Surface Nanostructuration and Wettability of Electrodeposited Poly(3,4-ethylenedioxyppyrrrole) and Poly(3,4-propylenedioxyppyrrrole) Films Substituted by Aromatic Groups

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1. INTRODUCTION

Controlling the surface wettability is fundamental for various applications in self-cleaning surfaces, oil/water separation membranes, and sensors or in microfluidics. Inspired by natural surfaces, the surface hydrophobicity is depending on both the surface energy and the surface roughness and morphology. Indeed, in nature, we can found species with various wetting properties. Superhydrophobic properties, characterized by both high contact angles and low hysteresis, are present in lotus leaves, cicada wings, or water strider’s legs. In opposite, parahydrophobic properties, characterized by both high contact angles and high hysteresis, are present in rose petals or gecko foot. The processes to create structured surfaces are numerous and imply different treatments (chemical, physical, mechanical...) such as etching, plasma, laser, lithography, or templating.

Following the used process, conducting polymers can form nanostructured materials. This is possible not only in solution by self-assembly but also directly on surfaces inducing a high influence of the surface properties. The electro-polymerization was revealed as a very interesting process because of an easy and fast control of the surface structures using various electrochemical parameters. In this process, a monomer is oxidized to form conducting polymers onto conductive substrates that are used as a working electrode such as gold, platinum, titanium, stainless steel, or indium tin oxide, whatever the surface geometry is (flat substrates, textured substrates, meshes, fabrics...). In this process, the monomer also plays a key role not only in the polymerization but also in the control of the surface morphology and wettability. Among the multiple possibilities, monomers of the 3,4-alkylenedioxyppyrrrole family such as 3,4-ethylenedioxyppyrrrole (EDOP) and 3,4-propylenedioxyppyrrrole (ProDOP) monomers because of their ultralow exceptional potential, leading to polymers with unique optoelectronic properties. Reynolds et al. were the first to report their substitution not only on the nitrogen but also on the bridge, leading to numerous synthesis possibilities. However, the substitution on the bridge needs the synthesis of each monomer in about eight steps. Moreover, the authors reported their exceptional optoelectronic properties including high conductivity, multicolor cathodic and anodic electrochromism, and rapid redox switching, but their surface morphology and hydrophobicity were not investigated.

Previously, it was found a way to obtain EDOP and ProDOP derivatives with hydroxyl groups on the bridge using epibromohydrin. These monomers could be easily functionalized by simple esterification reaction. Thanks to the presence of NH groups, superhydrophobic nanofibers were obtained with fluorinated chains.

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Here, for applications in water harvesting systems, we want to develop structured materials with parahydrophobic properties. Such materials are extremely interesting to collect water droplets even in arid or hot environments. For these applications, it is preferable to use substituents of lower hydrophobicity than fluorinated chains such as aromatic rings. Hence, we wanted to develop original EDOP and ProDOP monomers with various aromatic rings (Scheme 1). The resulting surfaces were investigated in order to determine significant effects on the surface morphology and wettability.

2. RESULTS AND DISCUSSION

2.1. Electrochemical Synthesis. Electrodepositions were performed in anhydrous acetonitrile containing 0.1 M Bu$_4$NClO$_4$ and 0.01 M monomer. The monomer oxidation potential was found to be between 0.96 and 1.12 V following the monomer used.

Then, it was very important to study the polymer growth by cyclic voltammetry because this technique gives extremely important information. It is known that the substituents induce steric hindrance during polymerization affecting both the polymer chain length and the resulting surface morphology. The substituent can also affect the polymerization capacity of the monomers by electrowithdrawing/electrodonating effects, but in our case, this is not the case because the substituents are sufficiently separated from the monomer. Indeed, the conductivity should be the highest in electrodeposition and the polymer insolubility. For example, the conductivity is affected by both the length of the polymer chain (different if we choose EDOP or ProDOT) and the presence of the substituent. Hence, the polymer conductivity and insolubility are very important if the polymer oxidation potential is very far from that of the monomer, and the intensity of its peak constantly increases after each scan without shift in potential.

The cyclic voltammograms are given in Figures 1 and 2. In the case of ProDOT derivatives (Figure 1), the voltammograms displayed superposed curves after each scan, indicating that the growth is homogeneous when the thickness increases, whatever the substitutes used here. Shifts to the high potentials indicate of extremely long polymer chain length. This parameter is extremely important in electropolymerization because the polymer insolubility increases when the polymer chain lengths. Moreover, differences in the polymer chain lengths can also change the resulting surface morphology. In the case of the EDOP derivatives (Figure 2), the substituents induce much higher steric hindrance. Only, EDOP-Ph and EDOP-Fluo display superposed curves after each scan.

2.2. Surface Properties. Then, the polymers were electrodeposited on 2 cm$^2$ gold plates and using different deposition charges ($Q$) from 12.5 to 400 mC cm$^{-2}$. The scanning electron microscopy (SEM) images are given in Figures 3 and 4, and the surface roughness and wettability in Tables 1 and 2.

First of all, the surfaces are not extremely rough (Tables 1 and 2), as obtained with EDOT or ProDOT derivatives. This is in agreement with previous works, in which the authors show that one of the main factors influencing on the surface morphology is the solubility of the oligomers formed in the first instances of the polymerization. The presence of NH groups induces, here, a high increase in the polymer solubility reducing the surface structurations.

However, some of the polymer films are nanoporous. This is the case of the films obtained with ProDOT-Ph, ProDOT-BiPh, and EDOP-diPh, whereas others are nanostructured such as the films obtained with ProDOT-Na, EDOT-BiPh, EDOP-Na, and EDOP-Fluo. The presence of nanostructure/nanoporosity is very important and can induce an important increase in the surface hydrophobicity. Indeed, at low deposition charge, all of the surfaces are hydrophilic, indicating that all of these polymers are intrinsically hydrophilic. This is not surprising because of the high polarity of the NH groups, whereas the aromatic substituents are not very apolar, compare the linear alkyl or fluorinated chains. The highest hydrophobicity up to about 116° is obtained with EDOP-diPh at 400 mC cm$^{-2}$ (Figure 5), for which the surface was both nanoporous and with a high surface roughness ($R_a > 500$ nm). This increase is not possible using the Wenzel equation ($\cos \theta = r \cos \theta^\circ$ where $r$ is a roughness parameter) because the surface roughness would increase the surface hydrophilicity. Indeed, the Wenzel equation describes the case where the water droplet enters in all surface roughness leading to a full solid—liquid interface. With this equation, it is possible to increase $\theta$ but only if the contact angle of the smooth surface ($\theta^\circ$) is above 90° (intrinsically hydrophobic).

Only the Cassie—Baxter can explain these results, indicating the presence of air between the surface and the water droplet. The Cassie—Baxter equation is $\cos \theta = r_f \cos \theta^\circ + f - 1$, where $r_f$ is the roughness ratio of the substrate wetted by the liquid, $f$...
is the solid fraction, and \((1 - f)\) is the air fraction. Indeed, because of the presence of surface nanoporosity, air is trapped between the surface and the water droplet leading to an increase in \(\theta\) even if the polymer is intrinsically hydrophilic. As a consequence, these states are intermediate states between the Wenzel and Cassie-Baxter states. Moreover, there is absolutely no direct link between the roughness and wettability. There is a link between the roughness parameter \(r\), which is different from the surface roughness (\(R_s\) or \(R_q\)), but only if the surfaces are in the "Wenzel state". This is not the case here because of the presence of air trapped between the surface and the water droplet.

It should also be noticed that compared to previous works on PEDOP or ProDOP polymers substituted on the bridge, the results with linear or branched alkyl chains gave higher parahydophobic properties because of the possible formation of long nanofibers structures, depending on their length.19,30

3. CONCLUSIONS

Here, in the aim to prepare parahydophobic materials (both high contact angles and high hysteresis), we investigated the electropolymerization of novel EDOP and ProDOP monomers with aromatic rings on the 3,4-alkylenedioxy bridge and studied their surface morphology and wettability. We demonstrated the influence of the nature of the aromatic ring (phenyl, biphenyl, diphenyl, naphthalene, fluorene, and pyrene) and the polymerizable core (EDOP or ProDOP) on the surface properties. The best results were obtained with both EDOP and diphenyl, with which extremely high hydrophobic properties (up to 116°) are obtained, even if...
the polymers are intrinsically hydrophilic. The synthesis strategy is extremely interesting and will open new lead to investigating many other molecules. Moreover, these surfaces could be excellent candidates in the future, for example, in water harvesting systems and in water/oil separation membranes.

4. EXPERIMENTAL SECTION

4.1. Monomer Synthesis and Characterization. For the monomer synthesis, the key molecules were ProDOP-OH and EDOP-OH as shown in Scheme 2. These intermediates were obtained in eight steps from iminodiacetic acid, as reported in the literature. Indeed, from intermediate 1, it is possible to obtain and separate the EDOP and ProDOP derivates thanks to epibromohydrin, following by nitrogen deprotection, saponification, and decarboxylation.

Then, the substituents were grafted by simple esterification reaction. All of the acids used here were purchased from Sigma-Aldrich. For that, 1.2 equiv of the corresponding acid, 0.31 g of N-(3-dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (0.0015 mol, 1.2 equiv), and 20 mg of N,N-dimethylaminopyridine were added to 20 mL of absolute dichloromethane. After 30 min at room temperature, the mixture was added to 20 mL of absolute acetonitrile containing 0.2 g of ProDOP-OH or EDOP-OH (0.0013 mol, 1 equiv). After stirring for 24 h at room temperature, the products were purified by column chromatography using tetrahydrofuran/petroleum ether 60:40 as an eluent. Here, it was also extremely important to add 10% of triethylamine in the silica gel and in the eluent because of the product sensitivity.

4.1.1. ProDOP-Ph: 2,3,4,7-Tetrahydro-[1,4]dioxepino[2,3-c]pyrrol-3-yl 2-Phenylacetate. Yield 51%; crystalline solid; mp 127.1 °C; δH (200 MHz, CDCl3): 7.31 (m, 5H), 7.20 (s, 1H), 6.32 (d, J = 3.3 Hz, 2H), 5.19 (m, 1H), 4.23 (dd, J = 12.5 Hz, J = 4.9 Hz, 2H), 4.06 (dd, J = 12.5 Hz, J = 2.7 Hz, 2H), 3.73 (s, 2H); δC (100 MHz, CDCl3): 171.01, 138.85, 135.76, 133.63, 129.28, 128.61, 127.20, 125.50, 103.11, 73.23, 72.52, 41.08; MS (ESI LC/MS): m/z [M – H]+ 274.00.

4.1.2. ProDOP-biPh: 2,3,4,7-Tetrahydro-[1,4]dioxepino[2,3-c]pyrrol-3-yl 2-([1,1′-Biphenyl]-4-yl)acetate. Yield 71%; crystalline solid; mp 137.8 °C; δH (200 MHz, CDCl3): 7.58...
Figure 3. SEM images of the polymer surfaces obtained from ProDOP derivatives for a deposition charge of 400 mC cm\(^{-2}\); working electrode: 2 cm\(^2\) Au-coated Si wafer.

Figure 4. SEM images of the polymer surfaces obtained from EDOP derivatives for a deposition charge of 400 mC cm\(^{-2}\); working electrode: 2 cm\(^2\) Au-coated Si wafer.

Table 1. Roughness (\(R_s\) and \(R_m\)) and Wettability Data for the ProDOP Polymers; Working Electrode: 2 cm\(^2\) Au-Coated Si Wafer

| polymer      | deposition charge \(\text{[mC cm}^{-2}\) | \(R_s\) [nm] | \(R_m\) [nm] | \(\theta_w\) [deg] |
|--------------|----------------------------------------|----------------|----------------|------------------|
| ProDOP-Ph    | 12.5                                   | 15 ± 2.3       | 27 ± 2.6       | 76 ± 4.2         |
|              | 25                                     | 21 ± 1.8       | 32 ± 6.4       | 77 ± 3.8         |
|              | 50                                     | 15 ± 2.3       | 23 ± 6.2       | 83 ± 6.3         |
|              | 100                                    | 90 ± 11        | 117 ± 9.8      | 89 ± 6.2         |
|              | 200                                    | 118 ± 6.2      | 153 ± 14       | 74 ± 5.8         |
|              | 400                                    | 200 ± 50       | 315 ± 65       | 92 ± 7.2         |
| ProDOP-BiPh  | 12.5                                   | 16 ± 7.9       | 36 ± 5.5       | 65 ± 8.5         |
|              | 25                                     | 20 ± 4.0       | 50 ± 10        | 62 ± 11          |
|              | 50                                     | 9.2 ± 1.5      | 12 ± 1.5       | 88 ± 3.2         |
|              | 100                                    | 14 ± 4         | 25 ± 7.1       | 96 ± 2.6         |
|              | 200                                    | 19 ± 5         | 34 ± 8.4       | 91 ± 2.2         |
|              | 400                                    | 288 ± 24       | 370 ± 48       | 99 ± 6.8         |
| ProDOP-diPh  | 12.5                                   | 14.6 ± 2.3     | 24 ± 8.4       | 76 ± 9.8         |
|              | 25                                     | 10.5 ± 1.0     | 13 ± 1.1       | 88 ± 4.2         |
|              | 50                                     | 43.9 ± 6.2     | 55 ± 6.4       | 87 ± 2.5         |
|              | 100                                    | 61 ± 11        | 100 ± 14       | 85 ± 3.3         |
|              | 200                                    | 191 ± 31       | 277 ± 37       | 86 ± 3.0         |
|              | 400                                    | 526 ± 35       | 818 ± 70       | 99 ± 4.2         |
| ProDOP-Na    | 12.5                                   | 12 ± 2.4       | 15 ± 3.3       | 82 ± 4.5         |
|              | 25                                     | 12 ± 1.4       | 22 ± 5.8       | 82 ± 4.9         |
|              | 50                                     | 11 ± 1.4       | 16 ± 5.7       | 85 ± 4.7         |
|              | 100                                    | 9.1 ± 1.0      | 17 ± 4.4       | 95 ± 10          |
|              | 200                                    | 29 ± 1.7       | 55 ± 8.6       | 99 ± 5.3         |
|              | 400                                    | 105 ± 9        | 183 ± 74       | 96 ± 6.3         |
| ProDOP-Fluo  | 12.5                                   | 15 ± 4.9       | 33 ± 10        | 73 ± 4.6         |
|              | 25                                     | 34 ± 4.6       | 53 ± 12        | 75 ± 4.6         |
|              | 50                                     | 25 ± 11        | 37 ± 15        | 67 ± 3.9         |
|              | 100                                    | 27 ± 12        | 39 ± 17        | 88 ± 3.2         |
|              | 200                                    | 127 ± 33       | 172 ± 18       | 86 ± 2.1         |
|              | 400                                    | 219 ± 31       | 324 ± 26       | 97 ± 3.2         |
| ProDOP-Py    | 12.5                                   | 9.5 ± 1.2      | 21 ± 1.6       | 74 ± 4.0         |
|              | 25                                     | 8.4 ± 3.1      | 12 ± 4.2       | 78 ± 11          |
|              | 50                                     | 8.0 ± 1.2      | 12 ± 5.0       | 80 ± 7.6         |
|              | 100                                    | 8.9 ± 2.1      | 14 ± 5.8       | 81 ± 3.6         |
|              | 200                                    | 14 ± 2.9       | 22 ± 5.7       | 84 ± 3.5         |
|              | 400                                    | 115 ± 35       | 156 ± 66       | 80 ± 4.1         |

(m, 4H), 7.41 (m, 5H), 7.19 (s, 1H), 6.33 (d, J = 3.3 Hz, 2H), 5.22 (m, 1H), 4.26 (dd, J = 12.5 Hz, J = 4.9 Hz, 2H), 4.08 (dd, J = 12.5 Hz, J = 2.7 Hz, 2H), 3.78 (s, 2H); δ\(_C\) (100 MHz, CDCl\(_3\)): 171.00, 140.77, 140.18, 138.88, 135.77, 132.64, 129.72, 128.74, 127.37, 127.26, 127.07, 125.50, 103.14, 73.33, 72.53, 40.71; MS (ESI LC/MS): m/z [M + H]^+ 350.00.

4.1.3. ProDOP-diPh: 2,3,4,7-Tetrahydro-[1,4]dioxepino-(2,3-c)pyrrol-3-yl 2,2-Diphenylacetate. Yield 61%; crystalline solid; mp 133.1 °C; δ\(_\text{H}(200 MHz, CDCl}_{3}\)): 7.32 (m, 10H), 7.09 (s, 1H), 6.1 (s, J = 3.3 Hz, 2H), 5.26 (m, 4H), 5.14 (s, 1H), 4.18 (dd, J = 12.4 Hz, J = 5.0 Hz, 2H), 4.09 (dd, J = 12.4 Hz, J = 3.1 Hz, 2H); δ\(_C\) (100 MHz, CDCl\(_3\)): 171.86, 138.81, 138.33, 128.62, 128.57, 128.54, 127.34, 103.00, 73.44, 72.40, 56.73; MS (ESI LC/MS): m/z [M + H]^+ 350.00.

4.1.4. ProDOP-Na: 2,3,4,7-Tetrahydro-[1,4]dioxepino(2,3-c)pyrrol-3-yl 2-(Naphthalen-2-yl)acetate. Yield 86%; liquid; δ\(_\text{H}(200 MHz, CDCl}_{3}\)): 7.72 (m, 4H), 7.39 (m, 3H), 7.11 (s, 1H), 6.24 (d, J = 3.3 Hz, 2H), 5.13 (m, 1H), 4.17 (dd, J = 12.5 Hz, J = 4.9 Hz, 2H), 3.98 (dd, J = 12.5 Hz, J = 2.7 Hz, 2H), 3.82 (s, 2H); δ\(_C\) (100 MHz, CDCl\(_3\)): 170.99, 138.86, 133.44,
Table 2. Roughness ($R_a$ and $R_v$) and Wettability Data for the EDOP Polymers; Working Electrode: 2 cm² Au-Coated Si Wafer

| polymer      | deposition charge [mC cm⁻²] | $R_a$ [nm] | $R_v$ [nm] | $θ_a$ [deg] |
|--------------|-----------------------------|-----------|-----------|-------------|
| EDOP-Ph      | 12.5                        | 12 ± 1.8  | 16 ± 4.8  | 75 ± 5.5    |
|              | 25                          | 10 ± 1.5  | 14 ± 4.3  | 86 ± 4.9    |
|              | 50                          | 8.8 ± 1.1 | 12 ± 1.5  | 77 ± 4.2    |
|              | 100                         | 7.1 ± 1.2 | 9.9 ± 1.3 | 75 ± 2.0    |
|              | 200                         | 39 ± 10   | 56 ± 15   | 81 ± 1.4    |
|              | 400                         | 162 ± 35  | 438 ± 95  | 87 ± 4.0    |
| EDOP-BiPh    | 12.5                        | 12 ± 3.5  | 29.5 ± 7.3| 66 ± 10     |
|              | 25                          | 9.6 ± 1.2 | 12 ± 1.7  | 92 ± 3.4    |
|              | 50                          | 9.3 ± 0.8 | 14 ± 4.1  | 76 ± 5.8    |
|              | 100                         | 16 ± 5.3  | 30 ± 10.5 | 93.9 ± 2.7  |
|              | 200                         | 50 ± 20   | 81 ± 35   | 103 ± 5.5   |
|              | 400                         | 700 ± 190 | 1430 ± 270| 106 ± 2.7   |
| EDOP-diPh    | 12.5                        | 20.5 ± 7.2| 42 ± 18   | 68 ± 11     |
|              | 25                          | 19 ± 2.9  | 40 ± 19   | 73 ± 6.4    |
|              | 50                          | 11 ± 1.2  | 22 ± 5.6  | 87 ± 1.4    |
|              | 100                         | 155 ± 16  | 210 ± 18  | 97 ± 2.0    |
|              | 200                         | 171 ± 22  | 228 ± 33  | 103 ± 4.6   |
|              | 400                         | 277 ± 81  | 400 ± 131 | 116 ± 5.6   |
| EDOP-Na      | 12.5                        | 11 ± 1.1  | 13 ± 1.1  | 82 ± 2.1    |
|              | 25                          | 10 ± 2.6  | 19 ± 8.7  | 81 ± 1.2    |
|              | 50                          | 11 ± 0.7  | 24 ± 1.0  | 84 ± 1.3    |
|              | 100                         | 23 ± 3.9  | 38.5 ± 16 | 87 ± 4.3    |
|              | 200                         | 160 ± 65  | 213 ± 78  | 90 ± 4.3    |
|              | 400                         | 96 ± 35   | 144 ± 41  | 114 ± 7.2   |
| EDOP-Fluo    | 12.5                        | 16 ± 7.2  | 35 ± 13   | 75 ± 9.2    |
|              | 25                          | 14 ± 2.0  | 34 ± 19   | 66 ± 7.9    |
|              | 50                          | 16 ± 2.5  | 25 ± 9.1  | 97 ± 4.4    |
|              | 100                         | 17 ± 9.4  | 22.1 ± 11 | 96 ± 4.5    |
|              | 200                         | 46 ± 22   | 80.6 ± 31 | 97 ± 3.9    |
|              | 400                         | 116 ± 23  | 156 ± 22  | 88 ± 4.8    |
| EDOP-Py      | 12.5                        | 16 ± 2.8  | 41 ± 12   | 67 ± 9.4    |
|              | 25                          | 10 ± 1.3  | 13 ± 1.8  | 82 ± 2.9    |
|              | 50                          | 11 ± 4.6  | 15 ± 5.8  | 62 ± 6.3    |
|              | 100                         | 10 ± 0.5  | 15 ± 1.8  | 89 ± 1.6    |
|              | 200                         | 117 ± 28  | 174 ± 55  | 75 ± 2.4    |
|              | 400                         | 121 ± 23  | 198 ± 40  | 79 ± 5.1    |

Yield 46%; liquid; δ (2,3-c)pyrrol-3-yl 2-(9H-Fluoren-9-yl)-acetate. Yield 49%; crystalline solid; mp 163.1 °C; δ (200 MHz, CDCl3): 7.75 (m 2H), 5.28 (m, 1H), 4.14 (dd, J = 12.6 Hz, J = 5.0 Hz, 2H), 4.08 (dd, J = 12.4 Hz, J = 3.0 Hz, 2H), 2.90 (m, 2H); δ (100 MHz, CDCl3): 171.61, 146.00, 130.80, 128.50, 127.19, 124.34, 119.94, 103.08, 73.15, 72.51, 43.48; MS (ESI LC/MS): m/z [M − H]^+ 324.07.

4.1.6. **ProDOP-Fluo:** 2,3,4,7-Tetrahydro-[1,4]dioxygeno-(2,3-c)pyrrol-3-yl 2-(9H-Fluoren-9-y)-acetate. Yield 49%; liquid; δ (200 MHz, CDCl3): 7.75 (m 2H), 7.52 (m, 2H), 7.36 (m, 4H), 7.20 (s, 1H), 6.22 (d, J = 3.3 Hz, 2H), 5.28 (m, 1H), 4.43 (m, 3H), 4.18 (dd, J = 12.4 Hz, J = 5.0 Hz, 2H), 4.08 (dd, J = 12.4 Hz, J = 3.0 Hz, 2H), 2.90 (m, 2H); δ (100 MHz, CDCl3): 171.61, 146.00, 130.80, 128.50, 127.19, 124.34, 119.94, 103.08, 73.15, 72.51, 43.48; MS (ESI LC/MS): m/z [M − H]^+ 324.07.

Figure 5. Example of contact angle measured on PEDOP-diPh with a deposition charge of 400 mC cm⁻².

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electrodes were used to connect an electrochemical cell to the potentiostat. A glassy carbon rod was used as a counter-electrode, and a SCE was used as the reference electrode. As the working electrode, a platinum tip (surface = 3.14 mm²) was first used in order to study electropolymerization, whereas 2 cm² Au-coated Si wafers were used for surface characterization. The Au-coated Si wafers were placed opposite to the counter electrode with a distance of about 2 cm, whereas the reference electrode was placed anywhere.

Ten milliliters of anhydrous acetonitrile containing 0.1 M tetrabutylammonium perchlorate (Bu₄NClO₄) and 0.01 M monomer was inserted inside the electrochemical cell. The solution was degassed under argon before each experiment.

4.3. Surface Characterization. The surface morphology was investigated by SEM. A 6700F microscope of JEOL was used. For the surface wetting properties, a DSA30 goniometer of Krüss was used. For that 2 μL water droplets were placed on the surface and the apparent contact angles were taken at the triple point. The arithmetic (Ra) and quadratic (Rq) surface roughness were determined with a WYKO NT1100 optical profiling system from Bruker. For that these measurements were realized with the working mode high mag phase-shift interference, the objective 50 ×, and the field of view 0.5 ×. Each data given in the paper is a mean of five measurements. The measurements were not determined at the edge of the plates because of differences in the polymer growth observed here.

Scheme 2. Synthesis Way to the Monomers

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REFERENCES

(1) Szczepanski, C. R.; Guittard, F.; Darmanin, T. Recent Advances in the Study and Design of Parahydrophobic Surfaces: From Natural Examples to Synthetic Approaches. Adv. Colloid Interface Sci. 2017, 241, 37–61.
(2) Marmur, A. Hydro- Hygro- Oleo- Omni-phobic? Terminology of Wettability Classification. Soft Matter 2012, 8, 6867–6870.
(3) Su, B.; Tian, Y.; Jiang, L. Bioinspired Interfaces with Superwettability: From Materials to Chemistry. J. Am. Chem. Soc. 2016, 138, 1727–1748.
(4) Nosonovsky, M.; Bhushan, B. Superhydrophobic Surfaces and Emerging Applications: Non-Adhesion, Energy, Green Engineering. Curr. Opin. Colloid Interface Sci. 2009, 14, 270–280.
(5) Darmanin, T.; Guittard, F. Superhydrophobic and Superoleophobic Properties in Nature. Mater. Today 2015, 18, 273–285.
(6) Koch, K.; Bhushan, B.; Barthlott, W. Diversity of Structure, Morphology and Wetting of Plant Surfaces. Soft Matter 2008, 4, 1943–1963.
(7) Feng, L.; Zhang, Y.; Xi, J.; Zhu, Y.; Wang, N.; Xia, F.; Jiang, L. Petal Effect: A Superhydrophobic State with High Adhesive Force. Langmuir 2008, 24, 4114–4119.
(8) Sun, Z.; Liao, T.; Sheng, L.; Kim, J. H.; Dou, S. X.; Bell, J. Fly Compound-Eye Inspired Inorganic Nanostructures with Extraordinary Visible-Light Responses. Mater. Today Chem. 2016, 1–2, 84–89.
(9) Yong, J.; Chen, F.; Yang, Q.; Jiang, Z.; Hou, X. A Review of Femtosecond-Laser-Induced Underwater Superoleophobic Surfaces. Adv. Mater. Interfaces 2018, 5, 1701370.
(10) Cheng, Y.; Yang, H.; Yang, Y.; Huang, J.; Wu, K.; Chen, Z.; Wang, X.; Lin, C.; Lai, Y. Progress in TiO₂ Nanotube Coatings for Biomedical Applications: A Review. J. Mater. Chem. B 2018, 6, 1862–1886.
(11) Liu, H.; Wang, Y.; Huang, J.; Chen, Z.; Chen, G.; Lai, Y. Bioinspired Surfaces with Superamphiphobic Properties: Concepts, Synthesis, and Applications. Adv. Funct. Mater. 2018, 28, 1707415.
(12) Zhang, S.; Huang, J.; Tang, Y.; Li, S.; Ge, M.; Chen, Z.; Zhang, K.; Lai, Y. Understanding the Role of Dynamic Wettability for Condensate Microdrop Self-Propelling Based on Designed Superhydrophobic TiO₂ Nanostructures. Small 2017, 13, 1600687.
(13) Lai, Y.; Huang, J.; Cui, Z.; Ge, M.; Zhang, K.-Q.; Chen, Z.; Chi, L. Recent Advances in TiO2-Based Nanostructured Surfaces with Controllable Wettability and Adhesion. Small 2016, 12, 2203–2224.

(14) Lai, Y.; Pan, F.; Xu, C.; Fuchs, H.; Chi, L. In Situ Surface-Modification-Induced Superhydrophobic Patterns with Reversible Wettability and Adhesion. Adv. Mater. 2013, 25, 1682–1686.

(15) Darmanin, T.; Godeau, G.; Guittard, F. Superhydrophobic, Superooleophobic and Underwater Superooleophobic Conducting Polymer Films. Surf. Innovations 2018, DOI: 10.1680/jsuin.18.00006.

(16) Zhao, Y.; Stejskal, J.; Wang, J. Towards Directional Assembly of Hierarchical Structures: Aniline Oligomers as the Model Precursors. Nanoscale 2013, 5, 2620–2626.

(17) Tan, L.; Cao, L.; Yang, M.; Wang, G.; Sun, D. Formation of Dual-Responsive Polystyrene/Polyaniline Microspheres with Sea Urchin-Like and Core–Shell Morphologies. Polymer 2011, 52, 4770–4776.

(18) Im, S. G.; Gleason, K. K. Systematic Control of the Electrical Conductivity of Poly(3,4-ethylenedioxythiophene) via Oxidative Chemical Vapor Deposition. Macromolecules 2007, 40, 6552–6556.

(19) Diouf, D.; Diouf, A.; Mortier, C.; Darmanin, T.; Dieng, S. Y.; Guittard, F. Poly(3,4-propylenedioxyxypyrrole) Nanofibers with Branched Alkyl Chains by Electropolymerization to Obtain Sticky Surfaces with High Contact Angles. ChemistrySelect 2017, 2, 9490–9494.

(20) Qu, L.; Shi, G.; Chen, F.; Zhang, J. Electrochemical Growth of Poly(3,4-ethylenedioxyxypyrrole) Microcontainers. Macromolecules 2003, 36, 1063–1067.

(21) 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-ethylenedioxyxypyrrole) Nanorod Arrays. Adv. Funct. Mater. 2013, 23, 3212–3219.

(22) Krompiec, M. P.; Baxter, S. N.; Klimareva, E. L.; Yufit, D. S.; Congrave, D. G.; Britten, T. K.; Perepichka, I. F. 3,4-Phenylenedioxyxypyrroles (PheDOTs) Functionalized with Electron-Deficient Side Groups. Chem. C 2018, 6, 3743–3756.

(23) Shao, S.; Shi, J.; Murtaza, I.; Xu, P.; He, Y.; Ghosh, S.; Zhu, X.; Perepichka, I. F.; Meng, H. Exploring the Electrochromic Properties of Poly(thieno[3,2-b]thiophene)s Decorated with Electron-Deficient Side Groups. Polym. Chem. 2017, 8, 769–784.

(24) Merz, A.; Schropp, R.; Dötterl, E. 3,4-Dialkoxyxypyroles and 2,3,7,8,12,13,17,21-octaalkoxyporphyrins. Synthesis 1995, 795–800.

(25) Schotland, P.; Zong, K.; Gaupp, C. L.; Thompson, B. C.; Thomas, C. A.; Giurgiu, I.; Hickman, R.; Abboud, K. A.; Reynolds, J. R. Poly(3,4-alkylenedioxyxypyrrole)s: Highly Stable Electronically Conducting and Electrochromic Polymers. Macromolecules 2000, 33, 7051–7061.

(26) Arroyave, F. A.; Reynolds, J. R. 3,4-Propylenedioxyxypyrrole-Based Conjugated Oligomers via Pd-Mediated Decarboxylative Cross Coupling. Org. Lett. 2010, 12, 1328–1331.

(27) Walczak, R. M.; Reynolds, J. R. Poly(3,4-alkylenedioxyxypyrroles): The PXDOPs as Versatile Yet Underutilized Electroactive and Conducting Polymers. Adv. Mater. 2006, 18, 1121–1131.

(28) Zong, K.; Reynolds, J. R. 3,4-Alkylenedioxyxypyrroles: Functionalized Derivatives as Monomers for New Electron-Rich Conducting and Electroactive Polymers. J. Org. Chem. 2001, 66, 6873–6882.

(29) Darmanin, T.; Guittard, F. Enhancement of the Superoxoleophobic Properties of Fluorinated PEDOP using Polar Glycol Spacers. J. Phys. Chem. C 2014, 118, 26912–26920.

(30) Mortier, C.; Darmanin, T.; Guittard, F. Major Influence of the Hydrophobic Chain Length in the Formation of Poly(3,4-propylenedioxyxypyrrole) (PPProDOP) Nanofibers with Special Wetting Properties. Mater. Today Chem. 2018, 7, 65–75.

(31) Mortier, C.; Darmanin, T.; Guittard, F. Direct Electrodeposition of Superhydrophobic and Highly Oleophobic Poly(3,4-ethylenedioxyxypyrrole) (PEDOP) and Poly(3,4-propylenedioxyxypyrrole) (PPProDOP) Nanofibers. ChemNanoMat 2017, 3, 885–894.