Nanoporous carbon thin films produced by plasma immersion ion implantation of self-assembled block-copolymer nanotemplates

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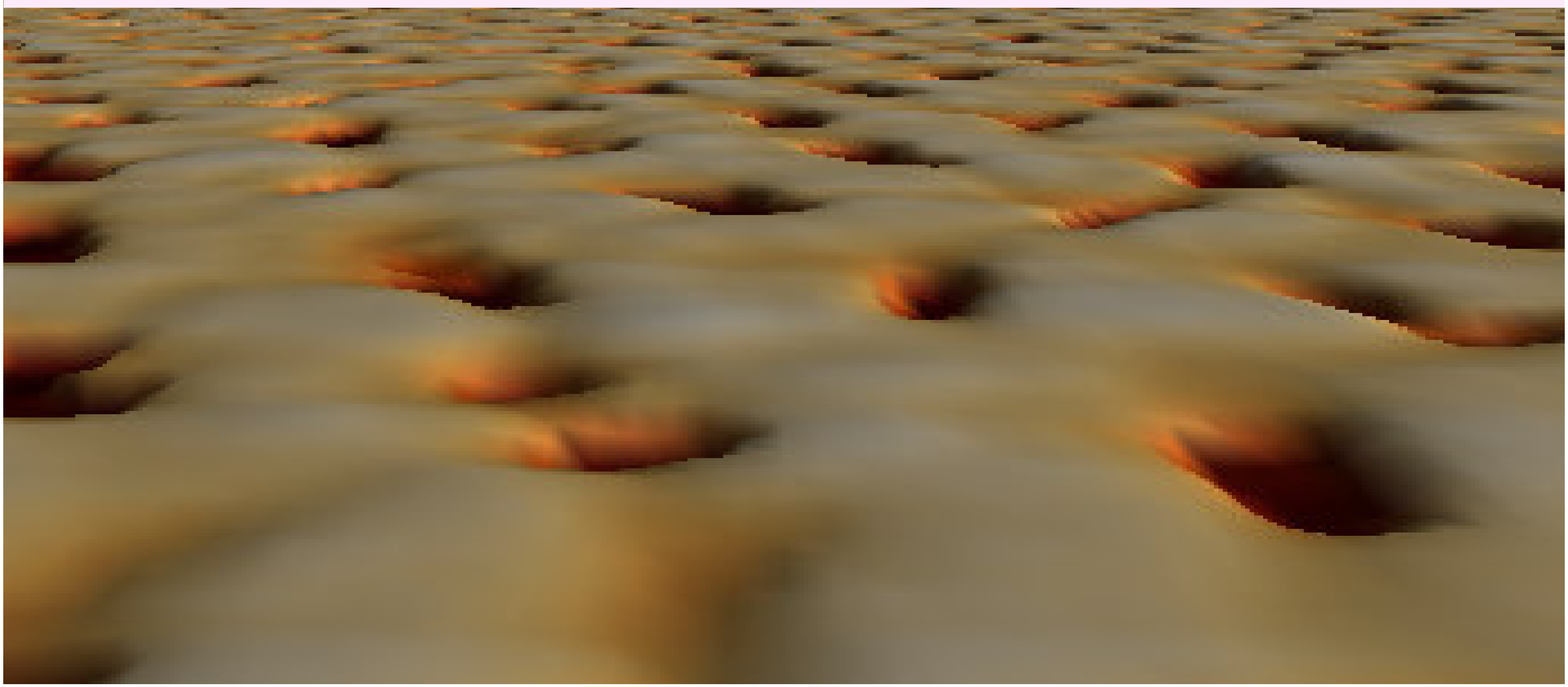
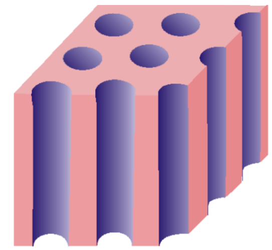


Block-copolymer self-assembly:

the route to producing highly ordered nano-structured thin films.



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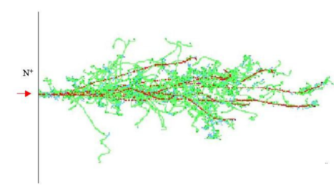
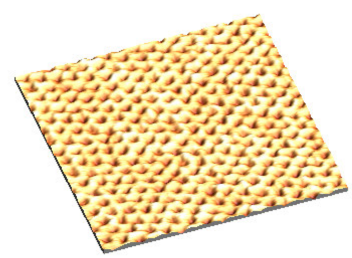
Plasma immersion ion implantation:

enhances properties (weariness, bio-compatibility *etc*) of polymer films via carbonization reactions.

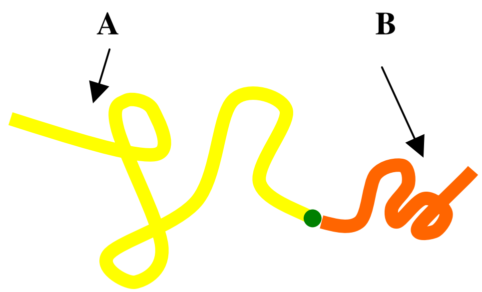


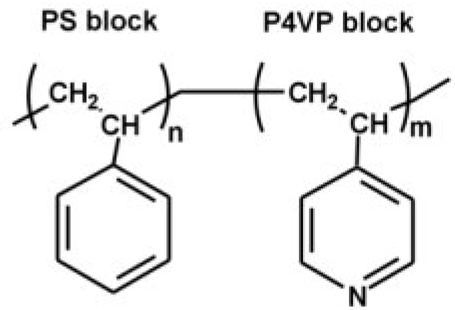
Carbonized nanoporous thin films:

a promising material for the membrane technologies, catalysis supports *etc.* - *Goal*



I. Self-assembly of block-copolymers





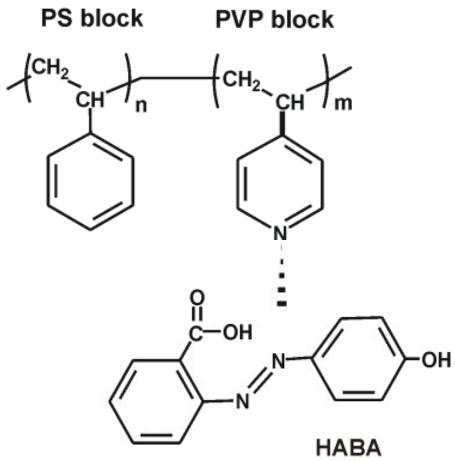
Mutual immiscibility of the A and B polymers

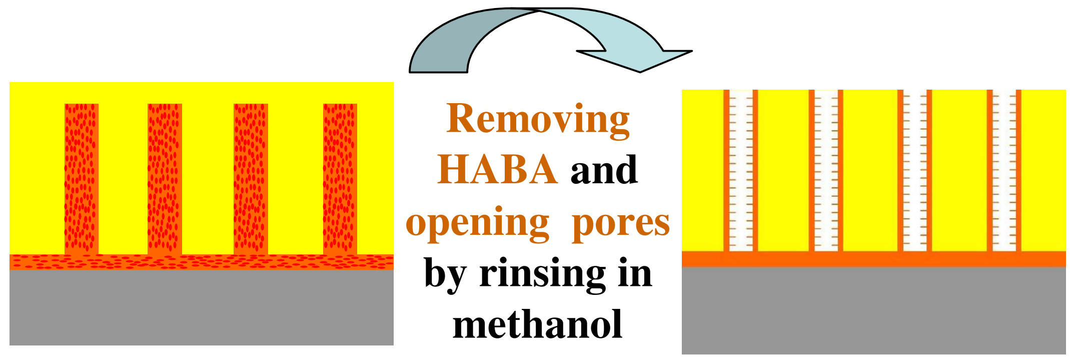
Impossibility of macro-phase segregation (*because of covalent bonding of the A and B components*)

Micro-phase separation (self-assembly).

Materials and fabrication of nanoporous BC films

Diblock copolymer (PS-b-P4VP) + HABA **2-(4-Hydroxyphenylazo)benzoic acid (HABA)**



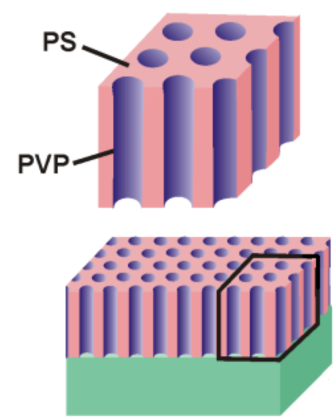


Self assembly of PS-b-P4VP+HABA

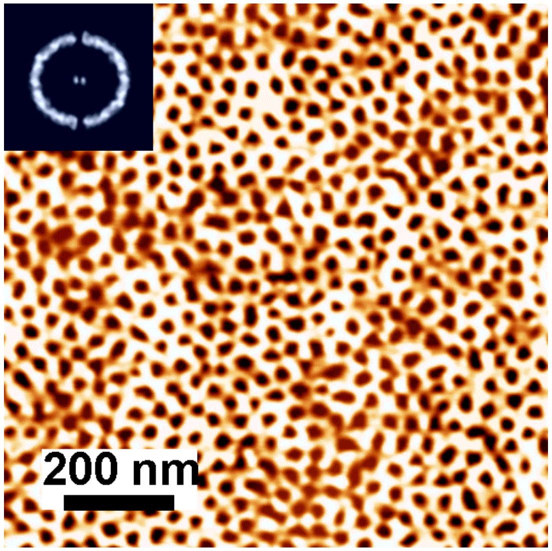
Porous PS-b-P4VP film

Typical characteristics of the film:

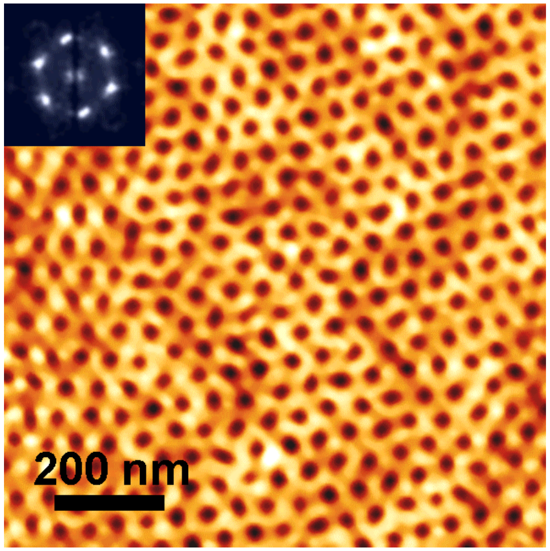
- **Thickness, h = 15-100 nm.**
- **Pore diameter, d_P = 8-10 nm.**
- **Inter-pore distance, d_i = 27 nm.**



Annealing of the BC-films is required for obtaining spatially ordered morphologies



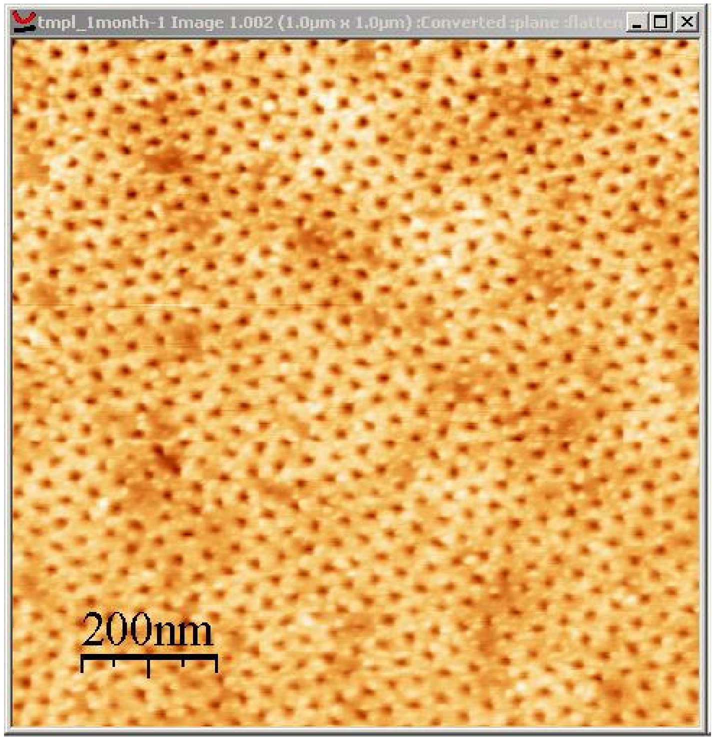
No annealing
(„as deposited")

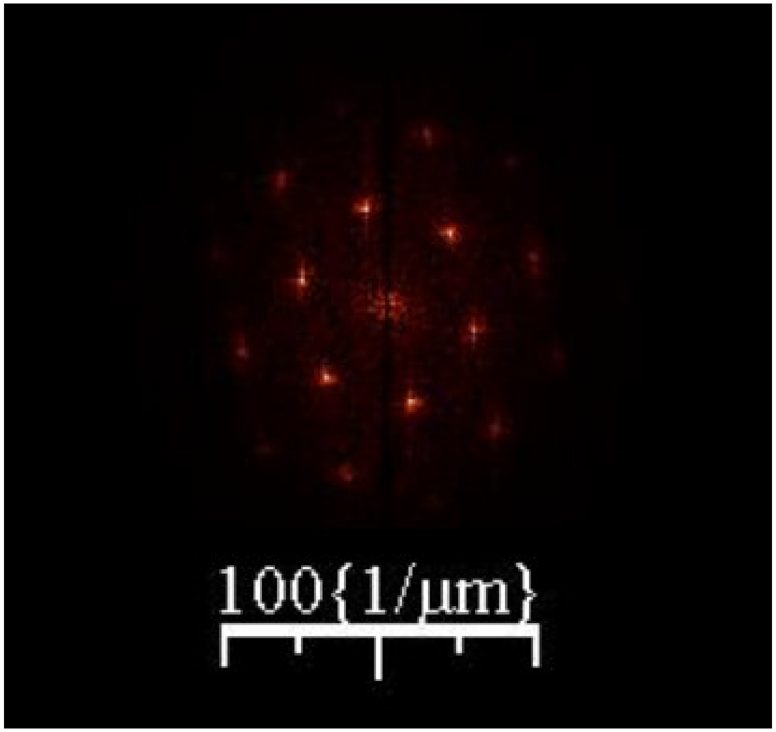


Annealed in
saturated vapor of
1,4 dioxane

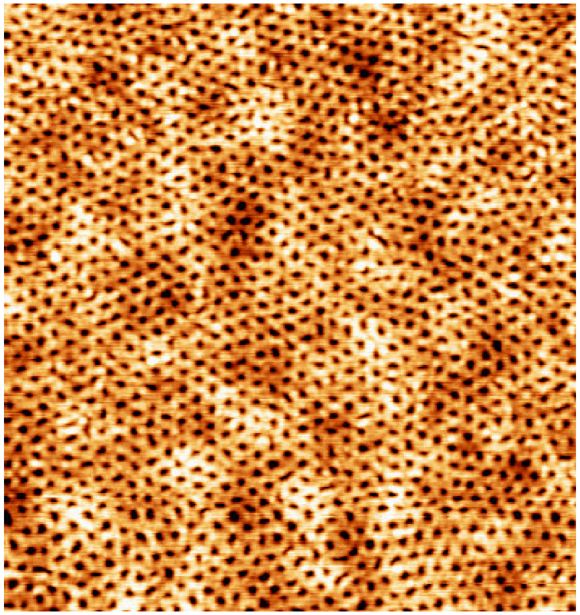
Annealing is done prior to washing HABA

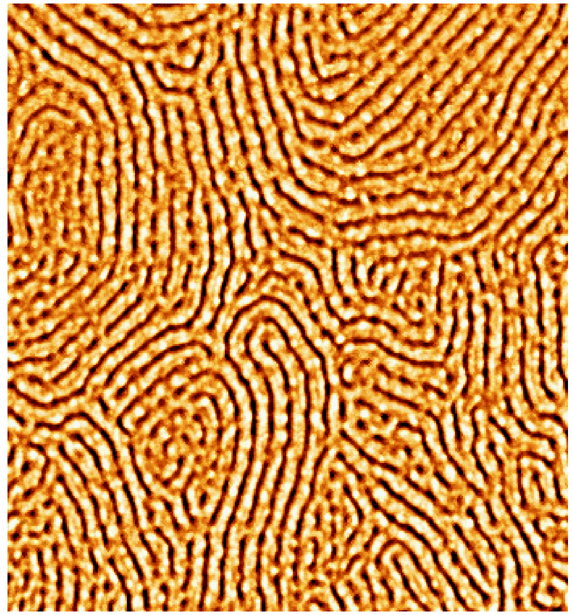
A sample annealed during 1 month – very good hexagonal order

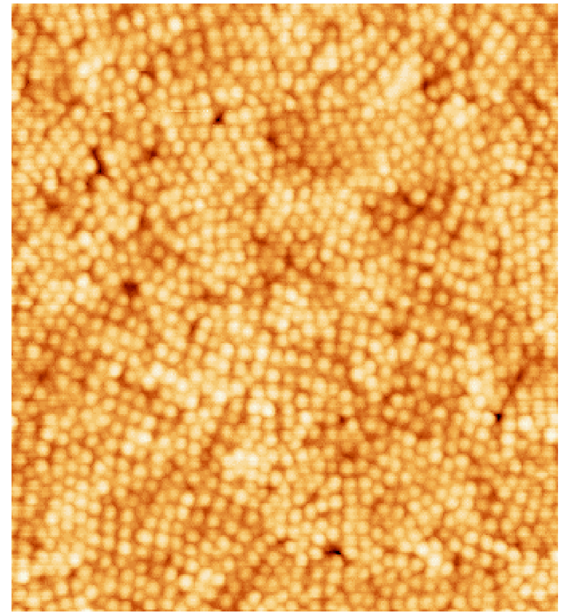




Morphology of the BC template for different volume fraction of PS and (P4VP+HABA) blocks

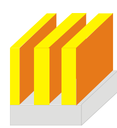




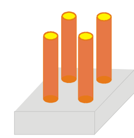


PS-b-P4VP(40000-5600)
PS:(P4VP+HABA))≈ 7:3

PS-b-P4VP(32900-8080)
PS:(P4VP+HABA)≈5:5



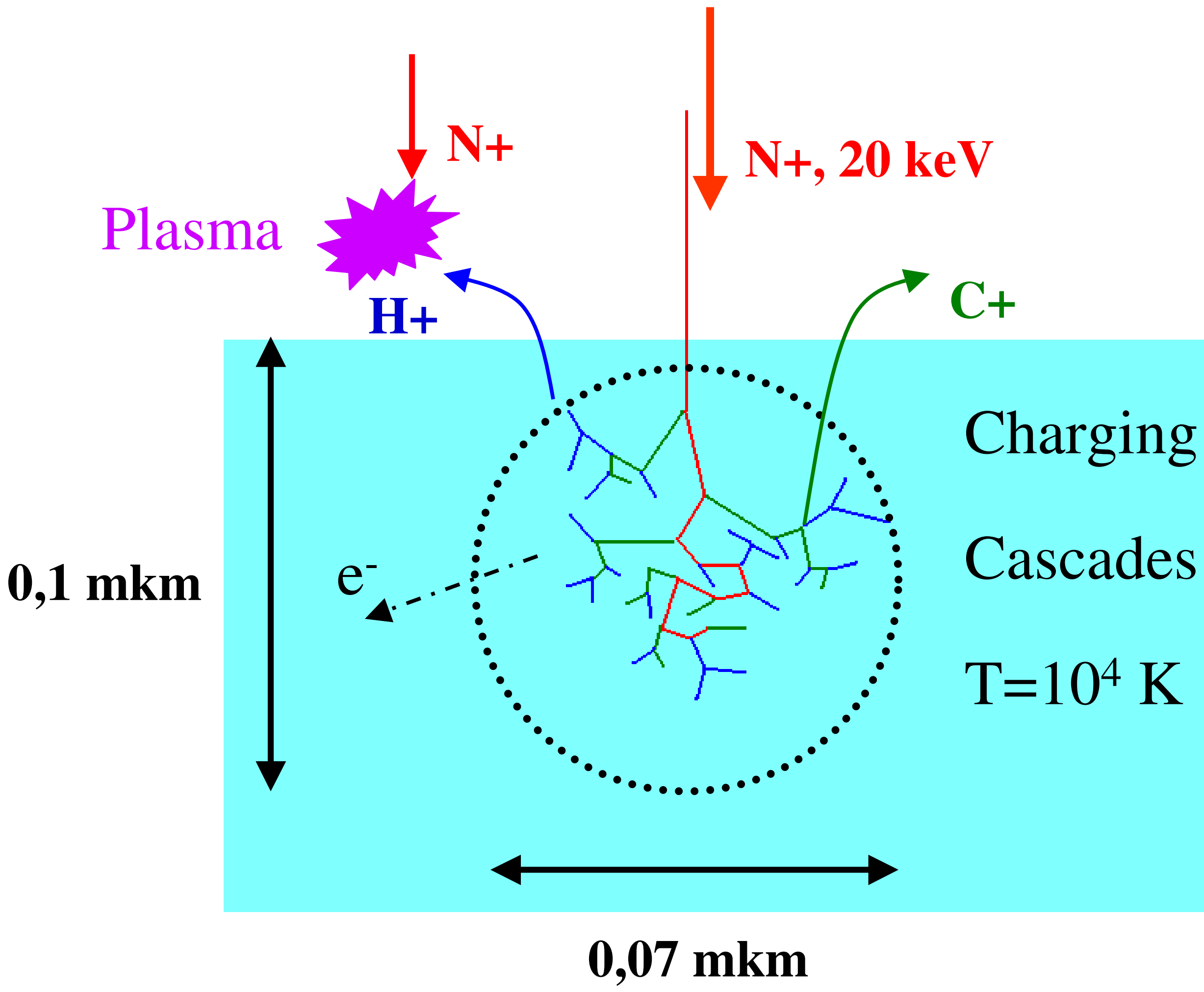
PS-b-P4VP(12000-11800)
PS:(P4VP+HABA)≈3:7



PS forms matrix, P4VP+HABA fills the pores

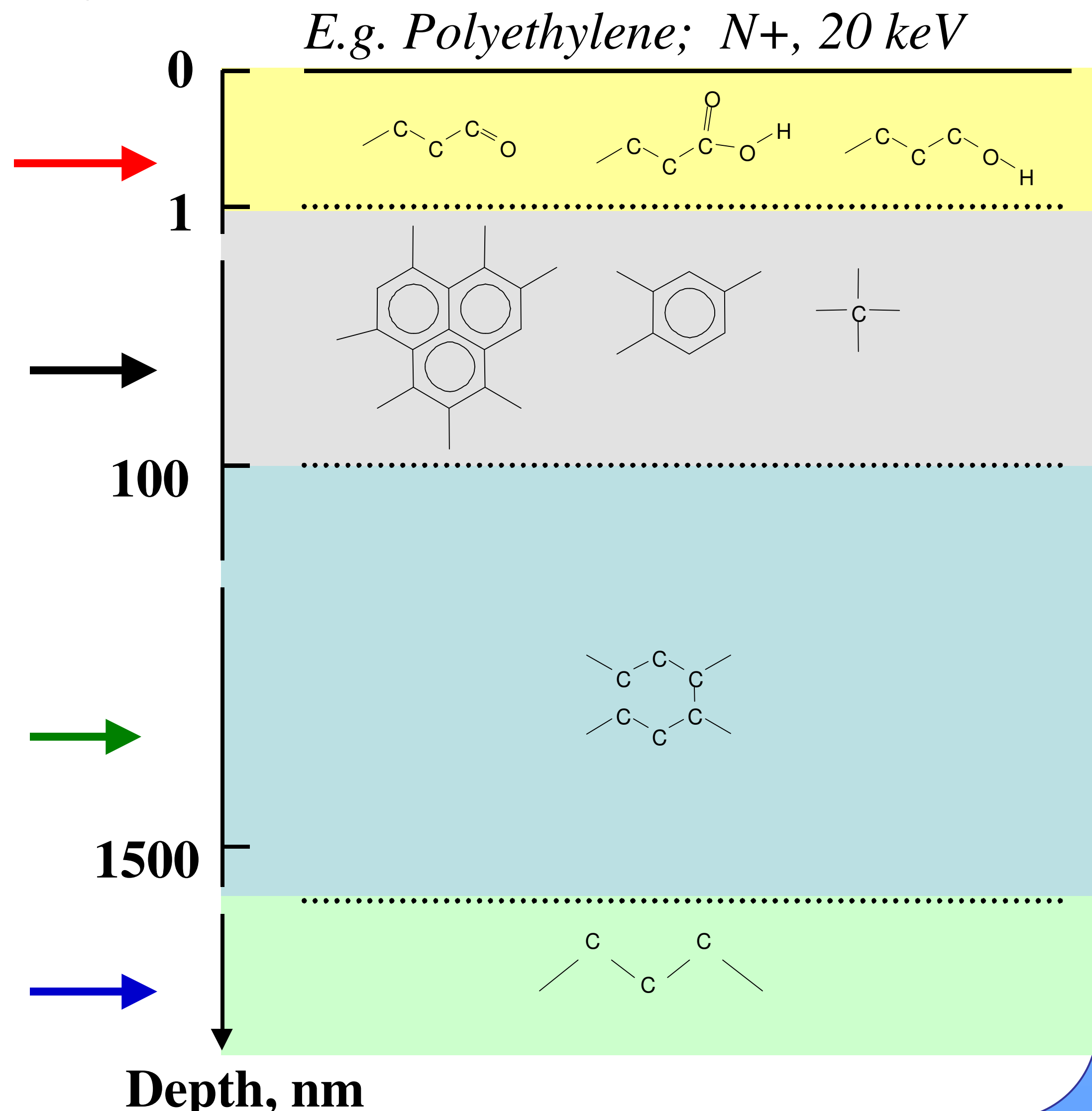
P4VP+HABA forms matrix, PS -cylinders

II. Ion Beam - Polymer interaction

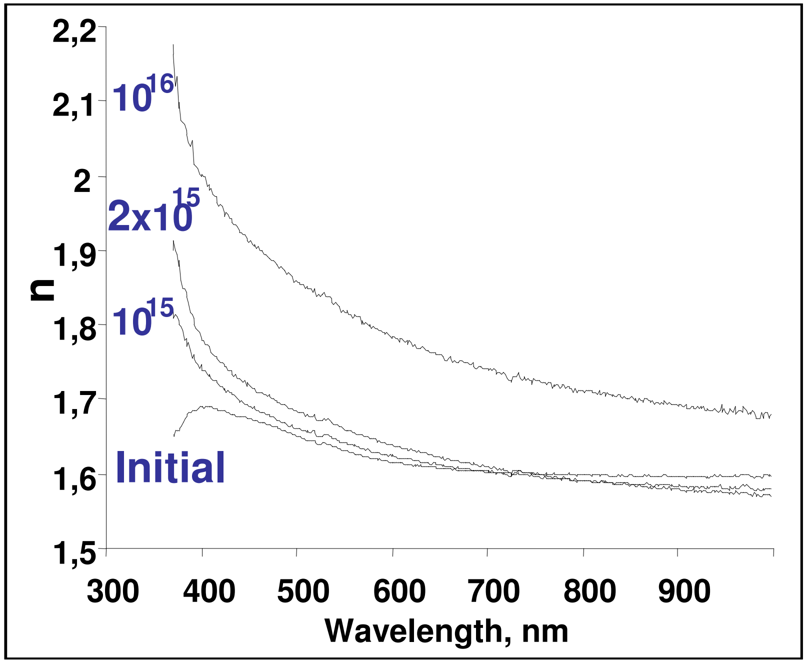


Layer structure of polymer after ion beam treatment

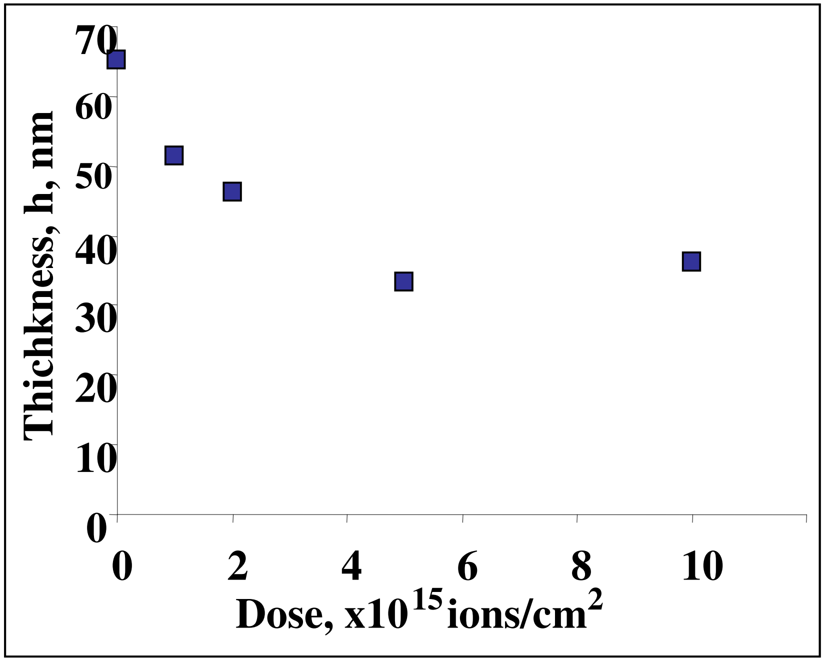
- <u>Oxidized layer</u>
  - Wetting angle
  - UV reflection spectra
  - XPS spectra
- <u>Carbonised layer</u>
  - FTIR ATR spectra
  - UV transmission spectra
- <u>Crosslinked layer</u>
  - Gel-fraction
  - Mechanical properties
- <u>Unchanged layer</u>
  - IR transmission spectra



III. Block-copolymer nanoporous films after PIII treatment

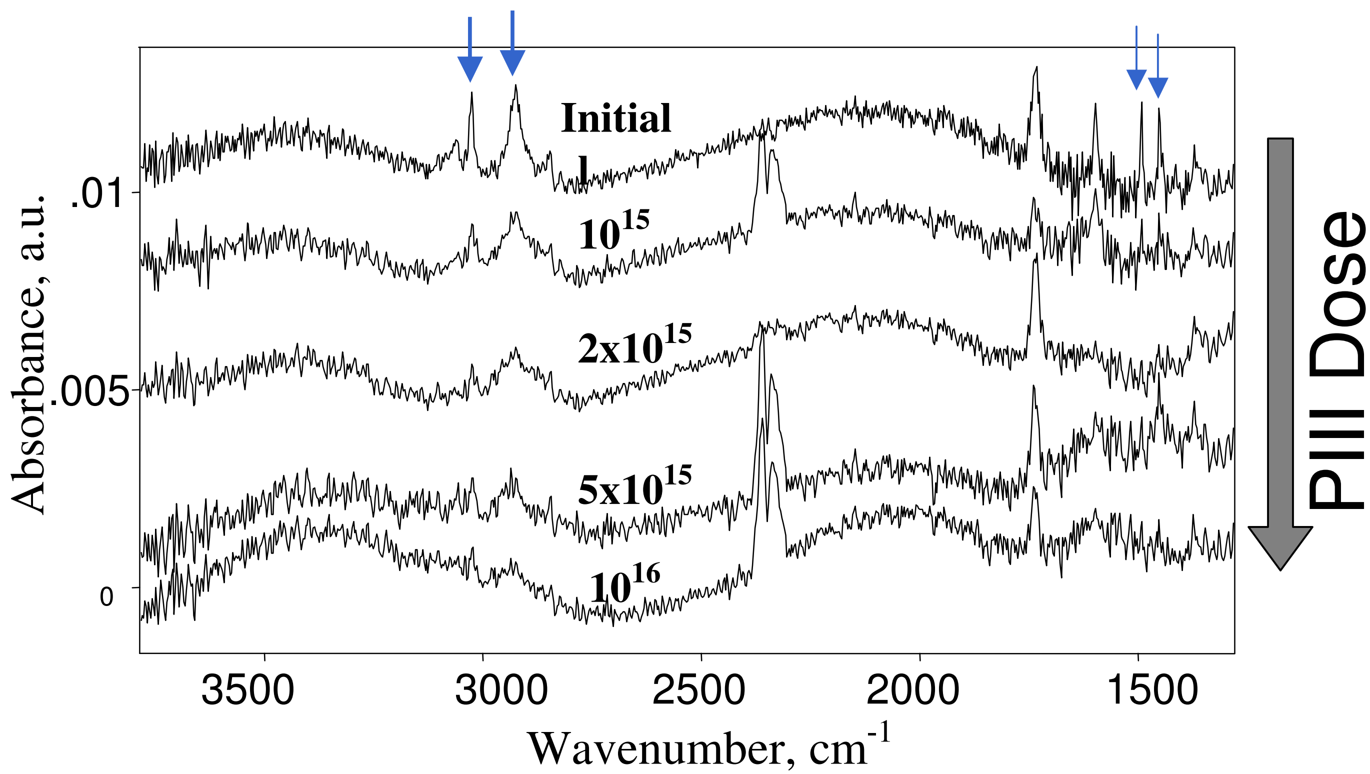


Real part of refractive index of PS-PVP templates after different doses of PIII.



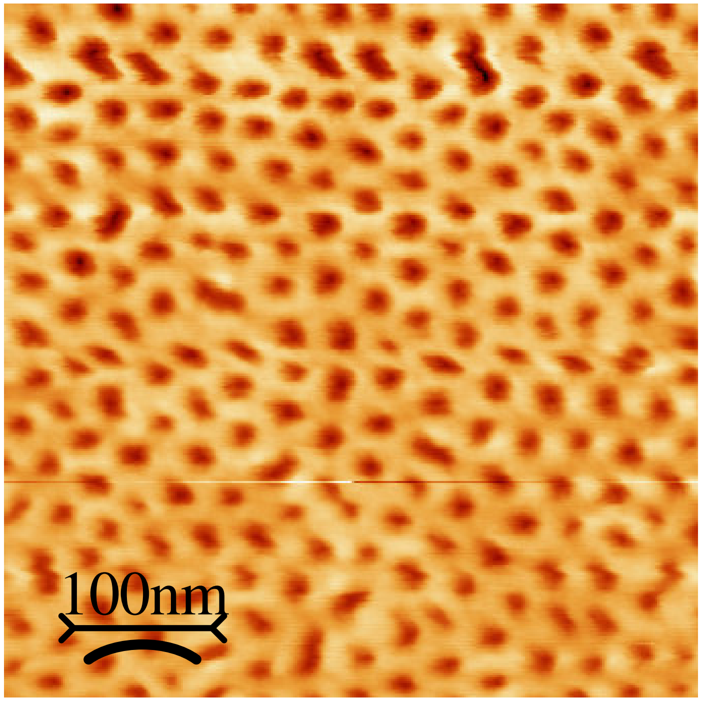
Thickness of a 65 nm BC film after PIII of different dozes.

FTIR transmittance spectra of PS-P4VP target after PIII by nitrogen ions (20 keV energy)

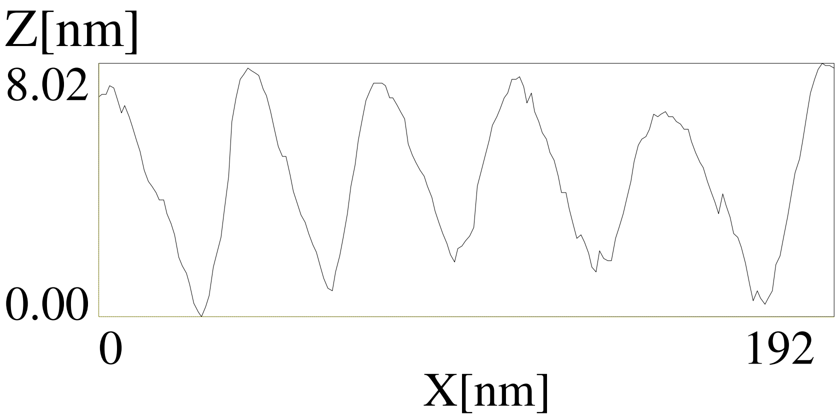


Polystyrene peaks.

AFM analysis of the PIII-treated nanoporous films

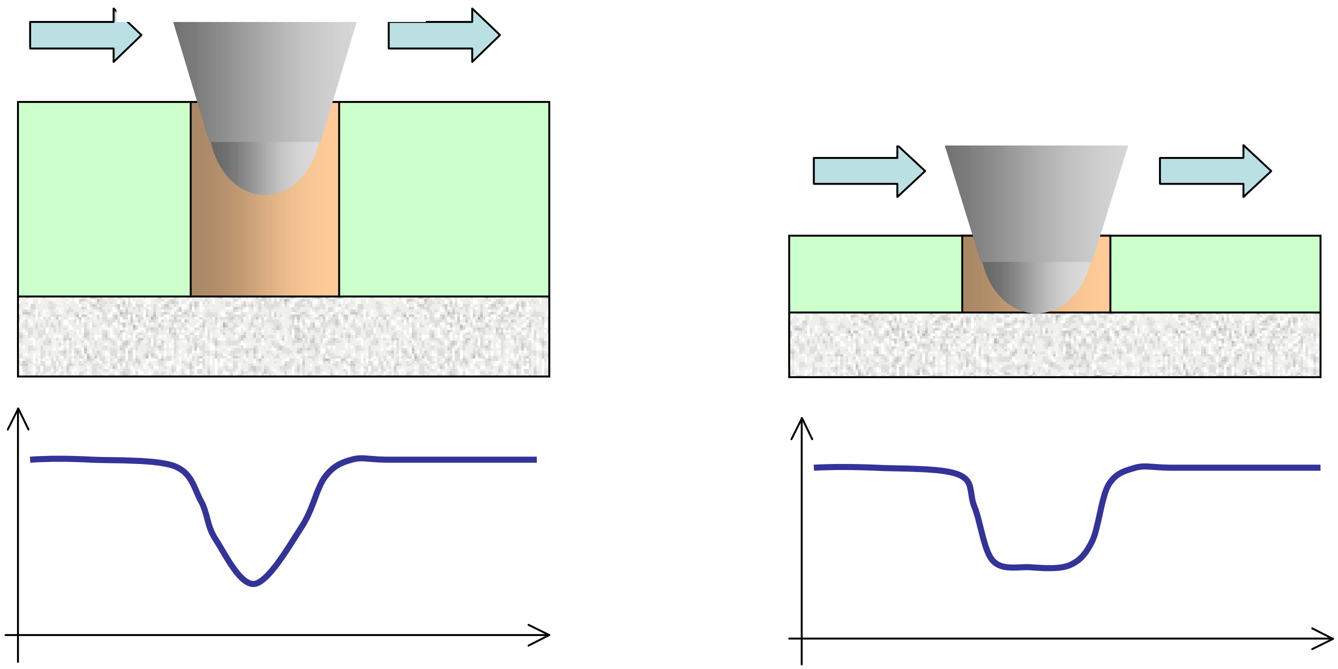


AFM topography image of the PIII-treated nanoporous film (implantation doze 5x10^{15} cm^{-2}).



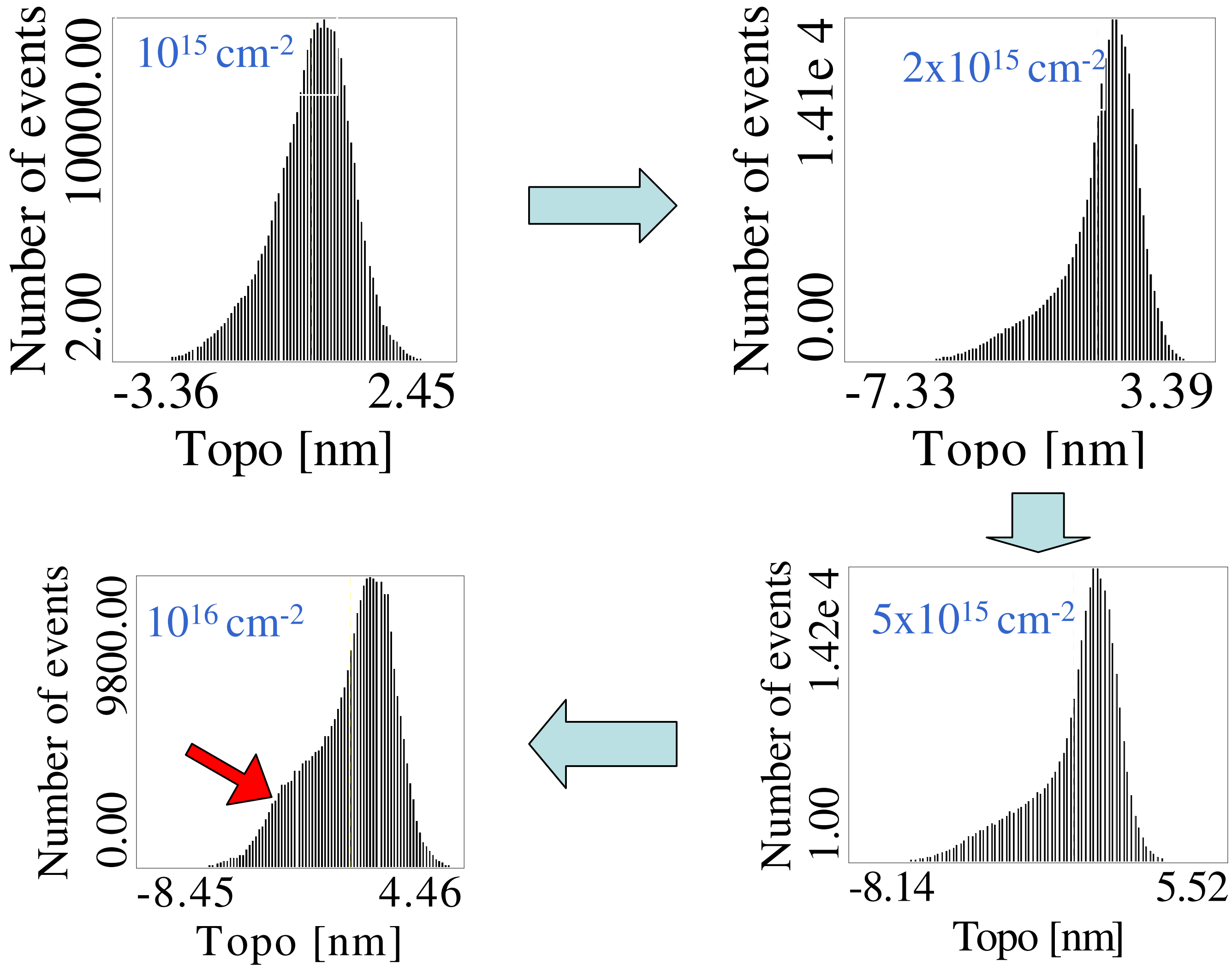
Height profile across 5 pores

AFM analysis of the PIII-treated nanoporous films

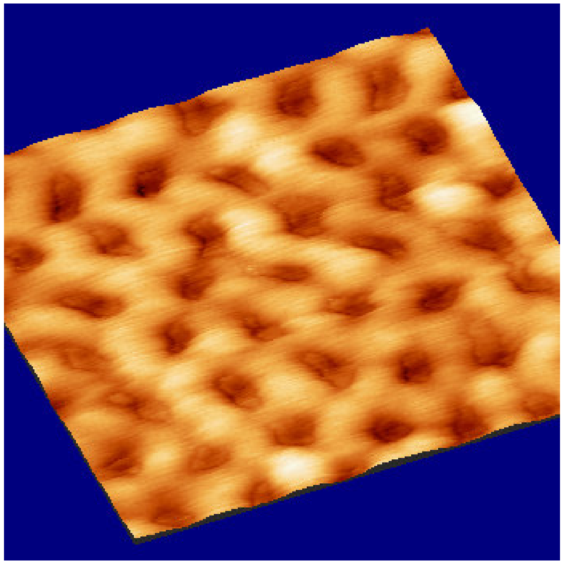


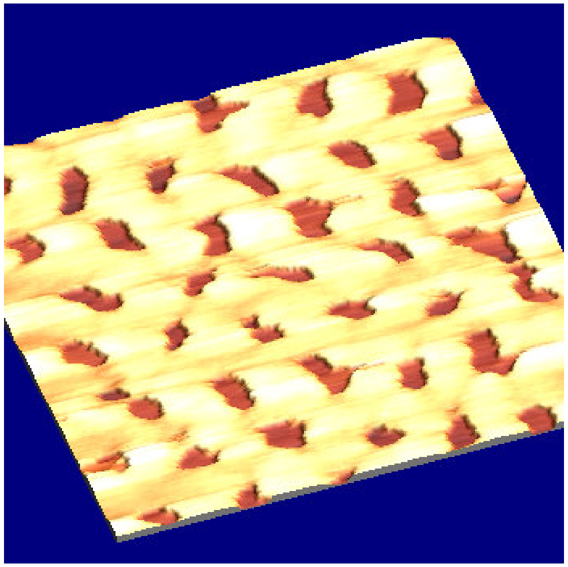
The height profiles for the high
and low aspect ratio pores
(left and right figures, respectively)

Statistical analysis of the AFM topography scans



Statistical analysis of the AFM height profiles





Summary

-PIII treatment preserves the ordered morphology of the BC films !

- Self-assembled block-copolymer films constitute a good precursor material for the manufacture of nanoporous carbon films.

- Additional research (TEM, SEM) is required for the complete characterization of the films, in particular openness of the pores.

-Carbonized nanoporous thin films may find numerous applications as Membranes, supports for catalytic nanoparticles, *etc.*

Thank you for your attention