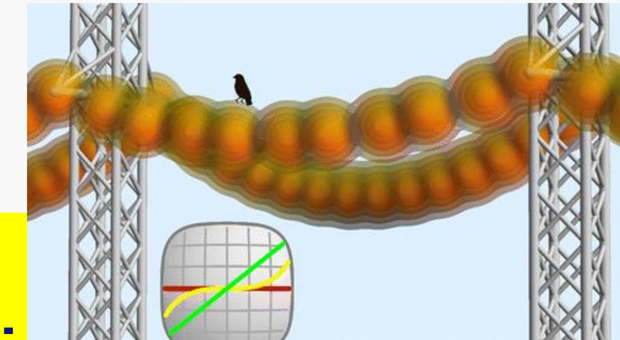
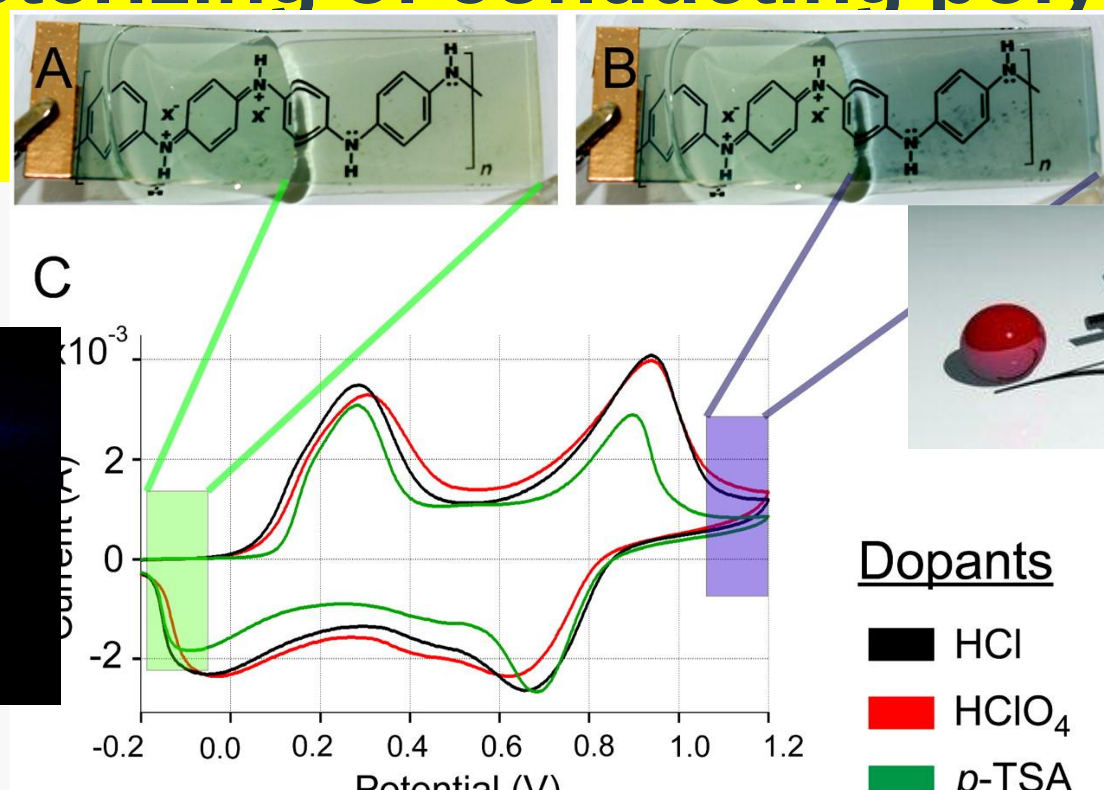
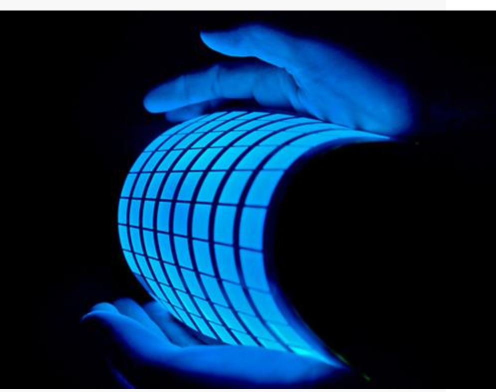
Goce Delcev University Stip, Macedonia

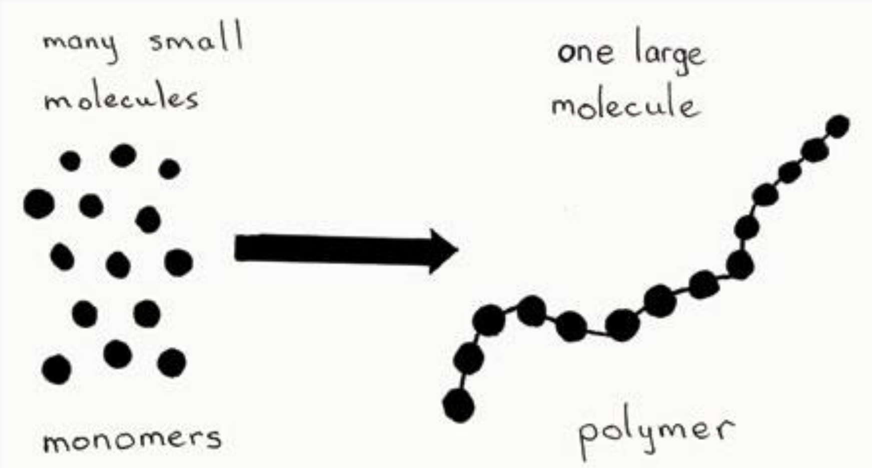


Prof. Dr Rubin Gulaboski

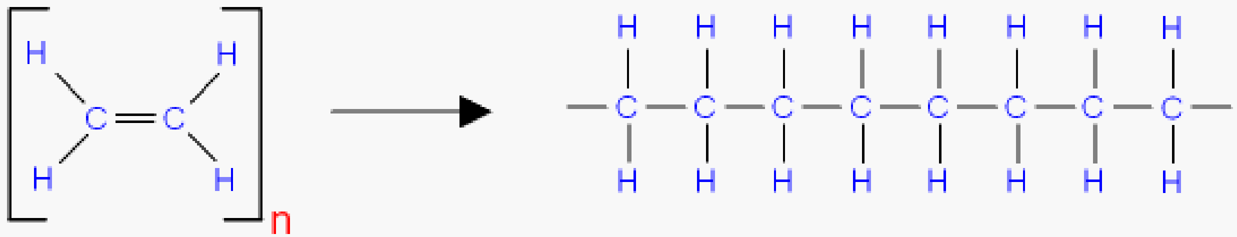
Voltammetric and Microscopic Methods for characterizing of conducting polymers







Polymerisation-process
of making large molecules
from smaller monomers which structure
repeats along the chain of the polymer

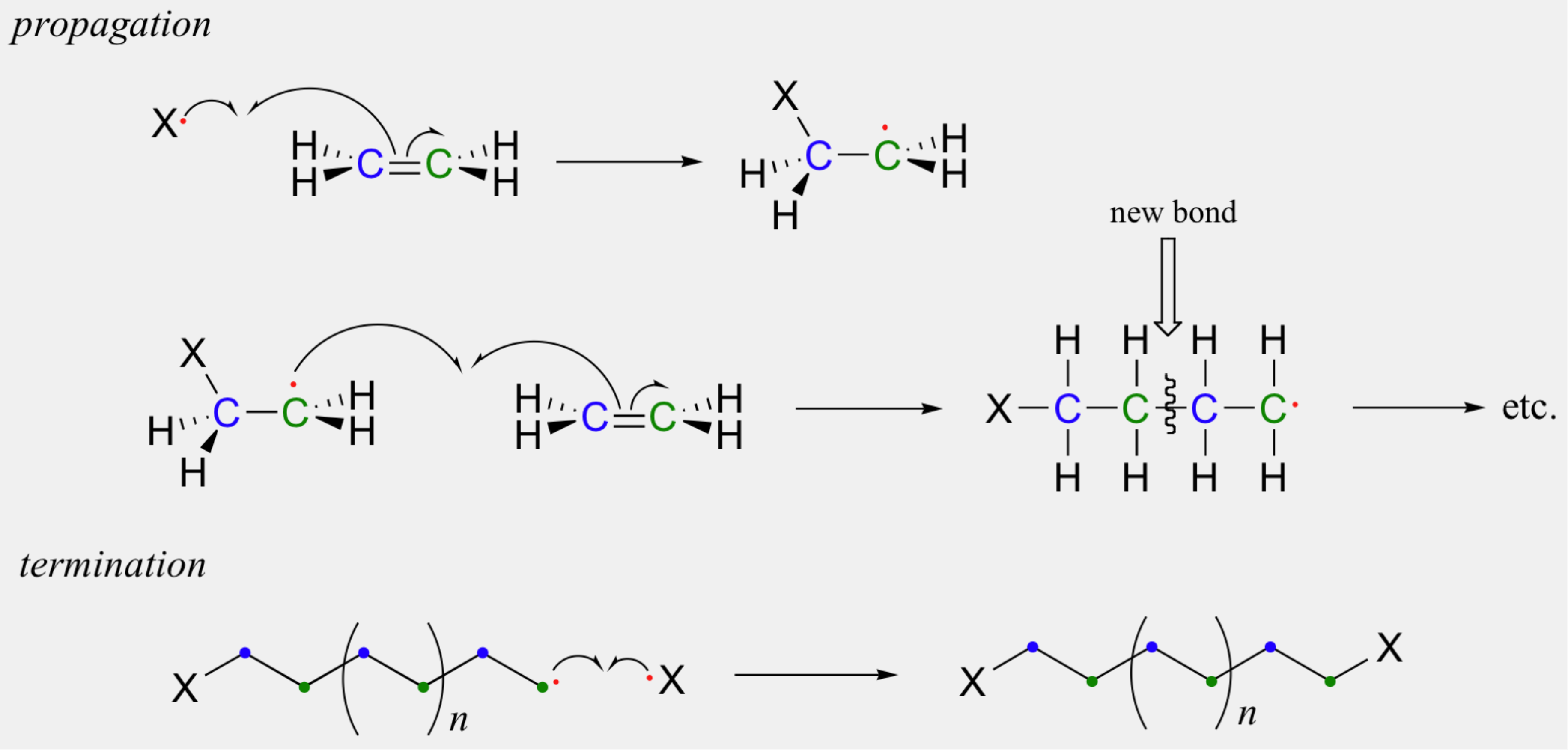


Many ethene molecules

Poly (ethene)

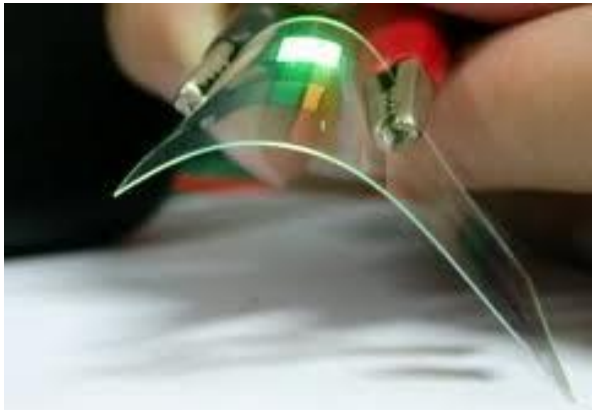
Mechanism of polymerisation

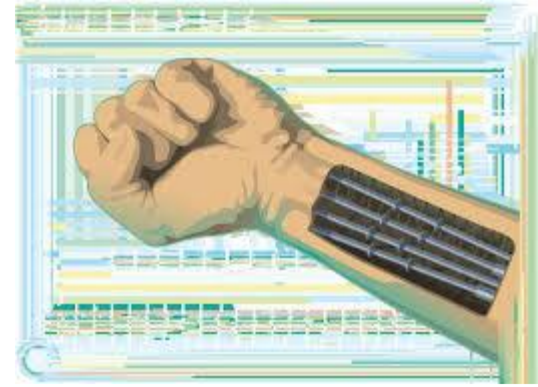
-***It is a radical reaction***!!!






Some Important Applications of polymers

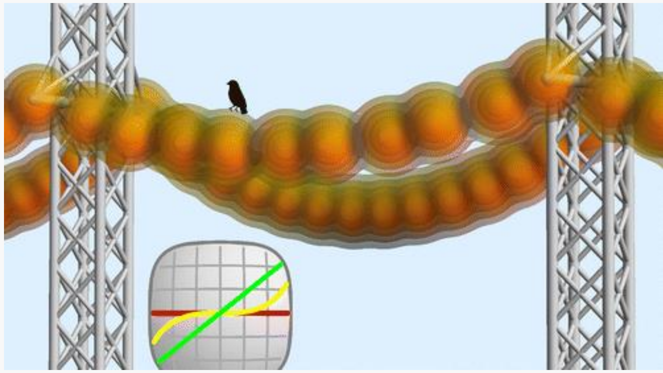




■ ■ ■ ■

Electrically conductive plastic

One has been taught that **plastics do not conduct electricity**. Usually plastics are used as insulation around the copper wires in ordinary electrical cables.



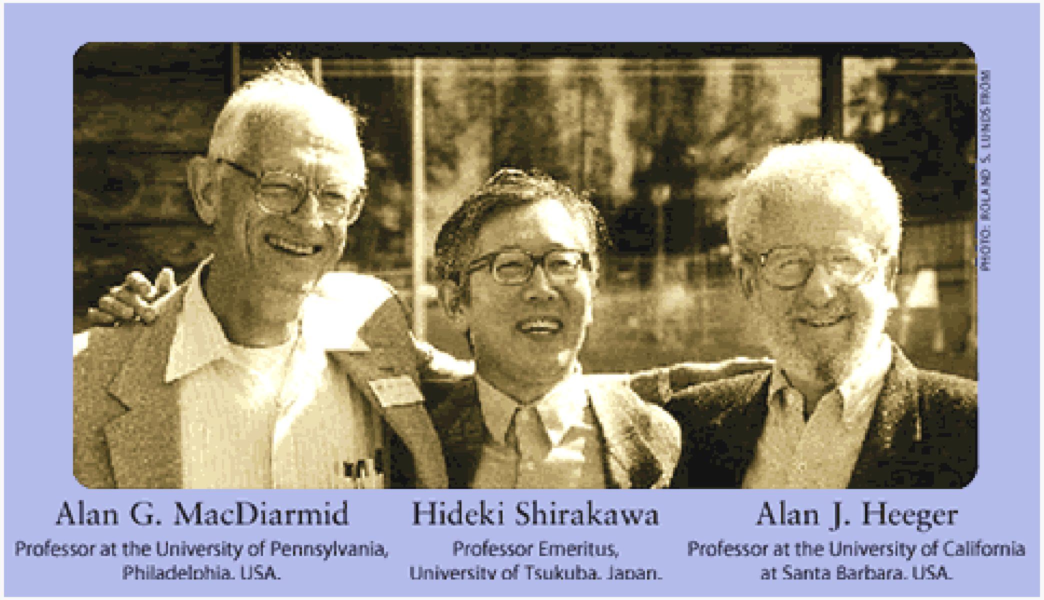


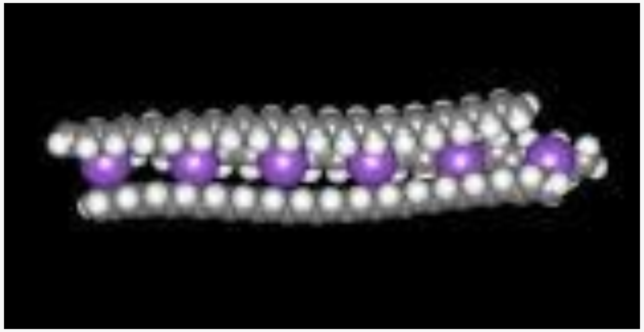
Photo acknowledged from report of Nobel Prize in Chemistry 2000

In 1977 three scientists Prof. A. J. Heeger, Prof. A. G. MacDiarmid and Prof. H. Shirakawa **cointidentaly** discovered and reported conductive properties of the alternating-bond conjugated polymers (Polyacetylene). They found that the polymer could be (n- or p-) doped to the metallic state and thereby transformed into a good electrical conductor.

* Nobel Prize in Chemistry 2000 being awarded to Profs. A. J. Heeger, A. G. MacDiarmid and H. Shirakawa (MacDiarmid A.G., "Synthetic metals: A novel role for organic polymers (Nobel Lecture)", *Angewandte Chemie, International Edition* **40**, 2581-2590, 2001)

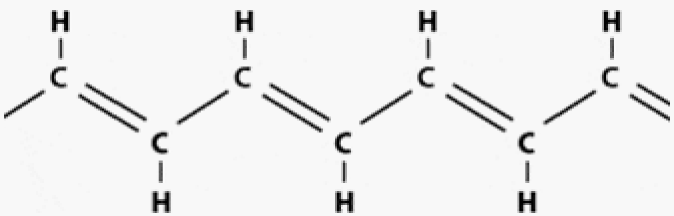
Polyacetylene created with Ziggler catalyst dopped by iodine gives conductive polyacetylene polymer

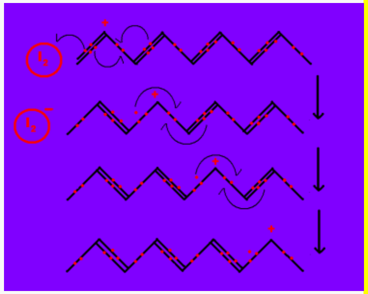
$+I_2 \longrightarrow$



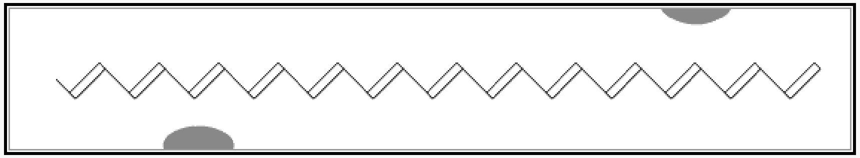
Conducting polymers

Polymers are molecules formed of many identical units (monomers) bound to each other. **For a polymer to be electrically conductive it must "imitate" a metal – the electrons in the bonds must be freely mobile and not bound fast to the atoms**. One condition for this is that the polymer consists of alternate single and double bonds, termed conjugated double **bonds**:

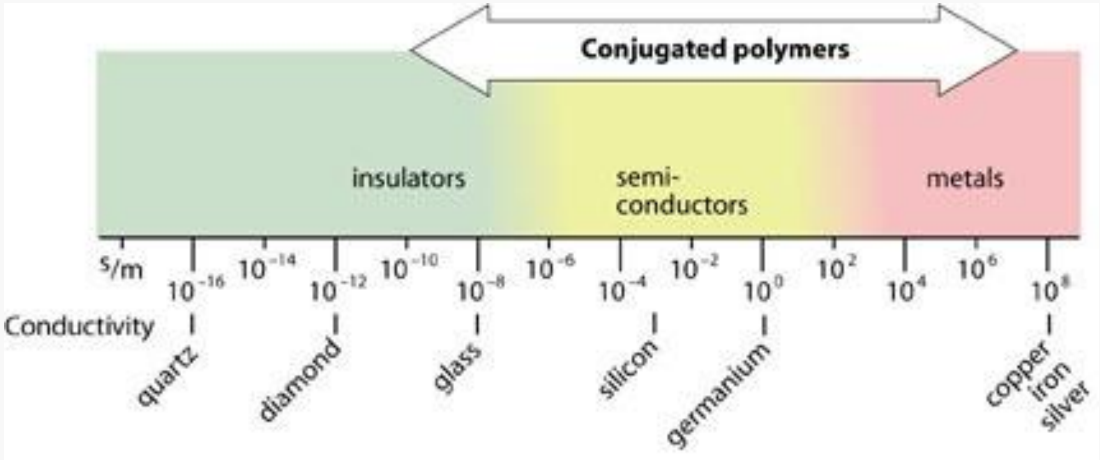




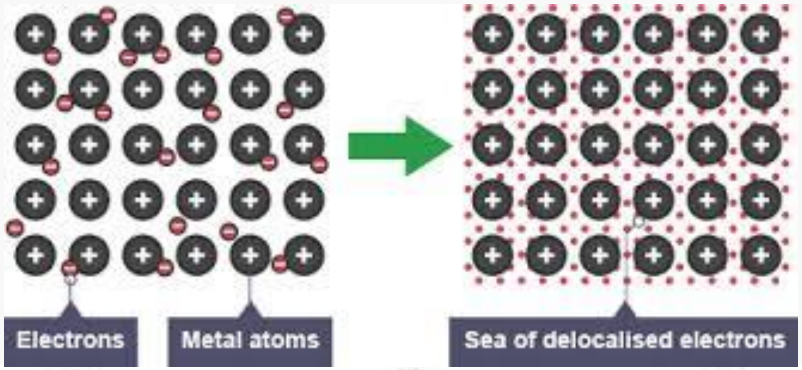
Example: Oxidation of Polyacetylene with iodine causes the electrons to be jerked out of the polymer, leaving "holes" in the form of positive charges that can move along the chain, thus leading to opening of an band gap and causes (semi)conductivity. (Nobel Prize in Chemistry 2000)

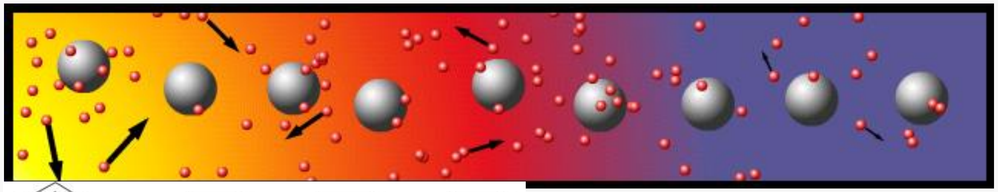


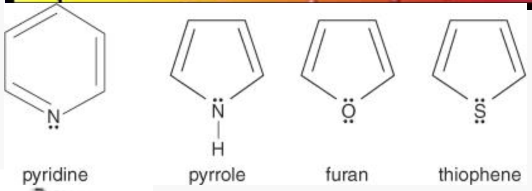
- low weight
- conductivity can be varied over a very broad area, from poor semi-conductors to metallic-level conductivity
- Excellent tolerance to corrosion
- large, flexible surfaces can be made relatively easily and cheaply

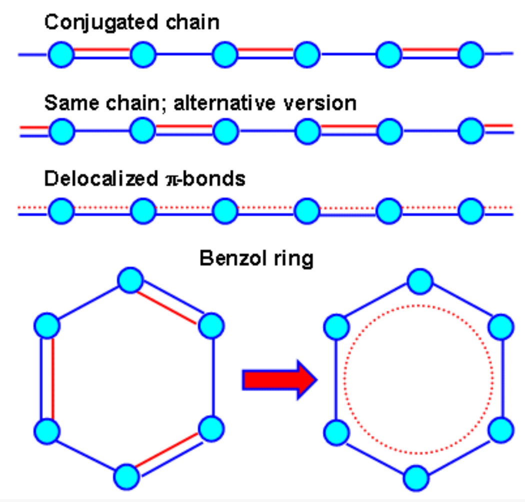


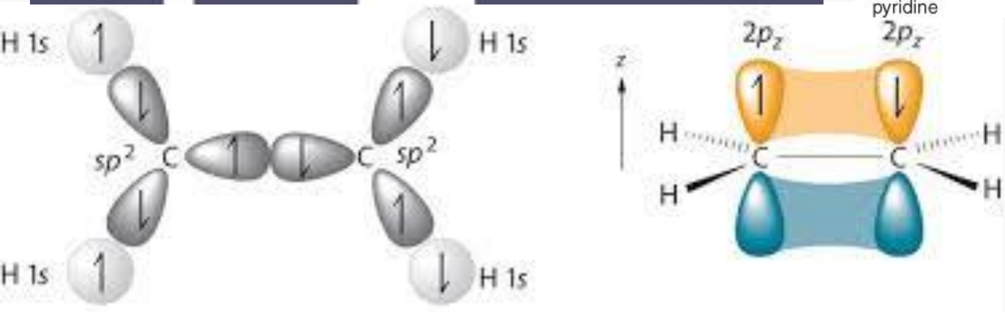
Conducting polymers have backbones of contiguous sp^2 hybridized carbon centers. One valence electron on each center resides in a p_z orbital, which is orthogonal to the other three sigma-bonds. The electrons in these delocalized orbitals have high mobility, when the material is "doped" by oxidation, which removes some of these delocalized electrons. Thus the p-orbitals form a band, and the electrons within this band become mobile when it is partially emptied.



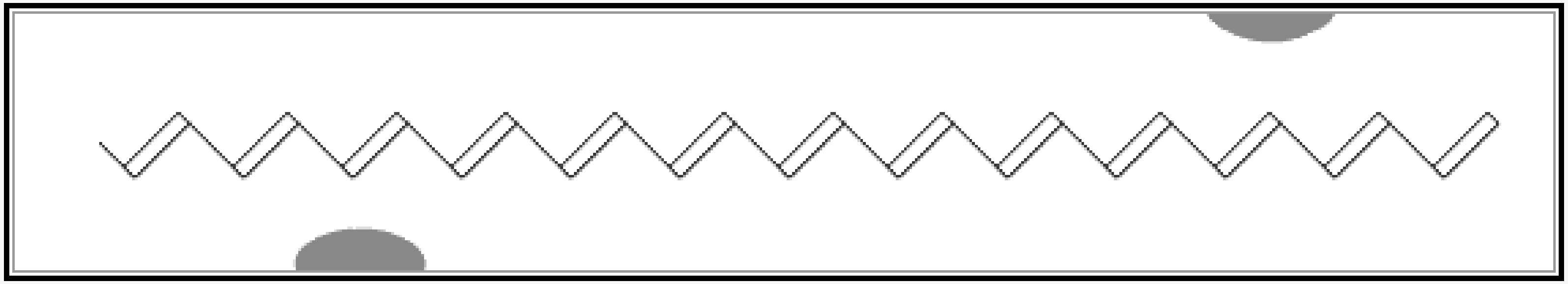








(a) C_2H_4 σ-bonded framework (b) C_2H_4 π bonding



Conducting Polymers

☯ Energy storage
(batteries, **supercapacitors)**

☯ Electrochromic devices
(smart Windows, mirrors, IR and microwave shutters)

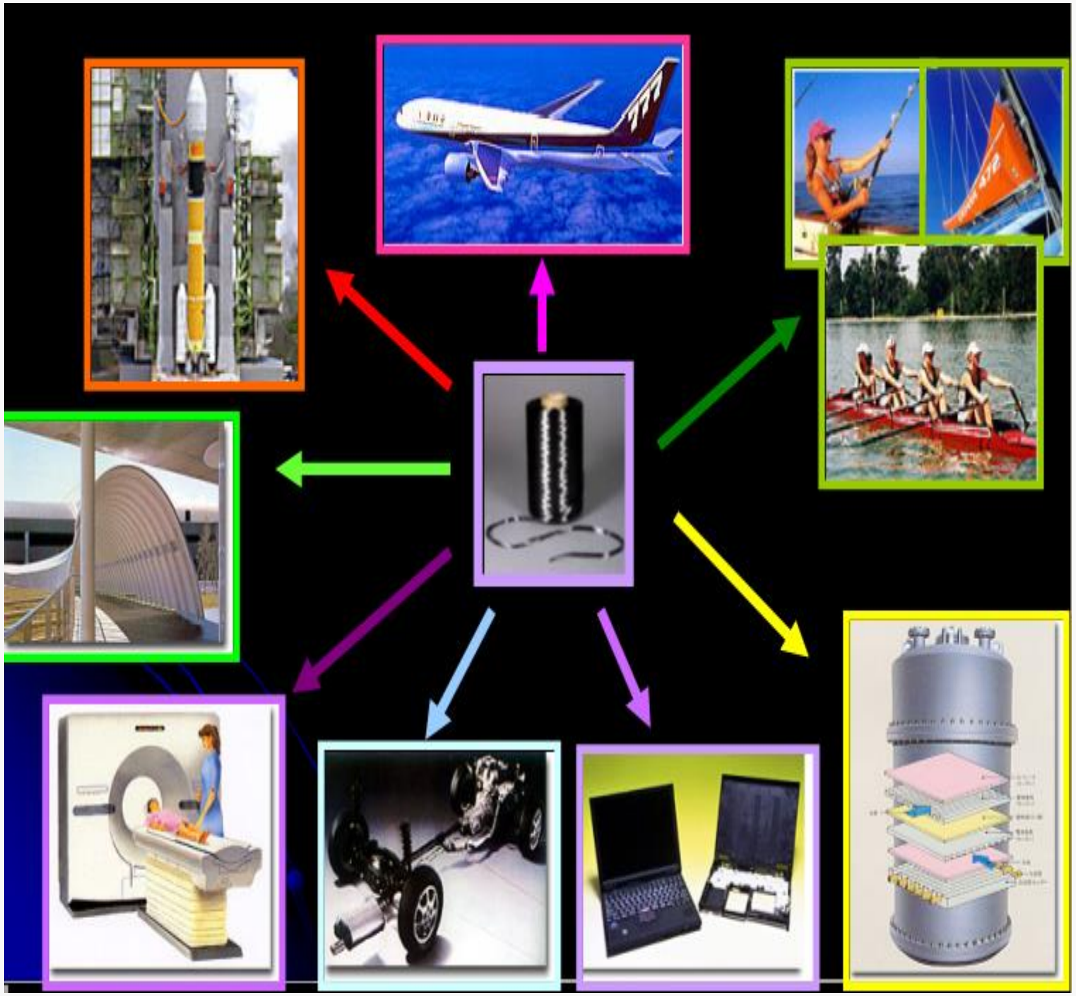
☯ Antistatic coatings
(displays, flat TV screens)

☯ Semiconductor devices
(Solar Cells)

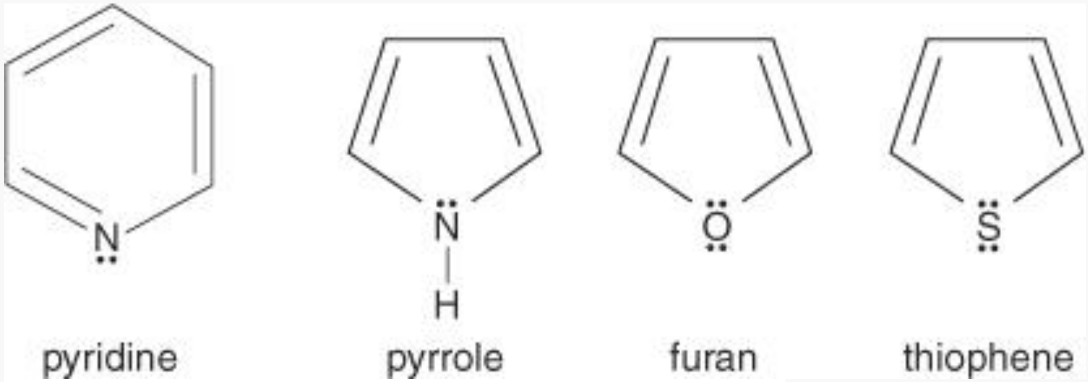
☯ Corrosion Protection

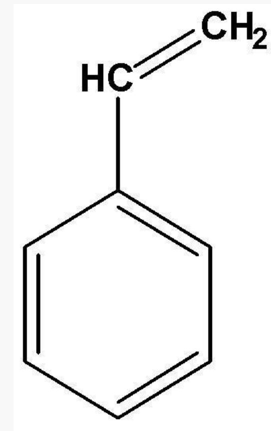
☯ Mechanical actuators

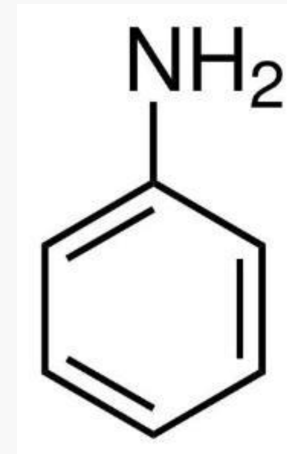
☯ Bio applications
(drug delivery systems, artificial muscles, biosensors)

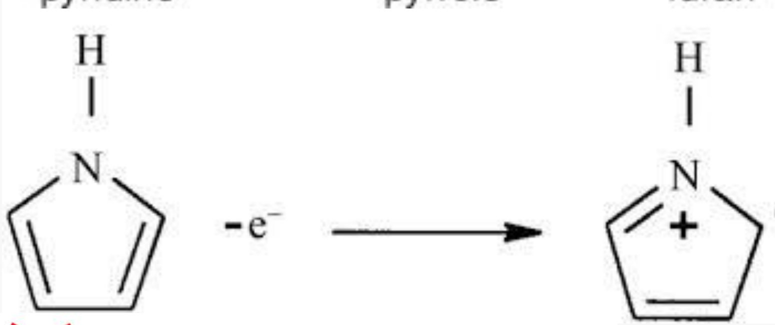


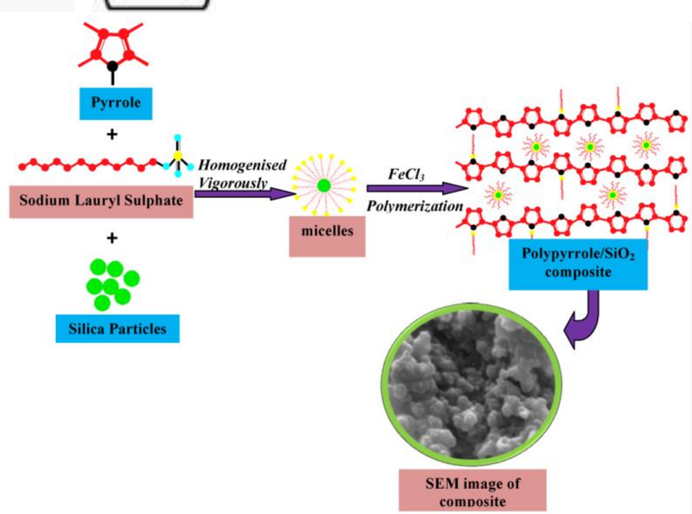
Monomers that are suitable for Synthesis of conducting polymers

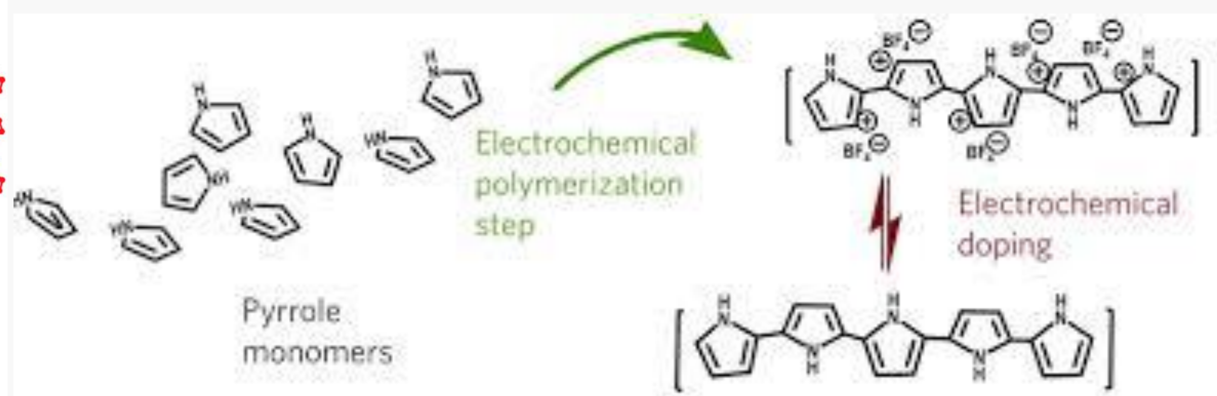




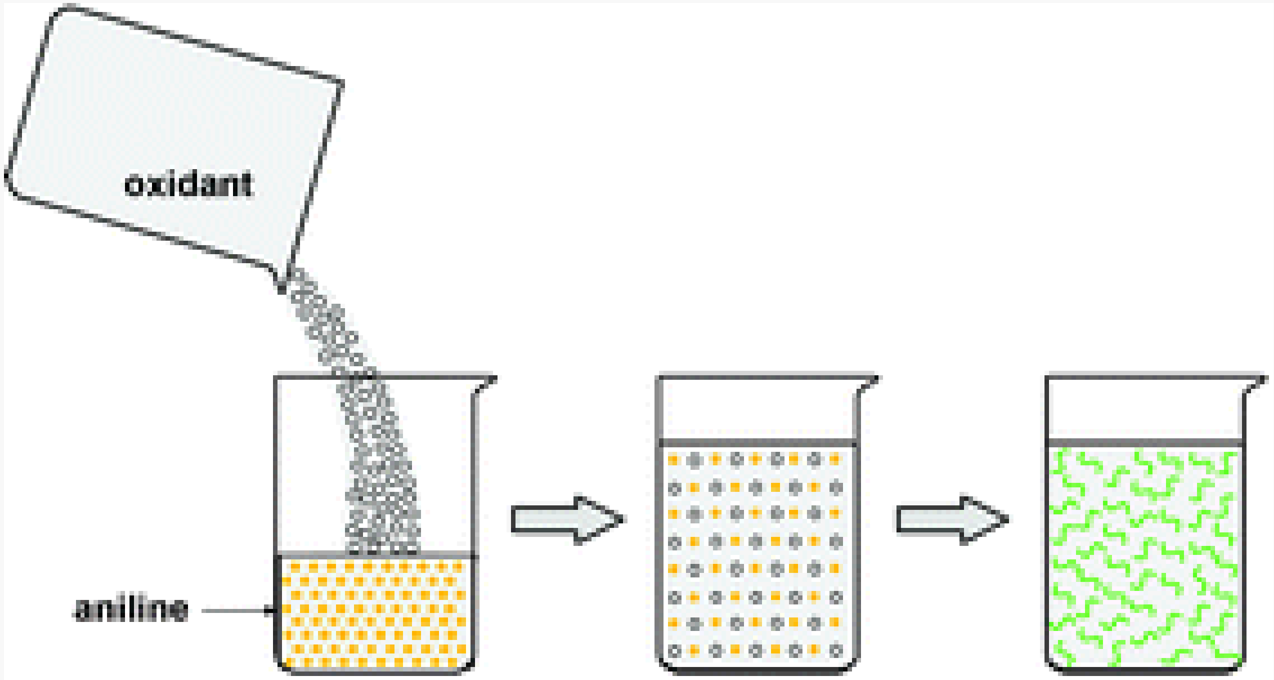




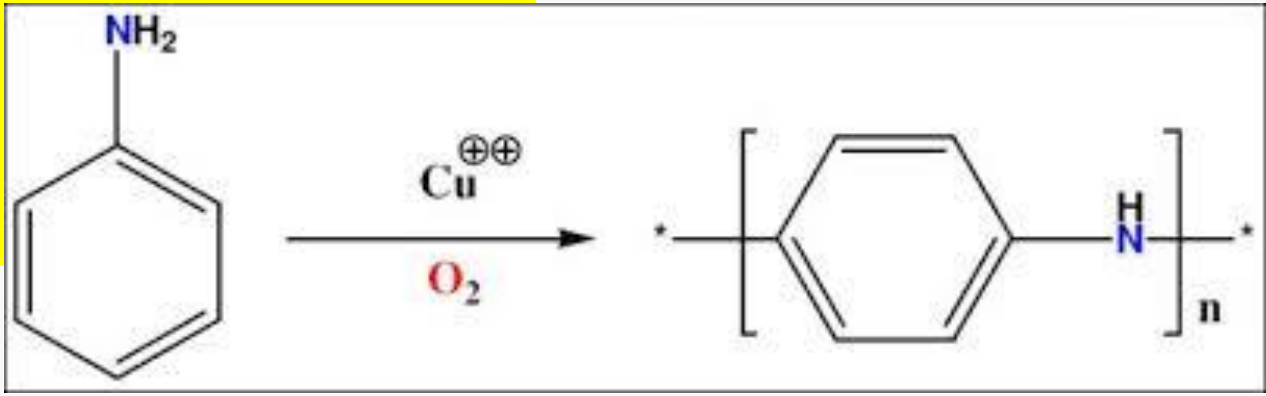




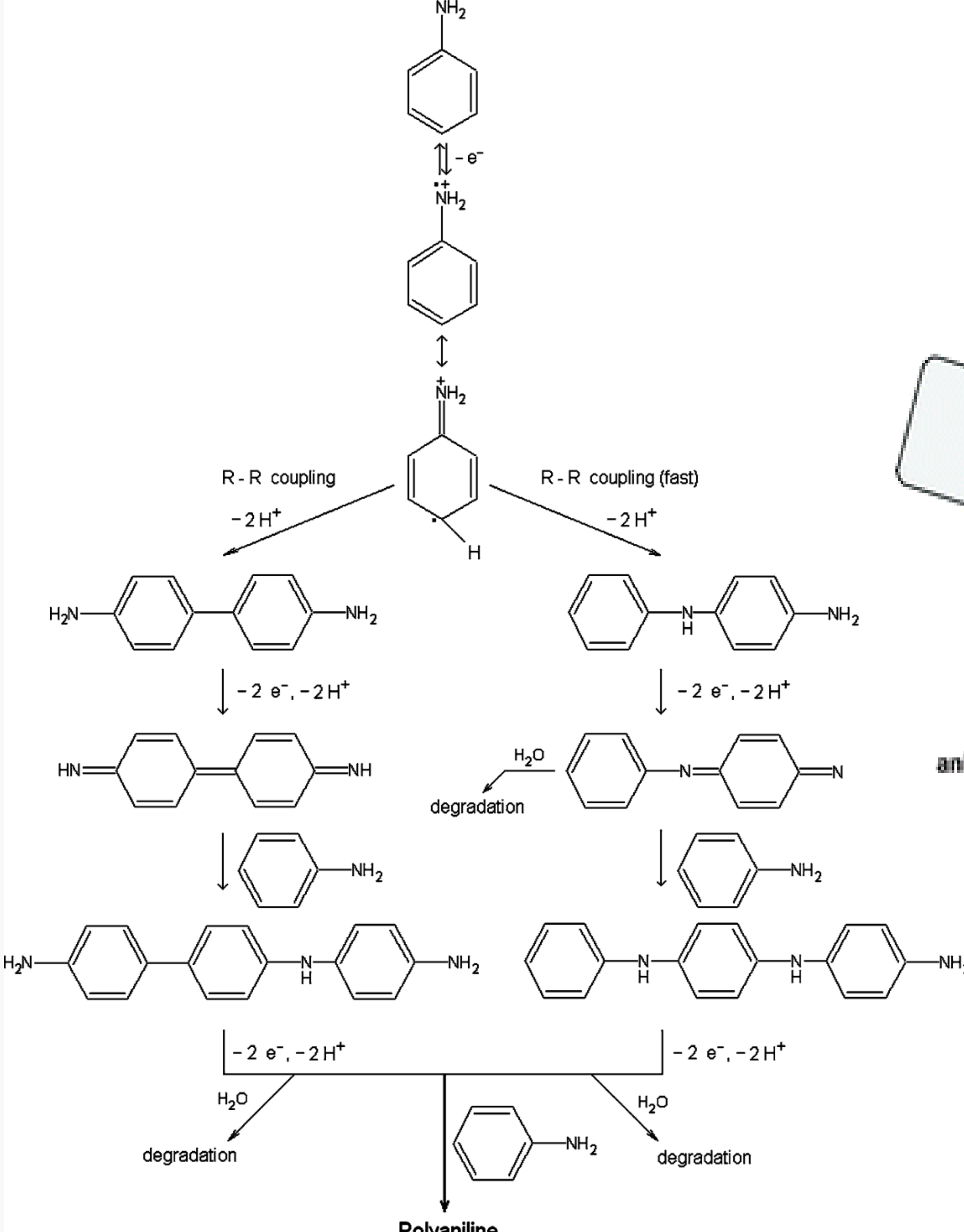
Chemical synthesis of conducting polymers

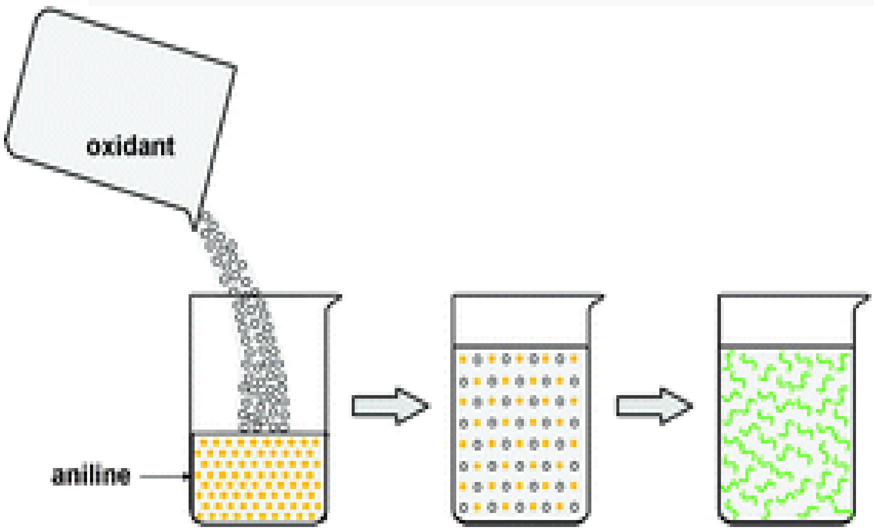


Conditions on which polymerization depends:
- -concentration of oxidant
- -pH
- -nature of electrolyte
- -temperature
- -time

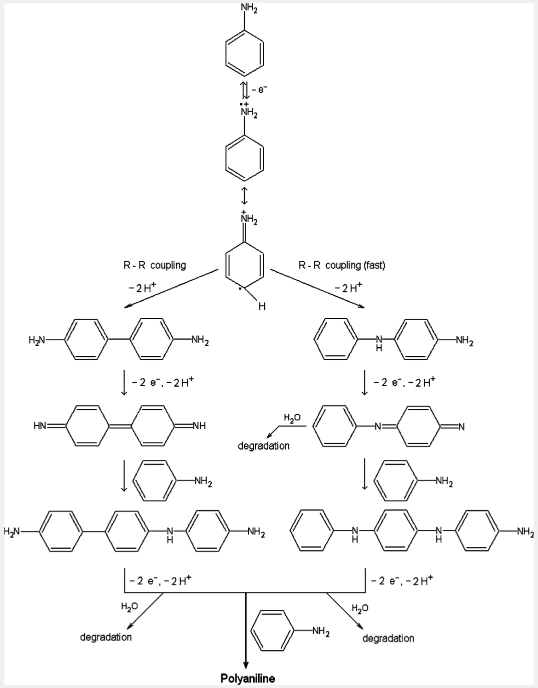


Oxidation of aniline
Synthesis of polyaniline-PANI





Problems that can arise by chemical polymerization method



-kinetics of polymer formation not easy to control

-side radical reactions

-mixture of polymers can be created

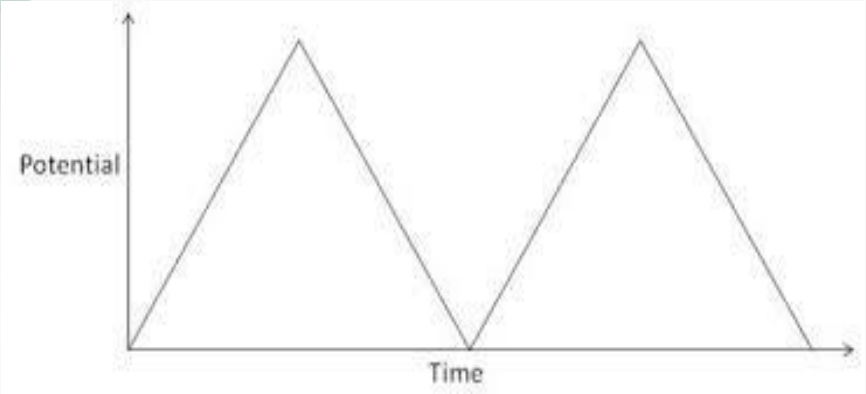
-structure of the polymer can not be uniform (role of intercalated Ions, processes of co-polymerization...)

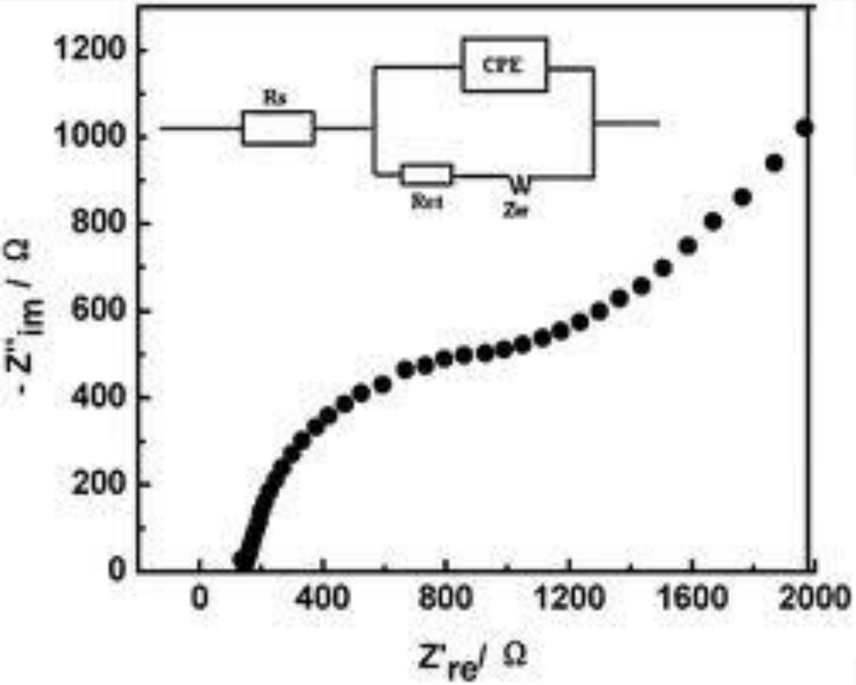
....
Suitable method for massive production of polymers

-for the sake of electrochemistry-a better way is the ELECTROCHEMICAL POLYMERIZATION METHODOLOGY

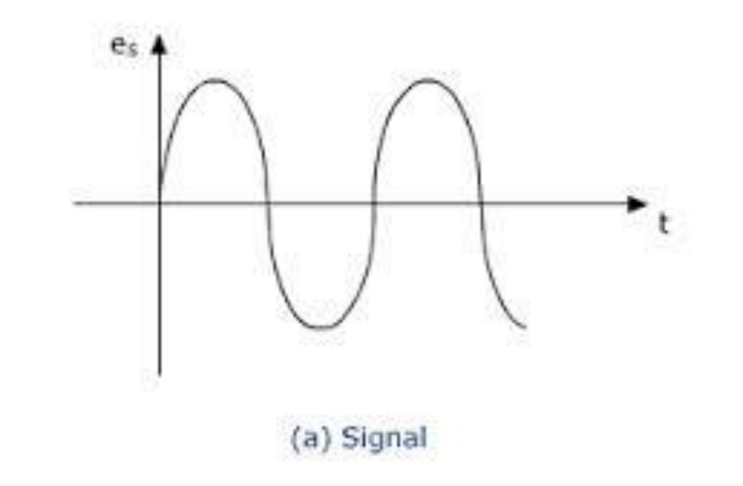
Electrochemical techniques for studying the features of the conductive polymers

CYCLIC VOLTAMMETRY

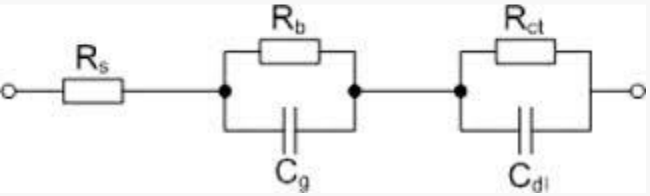


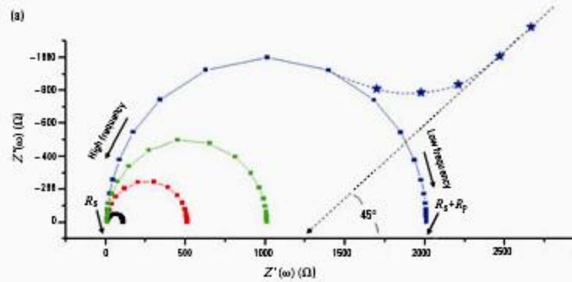


ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY-EIS



Electrochemical Impedance Spectroscopy





(AC) The excitation signal , expressed as a function of time , has the form

$$E(t) = E_0 \cos (wt)$$

In a linear system, **the response signal** , I_t , is shifted in phase (Φ) and has a different amplitude

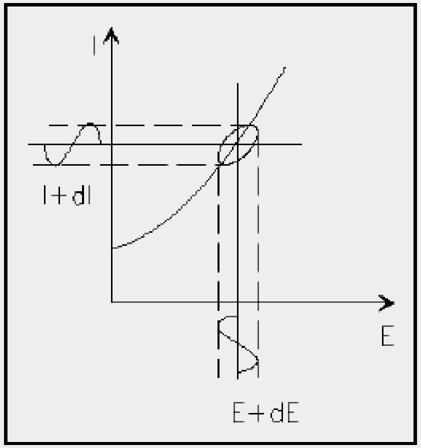
$$I(t) = I_0 \cos (wt - \Phi)$$

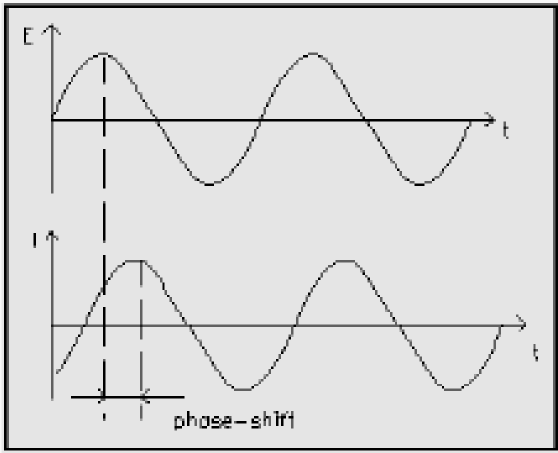
DC ohms law
R= E/I

Z = E(t) / I(t) = Zo [cos(wt) / cos(wt – Φ)]

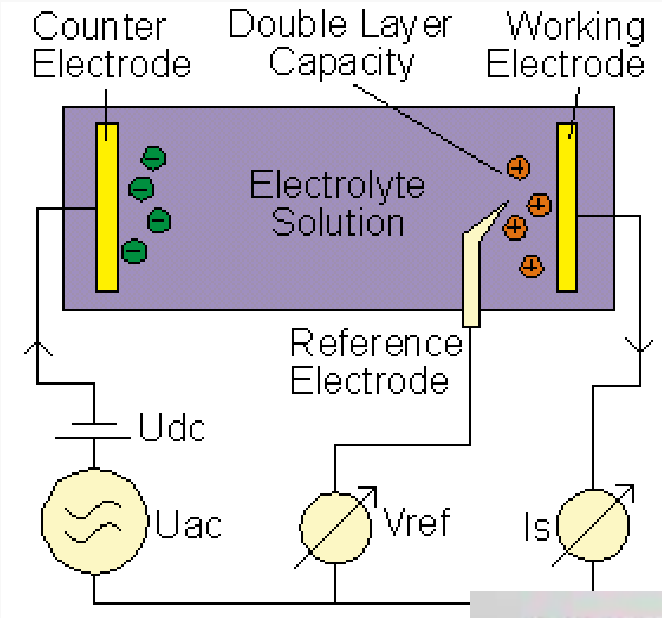
Using EULER's relationship
Exp (j **Φ**) = **cos Φ + jsin Φ**

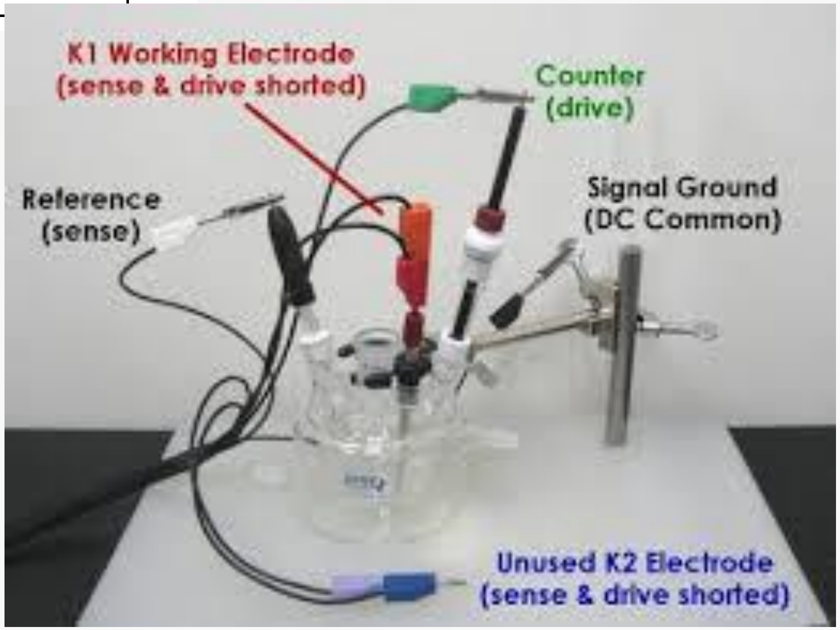
$$Z = Z_0(\cos \Phi + j\sin \Phi)$$





Common three-electrode cell are used in both techniques -a very simple set-up





Cyclic voltammetry provides basic information on the…

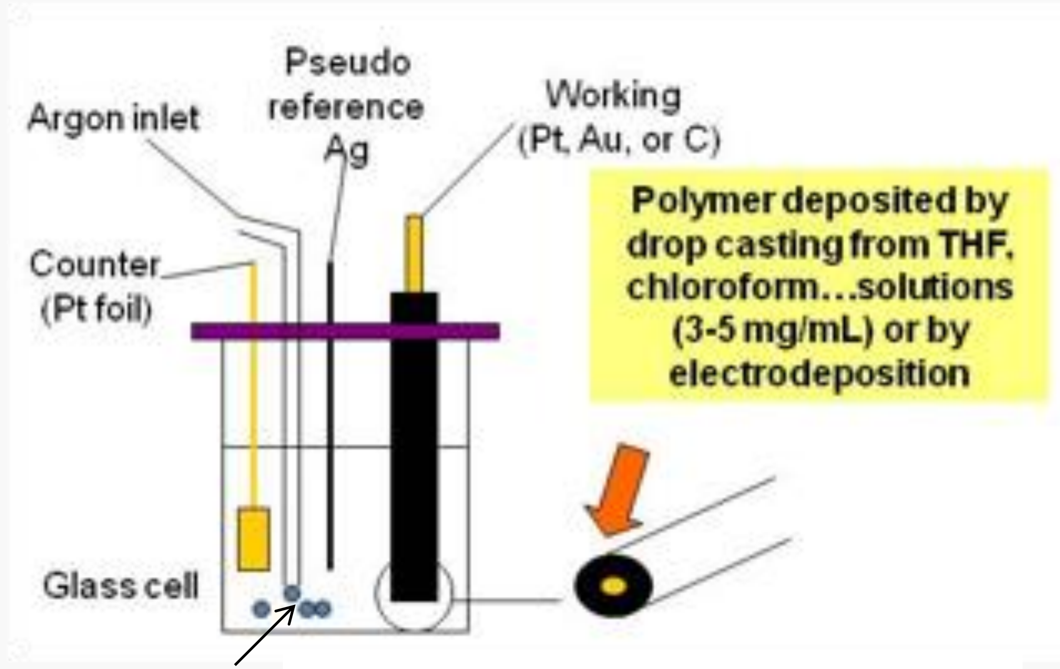
-**oxidation potential of the monomers,**

- **on film growth,**

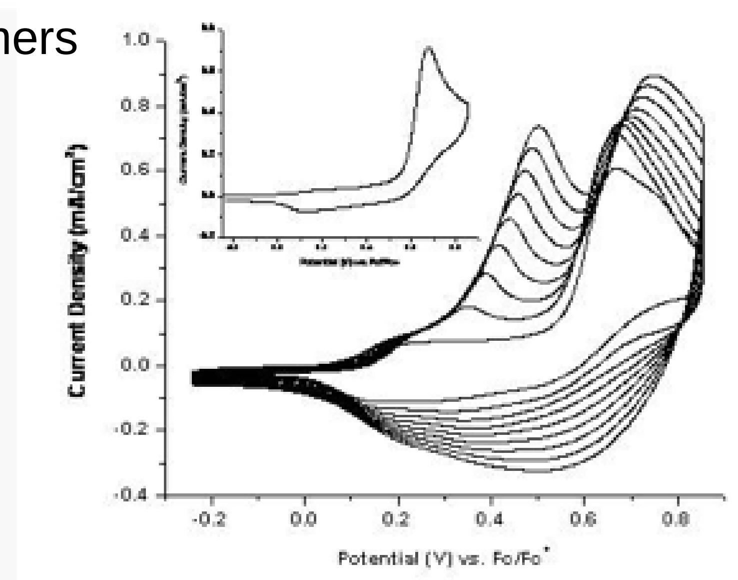
-**on the redox behavior of**
- **the polymer,**

and on the

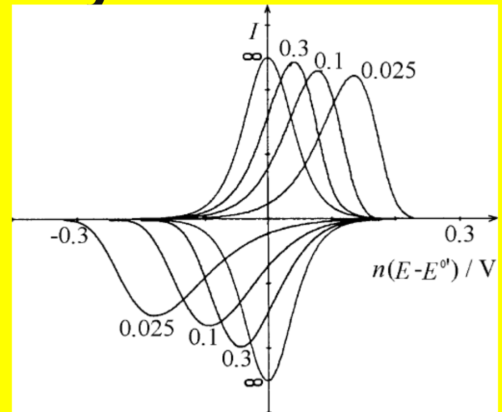
-**surface concentration (charge consumed by the polymer).**



monomers

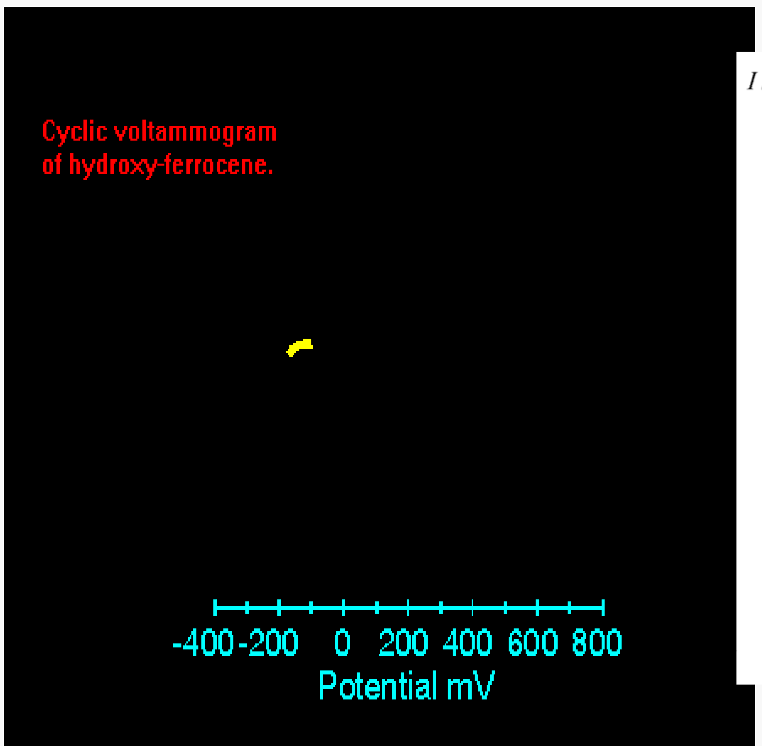


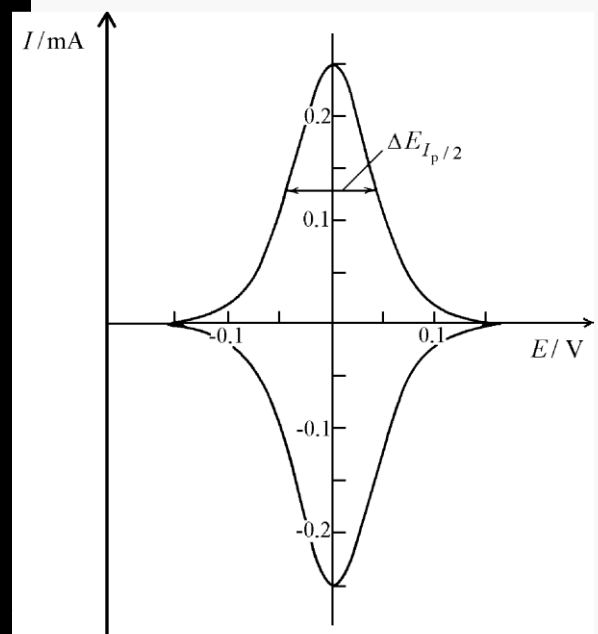
Conclusions can also be drawn from the cyclic voltammograms regarding the

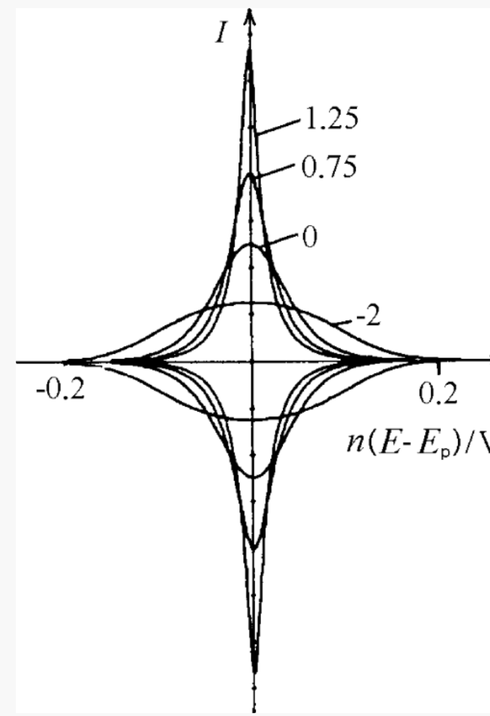


-rate of charge transfer
-charge transport processes, and the
-coupled chemical reactions…

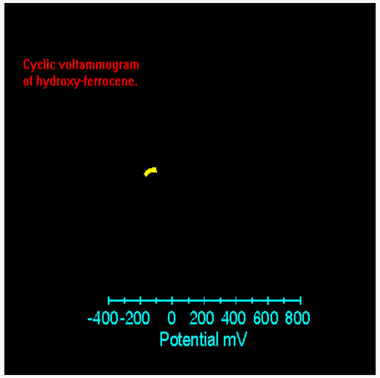
-interactions that occur within the polymer segments, at specific sites and between the polymer and the ions and solvent molecules.



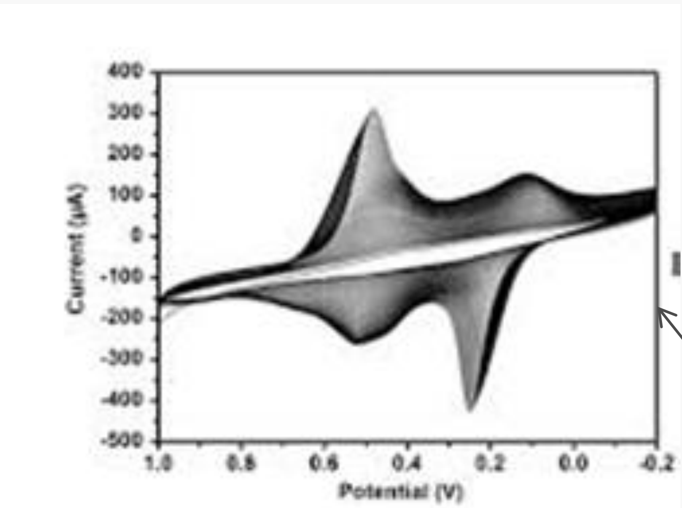




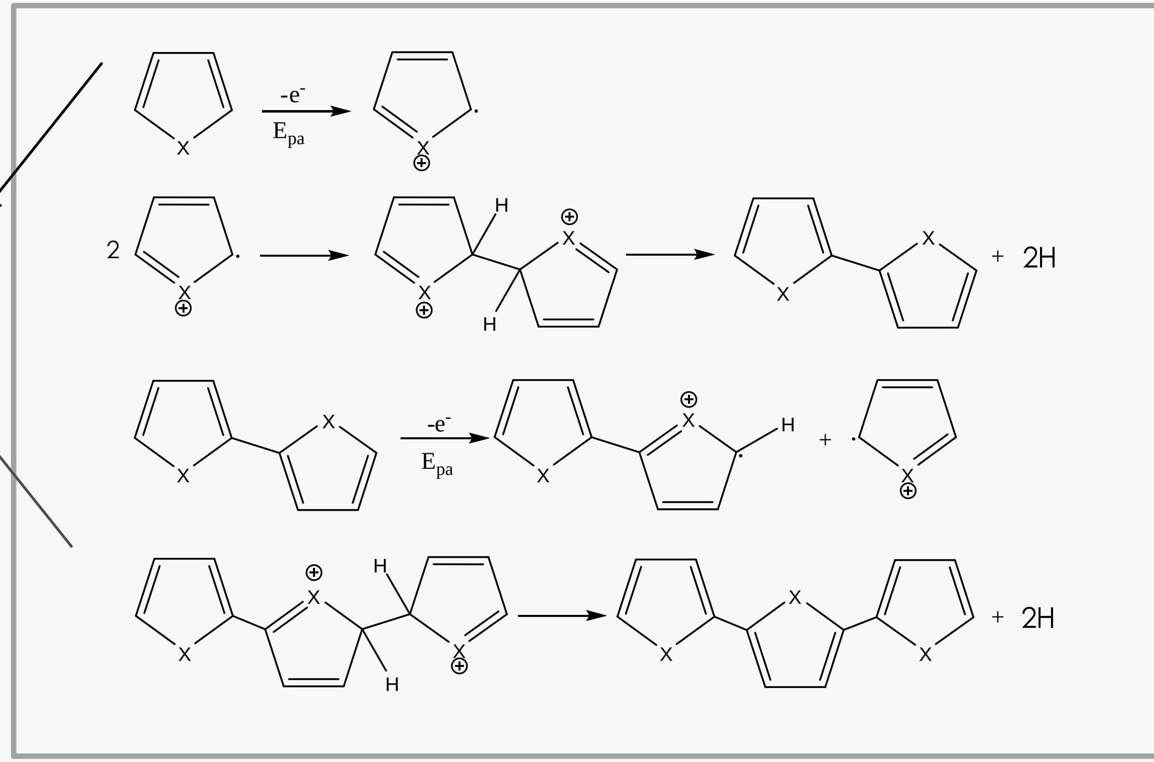
Cyclic Voltammetry (CV)



doping; reduction or oxidation.
Oxidation leaves "holes" in the form of positive charges that can move along the chain



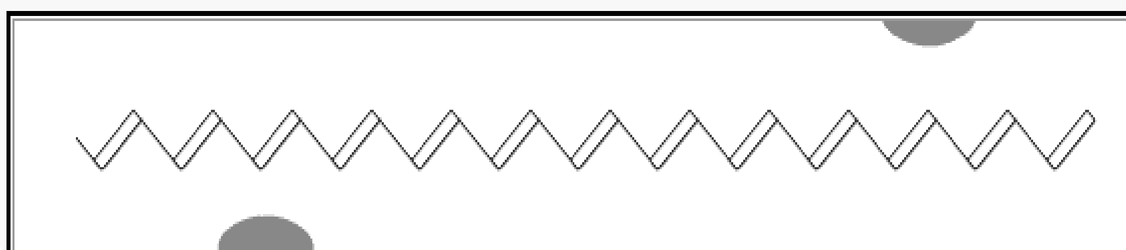
Polymer Electrogrowth



extremely useful for studying
electrode reaction mechanisms
&electropolymerization

Red ↔Ox + e-→X

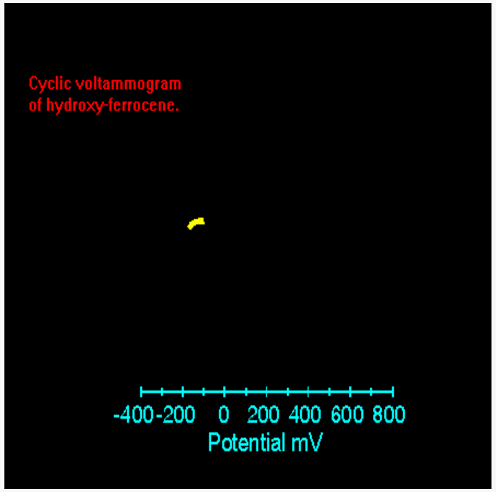
Monomer Free

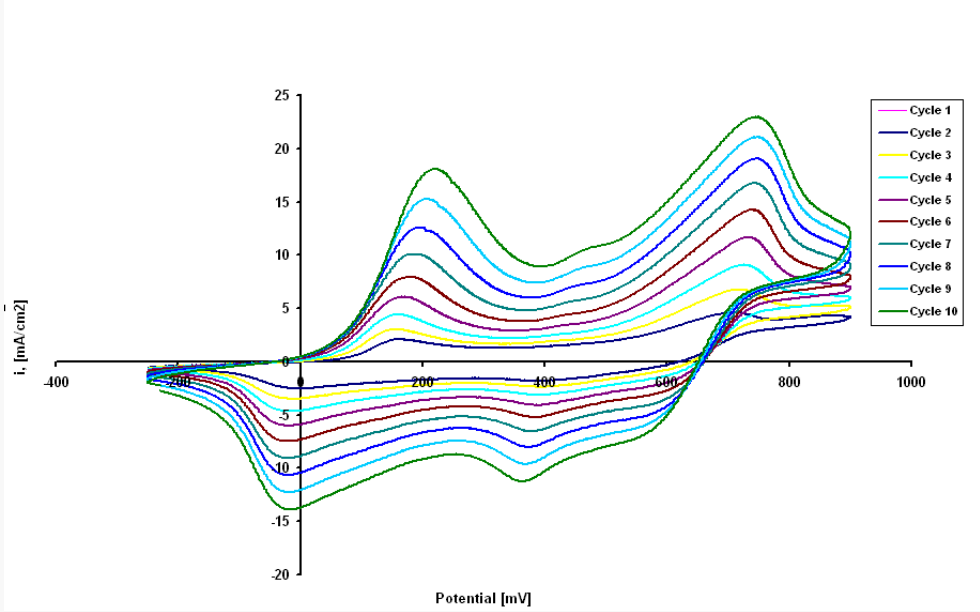


Electropolymerization mechanism of 5-membered heterocycles

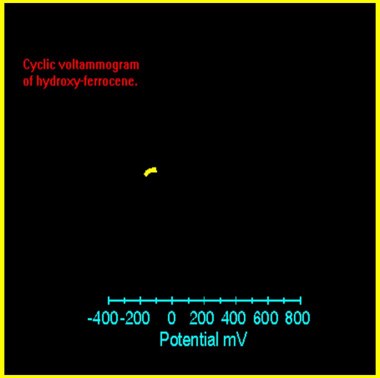
FACTOR AFFECTING THE POLIMERIZATION PROCESS AND THE STRUCTURE OF THE POLYMER FILM

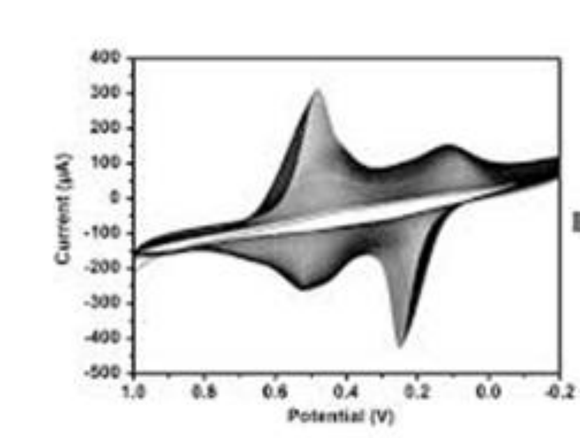
- -scan rate
- -initial and final potential
- -repetitive cyclization
- -type of the electrode material
- -type of the supporting electrolyte
- -pH of the solution
- -temperature
- -presence of co-adsorbants...





Cyclic voltammetry and Electrochemical impedance spectroscopy can provide a big range of valuable results





-kinetic parameters

-thermodynamic parameters

-insight into the redox transformation (redox mechanism

-insight into the influence of the various parameters used in the system studied

-insight into the chemical reactions occuring in the process of electropolymerization

-insight into the polymer growth

...

...

But,

Both techniques can not give us a visual impression of the structure of the polymer film

...they must be coupled by highly sophisticated microscopic Techniques in order to get complete characterization of the polymer film., i.e. <u>Atomic Force Microscopy and Scanining Electron Microscopy</u>

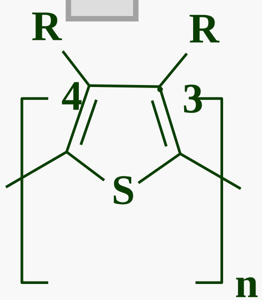
EXAMPLE: Electrochemical and microscopis study of the behavior of conductive polymers- Poly(3,4-alkylenedioxythiophene) Derivatives

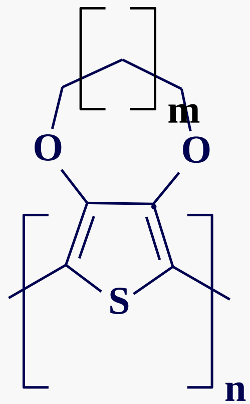
LONGER CONJUGATION LENGTH

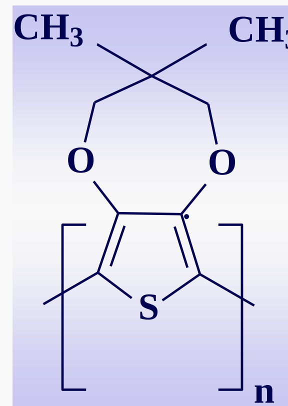
MORE ORDERED POLYMERS

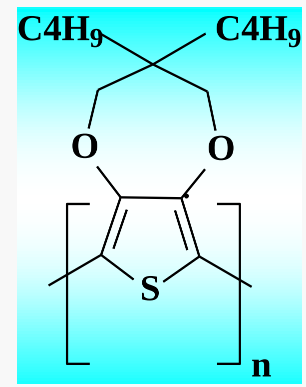
STABLE OXIDIZED FORM

LOW E_{ox}









Poly(3,4-dialkylthiophene)

Alkyl substitution to the monomer, lowers the E_{OX}

ProDOT-$(Me)_2$

ProDOT-$(Bu)_2$

Substitution at the 3- and 4- positions

CONDUCTIVITY

STERIC INTERACTIONS

INCREASING DEGREE OF CONJUGATION

J.Roncali,Chem.Rev.1997,97,173

ELECTROCHEMICAL EXPERIMENTS

Cyclic Voltammetric (CV)*Coating:*

10 mM ProDOT-$(Bu)_2$ in

0,1 M **$NaClO_4$/ACN & Bu_4NPF_6/ACN**

at diff.scan rates (mV s-1)

0,0 V – 1,6 V

Electrochem.Impedance Spectroscopy (EIS)

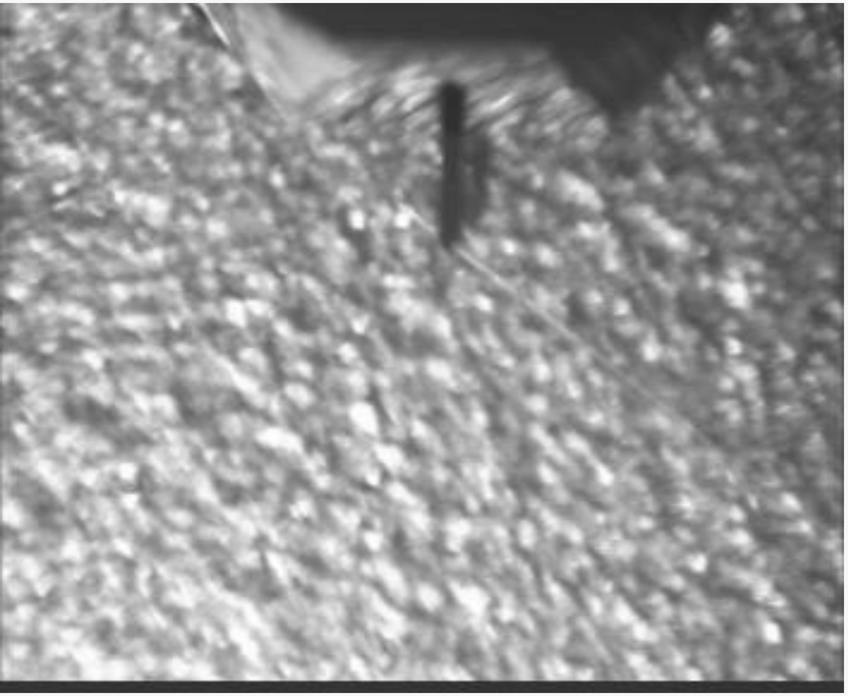
0,1 M $NaClO_4$/ACN

100 kHz -10 mhz

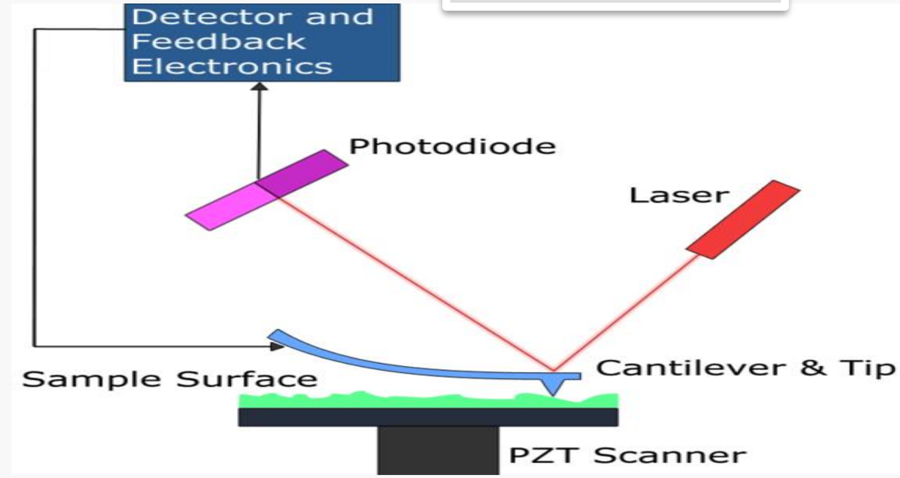
3 ELECTRODE SYSTEM

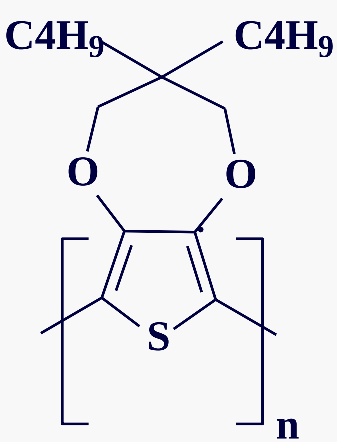
W.E. : CFSE (carbon felts electrode) , ITO (Indium Tinoxide electrode) ,Pt
R.E. : Ag wire
C.E. : Pt wire

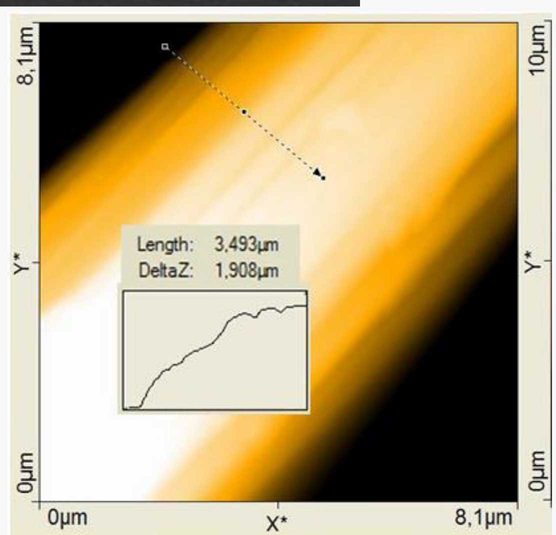
Atomic Force Microscopy (AFM)

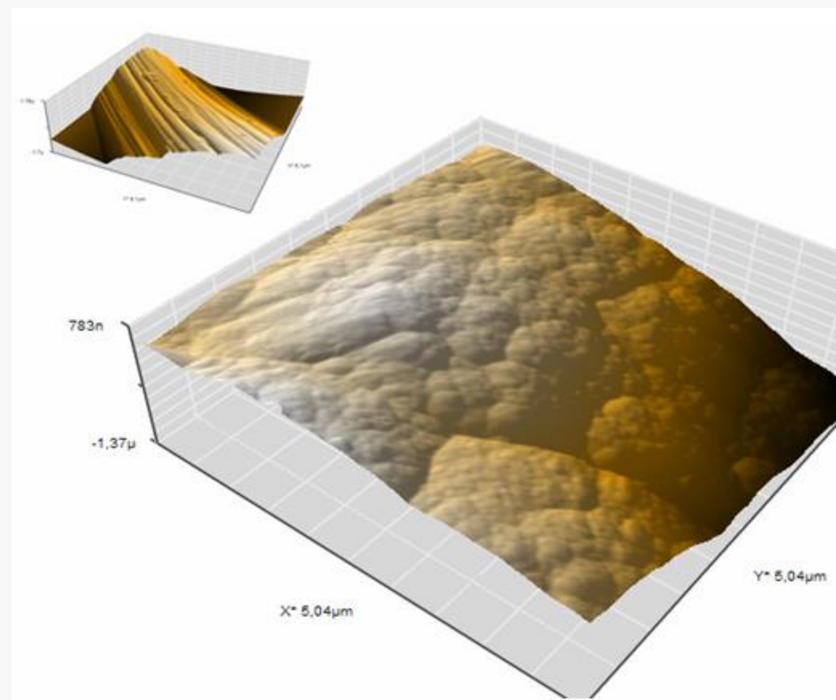


NON-CONTACT

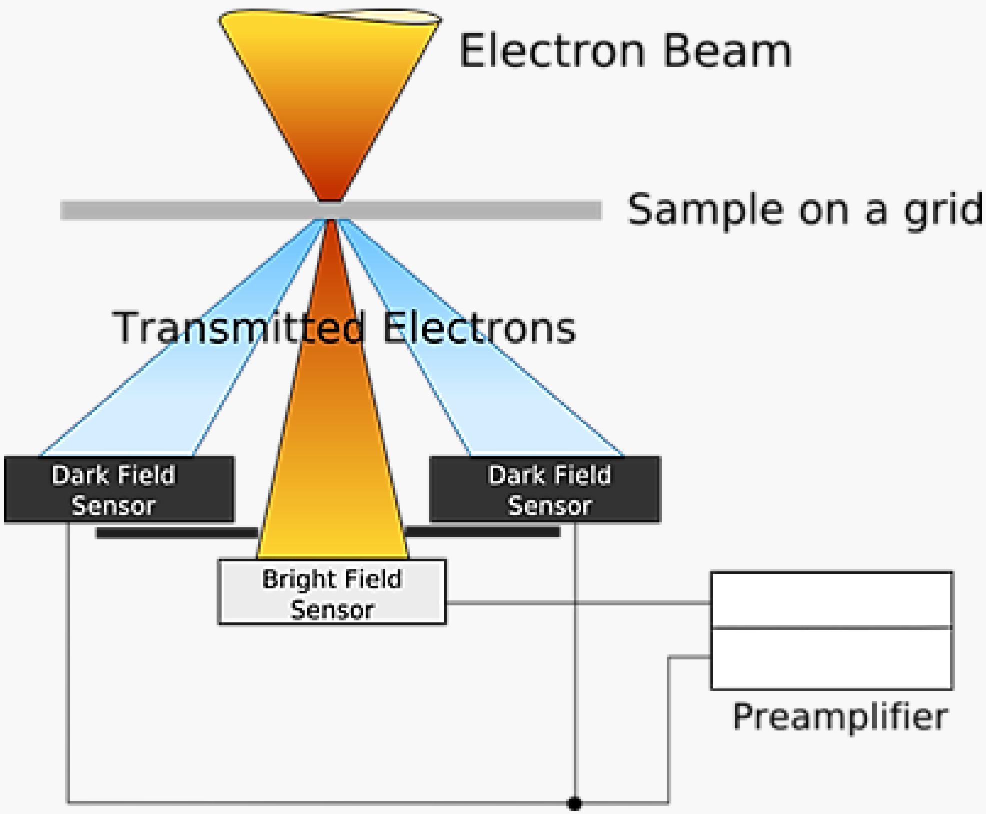


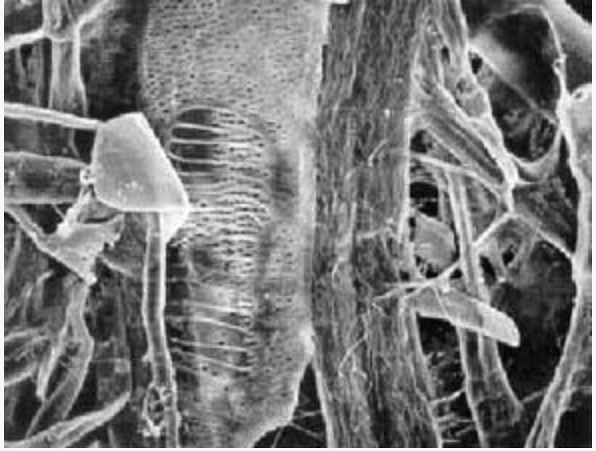


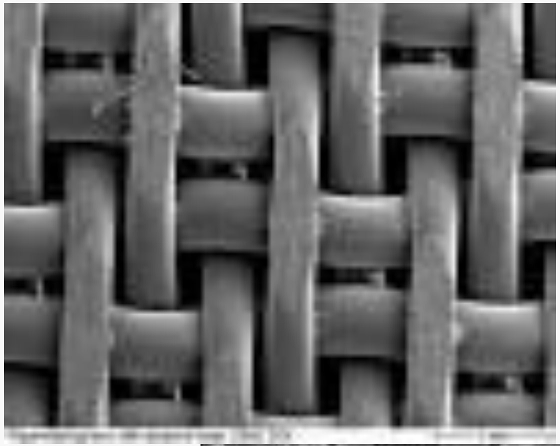


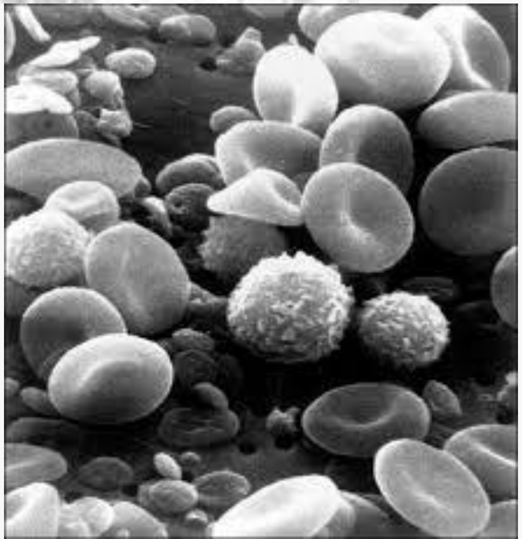


Scanning Electron Microscopy



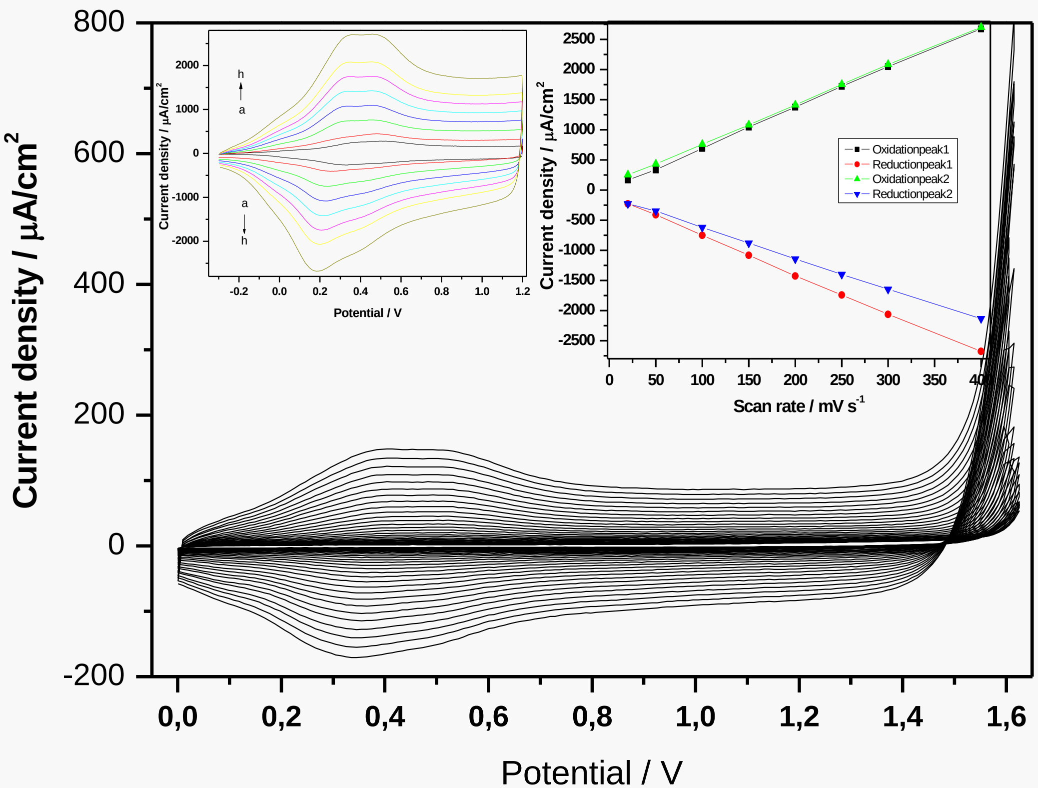


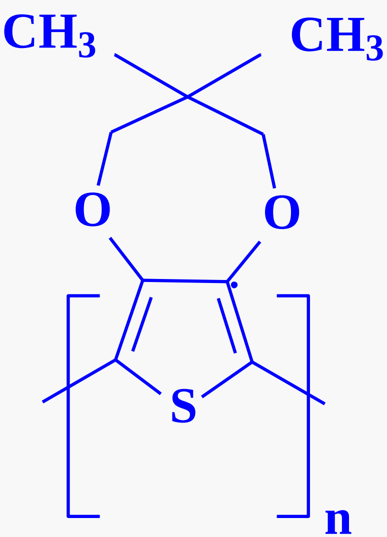




Experiment 1. Cyclic Voltammetric film growth

100 mV/s



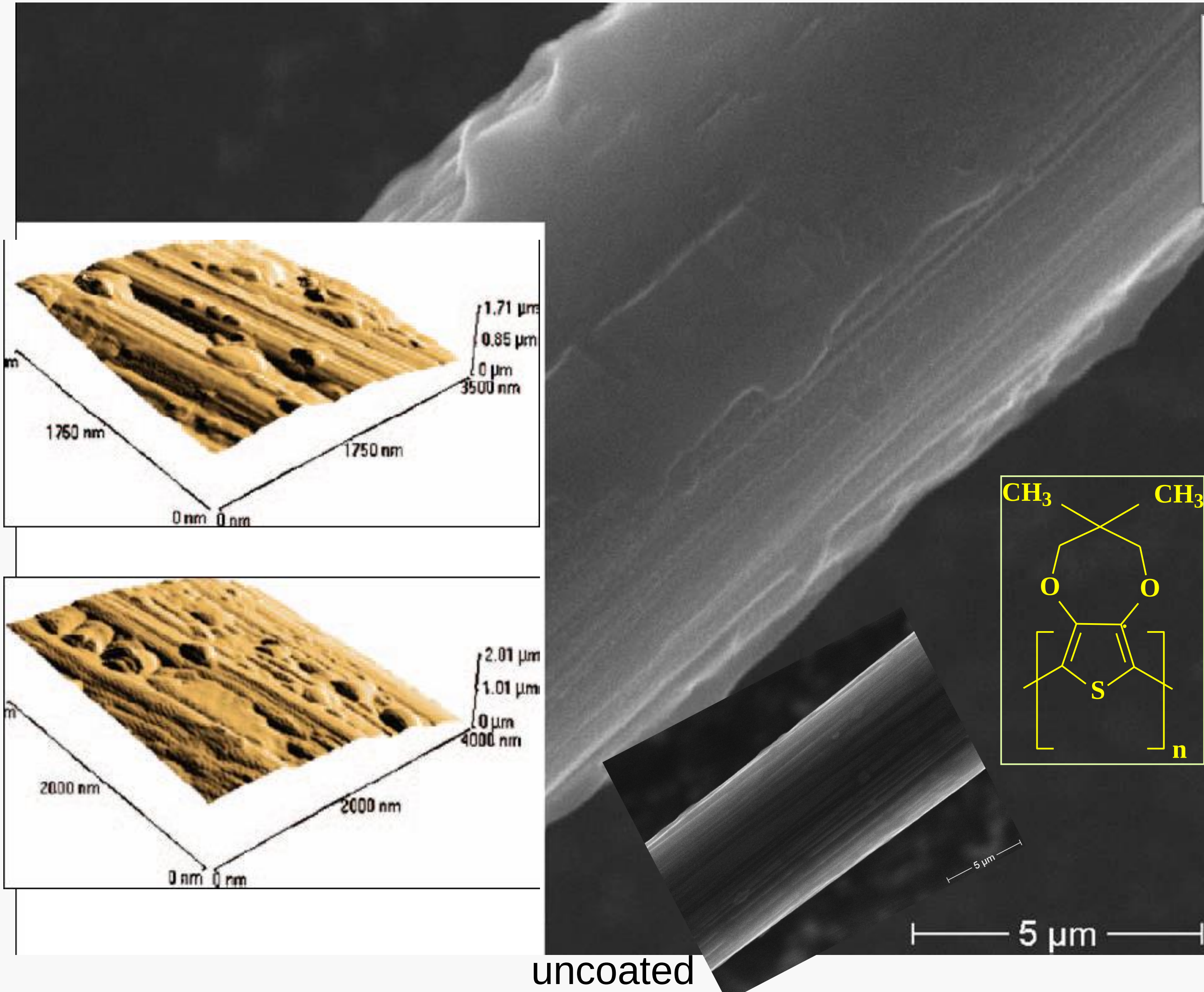


5mM ProDOT-Me$_2$ deposited at 100 mV/s, 10cycle in 0.1 M Bu_4NPF_6/ACN

EDX results of coatings

SEM & AFM

Electrocoated **2,2-Dimethyl-3,4 Propylenedioxythiophene** **on CFME**
in 0.1 M Bu_4NPF_6/ACN at scan rate: 400 mV/s, 10 cycle.



uncoated

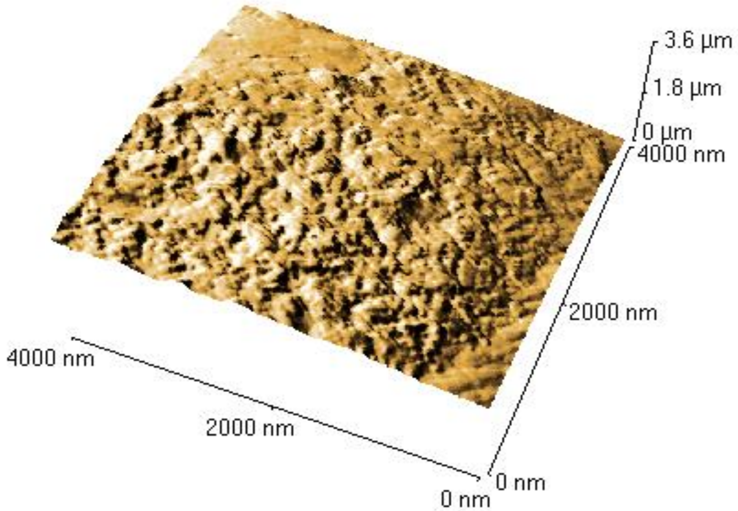
SCAN RATE EFFECT
400 mV/s

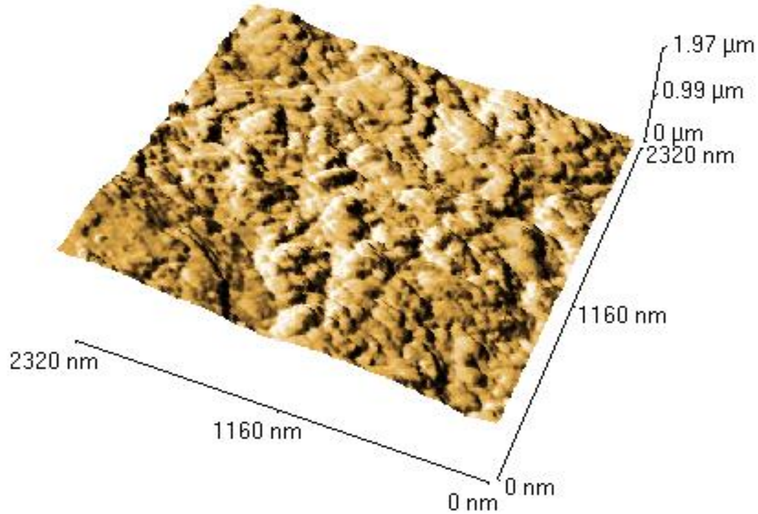
SEM & AFM

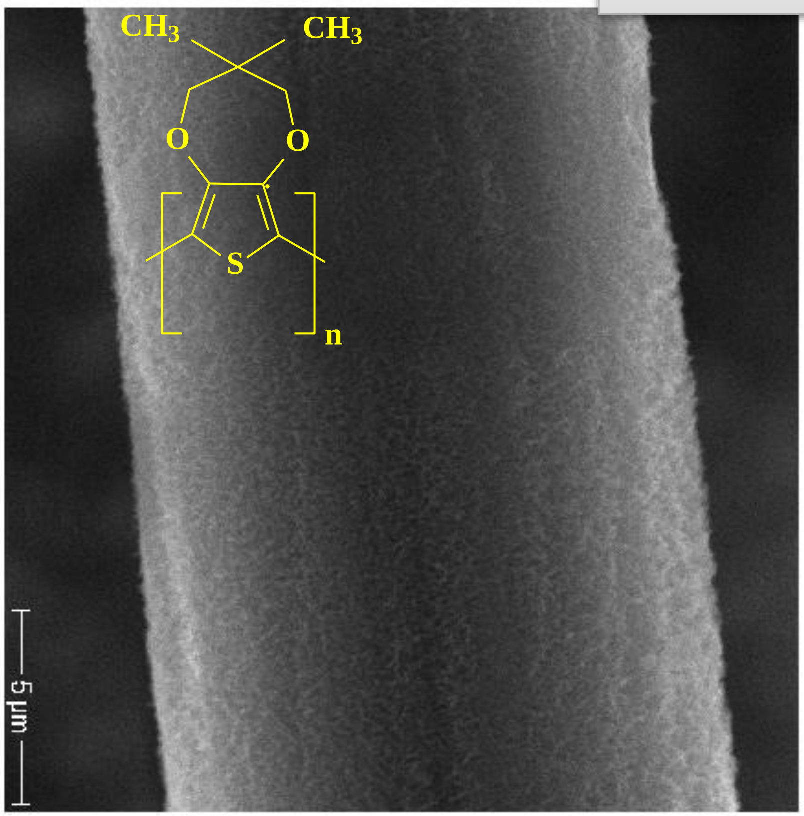
Electrocoated 2,2-Dimethyl-3,4 Propylenedioxythiophene on CFME

20 mV/s & 10 cycle

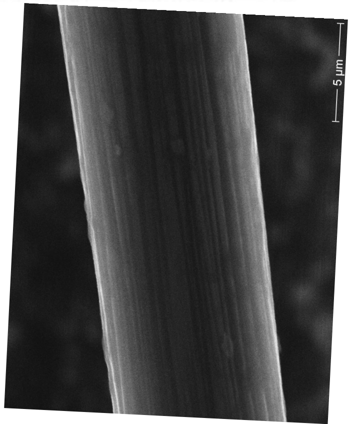
20 mV/s



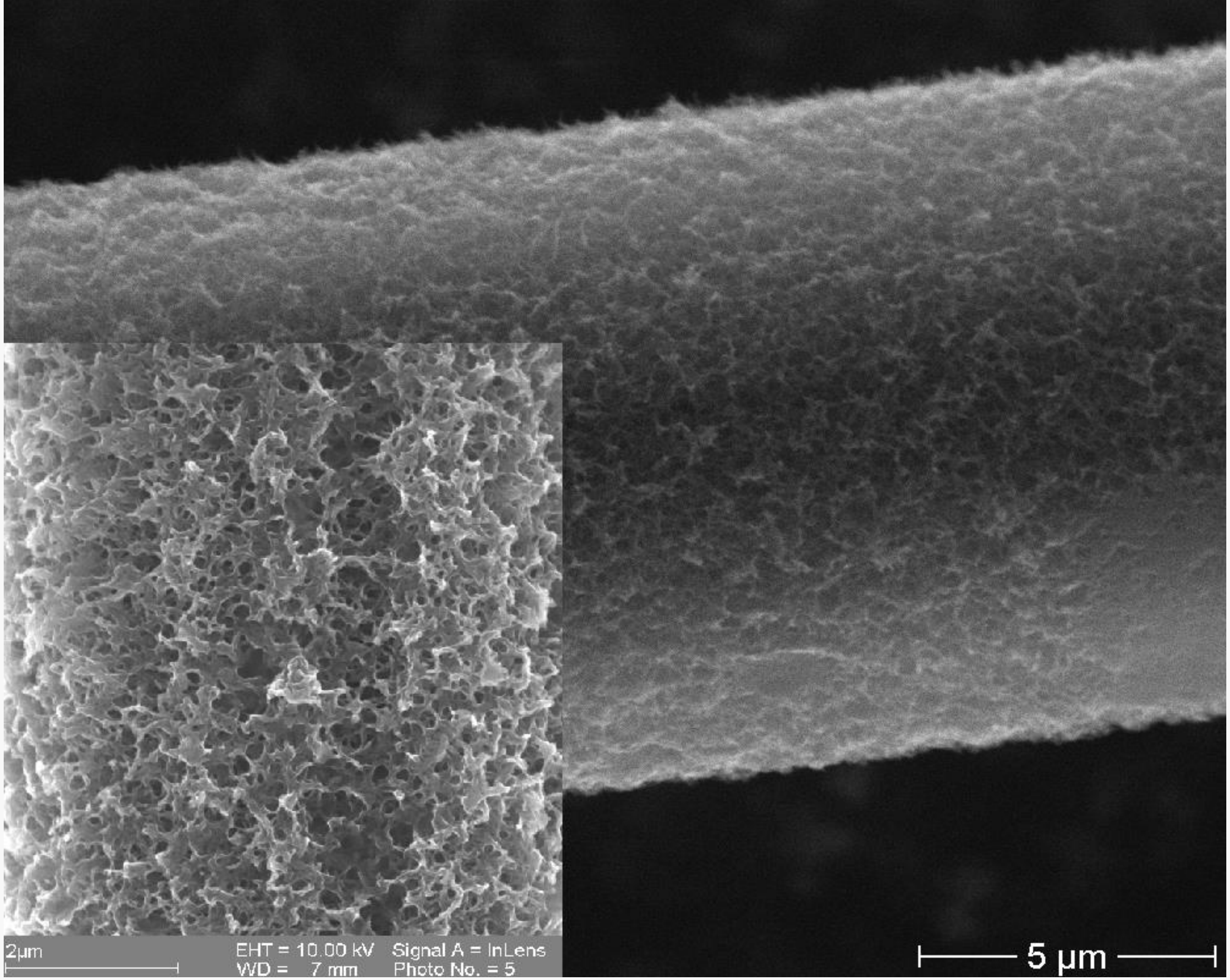


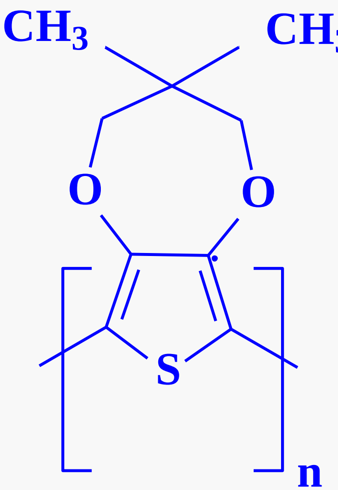


uncoated CF



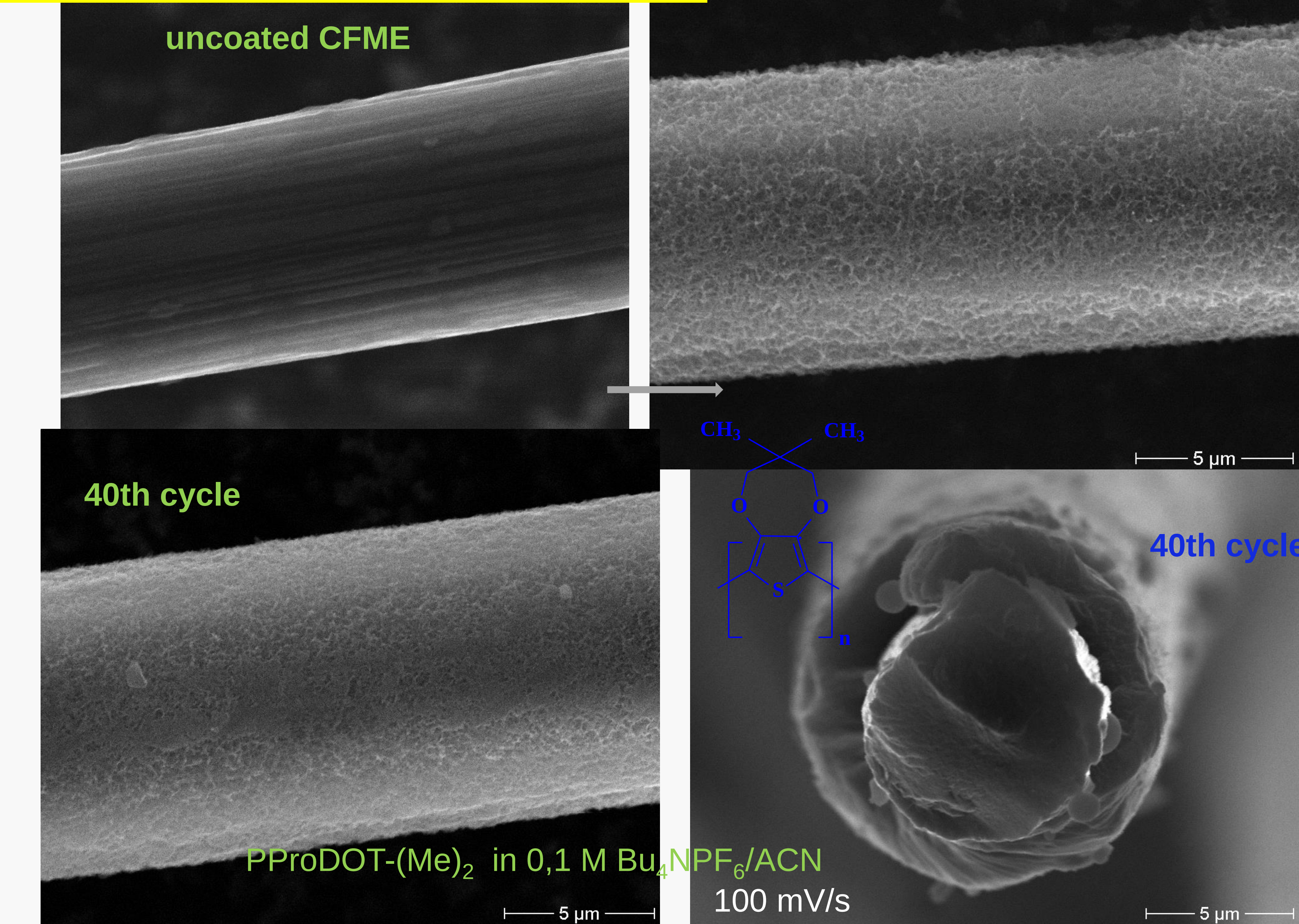
100 mV/s





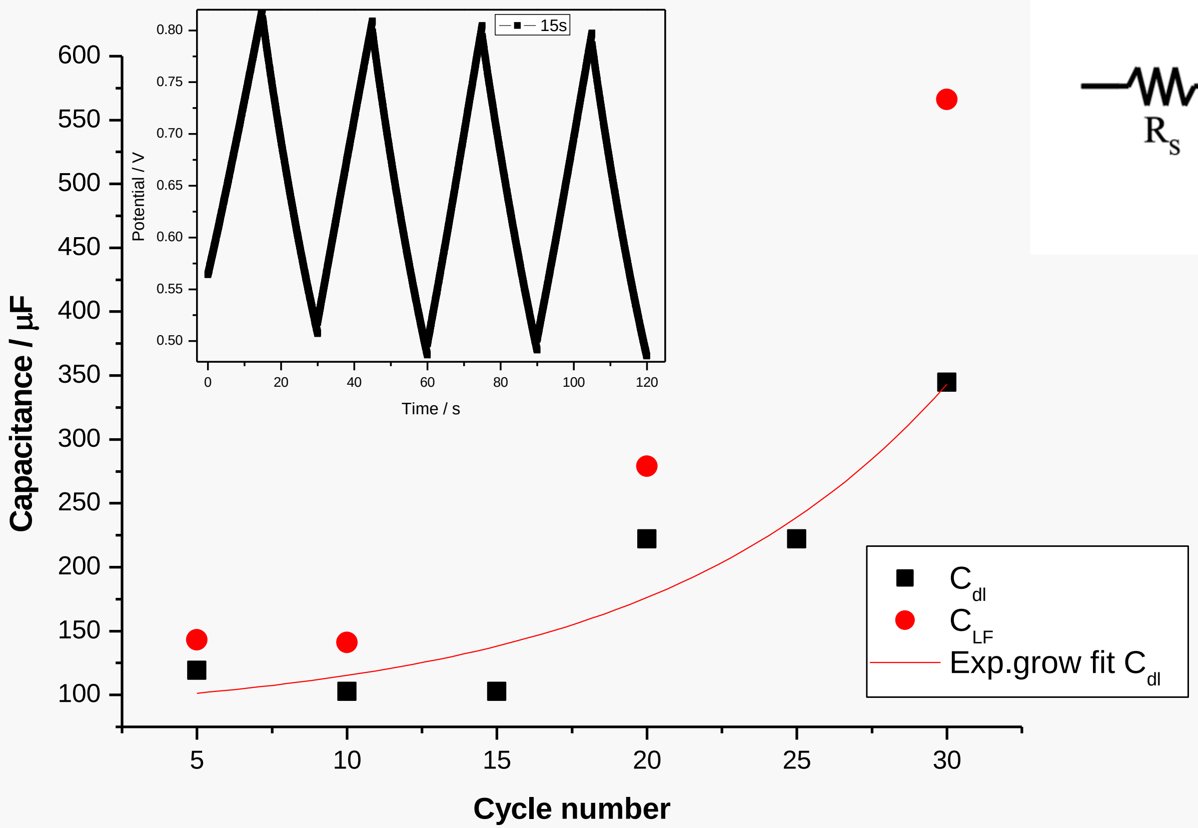
SEM picture of PProDOT-(Me)$_2$/CFME
in 0,1 M Bu_4NPF_6/ACN
scan rate:100 mV/s ,10 cycle, 2 different magnifications

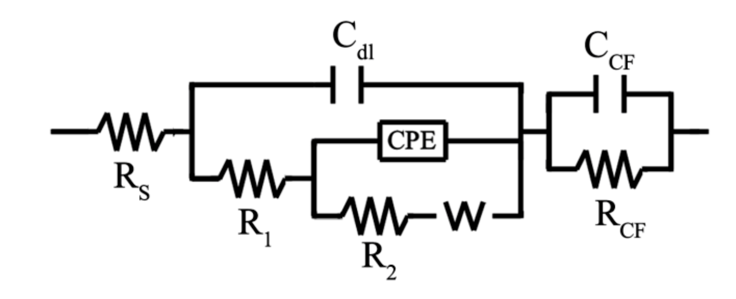
EFFECT OF CYCLIZATION (No OF CYLCES)



Capacitance vs scan no

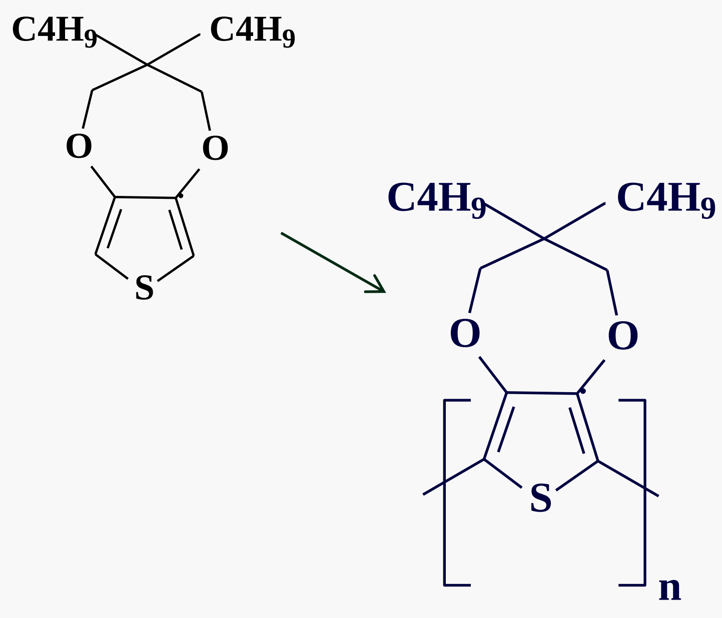
5mM ProDOT-Me_2 deposited at 100 mV/s in 0.1 M Bu_4NPF_6/ACN

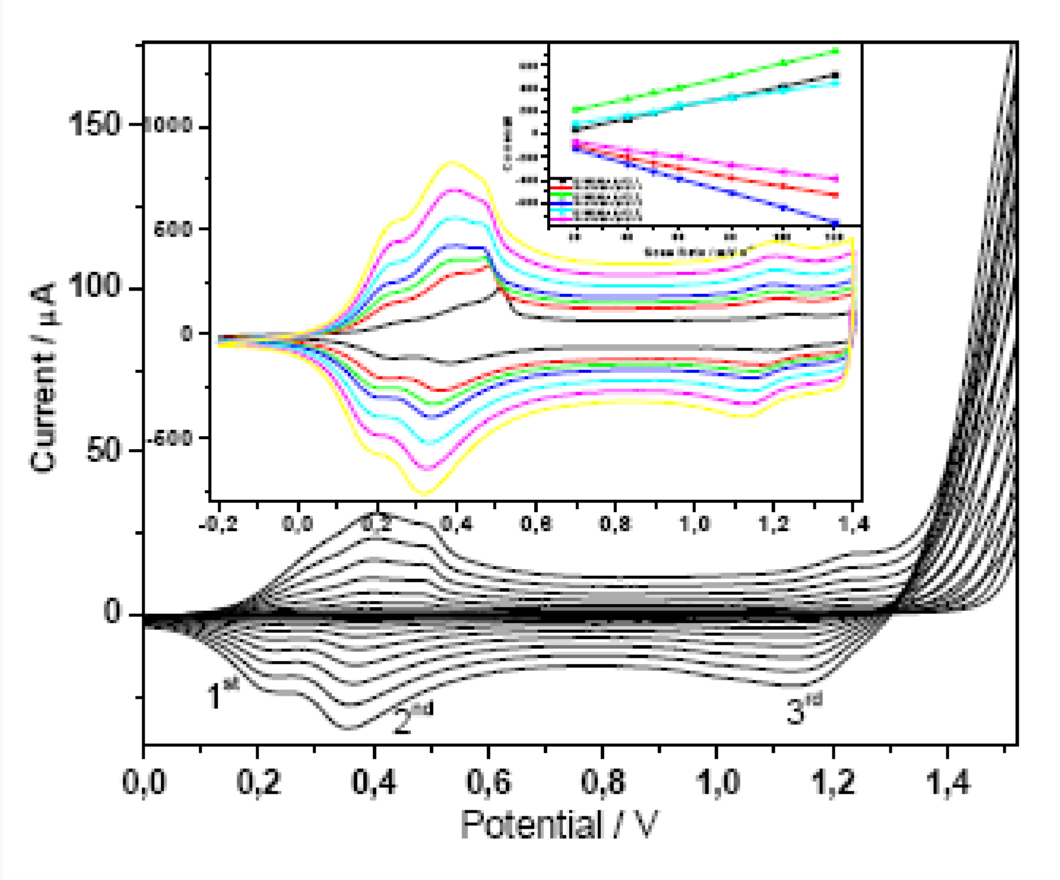




Poly(3,4-alkylenedioxythiophene) Derivatives

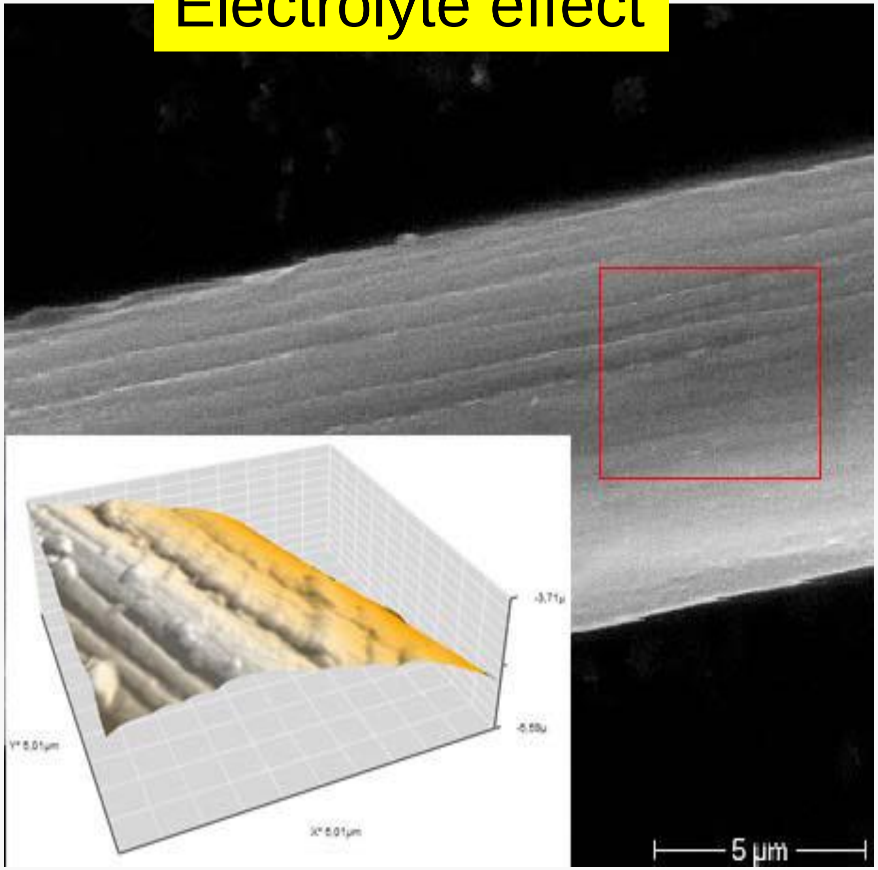
2,2 -dibutylpropylene dioxythiophene (PProDOT(Bu)$_2$)

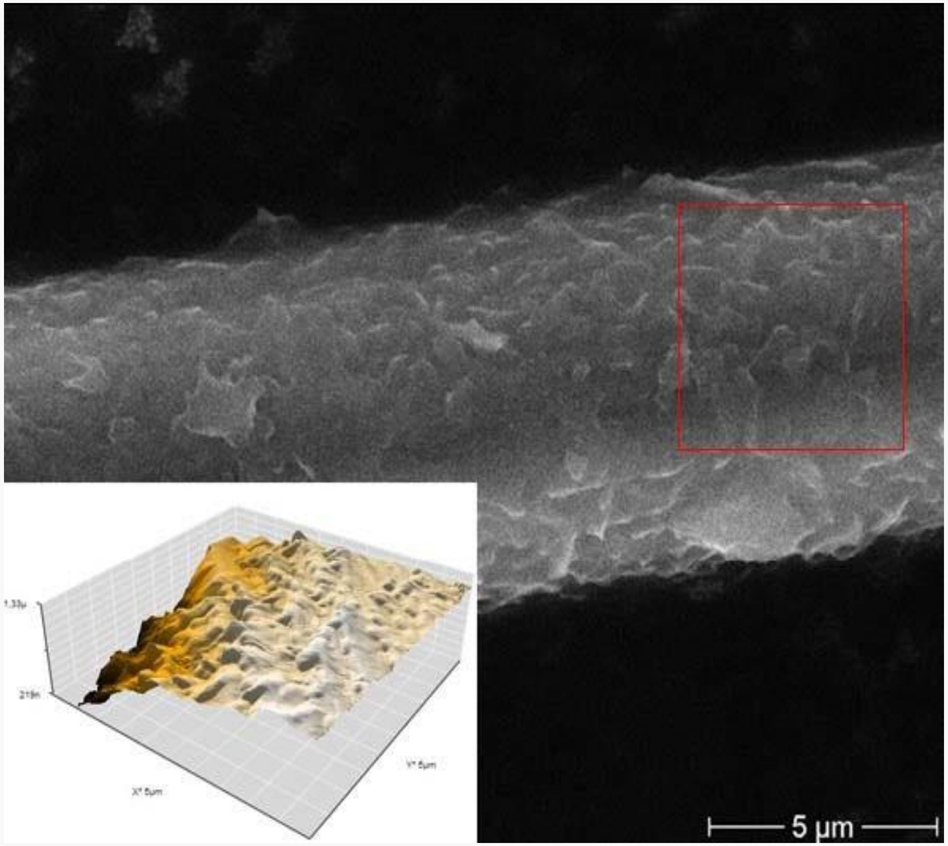




Atomic Force Microscopy (AFM)&SEM

Electrolyte effect



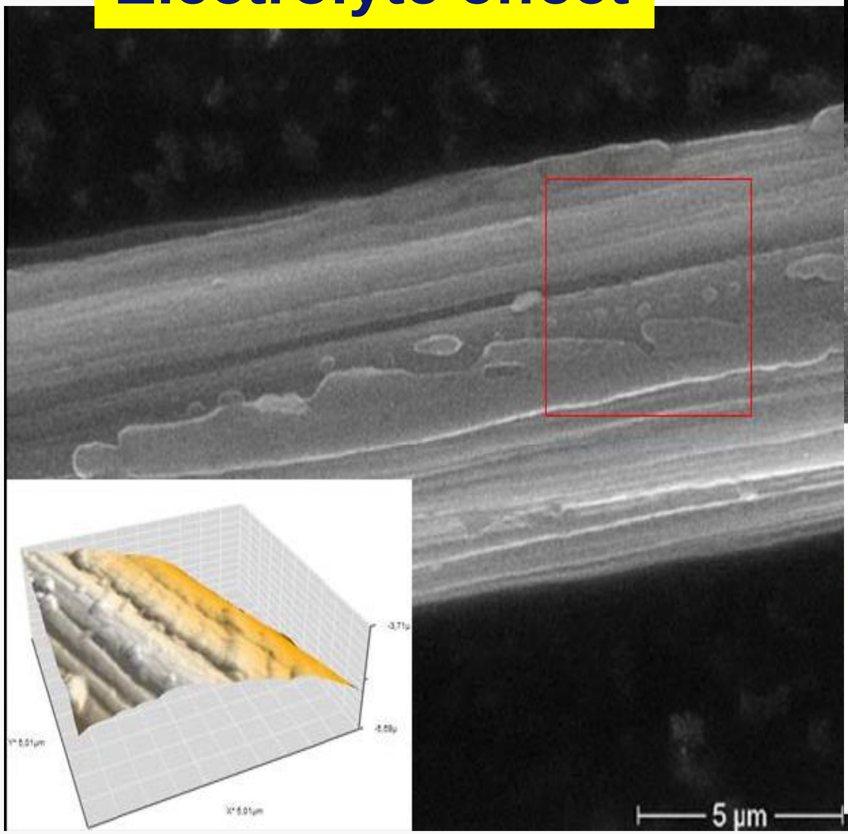


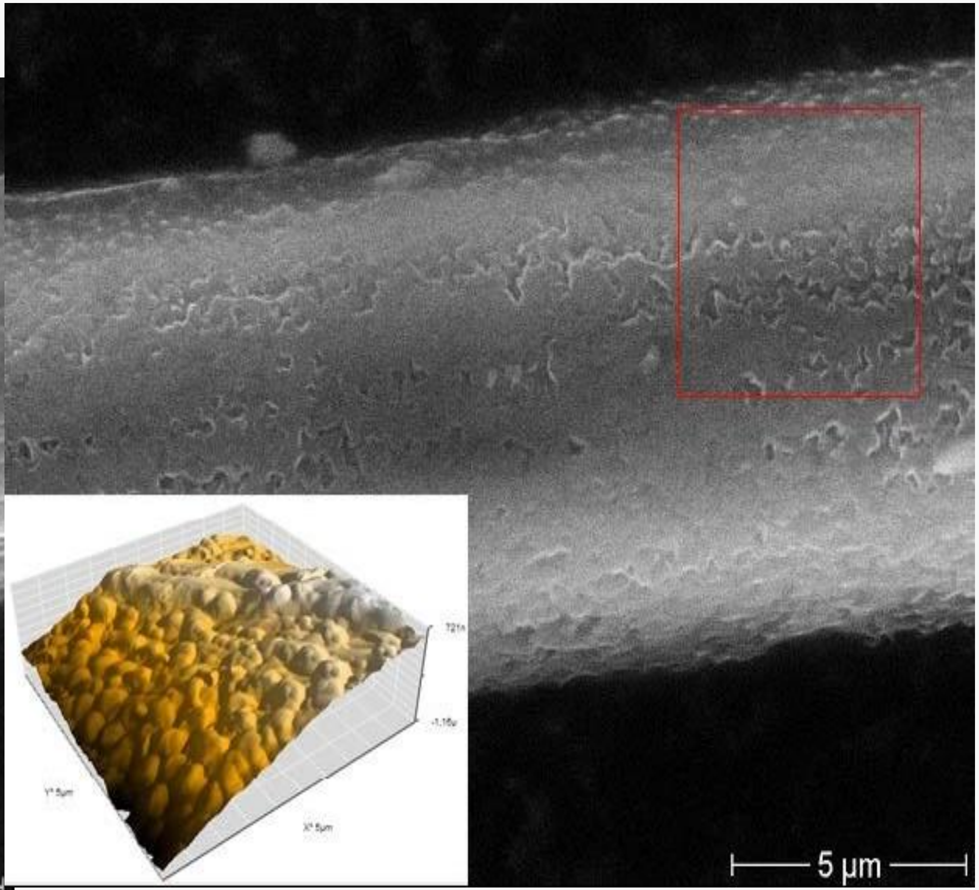
PProDOT-(Bu)$_2$/0,1 M **Bu_4NPF_6 /ACN**

PProDOT-(Bu)$_2$/0,1 M **Bu_4NBF_4/ACN**

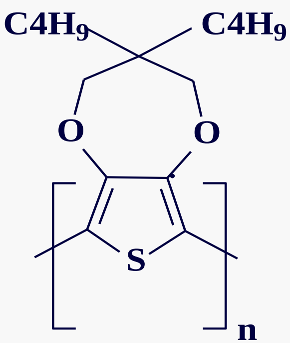
Atomic Force Microscopy (AFM)

Electrolyte effect



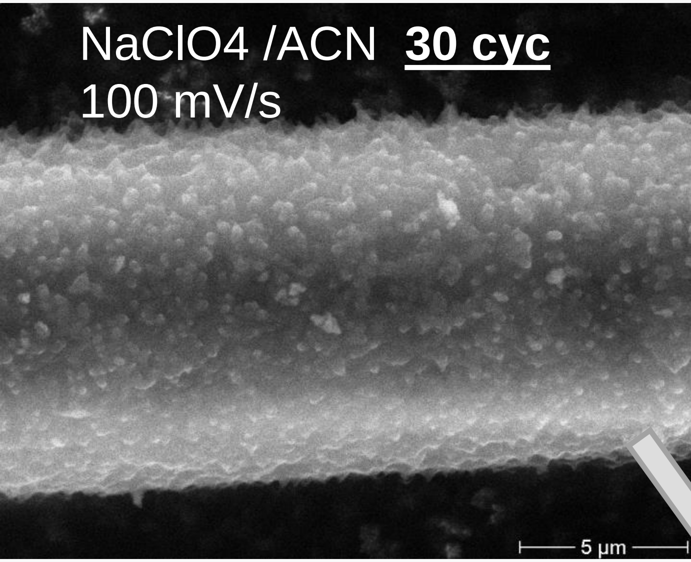


PProDOT-(Bu)2/0,1 M **Et_4N**ClO_4 /ACN

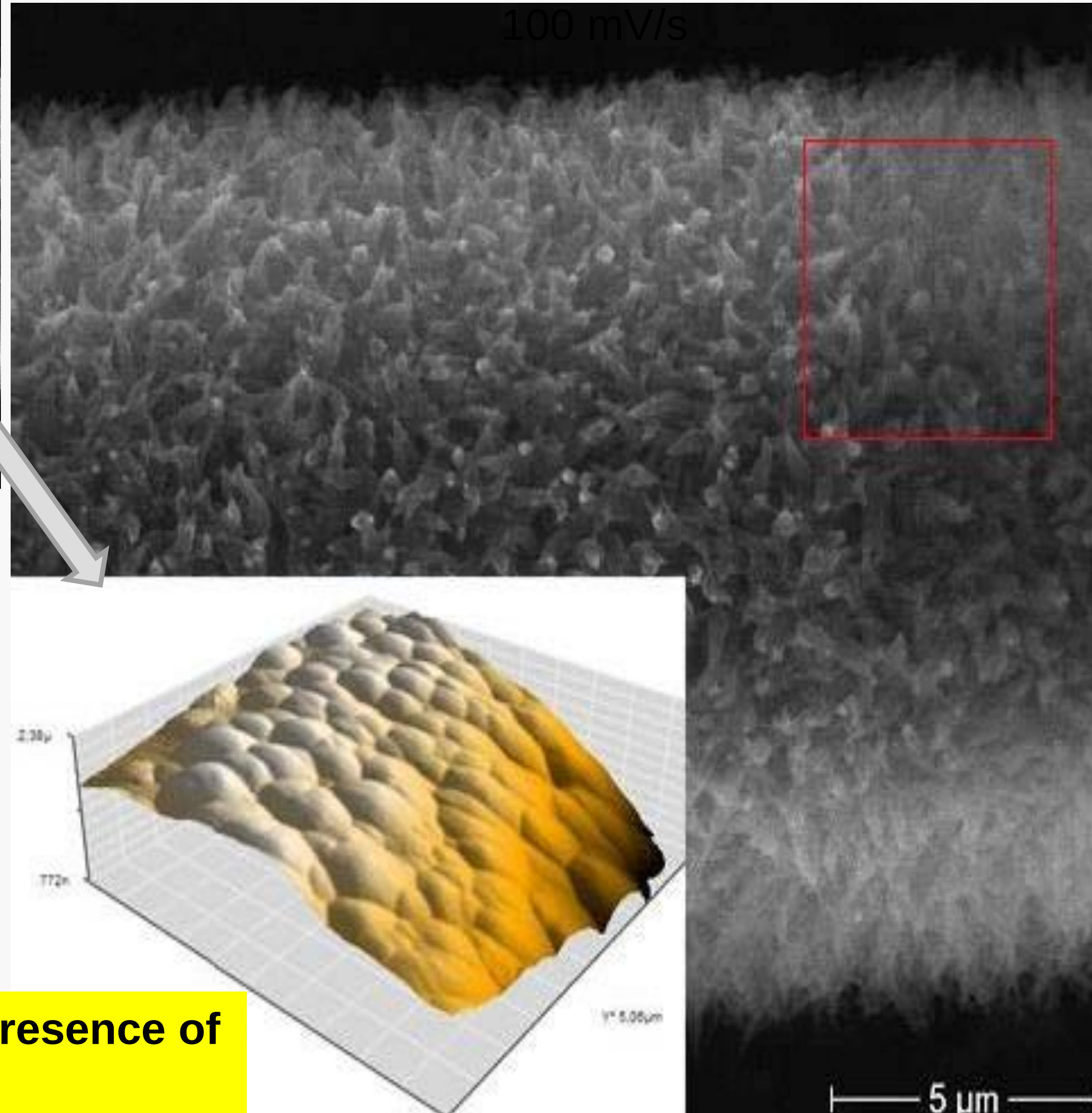


PProDOT-$(Bu)_2$/0,1 M LiClO_4/ACN

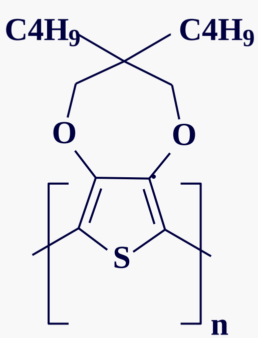
Atomic Force Microscopy (AFM)



0.1 M NaClO4/ACN **10 cycle**



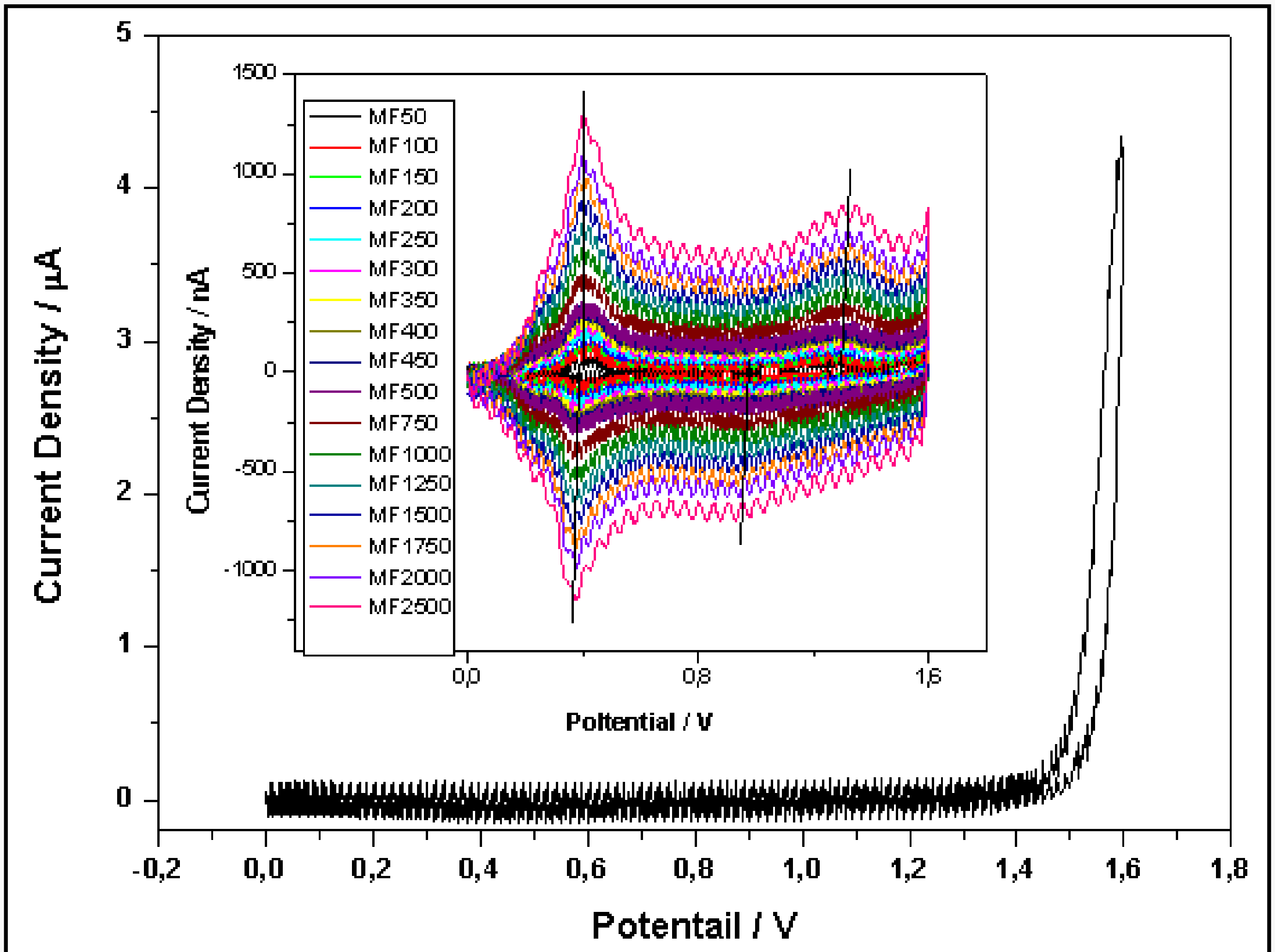
PProDOT-(Bu)2/0,1 M **$NaClO_4$ /ACN**

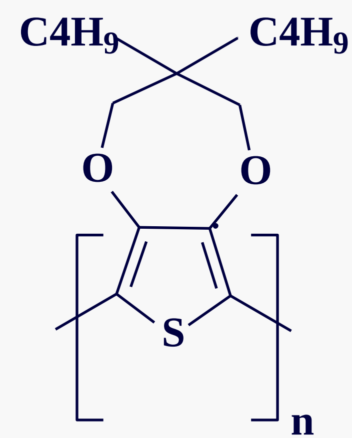


A uniform film is created in presence of NaClO4

Cycle Effect of PProDOT-Bu_2/Single CFME

1st CYCLE

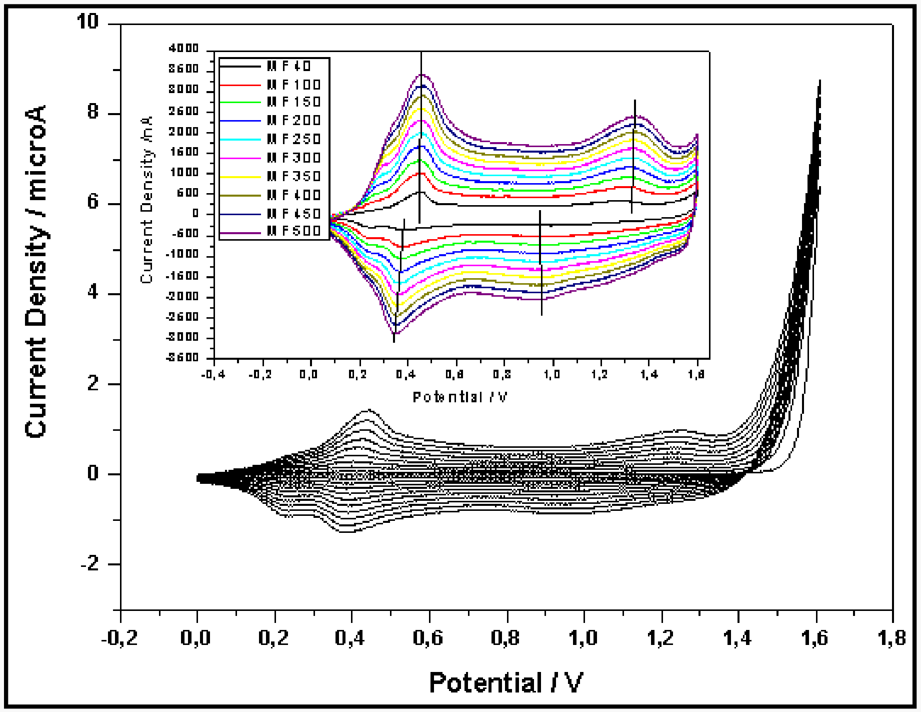




Cycle Effect of PProDOT-Bu_2/SCFME

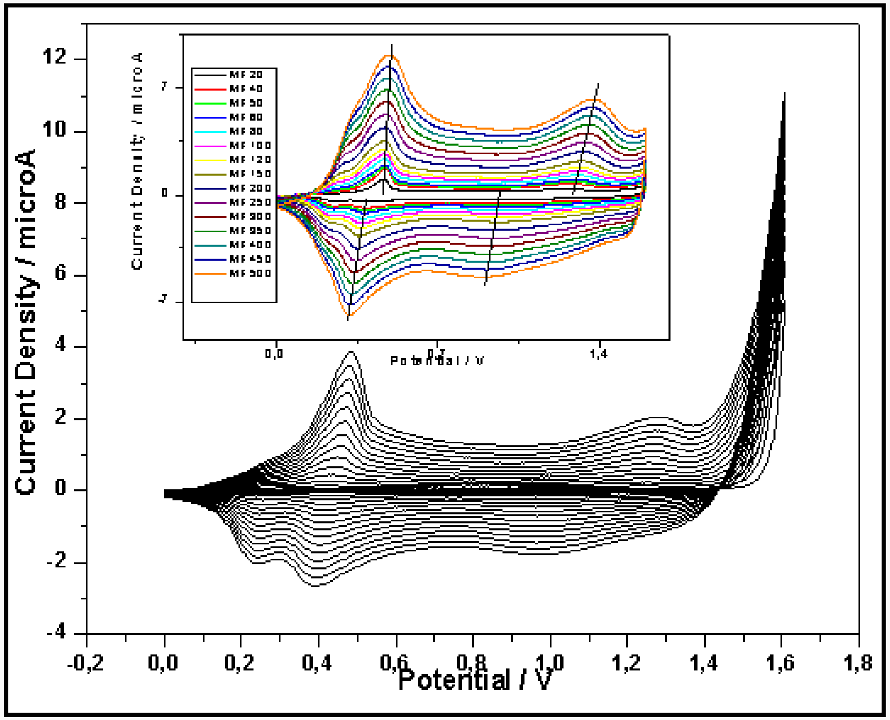
10 CYCLES

10 CYCLES



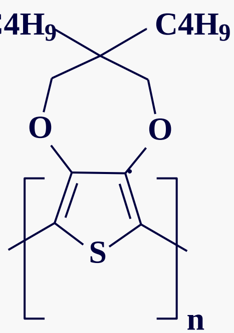
15 CYCLES

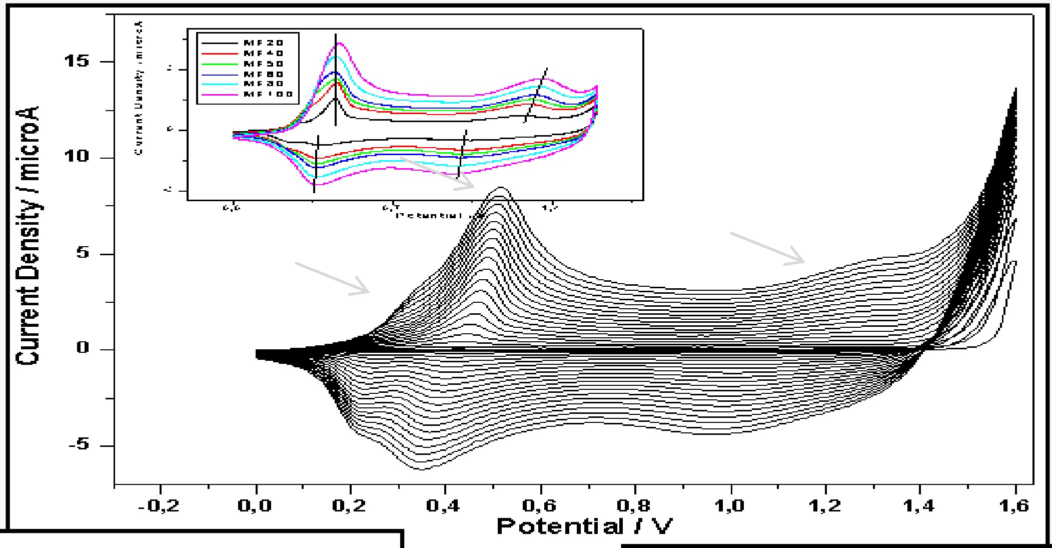
15 CYCLES

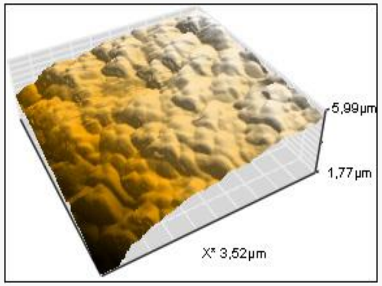


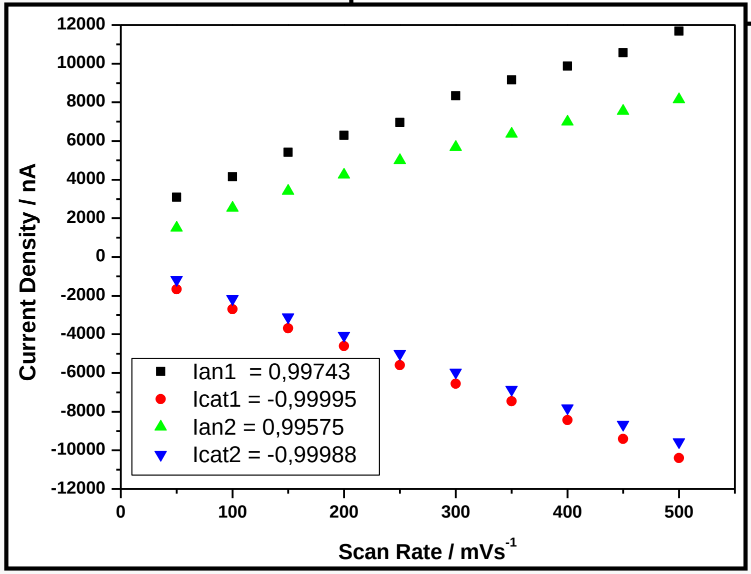
Cycle Effect of PProDOT-Bu_2/SCFME

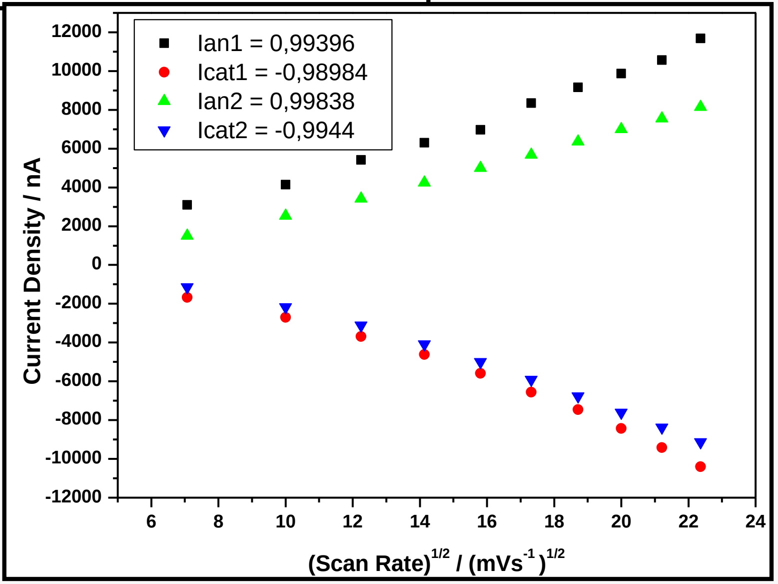
20 CYCLES





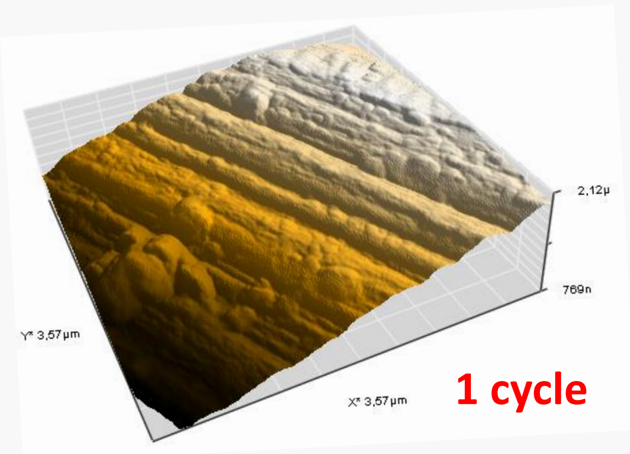


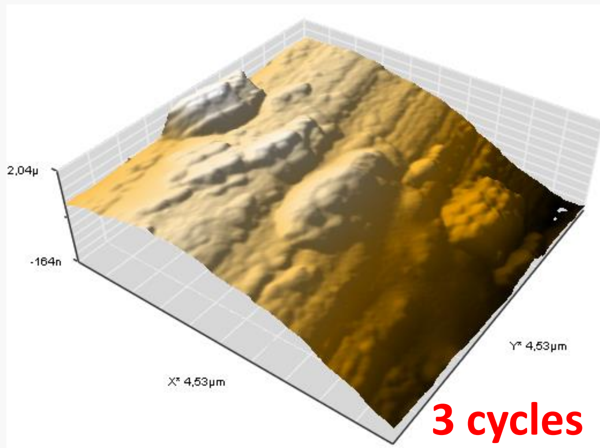


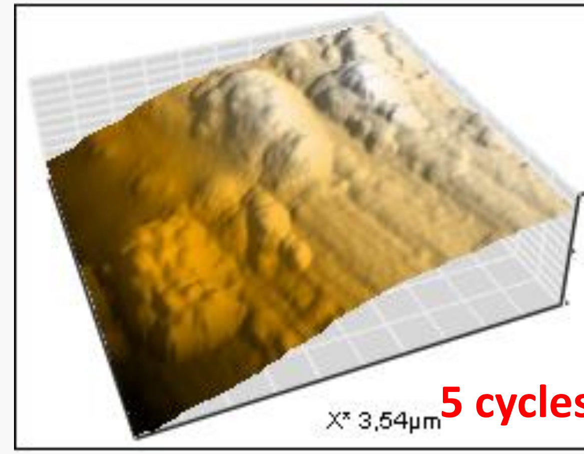


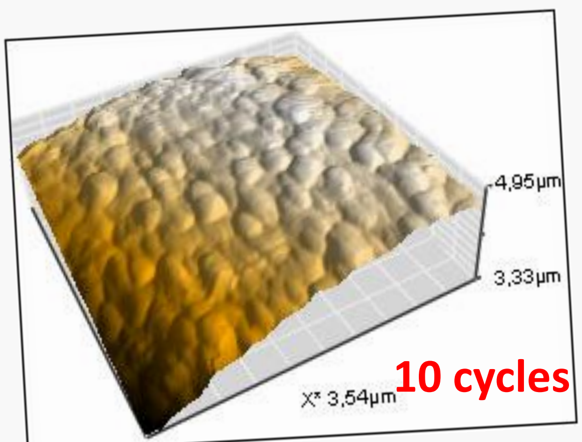
Cycle Effect of PProDOT-Bu_2/SCFME

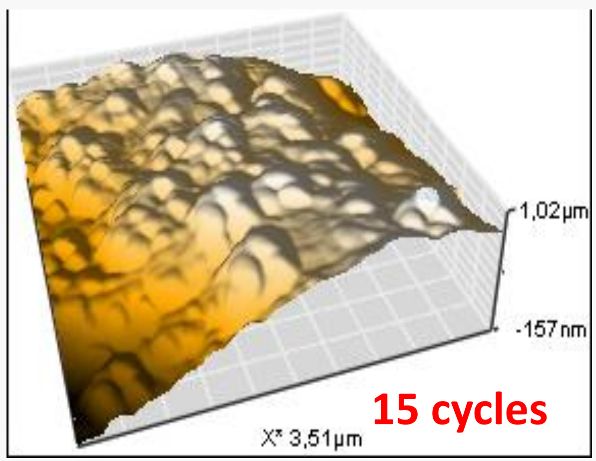
AFM

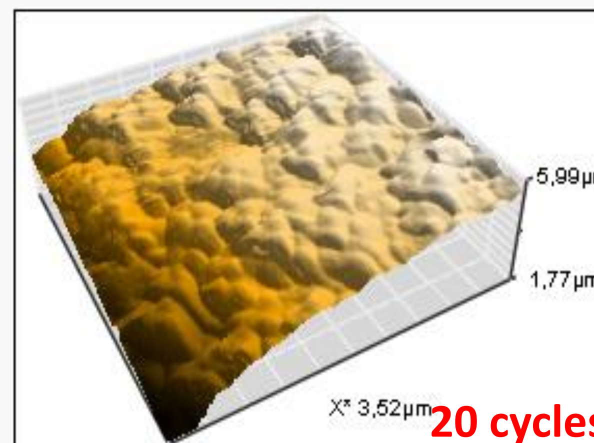






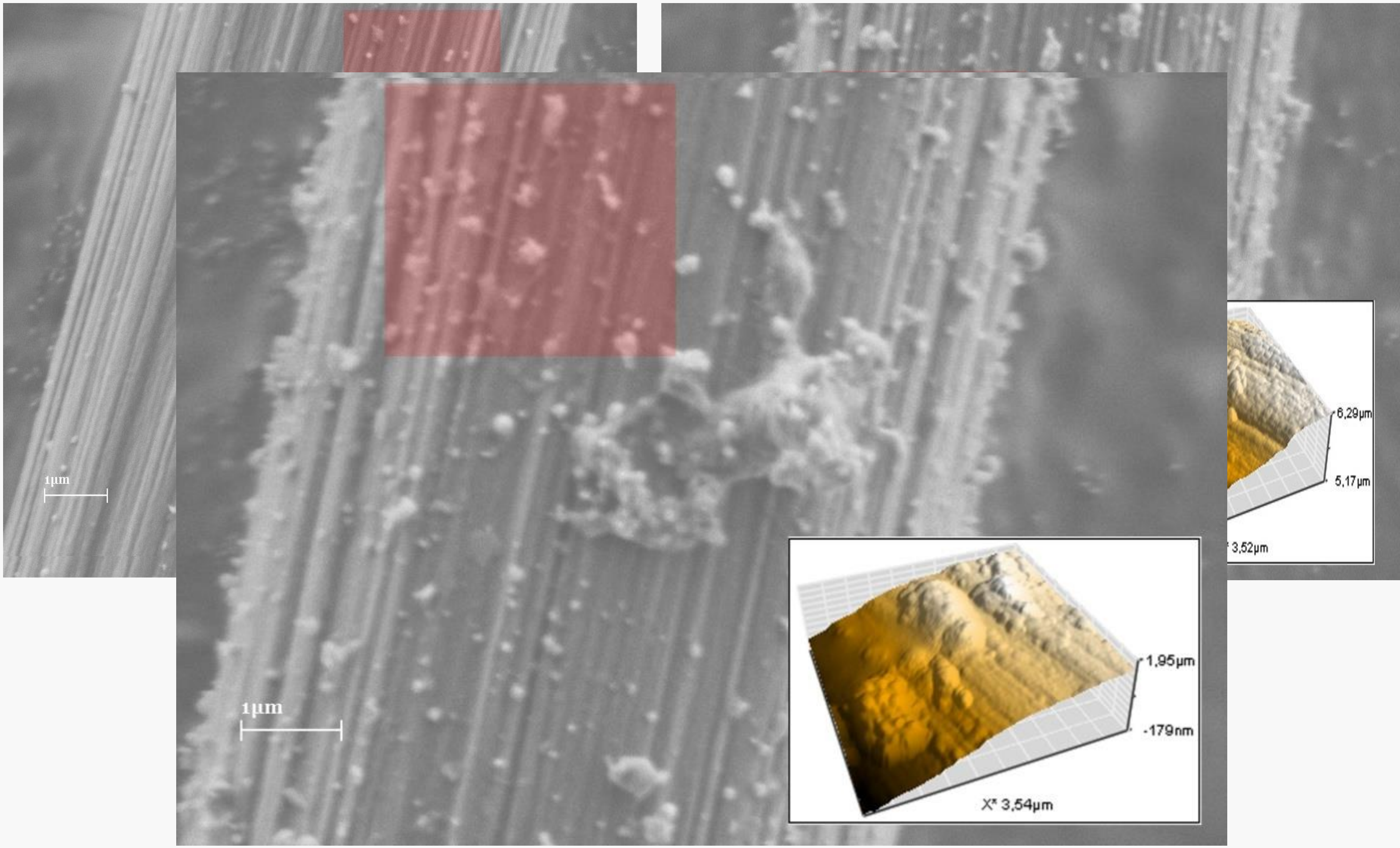




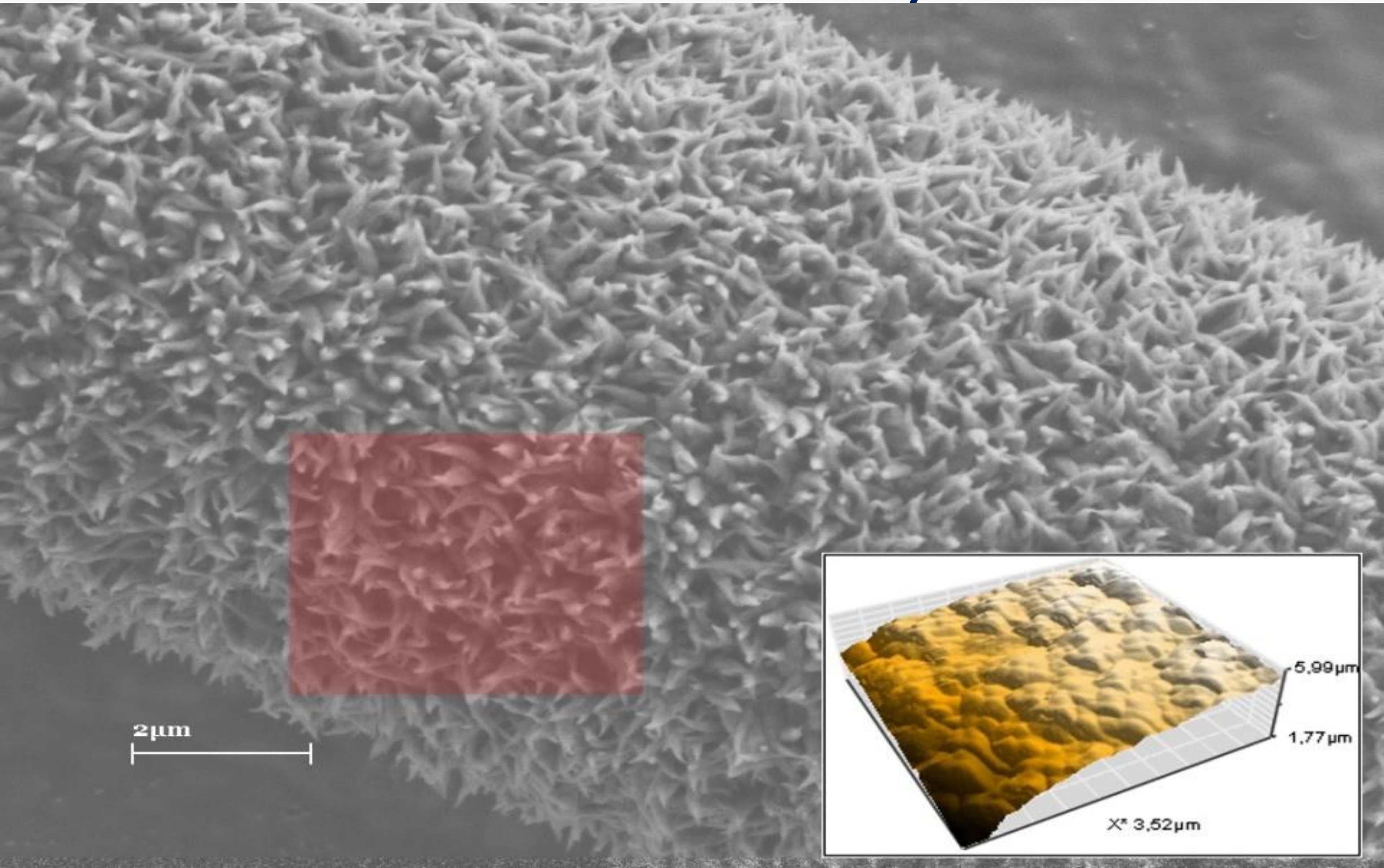


Cycle Effect of PProDOT-Bu_2/SCFME

SEM 1-3-5 Cycles

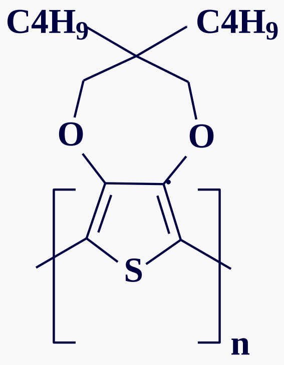


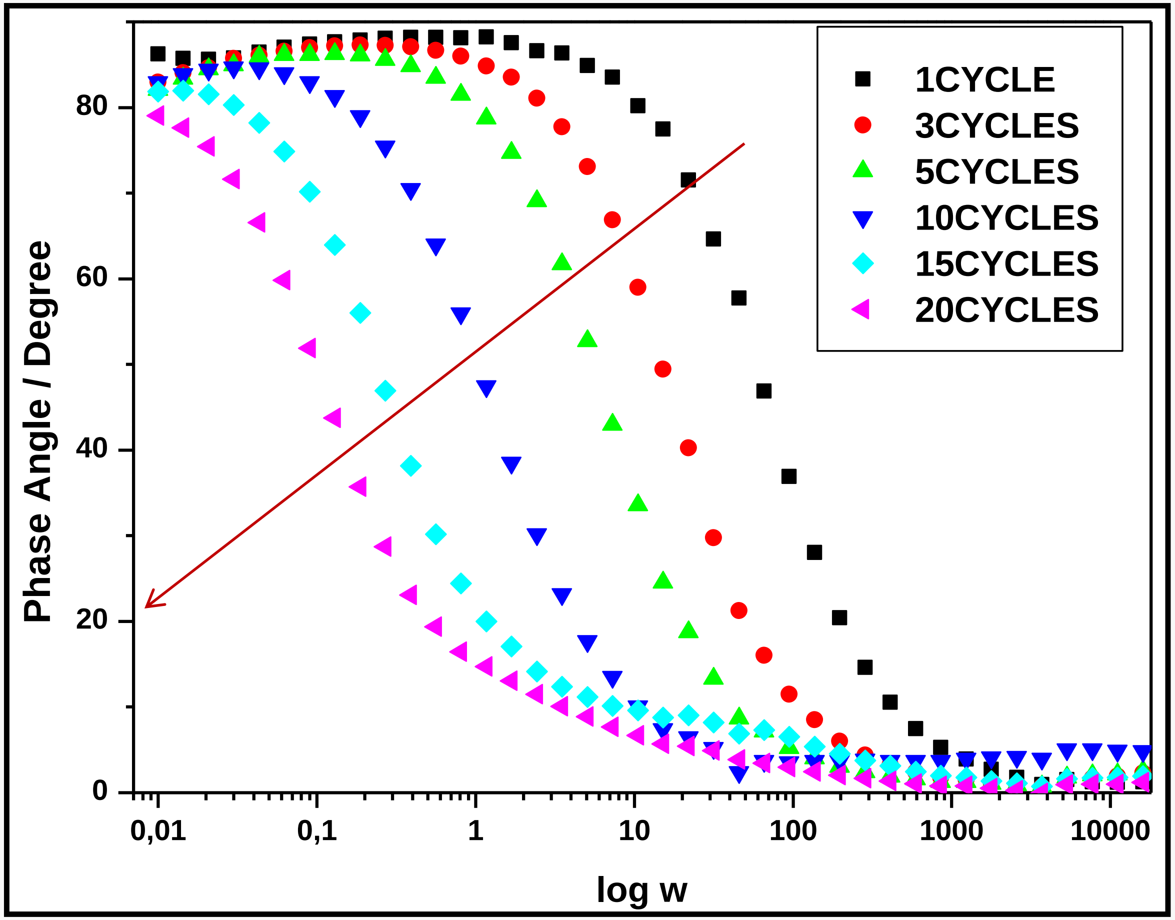
Cycle Effect of PProDOT-Bu_2/SCFME SEM 10-15- 20 cycles



Cycle Effect of PProDOT-Bu_2/SCFME

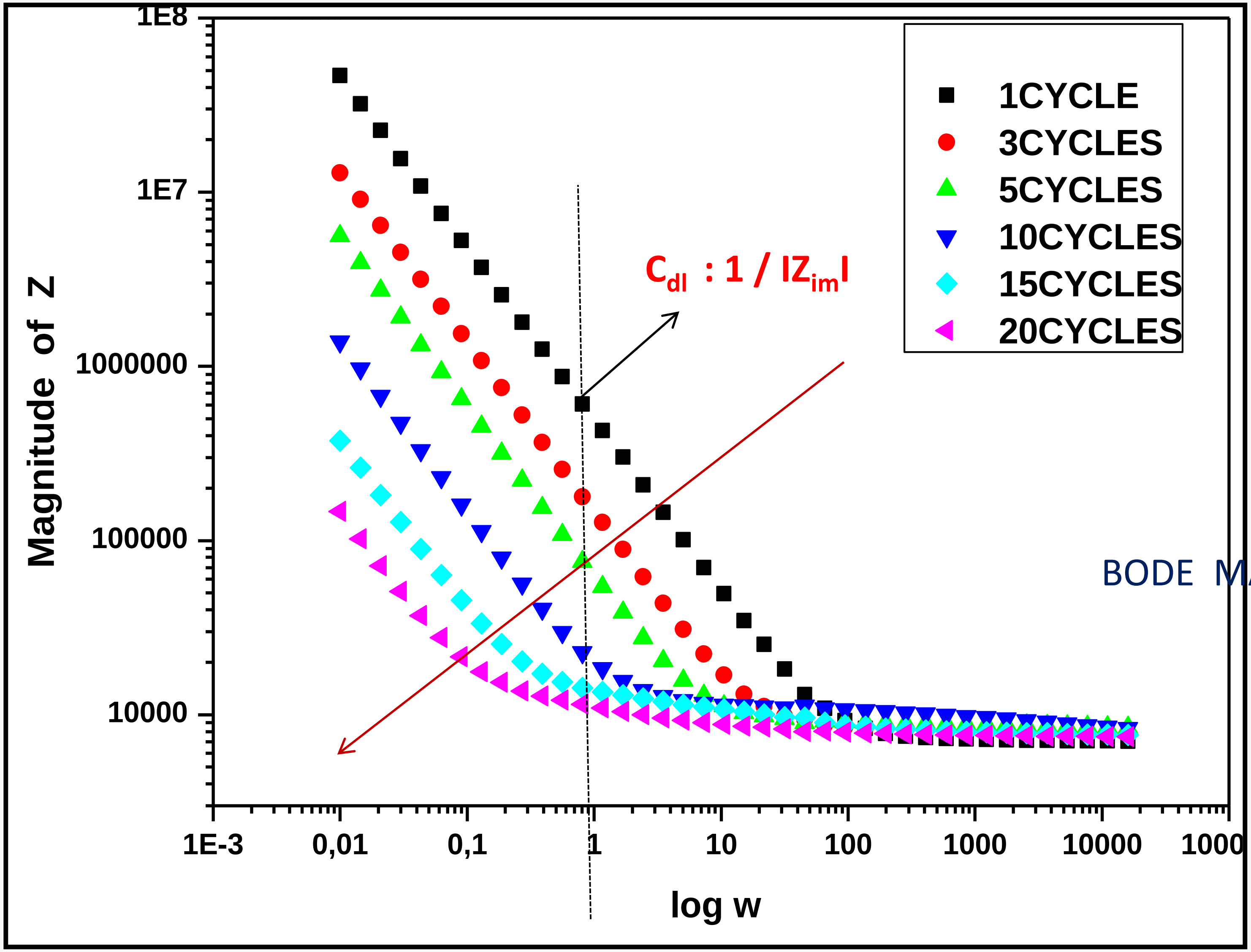
EIS





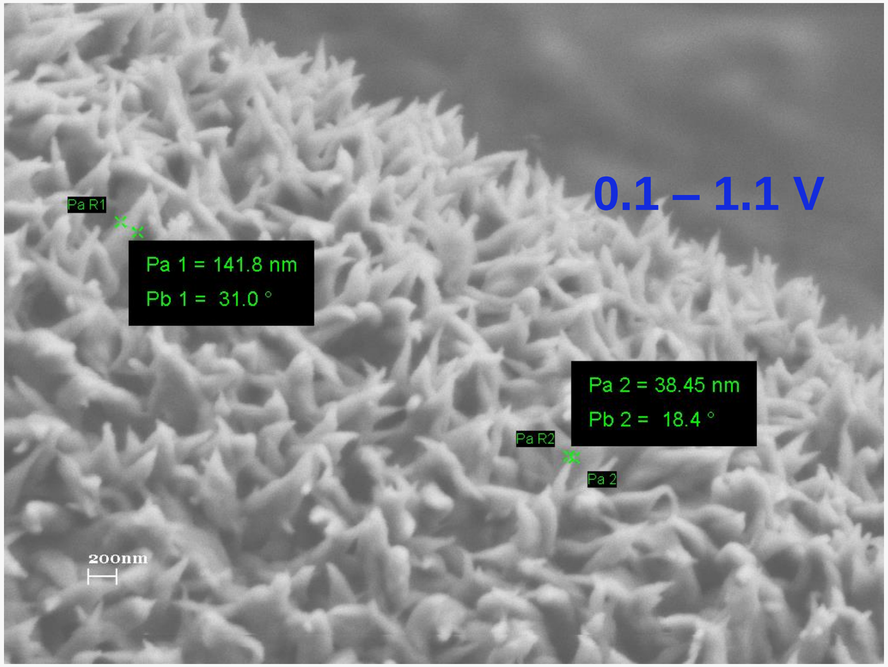
BODEPHASE

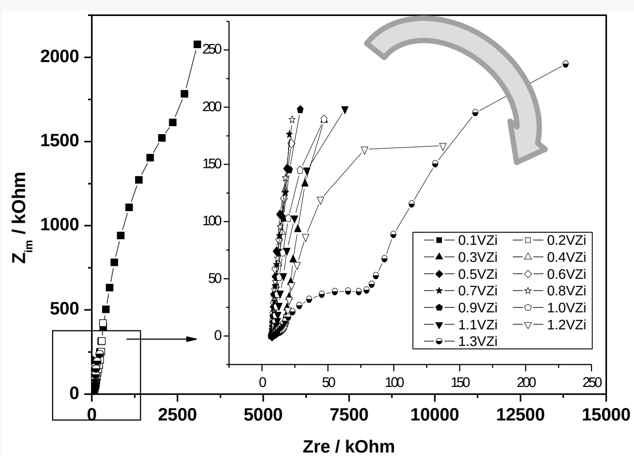
Cycle Effect of PProDOT-Bu_2/SCFME

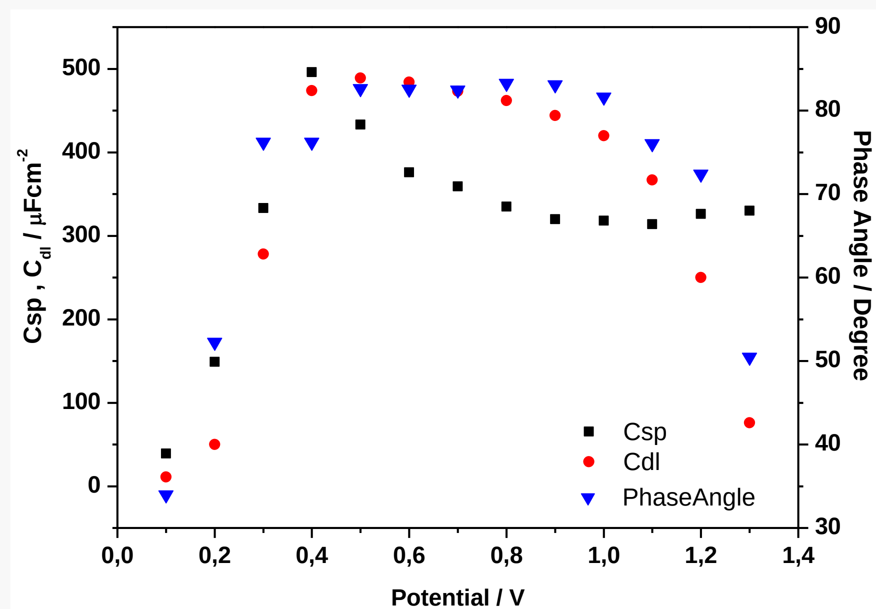


BODE MAGNITUDE

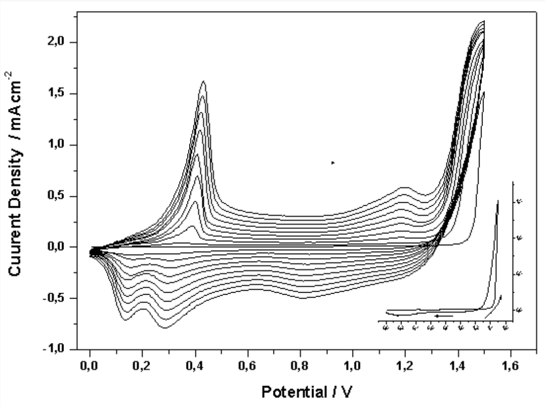
Potential Effect of PProDOT-Bu_2/CFSE



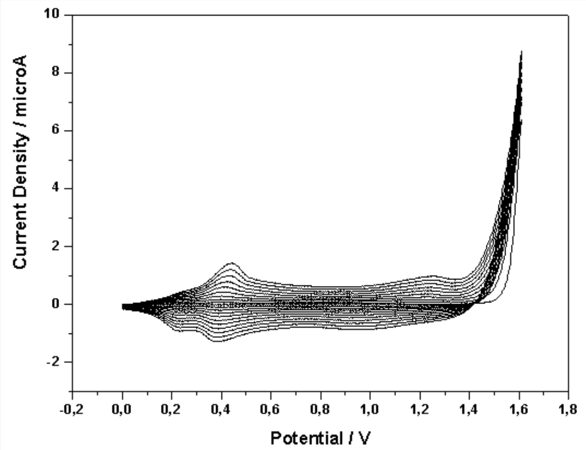




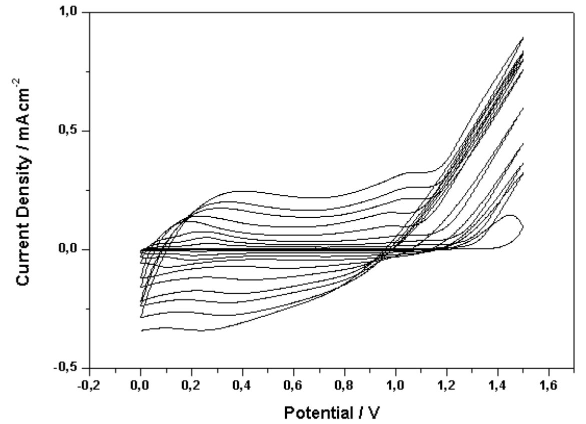
Substrate Effect of PProDOT-Bu_2



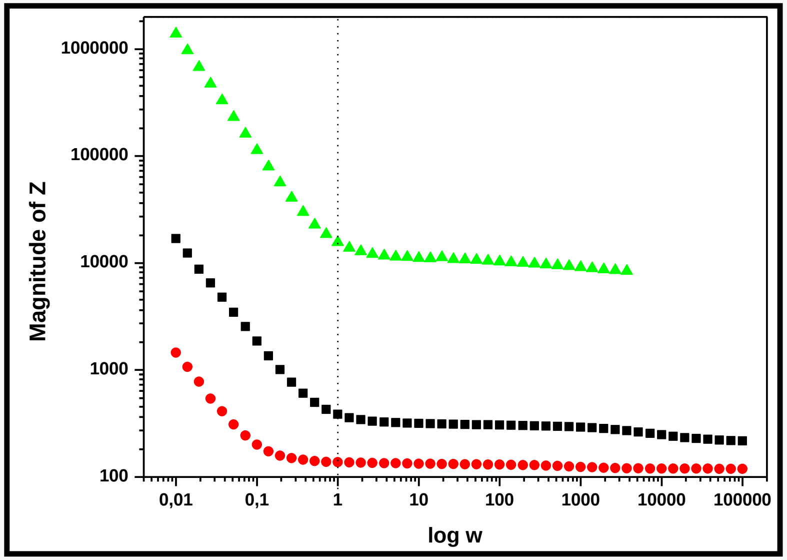
Pt

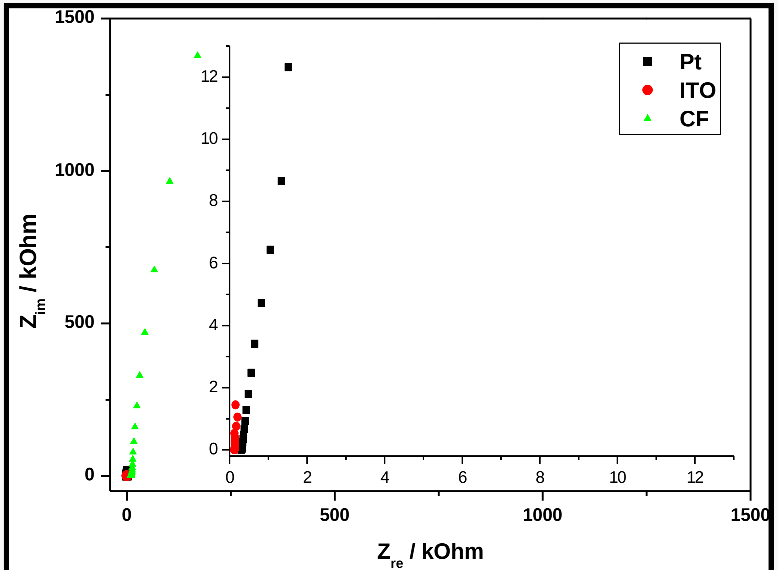


CFE



ITO





Conclusions

Performing modern voltammetry in present time-almost impossible task without having **<u>Modified electrodes</u>**

Cyclic voltammetry and EIS are cheap and reliable tools for mechanistic, kinetics and thermodynamic characterization of polymers

-**In respect to the solution chemistry methods**, **<u>electrochemical methods have numerous of advantages</u>** in respect to the polymer synthesis since

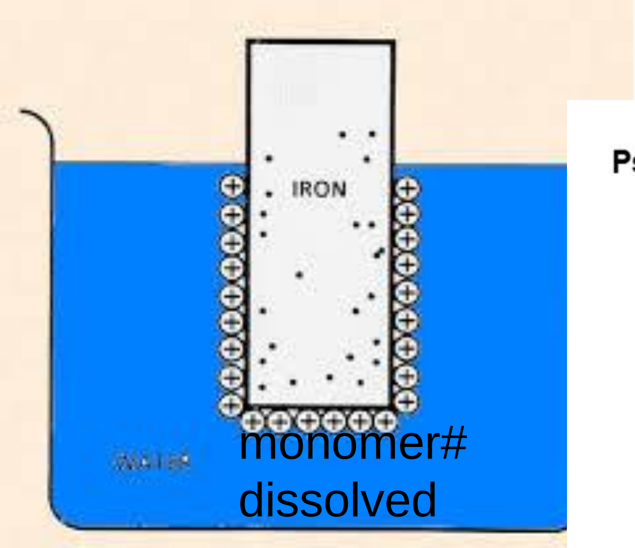
-polymerization process occurs only in a small part of the space (nearby the working electrode)

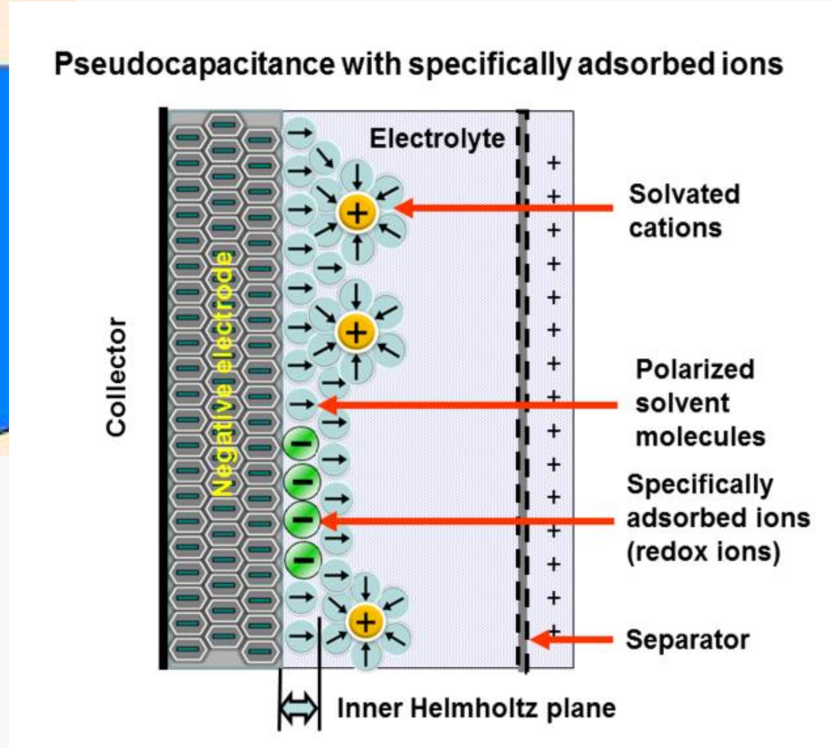
-kinetics of the polymerization process can be controlled by Applying appropriate potential

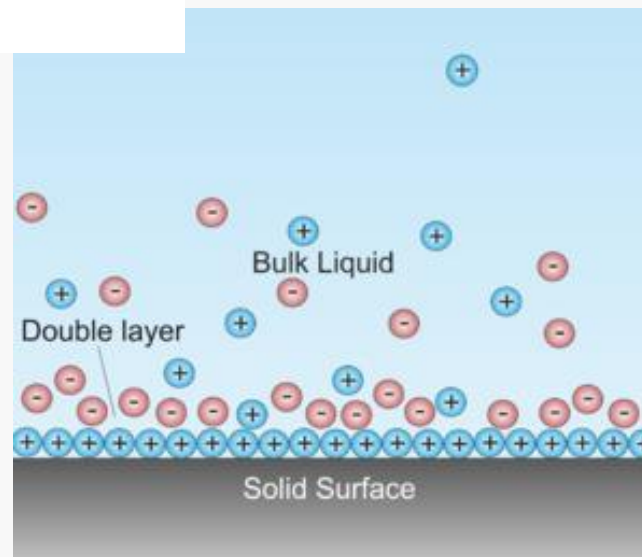
-growth of the polymer can be controlled

-...

but for the structural characterization of the polymers, one needs to couple the electrochemical techniques with microscopic techniques (AFM, SEM)







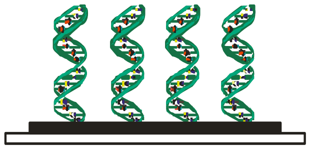
In **<u>Electrochemical polymerization</u>**
Polymerization takes place only in a very limited space
(only in electrical double layer nearby the working electrode)

Application of the conductive polymers in electrochemical sensors

Equipment for combinatorial polymer synthesis

DNA Arrays

Technology: entrapping into polymer matrix during EP



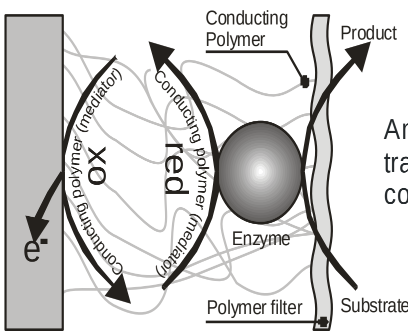
Hybridization detection:
- fluorescence [Livache]
- development of electro-chemical methods [Zhi]

Throughput: currently 96 electrodes, can be simply increased up to 384

Variations of Olygos: currently 4, can be increased.
A coupling with automated dispenser is possible

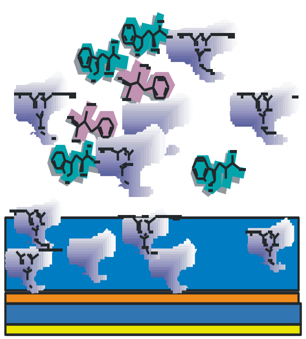
Cell volume: currently > 1.5 ml. Can be decreased, but it demands a new design

Enzymatic biosensors



Amperometric transducing method collaboration with ...

Moleculary imprinted polymers



MIP through electro-polymerization:
The 1-st works have been done by our co-workers (V, T), now 3 works more are published
the main problem of MIP - optimization

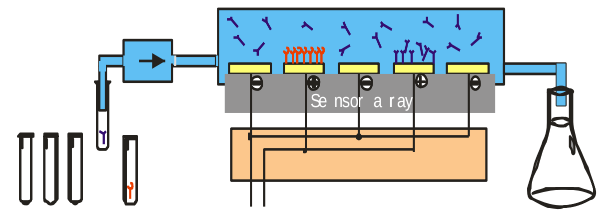
Throughput:
96 experiments per chip

Polymer filters for bio- and chemosensors

for any sensor with conductive polymers, as additional polymer layer

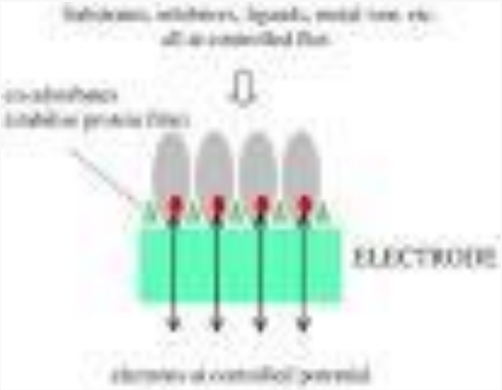
Throughput:
96 experiments per chip

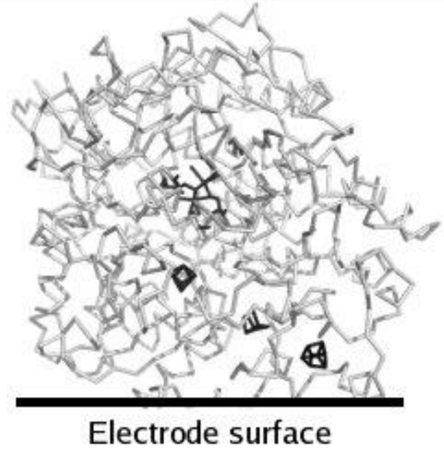
Electrically addressable immo-bilization of thiolated receptors

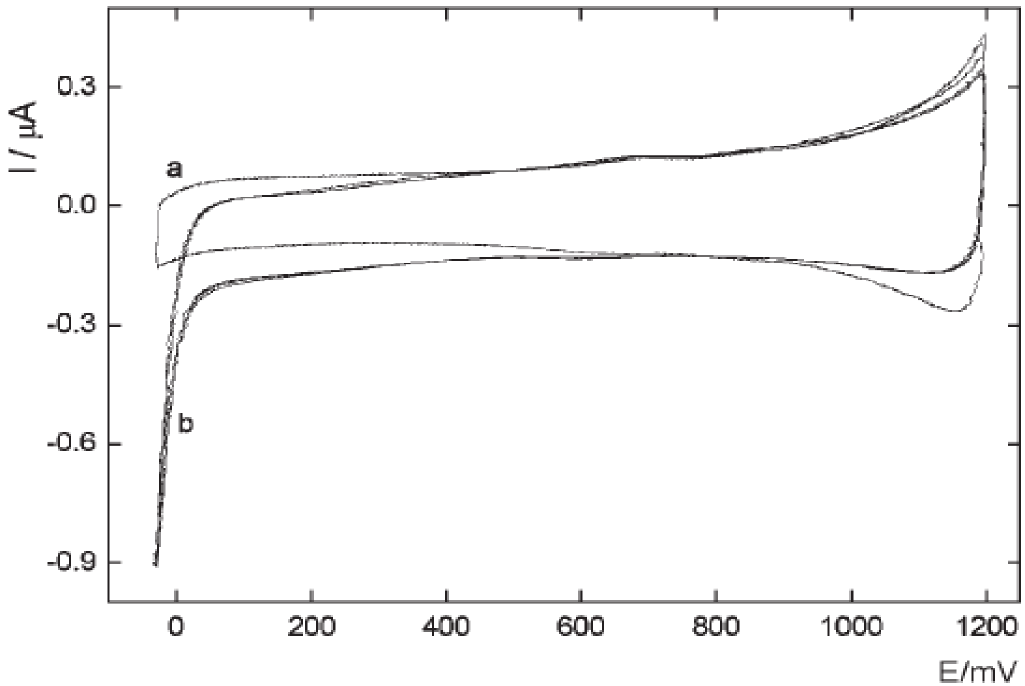


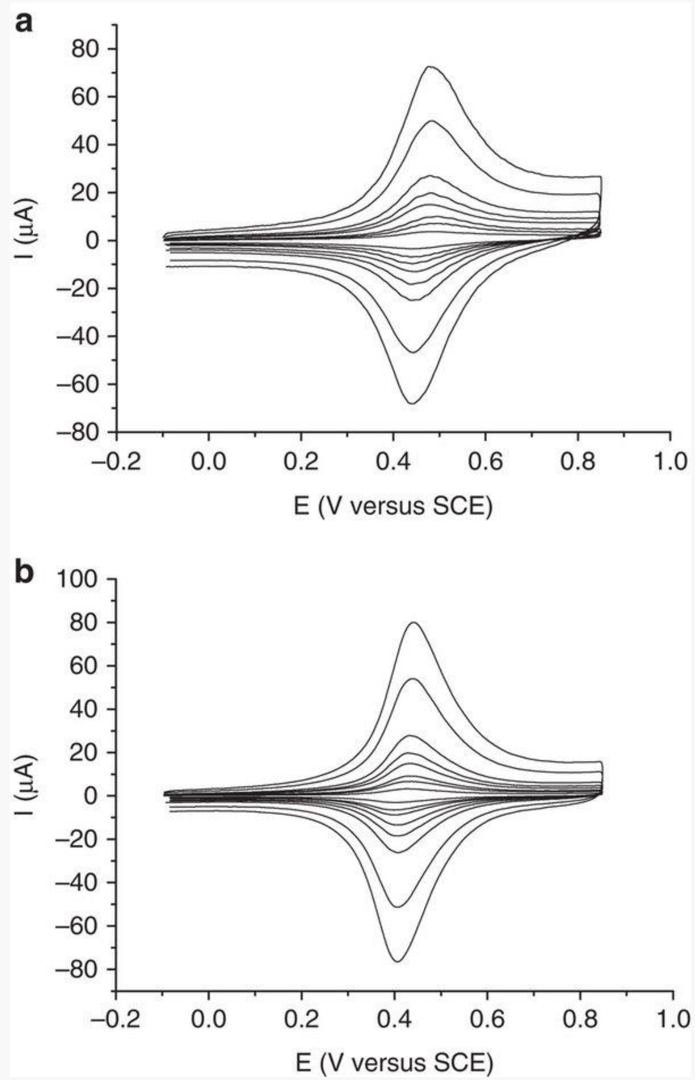
Throughput: currently 96 electrodes, but only up to 4 different thiols can be immobilized.
A coupling with automated dispenser is possible

Application of conductive polymers in protein-film voltammetry

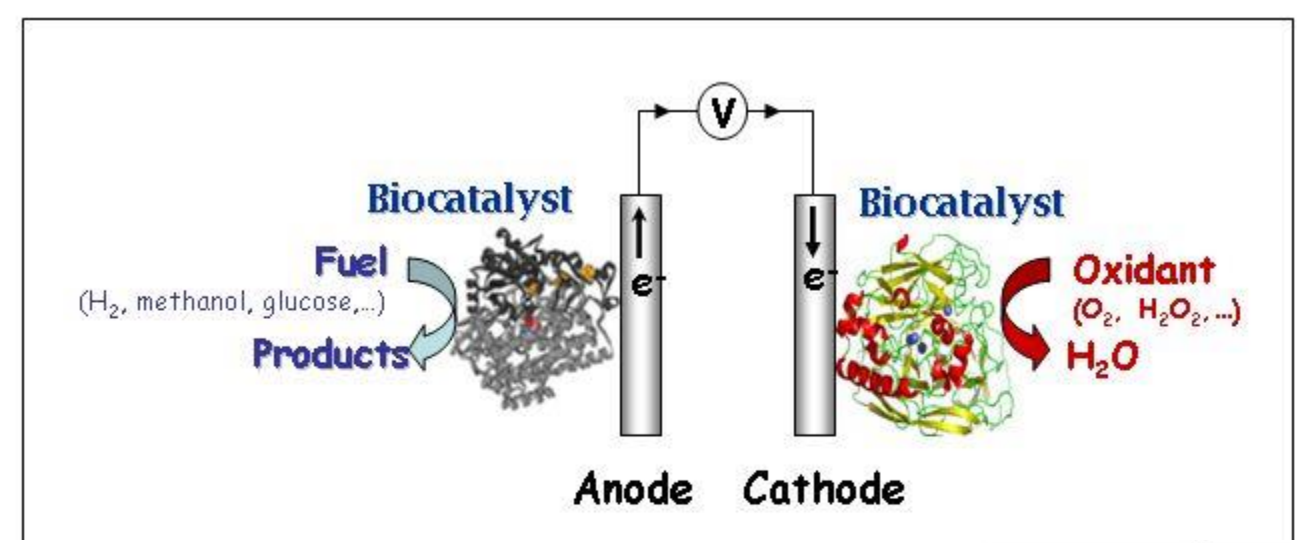


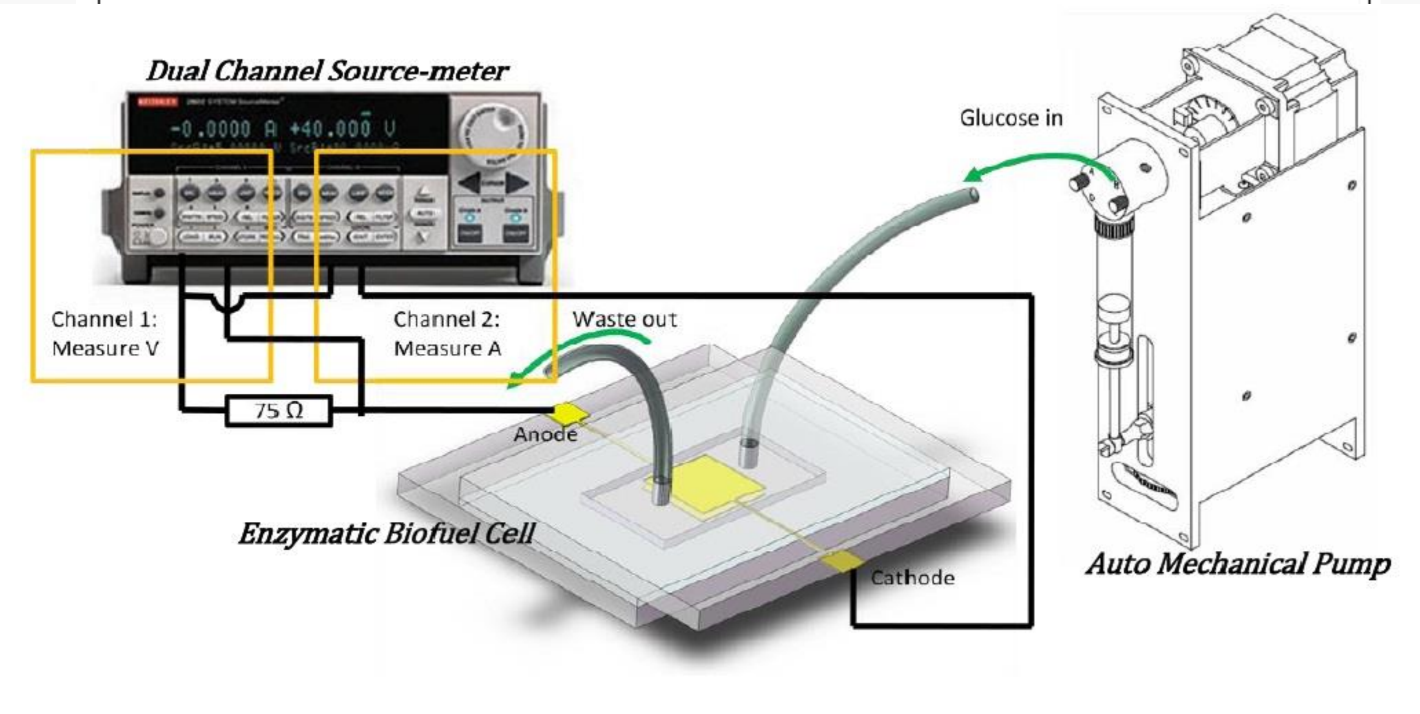




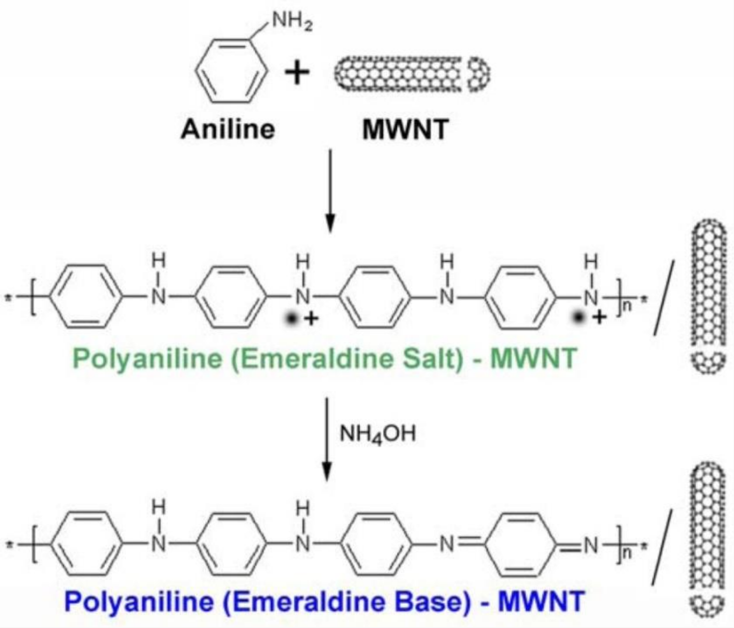


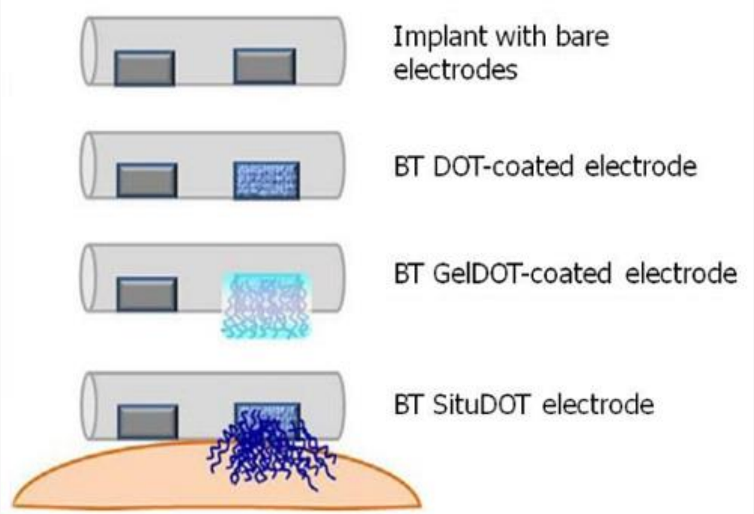
Application of the conductive polymers in bio-fuel cells

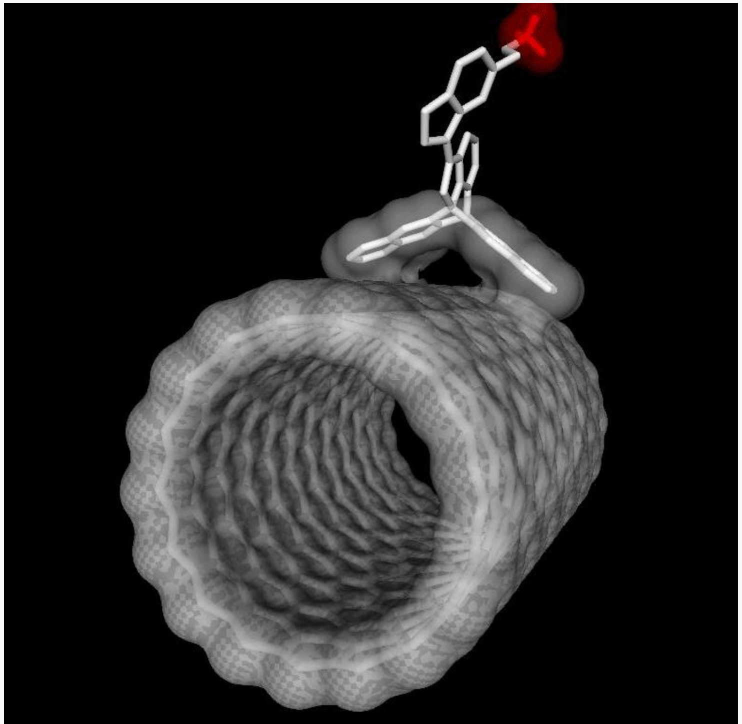


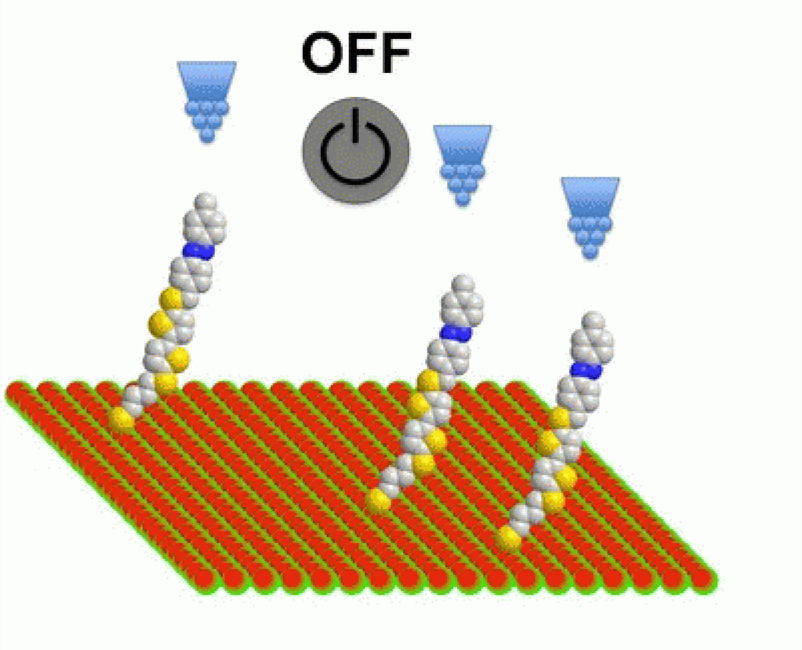


In the recent period, conductive polymers usually couple with nano-particles as modifiers for the working electrodes









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