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Nanocups and hollow microspheres formed by a one-step and templateless electropolymerization of thieno[3,4-*b*]thiophene derivatives as a function of the substituent

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ABSTRACT

Here we show a one-step and templateless approach to design nanocups and hollow microspheres structures by an electrochemical polymerization. Monomers derived from thieno[3,4-*b*]thiophene bearing linear, branched and aromatic substituents were successfully synthesized by a two-step synthetic route and electropolymerized yielding unique surface structures. First, we show the versatility of the thienothiophenes monomers to create different structures on the surfaces. More precisely, branched alkyl chains derivatives (Th-Br_n) are efficient to prepare densely packed hollow microspheres with different particle sizes. By contrast, aromatic substituents such as naphthyl groups (Th-Na) lead to vertically aligned nanocups. The mechanism of structure formation is direct related to the π-π stacking interaction between the molecules which drive a unidimensional growth with Th-Na yielding cups and a tridimensional growth with Th-Br_n yielding spheres during the electropolymerization. Since the process to obtain nanotubes is rare in the literature, the formation of nanotubular structures is evaluated using two different electrochemical methods: cyclic voltammetry and constant potential. The amount of gas (O_2 and/or H_2 as a function of the electrodeposition method) produced from trace water during the electropolymerization is crucial on the formation of porous structures. The growth of the larger nanocups is favored by cyclic voltammetry but their number is less important than at constant potential. Moreover, while parahydrophobic properties were obtained for all the families by cyclic voltammetry, hydrophilic surfaces were produced at constant potential. This first work showed the monomers synthesis, electrochemical polymerization and surface characterization of various thieno[3,4-*b*]thiophene derivatives for a potential application on surface science as in water transport and membrane design, for example.

1. Introduction

Conducting polymers are unique organic materials which present many properties, such as the good electrical and optical properties, easy synthesis and the possibility to prepare nanostructured materials [1]. They combine electronic and optical properties of metals and inorganic semiconductors with the attractive properties typically associated to conventional polymers, including mechanical flexibility and low-cost production. A potential good substitute for metals and semiconductors, conducting polymers can have their chemical, electrical and physical properties [2–4] tailored to the material specific needs or controlled through stimulation (pH, electricity, light, etc) [5–8]. Recent applications for the conducting polymers are as electrochromic devices [9–11], solar cells [12,13], supercapacitors [14,15], batteries [16,17], superconductors [18,19], etc.

One of the most studied conducting polymers is the polythiophene and its derivatives. This molecule has been of great interest because of their high electrical conductivity, electrochromism, high environmental and thermal stability and versatile redox properties [20]. Thiophene derivatives have also been the subject of increased attention/research in the materials field, mainly for 3,4-ethylenedioxythiophene (EDOT) with a wide application for solar cells [21–25]. Recently, an electrodeposited PEDOT was post-synthetically functionalized with alkyl, aryl and perfluorinated chains by a click reaction [26]. The surface wettability and morphology were deeply changed when the direct surface functionalization was compared with the nanoparticle-grafted

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surface functionalization due to the increase in the functionalizable surface area.

Inspired by nature [27–29], superhydrophobic and parahydrophobic materials have been calling attention for their several applications, such as water harvesting, self-cleaning coatings and membrane separation, for example [30]. These surfaces, characterized by high contact angles with water (θ_w), differ in their adhesive behavior. Superhydrophobic surfaces are found for high θ_w and low water adhesion (low hysteresis H and sliding angle α) while parahydrophobic surfaces were obtained with high θ_w and high water adhesion.

A famous engineering route towards to design nano and microstructured conducting polymers with a wide range of wettability is the electrochemical polymerization or electropolymerization [31,32]. This technique, classified as a "bottom-up" approach, presents many advantages towards the other techniques. The electropolymerization consists in a fast process that guarantees the polymerization, deposition and structuration of the film in only one-step. The monomer, dissolved in an appropriate electrolytic solution, is oxidized at the surface of an electrode by application of an anodic potential. Nevertheless, the electropolymerization do not only provide films with controllable surface morphology and wettability as well is considerably simpler, faster and more cost-effective technique when compared with the conventional chemical polymerization. The incorporation of substituents with different surface energies on the monomer is a way to achieve a range of surface wettability and varied morphologies. Bellanger and co-authors showed that the use of dodecyl spacers between the EDOP core and the fluorinated substituents yield surfaces with superhydrophobic and highly oleophobic properties [33]. Using the same framework, parahydrophobic surfaces were achieved with a very different morphology when aromatic substituents were used [34]. Using ProDOT as a model core, different wettability and surface roughness were also reported [35,36].

By electropolymerization, a templateless approach, it is also possible to form porous structures such as nanocups and nanotubes. The condition is the formation of gas bubbles during the electropolymerization process which will act as a template to create these structures. Shi and co-authors were the first to report the formation of polypyrrole microcontainers using an aqueous solution in the presence of a surfactant [37–39]. The role of the surfactant was to stabilize the gas bubbles and to make the structures grow around them. Very recently, it was also reported the possibility to obtain nanotubes in organic solvent and without surfactant. Trace water present in solution is sufficient to release gas bubbles, but the monomer must stabilize them. Thiophenes derivatives, such as 3,4-phenylenedioxythiophene (PhEDOT) and 3,4-naphthalenedioxythiophene (NaphDOT), were found to be excellent candidates to form vertically aligned nanotubes with parahydrophobic properties [40,41].

The thienothiophenes is a classification of fused thiophenes that have two annulated units and they are presented in four isomers (thieno[3,2-*b*]thiophene, thieno[3,4-*b*]thiophene, thieno[2,3-*b*]thiophene and thieno[3,4-*c*]thiophene). They are electron-rich structures allowing them to build conjugated and low band gap organic compounds. Especially, it was shown that thieno[3,2-*b*]thiophene and thieno[2,3-*b*]thiophene were also excellent candidates for the formation of porous structures in varied conditions [42,43]. Here, we investigate not only thieno[3,4-*b*]thiophene, but 12 derivatives differing by the substituent as shown in Scheme 1. The choice of this monomer core was made in order to find a favorable synthetic route to obtain a library of thienothiophene derivatives containing different substituents. The influence of the monomer side chain is mostly evaluated concerning the surface structuration and wetting behavior.

2. Materials and methods

2.1. Monomer synthesis and characterization

The thieno[3,4-*b*]thiophene derived monomers were synthesized following a two-step synthetic route starting from a Sonogashira coupling followed by a second step of cyclization (Scheme 2). The monomers were characterized by ^{1}H and ^{13}C NMR spectroscopy with a W-200 MHz and W-400 MHz (Bruker). Melting points of each monomer were determined *via* differential scanning calorimetry (Jade DSC-Perkin Elmer) using a thermal scan from 0 °C to 250 °C at a rate of 10 °C min^{-1}.

2.1.1. Synthesis of BrTh-SiMe$_3$: ((4-bromothiophen-3-yl)ethynyl) trimethylsilane

1.03 mmol of *bis*(triphenylphosphine)palladium (II) dichloride ($Pd(PPh_3)_2Cl_2$) and 1.03 mmol of CuI were suspended in 20 mL of diisopropylamine. After N_2 purging for 10 min, 20.7 mmol of 3,4-dibromothiophene and 20.7 mmol of trimethylsilylacetylene were added into the flask in sequence with N_2 purging. The solution was heated at 50 °C and let stirring for 7 h. The reaction was then allowed to cool until room temperature and the solvent was evaporated. Then, 100 mL of dichloromethane was added and the product was extracted twice with 50 mL of water and 50 mL of $NaHCO_3$ aqueous solution, dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the product was purified by column chromatography using silica gel and petroleum ether. Methodology adapted from Patra and co-authors [44]. Yield 49%; Yellow liquid; δ_H(200 MHz, $CDCl_3$): 7.47 (d, J = 3.4 Hz, 1H), 7.22 (d, J = 3.4 Hz, 1H), 0.26 (s, 9H); δ_C(100 MHz, $CDCl_3$): 129.78, 124.77, 122.94, 114.00, 98.00, 97.88, 0.02.

2.1.2. Synthesis of BrTh-C$_n$/BrTh-Br$_n$/BrTh-Aromatic (BrTh-X series)

To 40 mL of anhydrous methanol were added 1.03 mmol of *bis*(triphenylphosphine)palladium (II) dichloride ($Pd(PPh_3)_2Cl_2$) and 1.03 mmol of CuI. After N_2 purging for 10 min, 20.7 mmol of 3,4-dibromothiophene, 20.7 mmol of the correspondent alkyne and 20 mL of diisopropylamine were added into the flask in sequence with N_2 purging. The solution was heated at 85 °C and let stirring for 48 h. The reaction was then allowed to cool until room temperature and the solvent was evaporated. Then, 100 mL of dichloromethane was added and the product was extracted twice, washed with 50 mL of water and 50 mL of $NaHCO_3$ aqueous solution, dried over Na_2SO_4 and filtered. The solvent was removed under reduced pressure and the product was purified by column chromatography using silica gel and petroleum ether. Methodology adapted from Bae and co-authors [45].

2.1.2.1. BrTh-C$_4$: 3-bromo-4-(hex-1-yn-1-yl)thiophene. Yield 39%; Yellow liquid; δ_H(200 MHz, $CDCl_3$): 7.34 (d, J = 3.4 Hz, 1H), 7.21 (d, J = 3.4 Hz, 1H), 2.44 (t, J = 6.8 Hz, 2H), 1.65–1.45 (m, 4H), 0.95 (t, J = 7.1 Hz, 3H); δ_C(100 MHz, $CDCl_3$): 127.88, 125.38, 122.68, 114.02, 93.74, 74.14, 30.81, 22.09, 19.27, 13.76.

2.1.2.2. BrTh-C$_6$: 3-bromo-4-(oct-1-yn-1-yl)thiophene. Yield 41%; Yellow liquid; δ_H(200 MHz, $CDCl_3$): 7.34 (d, J = 3.4 Hz, 1H), 7.21 (d, J = 3.4 Hz, 1H), 2.43 (t, J = 6.8 Hz, 2H), 1.66–1.47 (m, 4H), 1.35–1.28 (m, 4H), 0.90 (t, J = 6.6 Hz, 3H); δ_C(100 MHz, $CDCl_3$): 127.88, 125.37, 122.68, 114.02, 93.81, 74.09, 31.50, 28.71, 28.67, 22.72, 19.58, 14.22.

2.1.2.3. BrTh-C$_8$: 3-bromo-4-(dec-1-yn-1-yl)thiophene. Yield 36%; Yellow liquid; δ_H(200 MHz, $CDCl_3$): 7.34 (d, J = 3.3 Hz, 1H), 7.21 (d, J = 3.4 Hz, 1H), 2.43 (t, J = 7.0 Hz, 2H), 1.65–1.58 (m, 2H), 1.51–1.44 (m, 2H), 1.31–1.29 (m, 8H), 0.88 (t, J = 6.6 Hz, 3H); δ_C(100 MHz, $CDCl_3$): 127.87, 125.38, 122.68, 114.03, 93.82, 74.09, 32.00, 29.36,