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

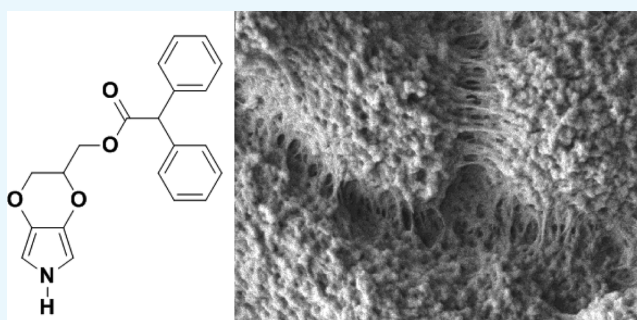
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ABSTRACT: In the aim to obtain parahydrophobic materials (both high contact angles and high hysteresis) for possible applications in water harvesting systems, we report the synthesis of novel 3,4-ethylenedioxyppyrrrole (EDOP) and 3,4-propylenedioxyppyrrrole (ProDOP) monomers with aromatic rings on the 3,4-alkylenedioxy bridge and the resulting conducting polymer films were prepared by electropolymerization. We show that the surface properties can be tuned by the nature of the aromatic ring (phenyl, biphenyl, diphenyl, naphthalene, fluorene, and pyrene) and the polymerizable core (EDOP or ProDOP). The best results are obtained with both EDOP and diphenyl, with which extremely high hydrophobic properties (up to 116°) are obtained, even if the polymers are intrinsically hydrophilic. These surfaces could be applied in the future, for example, in water harvesting systems or in water/oil separation membranes. The synthesis strategy is extremely interesting, and many other molecules will be envisaged in the future.



1. INTRODUCTION

Controlling the surface wettability is fundamental for various applications in self-cleaning surfaces, oil/water separation membranes, and sensors or in microfluidics.^{1–4} Inspired by natural surfaces, the surface hydrophobicity is depending on both the surface energy and the surface roughness and morphology.^{5–8} Indeed, in nature, we can find 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.^{5,6} In opposite, parahydrophobic properties, characterized by both high contact angles and high hysteresis, are present in rose petals or gecko foot.^{2,7,8} The processes to create structured surfaces are numerous and imply different treatments (chemical, physical, mechanical...) such as etching, plasma, laser, lithography, or templating.^{9–14}

Following the used process, conducting polymers can form nanostructured materials.^{15–18} This is possible not only in solution by self-assembly but also directly on surfaces inducing a high influence of the surface properties. The electropolymerization was revealed as a very interesting process because of an easy and fast control of the surface structures using various electrochemical parameters.^{19–23} 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) are exceptional monomers because of their ultralow exceptional potential, leading to polymers with unique optoelectronic properties.^{24–30} 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.^{25–28} 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.

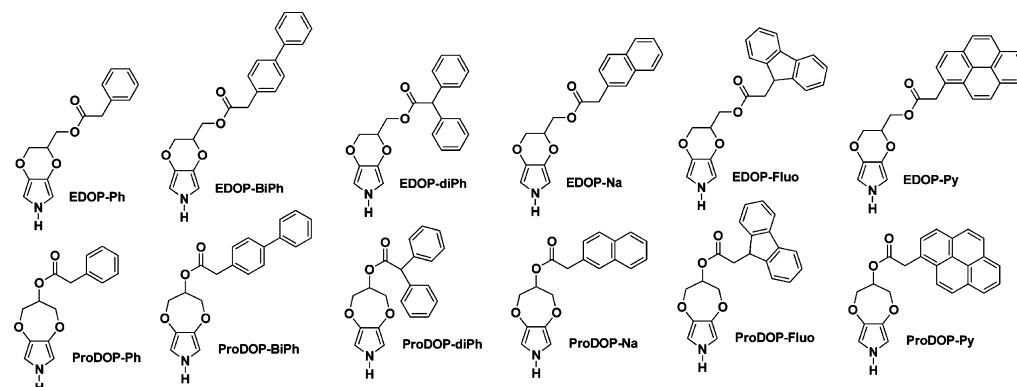
Previously, it was found a way to obtain EDOP and ProDOP derivatives with hydroxyl groups on the bridge using epibromohydrin.³¹ These monomers could be easily functionalized by simple esterification reaction. Thanks to the presence of NH groups, superhydrophobic nanofibers were obtained with fluorinated chains.

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Scheme 1. Original Monomers Studied in This Paper



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_4NClO_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 ProDOP) 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 are however observed with ProDOT-diPh, ProDOT-Fluo, and ProDOP-Py, indicating a significant steric hindrance. Moreover, using ProDOP derivatives, the polymer oxidation potentials [between -0.5 and 0 V vs saturated calomel electrode (SCE)] are very far from the monomer oxidation potentials, indicating 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_d) 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.³² 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 ProDOP-Ph, ProDOP-BiPh, and EDOP-diPh, whereas others are nanostructured such as the films obtained with ProDOP-Na, EDOP-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 ($R_a > 500\text{ nm}$). This increase is not possible using the Wenzel equation ($\cos \theta = r \cos \theta^Y$ where r is a roughness parameter) because the surface roughness would increase the surface hydrophilicity.³³ 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 θ but only if the contact angle of the smooth surface (θ^Y) 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.³⁴ The Cassie–Baxter equation is $\cos \theta = r_f \cos \theta^Y + f - 1$, where r_f is the roughness ratio of the substrate wetted by the liquid, f

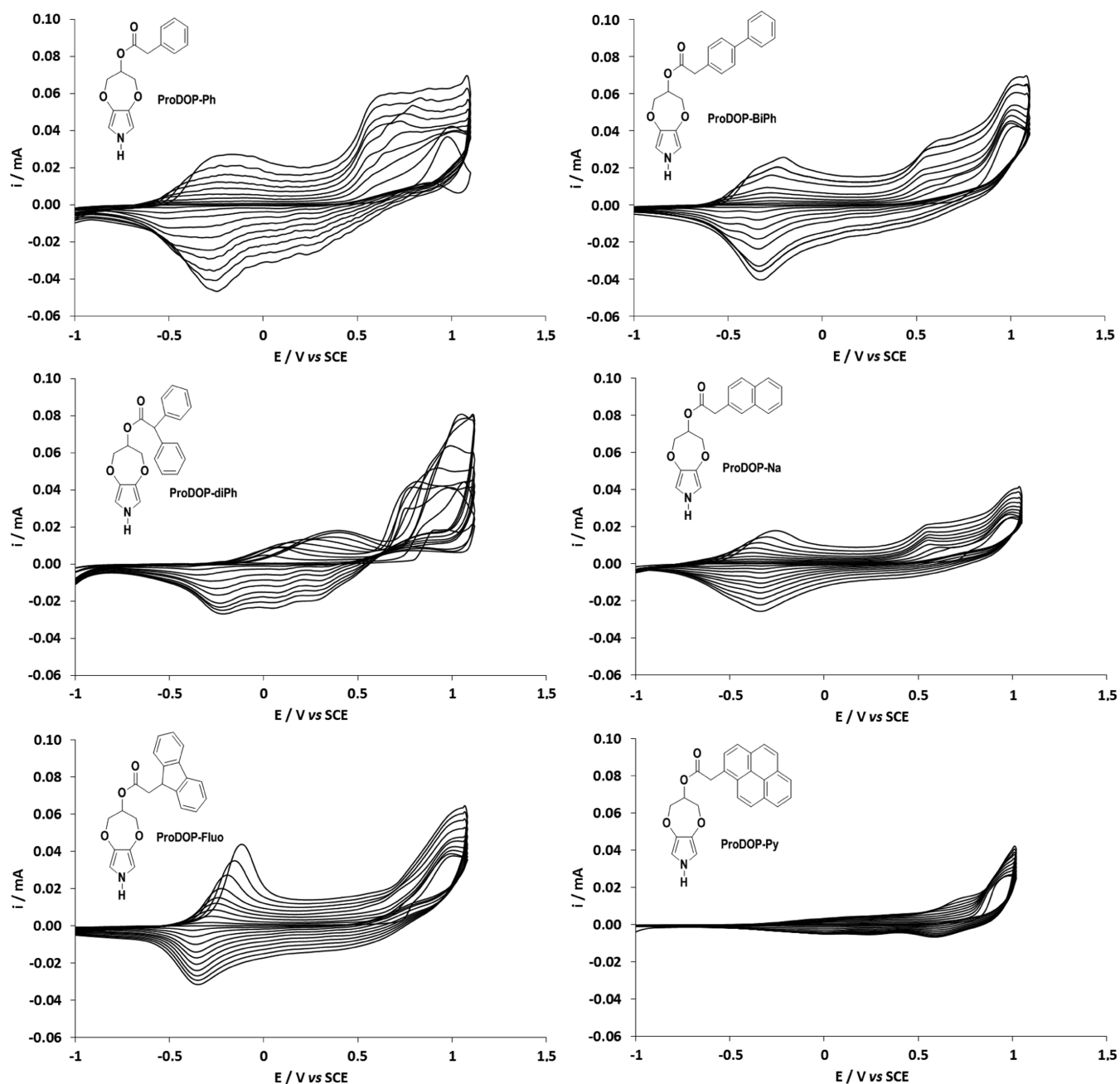


Figure 1. Cyclic voltammogram of the ProDOP monomers (0.01 M) in anhydrous acetonitrile containing 0.1 M Bu_4NClO_4 and at a scan rate of 20 mV s^{-1} ; working electrode: 3.14 mm^2 Pt tip.

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 θ 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_a 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

parahydrophobic properties because of the possible formation of long nanofiber structures, depending on their length.^{19,30}

3. CONCLUSIONS

Here, in the aim to prepare parahydrophobic 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

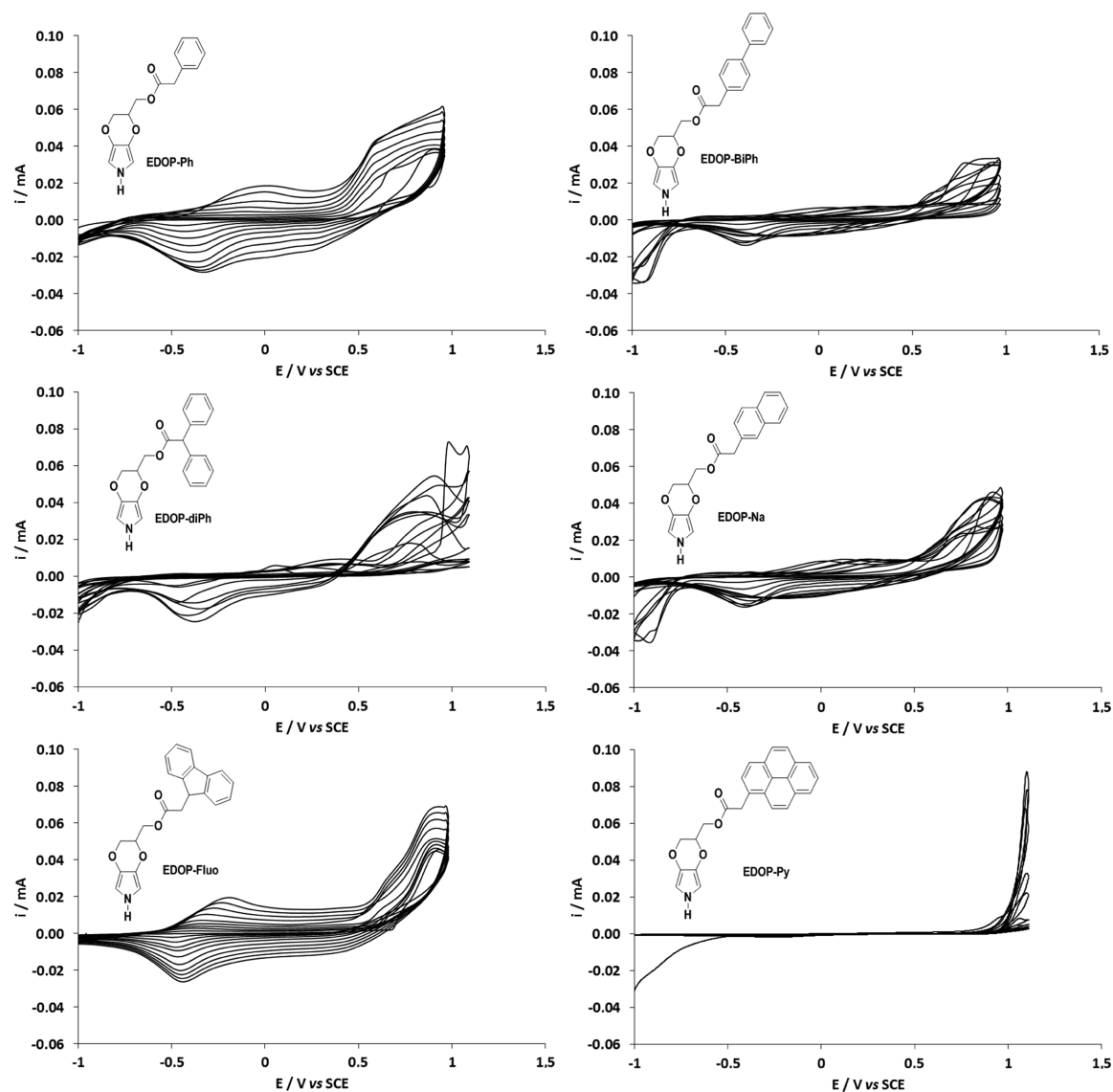


Figure 2. Cyclic voltammogram of the EDOP monomers (0.01 M) in anhydrous acetonitrile containing 0.1 M Bu_4NClO_4 and at a scan rate of 20 mV s^{-1} ; working electrode: 3.14 mm^2 Pt tip.

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.³¹ Indeed, from intermediate 1, it is possible to obtain and separate the EDOP and ProDOP derivatives 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; δ_{H} (200 MHz, CDCl_3): 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); δ_{C} (100 MHz, CDCl_3): 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 $[\text{M} - \text{H}]^+$ 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; δ_{H} (200 MHz, CDCl_3): 7.58

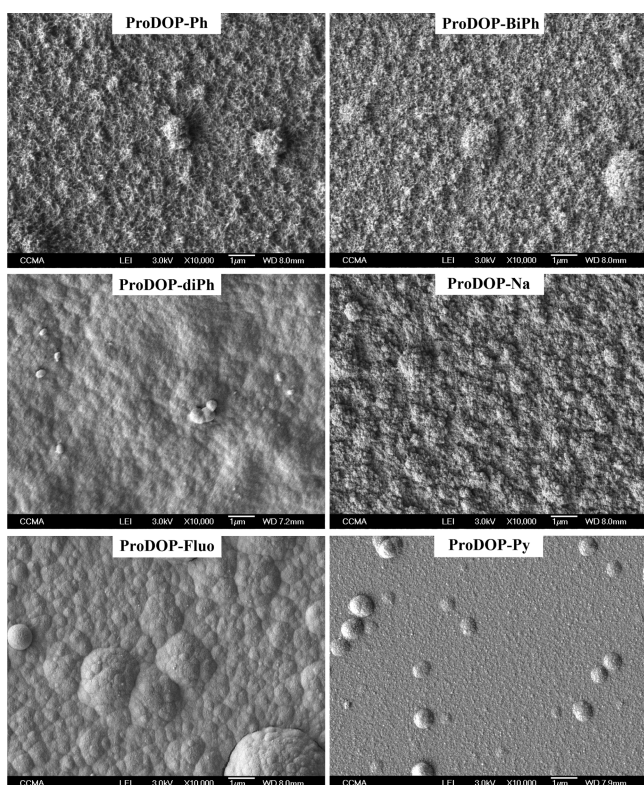


Figure 3. SEM images of the polymer surfaces obtained from ProDOP derivatives for a deposition charge of 400 mC cm^{-2} ; working electrode: 2 cm^2 Au-coated Si wafer.

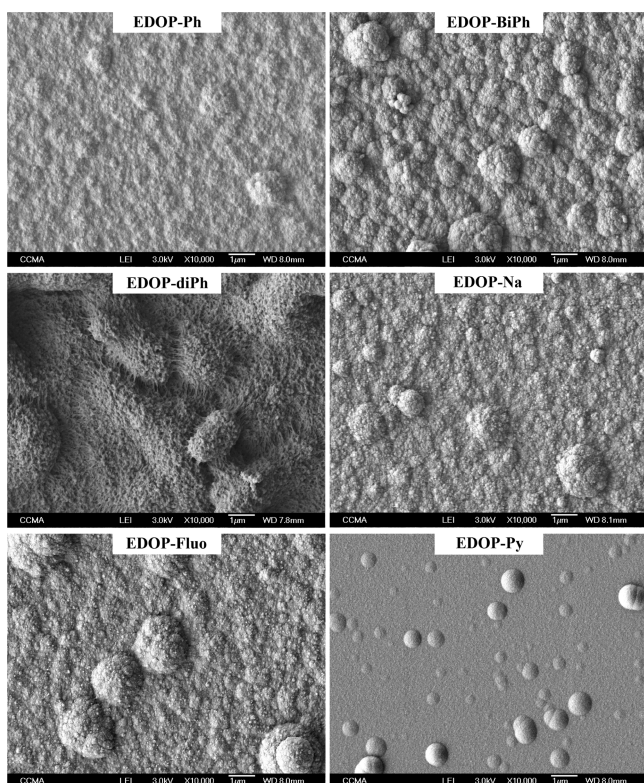


Figure 4. SEM images of the polymer surfaces obtained from EDOP derivatives for a deposition charge of 400 mC cm^{-2} ; working electrode: 2 cm^2 Au-coated Si wafer.

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

polymer	deposition charge [mC cm^{-2}]	R_a [nm]	R_q [nm]	θ_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
ProDOP-BiPh	400	200 ± 50	315 ± 65	92 ± 7.2
	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
ProDOP-diPh	200	19 ± 5	34 ± 8.4	91 ± 2.2
	400	288 ± 24	370 ± 48	99 ± 6.8
	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
ProDOP-Na	100	61 ± 11	100 ± 14	85 ± 3.3
	200	191 ± 31	277 ± 37	86 ± 3.0
	400	526 ± 35	818 ± 70	99 ± 4.2
	12.5	12 ± 2.4	15 ± 3.3	82 ± 4.5
	25	12 ± 1.4	22 ± 5.8	82 ± 4.9
ProDOP-Fluo	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
	12.5	15 ± 4.9	33 ± 10	73 ± 4.6
ProDOP-Py	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

(m, 4H), 7.41 (m, 5H), 7.19 (s, 1H), 6.33 (d, $J = 3.3 \text{ Hz}$, 2H), 5.22 (m, 1H), 4.26 (dd, $J = 12.5 \text{ Hz}$, $J = 4.9 \text{ Hz}$, 2H), 4.08 (dd, $J = 12.5 \text{ Hz}$, $J = 2.7 \text{ Hz}$, 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 $[\text{M} - \text{H}]^+$ 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 $133.1 \text{ }^\circ\text{C}$; δ_H (200 MHz, CDCl_3): 7.32 (m, 10H), 7.09 (s, 1H), 6.29 (d, $J = 3.3 \text{ Hz}$, 2H), 5.26 (m, 1H), 5.14 (s, 1H), 4.18 (dd, $J = 12.4 \text{ Hz}$, $J = 5.0 \text{ Hz}$, 2H), 4.09 (dd, $J = 12.4 \text{ Hz}$, $J = 3.1 \text{ Hz}$, 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 $[\text{M} - \text{H}]^+$ 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_H (200 MHz, CDCl_3): 7.72 (m, 4H), 7.39 (m, 3H), 7.11 (s, 1H), 6.24 (d, $J = 3.3 \text{ Hz}$, 2H), 5.13 (m, 1H), 4.17 (dd, $J = 12.5 \text{ Hz}$, $J = 4.9 \text{ Hz}$, 2H), 3.98 (dd, $J = 12.5 \text{ Hz}$, $J = 2.7 \text{ Hz}$, 2H), 3.82 (s, 2H); δ_C (100 MHz, CDCl_3): 170.99, 138.86, 133.44,

Table 2. Roughness (R_a and R_q) 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_q [nm]	θ_w [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 ± 4.7
	200	160 ± 65	213 ± 78	90 ± 4.3
	400	96 ± 25	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

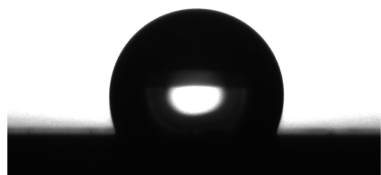


Figure 5. Example of contact angle measured on PEDOP-diPh with a deposition charge of 400 mC cm⁻².

132.51, 131.10, 128.29, 128.08, 127.71, 127.63, 127.29, 126.18, 125.84, 125.50, 103.13, 73.33, 72.52, 41.27; MS (ESI LC/MS): m/z [M - H]⁺ 324.07.

4.1.5. ProDOP-Fluo: 2,3,4,7-Tetrahydro-[1,4]dioxepino[2,3-c]pyrrol-3-yl 2-(9H-Fluoren-9-yl)acetate. Yield 49%; liquid; δ_H (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, 1H), 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_C (100 MHz, CDCl₃): 171.61, 146.00, 140.80, 138.80, 127.50, 127.19,

124.34, 119.94, 103.08, 73.15, 72.51, 43.48; MS (ESI LC/MS): m/z [M - H]⁺ 362.07.

4.1.6. ProDOP-Py: 2,3,4,7-Tetrahydro-[1,4]dioxepino[2,3-c]pyrrol-3-yl 2-(Pyren-1-yl)acetate. Yield 40%; crystalline solid; mp 163.1 °C; δ_H (200 MHz, CDCl₃): 8.18 (m, 5H), 8.00 (m, 4H), 7.20 (s, 1H), 6.32 (d, $J = 3.3$ Hz, 2H), 5.21 (m, 1H), 4.46 (s, 2H), 4.24 (dd, $J = 12.6$ Hz, $J = 4.9$ Hz, 2H), 4.04 (dd, $J = 12.6$ Hz, $J = 2.7$ Hz, 2H); δ_C (100 MHz, CDCl₃): 171.00, 131.29, 131.09, 130.92, 130.78, 129.45, 128.40, 128.01, 127.71, 127.38, 125.97, 125.51, 125.27, 125.17, 124.90, 124.73, 123.17, 73.44, 72.52, 39.24; MS (ESI LC/MS): m/z [M - H]⁺ 398.07.

98.65, 98.42, 72.01, 66.44, 63.10, 51.77;

4.1.7. EDOP-Ph: (3,6-Dihydro-2H-[1,4]dioxino[2,3-c]pyrrol-2-yl)methyl 2-Phenylacetate. Yield 41%; liquid; δ_H (200 MHz, CDCl₃): 7.31 (m, 5H), 7.10 (s, 1H), 6.20 (m, 2H), 4.30 (m, 3H), 4.11 (m, 1H), 3.96 (m, 1H), 3.68 (s, 2H); δ_C (100 MHz, CDCl₃): 171.25, 135.76, 133.58, 132.13, 131.88, 129.24, 128.61, 127.22, 125.50, 98.68, 98.47, 72.07, 66.51, 62.98, 41.06; MS (ESI LC/MS): m/z [M - H]⁺ 274.00.

4.1.8. EDOP-biPh: (3,6-Dihydro-2H-[1,4]dioxino[2,3-c]pyrrol-2-yl)methyl 2-([1,1'-Biphenyl]-4-yl)acetate. Yield 38%; liquid; δ_H (200 MHz, CDCl₃): 7.56 (m, 4H), 7.40 (m, 5H), 7.10 (s, 1H), 6.20 (m, 2H), 4.32 (m, 3H), 4.13 (m, 1H), 4.00 (m, 1H), 3.73 (s, 2H); δ_C (100 MHz, CDCl₃): 171.25, 140.72, 140.21, 138.86, 135.76, 132.59, 132.14, 129.68, 128.74, 127.37, 127.29, 127.06, 125.50, 98.68, 98.49, 72.09, 66.52, 65.84, 63.06, 40.67; MS (ESI LC/MS): m/z [M - H]⁺ 350.00.

4.1.9. EDOP-diPh: 2 (3,6-Dihydro-2H-[1,4]dioxino[2,3-c]pyrrol-2-yl)methyl 2,2-Diphenylacetate. Yield 45%; liquid; δ_H (200 MHz, CDCl₃): 7.31 (m, 10H), 7.10 (s, 1H), 6.18 (m, 2H), 5.09 (s, 1H), 4.38 (m, 3H), 4.10 (m, 1H), 3.90 (dd, $J = 11.5$ Hz, $J = 6.3$ Hz, 2H); δ_C (100 MHz, CDCl₃): 172.74, 138.29, 132.12, 131.85, 128.62, 128.58, 127.36, 98.66, 98.45, 72.00, 66.45, 63.09, 56.87; MS (ESI LC/MS): m/z [M - H]⁺ 350.07.

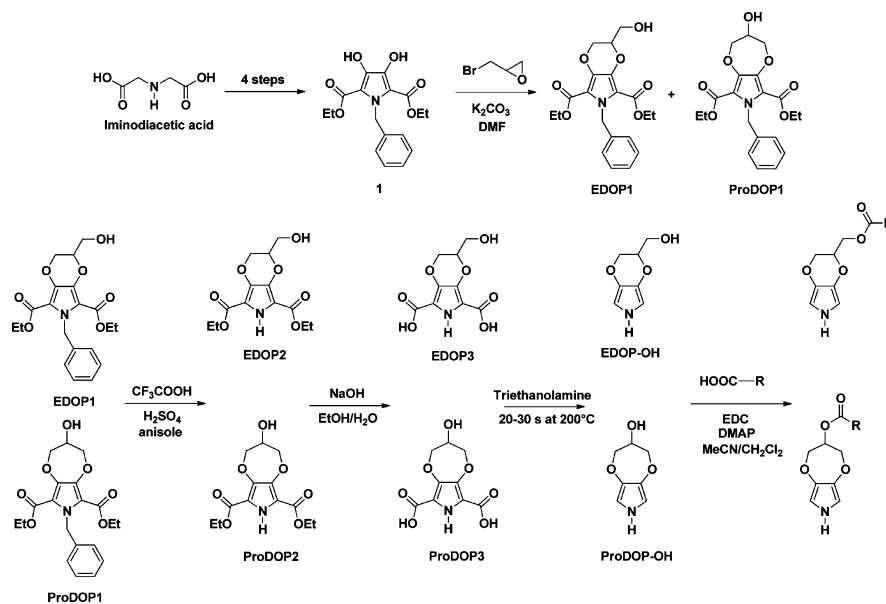
4.1.10. EDOP-Na: (3,6-Dihydro-2H-[1,4]dioxino[2,3-c]pyrrol-2-yl)methyl 2-(Naphthalen-2-yl)acetate. Yield 54%; liquid; δ_H (200 MHz, CDCl₃): 7.79 (m, 4H), 7.47 (m, 3H), 7.08 (s, 1H), 6.20 (m, 2H), 4.36 (m, 3H), 4.11 (m, 1H), 3.96 (m, 1H), 3.68 (s, 2H); δ_C (100 MHz, CDCl₃): 171.24, 135.77, 133.43, 132.51, 132.14, 131.88, 131.04, 128.31, 128.02, 127.67, 127.65, 127.25, 126.19, 125.88, 125.51, 98.69, 98.48, 72.08, 66.52, 63.06, 41.24; MS (ESI LC/MS): m/z [M - H]⁺ 324.00.

4.1.11. EDOP-Fluo: (3,6-Dihydro-2H-[1,4]dioxino[2,3-c]pyrrol-2-yl)methyl 2-(9H-Fluoren-9-yl)acetate. Yield 46%; liquid; δ_H (200 MHz, CDCl₃): 7.75 (m, 2H), 7.51 (m, 2H), 7.34 (m, 4H), 7.08 (s, 1H), 6.20 (m, 2H), 4.38 (m, 4H), 4.13 (m, 1H), 3.93 (dd, $J = 11.5$ Hz, $J = 6.6$ Hz, 2H), 2.90 (m, 2H); δ_C (100 MHz, CDCl₃): 171.97, 145.97, 140.78, 132.15, 131.88, 127.53, 127.20, 124.31, 119.96, 98.68, 98.48, 72.05, 66.49, 62.83, 43.47; MS (ESI LC/MS): m/z [M - H]⁺ 362.07.

4.1.12. EDOP-Py: (3,6-Dihydro-2H-[1,4]dioxino[2,3-c]pyrrol-2-yl)methyl 2-(Pyren-1-yl)acetate. Yield 58%; crystalline solid; mp 169.5 °C; δ_H (200 MHz, CDCl₃): 8.17 (m, 5H), 8.00 (m, 4H), 7.10 (s, 1H), 6.16 (m, 2H), 4.37 (m, 3H), 4.18 (m, 1H), 4.00 (m, 1H), 3.85 (s, 2H); δ_C (100 MHz, CDCl₃): 171.24, 132.06, 131.82, 131.28, 130.90, 130.75, 129.40, 128.32, 128.02, 127.59, 127.36, 125.99, 125.30, 125.17, 125.01, 124.86, 124.69, 123.11, 98.65, 98.42, 72.01, 66.44, 63.10, 39.20; MS (ESI LC/MS): m/z [M - H]⁺ 398.13.

4.2. Electropolymerization. The depositions were performed using an Autolab potentiostat of Metrohm. Three

Scheme 2. Synthesis Way to the Monomers



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 (R_a) and quadratic (R_q) 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 50X, and the field of view 0.5X. 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.

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Notes

The authors declare no competing financial interest.

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