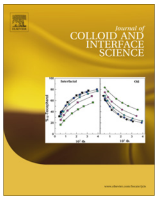
Journal of Colloid and Interface Science 408 (2013) 101–106

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis



Superoleophobic polymers with metal ion affinity toward materials with both oleophobic and hydrophilic properties

Thierry Darmanin, Frédéric Guittard *

Univ. Nice Sophia Antipolis, CNRS, LPMC, Groupe Surfaces & Interfaces, 06100 Nice , France

ARTICLE INFO

Article history:
Received 23 April 2013
Accepted 2 July 2013
Available online 18 July 2013

Keywords:
Oleophobicity
Hydrophilicity
Conductive polymers
Low fluorinated materials
Bioaccumulation

ABSTRACT

Bis(trifluoromethane)sulfonimide salts are used as electrolyte for the elaboration of superoleophobic properties by electrodeposition using a monomer containing a short perfluorobutyl (C_4F_9), separated from the polymer backbone by a long alkyl spacer, to reduce the mobility of these chains, and an amido connector to form complexes with ions. The electrodeposition in some of these electrolytes induces the formation of microstructures composed of nanosheets able to reach superoleophobic properties. When complexant ions (Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}) are used as cation of the electrolyte, these ions are incorporated in the polymer leading to a material with higher oleophobicity than hydrophobicity. Indeed, when a water droplet is deposited on the surface, the migration of the ions induces a decrease in the surface hydrophobicity, while the deposition of an oil droplet (diiodomethane or hexadecane) does not induce this migration. If the incorporation of these ions is not sufficiently stable for applications in oil/water separation, this work opens new strategies in the elaboration of both superoleophobic/oleophobic and superhydrophilic/hydrophilic materials. Such materials can also be used for the ion capture and release.

1. Introduction

Surfaces with very high oil-repellent properties, also named superoleophobic surfaces, are highly in demand for their potentials applications in microfluidic devices [1], oil transportation [2], anti-soil fabric[3] or printing technologies [4], for example. Due to the extremely low surface tension of oils, such surface properties are very difficult to obtain.

It was demonstrated that the combination of fluorinated materials with specific surface structures, known as re-entrant structures such as overhang, T-like or mushroom-like structures is ideal to reach such properties [5–8]. Indeed, if the Wenzel and Cassie–Baxter equations [9,10] are often used to predict the possibility to reach superhydrophobic properties, the presence of re-entrant structures induces a supplementary energy barrier between the Wenzel and the Cassie–Baxter by changing the liquid–vapor interface from concave to convex, which makes possible to stabilize the Cassie–Baxter state even with low surface tension liquids [11–14]. However, the elaboration of such surface structures by lithographic processes, which need various isotropic and anisotropic etchings, is too complex for industrial applications and other strategies were developed.

The electrochemical deposition of conducting polymers allows to induce the formation of various surface structures with an easy control of the polymer growth [15]. When a hydrophobic substituent is directly grafted to the monomer, the process can lead in one step to superhydrophobic or superoleophobic properties [16–20]. It was demonstrated that fluorinated 3,4-ethylenedioxypyrrole (EDOP) derivatives are, up to now, the best derivatives for the obtaining of superoleophobic properties, due to the self-organization of the polymer into nanoporous structures [20].

Due to the bioaccumulative potential of long perfluorinated substances [21–23], the elaboration of superoleophobic surfaces using short perfluorinated chains such as perfluorobutyl (C_4F_9) chains is a key challenge. However, this challenge is very difficult to reach due to the much lower intrinsic oleophobicity of perfluorobutyl tails, due to much lower interchain interactions, in comparison with perfluorohexyl or perfluorooctyl tails [24]. Previously, we showed the possibility to obtain superoleophobic properties with short perfluorobutyl (C_4F_9) chains using appropriate spacer and connector in order to reduce the mobility of these short fluorinated chains [25].

If most of superoleophobic surfaces reported in the literature are also superhydrophobic, surfaces being both superoleophobic/oleophobic and superhydrophilic/hydrophilic showed promising properties for oil/water separation [26–30]. However, such materials are extremely rare in the literature. In the literature, it was showed that the possibility to obtain both superoleophobic/oleophobic and superhydrophilic/oleophilic properties using polymers containing both oleophobic and hydrophilic groups [26,27]. For example, Zhang et al. obtained superhydrophilic and superoleophobic coating by spray casting suspensions containing a polymer (poly(diallyldimethylammonium perfluorooctanoate)) with both hydrophilic (ammonium + acetate groups) and oleophobic groups

---

* Corresponding author. Fax:+33492076156 email: guittard@unice.fr.
E-mail address: guittard@unice.fr (F. Guittard).

0021-9797/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2013.07.009

(perfluoroheptane) [26]. Other groups also reported the possibility to obtain materials with higher oleophobicity than hydrophobicity using polymers containing perfluorinated groups and other hydrophilic moieties (for example poly(ethylene glycol), carboxylic acid, hydroxyl) [27].

Here, we choose to introduce hydrophilic species and more precisely metal ions in the structure of a superoleophobic polymer. The monomer EDOP-C_{11}-NH-F_4, represented in Fig. 1, was chosen for the experiments. The amide connector between the polymer backbone and the fluorinated chain may form complexes with metal ions, as already shown in the literature [31]. The monomer was electrodeposited in presence of various complexant and non-complexant ions in order to investigate the effect of the ion incorporation on the surface properties. The surface properties were determined by contact angle measurements with three liquid probes (water, diiodomethane and hexadecane), optical profilometry and scanning electron microscopy.

2. Experimental

2.1. Electropolymerization conditions

The monomer EDOP-C_{11}-NH-F_4 was obtained in nine steps from iminodiacetic acid, following a procedure reported in the literature [32]. The electrolytes used for the experiments were bis(trifluoromethane)sulfonimide lithium ($LiTf_2N$), sodium ($NaTf_2N$), magnesium ($Mg(Tf_2N)_2$), calcium ($Ca(TF_2N)_2$), barium ($Ba(Tf_2N)_2$), triethylsulfonium ($SuTf_2N$), trihexyltetradecylphosphonium ($PhTf_2N$), tetrabutylammonium (Bu_4NTf_2N), 1-butyl-1-methylpyrrolidinium ($PyrTf_2N$), and 1-ethyl-3-methylimidazolium ($ImTf_2N$) salts. An electrochemical cell was connected to a potentiostat using a three-electrode system. After degassing with argon, 10 mL of anhydrous acetonitrile containing 0.1 M of an electrolyte and 0.01 M of EDOP-C_{11}-NH-F_4 was introduced. A large gold plate, a glassy carbon rod, and a satured calomel electrode (SCE) were used as working electrode, counter-electrode, and reference electrode, respectively. The determination of the monomer oxidation was determined by cyclic voltammetry. The deposition was performed at constant potential (E slightly lower to the monomer oxidation potential) and using a deposition charge (Qs) of 225 mC cm^{-2}. The deposition charge was chosen because it gave the best oleophobic properties.

2.2. Surface characterization

The apparent contact angles (θ) were determined using a goniometer for characterization of rough and chemically heterogeneous surfaces [33]a. Three probes liquid of different surface tension were used: water ($\gamma_L = 72.8$ mN/m), diiodomethane ($\gamma_L = 50.0$ mN/m), and hexadecane ($\gamma_L = 27.6$ mN/m). The angles were determined by depositing 2 μL droplets and using the sessile drop method. The surface morphology was determined by scanning electron microscopy using 6700F microscope of JEOL. The arithmetic (Ra) and quadratic surface (Rq) roughness as well as the surface area were determined using a Wyko NT 1100 optical microscopy of Bruker. Ra corresponds to the arithmetic average of the absolute values of the roughness profile, while Rq corresponds to the root mean square average of the roughness profile.

The analyzed areas were 182 μm× 239 μm. The roughness parameter *r* of the Wenzel equation was also determined by optical profilometry. It corresponds to the ratio of the real surface in contact with liquid to its projection onto the horizontal plane, as defined by de Gennes and co-authors [33]b.

3. Results and discussion

3.1. Surface wettability

Bis(trifluoromethane)sulfonimide salts were chosen because there are known to highly increase the surface hydrophobicity [34,35]. Using non-complexant ions (Su^+, Ph^+, Bu_4N^+, Pyr^+, Im^+), superhydrophobic surfaces were obtained with θ_{water} above 157° (Table 1). The dynamic contact angle measurements showed that the lowest adhesion of water droplet is obtained for $LiNTf_2N$ ($H_{water} = 21°$, $\alpha_{water} = 13°$). The fact that H and α are above 10° indicates that the water droplet is not in a Cassie–Baxter state but probably in an intermediate state between the Wenzel and the Cassie–Baxter states (High-stick Cassie impregnating state), as previously described by Bico, Quere, and Thiele [36,37]. Moreover, superoleophobic or highly oleophobic properties were obtained with each electrolyte showing the bis(trifluoromethane)sulfonimide salts are excellent candidates for obtaining highly oleophobic properties (Table 1). The best results were obtained with Bu_4NTf_2N and $LiNTf_2N$ for which $\theta_{hexadecane}$ of 130.0° and 126.9° were reached. However, hexadecane droplets remained stuck on these surfaces after inclination. Indeed, the decrease in the surface tension of the liquid probe induced, here, a high penetration of the liquid inside the surface roughness. As a consequence, water droplets are relatively close to the Cassie–Baxter state, while hexadecane droplets are closer to the Wenzel state. These results are exceptional for a polymer containing *F*-butyl tails and confirm the importance to reduce the mobility of these chains (here using a long alkyl spacer and an amide connector).

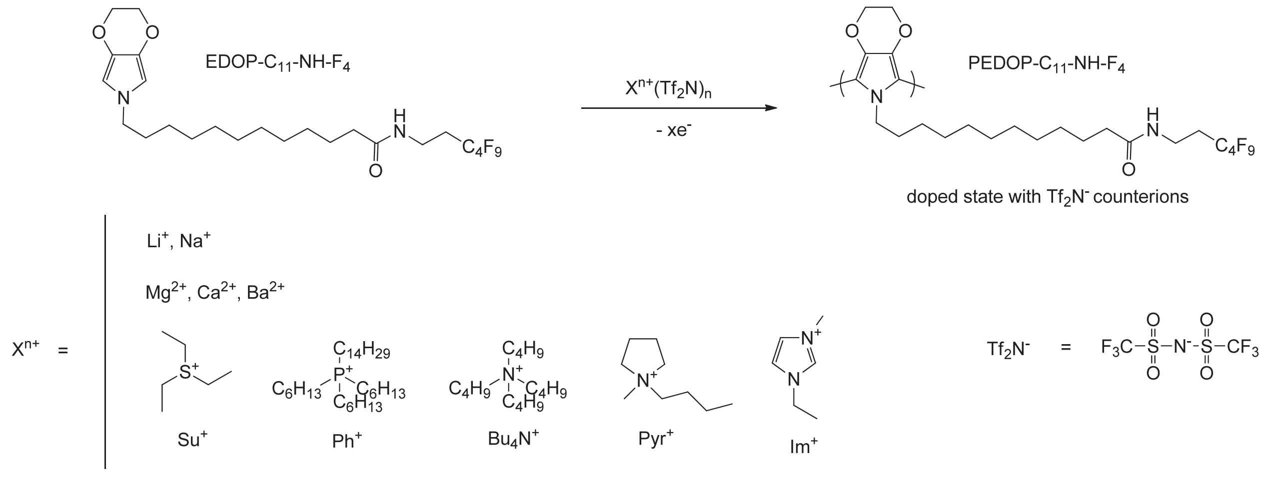


Fig. 1. Schematic representation of the electrodeposition.