Nano/microgel-embedding as a tool for thermosensitive hydrogels with enhanced swelling properties

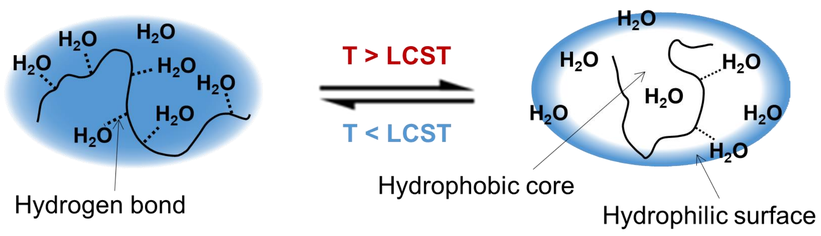
Charlotte Dai[1], Frédéric Demoly[2], Vincent Lapinte[1], Sébastien Blanquer[1*]

[1]Institut Charles Gerhardt de Montpellier, Université de Montpellier, CNRS, ENSCM, 34000 Montpellier, France / sebastien.blanquer@umontpellier.fr

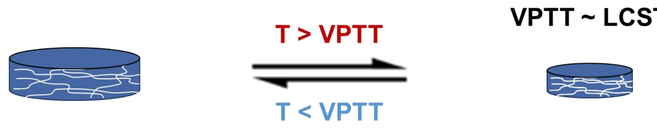
[2]ICB UMR 6303 CNRS, Université Marie et Louis Pasteur, UTBM, 90010 Belfort Cedex, France, Institut Universitaire de France

Current limitations of chemically crosslinked thermosensitive hydrogels

- **Lower Critical Solubility Temperature (LCST)** polymers[1]

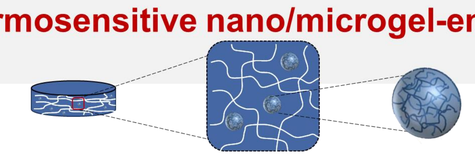


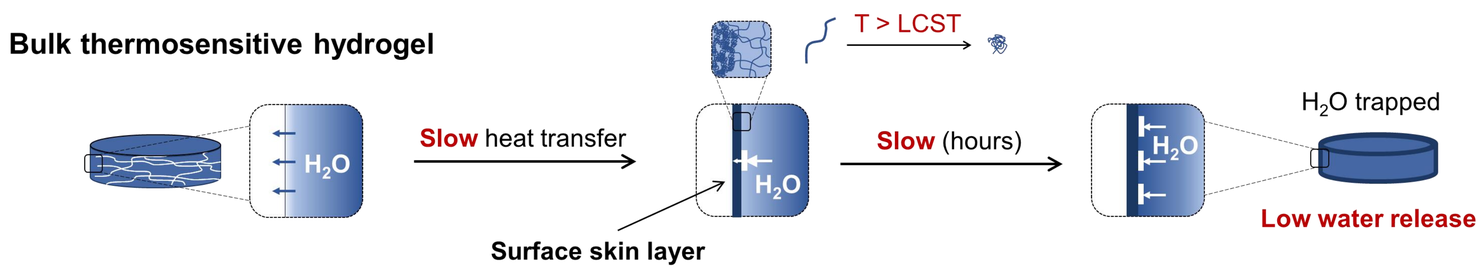
- **Volume Phase Transition Temperature (VPTT)** of hydrogels



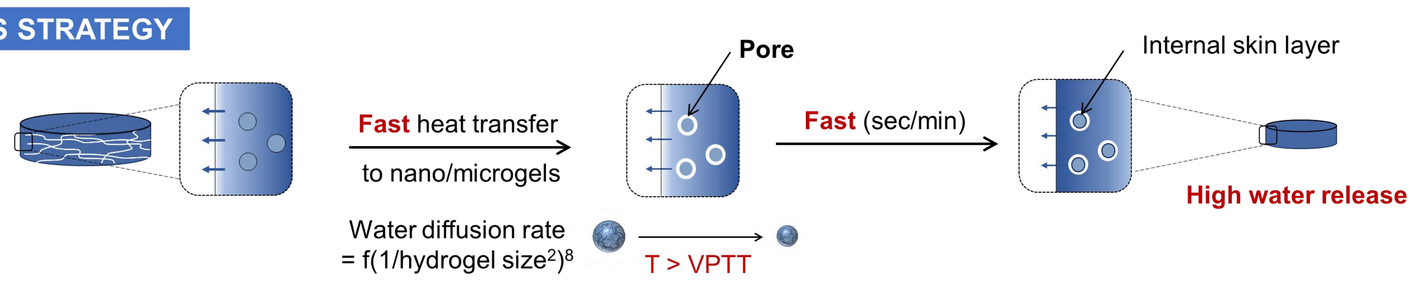
- Wide **applicability**: smart valves, grippers, drug delivery…
- **Slow responses, small deformations**

Adopted strategy: Thermosensitive nano/microgel-embedded thermosensitive hydrogels[2-7]





THIS STRATEGY



PNVCL

- *LCST around 32 °C*
- *Less toxic alternative to PNIPAM*

1 Study of bulk hydrogels

2 Synthesis of nano/microgels

3 Study of nano/microgel-embedding

- ❑ Swelling ratio at T (°C)?
- ❑ Swelling ratio difference?
- ❑ Kinetics?

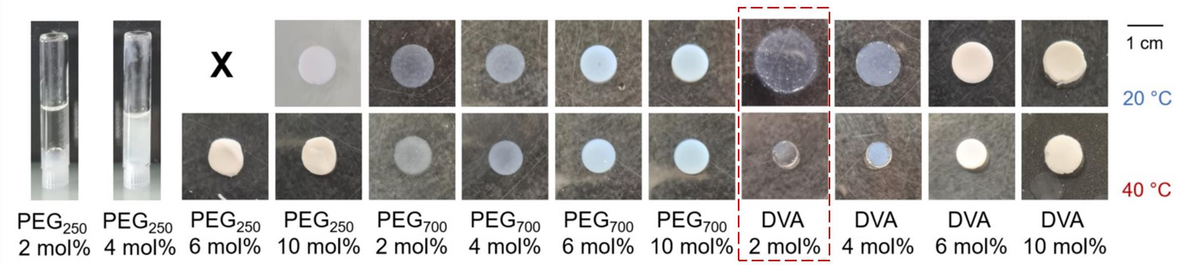
1 NVCL, **Crosslinker**, LAP, **H_2O/DEG**, UV irradiation 365 nm, 30 min ⟶ **Prepared PNVCL bulk hydrogels already exhibit high amplitude deformations**

- Influence of crosslinker type and crosslinker concentration on thermosensitivity

NVCL 25 wt%, H_2O/DEG 50/50 v/v, LAP 2 w/w% vs. NVCL + crosslinker

n ≈ 2-3 **$PEGDA_{250}$**
n ≈ 13-14 **$PEGDA_{700}$**

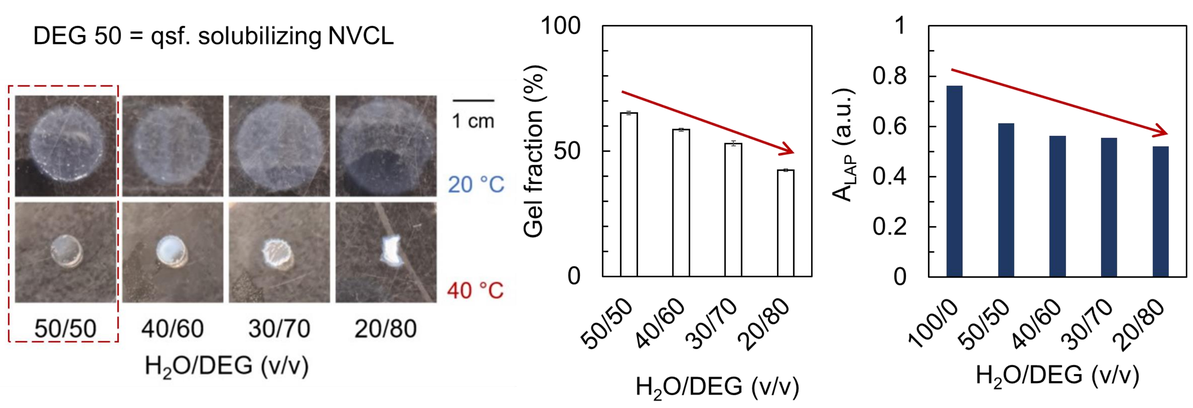
DVA



→ Better crosslinking with DVA vs. PEG700 vs. PEG250 (gel fraction 65% + ^{1}H NMR)
→ High deformability with DVA 2 mol% (water release 93 %)

- Influence of solvent composition on thermosensitivity

NVCL 25 wt%, DVA 2 mol%, LAP 2 w/w% vs. NVCL + crosslinker



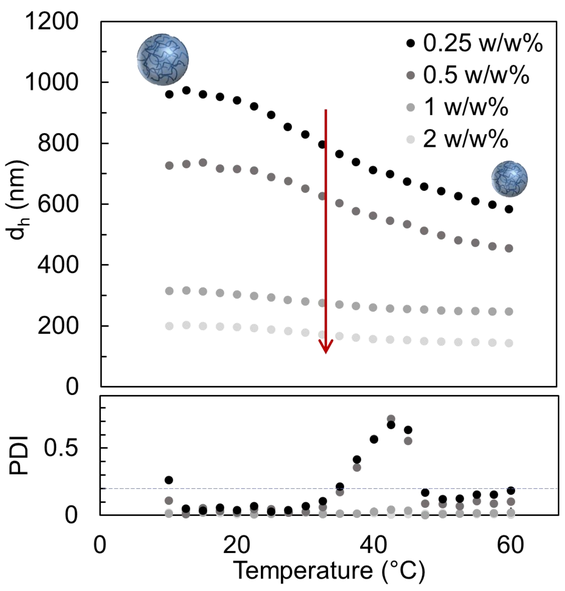
→ Lower gel fraction related to A_{LAP} decrease with increase in DEG content
→ Higher water release with increase in DEG content

1 NVCL, **Crosslinker**, KPS, **Stabilizer**, $NaHCO_3$ aq. buffer, 70 °C, 24 h ⟶ **PNVCL nano/microgels have tuneable sizes**

Dynamic Light Scattering (DLS) of diluted reaction medium

- Influence of stabilizer concentration on size

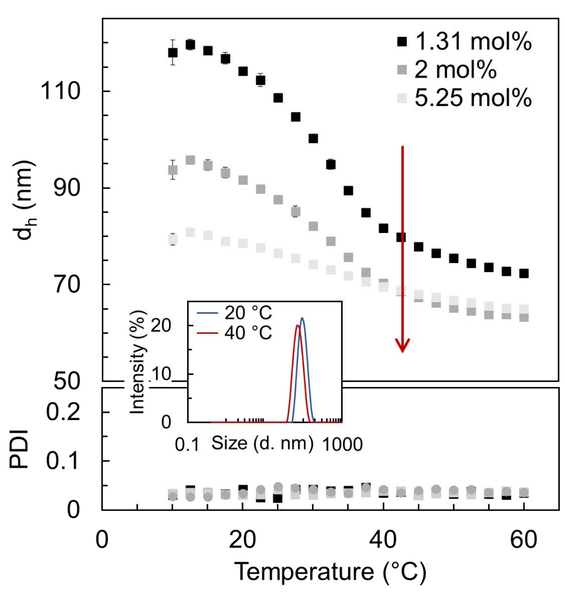
NVCL 1 wt%, DVA 2 mol%, $NaHCO_3$ and KPS 1 w/w% vs. NVCL + crosslinker



→ Smaller particles with increased SDS concentration

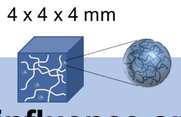
- Influence of crosslinker concentration

NVCL 1 wt%, SDS 4 w/w%, $NaHCO_3$ and KPS 1 w/w% vs. NVCL + crosslinker



→ Smaller particles with increased DVA concentration

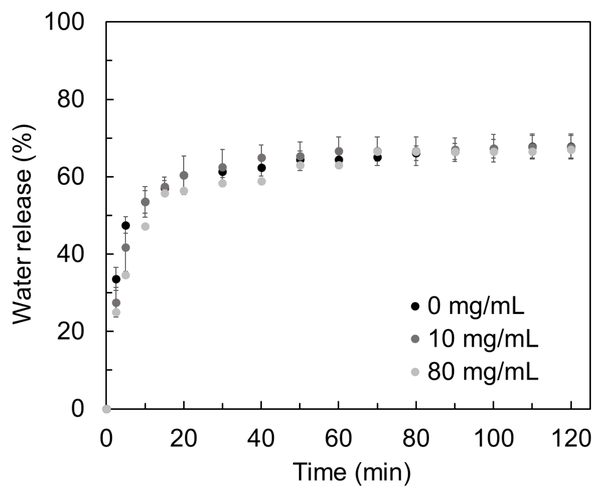
- ✓ Tuneable size (80 – 980 nm)
- ✓ Low dispersity (PDI < 0.2)
- ✓ VPTT around 32 °C
- ✓ Dispersible after drying

3 NVCL, Particles (**concentration,** size) ⟶ 

Under test conditions, nano/microgel-embedding has no influence on swelling properties

- Influence of nano/microgels concentration on swelling properties

Particles with DVA 2 mol%, SDS 4 w/w%

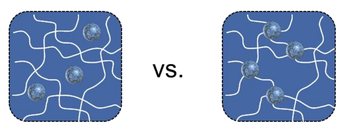


Deswelling kinetics from 20 °C to 40 °C

→ Incorporated particles have no influence on the water release nor on the deswelling kinetics

Perspectives

- ❑ Influence of particle size (nano vs. microgels)
- ❑ Nano/microgel-embedded vs. nano/microgel-crosslinked hydrogels[9]



References: 1. Sun S, Wu P. *J Phys Chem B*. 2011; 2. Hauck M, et al. *Advanced Materials*. 2023; 3. Zhang J, et al. *Macromol Rapid Commun*. 2005; 4. Zhang XZ, Chu CC. *Polymer*. 2005; 5. Gao Y, et al. *Chemical Engineering Journal*. 2023; 6. Wu P, Zhou H, Gao Y, et al. *Journal of Colloid and Interface Science*. 2024; 7. Liu J, et al. *Sensors and Actuators B: Chemical*. 2022; 8. Tanaka T, Fillmore DJ. *The Journal of Chemical Physics*. 1979; 9. Xia LW, et al. *Nature Communications*. 2013

A absorbance, **DEG** diethylene glycol, **d_h** hydrodynamic diameter (Z-average), **DVA** 3,9-Divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane, **Gel fraction (%)** = $m_{dried\ after\ washing}/m_{dried\ after\ UV}$ * 100, **KPS** potassium persulfate, **LAP** lithium phenyl-2,4,6-trimethylbenzoylphosphinate, **NIPAM** N-isopropylacrylamide, **NVCL** N-vinylcaprolactam, **PDI** polydispersity index, **PEGDA** polyethylene glycol diacrylate, **SDS** sodium dodecyl sulfate, **Swelling ratio at T (°C) SR_T (g/g)** = $m_{swollen\ at\ T\ after\ 24h}/m_{dried}$, **Water release (%)** = 100 * (1 – Mean $SR_{40\ °C}$ / Mean $SR_{20\ °C}$) or 100 * (1 – $area_{40\ °C}$ / $area_{20\ °C}$)

charlotte.dai@umontpellier.fr
www.icgm.fr