinated (*F*-hexyl and *F*-octyl) monomers derived from 3,4-ethylenedioxyppyrole (EDOP) and 3,4-propylenedioxyppyrole (ProDOP). These compounds EDOP and ProDOP differ by the presence of one additional methylene unit in the alkylendioxy bridge of ProDOP; Scheme 1 shows the molecular structures. The surface properties of the corresponding electrodeposited conductive polymers were evaluated and compared in terms of static and dynamic CA measurements and surface morphologies as determined by scanning electron microscopy (SEM).

Results and Discussion

Monomer Synthesis. Four original fluorinated EDOP and ProDOP derivatives containing either perfluorohexyl or perfluorooctyl chains were synthesized. The perfluoroalkyl chain, which has an electron-withdrawing effect, is sufficiently distant from the heterocycle to not affect the polymerization. To easily introduce perfluorinated chains into the monomers, it was necessary to obtain EDOP and ProDOP derivative precursors containing a hydroxyl group (Scheme 2, molecules 5–6).

First, EDOP and ProDOP were synthesized from iminodiacetic acid, following the route developed by Merz et al.;⁷⁸ the steps involved esterification of iminodiacetic acid, nitrogen protection, formation of the pyrrole heterocycle, formation of the EDOP or ProDOP heterocycle, nitrogen deprotection, hydrolysis, and decarboxylation. Then from EDOP and ProDOP, the formation of the key molecules 5 and 6 containing a hydroxyl group was performed by a modification of the

procedure developed by Zong and Reynolds,⁷⁹ using 2-*tert*-butyldimethylsilyloxyethyl tosylate and sodium hydride in THF, followed by silyl group deprotection with tetrabutylammonium fluoride (Bu_4NF) in THF. These molecules were obtained in good yields of 65–70%. Afterward, the four fluorinated monomers 1–4 were synthesized at room temperature in CH_2Cl_2 using *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC) and 4-dimethylaminopyridine (DMAP) as coupling agents. The overall yields for the syntheses of 1–4 from EDOP and ProDOP were ~40–55%.

Electrochemical Polymerization. The electrochemical polymerization was performed in anhydrous acetonitrile solutions containing 0.01 M monomer and 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6). The electrochemical polymerization was studied by cyclic voltammetry using a platinum disk working electrode and a saturated calomel electrode (SCE) as a reference. The oxidation potential of fluorinated EDOP ($E_{\text{peak,m}}^{\text{ox}} \approx 0.94$ V) was slightly lower than that for fluorinated ProDOP ($E_{\text{peak,m}}^{\text{ox}} \approx 0.98$ V). These monomer oxidation potentials are in agreement with literature values for nonsubstituted EDOP and ProDOP monomers.^{69,71} The electron-withdrawing effect of the fluorinated chain had no significant impact on the monomer oxidation potential because the fluorinated chain is sufficiently distant from the polymerizable heterocycle.

Consecutive cyclic voltammetry until a potential close to $E_{\text{peak,m}}^{\text{ox}}$ (denoted $E_{\text{p,opt}}^{\text{ox}}$) was achieved confirmed the polymerization and defined the redox potentials of the polymers. Cyclic voltammograms of the polymers showed reversible and stable redox processes, with two oxidation and reduction peaks for the fluorinated poly(3,4-ethylenedioxyppyrole) (PEDOP) and only one for the fluorinated poly(3,4-propylenedioxyppyrole) (PProDOP) (Figure 1 and Table 1). The half-wave potentials, $E_{1/2}$, of the fluorinated PProDOPs ($E_{1/2} \approx 0.38$ V) are higher than those of *N*-alkylated PProDOPs reported in the literature.^{69,71} Indeed, the rigidity of the perfluorinated chains may cause a greater distortion of the polymer backbone and therefore a reduction of the effective conjugation length. The half-wave potentials of the PEDOP derivatives ($E_{1/2} \approx 0.24$ V) are lower than those of the PProDOP derivatives. Increasing the fluorinated chain length has just a slight effect on the redox potentials of the corresponding polymers.

Wettability of the Films. To study the surface morphology and the surface properties, the polymers were deposited by chronoamperometry with an imposed potential of $E_{\text{p,opt}}^{\text{ox}}$ on gold plates with an optimal deposition charge of 225 mC/cm^2 , corresponding to a deposition time of ~5 min. This charge resulted in the best hydrophobic and oleophobic properties. Indeed, even though a deposition charge of 50 mC/cm^2 was sufficient to achieve the highest CA with water, a higher deposition of 225 mC/cm^2 was necessary to reach the highest CA with the oily liquid hexadecane.

CA measurements were performed with three solvents of different polarity: water ($\gamma_{\text{L}} = 72.8$ mN/m) to demonstrate the hydrophobicity and diiodomethane ($\gamma_{\text{L}} = 50.0$ mN/m) and hexadecane ($\gamma_{\text{L}} = 27.6$ mN/m) to explore the oleophobicity. In the literature,^{10–21} many oils with different surface tensions (hexadecane, rapeseed oil, salad oil, sunflower oil, etc.) have been used to determine surface oleophobicity, and there are claims that superoleophobicity occurs with different oils, requiring CAs in the range 130–165°. However, it is worth noting that there is a strong correlation between the measured

(70) Thomas, C. A.; Zong, K.; Schottland, P.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 222–225.

(71) Sönmez, G.; Schwendeman, I.; Schottland, P.; Zong, K.; Reynolds, J. R. *Macromolecules* **2003**, *36*, 639–647.

(72) Schottland, P.; Zong, K.; Gaupp, C. L.; Thompson, B. C.; Thomas, C. A.; Giurgiu, I.; Hickman, R.; Abboud, K. A.; Reynolds, J. R. *Macromolecules* **2000**, *33*, 7051–7061.

(73) Gaupp, C. L.; Zong, K.; Schottland, P.; Thompson, B. C.; Thomas, C. A.; Reynolds, J. R. *Macromolecules* **2000**, *33*, 1132–1133.

(74) Walczak, R. M.; Jung, J.-H.; Cowart, J. S., Jr.; Reynolds, J. R. *Macromolecules* **2007**, *40*, 7777–7785.

(75) Sönmez, G.; Schottland, P.; Zong, K.; Reynolds, J. R. *J. Mater. Chem.* **2001**, *11*, 289–294.

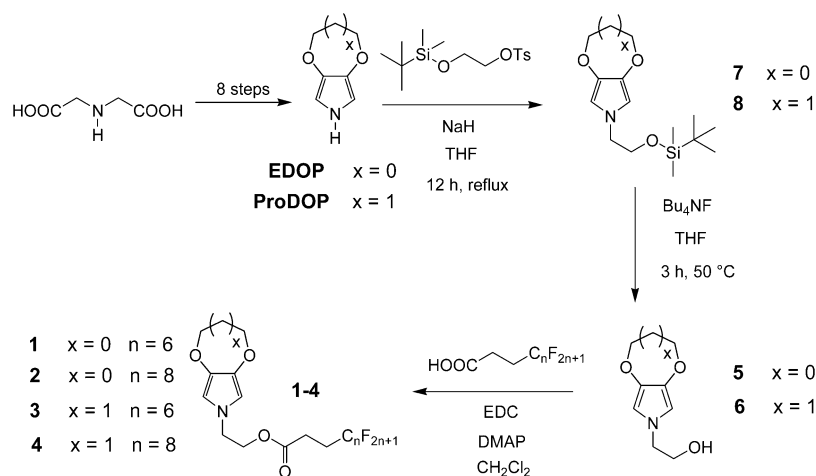
(76) Thompson, B. C.; Zong, K.; Schottland, P.; Reynolds, J. R. *Chem. Mater.* **2000**, *12*, 1563–1571.

(77) Zotti, G.; Zecchin, S.; Schiavon, G.; Groenendaal, L. B. *Chem. Mater.* **2000**, *12*, 2996–3005.

(78) Merz, A.; Schropp, R.; Dötterl, E. *Synthesis* **1995**, 795–800.

(79) Zong, K.; Reynolds, J. R. *J. Org. Chem.* **2001**, *66*, 6873–6882.

Scheme 2. Synthetic Route to Fluorinated 3,4-Alkylendioxyppyrrroles 1–4



CA and the oil surface tension: higher oil surface tension yields a larger CA. Thus, even if superhydrophobicity is determined with reference to a unique liquid probe (water), superoleophobicity strongly depends on the oil used. Here, the term superoleophobicity is used when the CA for hexadecane is greater than 140° . The measured CA values are gathered in Table 2.

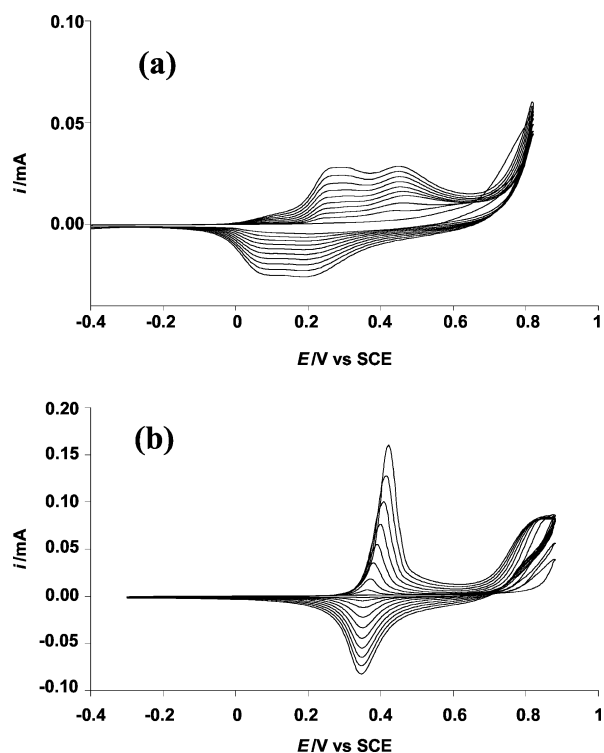


Figure 1. Cyclic voltammograms of (a) **1** and (b) **3** (0.01 M) on a Pt electrode recorded in 0.1 M $\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$.

Table 1. Electrochemical Data for the Monomers and Their Corresponding Polymers^a

monomer	$E_{\text{peak,m}}^{\text{ox}}$ (V)	$E_{\text{p,opt}}^{\text{ox}}$ (V)	$E_{\text{polymer}}^{\text{ox1}}$ (V)	$E_{\text{polymer}}^{\text{ox2}}$ (V)	$E_{\text{polymer}}^{\text{red1}}$ (V)	$E_{\text{polymer}}^{\text{red2}}$ (V)
1	0.94	0.82	0.28	0.45	0.07	0.18
2	0.94	0.82	0.30	0.45	0.10	0.20
3	0.97	0.88	0.42		0.34	
4	0.98	0.88	0.42		0.33	

^a All electrochemical data are given in V vs SCE.

Table 2. Static and Dynamic Contact Angles on Polymers Poly1 to Poly4 Electrodeposited on Gold (Salt: Bu_4NPF_6 ; $Q_s \approx 225 \text{ mC/cm}^2$)

	static contact angles (deg)			dynamic contact angles (deg) for water		
	water	diiodomethane	hexadecane	advancing	receding	H
Poly1	160	150	141	160	158	2
Poly2	161	152	145	161	159	2
Poly3	156	145	96	157	109	48
Poly4	160	152	120	161	122	39

Electrochemical polymerization of the four fluorinated monomers produced superhydrophobic films having static water CAs greater than 160° for Poly1, Poly2, and Poly4, but only the fluorinated PEDOPs (Poly1 and Poly2) were superoleophobic, with static hexadecane CAs greater than 140° . A considerable difference in the hexadecane CAs of Poly1 and Poly3 ($\sim 50^\circ$) was observed. For the ProDOP derivatives, the fluorinated tail length had almost no effect on hydrophobicity but had a significant effect on oleophobicity. In contrast, for the EDOP derivatives, no significant variation of lyophobicity was observed on lengthening the fluorinated tail. Most published work^{10–16,21} claims that superoleophobicity demands eight fluoromethylene units, but it can be seen here that it is also possible to obtain superoleophobic surfaces by decreasing the F -alkyl tail length by two fluoromethylene units. Importantly, this observation suggests that it is possible to construct such materials without PFOA (perfluorooctyl acid) precursors, which are well-known for their toxicity.⁸⁰

Moreover, the hysteresis and sliding angle measurements determined by the tilted-drop method [$<2^\circ$ ($\text{CA}_{\text{advancing}}/\text{CA}_{\text{receding}} \approx 160^\circ/158^\circ$) and $<3^\circ$ for Poly1 and Poly2, respectively] were extremely low, suggesting self-cleaning properties; this means that a water droplet rolls off the surface at a slight tilt angle (a movie showing this behavior is available). Water droplets can also easily bounce on the surfaces, confirming the very low adhesion between water droplets and the surfaces. In contrast, water droplets do not roll off the surfaces of Poly3 and Poly4, even with a tilt angle of 90° , as seen for the sticky superhydrophobic surfaces reported by Guo and Liu⁸¹ and Hess and co-workers⁸². On these sticky surfaces, the advancing and receding contact angles could not be determined by the tilted-

(80) Kudo, N.; Kawashima, Y. *J. Toxicol. Sci.* **2003**, *28*, 49–57.

(81) Guo, Z.-G.; Liu, W.-M. *Appl. Phys. Lett.* **2007**, *90*, 223111.

(82) Balu, B.; Breedveld, V.; Hess, D. W. *Langmuir* **2008**, *24*, 4785–4790.

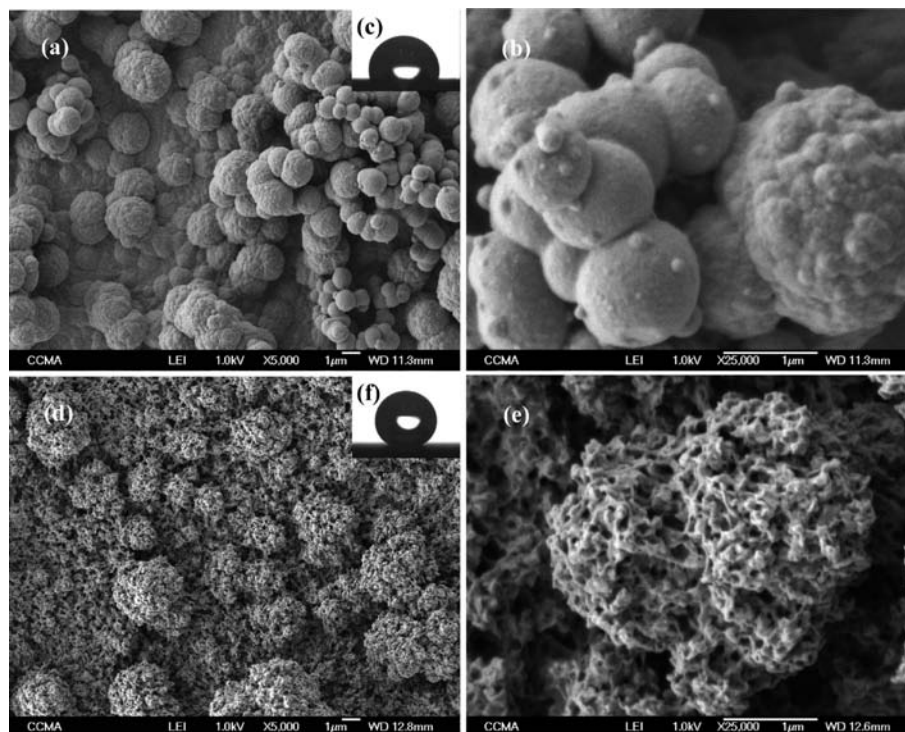


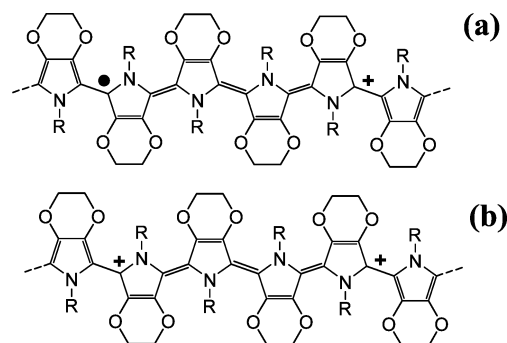
Figure 2. SEM images of Poly3 with magnifications of (a) 5000 \times and (b) 25000 \times and of Poly1 with magnifications of (d) 5000 \times and (e) 25000 \times . The films were electrodeposited on gold (salt: Bu₄NPF₆; $Q_s \approx 225 \text{ mC/cm}^2$); the scale bar represents 1 μm . (c, f) Pictures of a hexadecane droplets on (c) Poly3 and (f) Poly1 surfaces.

drop method, and a method previously reported in the literature⁸² was used. The values are gathered in Table 2. Thus, it would seem that the surface morphology of the fluorinated PEDOP films causes a higher distortion of the three-phase contact line than the surface morphology of fluorinated PProDOP films, according to the theory of Gao and McCarthy.⁴⁰ To confirm this supposition, the surfaces were studied by SEM in order to determine their surface morphologies.

Morphology of the Films. SEM images showed that electrochemical polymerization of the fluorinated 3,4-alkylenedioxy-pyrroles in Bu₄NPF₆ gave structured films (Figure 2). The fluorinated PProDOP surfaces (Poly3 and Poly4) appear to consist of spherical and cauliflower-like structures (Figure 2a,b). These nonporous structures are similar to those reported for fluorinated polythiophenes.^{65,66} In contrast, fluorinated PEDOP surfaces (Poly1 and Poly2) consist of very porous structures (Figure 2d,e). Interestingly, porosity features are structured on a nanometer length scale. Thus, the presence of one additional methylene in the alkylenedioxy bridge leads to surfaces without any obvious nanoporosity.

Nanoporosity. We suppose that the nanoporosity of the surfaces, especially that observed for the fluorinated PEDOPs (Poly1 and Poly2), is due to a more complex doping process. Indeed, two successive peaks were observed in the cyclic voltammograms (Figure 1a) of fluorinated PEDOP, corresponding to the formation of polaronic and bipolaronic forms⁸³ (Scheme 3), whereas only one peak was observed in the cyclic voltammograms of fluorinated PProDOP (Figure 1b). Thus, the flexibility of the propylenedioxy bridge in PProDOP may impede π -stacking interactions and hence the interchain dimerization of polarons. Consequently, the porosity at the molecular scale is higher in PProDOP, though this is not the case at the

Scheme 3. Examples of (a) Polaronic and (b) Bipolaronic Forms



microscopic scale. The differences observed at the microscopic scale can also be a consequence of different polymerization kinetics or perhaps interactions with the counteranions. If the nanoporosity were due to a difference in polymerization kinetics, PProDOP would be more porous than PEDOP because the polymer chain length and the interactions between the polymer chains are more important in PEDOP (EDOP derivatives polymerize more quickly than ProDOP analogues), as evidenced by the half-wave potentials. As the nanoporosity is observed only in the PEDOP films, it is probably due to the interactions with the counteranions and their diffusion inside the polymer. Indeed, the formation of bipolaronic forms needs a supplementary circulation of counteranions to neutralize the polymer. This discovery is encouraging, as it suggests that the design and synthesis of novel fluorinated electropolymerizable monomers could lead to a variety of new superoleophobic surfaces.

As these polymers are chemically very similar, the comparison between a fluorinated PEDOP and the homologous fluorinated PProDOP highlights the influence of surface morphology, in this case nanoporosity, on surface wettability. Thus, nan-

(83) Sadki, S.; Chevrot, C. *Electrochim. Acta* **2003**, *48*, 733–739.

oporosity, which was observed only with the fluorinated PEDOP, decreases the adhesion between the liquid droplets and the surface, explaining the very low hysteresis and sliding angle observed only for fluorinated PEDOP. This result is in agreement with the results of Yerushalmi-Rozen and co-workers,⁴⁸ in which Poly3 and Poly4 can be assimilated to their post structures and Poly1 and Poly2 to their pore structures. Indeed, the dimension and form of the pores, which are very important parameters that govern the wettability of the surfaces,^{45,47,48,84–86} seem to be “ideal”. As a consequence, the presence of these nanoporosities induces a very high discontinuity of the three-phase contact line that makes the support and movement of liquid droplets (both water and hexadecane) easier. This is the first time that superoleophobic nanoporous surfaces have been obtained by electrochemical polymerization. The development of nanoporous conducting polymer films has often demanded the use of nanostructured templates,^{87–89} which are themselves inconvenient to manipulate. This new example demonstrates the high impact of porosity size on the wettability with polar and also apolar liquids, in agreement with the work of Gao and co-workers¹⁸ on porous silicon films.

Conclusions

In this work, we have reported the synthesis and characterization of two kinds of fluorinated electropolymerizable monomers

derived from 3,4-alkylenedioxy pyrroles differing by one methylene unit in the alkylenedioxy bridge. The modification of the 3,4-alkylenedioxy bridge length appears to have a considerable influence on surface morphology of the corresponding electrodeposited polymer films. Here we have demonstrated that fluorinated EDOP gives superoleophobic and superhydrophobic films with extremely low hysteresis and sliding angles, whereas fluorinated ProDOP gives only superhydrophobic films with no sliding angle. The difference in wettability is attributed to the presence of nanoporosity in fluorinated PEDOP films, which increases the oil contact angles and makes the support and movement of liquid droplets easier. The nature of the central polymerizable unit (EDOP vs ProDOP) has a greater effect on surface antiwetting properties than does increasing the fluorine density (*F*-hexyl to *F*-octyl). These results point to exciting possibilities for generating new classes of materials with dual water- and oil-repellency, which themselves are quite stable and of potentially low toxicity.

Acknowledgment. T.D. thanks the French Ministry for a research grant. The authors thank J. Eastoe (Bristol Univ.) for discussions.

Supporting Information Available: Synthesis procedures and mass spectra of the molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA901392S

- (84) Extrand, C. W. *Langmuir* **2004**, *20*, 5013–5018.
(85) Patankar, N. A. *Langmuir* **2004**, *20*, 7097–7102.
(86) Patankar, N. A. *Langmuir* **2004**, *20*, 8209–8213.
(87) Li, M.; Yuan, J.; Shi, G. *Thin Solid Films* **2008**, *516*, 3836–3840.
(88) Luo, X.; Killard, A. J.; Morrin, A.; Smyth, M. R. *Chem. Commun.* **2007**, 3207–3209.

- (89) Joo, J.; Kim, B. H.; Park, D. H.; Kim, H. S.; Seo, D. S.; Shim, J. H.; Lee, S. J.; Ryu, K. S.; Kim, K.; Jin, J.-I.; Lee, T. J.; Lee, C. J. *Synth. Met.* **2005**, *153*, 313–316.