



Paris, Mercredi 15 Mars 2017



Auto-assemblage de biomolécules pour les biomatériaux de demain



Redouane BORSALI

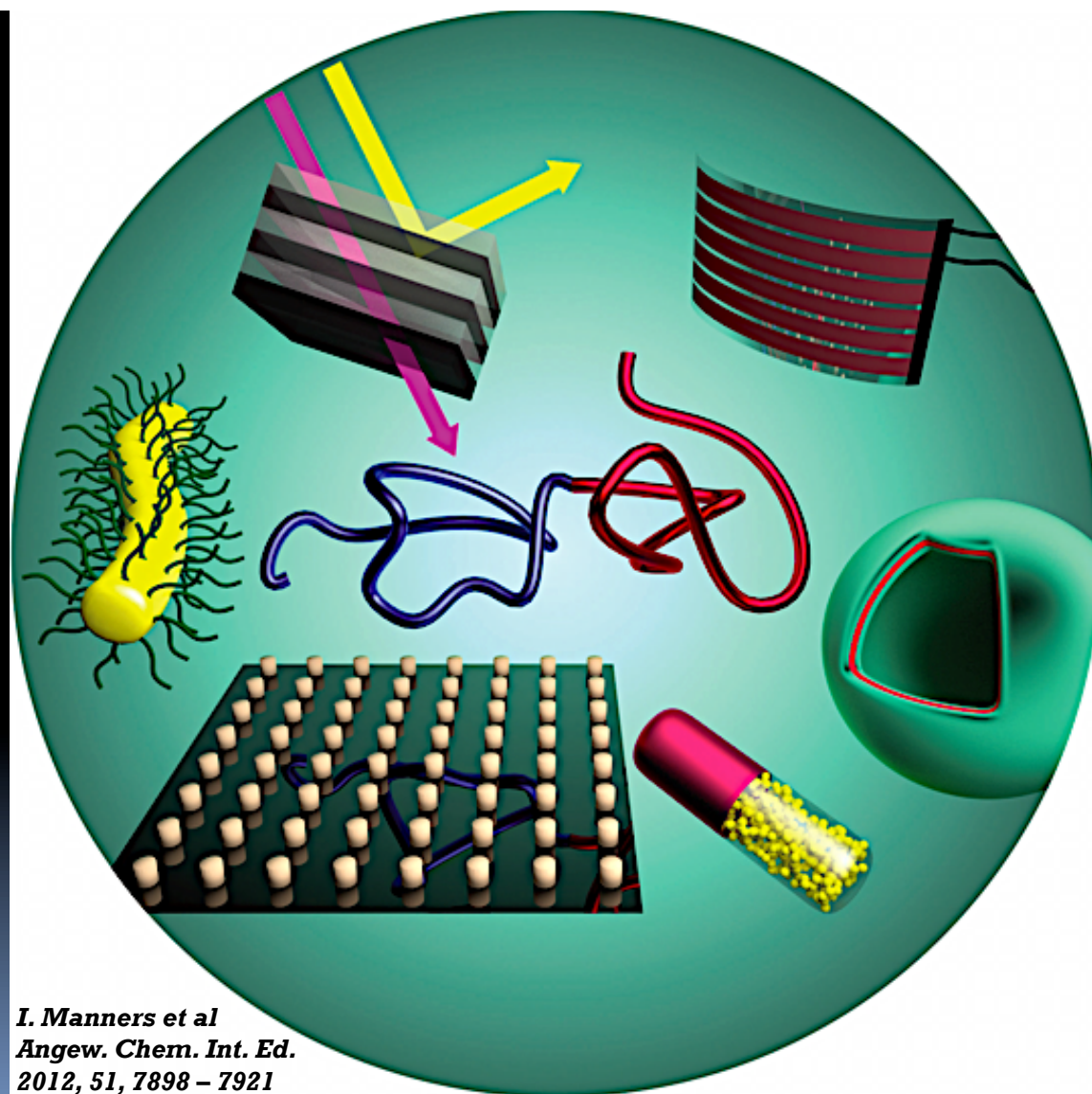
*CERMAV , UPR 5301
Univ. Grenoble Alpes, Grenoble, France*



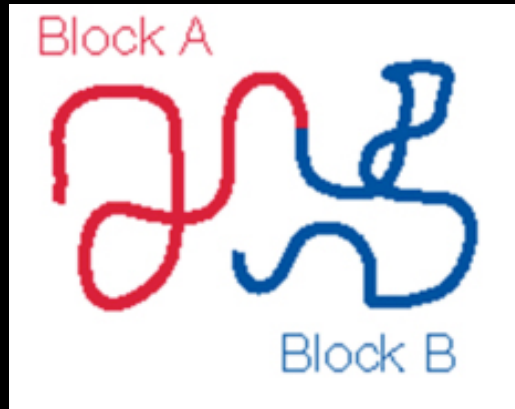
Aujourd'hui
les matériaux (nanostructurés)
sont produits
à partir de (macro)molécules
issues du **Pétrole**

Peux-t-on les produire
à partir de (macro)molécules
Issues de la **Biomasse** ?

Polymères Biosourcés ?
Carbohydrates ?



*I. Manners et al
Angew. Chem. Int. Ed.
2012, 51, 7898 – 7921*



Les polymères ou Copolymères issus du **Pétrole**

Système Classique
PS-PMMA

Peux-t-on les produire
à partir de la **Biomasse** ?

Copolymères à base de Carbohydrates

NOUVELLE CLASSE -> MATÉRIAUX NANOSTRUCTURES



STRATEGIE

PHILOSOPHIE
& OBJECTIFS

AUTO-ASSEMBLAGE DE GLYCOPOLYMERES

Copolymères à Blocs à base de Carbohydrates

“Philosophie” & Objectifs



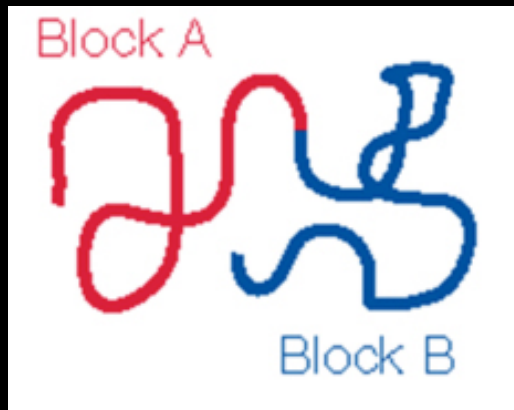
Concevoir, avec une chimie respectueuse de l'environnement, **et par auto-assemblage de briques élémentaires** (glycopolymères: copolymères biosourcés) **des biomateriaux** innovants à haute valeur ajoutée **pour des applications**

❖ Biomedicale, Cosmetique: **GlycoNanoparticules**

**NANOELECTRONIQUE
BIOINSPIREE**

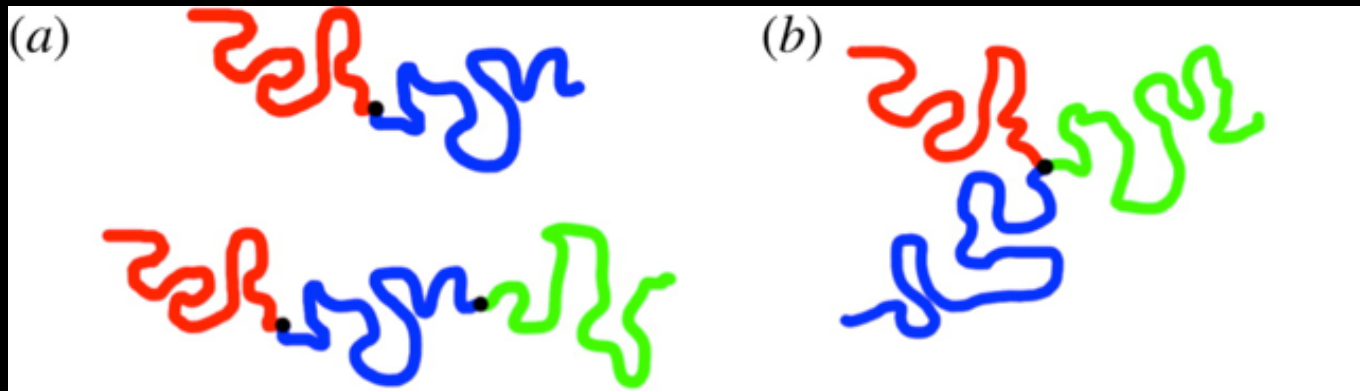
❖ Electronique Flexible (Nouvelle génération de nanolithography, Organique photovoltaïque, Bio-senseurs/Biocapteurs à haute sensibilité,...)

Les copolymères : un domaine de recherche fascinant !

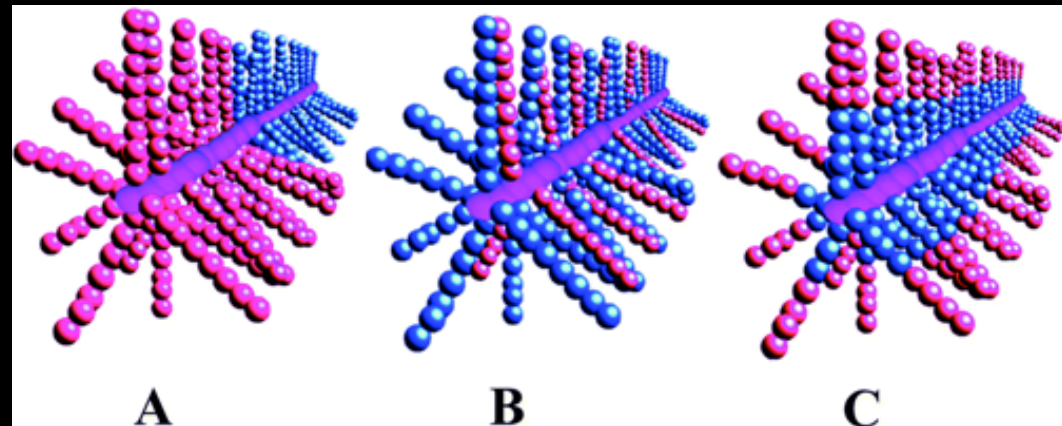


- Mass Molaire
- Fraction volumique
- Incompatibilité entre les blocs
- Flexibilité , rigidité, Hélicité,...
- Architecture : lineaire, cyclique, étoile, peigne,...
- Approche nanotechnologique
- Matériaux avancés
- Santé
- Microélectronique
- Gels
- Nanoparticules
- Films Surfaces
- ...

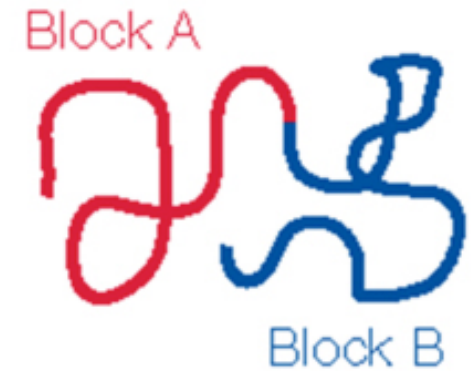
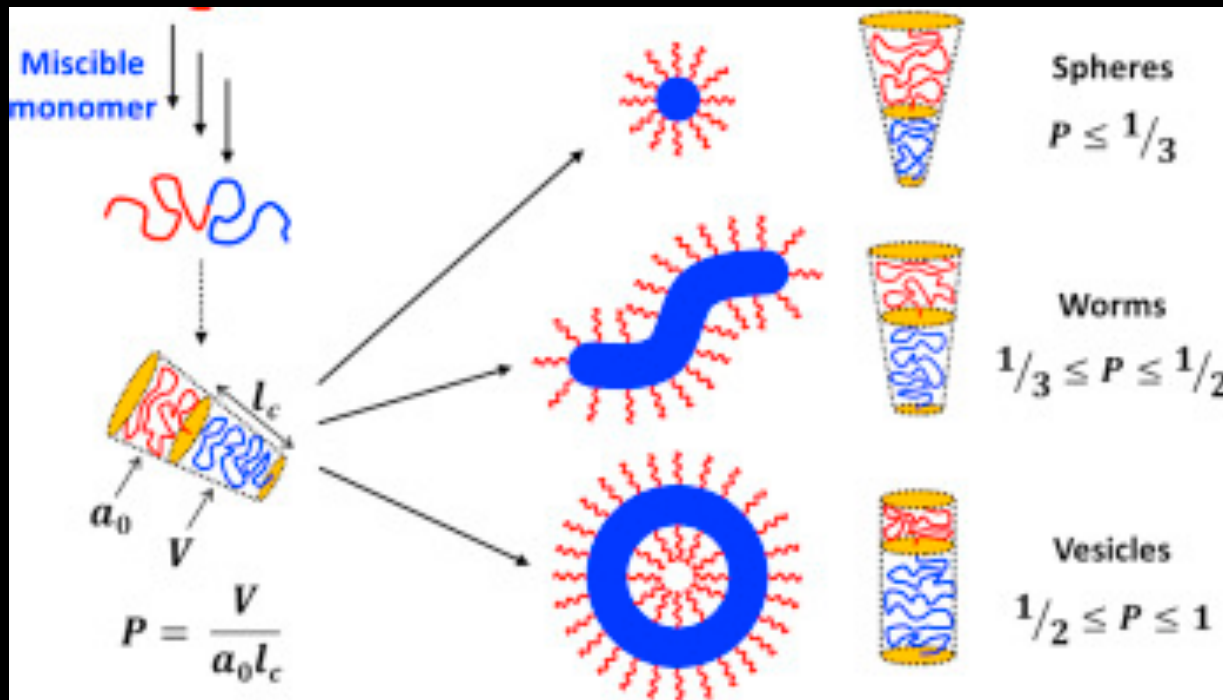
Copolymères à Blocs: Architectures à façon!



- Dibloc
- Triblocs
- Etoile
- Peigne
- ...



De la chaîne de copolymère à la nanoparticule en milieu aqueux



Nanoparticules

- Matériaux
- Santé
- Microelectronique-
- Optique
- Photovoltaïque
- ...

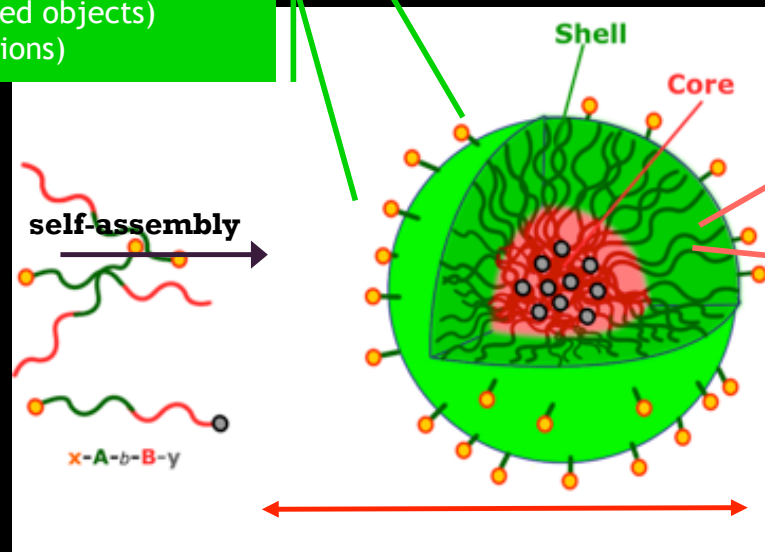
→ Paramètre Important: L'incompatibilité entre les blocs

Pourquoi les Nanoparticles Biosourcées: intérêt ?

*Encapsulation
et relargage contrôlé*

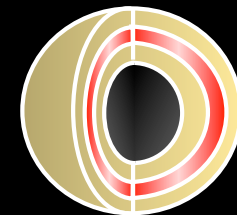
Hydrophilic polymer
Stability
Biocompatibility

Reactive group
(surface-functionalized objects)
(piloting functions)



Driving force of core segregation
hydrophobic interaction
electrostatic interaction (PIC)

Hydrophobic guest molecules
chemically or physically attached to the
micelle core



several tens of nm (10-500 nm)

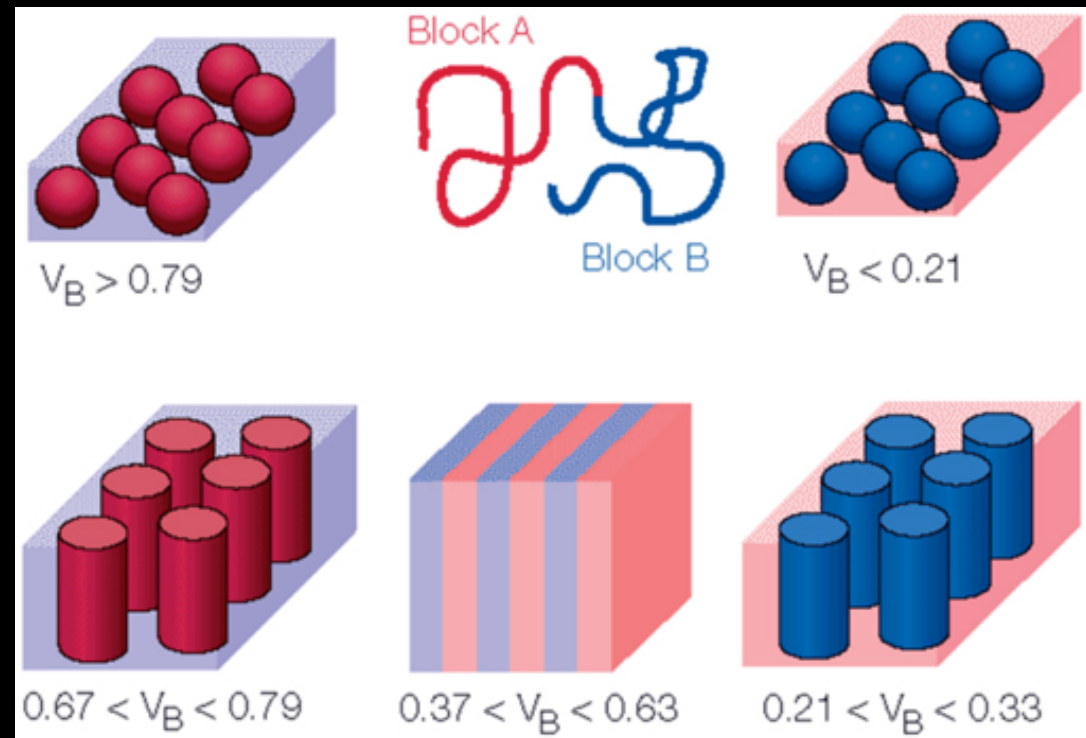
Adapted from Kataoka, K. et al. Adv. Drug Deliv. Rev. 2001, 47, (1), 113-131

Double Encapsulation

Des copolymères à Blocs aux films (surfaces) “intelligents” nanostructurés

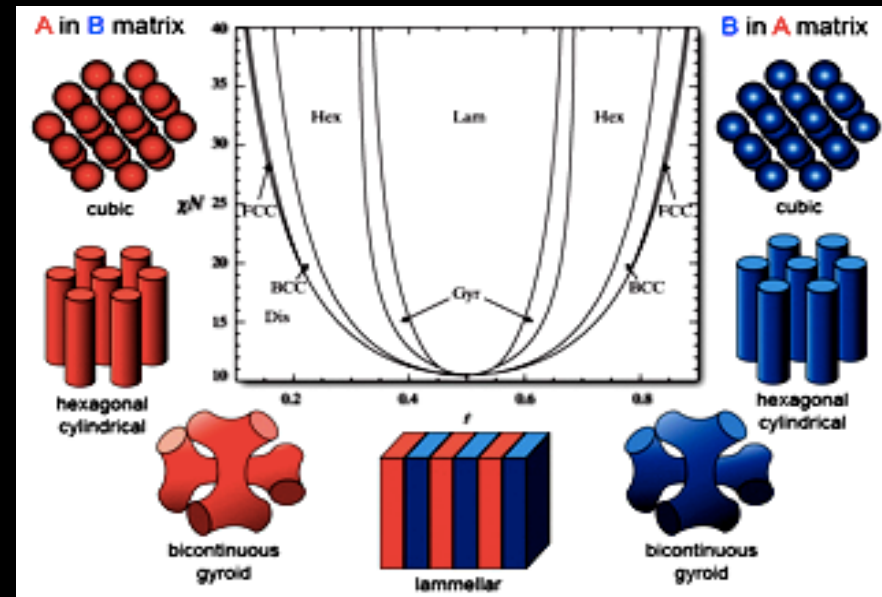
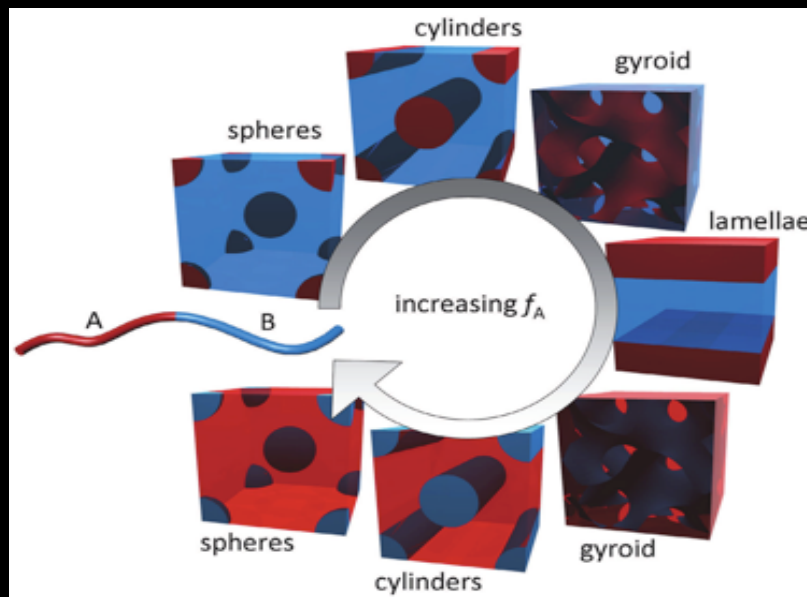
Films Minces

- Nanolithographie
- Microelectronique
- Optique
- Photovoltaïque
- Memoires à Transistors
- Biosenseurs
- Biocapteurs
- ...



Paramètre Important: L'incompatibilité entre les blocs

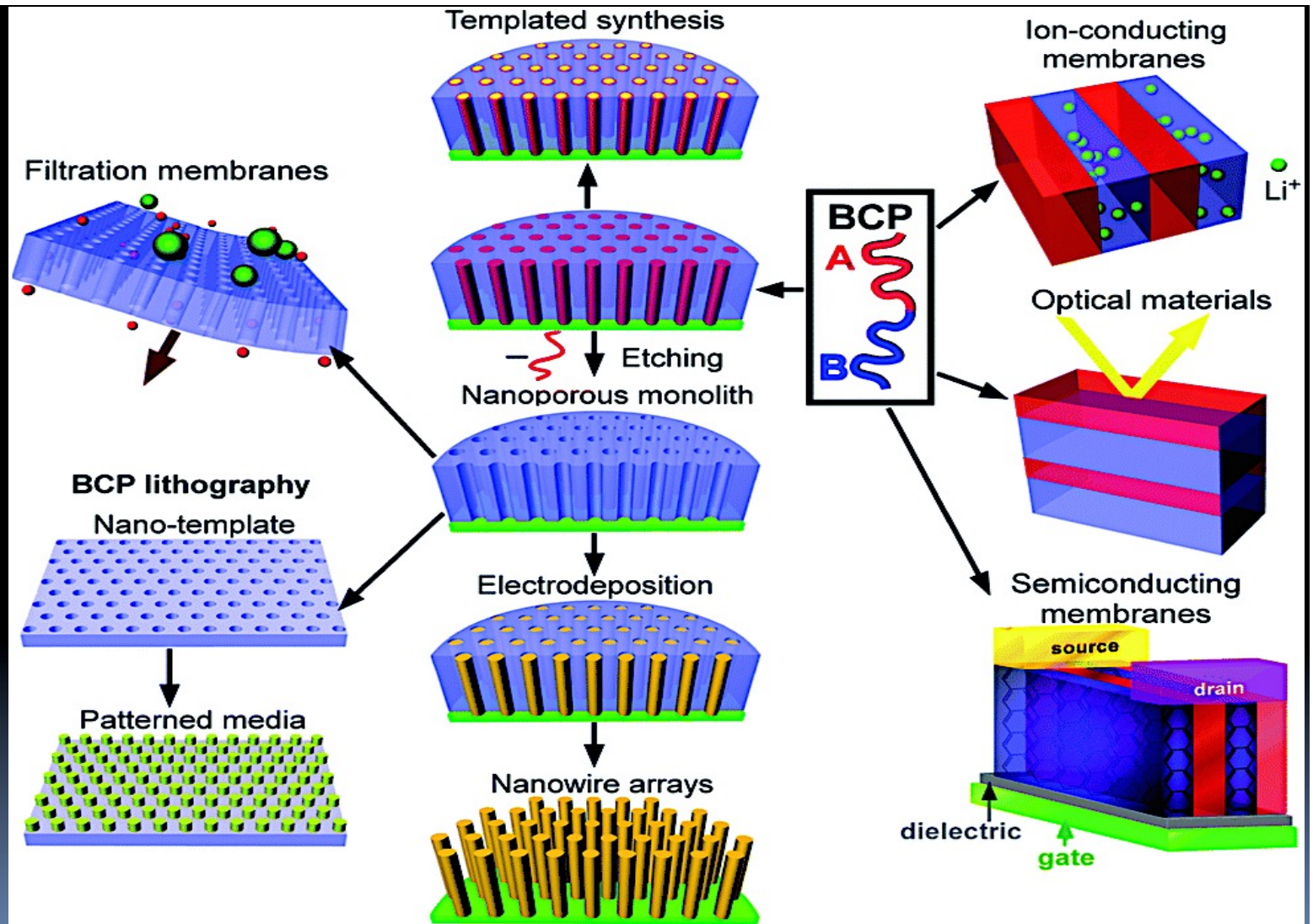
Les phases sont contrôlées par la fraction volumique f_A



Different phases formed by self-assembly of coil-coil diblock copolymers in the bulk (when the intermolecular interaction is sufficiently large) as a function of the volume fraction of one of the blocks (f_A). Other phases have also been reported for diblocks, and the phase diagrams of BCPs containing more than two blocks are considerably more complex. Switching out one or both coil blocks with a conjugated block that adopts a semi-flexible or rigid rod structure will also qualitatively change this phase diagram.

Intérêt des Films Minces

Dispositifs
Nanotechnologiques
Utilisant
Les Copolymères
à Blocs

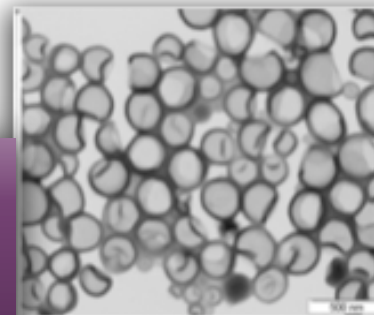


After Hanqiong Hu, Manesh Gopinadhan† and Chinedum O. Osuji in *Soft Matter*, 2014, 10, 3867-3889

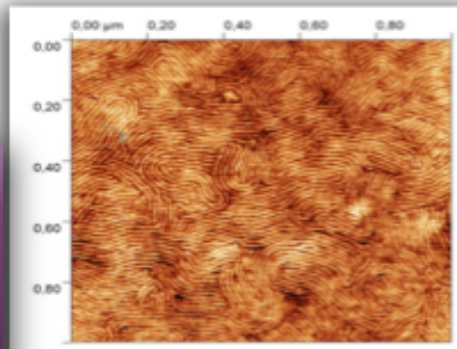
Copolymères
Biosourcés



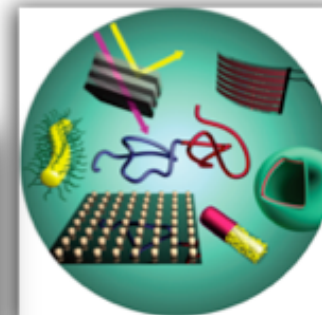
NANO-
PARTICULES



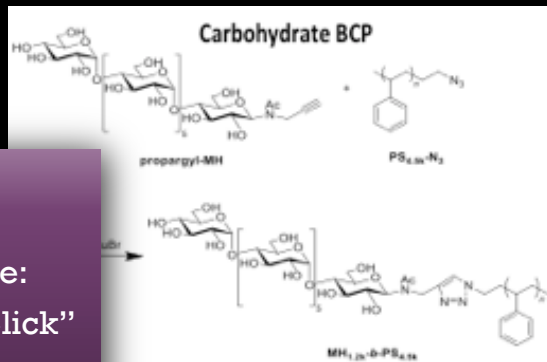
FILMS MINCES



APPLICATIONS



Synthèse:
Chimie "Click"



METHODES DE
PREPARATION

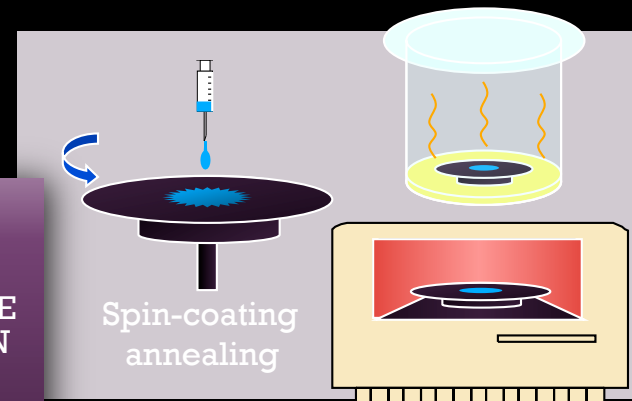
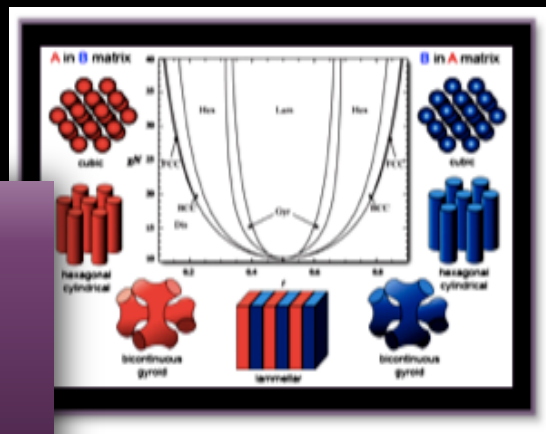
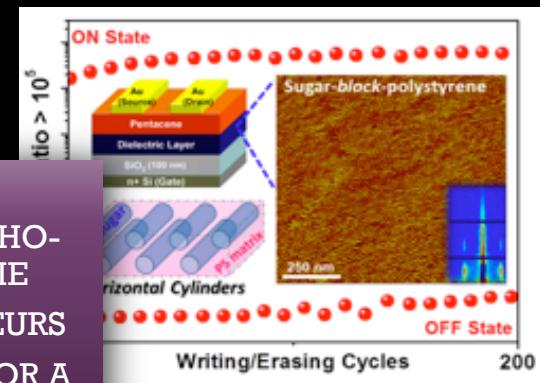


DIAGRAM
DE
PHASE



OPV,
NANOLITHO-
GRAPHIE
BIONSENSEURS
TRANSISTOR A
MEMORY



Permanents (5)

R. Borsali (DR, CNRS) –**Group Leader**

F. Dubreuil, MdC UJF

S. Halila (CR, CNRS)

I. Otsuka (CR, CNRS)

Technical Staff

C. Travelet (IE), CNRS

Visiting Prof, (2)

T. Isono

E. Minatti

Post-docs, Phds, (7)

M. Cardoso

L. Goujon

Y. Liao

E. Reynaud

L. Wang

Y. Wang

Phds, (3)

Y. Otsuka,

B. Sthéfani Caldas PhD, Brazil

M. Vestari PhD, Brazil

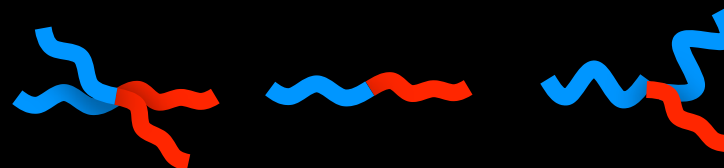
MASTERS & Interns (7)

Karine, Aynur, Christian, Rémy

Mariane, Anastasia, Coralie

Greenanofilms : N. Ballot

Polynat : F. Portello

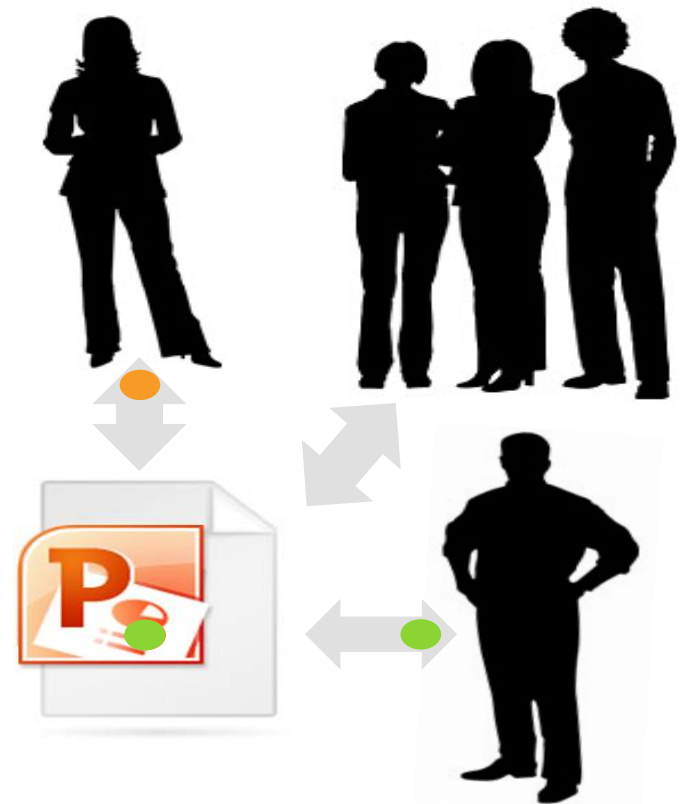


Year 2016 - « Self-Assembly of Glycopolymers »



Collaborations

Europe, Japan, Taiwan, Brazil, USA





Collaborations

CERMAV, Grenoble

K. AISSOU (PhD, Dr)
Y. OTSUKA (PhD)
S. FAYAD (PhD)
S. TALLEGAS (PhD)
I. OTSUKA (PhD, Dr)
S. HALILA (PhD, Dr)
S. FORT (PhD, Dr)
C. TRAVELET (Eng. CNRS)
C. ROCHAS (PhD, Dr)
R. BORSALI (PhD, Dr)

Collaboration SPrAM (CEA/CNRS/UJF)

P. RANNOU

Collaboration LTM, CEA-Leti

T. BARON (PhD, Dr)
R. TIRON (PhD, Dr)

Collaboration with Japan

T. SATOH (Hokkaido)
T. ISONO (Hokkaido)
T. KAKUCHI (Hokkaido)
H. SATO (TOSHIBA)
Y. SEINO (TOSHIBA)
T. AZUMA (TOSHIBA)
T. HAYAKAWA (Tokyo)
H. YOSHIDA (HITACHI)
S. NAGAHARA (Tokyo Electron)

Collaboration with Taiwan

W.-C CHEN (Prof)
Y. CHENG (Post-Doc)

Collaboration with Brazil

V. SOLDI (Prof)
E. MINATTI (Prof)
E. CURTI MUNIZ (Prof)

Collaboration with USA

R. PECORA (Prof), Stanford Univ., CA
G. WILLSON (Prof), C. J. ELLISON (Prof), UT, TX

....K€



TNO

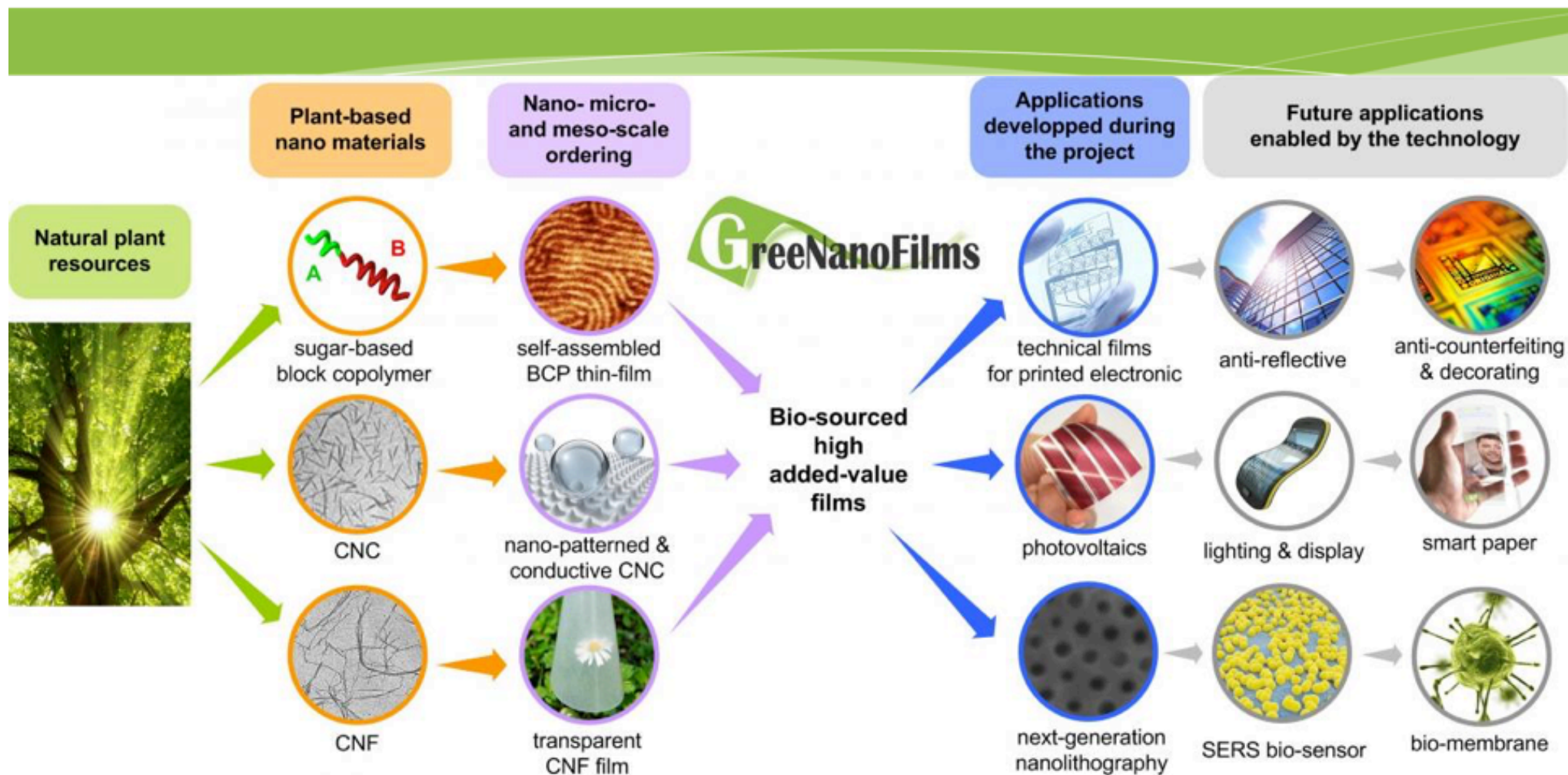


csem



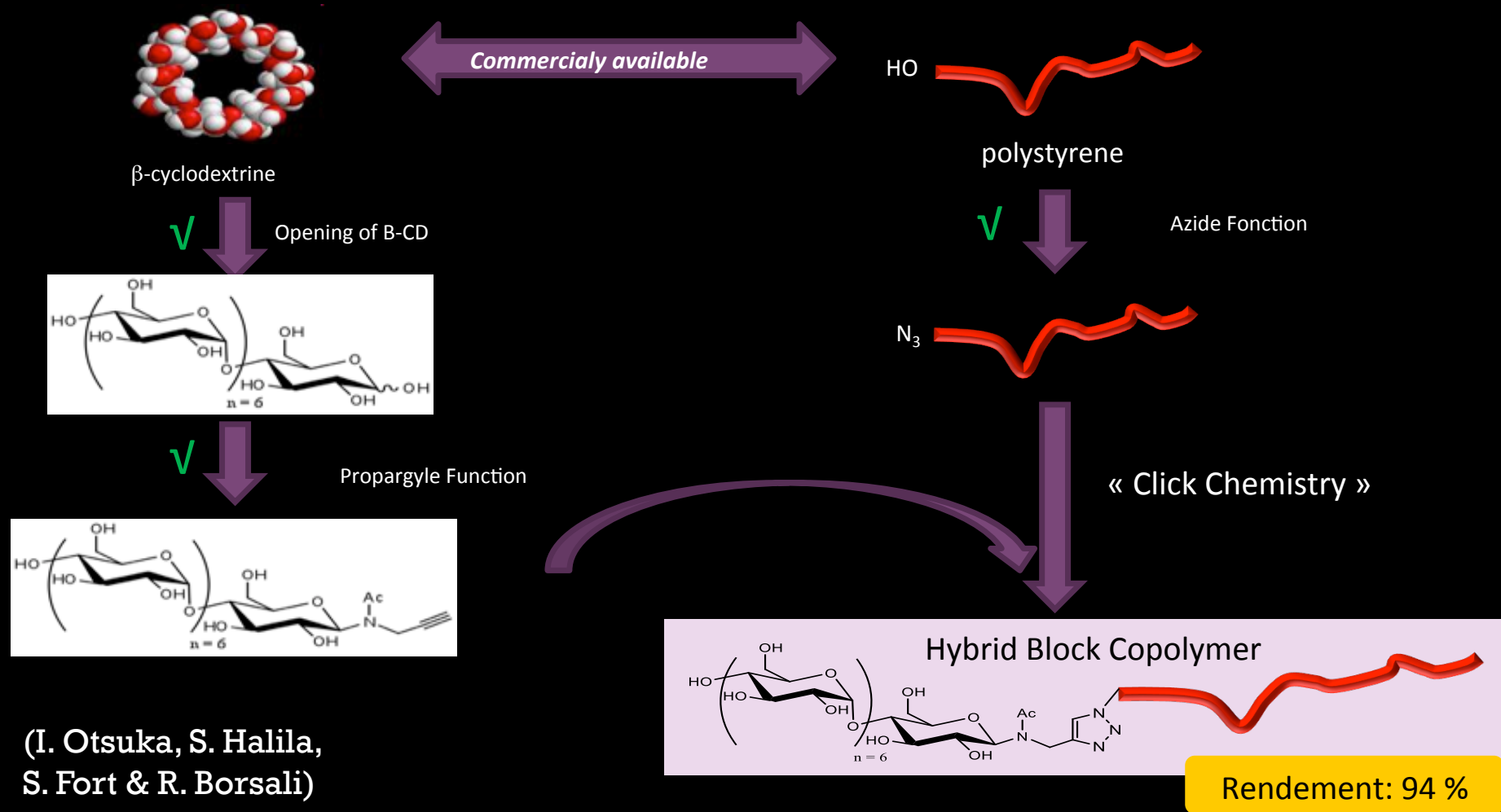
**Projet Européen
10 partners:
2014-2017**

Coordinateur: R. Borsali ; Budget : 5.2 M€



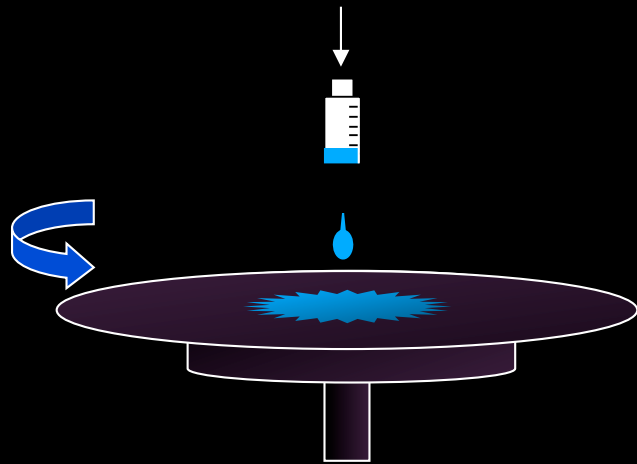
Synthèse de Copolymères Biosourcés?

NOUVELLE STRATEGY: Chimie « Click » : 1st system Maltoheptaose-*b*-Polystyrene - (2010)



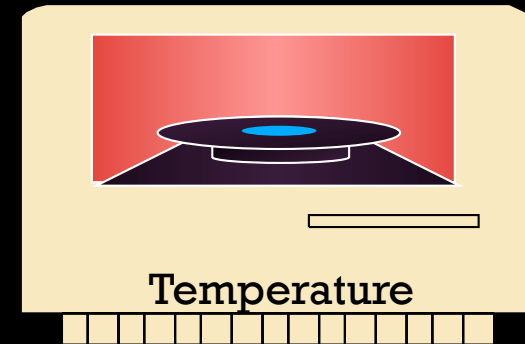
Films Minces

Solution de Copolymère Biosourcés

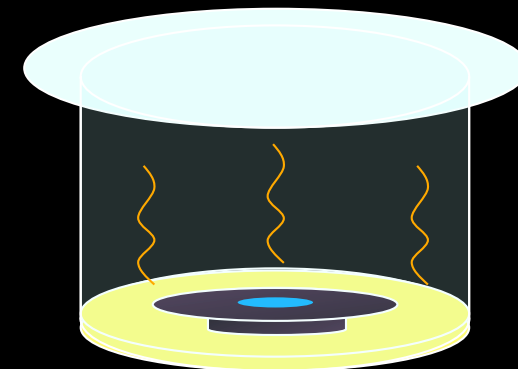


“spin-coating”

Recuit



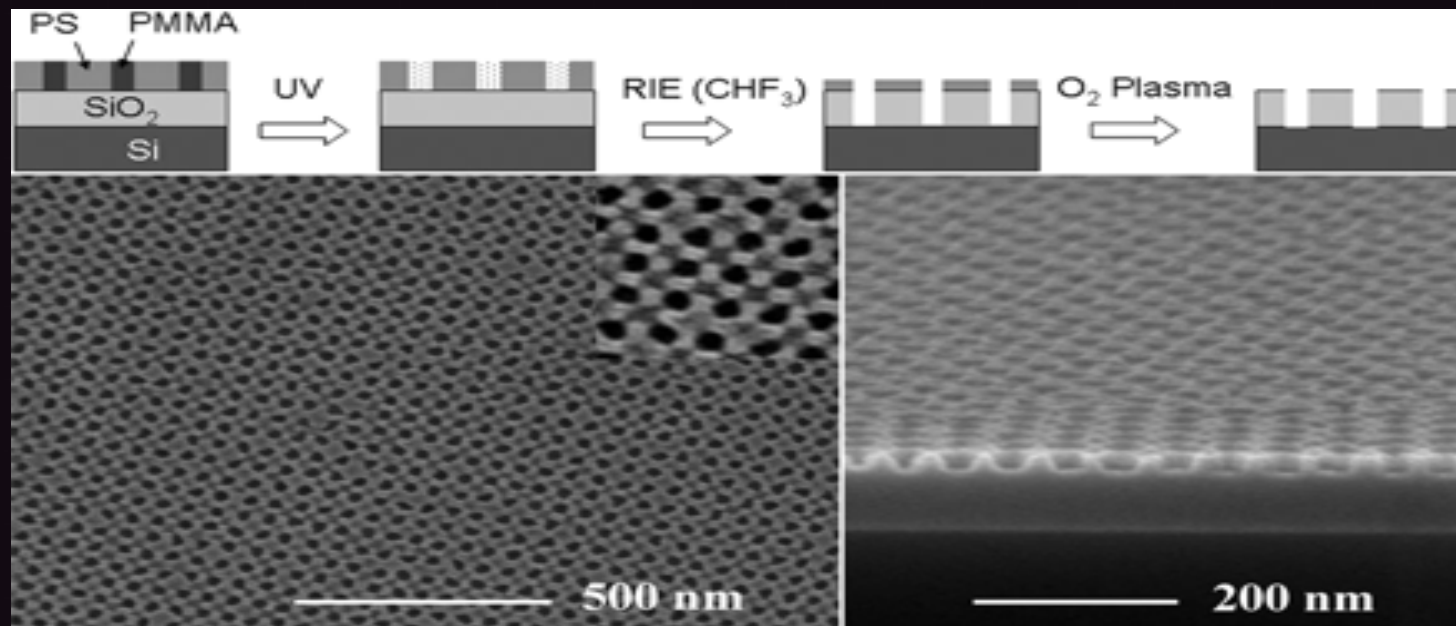
Temperature



Solvent et/ou micro-ondes

L'Etat de l'Art : Aujourd'hui

Schematic representation of pattern transfer
from supramolecular block copolymer thin films



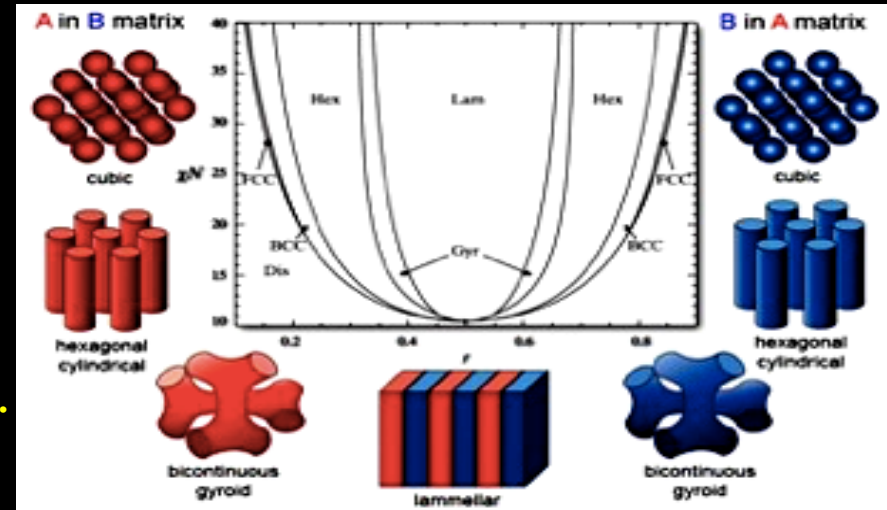
C. Tang et al., Science 322, 429 -432 (2008)

limits: ($L_p = 40$ nm, $L_s = 80$ nm)

Peux-t-on aller à des resolution importante?

Pourquoi : Augmenter les performances

- ✓ Nanolithographie
- ✓ Dispositifs Nano-electroniques (OPV...)
- ✓ Capacité de Stockage Importante
- ✓ Biosenseurs à Haute sensibilité/résolution,...



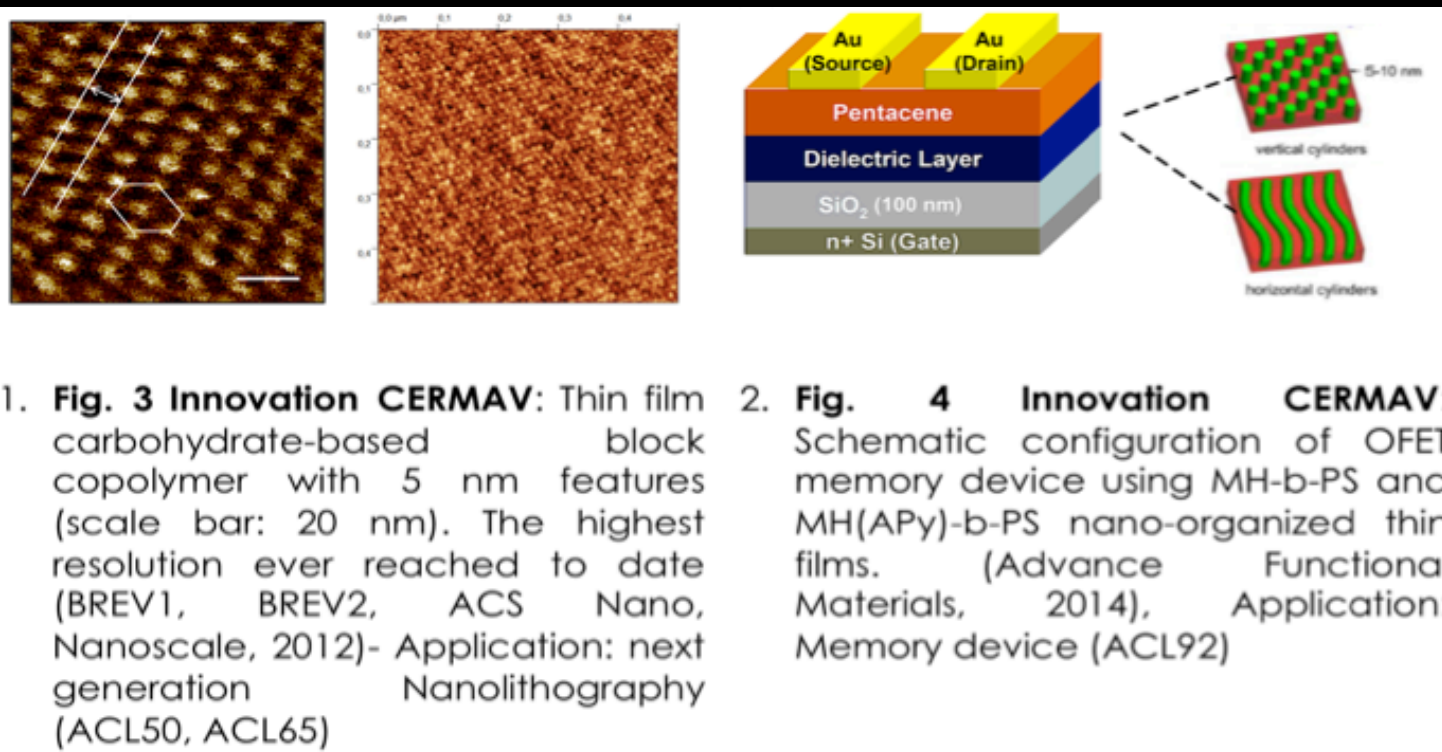
Comment :

Augmenter l'incompatibilité entre les blocs: paramètre χN

- ✓ Copolymères Biosourcés (très incompatible)
- ✓ Faible masse (petite domain)
- ✓ Haute résolution

Equipe Auto-assemblage de glycopolymères

Innovation 2012



Ultra-high resolution (5 nm) nano-organized thin films made from the self-assembly of bio-based block copolymer systems -never attained to date- for nano-electronic applications– Such innovation allowed the building up and coordination of the “Greenanofilms” FP7 European project, attracted several industries (PCAS, DISASOLAR, OBDUCAT) and others under discussions (Toshiba, JSR, Solvay and Arkema).

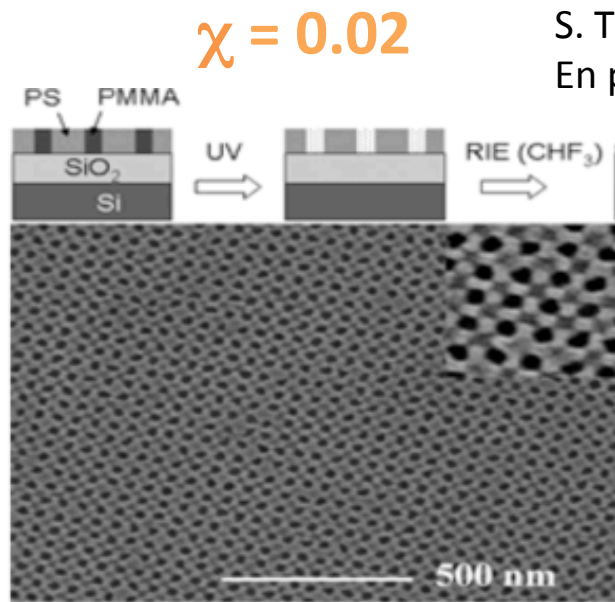


Figure 1. State-of-art: Thin film PS-PMMA block copolymer with **40nm features** (scale bar: 500 nm) after C. Tang et al., *Science* 322, 429 -432 (2008).

S. Tallegas, R. Borsali et al
En préparation– en 2017

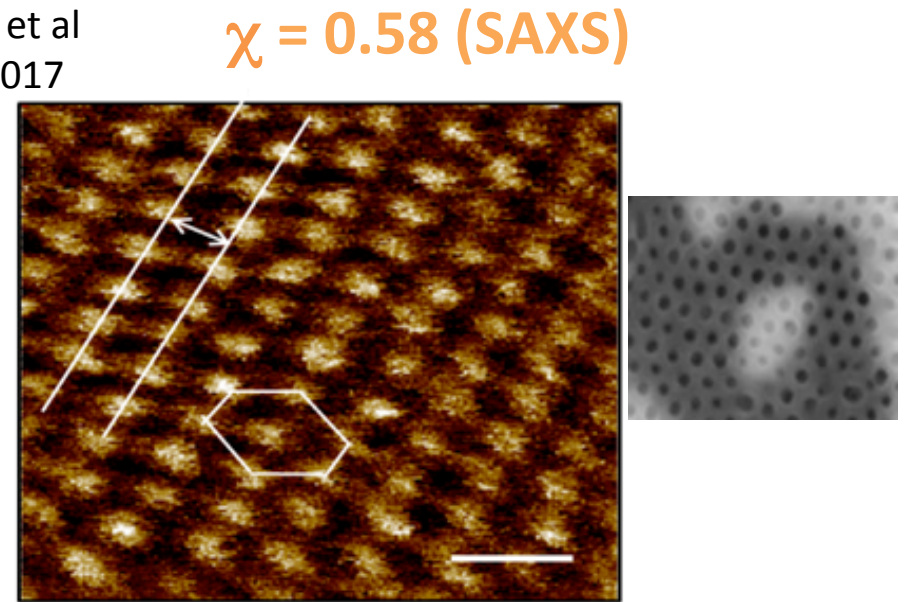


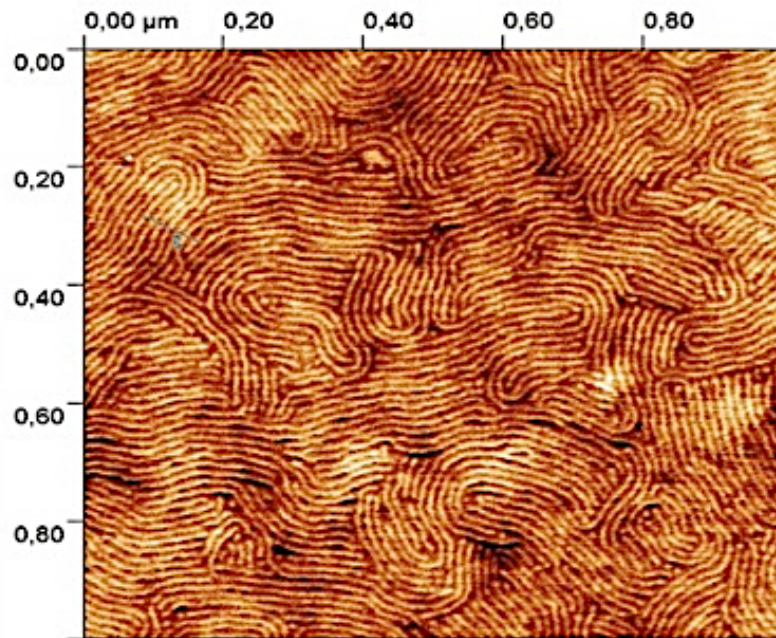
Figure 2. Innovation (CERMAV): Thin film carbohydrate-based block copolymer with **5 nm features** (scale bar: 20 nm) The highest resolution ever reached to date⁷ (*ACS Nano*). AFM image.

“Conventional” χ

Carbohydrate-BCP “HIGH” χ

Cushen, J.; Otsuka I; Bates, C.; Halila, S.; Fort, S.; Rochas, C.; Easley, J.; Rausch, E.; Thio, A.; Borsali, R.; Willson, G.; Ellison, C. **Oligosaccharide/Silicon-Containing Block Copolymers with 5 nm Features for Lithographic Applications.** *ACS Nano* , 2012, 6(4) 3424–3433

Aujourd'hui

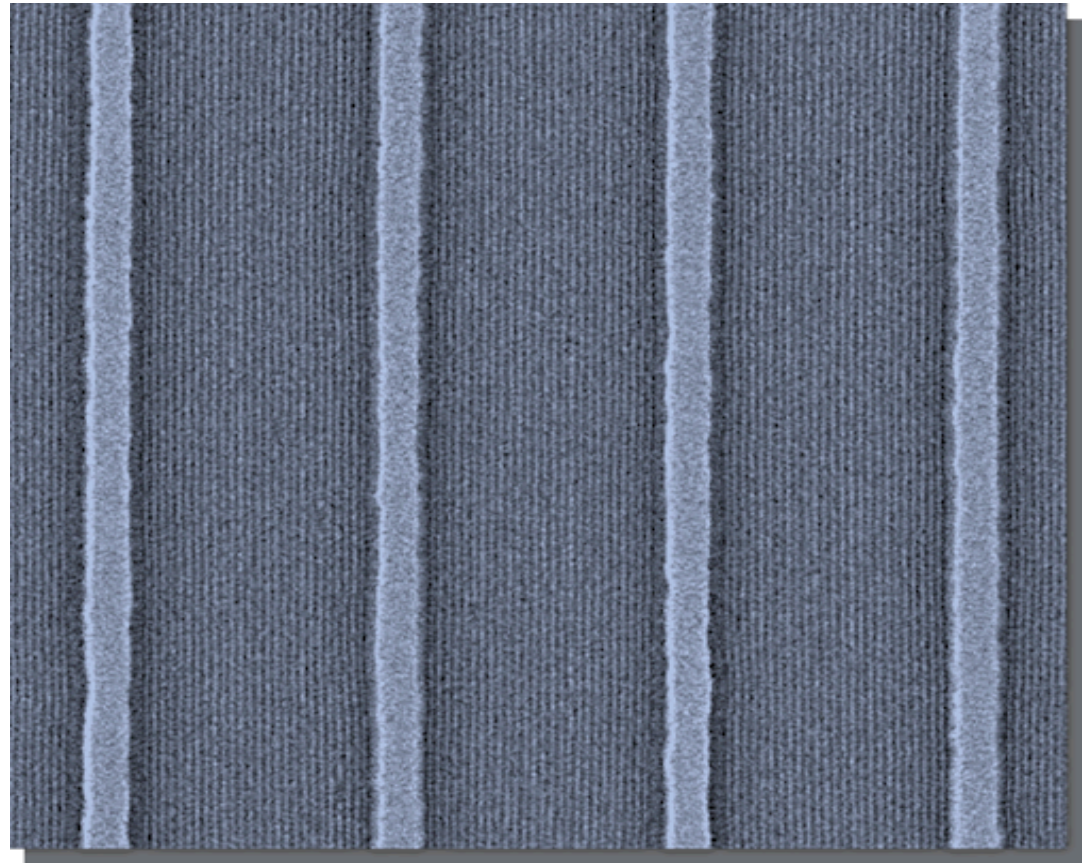


Resolution Sub_10 nm !
Copolymères Biosourcés



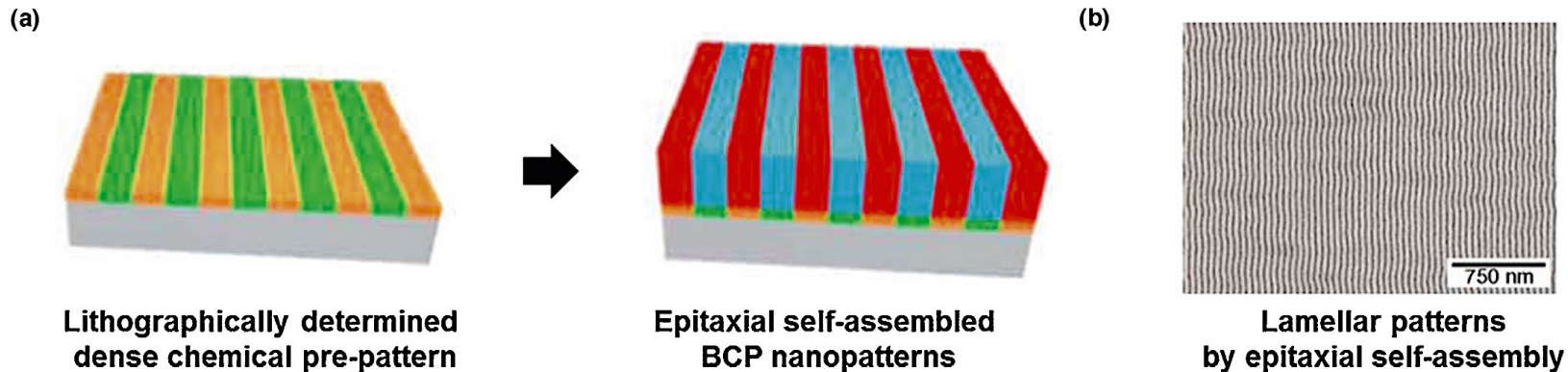
MH-*b*-PS

Objectif: Demain



DSA : “Directed Self-Assembly”

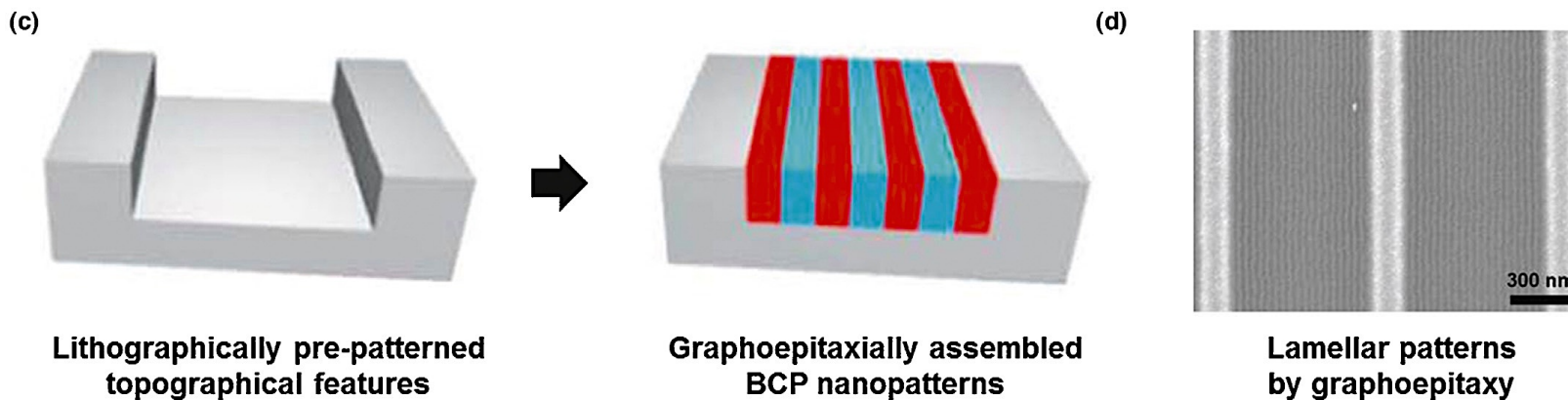
Epitaxial Self-Assembly



(a) Schematic illustration of epitaxial self-assembly exploiting nanoscopic chemical patterns to direct BCP self-assembly

(b) SEM image showing defect free lamellar patterns attained by epitaxial self-assembly

Graphoepitaxy



(c) Schematic illustration of graphoepitaxy utilizing topographic pattern to direct BCP assembly

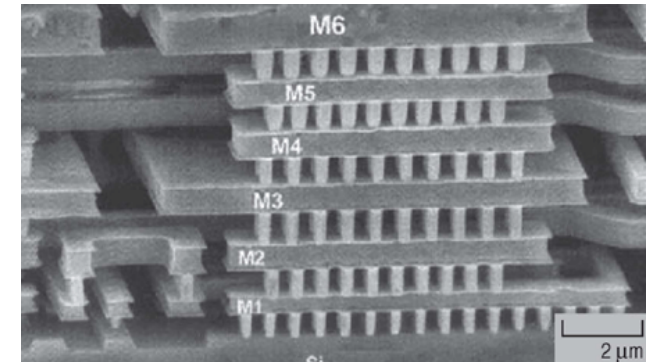
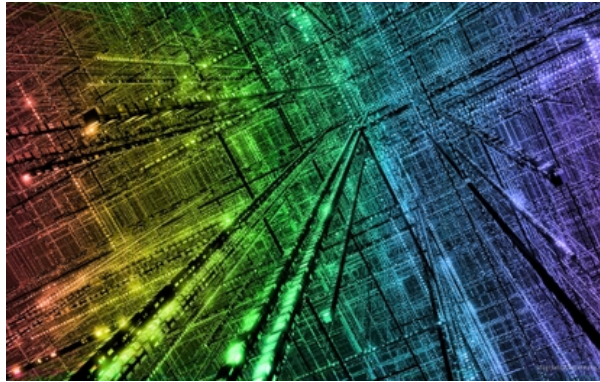
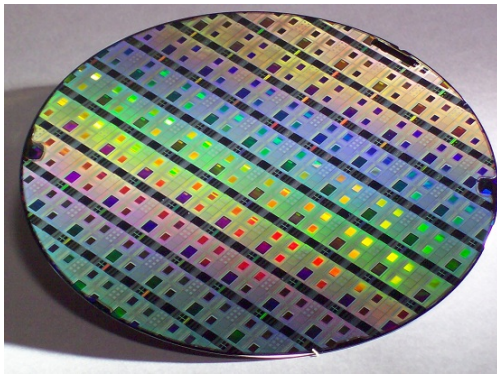
(d) SEM image showing highly aligned lamellar patterns prepared by graphoepitaxy

From
Seong-Jun Jeong
et al
Materials Today
Volume 16,
Number 12
December 2013

LA LITHOGRAPHIE EN MICROÉLECTRONIQUE

Lithographie: Étape de fabrication des motifs sur une puce

→ détermine la performance des microprocesseurs



Impératifs et contraintes de la filière CMOS:

- Forte capacité d'Intégration
- Haute résolution
- Control de l'alignement des domaines
- Faible défektivité
- Faible coût
- Rapidité de production

CMOS : "Complementary Metal Oxide Semiconductor"

C'est une technologie de fabrication de composants Électroniques (circuits intégrés) à très faible consommation.

Application 1 - DSA



Films Minces à base de Copolymères Biosourcés: Nanolithographie de nouvelle génération

Approche #1

Djamila Ouhab

Doctorat Janvier , 2016



PDMS-MH

Approche #2

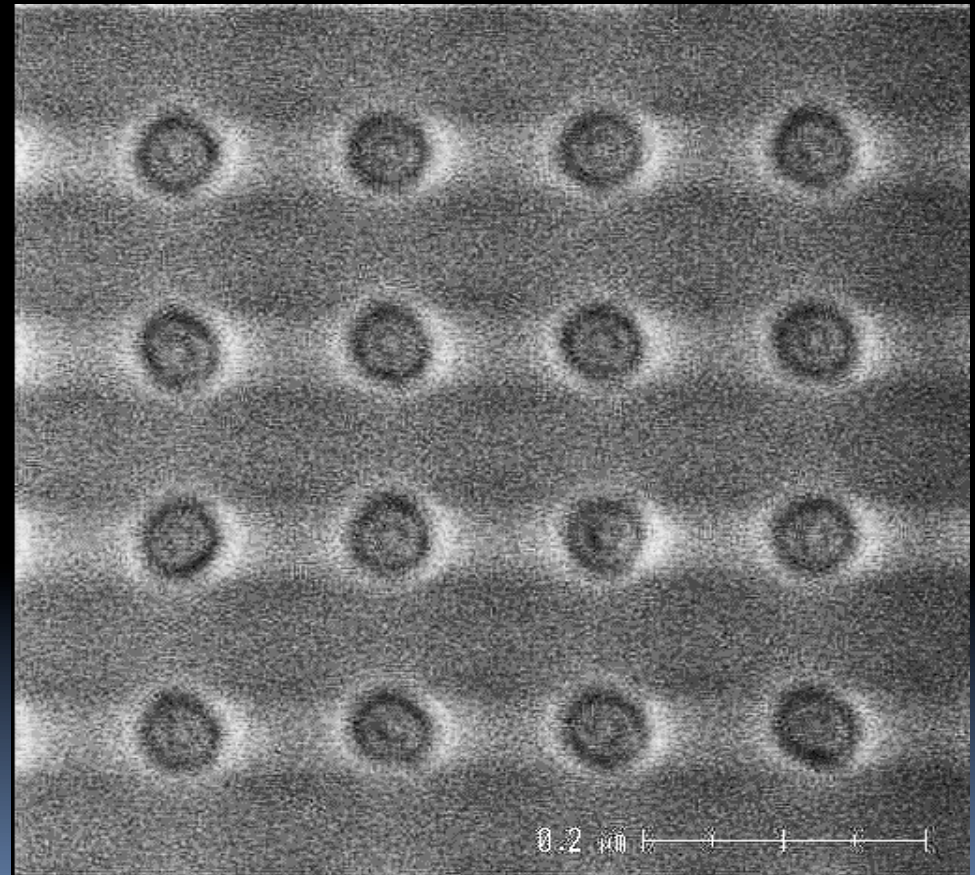
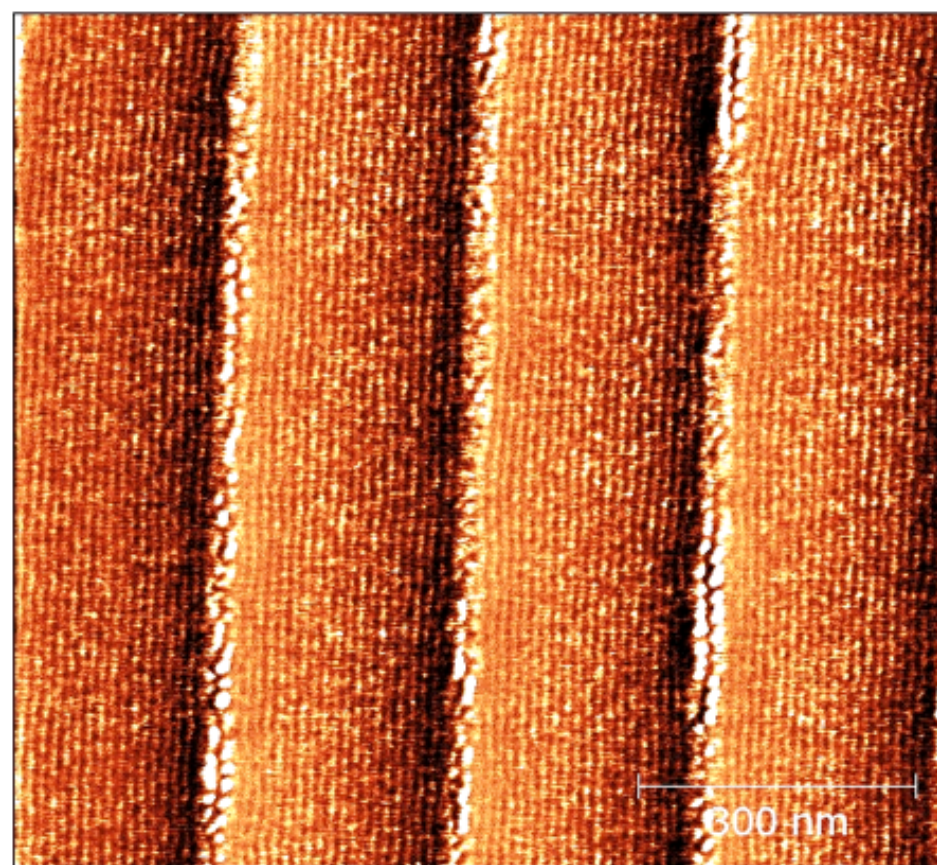
Lund Group

I. Maximov

PS-MH

Film minces à base de Copolymères Biosourcés
Résolution: Sub_10nm BCP PDMS-Oligosaccharide

CERMAV-CEA Leti, 2016, Phd D. Ouhab
Approche "DSA "



D. Ouhab, S. Halila, R. Tiron & R. Borsali (en préparation)

Application 2 - OPV



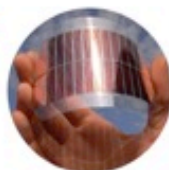
Films Minces à base de Copolymères Biosourcés: Photovoltaïque organique

Yoko Otsuka
Doctorat Janvier, 2017





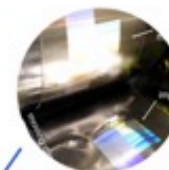
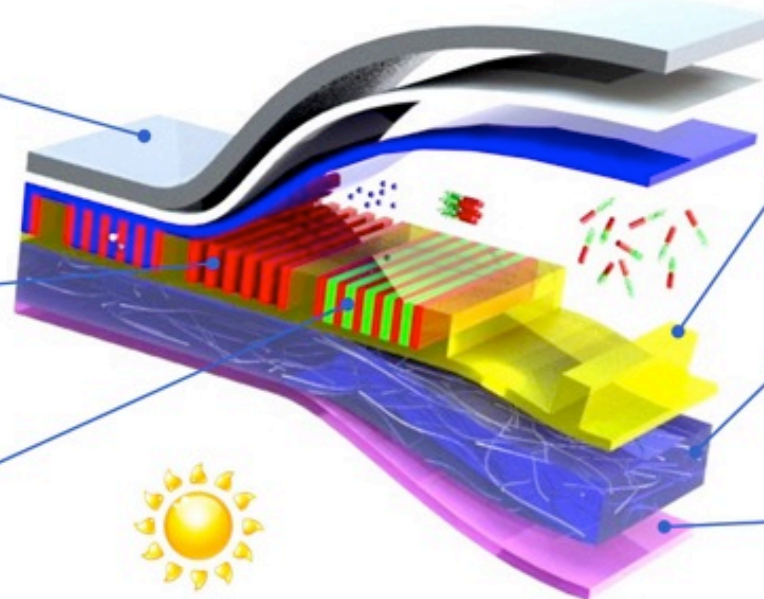
**Solar cell printing
& performance
characterization**
(efficiency, lifetime,
energy payback
LCA, sustainability)



**Carbohydrate etching
and acceptor filling**
(PCBM, ICBA)



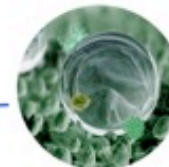
**Directed self-
assembling of sugar-
based semiconducting
block copolymer**
(P3HT, PCz)



**Nano-imprinting of
transparent
conductive anode**
(functionalized-CNC,
PEDOT:PSS)



**Transparent nano-
cellulose film**
(CNF, CNC)



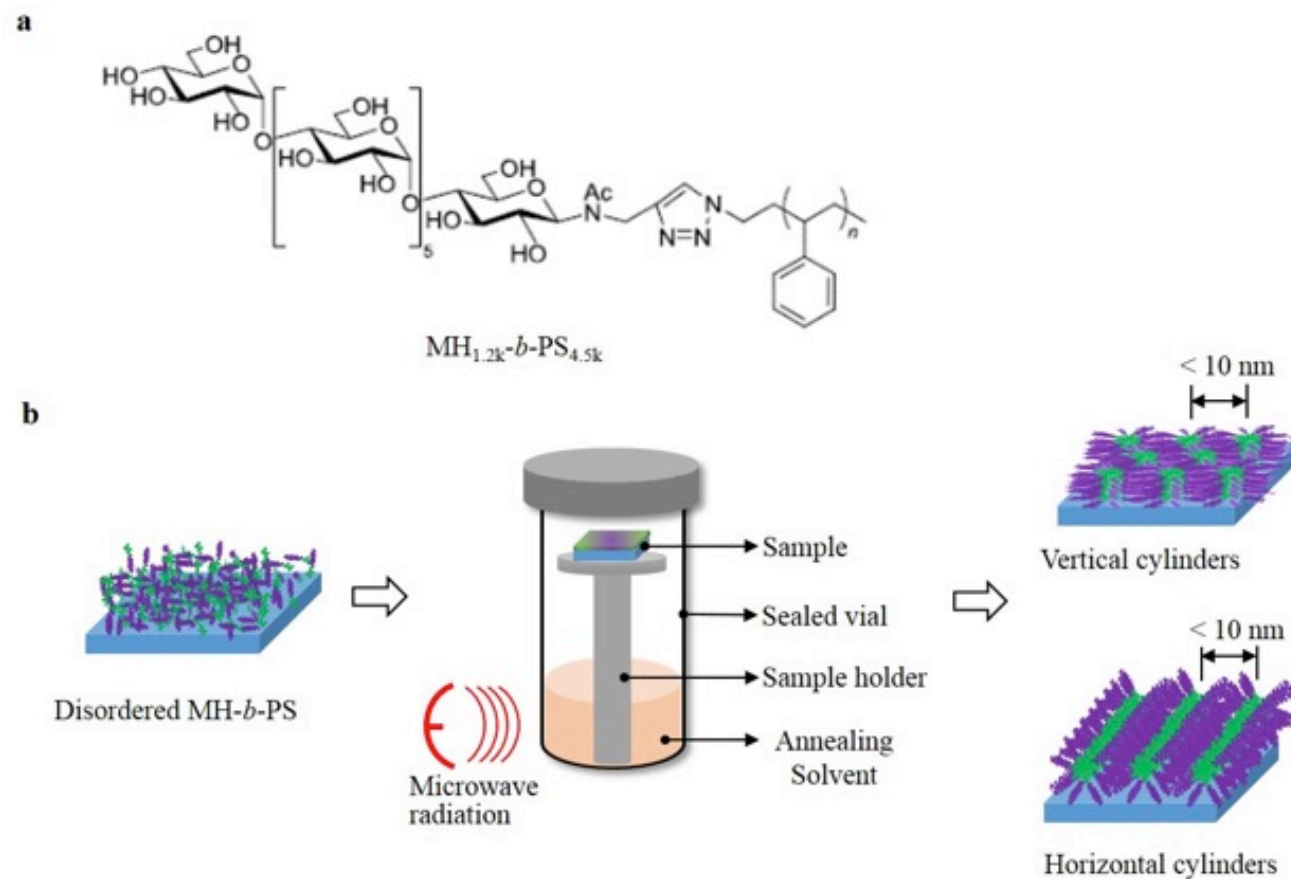
**Super-hydrophobic &
barrier coatings**
(lotus-like nano-
patterning, atomic layer
deposition &
chromatogenic grafting)



Auto-assemblage Ultra-rapide du PS-*b*-MH par micro-ondes



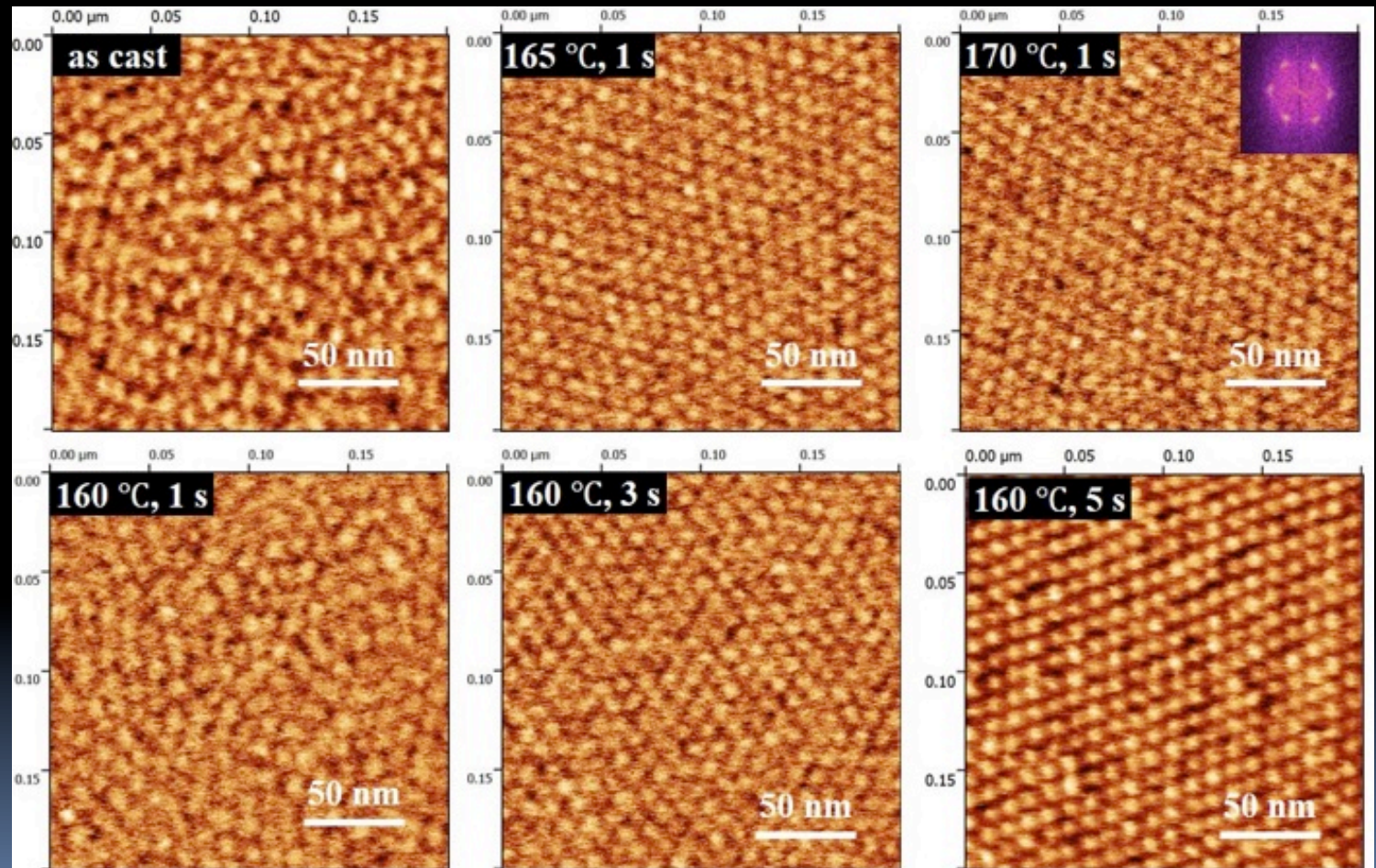
Yingjie LIAO
(Post-Doc 2016)



Auto-assemblage Ultra-rapide du PS-*b*-MH par micro-ondes

De l'heure
à la
Seconde !

CYLINDRES
PERPENDICULAIRES
de Carbohydrates



Y. Liao & R. Borsali (Submitted)

Application 3: Mémoires à Transistors

Films Minces à base de Copolymères Biosourcés: Mémoires à Transistors

Collaboration (cadre ANR Internationale France-Taiwan 2016-2018)

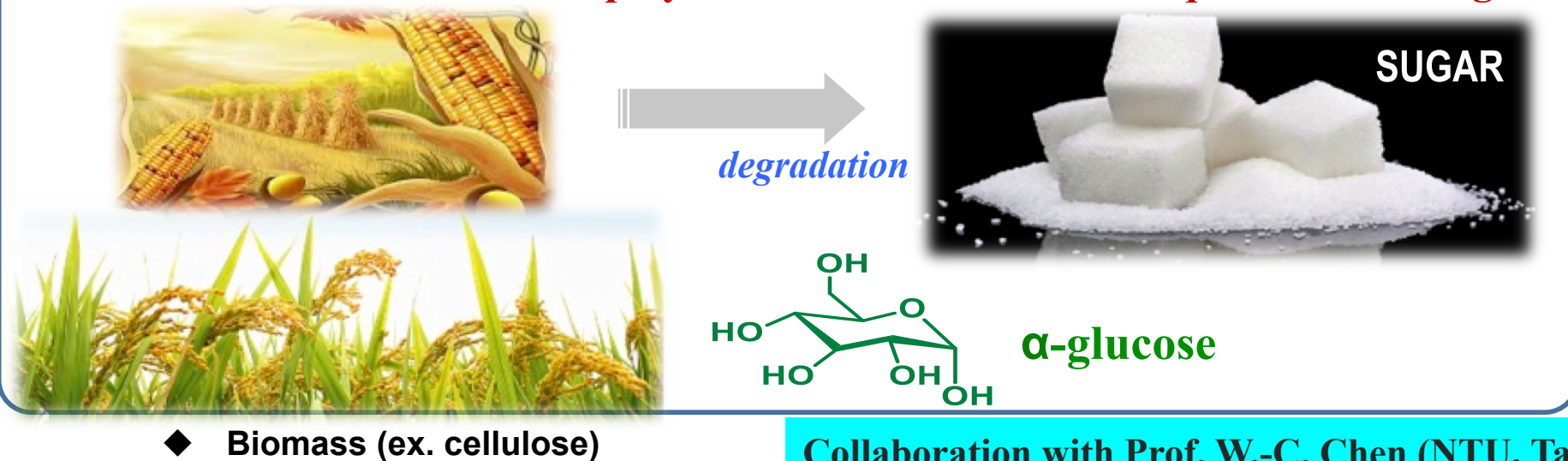
Prof Wen-Chang CHEN
National Taiwan University,
Taipei, Taiwan



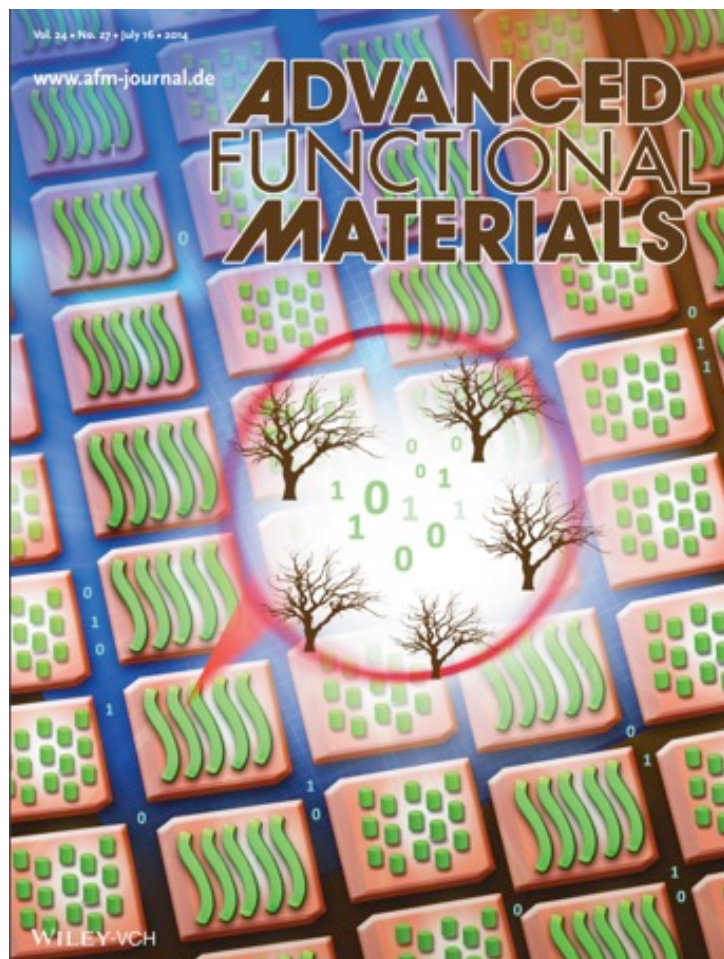
Aujourd'hui les dispositifs électroniques organiques contiennent en général une couche active de matériaux polymères à base de Pétrole



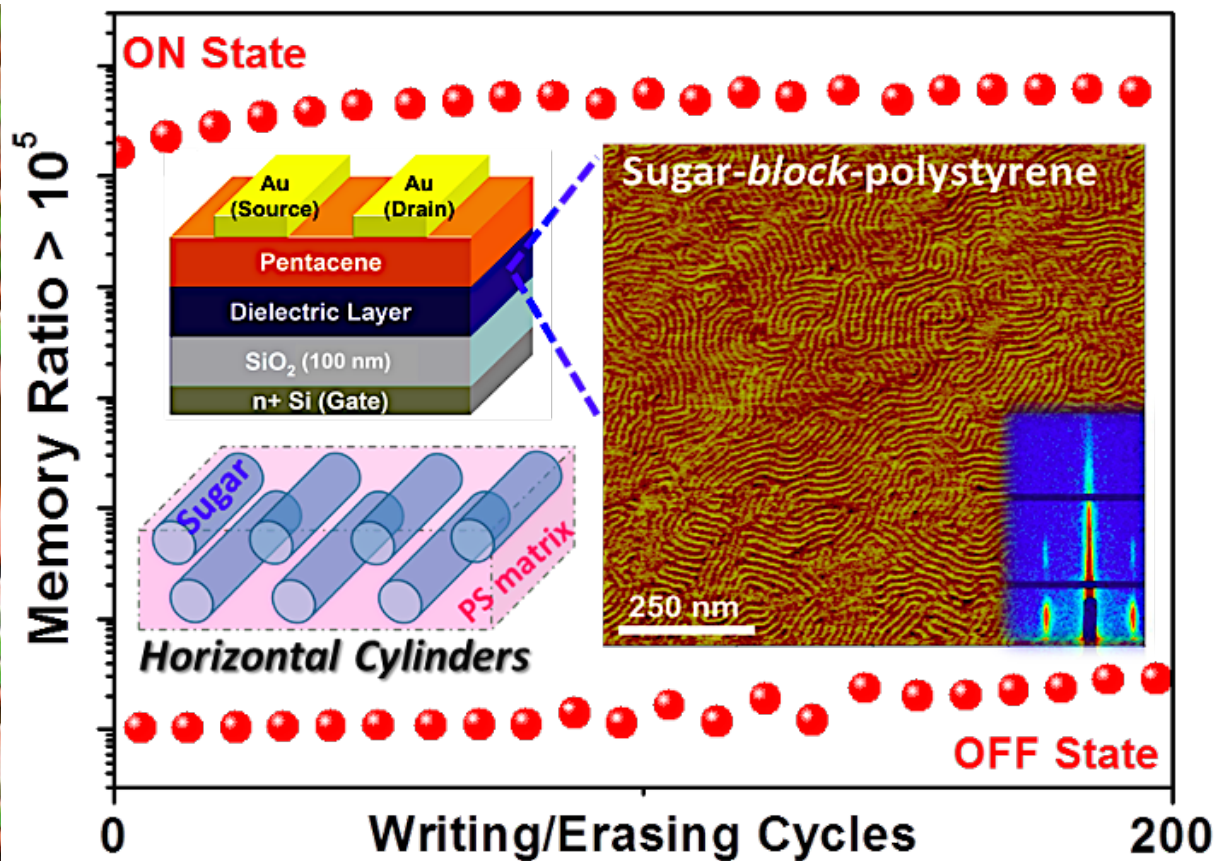
A la recherche de matériaux polymère Biosourcés: électronique de nouvelle génération



Collaboration with Prof. W.-C. Chen (NTU, Taiwan)



Featured on issue back cover

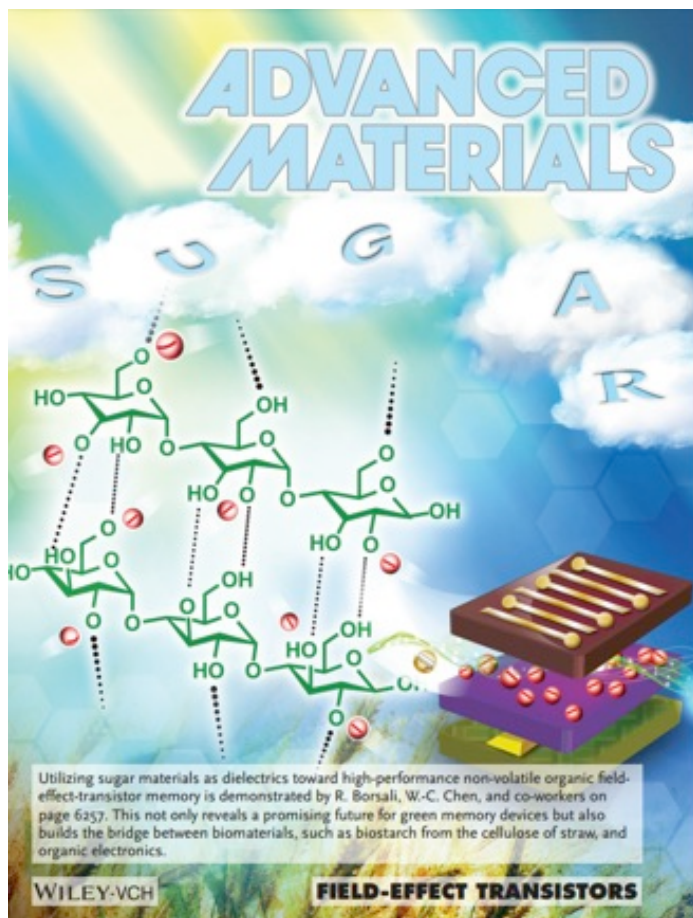


Y.-C. Chiu; I. Otsuka; S. Halila; R. Borsali; W.-C. Chen

“High-Performance Nonvolatile Transistor Memories of Pentacene Using the Green Electrets of Sugar-based Block Copolymers and Their Supramolecules”

Adv. Funct. Mater. -2014, Article first published online: 1 APR 2014, DOI: 10.1002/adfm.201304297

Advanced Materials 2016

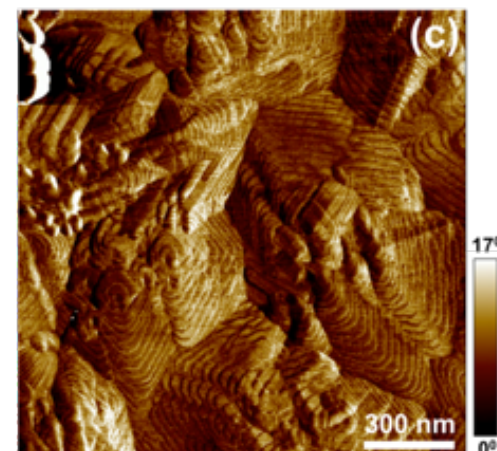
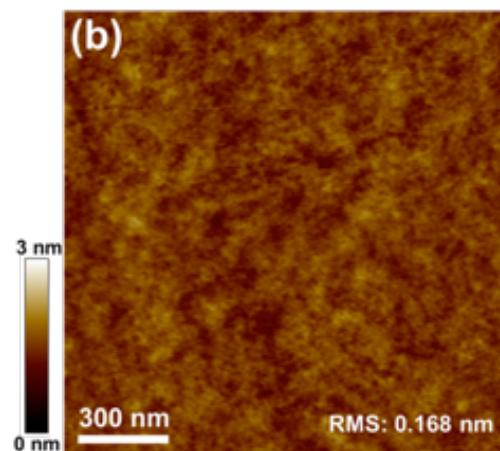
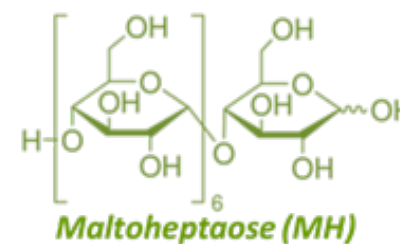
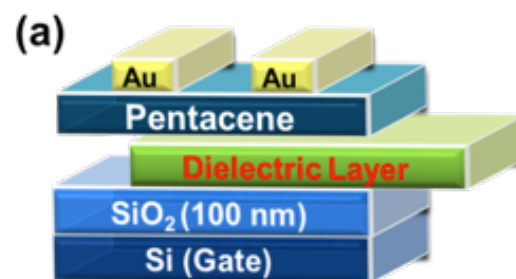


Featured on issue front Cover

Oligosaccharide Carbohydrate Dielectrics toward High Performance Non-Volatile Transistor Memory Devices

Yu-cheng Chiu, Han-sheng Sun, Wen-ya Lee, Sami Halila, Redouane Borsali,* And Wen-chang Chen*

Carbohydrates



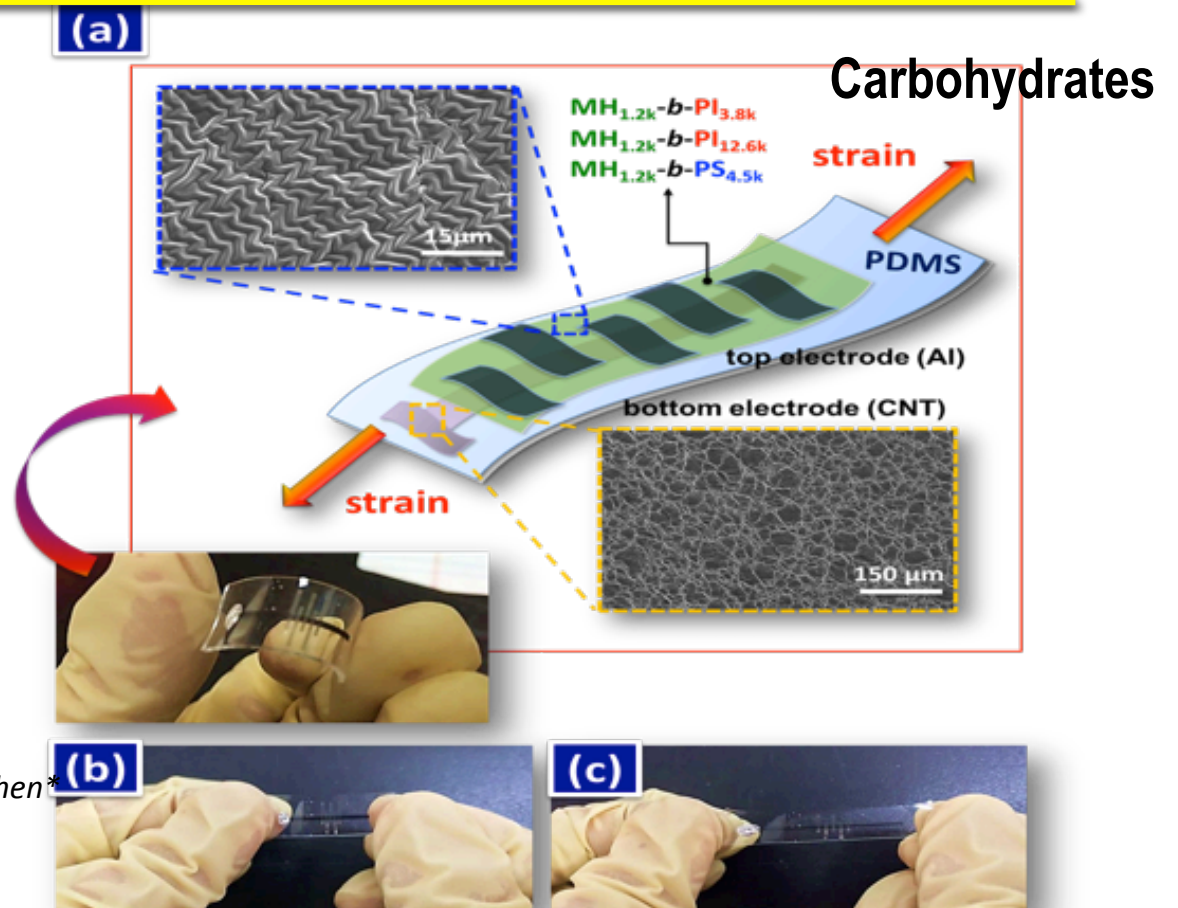
Dispositif de Transistors à mémoire étirable : Copolymère Biosourcé (MH-b-PI) utilisé comme couche active

Conception of Stretchable Resistive Memory Devices
based on Nanostructure-Controlled
Carbohydrate-*block*-Polyisoprene Block Copolymers



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Merci de votre attention

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