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Acids and alkali resistant sticky superhydrophobic surfaces by one-pot electropolymerization of perfluoroalkyl alkyl pyrrole

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ABSTRACT

Over the past few years, electropolymerization of semifluorinated monomers like thiophene or pyrrole has been used as a gentle and effective method to generate, in one step, stable superhydrophobic surfaces. The synthetic route mostly involves the coupling reaction between a carboxylic acid and an alcohol, using a carboxy group-activated reagent and a catalyst. As a consequence, the electroformed surfaces present high liquid repellency due to the concomitant effect of roughness and low surface energy. Nevertheless, the ester connector can be cleaved under acidic and basic conditions, preventing its use under a range of environmental conditions. To overcome this drawback, a new perfluoroalkyl alkyl pyrrole has been synthesized, the fluorinated segment being connected to the electropolymerizable part via an alkyl chain, and electropolymerized, leading to surfaces that exhibit a static contact angle with water superior to 150° and no sliding angle, over a wide pH range and with a long lifetime. This represents the first example of a pure conducting polymer surface with sticky superhydrophobicity not only in pure water but also in corrosive solutions such as acids and bases, giving rise to new prospects in practical applications.

1. Introduction

The wettability of a solid surface by liquids, particularly water and oil, represents a major and essential property both from an academic point of view and for many practical and industrial applications. Especially, the creation of super wetting (contact angle close to 0°) or/and super nonwetting (contact angle superior to 150°) surfaces has generated a great area of research. In general, the wettability of a solid substrate is governed by both the chemical composition of the extreme surface and its roughness and porosity. Controlling these two parameters has permitted the design and creation of organic, inorganic, and hybrid surfaces with special wettabilities [1]. Among the materials used, the conducting polymers have recently appeared as a very convenient and straightforward candidate for designing such surfaces. Indeed, a huge advantage consists in the possibility of obtaining structured films deposited directly onto a solid electrode, in one step and under mild conditions, by the electropolymerization technique. Moreover, the functionalization of the monomer before polymerization allows controlling the surface energy of the surface. For instance, stable superhydrophobic films of poly(alkylpyrrole) [2] and poly(fluorinated thiophene) [3] have been achieved by electropolymerization. More recently, the covalent binding of low free energy fluorinated chains on the ethylenedioxythiophene monomer before polymerization gave rise to a superhydrophobic behavior while conserving the superoleophilicity due to the polymer backbone. It holds the promise of an interesting candidate for the separation of water and oil [4].

In the large family of conducting polymers, due to the ease of substitution on the N and/or 3 positions together with a low oxidation potential, a high stability in the p-doped state, and a redox activity in aqueous media, polypyrrole (PPy) and its derivatives have been largely studied and used for different applications including sensors, batteries, etc. [5]. In the field of surface science, the introduction of low free energy substituents such as alkyl or fluorinated chains, by a prefunctionalization [2] or as a codopant [6], has permitted the obtaining of high or superhydrophobic PPy surfaces, depending on electrosynthesis conditions, while PPy itself is wettable by liquids [7]. Nevertheless, very few syntheses of fluorinated PPy, with the 2 and 5 positions free for the oxidative polymerization, have been reported in the literature [8]. It is only recently that our group reports the synthesis of pyrrole monomers connected to a fluorinated segment via an ester spacer [9]. The electrodeposited films showed high hydrophobicity and very good oil repellency. As known the ester group is sensitive to acidic or alkaline conditions and can cleave, leading to the loss of fluorinated segments and consequently to the loss of the high

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hydrophobic behavior. Thus, for application where acid and alkali resistance is needed, such as corrosion, it would be of interest to connect the fluorinated chain directly via an alkyl spacer.

This paper reports the synthesis of a perfluoroalkyl alkyl pyrrole, its electrochemical polymerization, and its thermal and surface properties, which are compared to nonsubstituted polypyrrole. The emphasis is on its wettability with acidic and alkaline aqueous solutions and the results are compared with the ones obtained with the polypyrrole films in which the fluorinated segments were connected via en ester linker, so as to be aware of the efficiency and the resistance of such surfaces. As a result, stable sticky superhydrophobic surfaces were obtained whatever the pH of the aqueous solution. They can have practical uses as in adhesion, lubrication, and anticorrosion protection in various environments, especially under harsh conditions.

2. Experimental

All organic reactions were carried out under nitrogen. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ solution with a Bruker AC 200 spectrometer. Silica gel (230–400 mesh, 40–63 μm) for column chromatography was purchased from Merck. Mass spectra were measured with a Thermo Quest Automass III spectrometer equipped with an electron ionization source (70 eV) and a quadripole analyzer, fitted with a TraceGC gas chromatograph.

2.1. Synthesis of the monomer

In a three-neck flask under nitrogen, pyrrolyl potassium salt (5 mmol, 526 mg) is dissolved in 2 mL of DMSO and then 5 mL of THF is added. A solution of perfluoroalkyl alkyl tosylate (5 mmol, 2.232 g) in about 2 mL of THF is slowly added to permit heat elimination. After a few hours stirring, the solution is poured into 50 mL of water saturated with sodium sulfate and extracted several times with diethyl ether. The organic phases are gathered, dried with $MgSO_4$, and concentrated to dryness under reduced pressure and the crude oil is purified by column chromatography.

Py-RF$_6$: 1-(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)-1H-pyrrole.

Yield: 49%; eluent: petroleum ether; colorless liquid; $\delta_H(CDCl_3)$: 6.65 (t, 2 H, H_{Py}, $^3J_{HH} = 2.0$ Hz), 6.17 (t, 2 H, H_{Py}, $^3J_{HH} = 2.0$ Hz), 3.93 (t, 2 H, Py-CH_2–CH_2, $^3J_{HH} = 6.9$ Hz), 1.53–2.18 (m, 6 H, $(CH_2)_3$–CF_2); $\delta_C(CDCl_3)$: 120.78 and 108.69 (C_{Py}), 49.50 (Py-CH_2), 31.38 (Py-CH_2–CH_2), 30.79 (t, CH_2–CF_2, $^2J_{CF} = 22.3$ Hz), 18.12 (t, CH_2–CH_2–CF_2, $^3J_{CF} = 3.9$ Hz); $\delta_F(CDCl_3)$: −126.61 (m, 2 F, CF_2–CF_3), −124.04 (m, 2 F, CF_2–CF_2–CF_3), −123.38 (m, 2 F, CF_2–CF_2–CF_2–CH_2), −122.42 (m, 2 F, CF_2–CF_2–CH_2), −114.97 (m, 2 F, CF_2–CH_2), −81.22 (tt, 3 F, CF_3, $^3J_{FF} = 10.5$ Hz, $^4J_{FF} = 2.6$ Hz); MS (EI, 70 eV): 441 (M^+).

2.2. Electropolymerization

The electrolytic solution (tetra-*n*-butylammonium hexafluorophosphate Bu_4NPF_6 puriss., electrochemical grade, from Fluka, 10^{-1} M in acetonitrile, anhydrous analytical grade, from Fluka) was degassed with argon prior to use and all experiments were carried out at room temperature. Cyclic voltammetry experiments were performed with an Autolab PGSTAT 30 potentiostat from Eco Chemie B.V. equipped with General Purpose Electrochemical System GPES software (version 4.9 for windows). The working electrode was either a platinum disk (area = 7.1 mm^2) or an ITO plate (area = a few cm^2) and the counterelectrode a glassy carbon rod. All potentials were relative to the calomel saturated electrode (CSE) reference electrode ($E' = 0.24$ V/NHE, i.e., the normal hydrogen electrode).

The polymer films for thermal and surface analysis were potentiostatically electroformed on ITO with an anodic limit close to the irreversible peak of the corresponding monomer, under the following conditions: applied voltage, 1.25 V; monomer concentration, 20 mM; reaction time, 300 s. The films were washed with acetonitrile to eliminate reactants and finally dried.

2.3. Thermal properties

The thermogravimetric measurements were made on a TGA 851^e from Mettler-Toledo. The microbalance has a precision of ±0.1 μg and was kept at constant temperature (22 °C) during analyses to avoid the variation of weight measurement with temperature. Samples of about 5 mg were placed into 70-μL alumina pans. The samples were heated from 35 °C to 950 °C at 7 K min^{-1} under synthetic air flow of 30 mL min^{-1}.

2.4. Surface characterization techniques

Contact angles measurements were performed using the sessile drop method on a Krüss DSA10 contact angle goniometer. The angles reported here were the averages of at least five measurements. They were recorded at 22 ± 1 °C using distilled water, buffer solutions, hydrochloric acid and hydroxide sodium solutions, and diiodomethane and hexadecane as wetting liquids. Water and hexadecane contact angles were taken as the index of the hydrophobicity and lipophobicity, respectively. Surface energy, γ, and its dispersive and polar components, denoted as γ^d and γ^p, respectively, were evaluated using the Owens, Wendt, Fowkes concept [10].

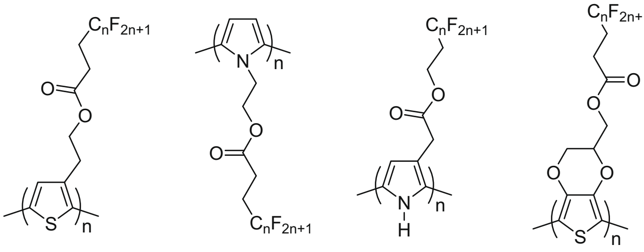

Fig. 1. Some semifluorinated electroformed polymers.

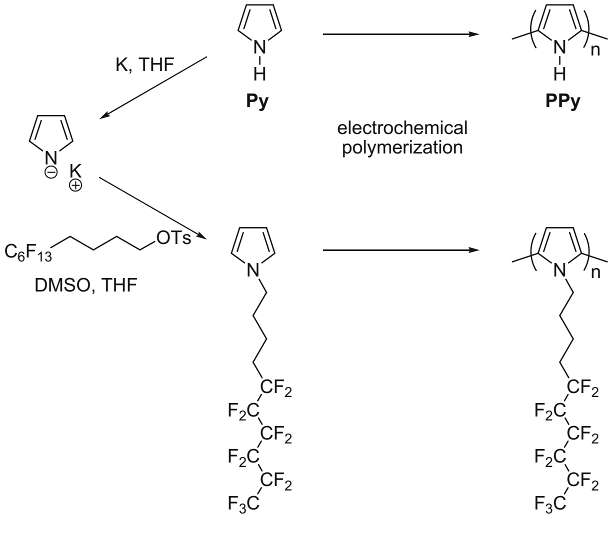

Fig. 2. Synthesis of the monomer and polymers.