

Supporting information

Pickering emulsions stabilized by thermoresponsive oligo(ethylene glycol)-based microgels: effect of temperature-sensitivity on emulsion stability

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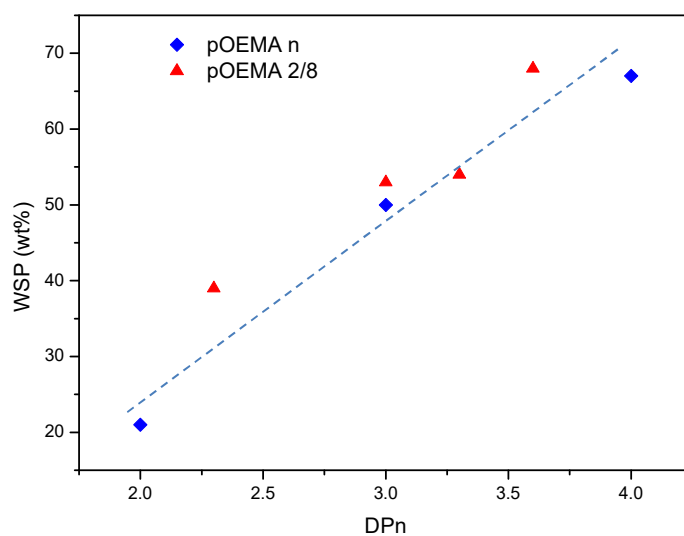


Figure S1. Evolution of the fraction of water-soluble species (WSP) as a function of microgel composition. The dotted line is a guide for the eye to evidence the linear variation of the WSP with EOn.

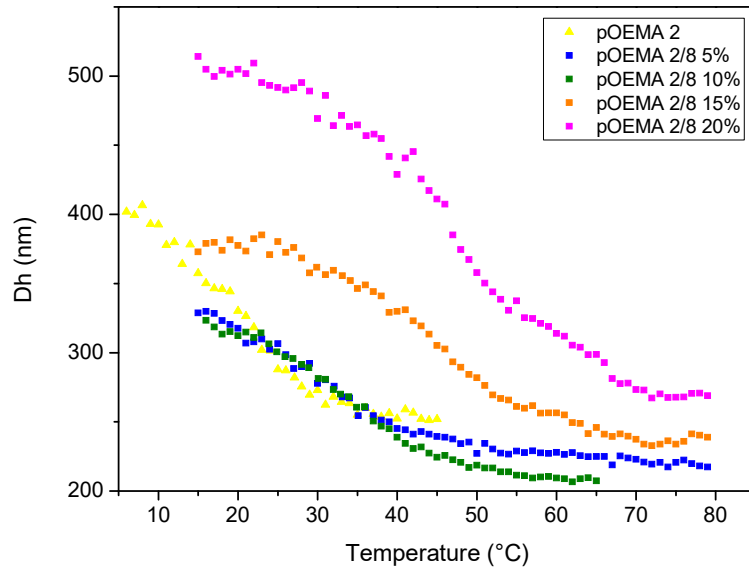
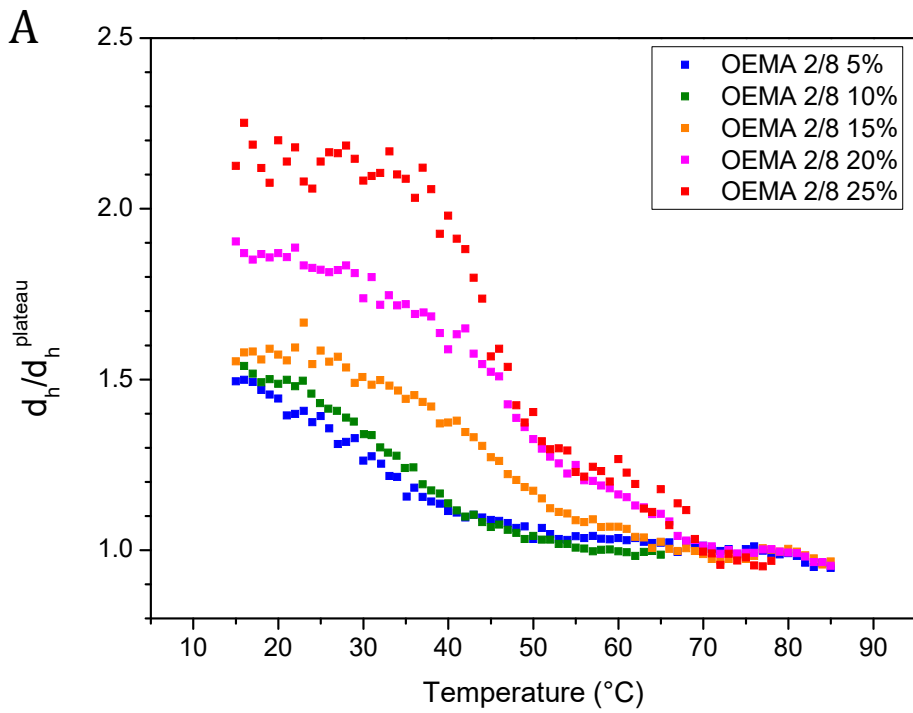


Figure S2. Close view of Fig. 3, showing the thermoresponsive behavior of microgels in pure water.



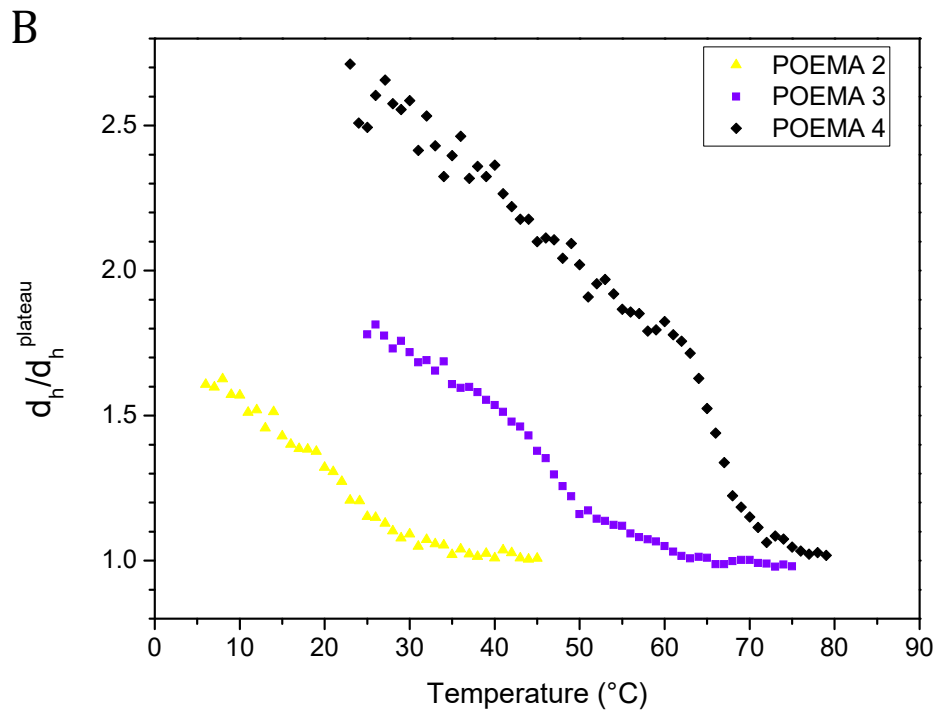


Figure S3. Normalized hydrodynamic diameter of the various nanogels as a function of temperature: pOEMA 2/8 series (A) and pOEMA n series (B).

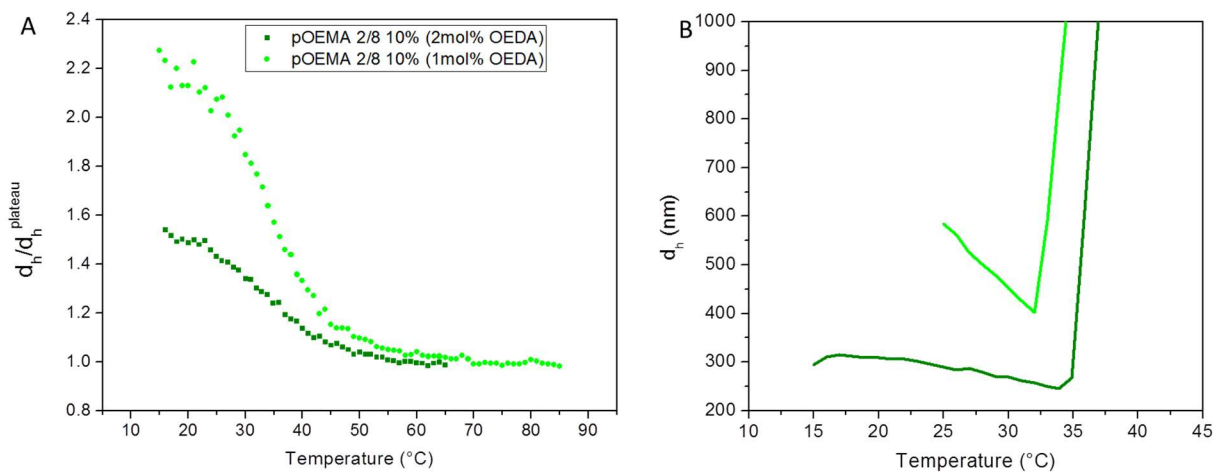


Figure S4. Influence of the cross-linking density on the thermoresponsive behavior of microgels (pOEMA 2/8 10 mol%): A. Evolution of the normalized hydrodynamic diameter in pure water, B. Evolution of the hydrodynamic diameter in 0.1 M NaCl, showing the onset of flocculation.

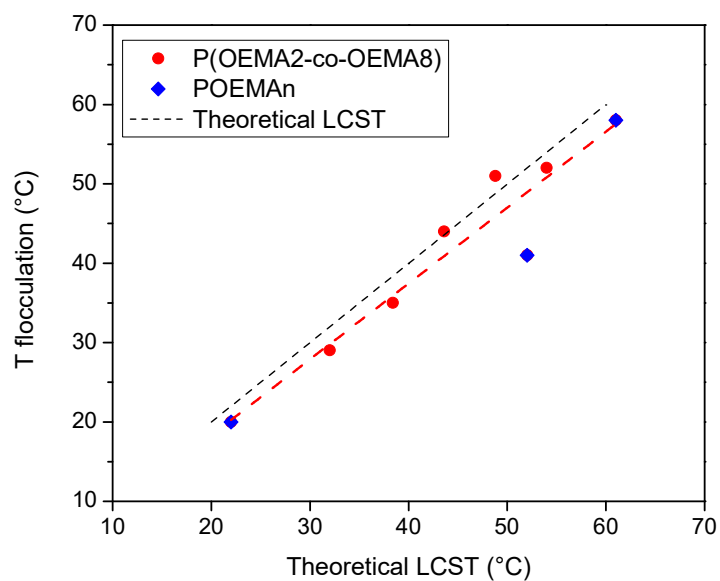


Figure S5. Correlation between the flocculation temperature and the theoretical LCST, obtained from [1, 2] for the homopolymers and [3] for the copolymers. The dotted black line correspond to unity that is to say to a perfect agreement between the theoretical LCST and the flocculation temperatures. The dotted red line is the best linear fit of the data.

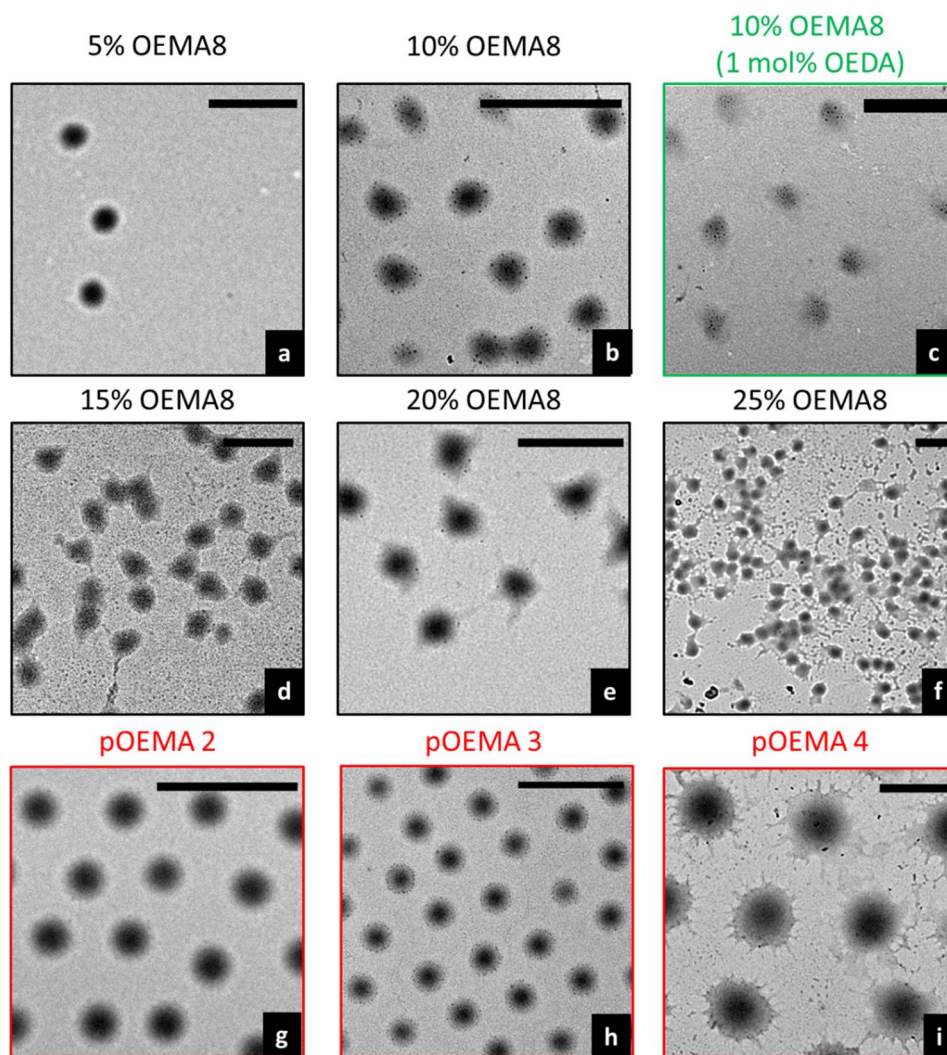


Figure S6. TEM views of the dried microgels: pOEMA 2/8, 5% (a), 10% (b, c), 15% (d), 20% (d), 25% (e), pOEMA n with n=2 (g), 3 (h), 4 (i). (c) and (d) were prepared with different cross-linker ratio, 2 mol%, and 1 mol% respectively.

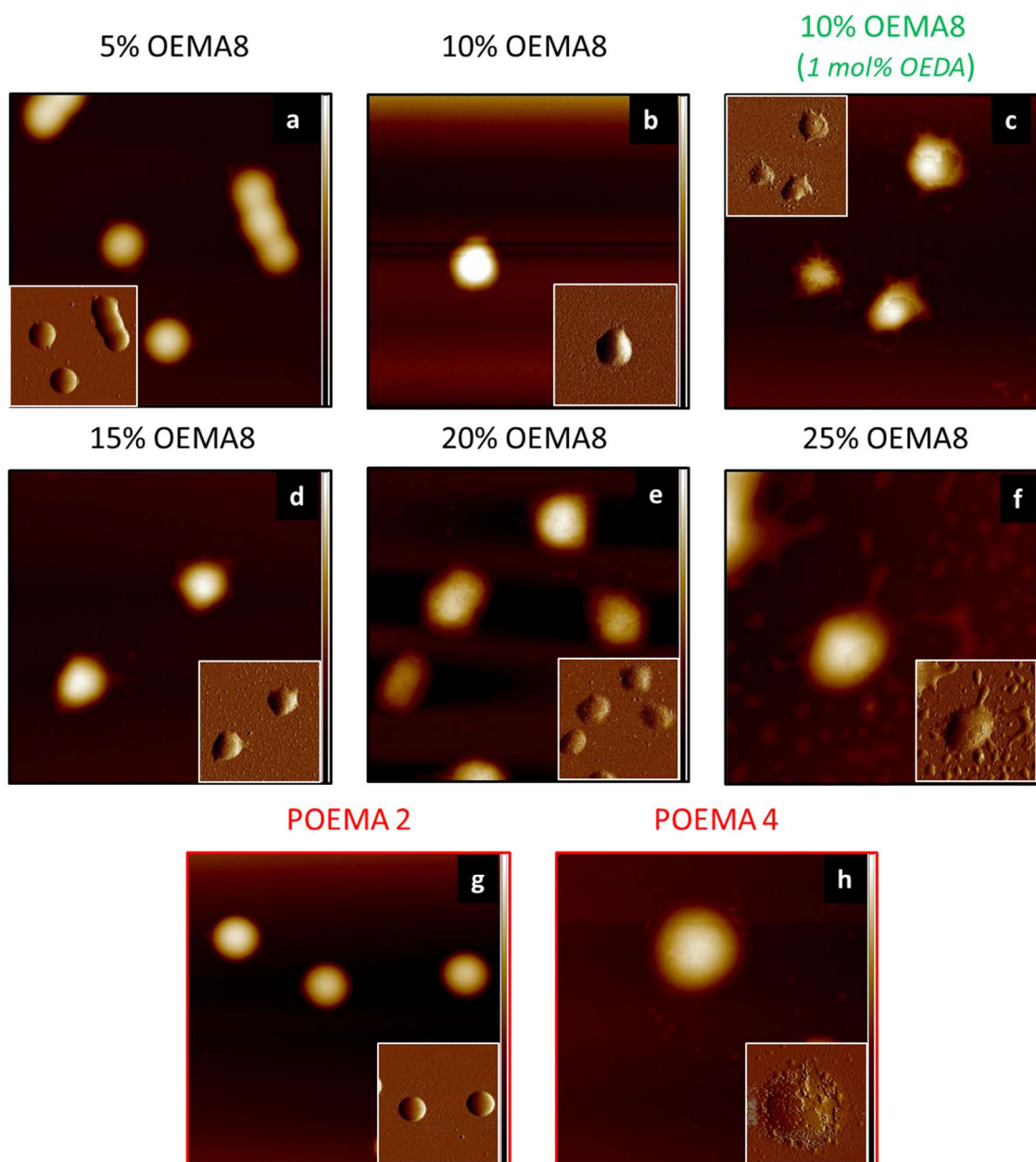


Figure S7. AFM images of the dried microgels. Height views and phase images insets of pOEMA 2/8, having 5 (a), 10 (b), 15 (d), 20 (d), 25 (e) pOEMA n with n=2 (g), 3 (h), 4 (i) with OEDA 2 mol%, and OEDA 1 mol% (c).

Table S8. AFM data

Microgel	FWHM (nm)	H _{max} (nm)	Ratio : H _{max} /FWHM
pOEMA 2/8 5%	370	140	0.38
pOEMA 2/8 10%	350	90	0.26
pOEMA 2/8 10% (1 mol% OEDA)	420	45	0.11
pOEMA 2/8 15%	400	80	0.2
pOEMA 2/8 20%	570	110	0.19
pOEMA 2/8 25%	750	83	0.11

pOEMA 2	370	130	0.35
pOEMA 4	850	105	0.12

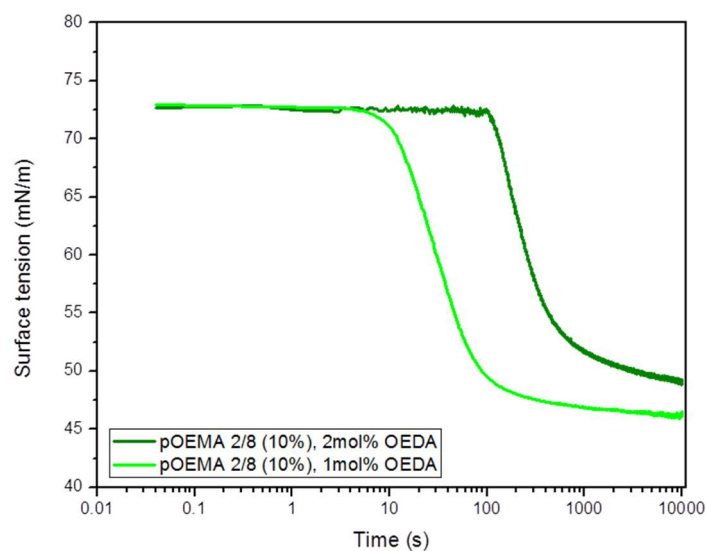


Figure S9. Influence of the cross-linking density on the surface tension for the pOEMA 2/8 containing 10 mol% of OEMA8.

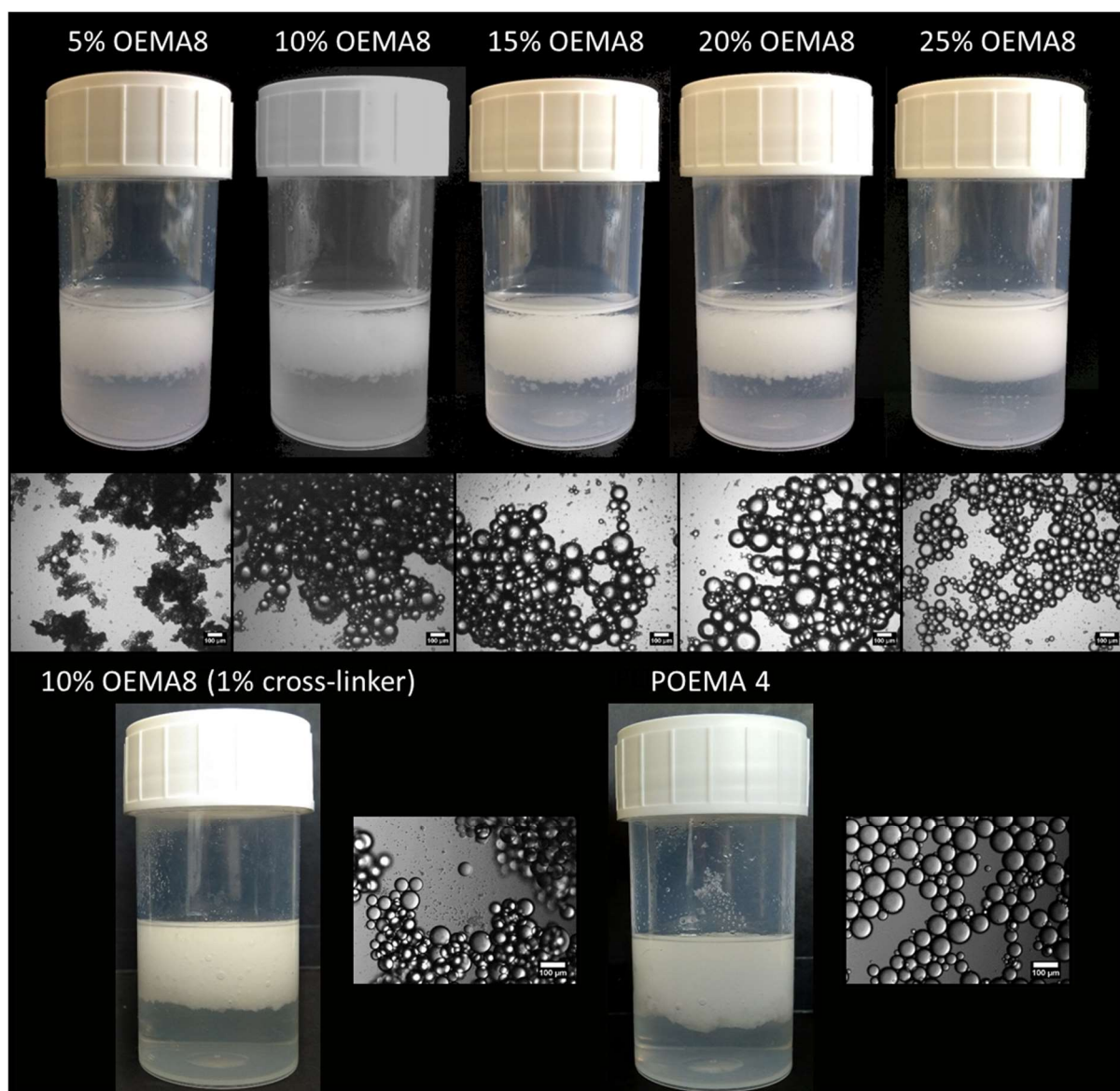


Figure S10. General view of the dodecane-in-water emulsions obtained using 0.05 wt% of microgels, at 22°C. The dodecane fraction is 30 wt%. Scale bar is 100 μm .

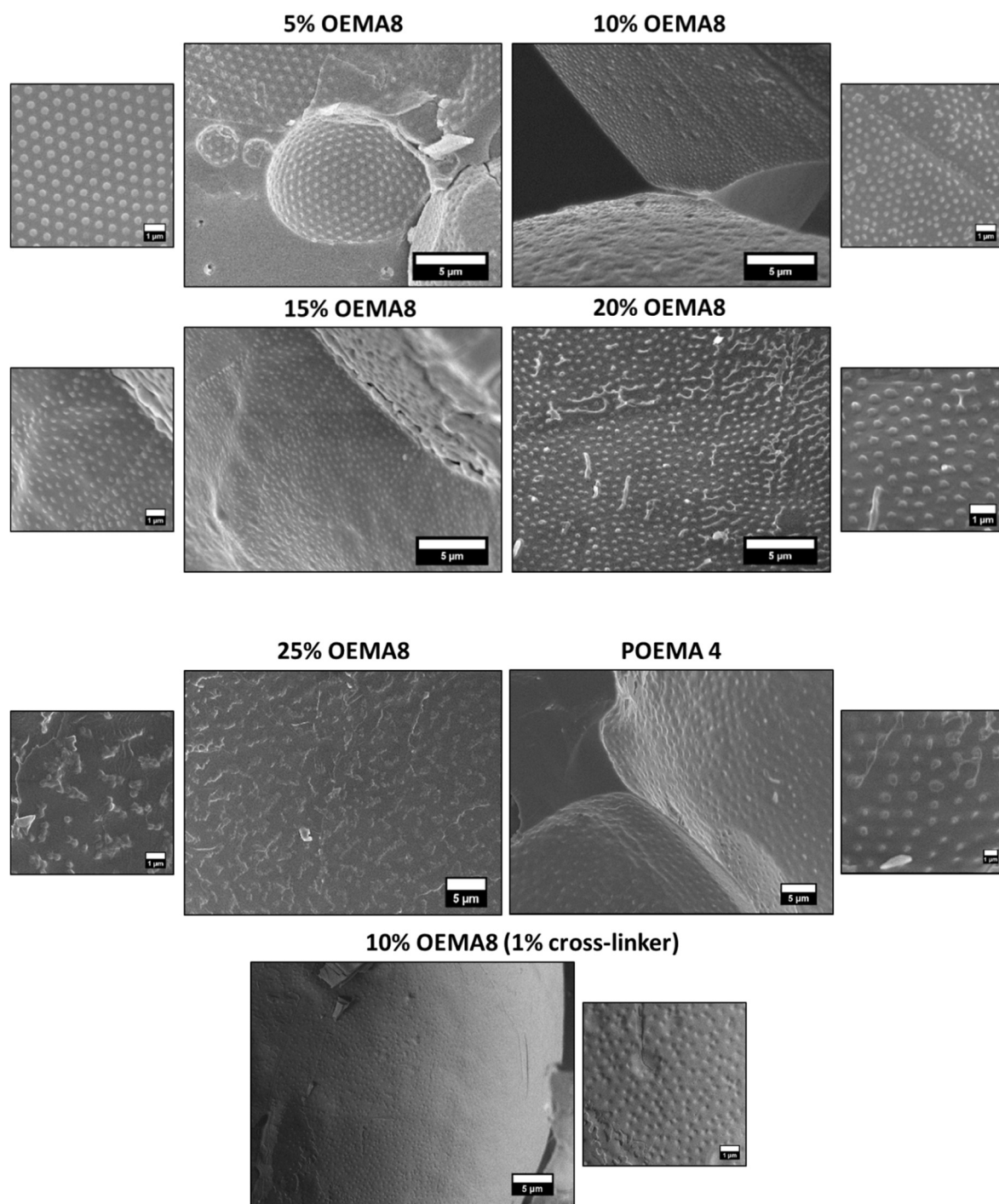


Figure S11. CryoSEM views of the microgels at the drop surface.

S12: Limited coalescence process

Limited coalescence arises in Pickering emulsions where particles are irreversibly anchored at the oil–water interface [4-6]. If the system is emulsified with a low amount of particles, the newly created droplets are insufficiently protected by the particles. When the agitation is

stopped, the droplets coalesce, thus reducing the total amount of oil–water interface. Since the particles are irreversibly adsorbed, the coalescence process stops as soon as the oil–water interface is sufficiently covered and the resulting emulsions exhibit remarkably narrow size distributions ($P < 30\%$) [6]. The final surface area of the droplets depends on the initial amount of particles and on their arrangement at the interface. For emulsions undergoing limited coalescence, the final interfacial particle coverage can be directly deduced from the surface average drop size, D . Indeed, the total interfacial area S_{int} of the emulsion is directly linked to D ($S_{int} = 6V_d/D$, where V_d is the oil volume). Assuming that all the particles are adsorbed, the interface area that the particles may cover is estimated from their equatorial section $S_{eq} = n_{particles} \pi (d_{H \text{ at } 22^\circ\text{C}}/2)^2$, where $n_{particles}$ is the total number of particles deduced from Eq. 3 and $d_{H \text{ at } 22^\circ\text{C}}$ is their hydrodynamic diameter at 22°C . The surface coverage, C , defined as $C = S_{eq}/S_{int}$ can thus be estimated after measuring D :

$$\frac{1}{D} = \frac{n_{particles} \pi d_{H \text{ at } 22^\circ\text{C}}^2}{24 C V_d} = \frac{S_{eq}}{6 C V_d} \quad (2)$$

Following the work published by Lele *et al.* [7] it was considered that a particle is composed of 71 wt.% of polymer and 29 wt.% of bound water at 50°C . From the hydrodynamic particle diameter, $d_{H \text{ at } 50^\circ\text{C}}$, measured by DLS at 50°C , the particle number $n_{particles}$ was estimated as:

$$n_{particles} = \frac{6m_{polymer}}{\pi (d_{H \text{ at } 50^\circ\text{C}})^3} \left(\frac{1}{\rho_{polymer}} + \frac{0.29}{0.71 \rho_{water}} \right) \quad (1)$$

where $\rho_{polymer} = 1.15 \text{ g.cm}^{-3}$ [8], and $\rho_{water} = 0.988 \text{ g.cm}^{-3}$ are respectively the polymer and water densities.

Equation 2 shows that the surface coverage characterizing the particle packing at the interface can directly be deduced from a drop size measurement in the low particle concentration regime where the average inverse droplet diameter is proportional to S_{eq}/V_d .

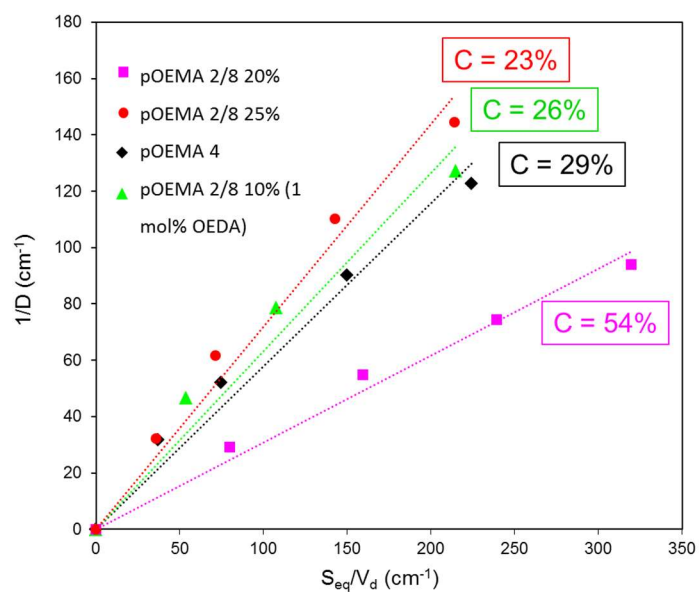


Figure S13. Limited coalescence process of the four samples: pOEMA 2/8 20%, pOEMA 2/8 25%, pOEMA 4 and pOEMA 2/8 10% with 1 mol% of cross-linker; $T=22^{\circ}\text{C}$.

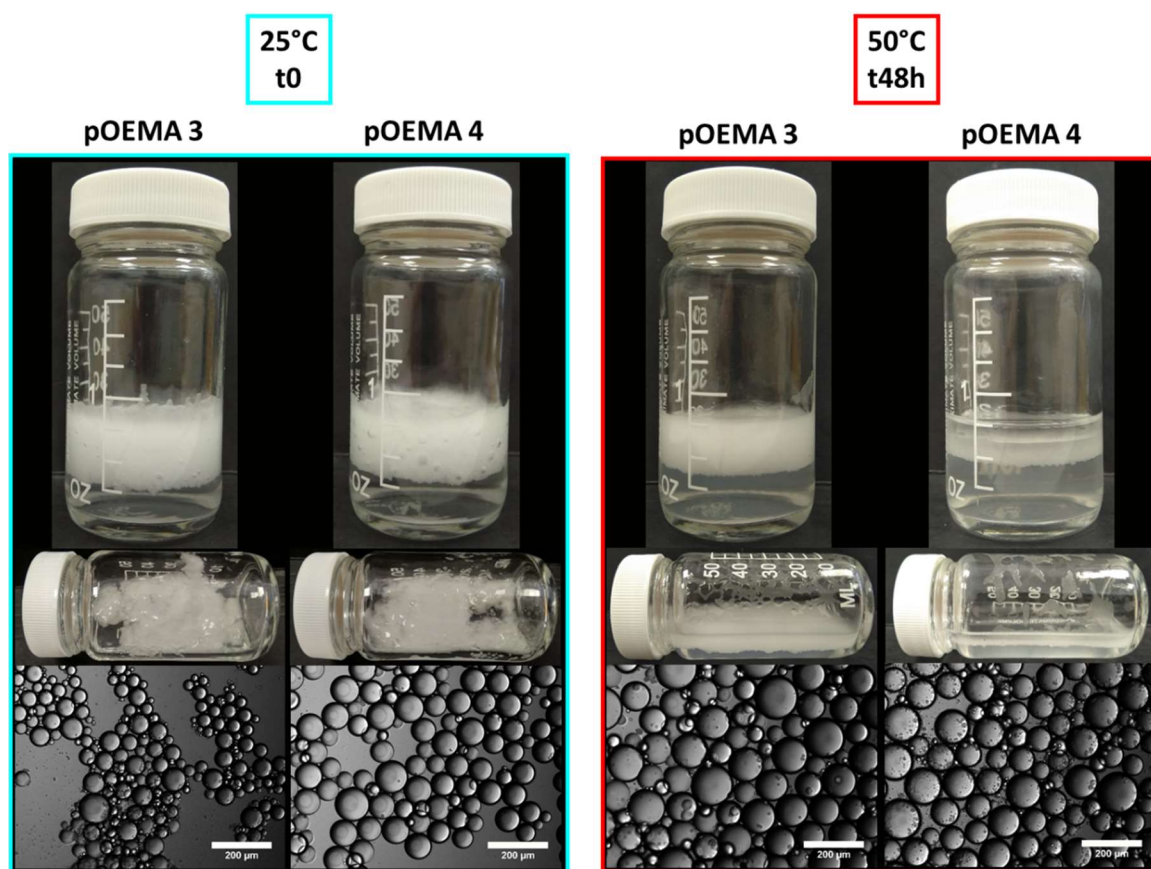


Figure S14. Thermal stability at 22°C and after 48 hours at 50°C of emulsions stabilized by pOEMA n.

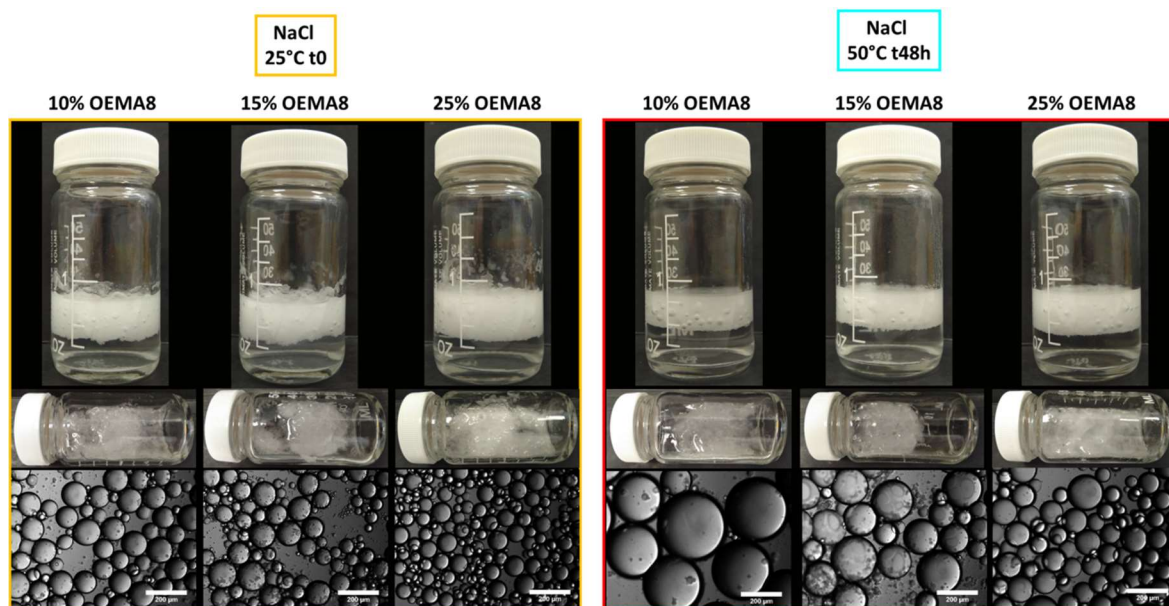


Figure S15. Evolution of the emulsion properties and stability upon temperature increase; in NaCl 0.1M. Emulsions stabilized by different microgels: pOEMA 2/8 containing respectively 10, 15, and 25% of OEMA 8. The micrographs show the emulsion in the quiescent state, after creaming (top row), after tilting the vial (intermediate row) and optical microscopy images of the drops (low row, scale bar is 200 μm) at 22°C and 50°C.

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