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# Versatile photoactive latex particles for singlet oxygen production as a tool for sustainable solutions

Guillaume Mageste, Ali Aboudzadeh, Charlene Boussiron, Luca Petrizza, Sylvie Lacombe, Thierry Pigot, Mickaël Le Behec, Maud Save

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## Interest of the study

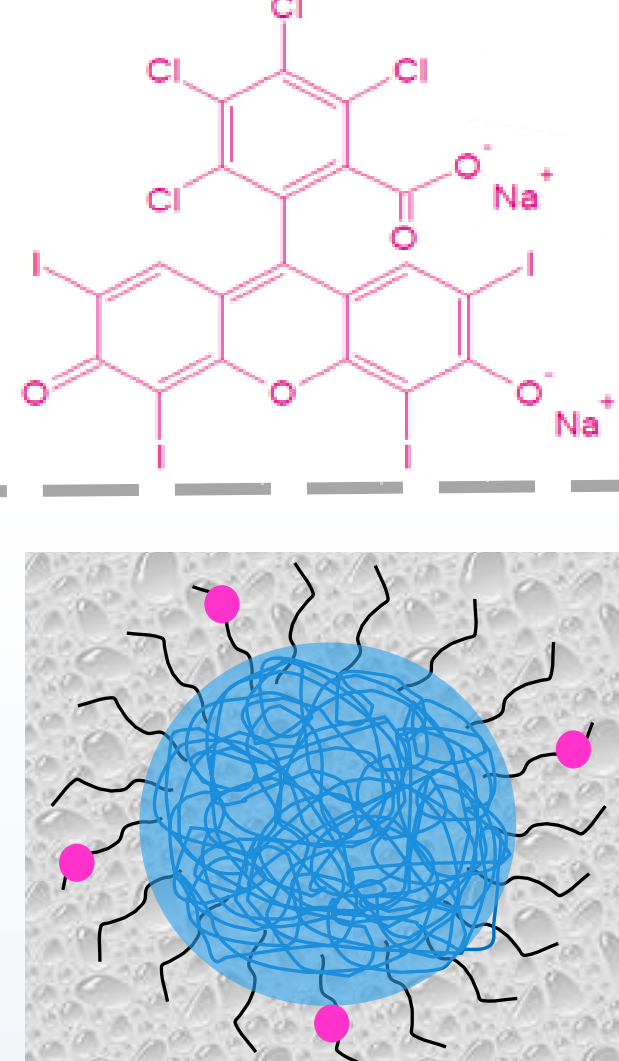
### State of the art

### Rose Bengal for singlet oxygen production

Limitations: Sensitive to photobleaching  
Difficult to recycle

### Objectives

Low energy light in visible range (LED 550 nm)



Energy transfer from excited Rose Bengal state to oxygen at ground state

Less sensitive to photobleaching  
Easier to recycle  
Versatile applications (film forming)

## Rose Bengal covalent grafting on polymer colloids for singlet oxygen production

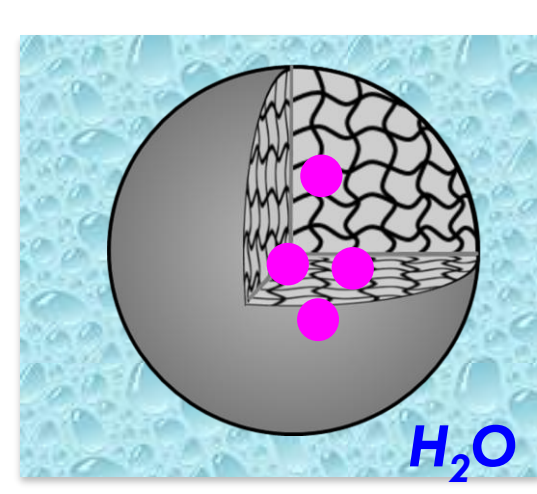
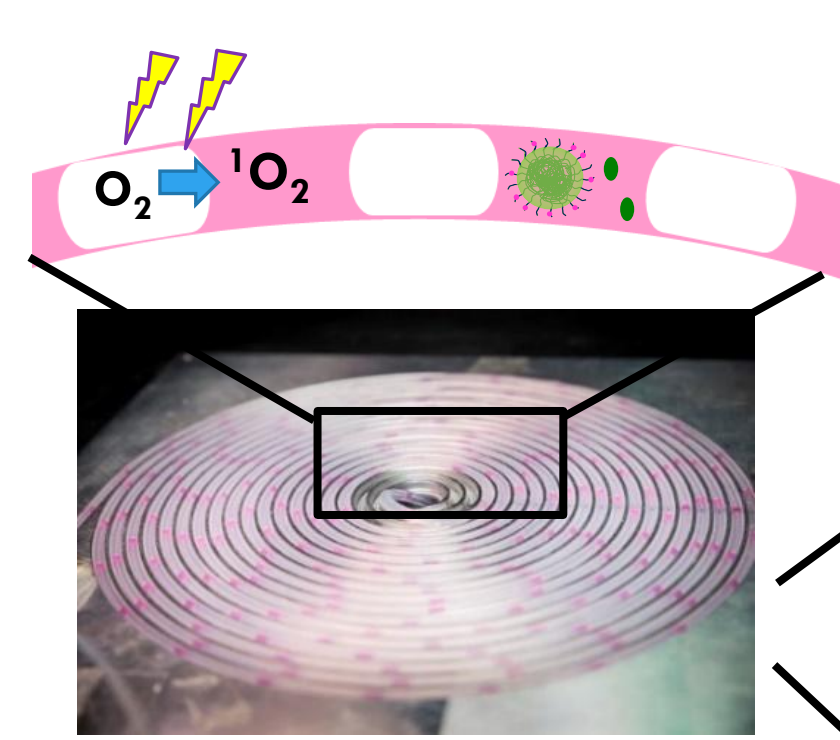
## Applications

### Oxygenation of biobased molecules

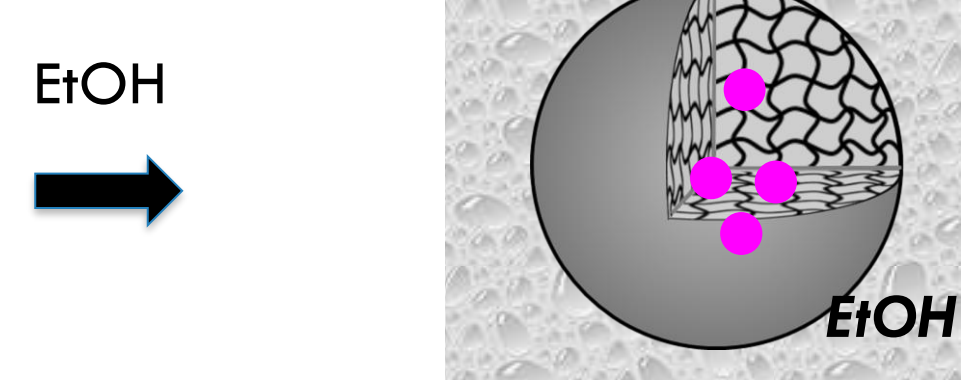
### Flow photochemistry

### 2 generations of ethanolic dispersions of Rose-Bengal polymer particles

Collaboration R. Radjagobalou, A. Desriac, J-F. Blanco, K. Loubière



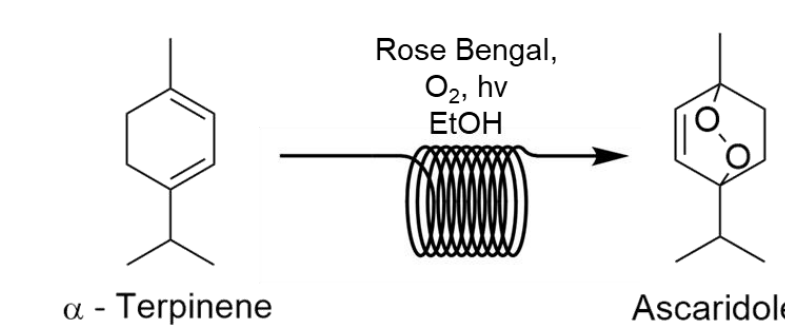
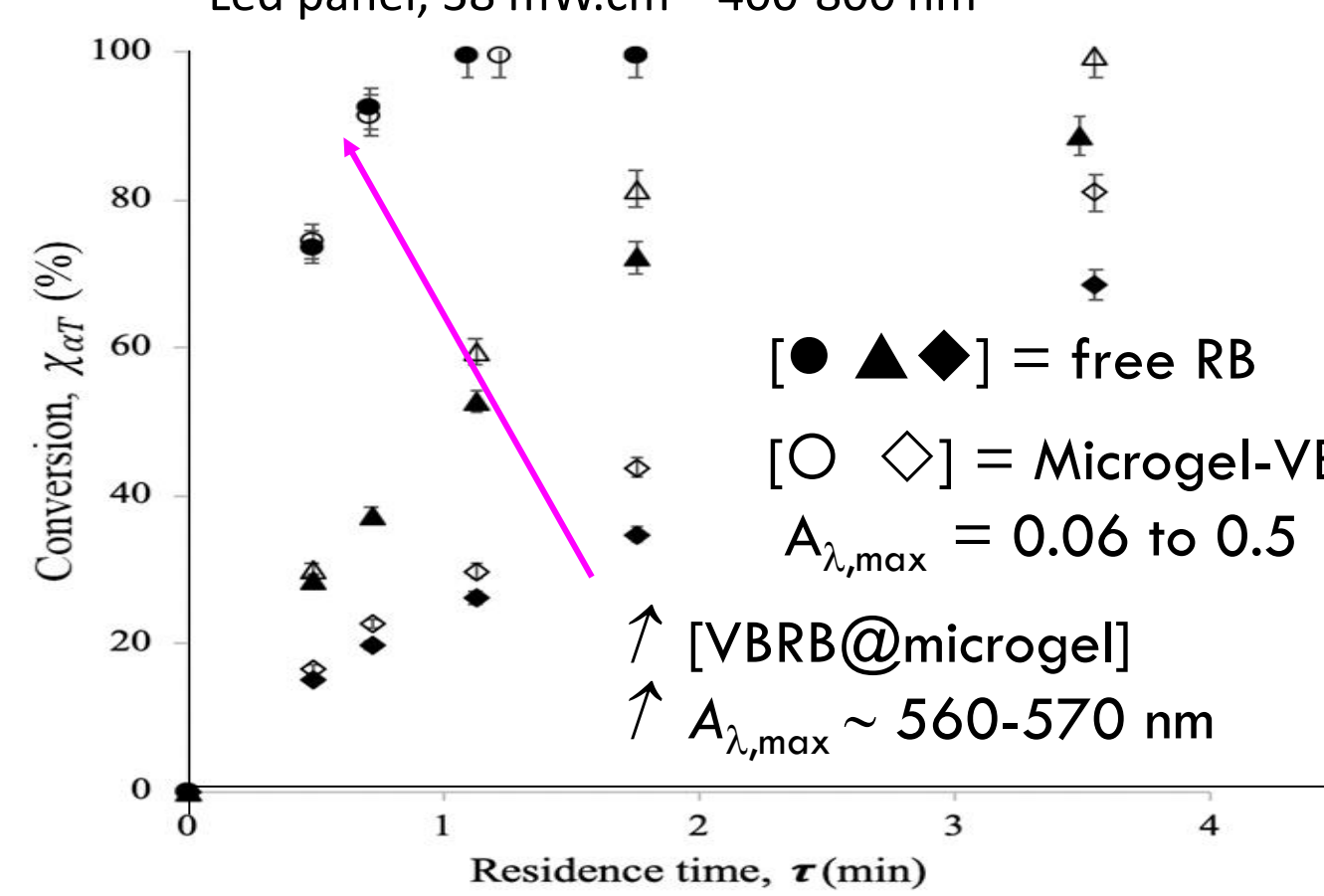
Latent colloids  
 $\phi_{\Delta}^{1O_2} \sim 0.03$



Photoactive microgels  
 $\phi_{\Delta}^{1O_2} \sim 0.37$

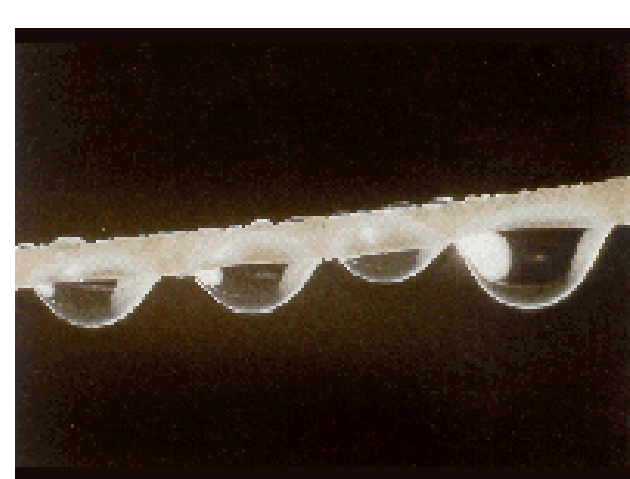
✓ OFF/ON photosensitized production of  $^1O_2$  with Poly(N-vinylcaprolactam) microgels<sup>[1]</sup>

Conversion of alpha-terpinene versus time for free RB and microgel-VBRB<sup>[2]</sup>  
Led panel, 38 mW.cm<sup>-2</sup> 400-800 nm

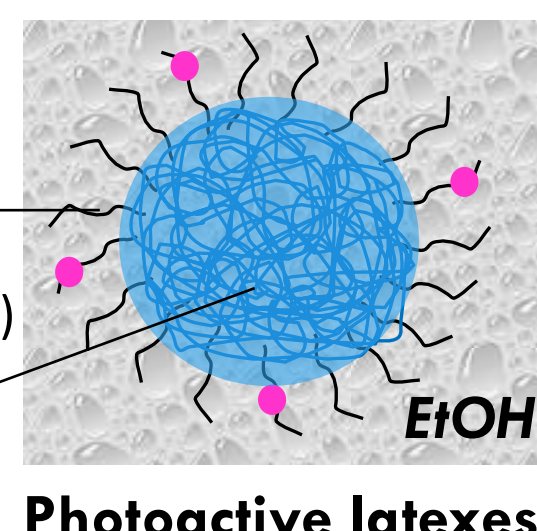


- ✓ 100% conversion  $\alpha$ -terpinene into ascaridole / Reactivity RB particles ~ free RB
- ✓ Very short residence times (< 6 min)
- ✓ Low photobleaching (RB- colloids < 1- 5 %)
- ✓ High Selectivity to produce ascaridole
- ✓ Similar efficiency for all latex particles Dh / DP block core-shell copolymer particles

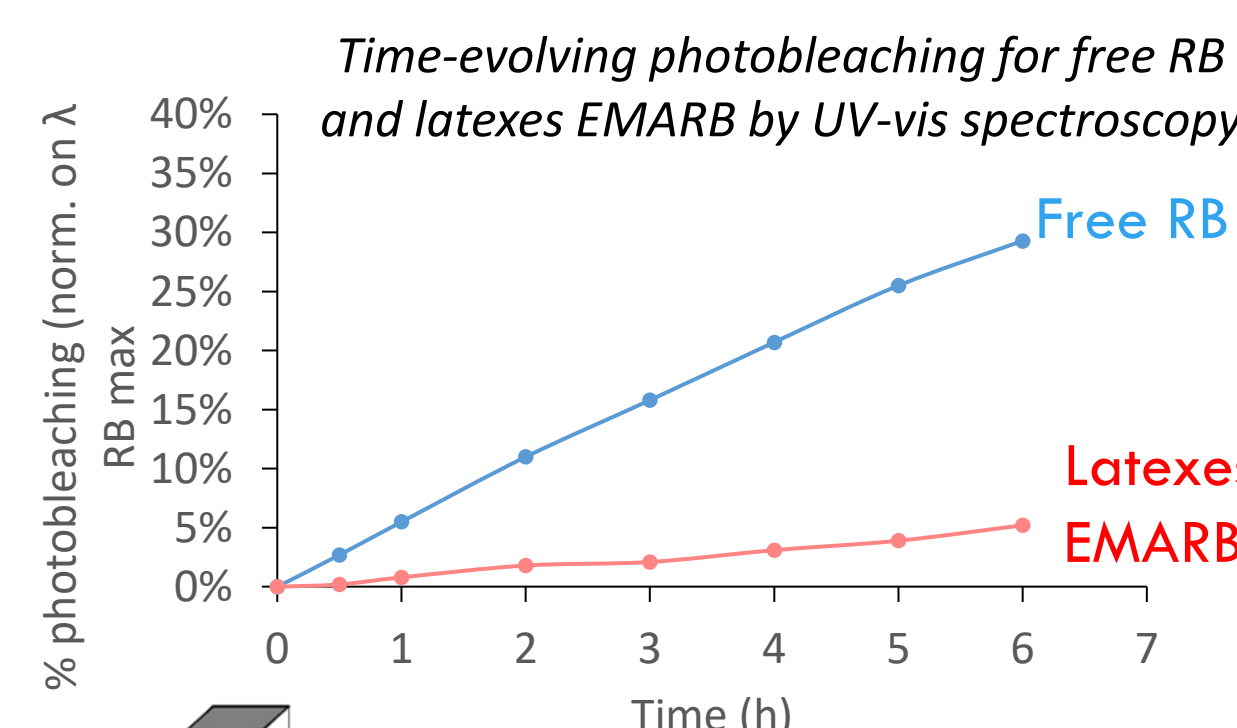
### Separation procedures



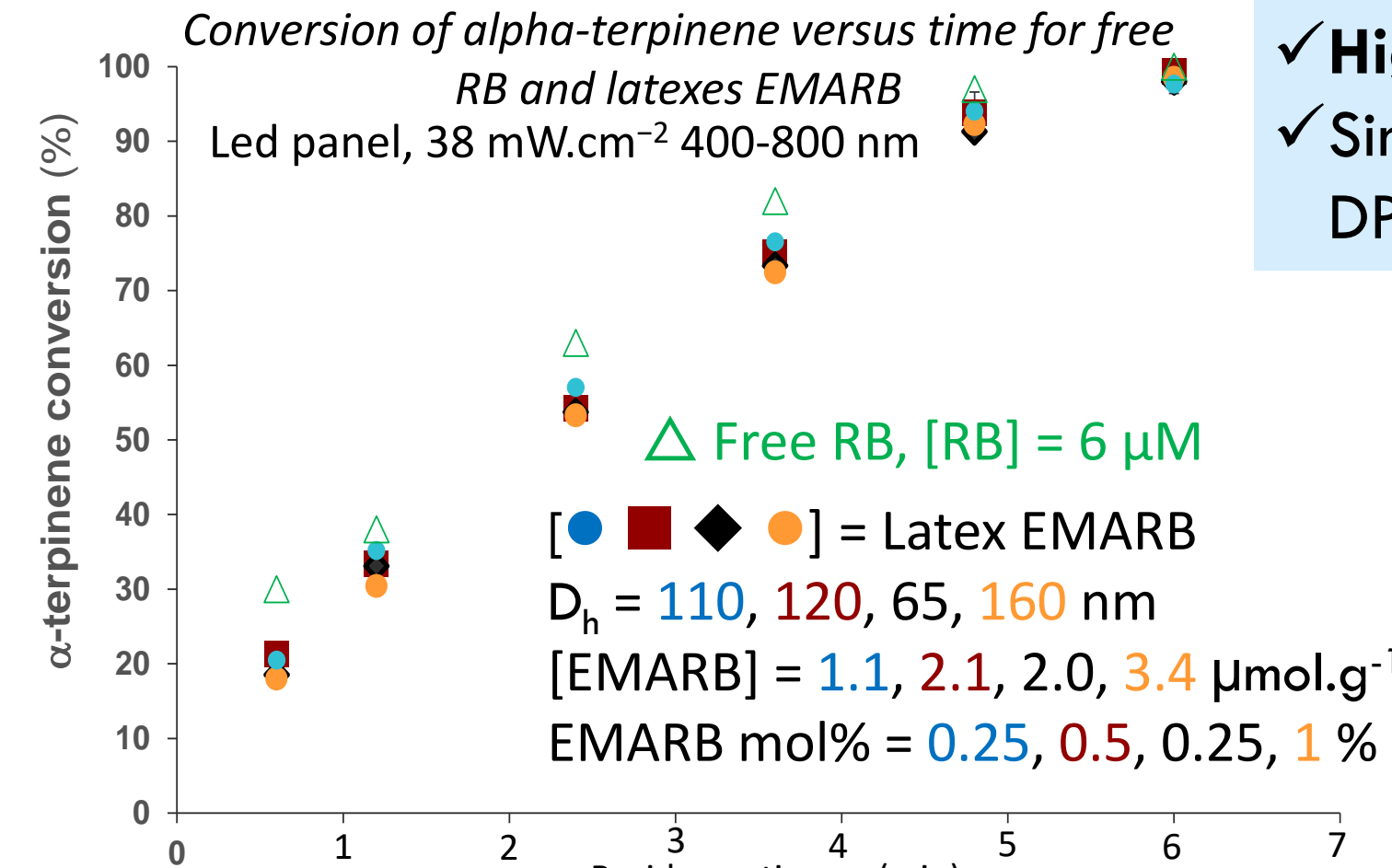
Poly(oligo(ethylene glycol) methyl ether methacrylate)  
Poly(benzyl methacrylate)



Photoactive latexes  
 $\phi_{\Delta}^{1O_2} \sim 0.6$



✓ Latexes are less sensitive to photobleaching than free RB



Quantum yield of singlet oxygen production  
 $\phi_{\Delta}^{1O_2} = \frac{n^{1O_2}}{n_{photons,abs,PSens}}$   
 $\phi_{\Delta}^{1O_2}$  (free RB) ~ 0.8

300 W Xe lamp, 25 mW.cm<sup>-2</sup>  
400-800 nm to enhance photobleaching to assess Free vs grafted properties

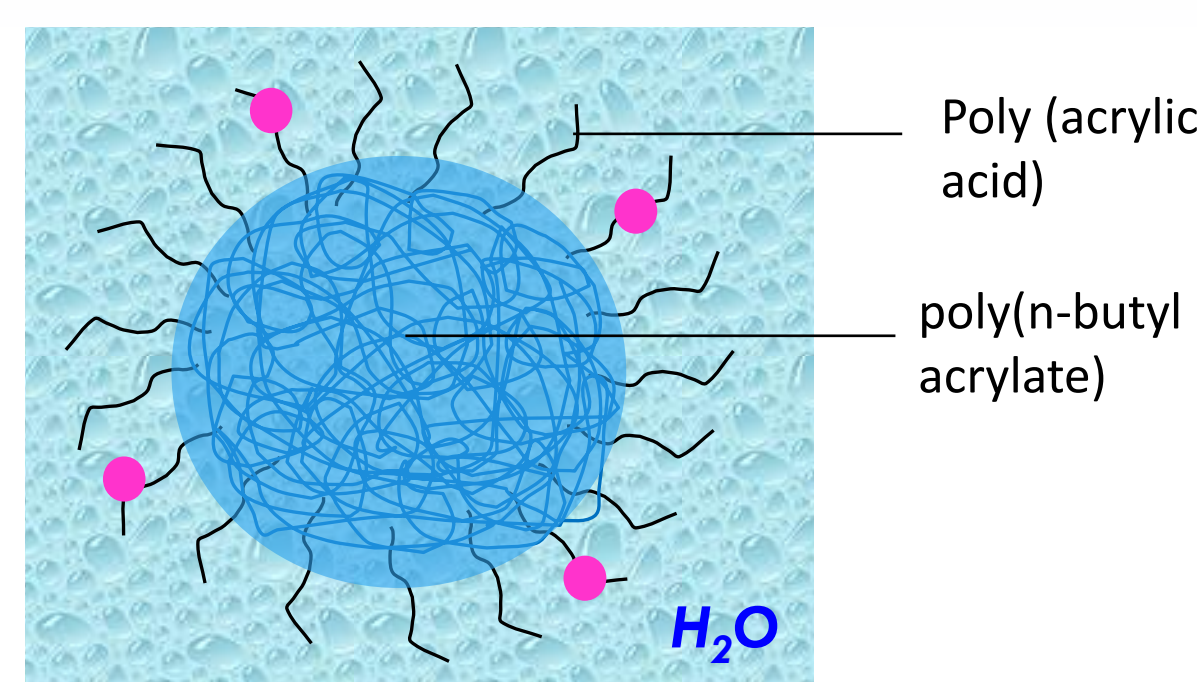
### Antibacterial Photoactive coating

### Film forming latex

### Mechanical properties



Collaboration Helen Minsky, Constantino Creton (ESPCI), Virginie Pellerin (IPREM, AFM)

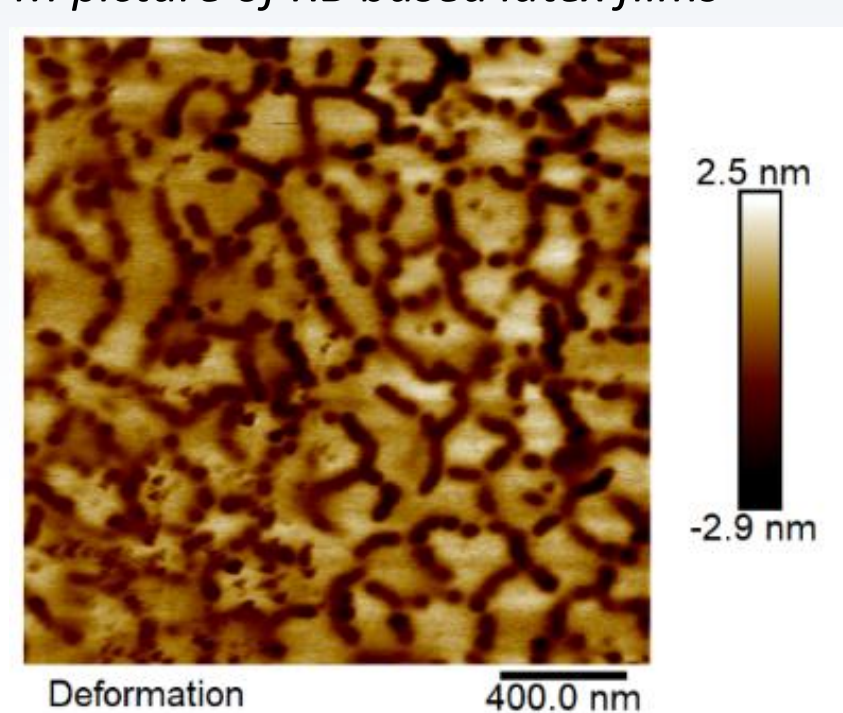


Surfactant-free core-shell photoactive latexes<sup>[3] [4]</sup>

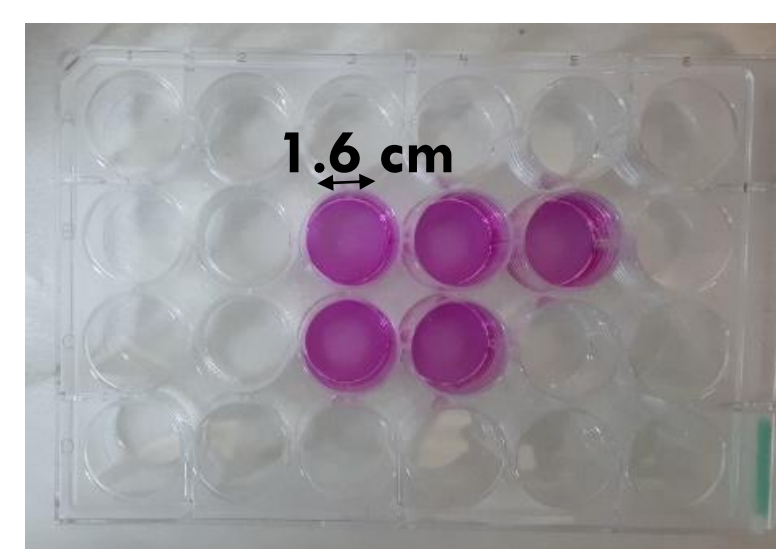
Aqueous solution of *Escherichia Coli* Gram negative bacteria in Tryptic soy broth/PBS



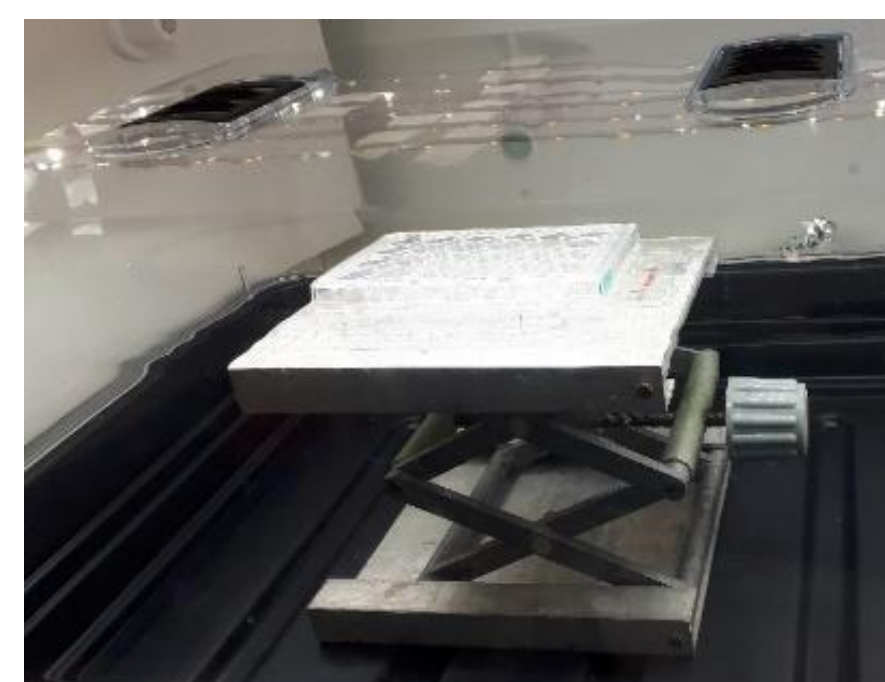
AFM picture of RB based latex films



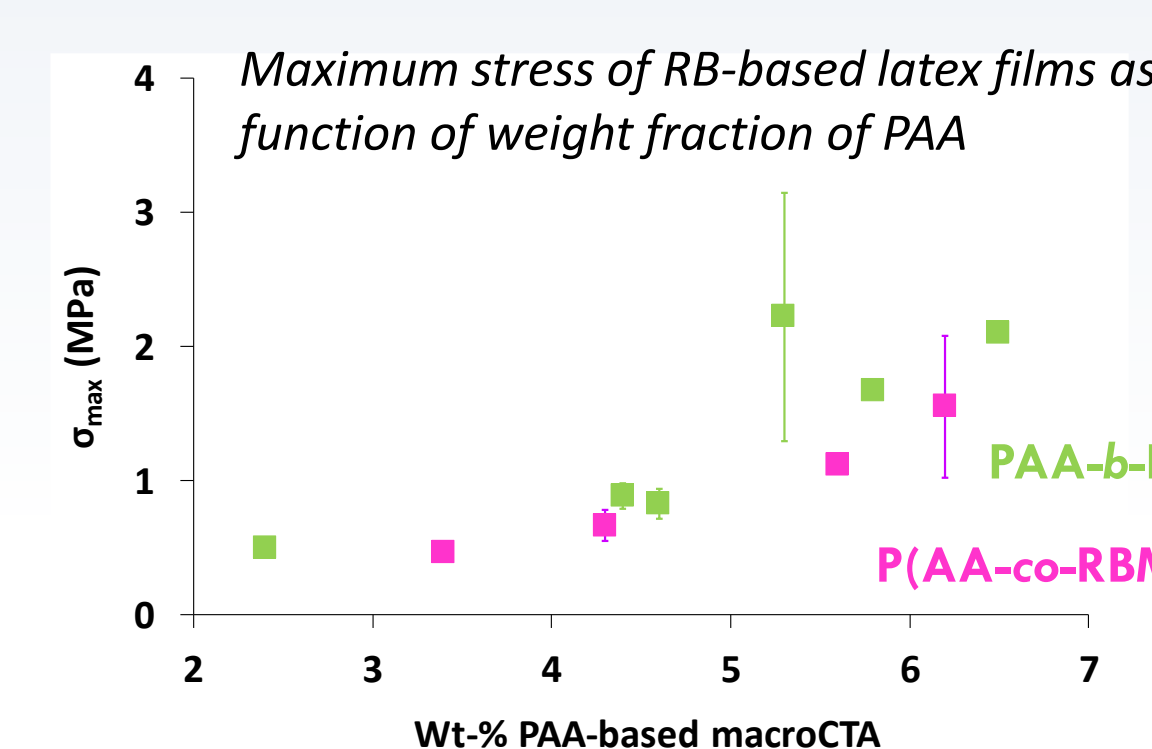
Casted annealed P(AA-co-EARB<sub>0.1%</sub>)<sub>70</sub>-b-PnBA<sub>700</sub> latex



Cell culture well plate 24 well, material: PS



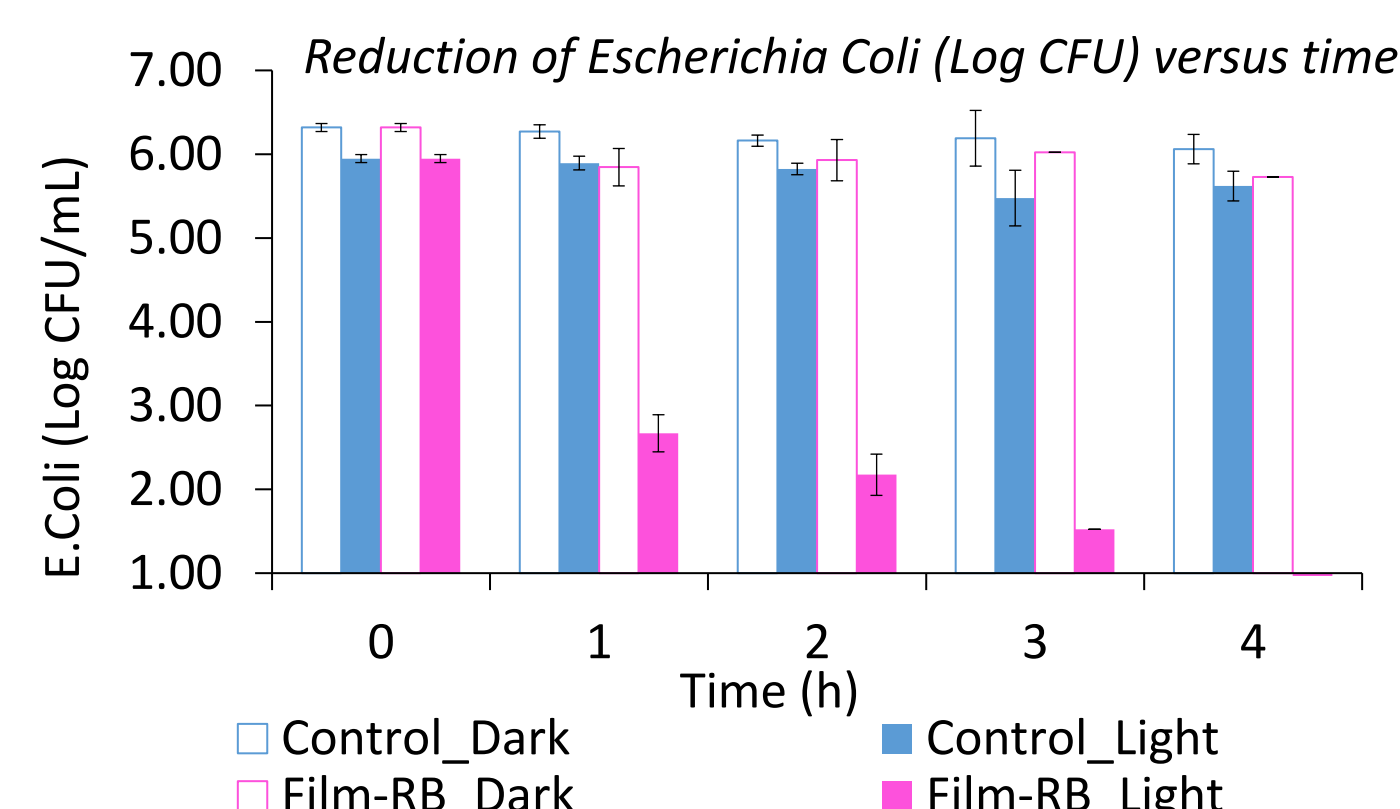
White led panel (5 mW.cm<sup>-2</sup>)



- ✓ Tunable mechanical properties according to PAA fraction
- ✓ Similar trend in the presence of photosensitizer in the shell

### Antibacterial activity against E.Coli

Collaboration P. Fernandez S. McMichael  
Ulster University



- Coating prepared by simple casting of film-forming polyacrylic waterborne latex
- ✓ Low level of leaching
- ✓ Low contact toxicity
- ✓ Inactivation of *E. Coli* bacteria under white light in 4 hours: efficient antibacterial coating

## Green Chemistry

## Conclusion

- Waste prevention**  
Recycle photosensitizer Supported on polymer colloids  
Separation procedures
- Atom economy**  
Photon Reduced steps  $h\nu$
- Hazard reduction**  
 $O_2$  from air as reactant  
Low energy LED sources / visible light
- Energy efficiency**  
Room T° photochemistry  
Process intensification Flow photochemistry  
Good level of photostability
- Safer solvents**  
Polymerization in dispersed media  
Eco-friendly solvent (EtOH, H<sub>2</sub>O)
- Renewable feedstocks**  
Carbon footprint  
Biobased feedstock photo-oxidized

- Syntheses of **photoactive** Rose Bengal based polymer particles
- **Versatile** media from polymer colloids (water, ethanol)
- **Versatile** and promising applications (coating->surface disinfection ; flow photooxygenation)

### Acknowledgements

The research projects have received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 893426 from ANR (APOFLOW project ANR-21-CE06-0038-01 and ANR-15-CE08-0005).

### References

- [1] L. Petrizza, M. Le Behec, E. Decompte, H. El Hadri, S. Lacombe, M. Save *Polymer Chemistry*. **2019**, *10*, 3170
- [2] M. Save, K. Loubière et coll. *ACS Sust. Chem. & Eng.* **2020**, *8*, 18568
- [3] C. Boussiron, M. Le Behec, L. Petrizza, J. Sabalot, S. Lacombe, M. Save *Macromol. Rapid. Commun.* **2018**, p 1800329.
- [4] C. Boussiron, M. Le Behec, J. Sabalot, S. Lacombe, M. Save *Polymer Chemistry* **2021**, *12*, 134 - 147