



Effect of hydrocarbon chain branching in the elaboration of superhydrophobic materials by electrodeposition of conducting polymers

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ABSTRACT

Here, we study for the first time the influence of hydrocarbon chain branching on the formation of surface structures and on superhydrophobic properties obtained by electrodeposition of conducting polymers. Two series of 3,4-ethylenedioxythiophene (EDOT) derivatives with branched hydrocarbon chains were synthesized and the surface properties were compared with linear hydrocarbon chains. We show that hydrocarbon chain branching reduces the intrinsic hydrophobicity of the substituent. As a consequence, the branching can lead to smoother films, due to the increase in the solubility of the oligomers formed in the first instances of the polymerization, than that obtained with linear hydrocarbon chains. Here, highly structured films with non-wetting properties close to superhydrophobic properties are obtained with linear hydrocarbon chains from a total number of carbon of 8 while relatively smooth hydrophobic films are obtained with branched hydrocarbon chains. This work is extremely important in the control of the surface properties of electrodeposited conducting polymers.

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1. Introduction

Nowadays, it is well-known that superhydrophobic surfaces come from appropriate combination of surface chemistry and surface structures. This property exists in nature [1–4] and is of particular interest for technological, economic and environmental reasons in various fields such as apparel, biomedical, aeronautics or building for example [5–7]. That is why, since 2000s, scientists have been developing several techniques to mimic the nature and to produce superhydrophobic surfaces from various substrates [8–11]. One of the strategies to fabricate these surfaces involves the use of a low-surface energy material such as fluorocarbon, hydrocarbon and silicone materials. Electrochemical polymerization is a method inducing the formation of a structured film during polymerization process. The surface structures depend not only on the electrochemical parameters but also on the monomer chemical structure [12–17]. By changing the chemical core structure or the length of the hydrophobic part, various structures could be obtained from fibers to cauliflower-like morphologies. Among the polymerizable cores, 3,4-ethylenedioxythiophene (EDOT) has unique advantages such as exceptional polymerization capacity, extremely fast deposition and the possibility to deposit many kinds of fiber structures. In many cases, linear hydrocarbon chains were grafted onto the electropolymerizable core before the electropolymerization process

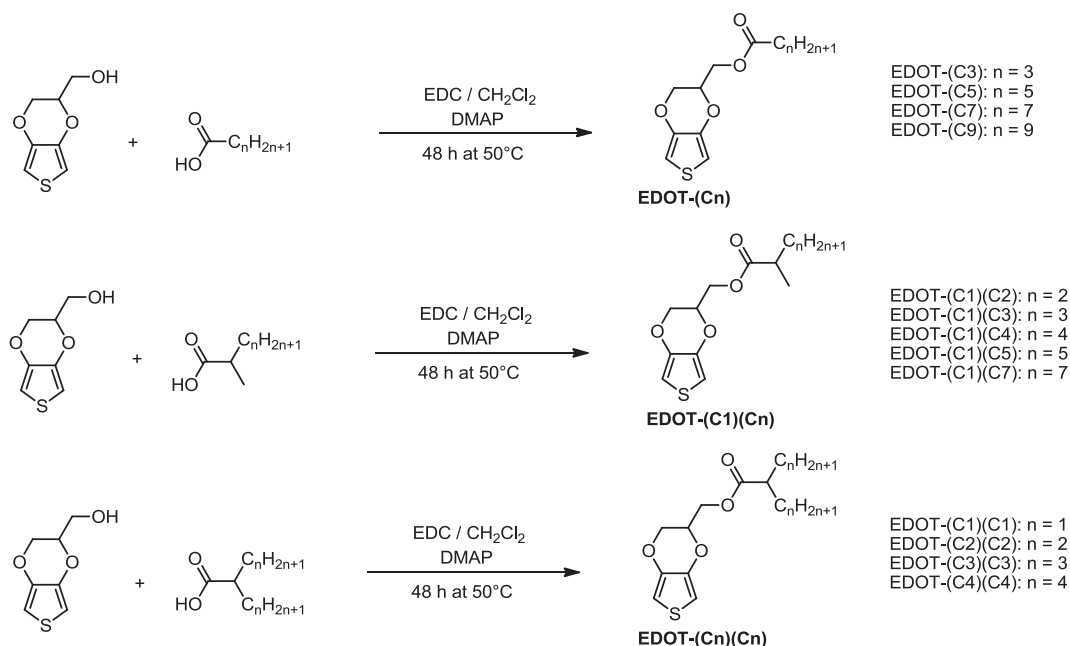
[18–22]. However, as far we know, the influence of the branching of hydrocarbon chains was not investigated in the field of superhydrophobic polymer from electrochemical polymerization process although it could have an impact on the resultant film morphology and therefore on the wettability of the film. Indeed, it is known that the branching of alkyl chains can affect the optical and electronic properties of conducting polymers [23,24]. Recent works on low surface energy surfactants have proved that hyperbranched hydrocarbon surfactants could be a real alternative to fluorocarbon ones because they presented similar interfacial properties [25,26]. The purpose of this study is to evaluate the influence of the chemical organization of the hydrophobic part (hydrocarbon chain) onto the resultant surface properties. Is it possible to replace one long linear hydrocarbon chain by two short ones keeping the same wetting properties? Here, we show that the chemical organization of a hydrocarbon chain induces a change on the wetting properties of electrodeposited conducting polymer films. We report the synthesis of the linear and branched monomers, their electropolymerization and the surface characterizations of the corresponding electrodeposited films.

2. Experimental

2.1. Electropolymerization

The monomers used for the electropolymerization are shown in [Scheme 1](#). The electrochemical polymerizations were performed in a three-electrode cell composed with either a platinum disk or a gold

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Scheme 1. Synthetic way to EDOT derivatives with linear and branched alkyl chains.

plate as a working electrode, a glassy carbon bar as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. These three electrodes were connected to a PGSTAT100 potentiostat from Metrohm with General Purpose Electrochemical System (GPES) software. All the experiments were performed in anhydrous acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) and 0.01 M of monomer. All solutions were degassed during 30 min before making the experiments. In a typical study of polymerizability of a monomer, the oxidation potential of the monomer was first measured using a fast cyclic voltammetry method (1 scan from 0 to 2 V at a scan rate of $0.1 \text{ V} \cdot \text{s}^{-1}$). The oxidation potential range for these monomers was 1.51–1.59 V. To study the surface properties of the electrodeposited polymers, a gold plate of about 1 cm^2 (silicon wafer coated by 20 nm chromium + 150 nm gold purchased from Neyco) replaced the platinum disk as working electrode and the polymers were electrodeposited at a constant potential slightly lower than their own oxidation potential. For each polymer, various deposition charges (Q_s) were performed. Indeed, if the film thickness does not depend not only on Q_s but also on the film compacity and porosity, Q_s gives the amount of polymer deposit on the surface.

2.2. Surface analyses

DSA30 goniometer from Krüss equipped with DSA4 software was employed to measure water contact angles. The apparent contact angles (θ) were determined using the sessile drop method while the dynamic contact angles, the hysteresis (H) and the sliding angles (α) were obtained with the tilted-drop method. The tilted-drop method consists in a deposition of a $6 \mu\text{L}$ liquid droplet on the surface. Then, the surface is inclined until the droplet rolls off the surface. The maximum contact angle is called α . The advanced and receding contact angles, and as a consequence H, are taken just before the droplet rolls off the surfaces. The angle in the moving direction is the advanced contact angle and that in the opposite direction is the receding contact angles.

The surface morphology was determined by scanning electron microscopy (SEM) using a 6700F microscope from JEOL. The arithmetic (R_a) and quadratic surface (R_q) roughness were measured with a Wyko NT 1100 optical microscope from Bruker. Each value corresponds

to an average of 5 measurements at different points of the surface. The analyzed areas were $182 \mu\text{m} \times 239 \mu\text{m}$.

3. Results and discussion

3.1. Surface wetting measurements

The apparent water contact angle (θ) as a function of the number of carbons in the hydrophobic part for a deposition charge of $100 \text{ mC} \cdot \text{cm}^{-2}$ is presented in Fig. 1. This graph shows that for PEDOT-(Cn)(Cn), which contains symmetric branching, θ was in little lower than that of PEDOT-(C1)(Cn), which contains asymmetric branching. However, θ of the polymers with branched hydrocarbon chains (PEDOT-(Cn)(Cn) and PEDOT-(C1)(Cn)) was much lower than that of the polymers with linear hydrocarbon chains PEDOT-(Cn) especially for a high total number of carbons (>8). In addition, in the case of polymers with a linear hydrocarbon chains, a state relatively close to superhydrophobicity was successfully reached for 8 and 9 carbons,

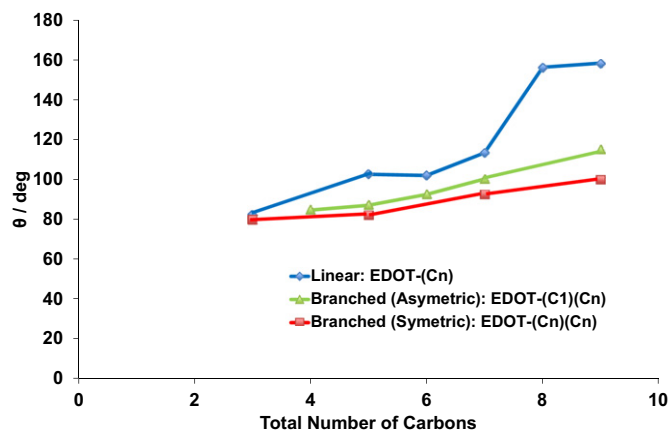


Fig. 1. Apparent water contact angle (θ) as a function of the number of carbons in the hydrophobic substituent for the different polymers; $Q_s = 100 \text{ mC} \cdot \text{cm}^{-2}$.

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