

# INGENIERIE DES MATERIAUX POLYMERES

## Chemistry of Polymers

by

Etienne Fleury, Philippe Chaumont and Mohamed Taha

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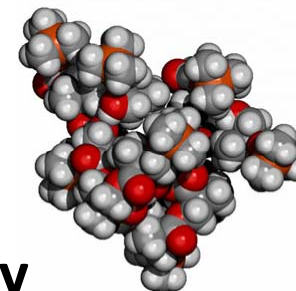
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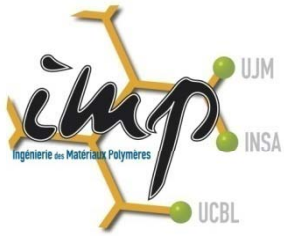


# CHEMISTRY OF POLYMERS

## ***OBJECTIVES***

- To develop
  - \* basic research in macromolecular chemistry
  - \* Chemical tools in cooperation to the other lab. Activities (design of macromolecular architectures and morphologies for given functionality(ies))
- To integrate sustainability in research approaches
- To get innovative approaches for designing and functionalizing macromolecular architectures



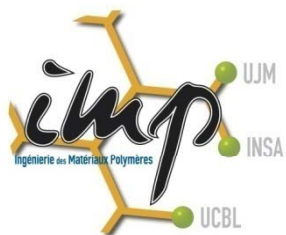


# CHEMISTRY OF POLYMERS

## ***COMPETENCES***

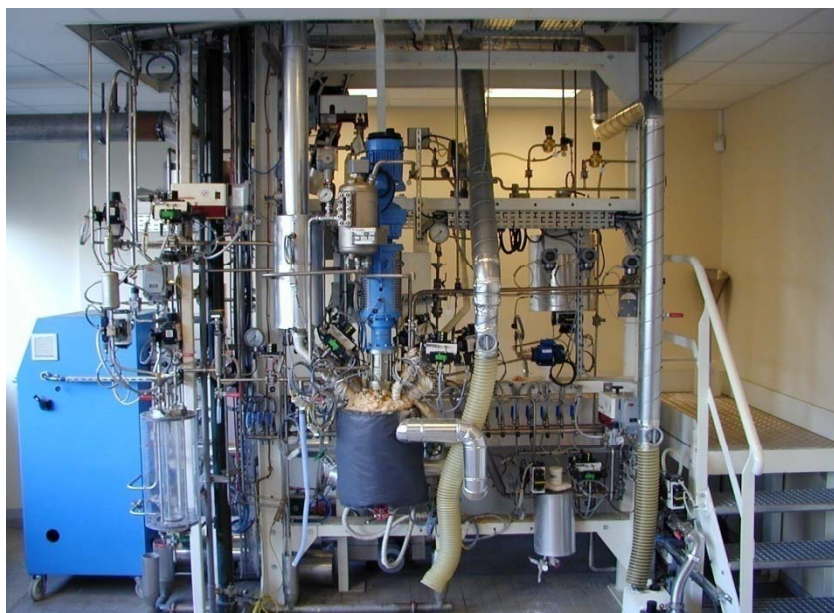
- \* Molecular Chemistry**
- \* Chemical Modification of Polymers and Polysaccharides**
- \* Chemistry of Polymerization**
  - Polycondensation / Polyaddition**  
**=> PU, Polyepoxy, Polyamide, Polyester...,**
  - Ring-Opening Polymerization**  
**=> Lactides, Glycolides, Cyclosiloxane..,**
  - Radical Polymerization**  
**=> Free-radical, NMP, RAFT, ATRP**
- \* Polymerization Processes (dispersed media, High T°, Sol Gel, SC CO<sub>2</sub>,...)**
- \* Chemical and Microstructure Analysis**





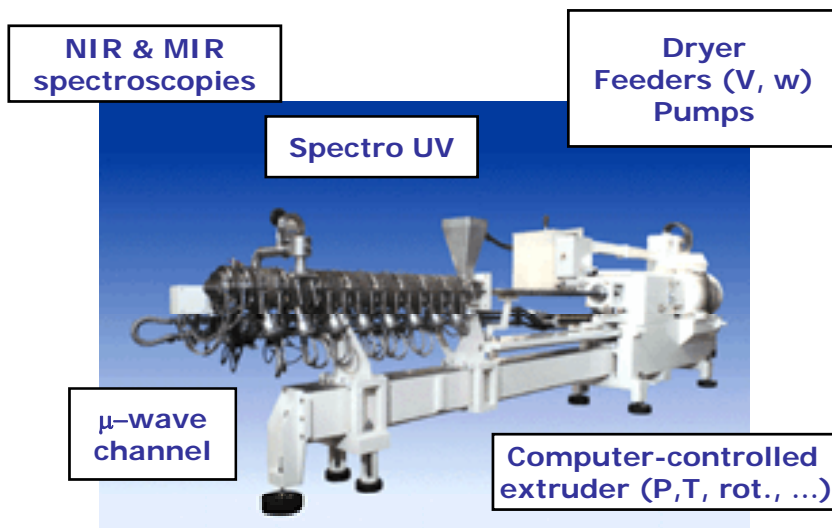
## ***SPECIFIC TOOLS***

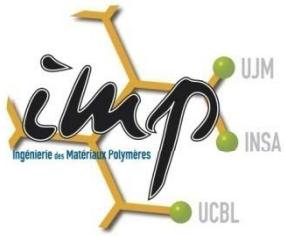
**Pilot reactor for polyesters synthesis  
(8.5L, 290°C, 7bars)**



**Pilot reactor for polyamides synthesis  
(1L, 350°C, 50 bars)**

## **CHEMISTRY OF POLYMERS**





# CHEMISTRY OF POLYMERS

## ***TOPICS***

### **TOPIC #I : Molecular & Macromolecular Engineering**

**I.1 Macromolecular Engineering in Molten State**

**I.2 Polymers with Controlled Architecture**

**I.3 « New » (macro)molecular Chemistry from Soft Conditions  
and/or Selective and/or Reversible Reactions**

### **TOPIC #II : Chemistry & Sustainable Development**

**II.1 Chemistry for Reactive Extrusion**

**II.2 Non Toxic Processes**

**II.3 Biosourced Polymers**

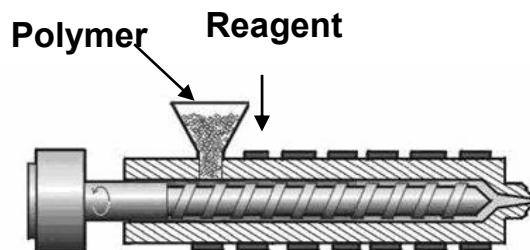
**II.4 Modification of polysaccharides**

### **TOPIC #III : Surfaces & Interfaces Chemistries**

**III.1 Synthesis of Nano-objects**

**III.2 Functionalization of Planar Surfaces**

**III.3 Functionalization of Fillers**

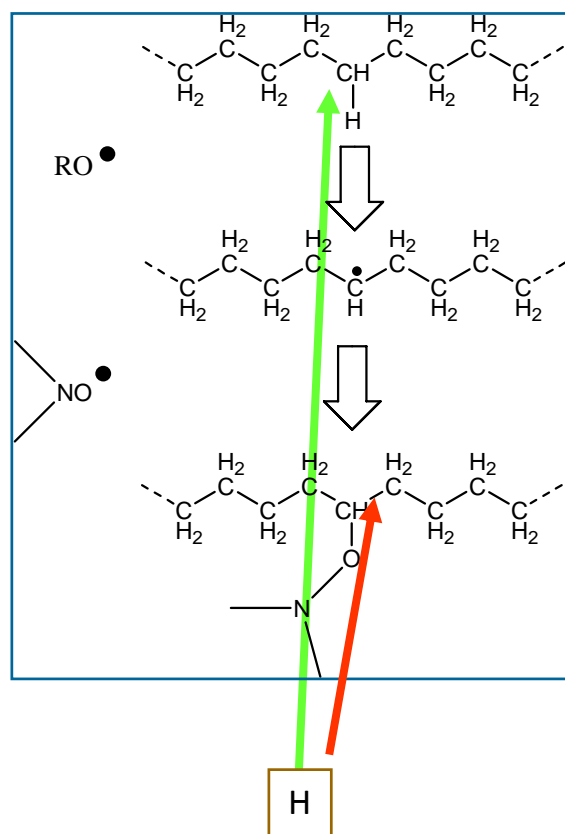


# CHEMISTRY OF POLYMERS

LDPE + peroxide

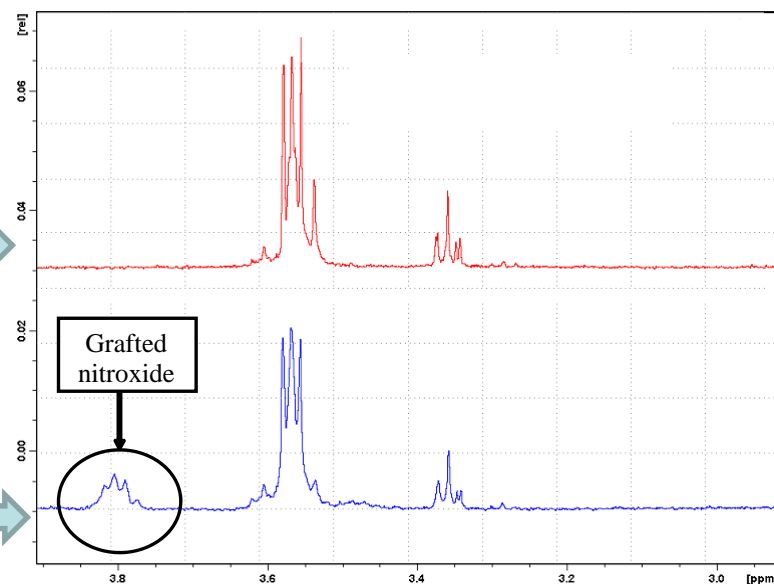
## TOPIC #1 : Molecular & Macromolecular Engineering

### 1.1 Macromolecular Engineering in Molten State



without TEMPO

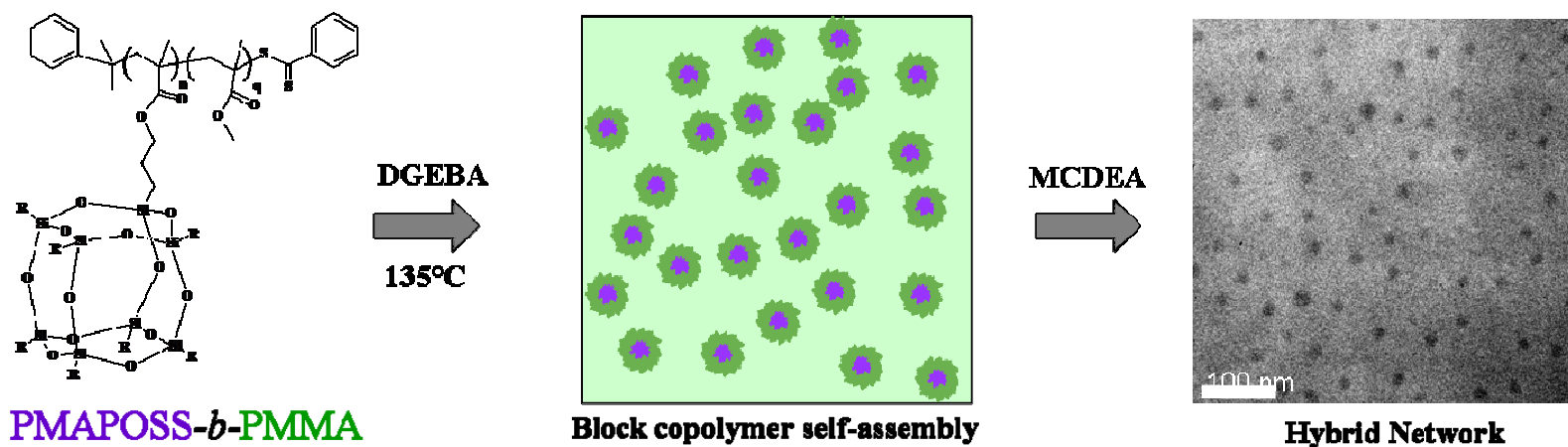
with TEMPO



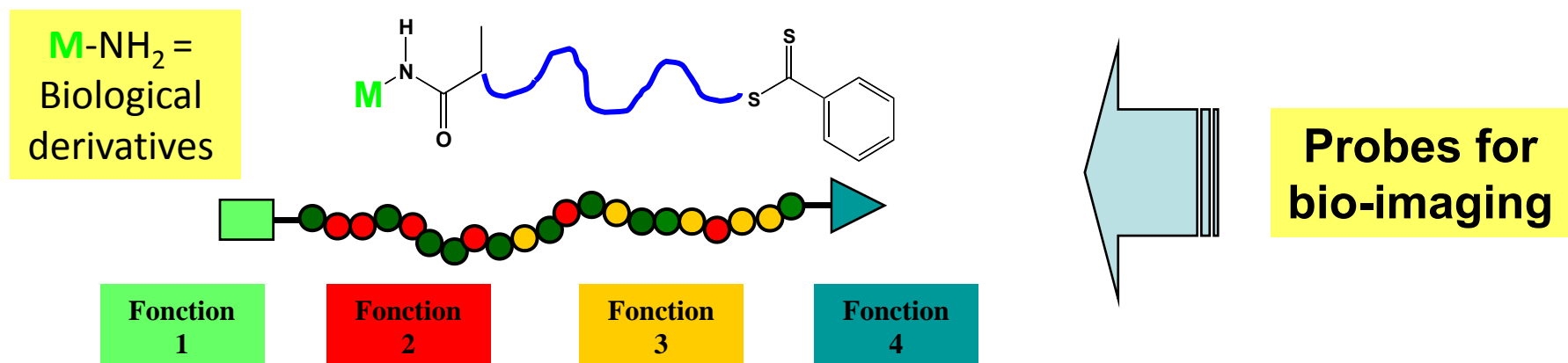
- Badel T., Beyou E., Bounor-Legare V., Chaumont P., Flat J.J., Michel A.  
J. of Polym. Sci. Part A (2007) 5215-5226
- Ibid Macromolecular Material and Engineering (2012)
- Akbar S., Beyou E., Chaumont P., Mazzolini J., Espinosa E., D'Agosto F., Boisson C.  
J. of Polym. Sci. Part A (2011) 957-965

## TOPIC #1 : Molecular & Macromolecular Engineering

### I.2 Polymers with Controlled Architecture



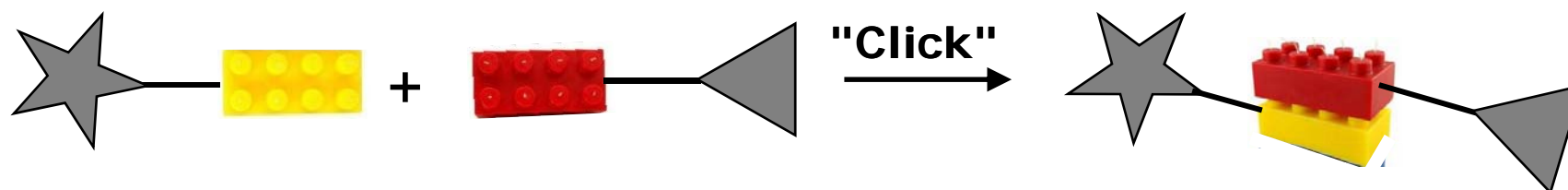
Deng Y., Bernard J., Alcouffe P., Galy J., Dai L., Gérard J. F. J. of Polym. Sci. Part A-Polymer Chemistry (2011) 4343-4352



# CHEMISTRY OF POLYMERS

## TOPIC #I : Molecular & Macromolecular Engineering

### I.3 « New » (macro)molecular Chemistry from Soft Conditions and/or Selective and/or Reversible Reactions



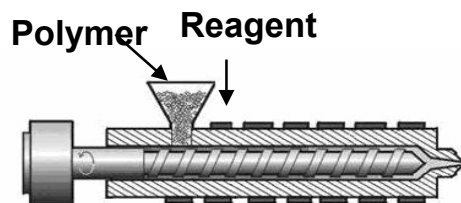
**"Click Chemistry" : Sharpless et al. 2001 =>  
chemio-selectivity, robustness, atom economy,...**

- 1,3-dipolar cycloaddition (Huisgen)
- Radical addition thiol-ene
- Dipolar Cycloaddition [4+2] (Diels Alder)
- Oximes / hydrazones
- ...

Binauld S., Damiron D., Hawker C. J., Connal L. A., Drockenmuller E. Macromolecular Rapid Communications (2011) 147-168

Magana, S., Zerroukhi, A., Jegat, C., Mignard, N. Reactive & Functional Polymers (2010) 70, 442-448

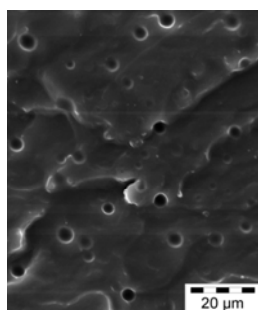
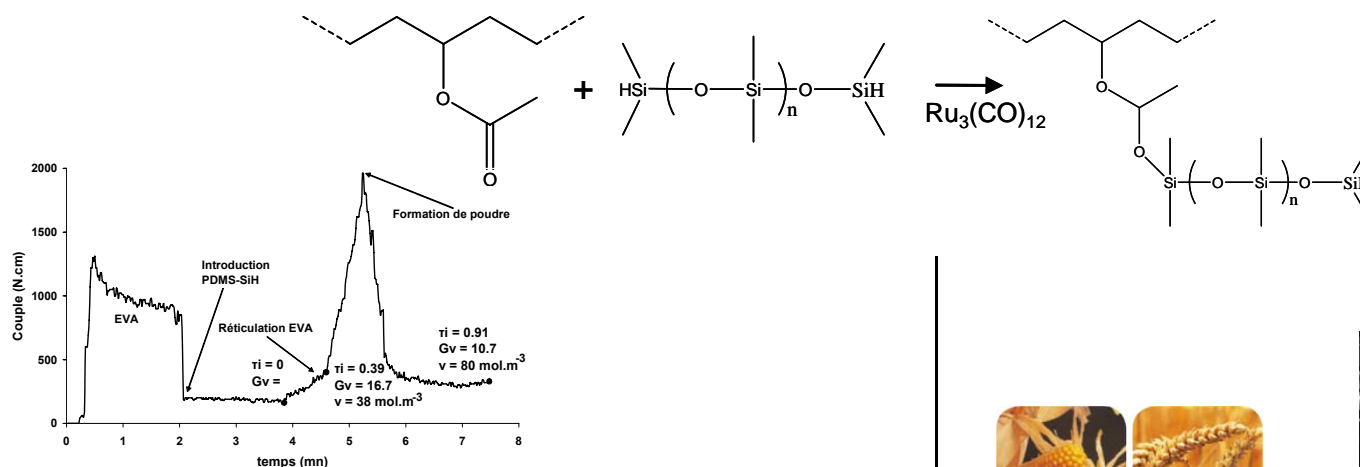




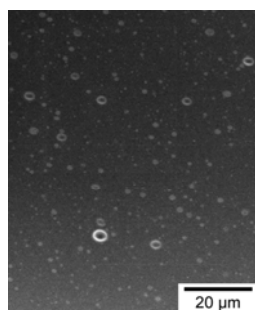
# CHEMISTRY OF POLYMERS

## TOPIC #II : Chemistry & Sustainable Development

### II.1 Chemistry for Reactive Extrusion



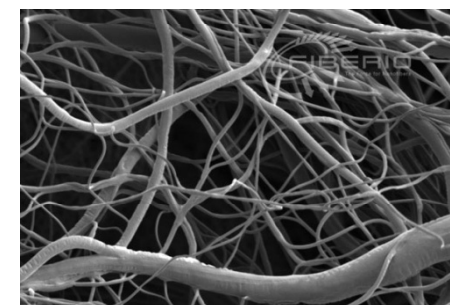
**Non reactive  
blend EVA/PDMS-SiH**



**Reactive Blend  
EVA/PDMS-SiH**



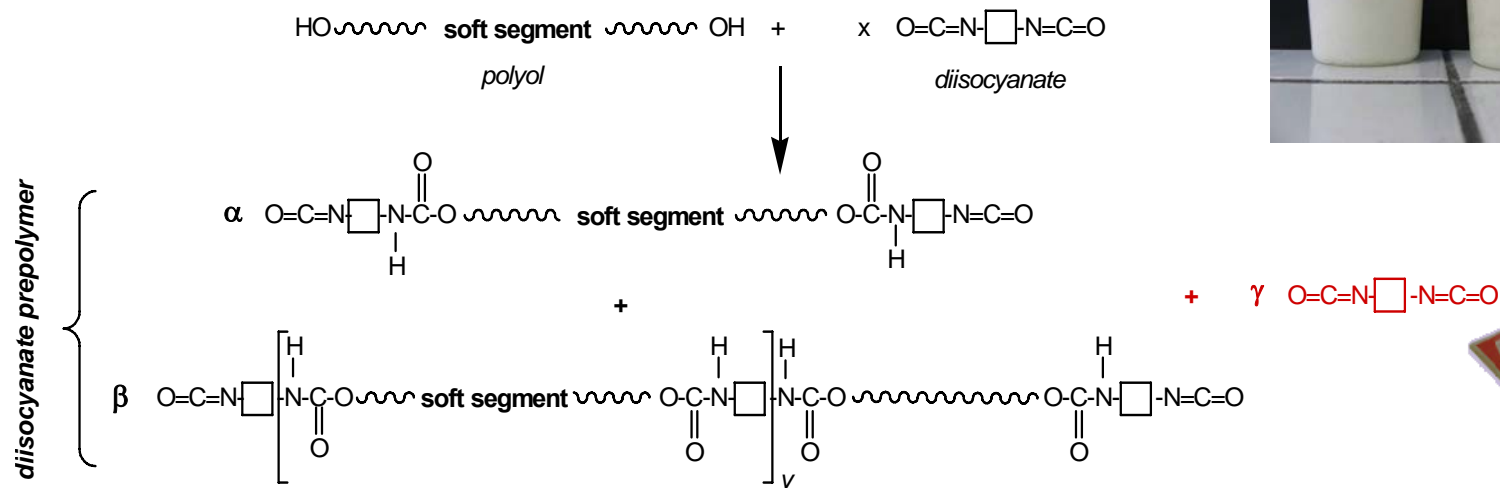
**Starch**



**Polyesters  
=> PC, PG, PLA**

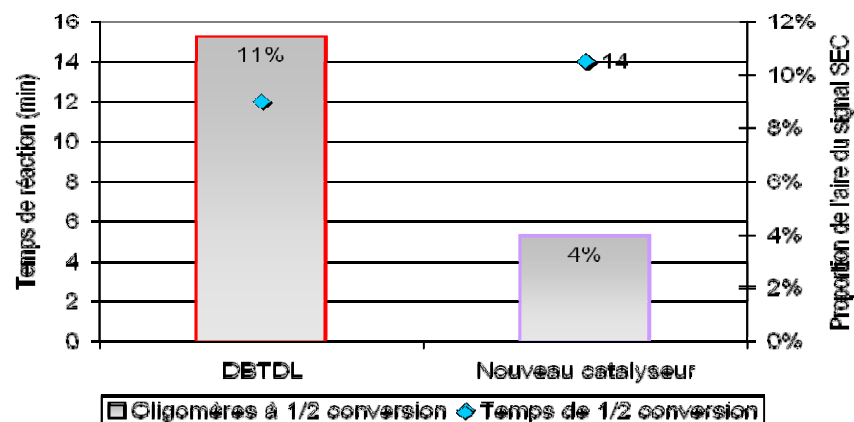
## TOPIC #II : Chemistry & Sustainable Development

### II.2 Non Toxic Processes



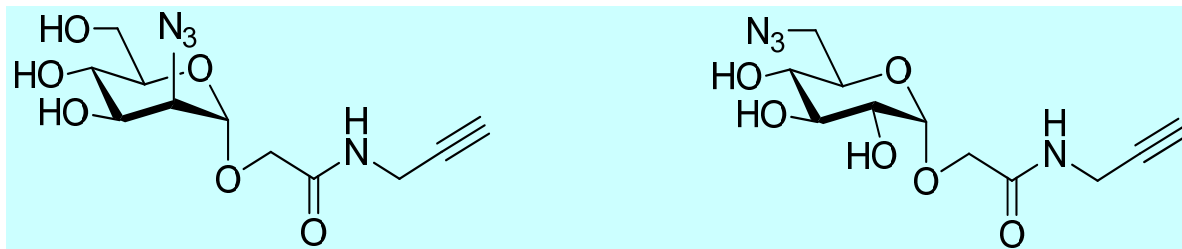
- Residual monomers

- Catalysts

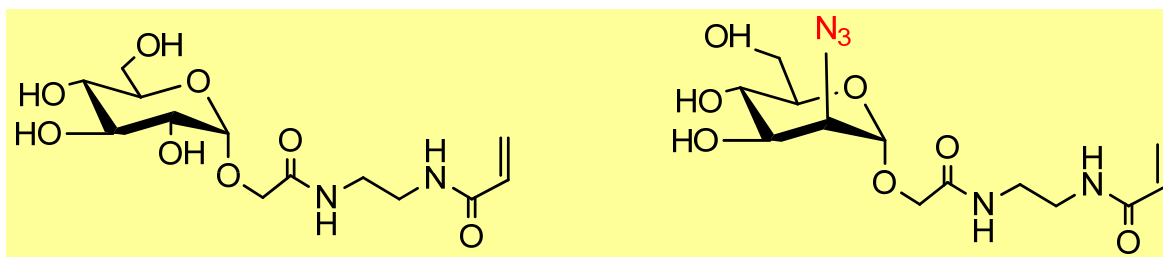
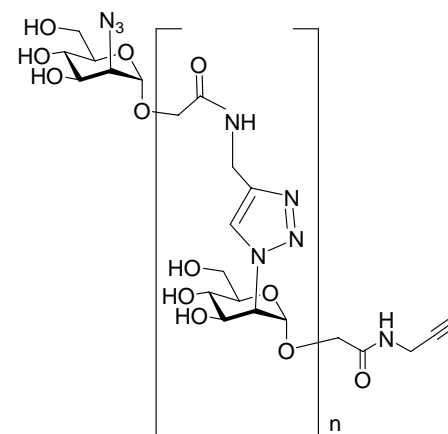


## TOPIC #II : Chemistry & Sustainable Development

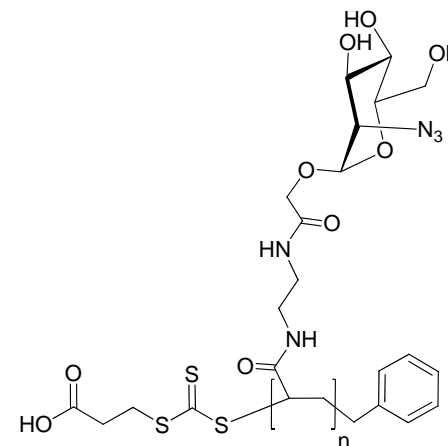
### II.3 Biosourced Polymers

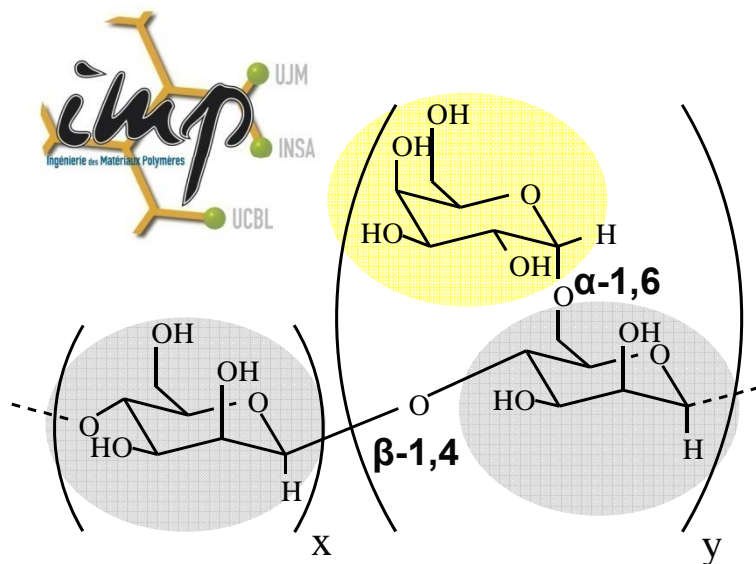


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Abdelkader, S. Moebis, J. Bernard, Y. Queneau, E. Fleury,  
J. Polym. Sci. Pol. Chem. 2011, 49, 1309-1318





# CHEMISTRY OF POLYMERS

## TOPIC #II : Chemistry & Sustainable Development

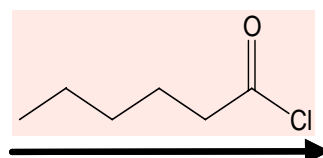
### II.4 Modification of polysaccharides

## Galactomannan

Guar esterifications  
in ionic liquids



5 %  
in BMIMCl



surfactant



3 %  
in  $\text{H}_2\text{O}$

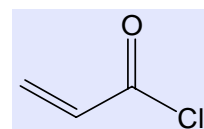


DS = 0.12

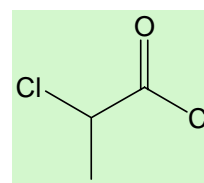
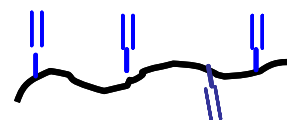
10 %  
in  $\text{CHCl}_3$



DS = 2.70



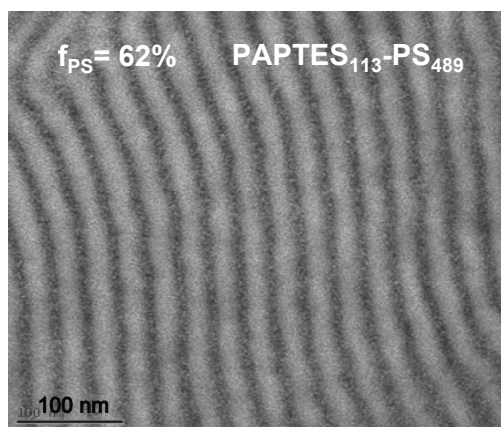
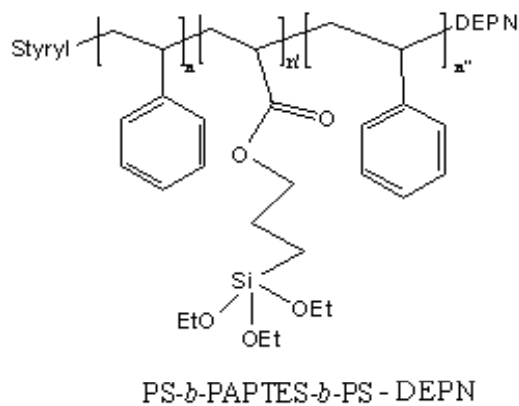
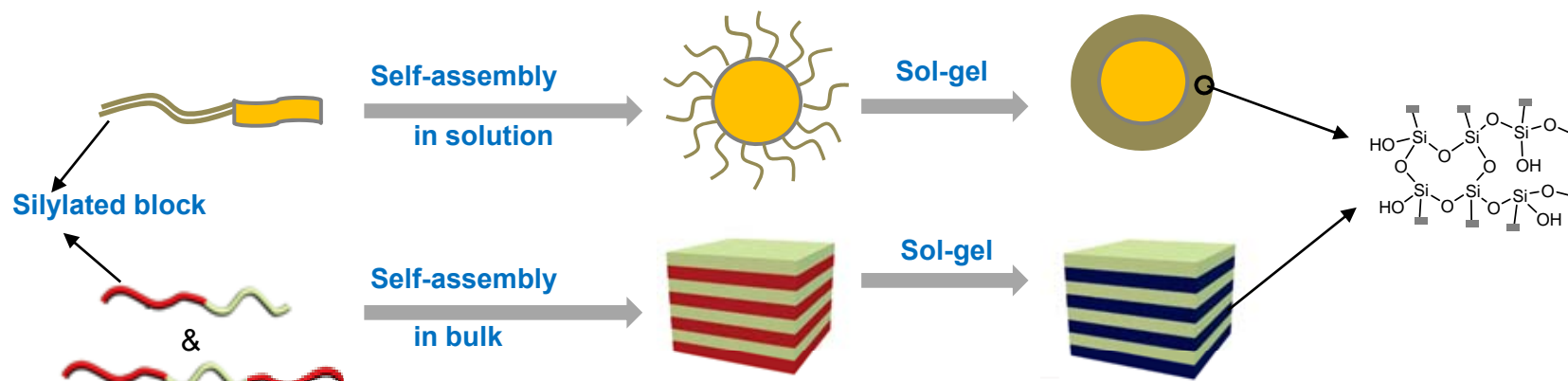
macromonomer



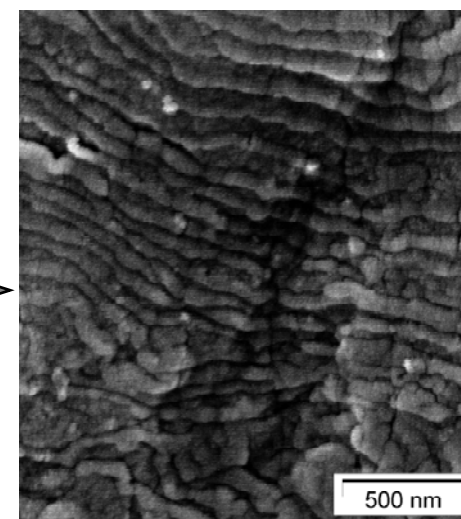
Chemical network

## TOPIC #III : Surfaces & Interfaces Chemistries

### III.1 Synthesis of Nano-objects



1) HCl, 1M  
2) Calcination  
800°C

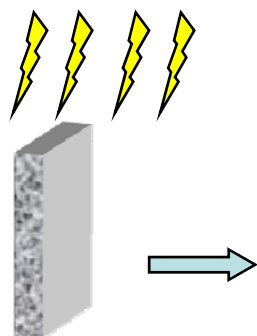




## TOPIC #III : Surfaces & Interfaces Chemistries

### III.2 Functionalization of Planar Surfaces

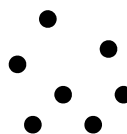
Irradiation



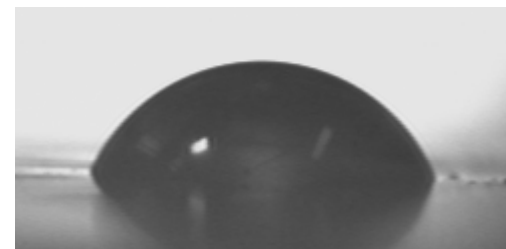
Radical



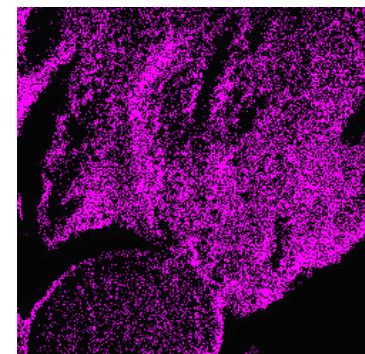
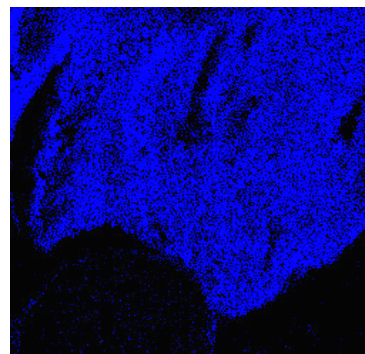
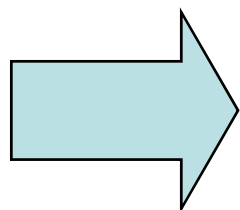
+



Grafting from



Copolymer  
(PVDF/PA 6-6)-g-PHEMA



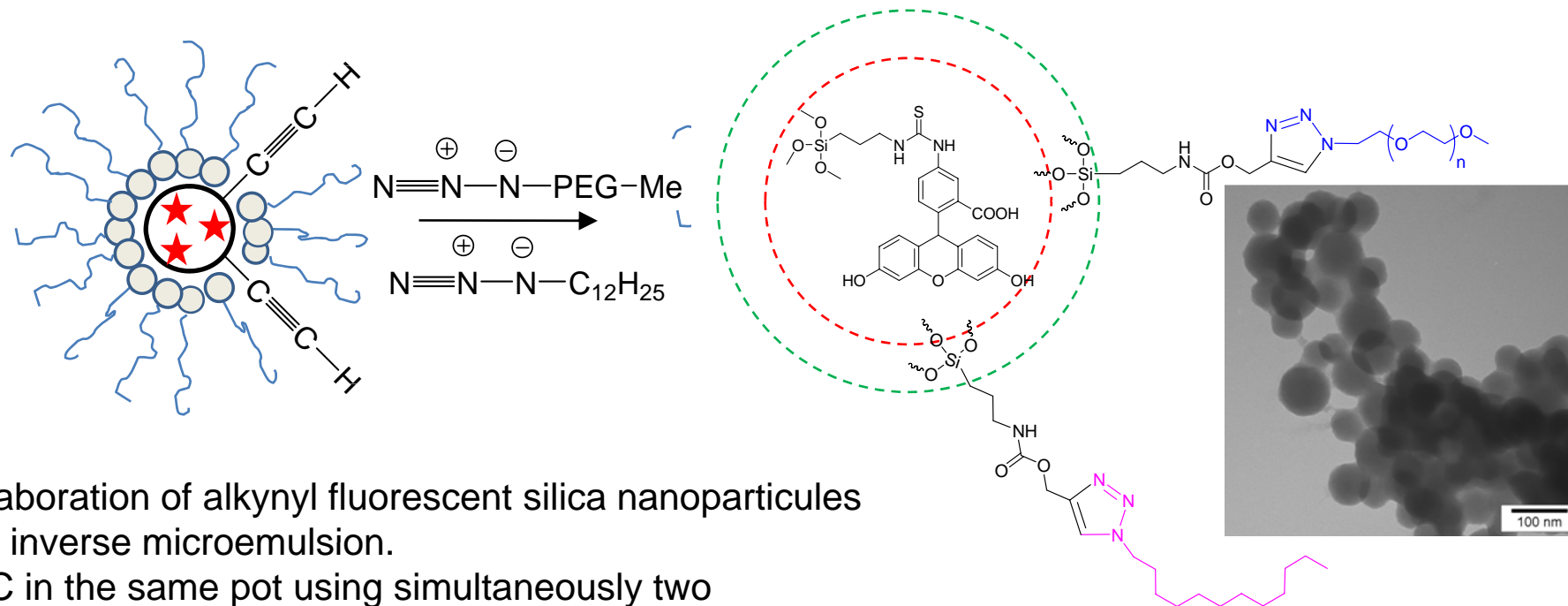
$^{19}\text{F}$

(MEB/EDX)

$^{16}\text{O}$

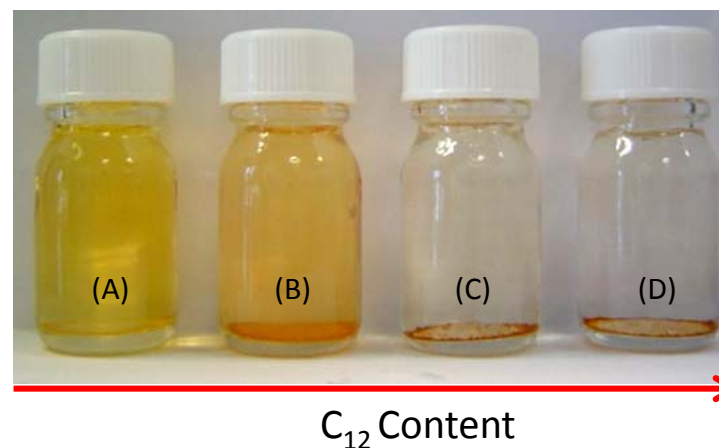
## TOPIC #III : Surfaces & Interfaces Chemiseries

### III.3 Functionalization of Fillers



Elaboration of alkynyl fluorescent silica nanoparticules by inverse microemulsion.  
CC in the same pot using simultaneously two reactants of various HLB

Colloidal stabilization of mixed MEG-dodecyl silica nanoparticles in water.  
MPEG:C<sub>12</sub> = 100:0 (A); 75:25 (B); 50:50 (C); 25:75 (D)



# CHEMISTRY OF POLYMERS

## *Permanent Staff*

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