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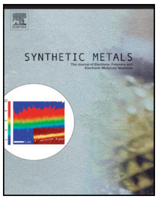

Superhydrophobic surface properties with various nanofibrous structures by electrodeposition of PEDOT polymers with short fluorinated chains and rigid spacers

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ABSTRACT

In the aim to produce superhydrophobic surface properties, the nanofibers are excellent candidates due to the possible control in the water adhesion by the nanofiber characteristics, for example. Here, we report the growth of nanofibers with various assemblies directly on surfaces by electropolymerization. For this purpose, an original 3,4-ethylenediothiophene monomer was synthesized. The monomer contains a short fluorinated chain (C_4F_9) in order to preserve the nanofiber morphology and a highly rigid methoxybenzothioate spacer for the reduction of the mobility. In this work, we show that various nanofibrous structures and superhydrophobic properties can be obtained by modifying the electrolyte while the surface roughness can also be controlled by the number of deposition scans. The nanofibrous polymers could be used to control the attachment and growth of cells or bacteria.

1. Introduction

Superhydrophobic surfaces, defined as surfaces with apparent water contact angles (θ) larger than 150° and low hysteresis, can be designed for many practical applications such as self-cleaning textiles, optical devices, sensors, solar cells, batteries, microfluidic devices, oil/water separation membranes, droplets manipulation, water purification, drag reduction, drug delivery, catalysis or for the inhibition of the corrosion and bacterial adhesion [1–3]. The study of the surface morphology and chemical composition of natural superhydrophobic surfaces pointed out the importance of these two parameters on the surfaces wettability [4–6]. Indeed following the Wenzel and Cassie–Baxter equations [7,8], a surface roughness is essential for generating superhydrophobic properties while the adhesion properties can be tuned with the surface topography parameters and intrinsic hydrophobicity of the materials. To enhance the surface roughness, various methods have been developed, which are usually regrouped in two categories: the top–down approaches (for example lithography or templating, plasma etching) and the bottom–up approaches (for example layer-by-layer assembly, assembly of particles or electrochemical polymerization) [9–12]. In order to control the adhesion of superhydrophobic materials, the use of nanofibers to structure the surface is a key parameter [13]. Indeed, the adhesion can be controlled by playing on the nanofibers length, diameter, the inter-fiber distance, their orientation to the substrate or their surface chemistry [14,15]. For example, the gecko is able to walk on vertical surfaces thanks to intrinsic hydrophilic micron-sized dense setal hairs on their feet [16,17].

Conducting polymers can produce nanofiber morphology during their synthesis [18–20]. Due to the presence of hydrogen bonds, polyaniline is actually the most used conducting polymer. Nanofibers as well as nanofiber-assemblies such as rambutan-like or dandelion-like structures could be produced in solution [21–23]. Due to exceptional optical and electronic properties, poly(3,4-ethylenedioxythiophene) (PEDOT) and their derivatives are unique conducting polymers [24–27]. However, it is often necessary to use nanostructured materials [28], surfactants [29] or chemical seeds [30] to produce PEDOT nanofibers in solution. Hopefully, the template-less electrodeposition process can induce the formation of PEDOT nanofibers directly on a substrate used as working electrode [31–35]. The process consists in a monomer oxidation using a potentiostat. The PEDOT nanofiber characteristics can be easily controlled with the used electrolyte or

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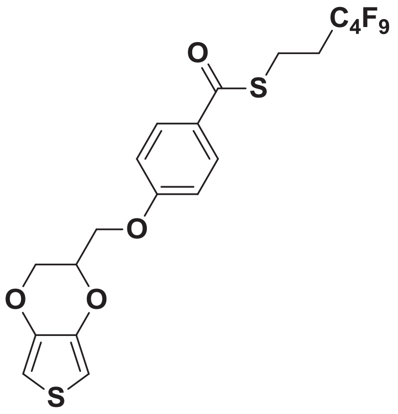


Scheme 1. Original monomer studied in with work.

deposition method. In order to tune both the nanofiber characteristics and the surface hydrophobicity and adhesion, the best way is to introduce a hydrophobic or hydrophilic substituent. Indeed, various fluorocarbon and hydrocarbon chains were introduced and it was shown that the nanofiber characteristics were highly dependent on the substituent intrinsic hydrophobicity and that short hydrophobic chains are preferred to preserve the nanofiber morphology while long hydrophobic chains often lead to spherical or cauliflower-like structures [34,35]. Moreover, the use of short fluorinated chains allows to reduce the bioaccumulative potential of fluorinated materials. Indeed, it was demonstrated that the bioaccumulative potential is dependent on the fluorinated chains and that materials with short fluorinated chains can be envisaged as non-bioaccumulative alternatives [36].

Here, we report the formation of superhydrophobic nanofibrous structures using the original monomer represented in Scheme 1. The monomer bears a short fluorinated chain (C_4F_9). Due to much lower intermolecular interactions, the short C_4F_9 chains are very mobile in comparison to long C_8F_{17} chains, which is sometimes problematic because the substituent rigidity is an important parameter in the properties of conducting polymers. Hence, a highly rigid methoxybenzothioate spacer was chosen in order increase the substituent rigidity while preserving nanofibrous morphologies.

2. Experimental

2.1. Synthesis

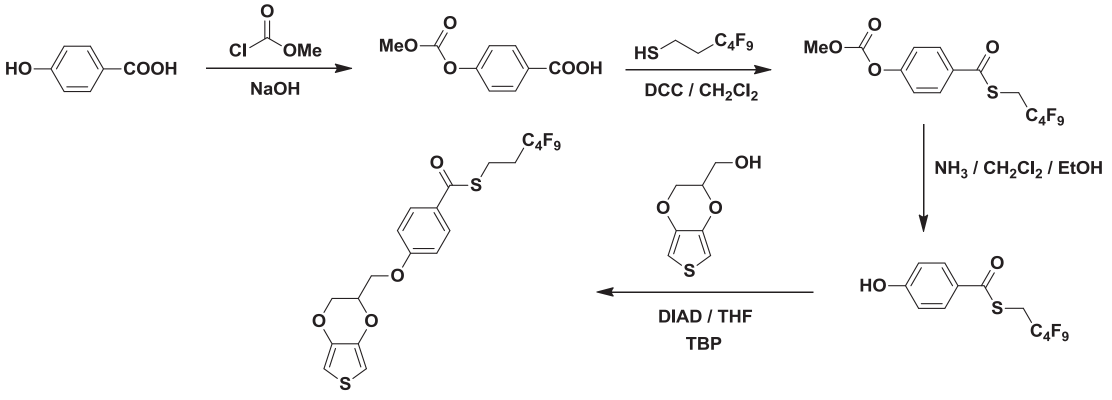
In this work, an EDOT derivative incorporating a rigid segment with a perfluorobutyl chain (C_4F_9) was synthesized following the chemical way schematized in Scheme 2. The rigid segment (*S*-3,3,4,4,5,5,6,6,6-nonafluorohexyl 4-hydroxybenzothioate) consists in a rigid single phenyl group bound to a pro-mesogenic perfluoroalkyl tail by a thioester connector and its introduction to synthesize many liquid crystalline molecule was already be reported [37,38]. Their incorporation in EDOT was performed from (2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl)methanol and via a Mitsunobu reaction with diisopropylazodicarboxylate (DIAD) and tributylphosphine (TBP) in anhydrous THF. More precisely, DIAD (0.8 ml, 3.9 mmol) was slowly added to a solution of (2,3-dihydrothieno[3,4-*b*][1,4]dioxin-2-yl) methanol (0.33 g, 2.0 mmol), TBP (1 ml, 3.9 mmol) and *S*-3,3,4,4,5,5,6,6,6-nonafluorohexyl 4-hydroxybenzothioate (0.8 g, 2.0 mmol), in absolute THF under exclusion of light and argon. The reaction mixture was stirred during two days at 48 °C. The solvent was then removed and hexane (5 ml) was added. After vigorous stirring, the product precipitated. After purification by column chromatography (silica gel; eluent = dichloromethane) the products were yielded as white solids.

2.1.1. S-3,3,4,4,5,5,6,6,6-nonafluorohexyl 4-((2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxy)benzothioate

Yield 51%. White solid. m.p. 133 °C. 200 MHz ^{1}H NMR ($CDCl_3$): δ 2.48 (tt, $^3J_{H,F} = 7.8$ Hz, $^2J_{H,H} = 18.1$ Hz, 2H), 3.27 (t, $^3J_{H,F} = 7.8$ Hz, 2H), 4.17–4.39 (m, 4H), 4.57 (m, 1H), 6.38 (s, 2H), 6.94 (d, $^3J_{H,H} = 8.9$ Hz, 2H), 7.94 (d, $^3J_{H,H} = 8.9$ Hz, 2H). 50 MHz ^{13}C NMR ($CDCl_3$): δ 19.96 (t, *J* 4.6), 31.77 (t, *J* 21.5), 65.59, 66.30, 71.60, 100.16, 114.44, 129.52, 130.03, 140.86, 141.85, 162.51, 189.21. 188 MHz ^{19}F NMR ($CDCl_3$): −126.45 (m, 2F), −124.77 (m, 2F), −115.17 (m, 2F), −81.42 (m, 3F); IR ν_{max}(cm^{-1}): 3112, 2928, 1653 (SC=O), 1599, 1483, 1249, 1218, 1130 cm^{-1}. MS (70 eV, *m*/*z*): 554 (M^+, 7%), 275 ($C_{14}H_{11}O_4S^{+\bullet}$, 82%), 155 ($C_7H_7O_2S^{+\bullet}$, 27%), 121 ($C_7H_5O_2^{+\bullet}$, 100%).

2.2. Electrochemical polymerization

The electrochemical polymerization of the monomer was performed in anhydrous acetonitrile and using different electrolytes (0.1 M): tetrabutylammonium perchlorate (Bu_4NClO_4), tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), tetrabutylammonium trifluoromethanesulfonate ($Bu_4NCF_3SO_3$),



Scheme 2. Synthesis of the monomer.