

Nanotecnologia: construindo desde a escala nanométrica

- Síntese química
 - Fazendo moléculas e macromoléculas
- Auto-organização
 - Também um problema de Biologia, Filosofia, Sociologia
- Nanomanipulação
 - A manipulação individual de átomos

Auto-organização

(auto-ordenamento, auto-montagem,
self-arraying, self-organization)

- Formação de estruturas usando ligações não-covalentes
 - Coordenativa
 - Pontes de hidrogênio
 - Eletrostática
 - van der Waals
 - “Ligação hidrofóbica”
- É a base da *química supramolecular*
 - *Jean-Marie Lehn, Prêmio Nobel (1988)*

Produtos de auto-organização

- Organização de moléculas, átomos e íons em cristais
 - Vidros, géis, elastômeros
- Micelas, emulsões (sabão, leite)
- Macro-cristais
 - Opala, cristais fotônicos
- Fibras super-resistentes
 - Celulose, Kevlar, seda de aranhas

Micelização

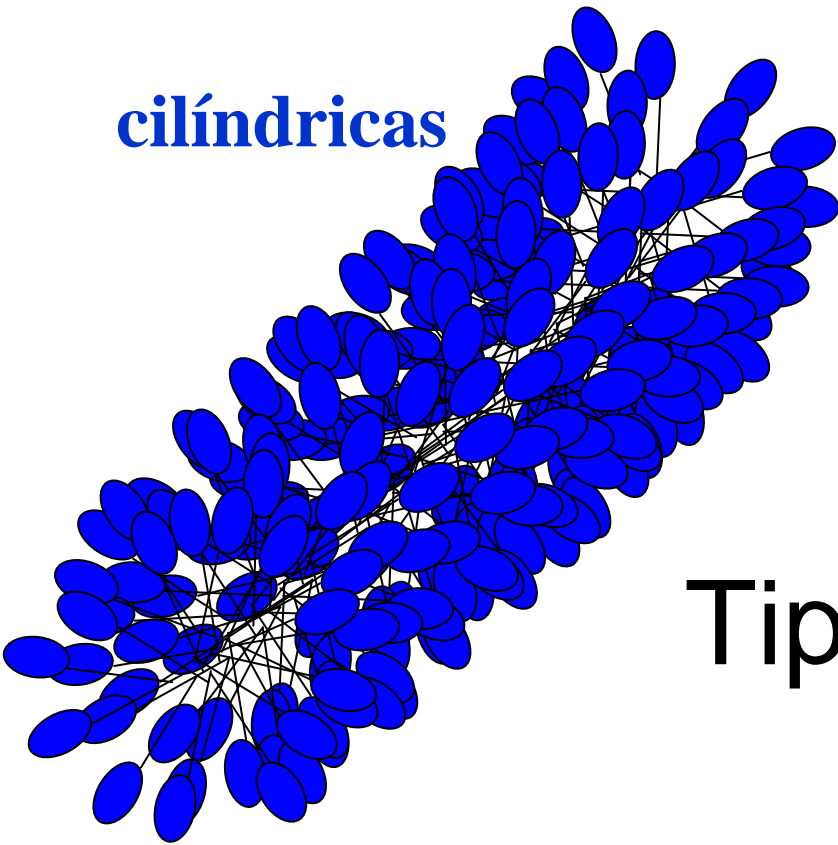
- Compostos anfifílicos
 - dois grupos, com características de *polaridade* ou de *solubilidade* opostas
- É muito importante o **tamanho** dos dois grupos
 - compostos de baixa e de alta massa molar.

Micelização

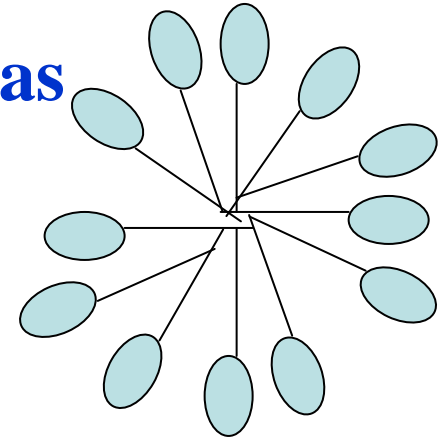
- Compostos anfifílicos
 - Surfactantes
 - Copolímeros-bloco
- Separação de fases em micro-escala
 - Nucleação e crescimento: dispersões
 - Binodal
 - Fases bicontínuas
 - Espinoidal



cilíndricas

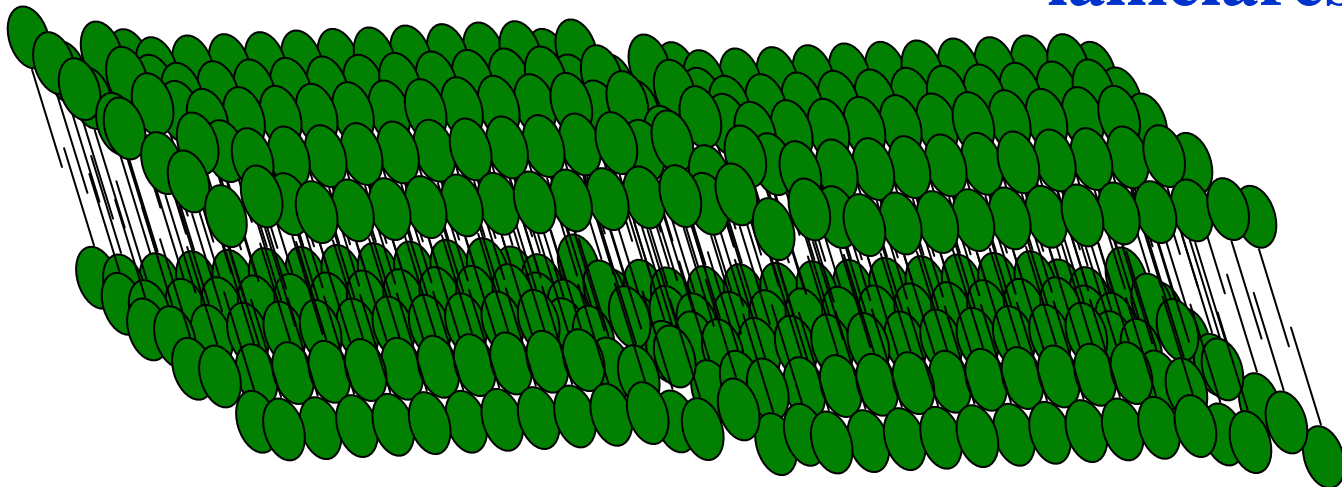


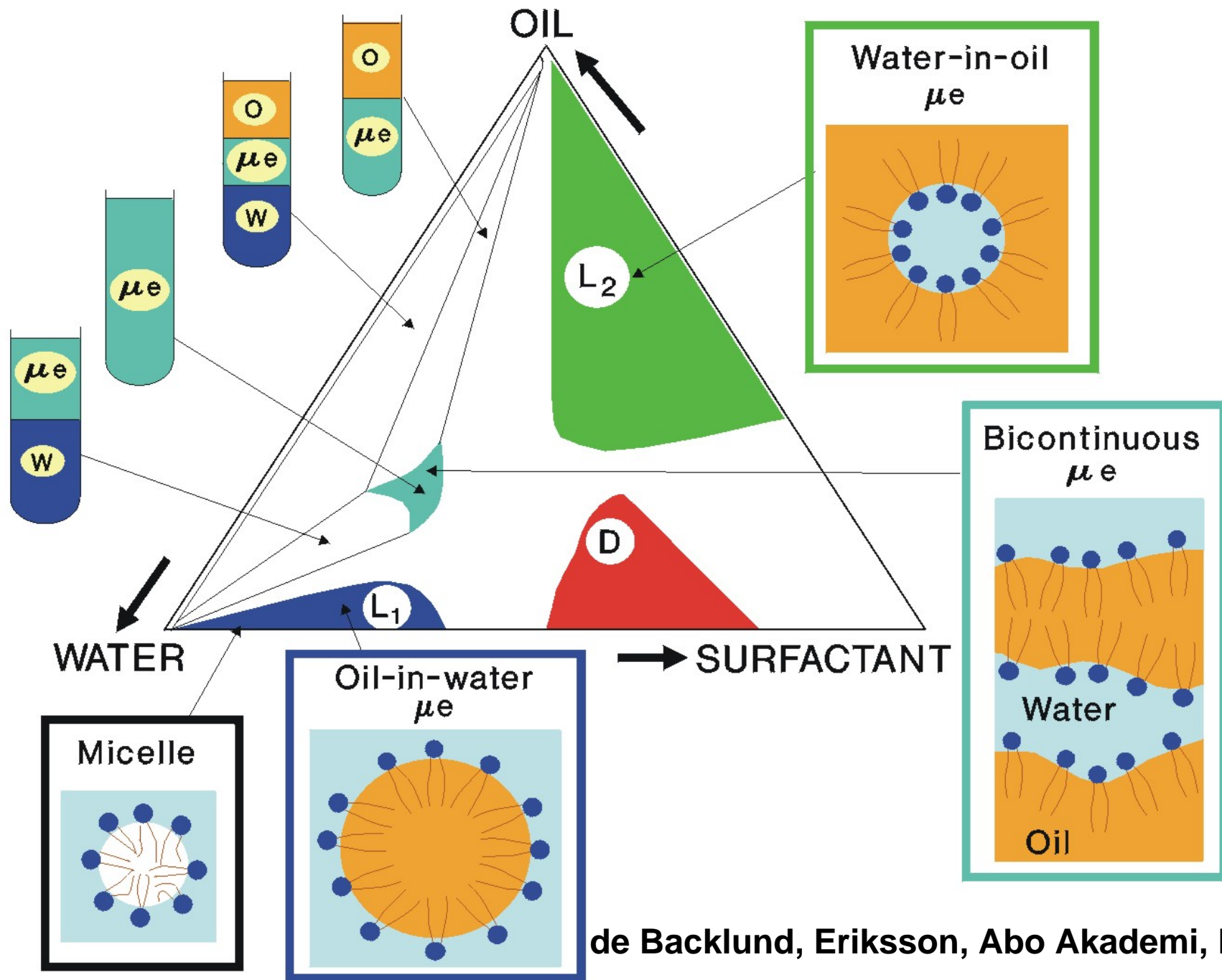
esféricas



Tipos de micelas em água

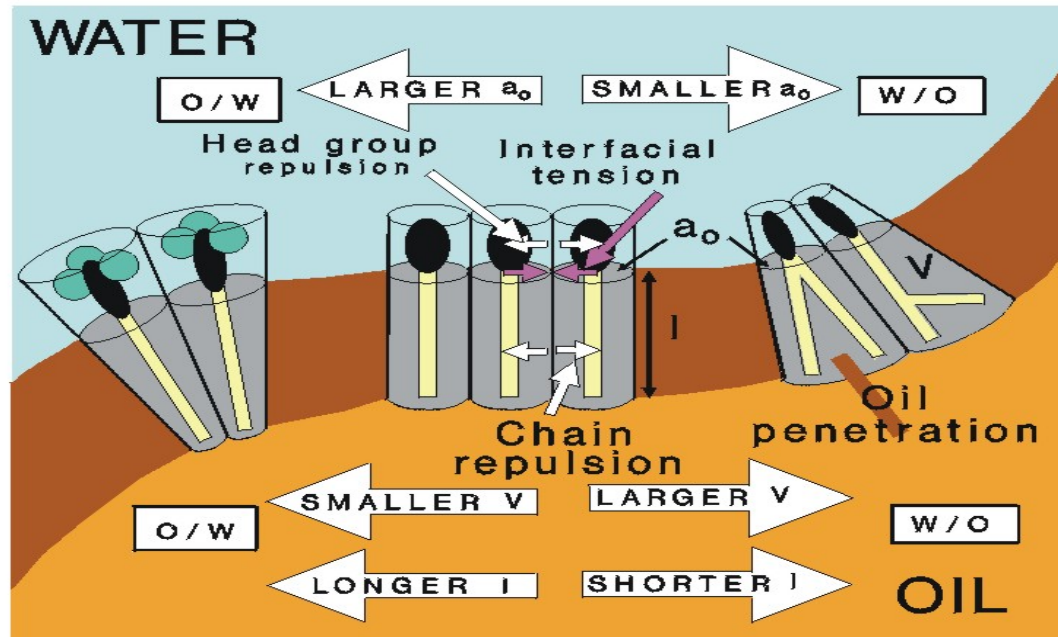
lamelares





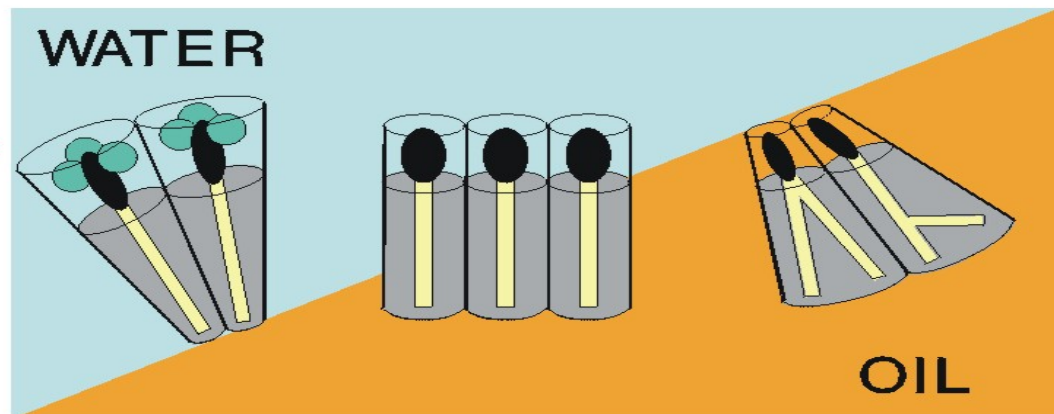
$P =$
 packing
 parameter

$$= \frac{V}{a_o l}$$



P	1/3	1/2	1	2	3
HLB	40	20	10	2	1

HLB =
 hydrophile -
 lipophile
 balance

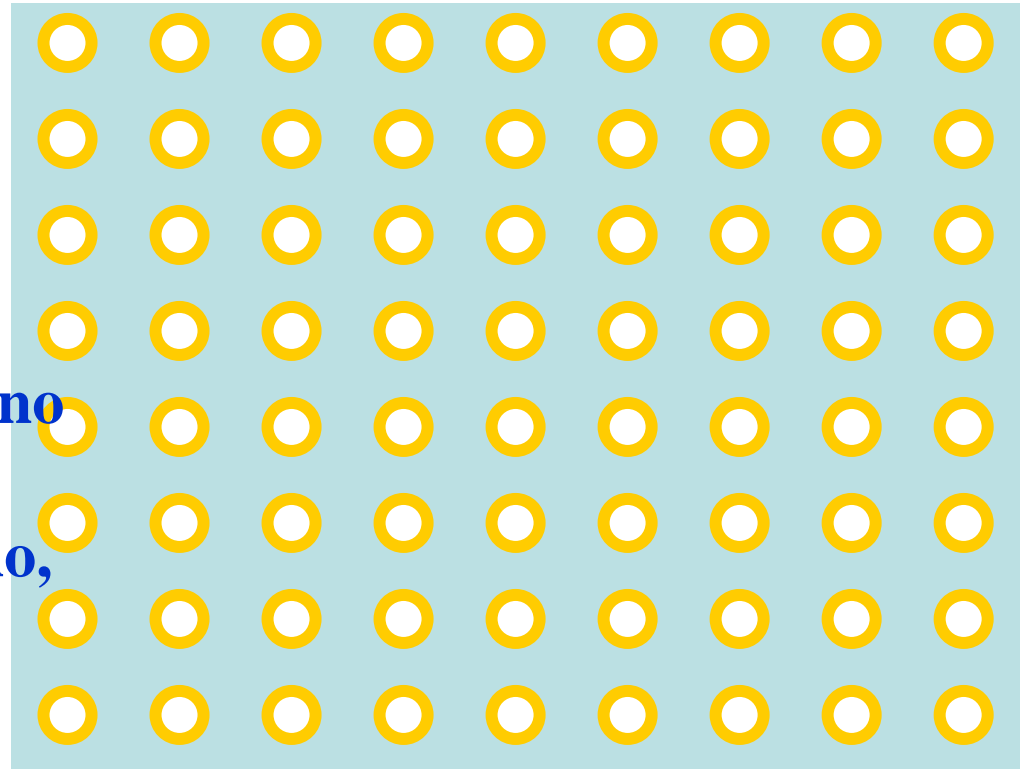


copolímero PPQ-PS

poli(fenilquinolina)-b-poliestireno

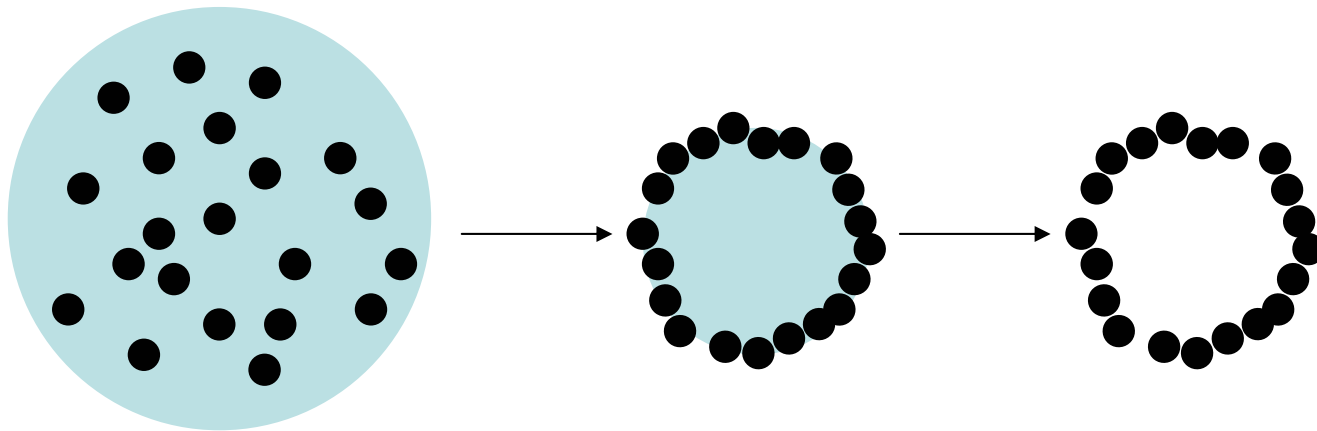
**S.A.Jenekhe e X.L.Chen, Science 283(1999)372:
exemplo de material fabricado por auto-
ordenamento**

**A secagem de uma
solução em sulfeto de carbono
produz um filme em que
a fase contínua é poliestireno,
com furos regulares de
2 microns de diâmetro.**



Formação de partículas ocas

- Secagem em spray
- Cinzas de casca de arroz e “*fly-ash*”



Formação de nanoestruturas por síntese

JOC *Article*

Synthesis of Anthropomorphic Molecules: The NanoPutians

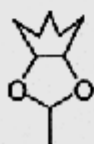
Stephanie H. Chanteau and James M. Tour*

*Department of Chemistry and Center for Nanoscale Science and Technology, MS 222, Rice University,
Houston, Texas 77005*

tour@rice.edu

Received June 27, 2003

Described here are the synthetic details en route to an array of 2-nm-tall anthropomorphic molecules in monomeric, dimeric, and polymeric form. These anthropomorphic figures are called, as a class, NanoPutians. Using tools of chemical synthesis, the ultimate in designed miniaturization can be attained while preparing the most widely recognized structures: those that resemble humans.



NanoMonarch (18)



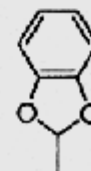
NanoTexan (19)



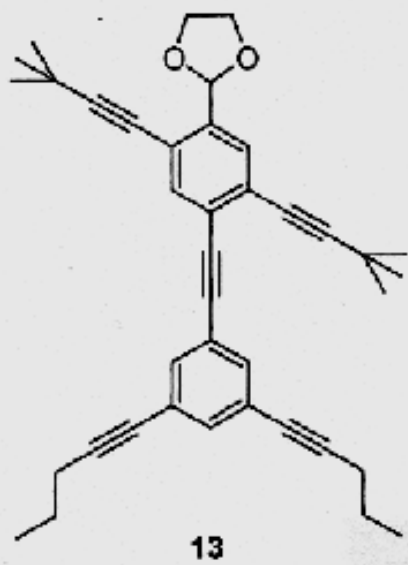
NanoScholar (20)



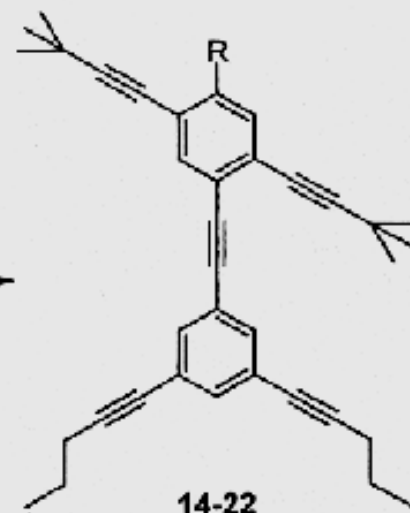
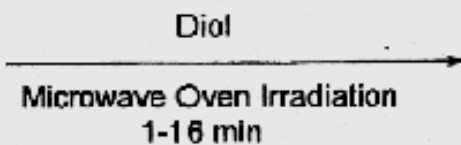
NanoBaker (21)



NanoChef (22)

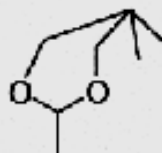


13
NanoKid

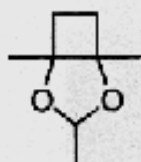


14-22

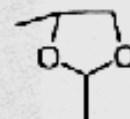
R = acetal head and neck



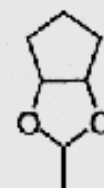
NanoAthlete (14)



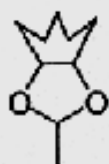
NanoPilgrim (15)



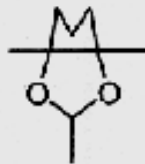
NanoGreenBeret (16)



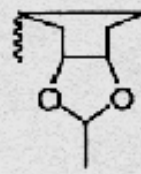
NanoJester (17)



NanoMonarch (18)



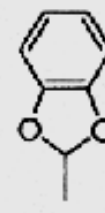
NanoTexan (19)



NanoScholar (20)

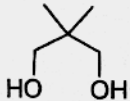
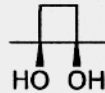
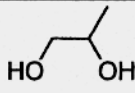
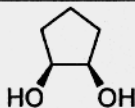
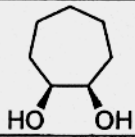
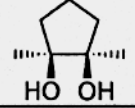
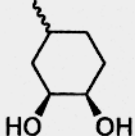
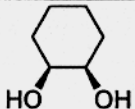
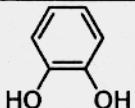


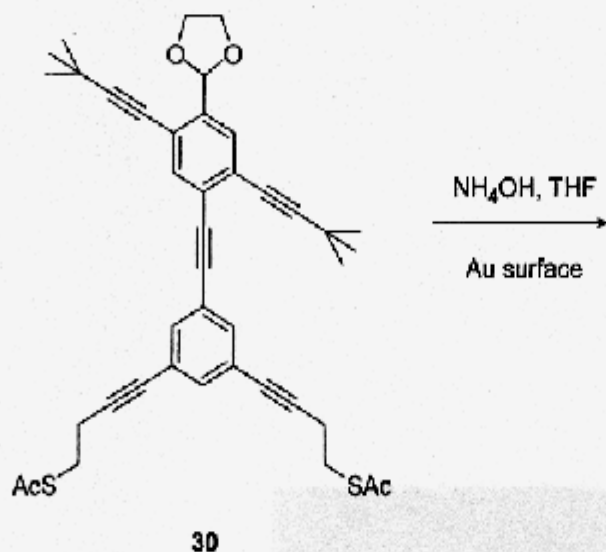
NanoBaker (21)



NanoChef (22)

TABLE 1. Conversion of NanoKid (13) into the NanoProfessionals 14–22 Using Microwave Irradiation in the Presence of Selected Diols

Entry	Diol ^a	Equiv. of Diol	Irradiation (min)	NanoPutian	Yield (%)	Diastereomeric ratio ^b
1		20	7	14	91	---
2		11	13	15	25 ^d	55 : 45
3		100	1	16	85	1 : 1
4		20	7	17	94	10 : 3
5		5	10	18	87	10 : 3
6		9	9	19	24 ^d	3.2 : 1
7		20	16	20	90	17 : 12 : 12 : 9
8		15	10	21	84	1.6 : 1
9 ^c		22	---	22	9 ^d	---



Auto-
organizando
nanoestruturas:
monocamadas
de tióis em ouro
(Whitesides)

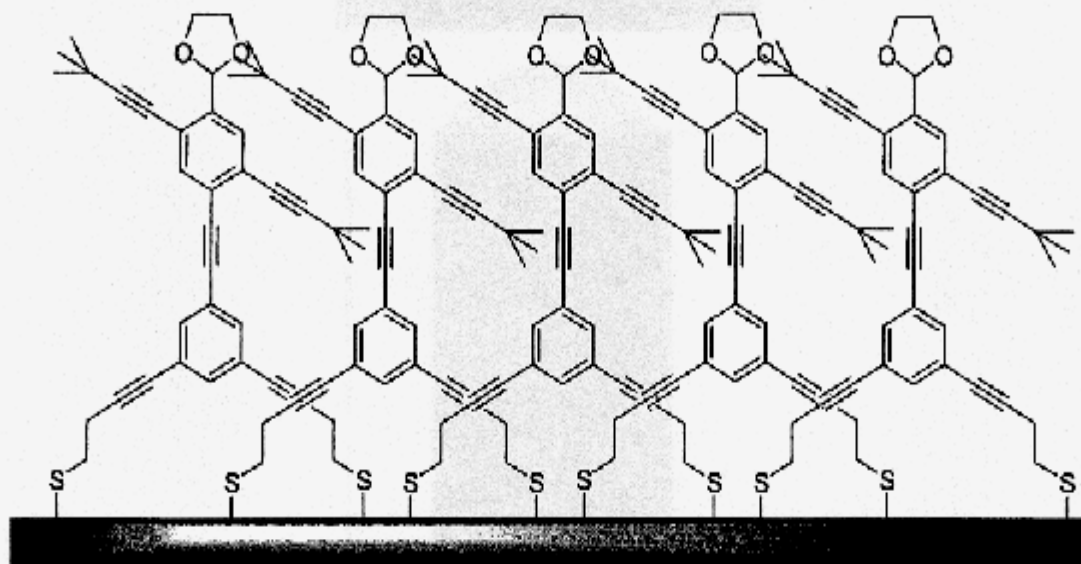


FIGURE 3. Self-assembly of **30** on a gold surface. Surface packing is greater than represented here since monolayer coverage was achieved.

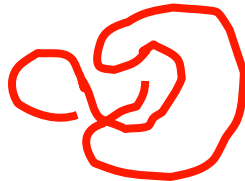
Nanofabricação: fazendo carros, átomo por átomo?

- O número de Avogadro é 6.10^{23} atoms/mol.
- Para montar um grama de átomos por nanomanipulação, é necessário *fazer* 6.10^{21} movimentos.
- Portanto, uma planta com **um bilhão de máquinas montadoras**, cada uma capaz de montar **um milhão de átomos por segundo...**
- ...consome **6 milhões de segundos** (ou 2.3 meses) para montar apenas um grama de átomos.

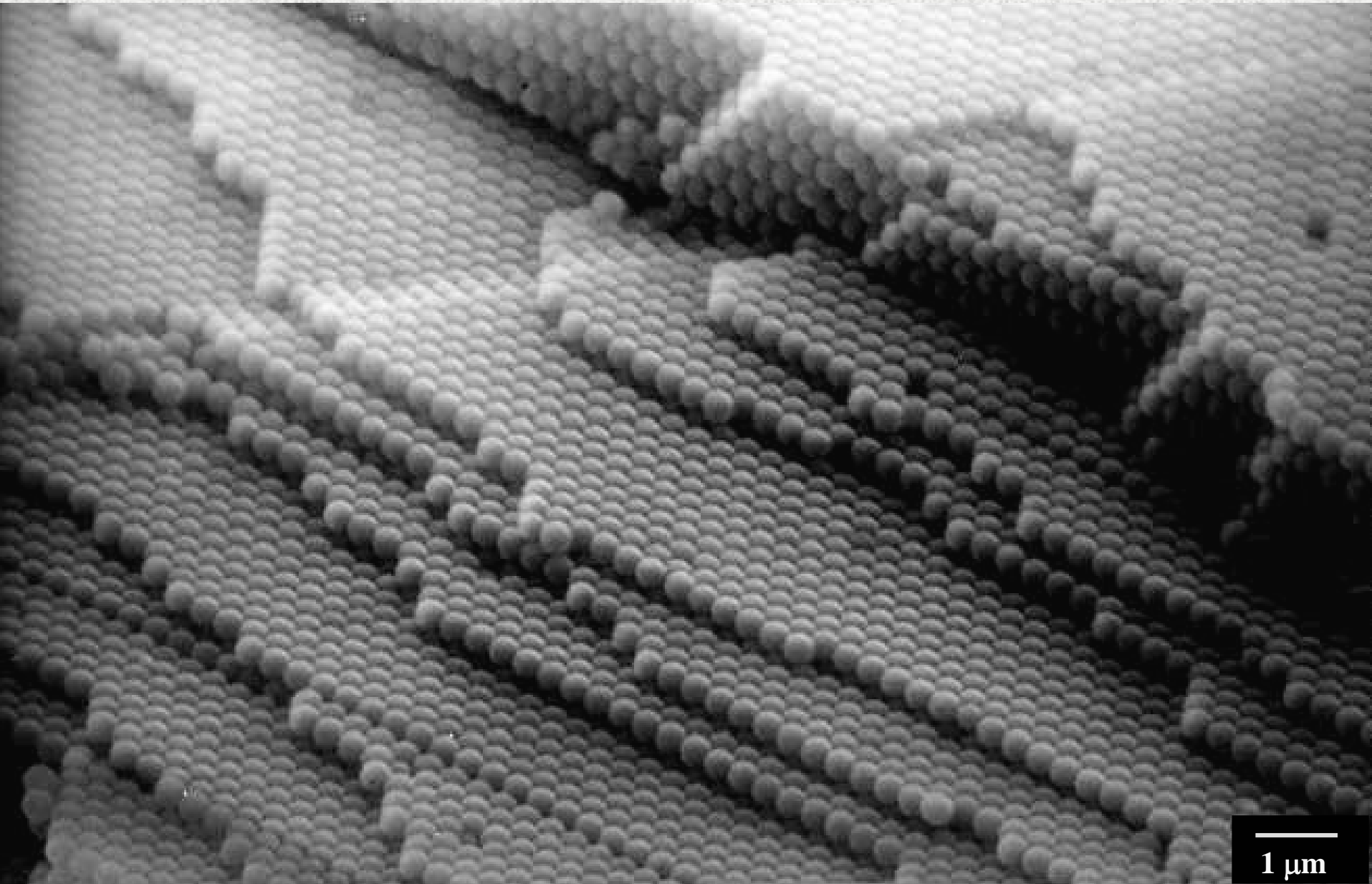
Estruturas nanométricas em polímeros

- Unidades monoméricas ($-\text{CH}_2-\text{CH}_2-$)
 - Propriedades funcionais
- Cadeias
 - Entrelaçamento
 - Barreira à rotação, flexibilidade e T_g
 - Coesão
 - Plasticidade, rigidez
 - Tenacidade
- Estruturas supramoleculares
 - Cristais
 - Líquidos cristalinos
 - Redes
- Superfície
 - Adesão, limpeza, atrito, dureza

...são conhecidas e exploradas há muito tempo.



Auto-organização de partículas de poliestireno,



1 μm

Novos tipos de nanodomínios em polímeros

Muitos tipos

- Argilas e nanotubos em nanocompósitos
 - Nanopartículas
 - Nanodomínios elétricos

Novas propriedades

Novas funções

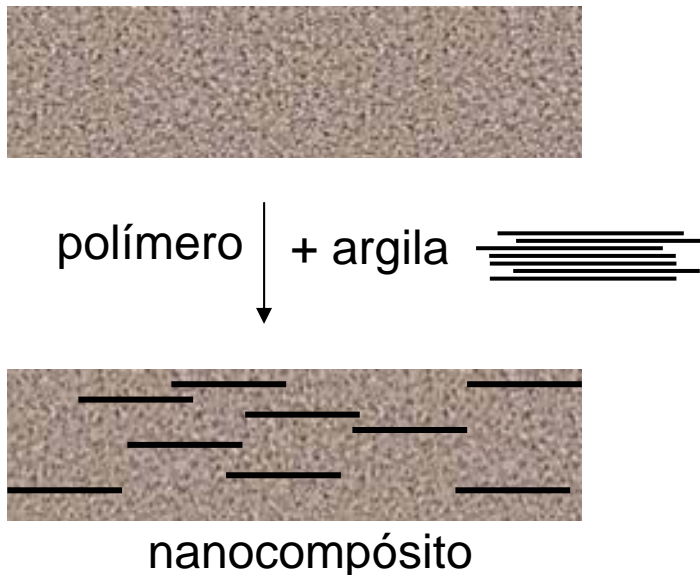
Novas estruturas

Estrutura nanométrica⇒ propriedades macroscópicas

- As propriedades macroscópicas permitem aos materiais exercerem funções úteis
- Dão valor econômico, social e estratégico a substâncias químicas e materiais.
- Como gerar:
 - Resistência à tração, elasticidade, emissão de luz, condução elétrica, magnetismo...?

Design de um produto nanotecnológico: nanocompósito

- Gerar novos materiais poliméricos aproveitando Nanotecnologia



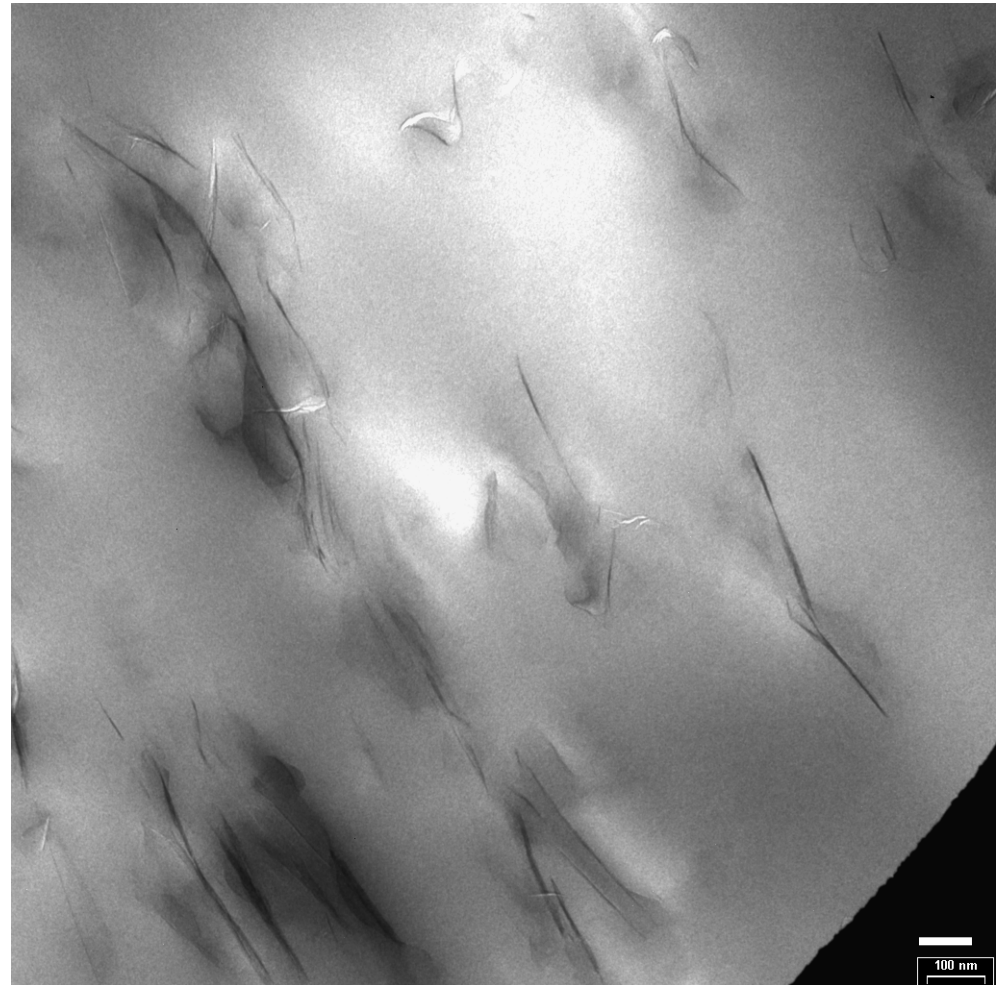
- Separar lâminas de silicato, dispersar e orientar as lâminas em matriz de polímero.
- A permeabilidade do polímero a gases pode ser reduzida a 10% ou menos.
- A resistência do polímero à flexão diminui: aumento da temperatura de trabalho.
- Coeficiente de armazenamento elástico aumenta.

Como se faz

- A argila tratada com um sal de **amônio quaternário**
- Resulta argila **organofílica**
- Argila organofílica é misturada ao polímero em extrusora
- Nos casos de sucesso, a argila se dispersa no polímero na forma de **lamelas com espessura nanométrica**
- Perguntas: interações entre argilas, alinhamento?

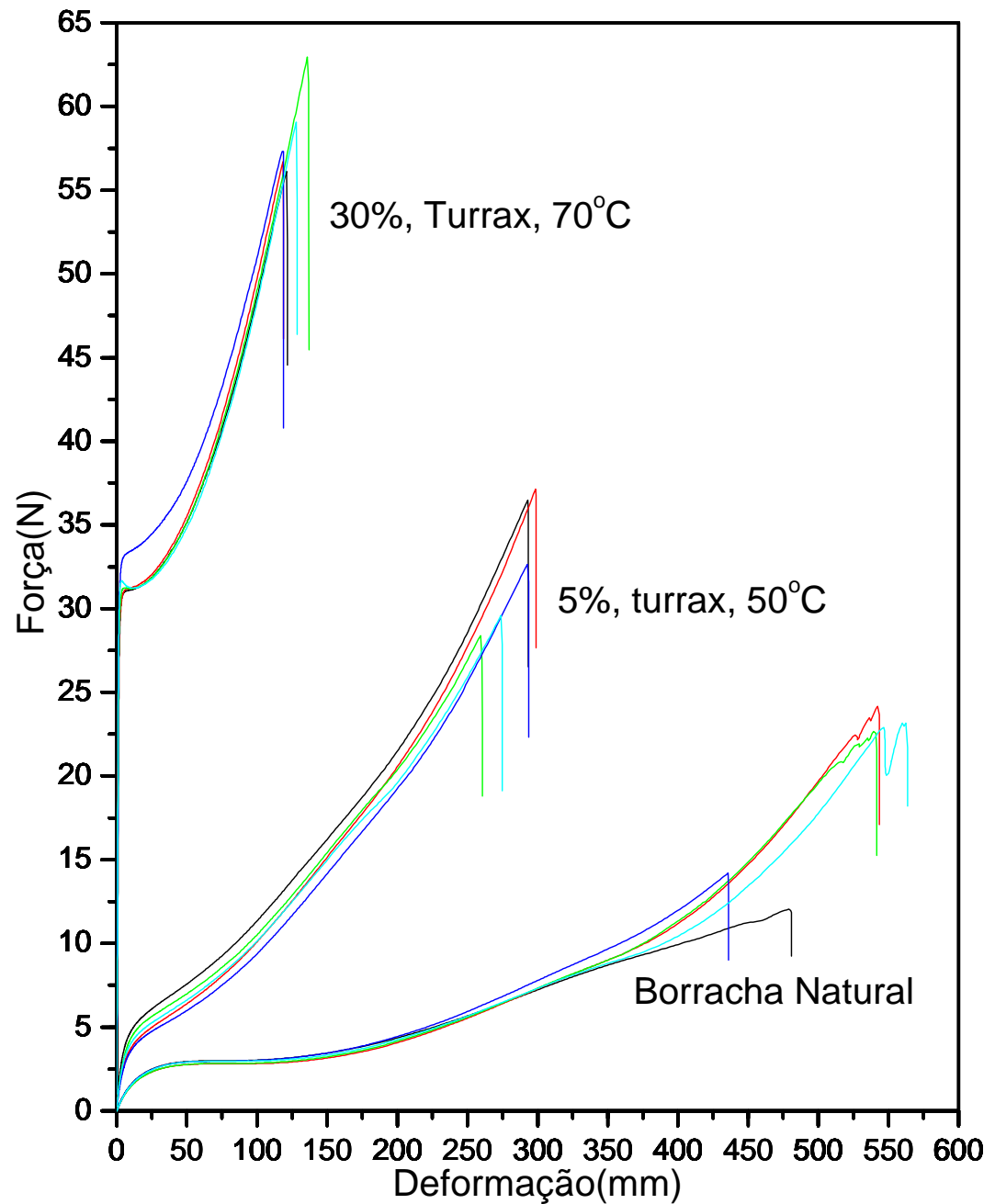
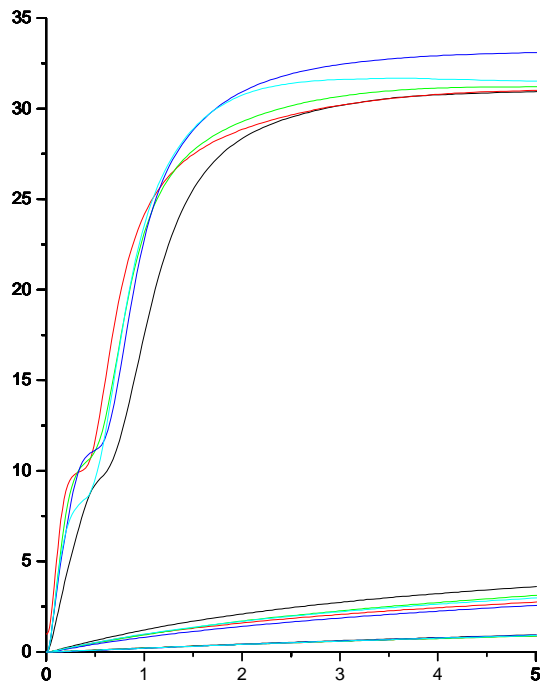
Nanocompósitos de látex

- Água é o melhor esfoliante conhecido, de argila
- Água é o dispersante de látexes
- Látex + argila em água
- Depois de seco: nanocompósito

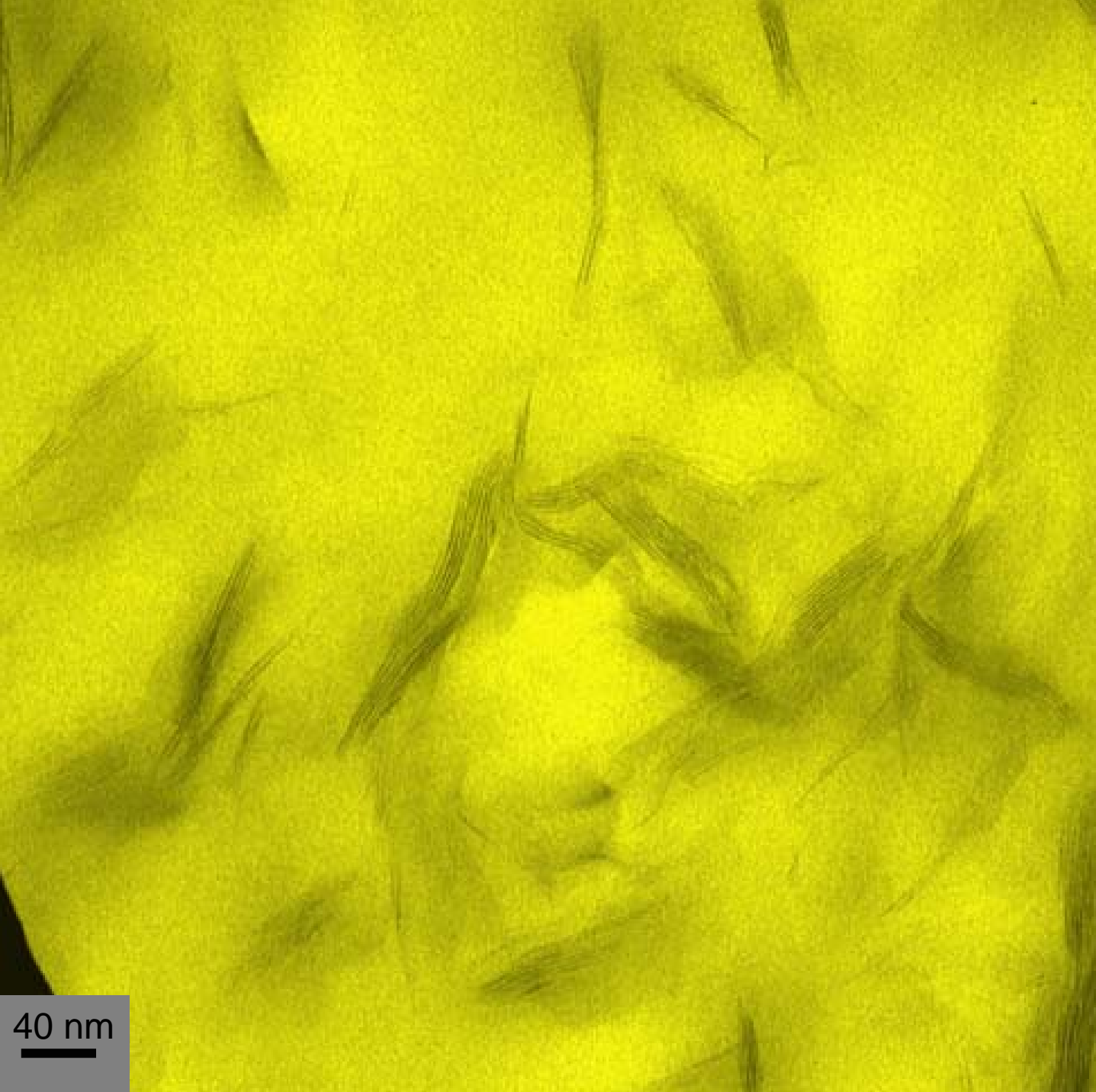


100 nm

Propriedades mecânicas inéditas



**Nanocompósito
polímero-argila**

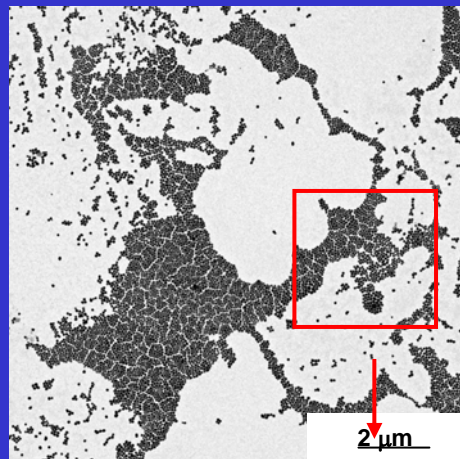


40 nm

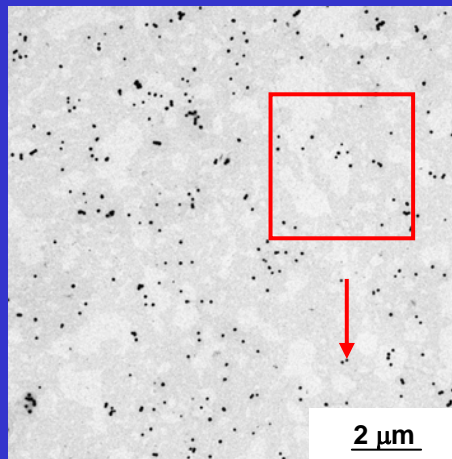
TEM images of silica particles

Effect of different surfactants

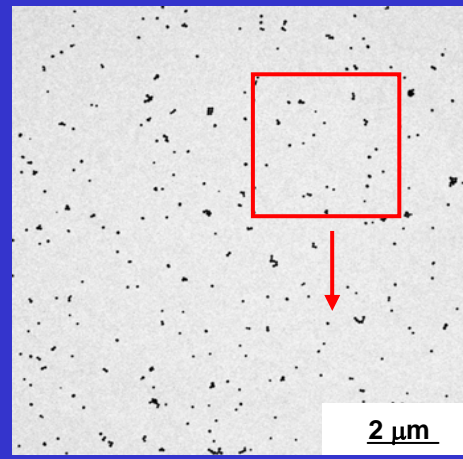
No surfactant



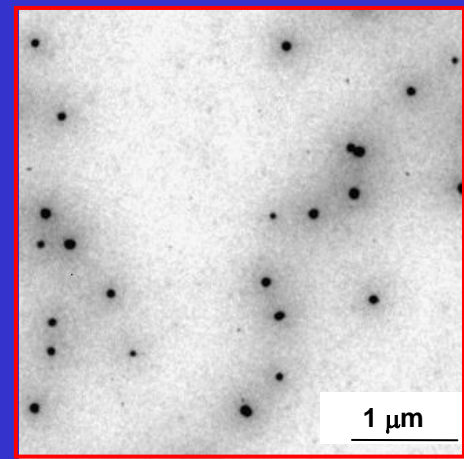
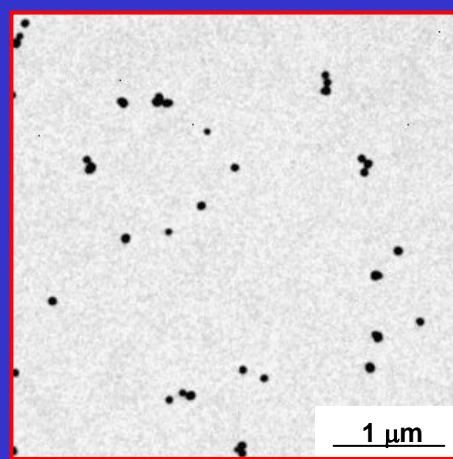
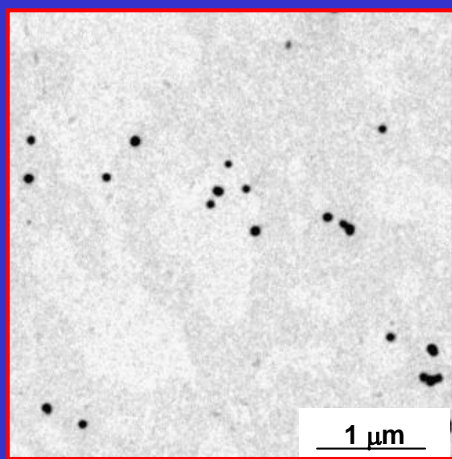
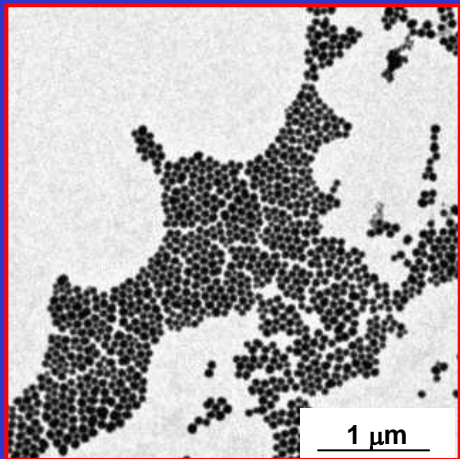
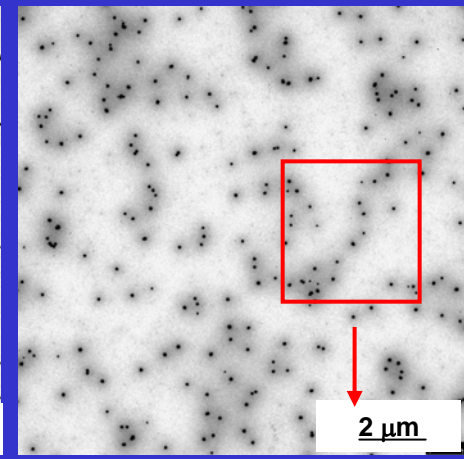
SDS $10^{-1}\ \text{M}$



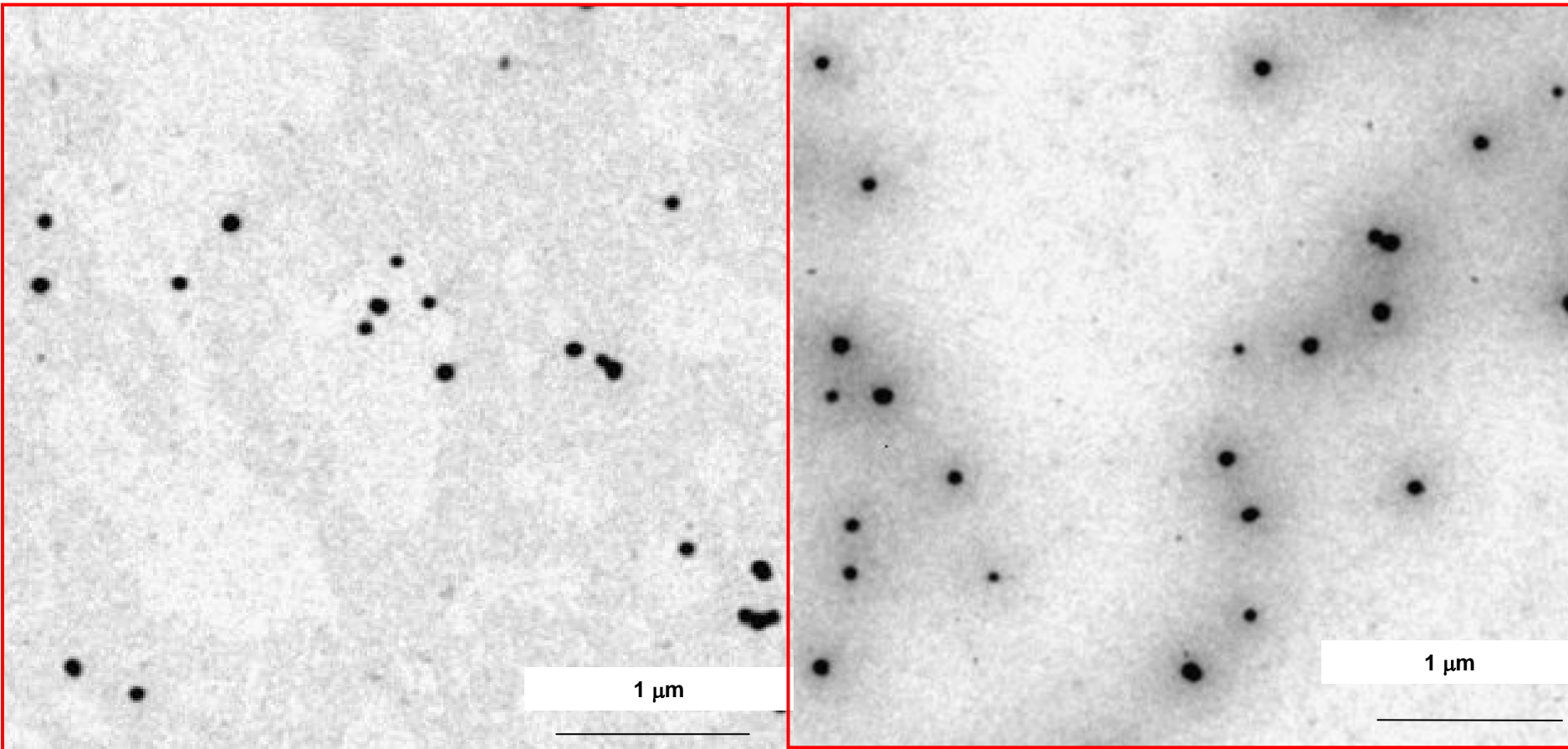
CTAB $10^{-1}\ \text{M}$



RENEX $10^{-1}\ \text{M}$



Padrões de secagem de dispersões

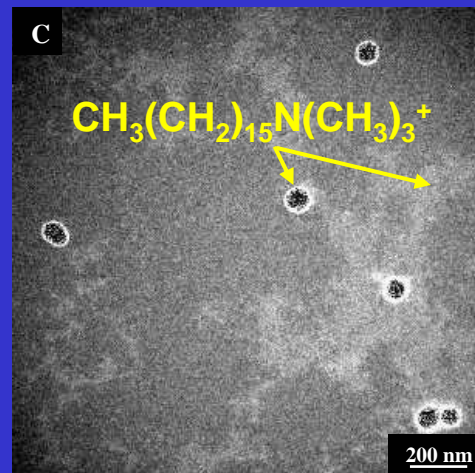
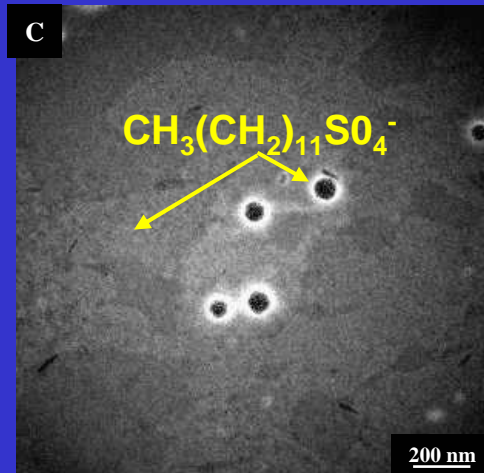
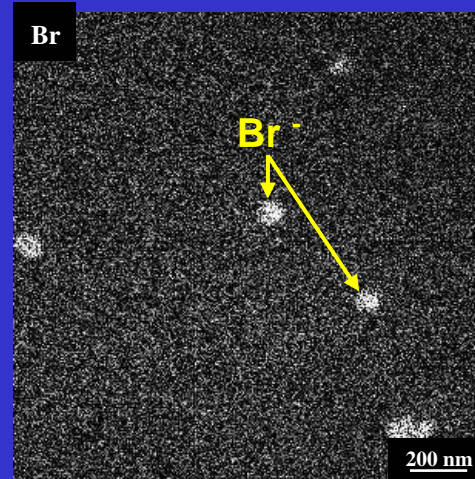
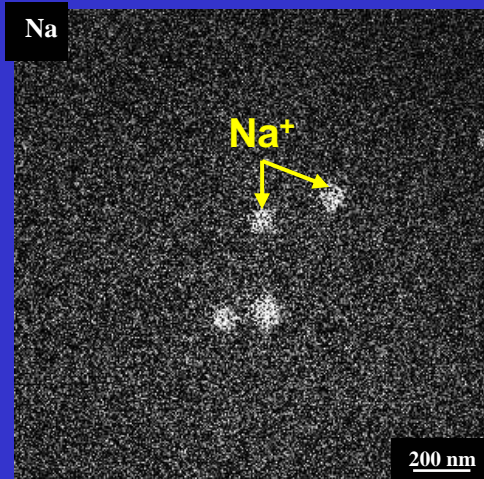


Counter-ion adsorption

Elemental maps of sodium, bromide and carbon

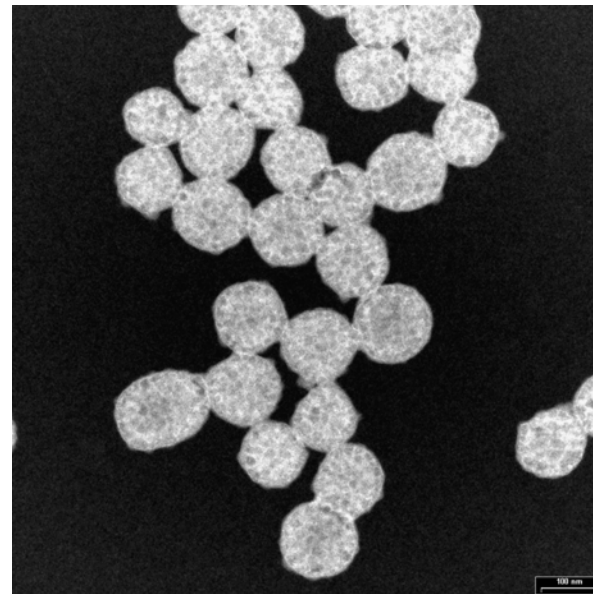
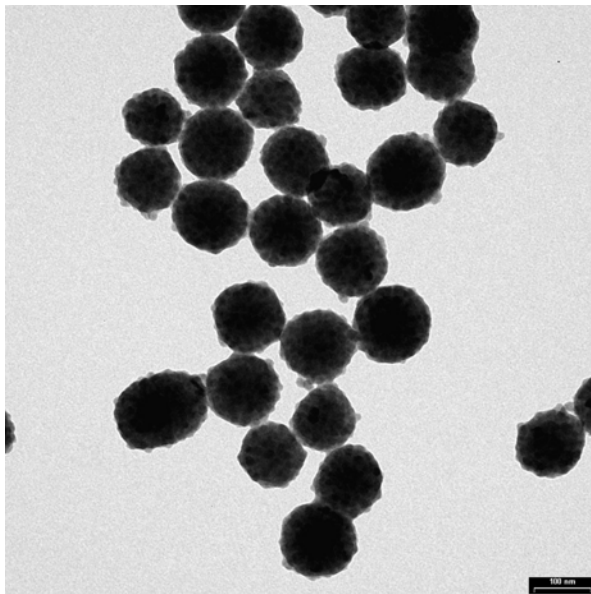
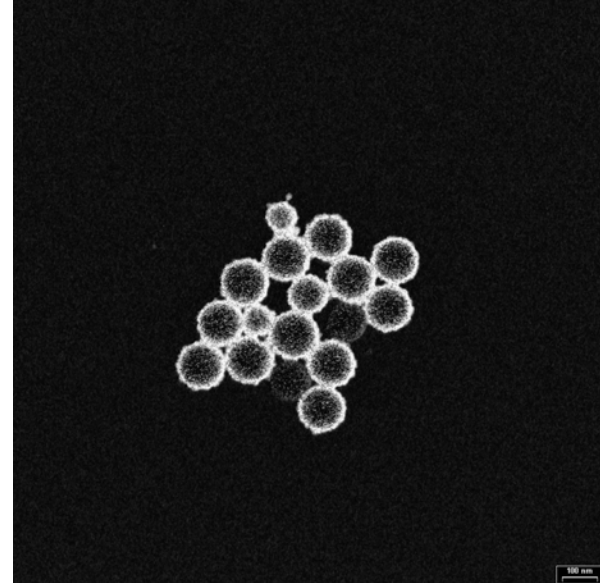
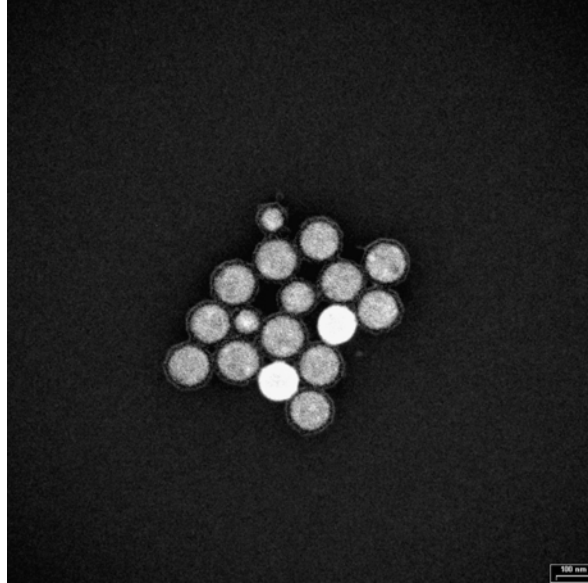
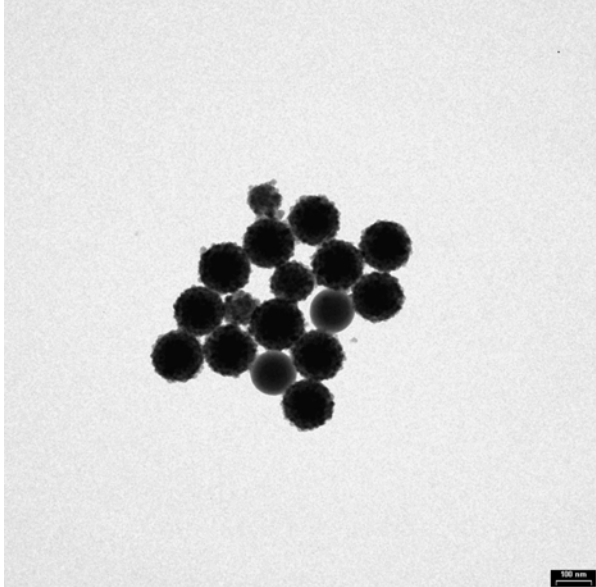
SDS 10^{-1} M

CTBA 10^{-1} M



■ The counter-ions are detected within the particles.

■ Counter-ion distribution over the background does not match surfactant.



Nanopartículas de sílica em látex: a posição da sílica depende da hidrofilicidade do polímero: poliestireno e poli(4-vinil piridina)

437 patentes no USPTO <nanocomposite and polymer>: 50 entre 30/3 e 17/8/2004

- [6,777,480 Networked polymer/clay alloy](#)
- [6,777,479 Polyamide nanocomposites with oxygen scavenging capability](#)
- [6,773,823 Sequential synthesis of core-shell nanoparticles using reverse micelles](#)
- [6,770,697 High melt-strength polyolefin composites and methods for making and using same](#)
- [6,765,049 High acid aqueous nanocomposite dispersions](#)
- [6,764,617 Ferromagnetic conducting lignosulfonic acid-doped polyaniline nanocomposites](#)
- [6,762,237 Nanocomposite dielectrics](#)
- [6,762,233 Liquid crystalline composites containing phyllosilicates](#)
- [6,759,446 Polymer nanocomposite foams](#)
- [6,758,148 Fire blocking method and apparatus](#)
- [6,757,094 Optical shutter assembly](#)
- [6,756,444 Oxygen scavenging polyamide compositions suitable for pet bottle applications](#)
- [6,753,360 System and method of preparing a reinforced polymer by supercritical fluid treatment](#)
- [6,750,282 Flameproof polymer composition](#)

- Sequestro de oxigênio (cerveja)
- Fundido resistente
- Condutor ferromagnético
- Dielétrico
- Espuma sólida
- Anti-chama
- Processamento supercrítico
- Filme fino resistivo
- Meio para registro de imagens, detector de radiação, guias de onda, registro magnético, memória ótica 3D, chaves ópticas, membranas, eletrodos, catalisadores...

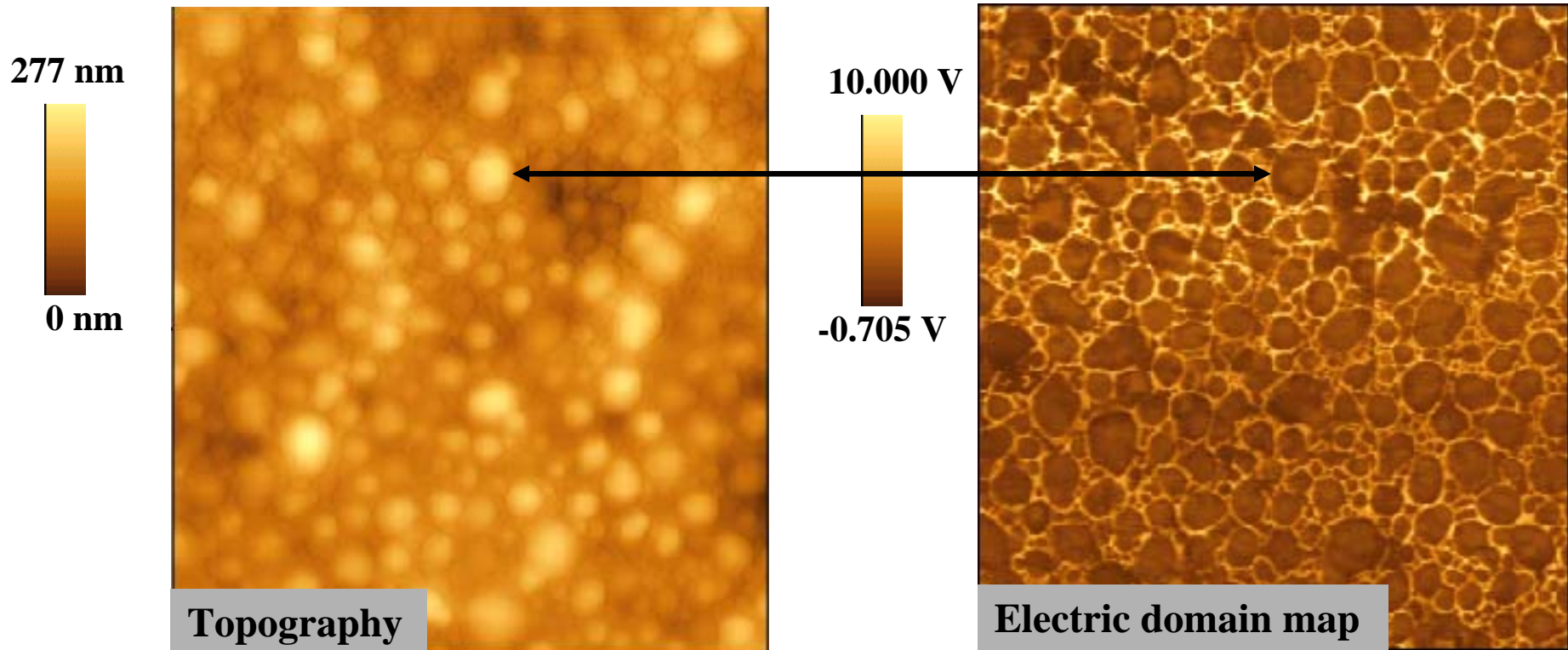
GROWTH

U.S. nanomaterials markets to expand significantly

					ANNUAL GROWTH
\$ MILLIONS	2002	2007	2012	2020	2002-20
Minerals	\$140	\$675	\$2,100	\$11,500	28%
Metals	45	150	500	3,000	26
Polymers & chemicals	5	175	1,400	15,500	56
New materials ^a	10	100	500	5,000	41
TOTAL	\$200	\$1,100	\$4,500	\$35,000	33%

^a Includes carbon nanotubes. **SOURCE:** Freedonia Group

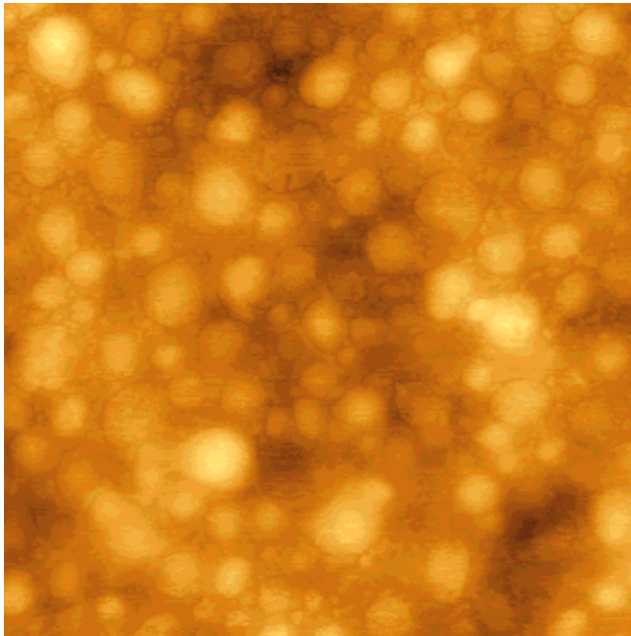
Natural rubber film topography (non-contact AFM) and scanning electric potential (SEPM) images



**Individual particles are observed as elevations.
Negative cores dispersed in a positive matrix.**

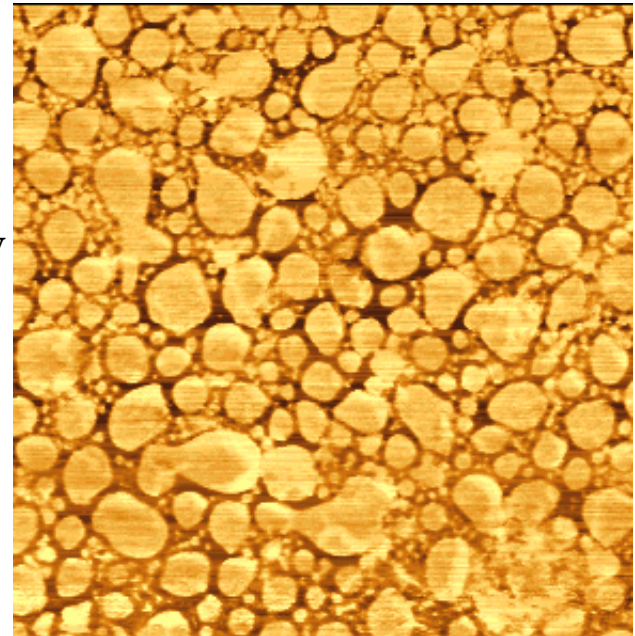
Natural Rubber Latex Film: hard and soft domains

276 nm
0 nm



Topography

0,875 V
-1,221 V

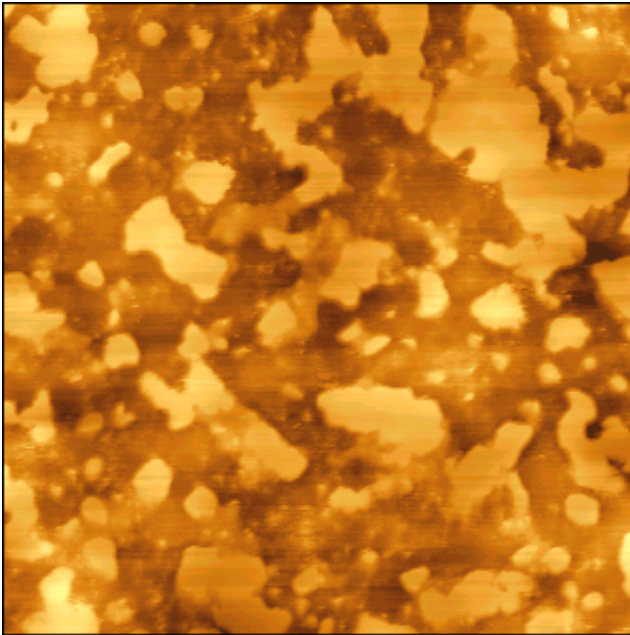


Phase Contrast

Phase contrast images show bright (soft) particles surrounded by stiffer (darker) domains, at the particle interfaces.

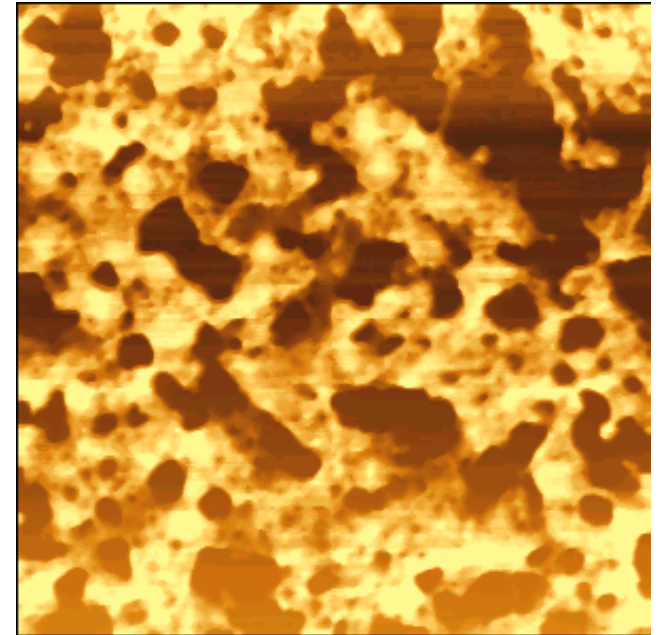
Natural Rubber Latex - Polyphosphate Film: hard and soft domains

321 nm
0 nm



5 μm
Topography

-0.538 V
-1.488 V

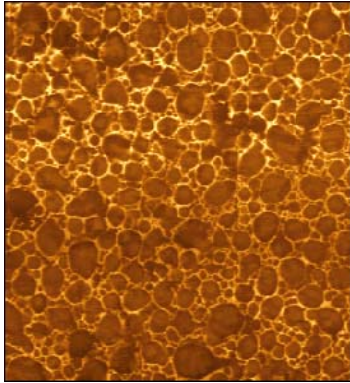


5 μm
Phase Contrast

10.000 V



-0.705 V



**Electric domain map
of the (unstabilised)
dry latex film surface**

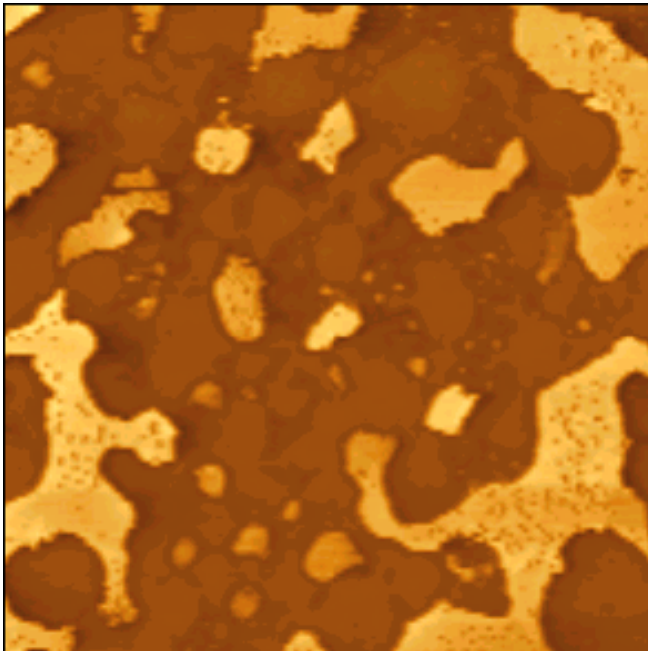
PP/NR film surface

**PP/NR film surface in
contact with the glass**

4.50 V



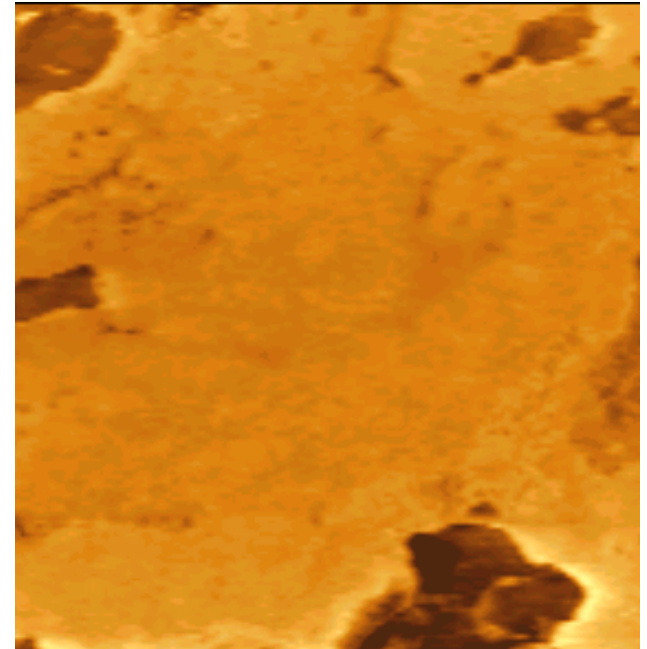
-8.56 V



10.57 V



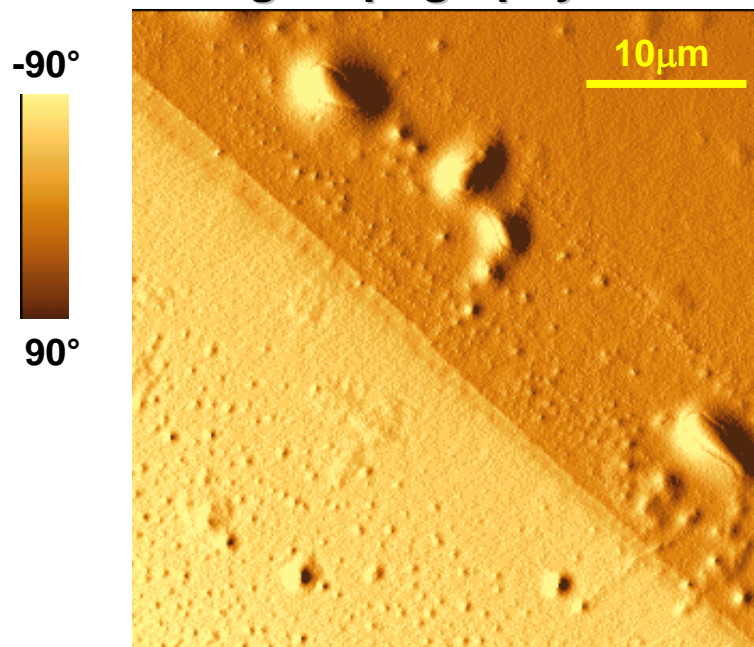
-2.43 V



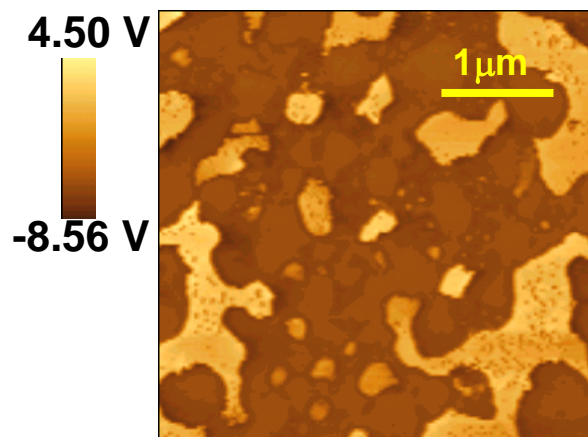
Natural rubber + sodium polyphosphate film

topography and scanning electric potential (SEPM) images

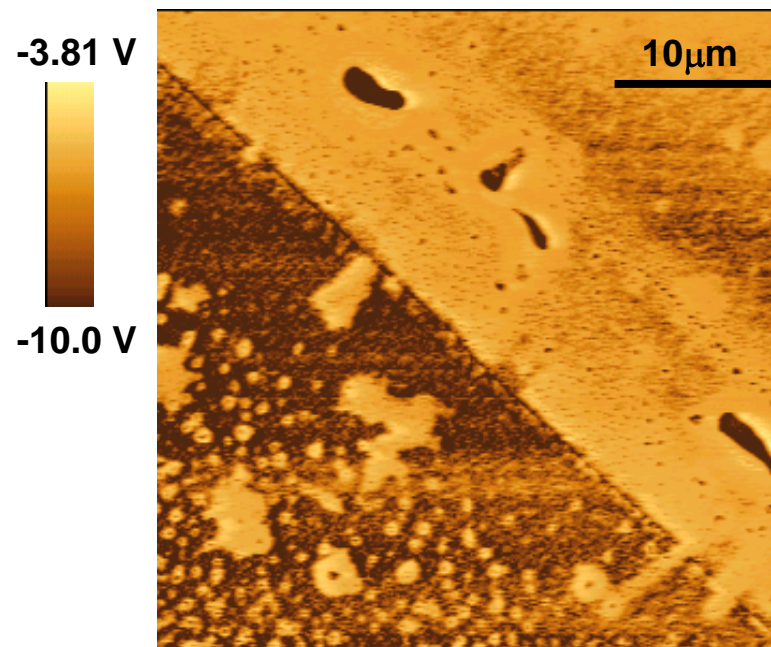
Shading Topography - Fracture



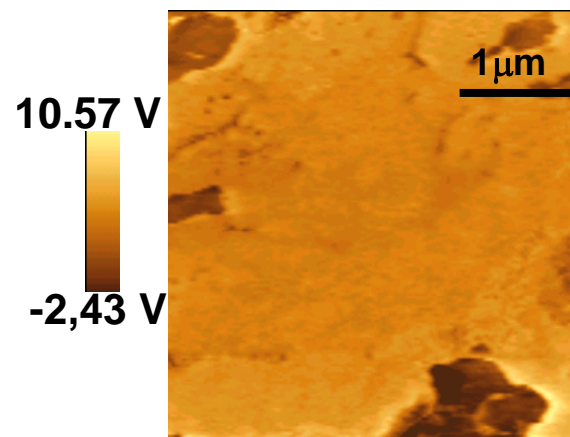
PP/NR film (air) surface



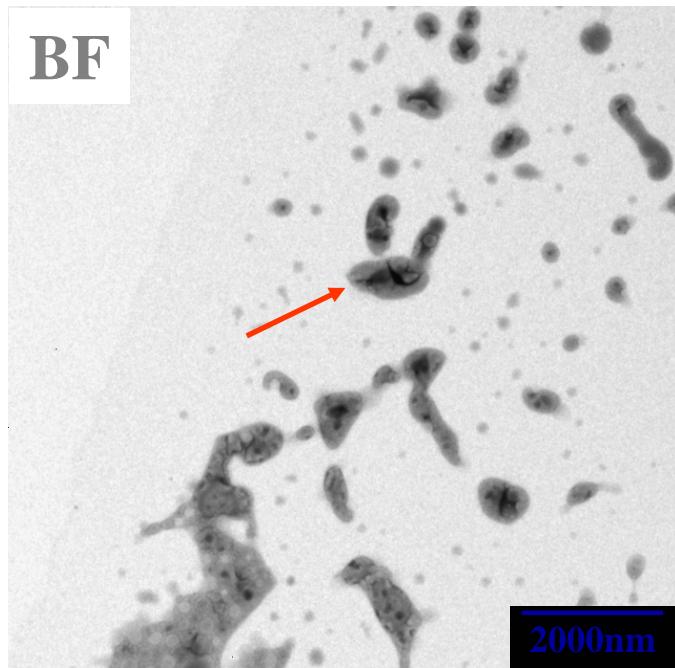
SEPM - Fracture



PP/NR film surface in contact with the glass

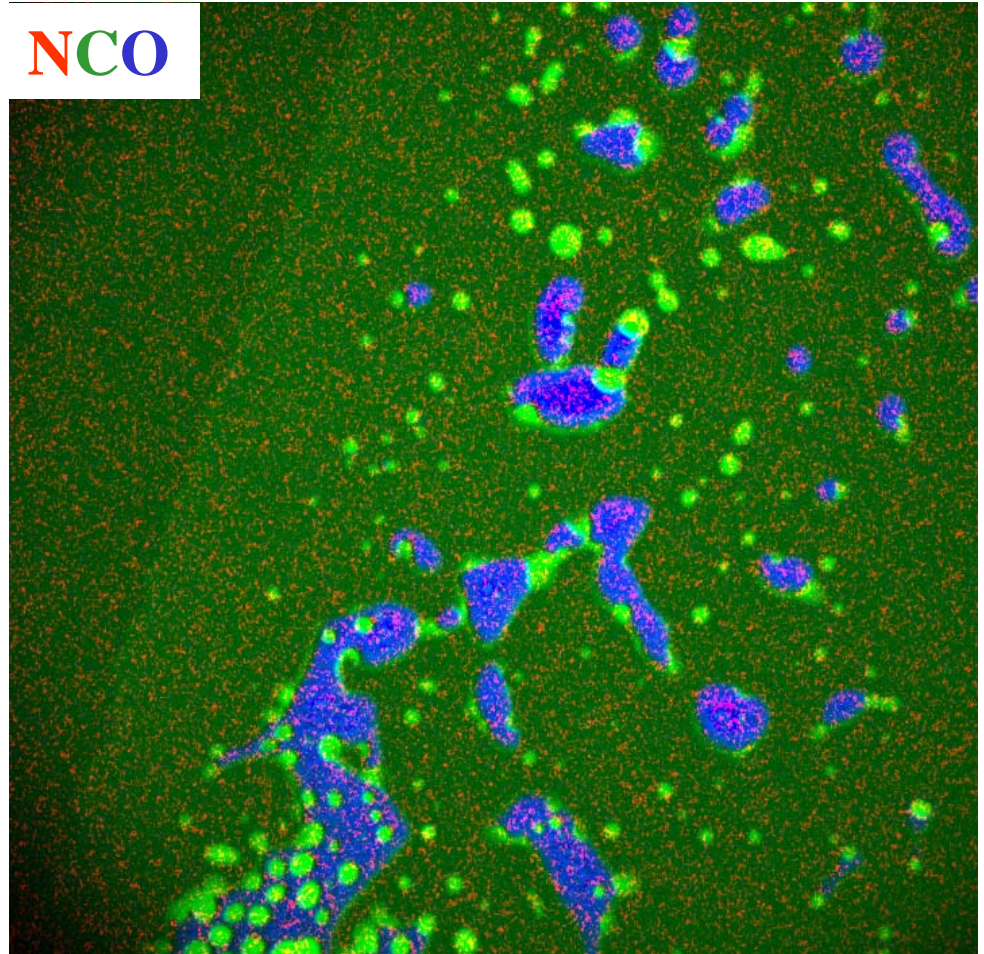


BF

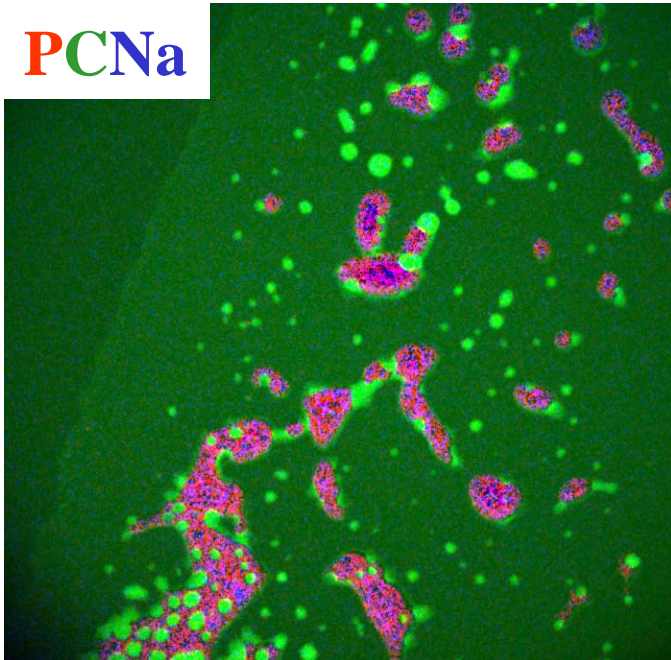


Compatibilidade entre uma fase orgânica e outra, inorgânica

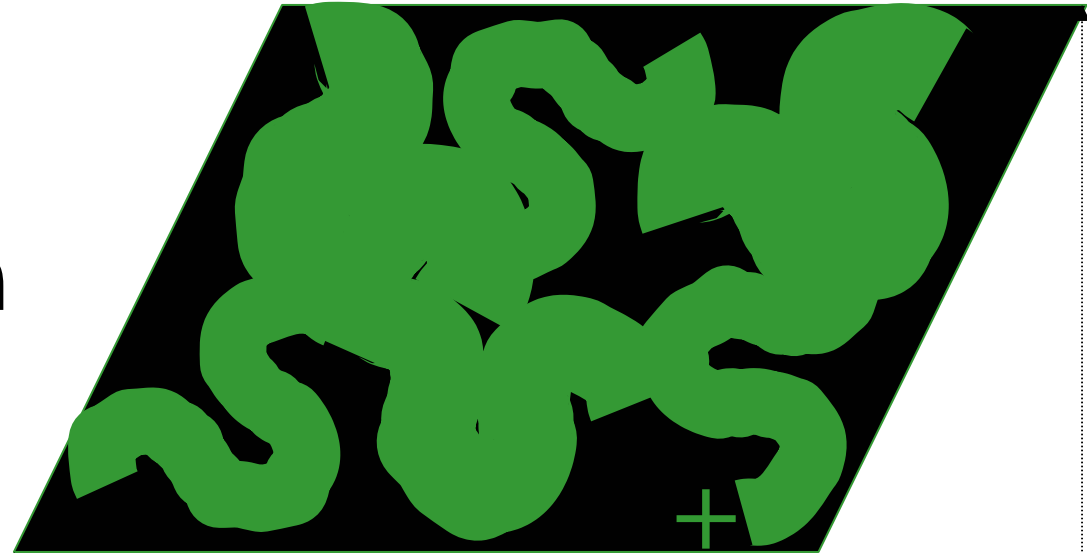
NCO



PCNa



**A model for
adhesion
improvement on
glass:
the PP-rubber
film has charged
domains, which
bind to the
replicating
surface.**



Rippel, Polymer 2004