Hydrocarbon superhydrophobic polymers from electrochemical polymerization: an alternative to fluorine?

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HYDROCARBON SUPERHYDROPHOBIC POLYMERS FROM ELECTROCHEMICAL POLYMERIZATION: AN ALTERNATIVE TO FLUORINE?

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Glossary

AAO	Anodic Aluminum Oxide
AFM	Atomic Force Microscopy
Bu_4NBF_4	Tetrabutylammonium tetrafluoroborate
$Bu_4NC_4F_9SO_3$	Tetrabutylammonium nonafluorobutanesulfonate
$Bu_4NC_8F_{17}SO_3$	Tetrabutylammonium heptadecafluorooctanesulfonate
$Bu_4NCF_3SO_3$	Tetrabutylammonium trifluoromethanesulfonate
Bu_4NClO_4	Tetrabutylammonium perchlorate
Bu_4NPF_6	Tetrabutylammonium Hexafluorophosphate
CV	Cyclic Voltammetry
d	Doublet
dd	Doublet of doublet
DMAP	4-(dimethylamino)pyridine
DMF	Dimethylformamide
$E_{1/2}$	Half-wave potential
ECA	ethyl-cyanoacrylate
EDC	*N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride
EDOT	3,4-Ethylenedioxythiophene
EOTT	3,4-Ethyleneoxythiathiophene
EOTT	3,4-ethyleneoxythiathiophene
E^{ox}	Monomer oxidation potential
$E_{ox,\ polym}$	Polymer oxidation potential
E_{ox}	Monomer oxidation potential

$E_{ox,opt}$	Optimal oxidation potential
$E_{red,\ polym}$	Polymer Reduction Potential
GC-MS	Gas Chromatography coupled with Mass Spectroscopy
H_{liquid}	Hysteresis measured with liquid droplet
HDPE	High Density Poly(ethylene)
HFDT	Heptadecafluoro-1-decanethiol
J	Coupling Constant
LbL	Layer-by-Layer
LDPE	Low Density Poly(ethylene)
m	Multiplet
m.p.	Melting point
$NaClO_4$	Sodium perchlorate
NMR	Nuclear Magnetic Resonance
PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile
PANI	Polyaniline
PC	Polycarbonate
PCL	Polycaprolactone
PDMS	Poly(dimethylsiloxane)
PE	Polyethylene
PECA	Poly(ethyl-cyanoacrylate)
PEDOT	poly(3,4-ethylenedioxythiophene)
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEI	Poly(ethyleneimine)
PEOTT	poly(3,4-ethyleneoxythiathiophene)
PET	Polyethylene terephthalate

PFDA	Poly(heptadecafluorodecylacrylate)
PFO^-	Perfluorooctanoate anion
PFTDS	*1H,1H,2H,2H*-perfluorodecyltrichlorosilane
PHFMA	Poly(2,2,3,4,4,4-hexafluorobutyl methacrylate)
PMETAC	Poly[2-(methacryloyloxy)ethyltrimethylammonium chloride]
PMMA	Poly(methyl methacrylate)
PNIPAAm	Poly(N-isopropylacrylamide)
POSS	Polyhedral oligomeric silsesquioxane
PP	Poly(propylene)
PProDOT	Poly(3,4-propylenedioxythiophene)
PProDOP	Poly(3,4-propylenedioxypyrrole)
PS	Poly(styrene)
Pt	Platinum
PTFE	Poly(tetrafluoroethylene)
pTSA	*p*-toluenesulfonic acid
PU	Polyurethane
PUA	Polyurethane acrylate
PVC	Poly(vinyl chloride)
PVDF	Poly(vinylidene fluoride)
PVDMA	Poly(2-vinyl-4,4-dimethylazlactone)
Qs	Deposition charge
r	Wenzel Roughness factor
r.t.	Retention time
R_a	Arithmetic Roughness
R_q	Root Mean Square Roughness
s	Singlet

SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy
sept.	Septuplet
sext.	Sextuplet
SI-ATRP	Surface-Initiated Atom Transfer Radical Polymerization
t	Triplet
TEOS	Tetraethyl orthosilicate
THF	Tetrahydrofuran
tt	Triplet of triplet
UV	Ultra-violet
α_{liquid}	Sliding angle measured for liquid
γ_{LV}	Interfacial tension between Liquid-Vapor
γ_{SL}	Interfacial tension between Solid-Liquid
γ_{SV}	Interfacial tension between Solid-Vapor
δ	Chemical shift
θ_a	Advancing angle
θ^{CB}	Apparent contact angle determined by Cassie-Baxter equation
θ_{diiodo}	Static diiodomethane contact angle
θ_r	Receding angle
θ^{W}	Apparent contact angle determined by Wenzel equation
θ_{water}	Static water contact angle
θ_{water}	Water contact angle
θ^{Y}	Contact angle of Young's equation
ϕ_a	Air Fraction
ϕ_S	Solid fraction

Introduction

From a chemist's point of view, making anhydrophobic surface is possible by using an hydrophobic bulk or by making surface modifications such as coating the surface with a polymer, activating and grafting hydrophobic molecules onto the surface, making self-assembled monolayers onto the surface or depositing self-assembled monolayers or hyperbranched polymers for example (Figure 1). With all these techniques, hydrophobic surfaces are mainly flat.

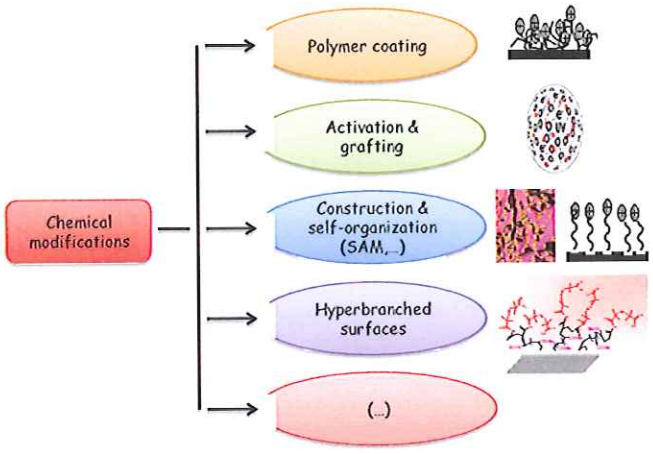


Figure 1. Examples of chemical modifications to produce hydrophobic surfaces.

The hydrophobicity comes from the intrinsic hydrophobicity of the bulk or the deposited species. The water-repellency is evaluated by measuring the contact

angle between the water droplet's tangent and the solid surface's tangent. With these techniques described in Figure 1, the highest water contact angle we could obtain was 120° which corresponds to the smooth surface of poly(tetrafluoroethylene) (PTFE). In 2000, Genzer and his co-workers previously stretched their surface before grafting a self-assembled monolayer of fluorinated compounds (Genzer, J; Efimenko, K. Science **2000**, *290*, 2130-2133). From this technique, they deposited a mechanically assembled monolayer (MAM) instead of a self-assembled monolayer (SAM. Thus, they enhanced the density of the grafted molecules and they increased the water-repellency with a water contact angle of130-135°.

Fluorinated compounds are often employed to fabricate hydrophobic surface. The advantages are their chemical and thermal inertia as well as their low surface energy. However due to their chemical inertia, long fluorinated tails are not easily degradable. As a consequence, it is very difficult or quasi impossible for the body of living species to eliminate these compounds. Long fluorinated tails are thus considered as bioaccumulable species. In opposition to synthetic pathway proposed in literature, in nature, we can find surfaces with extreme water-repellency properties (i.e. on which water droplets remained spherical) without

using fluorine chemistry. These surfaces are named superhydrophobic. This phenomenon could be explained by an appropriate combination of either morphology, either roughness or surface structuration and low surface energy raw materials. Hence, the main subject of this research work was to find alternative to fluorine chemistry by the preparation of superhydrophobic material within hydrocarbon series.

In literature, several techniques to produce superhydrophobic surfaces have been described. Amongst them, electrochemical polymerization allowed the design of surfaces withspecial wettability and especially the possibility to obtain superhydrophobic surfaces. The main advantages of this technique are:

- The speed: the deposition and the surface structuration occur at the same time
- The versatility: an accurate design of the monomer chemical structure influences the resultant morphology and properties. it is also possible to control the morphology through the electrochemical parameters (deposition charge, supporting electrolyte, solvent, deposition technique, etc)

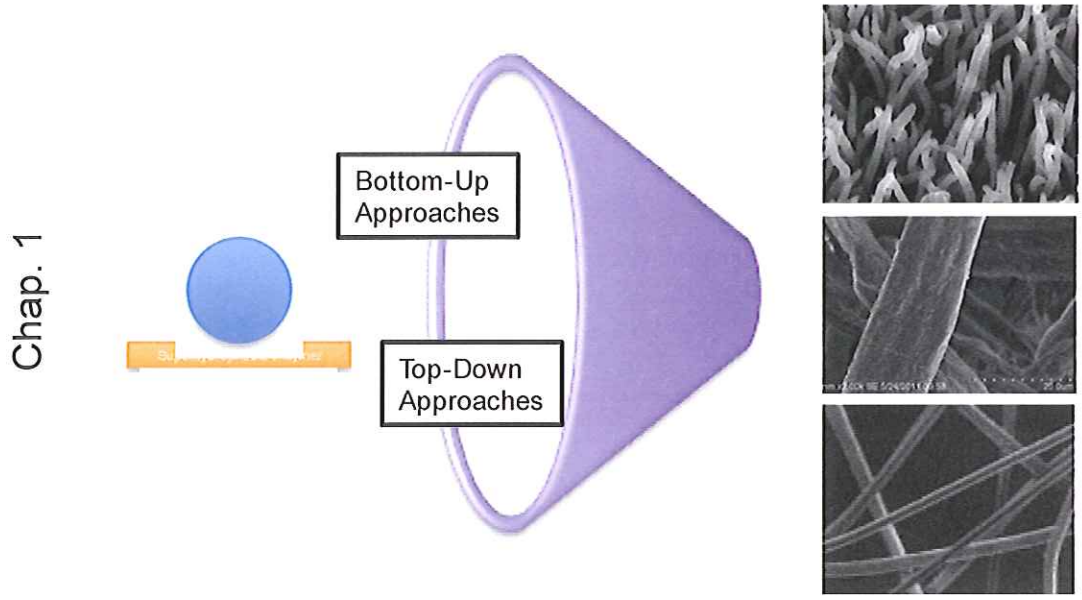
In this thesis, the challenges were:

1. To make an assessment of the existed techniques to produce superhydrophobic surfaces with polymer material
2. To focus on superhydrophobic fibrous polymers since fibers present many practical applications
3. To produce superhydrophobic surfaces with hydrocarbon conducting polymers
4. To evaluate the influence of chemical and physical part onto the wetting properties
5. To compare hydrocarbon conducting polymers with fluorinated analogues
6. To study the impact of the polymerizable core onto the properties.

All these challenges can be summed up in Figure 2.

This work is thus divided into four chapters. First, we will present areview of the techniques employed to obtain superhydrophobic polymers then superhydrophobic fibrous polymer surfaces. The second chapter is devoted to one particular hydrocarbon ethylenedioxythiophene (EDOT) series. We will see if superhydrophobicity could be reached with these polymers and if we can get chemical and physical parts impacting onto the wetting properties. Finally, the fourth chapter will describe the surfaces properties comparison between

hydrocarbon and fluorinated surfaces as well as the influence of polymerizable core onto the resultant surface properties.



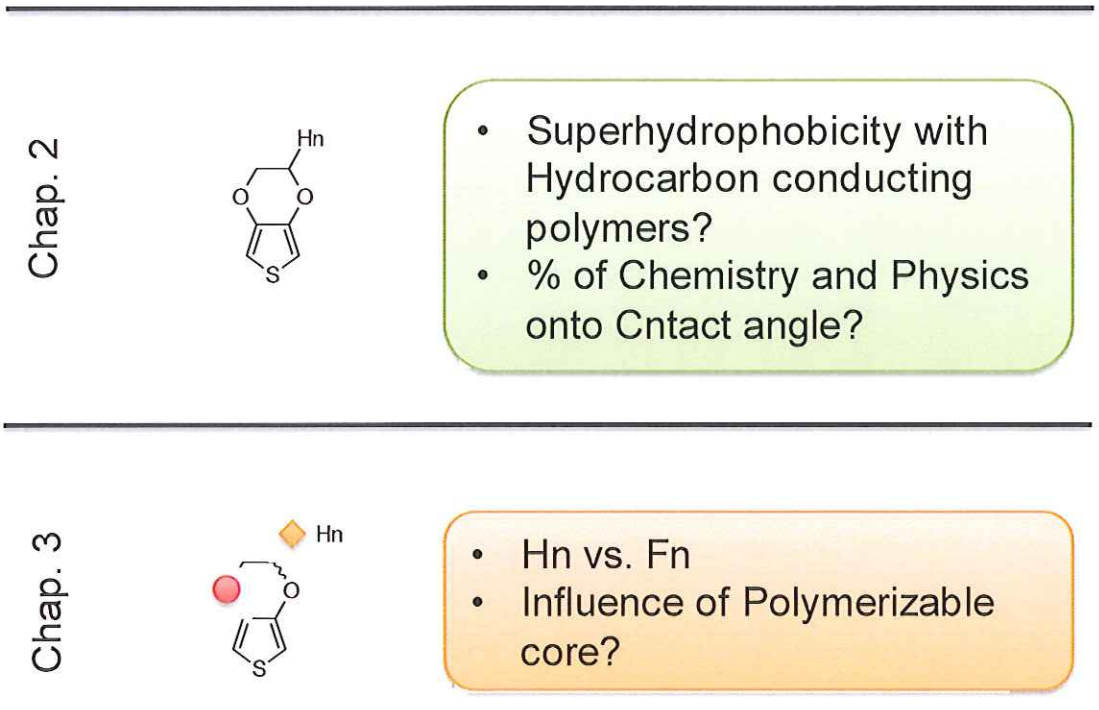


Figure 2. Thesis synoptic representation.