Stimuli Responsive Nanostructured Porous Network from Triblock Copolymer Self-assemblies

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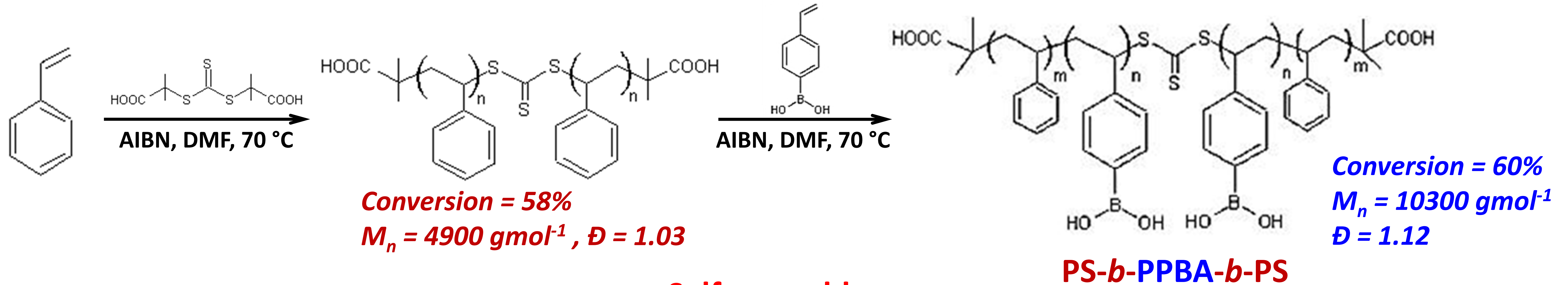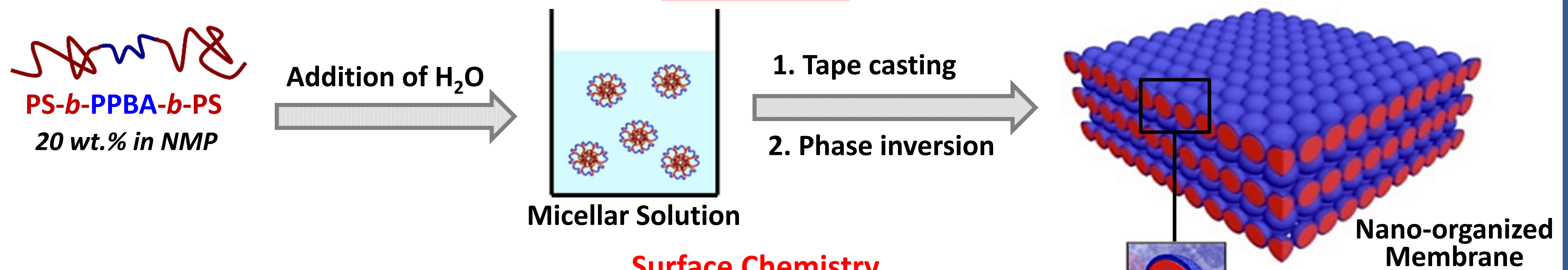
Preparation of Smart Membranes using Supramolecular Chemistry

ABA triblock amphiphilic copolymer is synthesized using RAFT chemistry. The self-assembled micelles of this copolymer are then used to prepare nano-organized porous films that could be used as filtration membranes. A novel strategy is developed to build the nanostructures and perform their self-assembly using reversible and non-covalent interactions to create free volume between the micelles, thus giving tuneable porosity to the film. The self-assembly of block copolymer, occurs at high concentration through solvent evaporation, which induces a progressive decrease of the inter-micellar distance, and results in the formation of an in-situ network of micelles and the final porous film. Subsequent permeability tests were conducted under different stimuli (pH and UV), generating cross-linking and chemical exchange reactions, to ensure the best balance between permeability and mechanical strength. This work highlights an original strategy for pore size control, and provides new insights towards the design of stimuli-responsive materials.
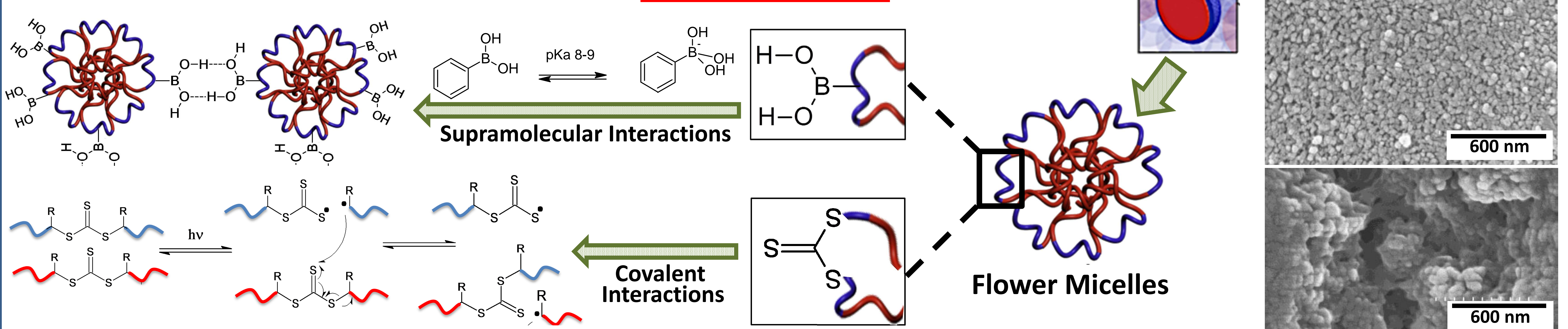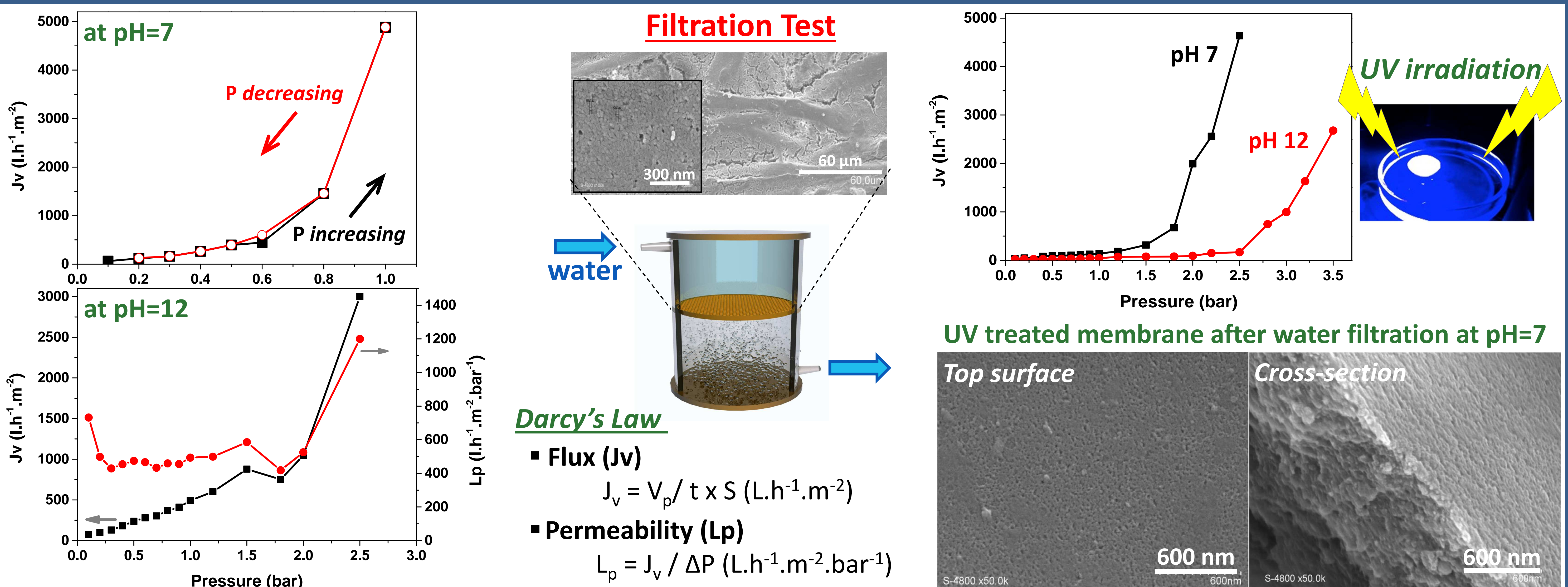
RAFT Synthesis of ABA Triblock copolymer

AIBN, DMF, 70 °C

Conversion = 58%
M_n = 4900 gmol^{-1} , Đ = 1.03

AIBN, DMF, 70 °C

Conversion = 60%
M_n = 10300 gmol^{-1}
Đ = 1.12

PS-*b*-PPBA-*b*-PS

Self-assembly

PS-*b*-PPBA-*b*-PS
20 wt.% in NMP

Addition of H$_2$O →

Micellar Solution

1. Tape casting
2. Phase inversion →

Nano-organized Membrane

600 nm

600 nm

Surface Chemistry

Supramolecular Interactions

pKa 8-9

Covalent Interactions

hv

Flower Micelles

Filtration Test

at pH=7

P *decreasing*

P *increasing*

Jv (L.h^{-1}.m^{-2})

at pH=12

Jv (L.h^{-1}.m^{-2})

Pressure (bar)

Lp (L.h^{-1}.m^{-2}.bar^{-1})

water

300 nm   60 µm

Darcy's Law

- **Flux (Jv)**

$$J_v = V_p / t \times S \ (L.h^{-1}.m^{-2})$$

- **Permeability (Lp)**

$$L_p = J_v / \Delta P \ (L.h^{-1}.m^{-2}.bar^{-1})$$

pH 7

pH 12

Jv (L.h^{-1}.m^{-2})

Pressure (bar)

UV irradiation

UV treated membrane after water filtration at pH=7

Top surface   *Cross-section*

600 nm   600 nm

Conclusions

- **Lp at *pH 7* > Lp at *pH 12***
- **Number of interactions ↗ Pore size ↘**
- **The flux steady-state range at *pH 12* > *pH 7***
- **morphological switch;**
    - only at higher pressure
    - From *Compact* to *Cubic*

P↑
P↓

Compact Stacking
Tortuous Trajectory

Cubic Stacking
Straight Trajectory

Adequate selection of the conditions allows the *modulation* of the membrane properties

Lp (L.h^{-1}.m^{-2}.bar^{-1})

UV

pH7   pH12

P (bar)

UV   UV

pH7   pH12