Electronic Supplementary Information

A Mechanistic Investigation of Pickering Emulsion Polymerization

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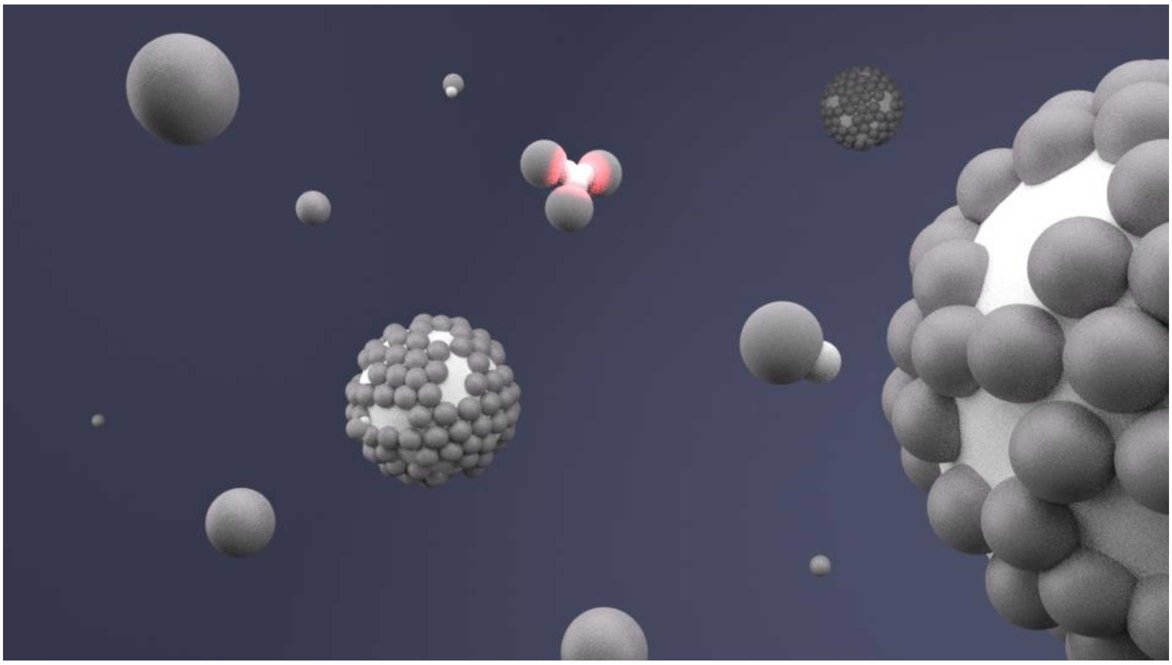

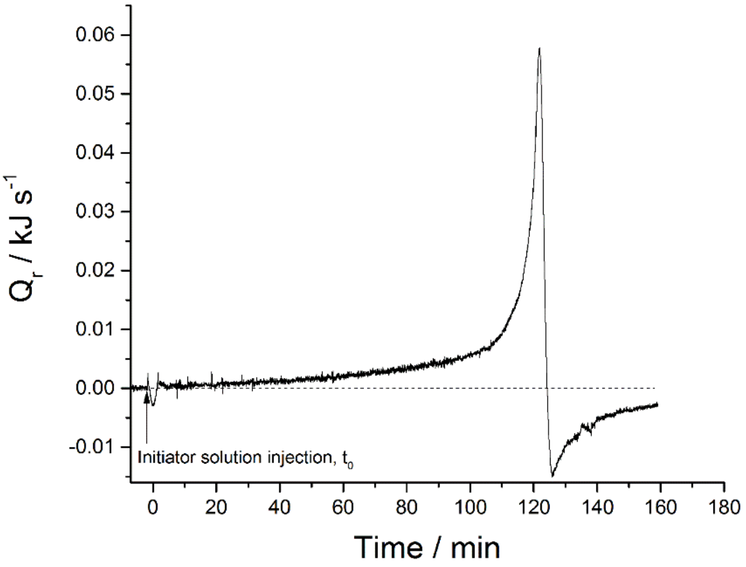

Figure S1. Variation of the heat of reaction (Q_r) for the Pickering emulsion polymerization of methyl methacrylate (MMA) and SiO_2 for SiO_2/M = 0.00 w/w.

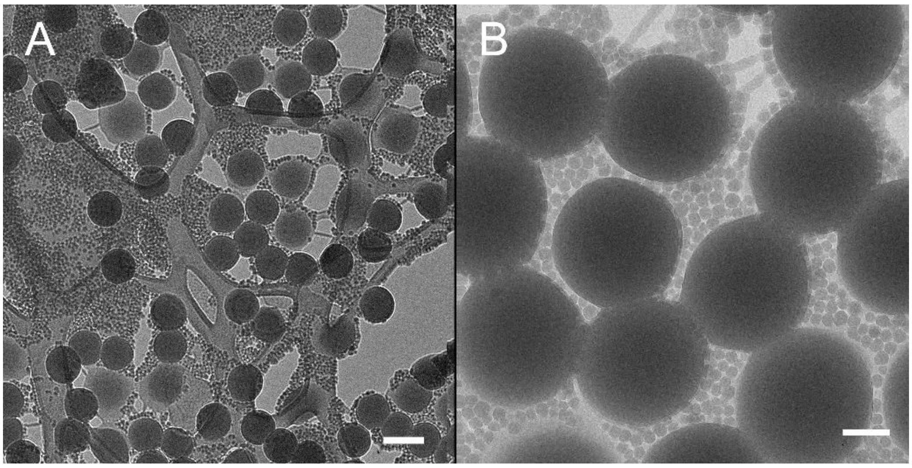

Figure S2. Cryo-TEM pictures of soap-free monomer-swollen PMMA latex particles (average diameter ~ 180 nm) in the presence of Ludox TM-40 at pH 4.5. Scale bars a) 400 nm and b) 100 nm.

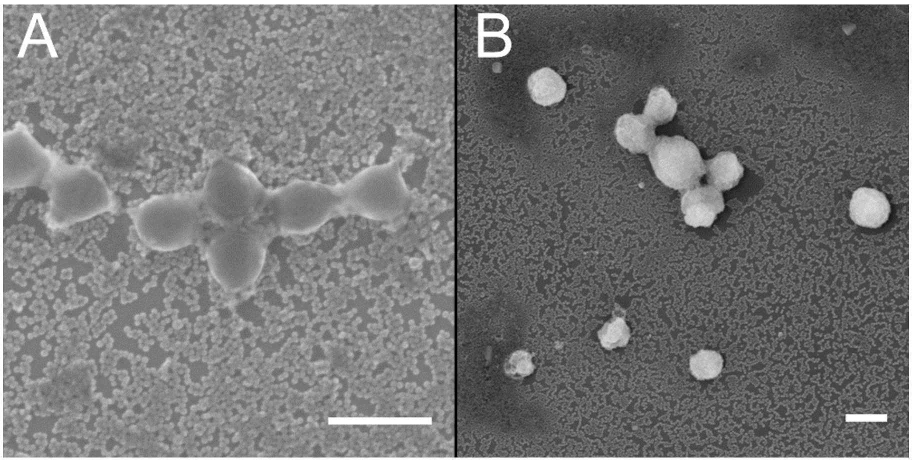

Figure S3. SEM pictures of a) 280 nm PMMA latex particles swollen with MMA in the presence of colloidal SiO_2 and b) of a 350 nm PMMA latex swollen with MMA and in the presence of colloidal SiO_2 after the application of ultrasounds. Scale bar 500 nm.

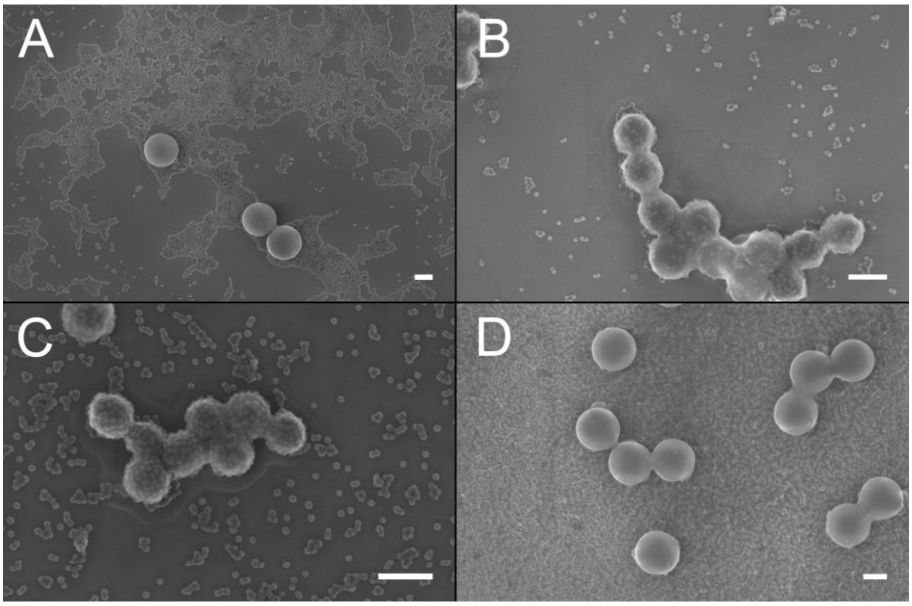

Figure S4. SEM images of the latex particles resulting from the Pickering emulsion polymerization of styrene a) in the absence of comonomer, in the presence of b) 1.0 wt% (with respect to styrene) and c) 3.0 wt% of di(ethylene glycol) ethyl ether acrylate, in the presence of d) 1.0 wt% of methacrylic acid. Scale bars 300 nm.

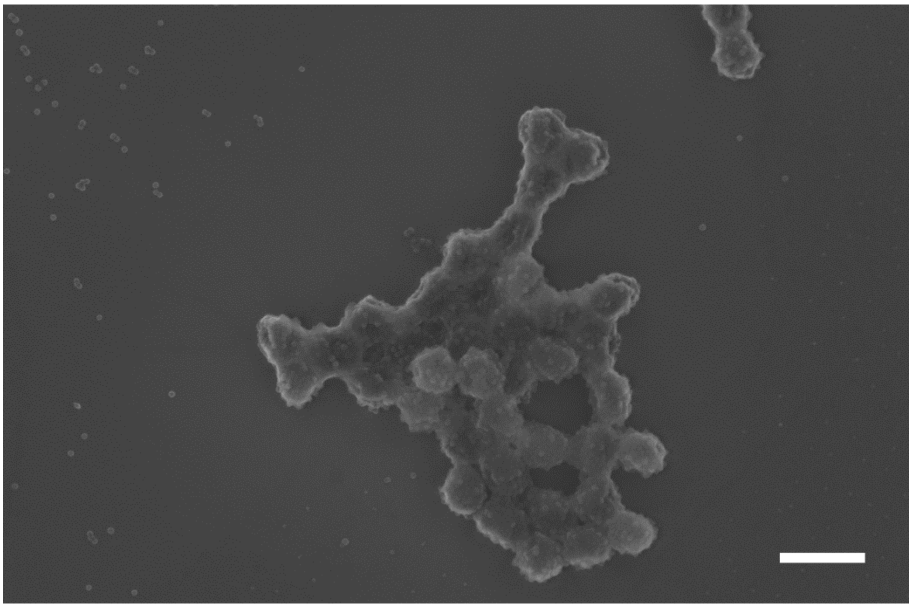

Figure S5. Pickering emulsion polymerization of MMA in the presence of colloidal SiO_2 for SiO_2 = 0.50 w/w. Scale bar 500 nm.

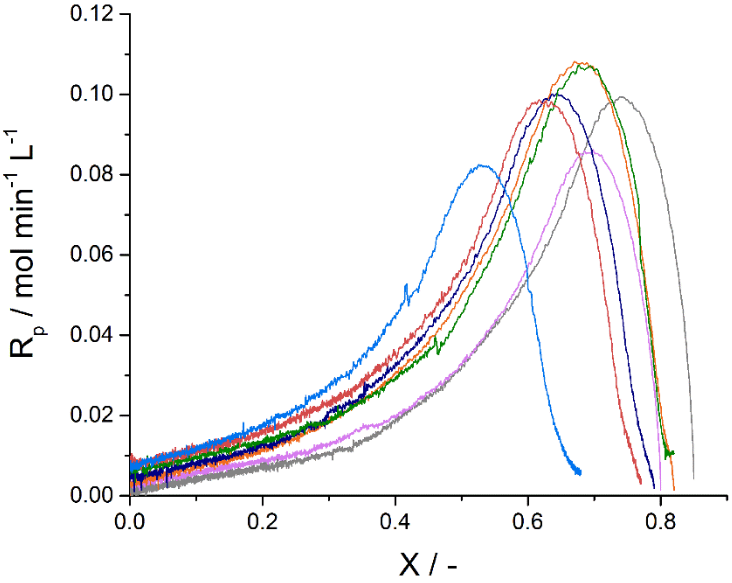

Figure S6. Variation in the polymerization rate (R_p) for the Pickering emulsion polymerization of MMA in the presence of nanosilica. SiO_2/M = 0.00 (grey), 0.10 (pink), 0.50 (orange), 0.75 (dark blue), 1.00 (green), 1.50 (red), 2.00 (light blue) w/w.

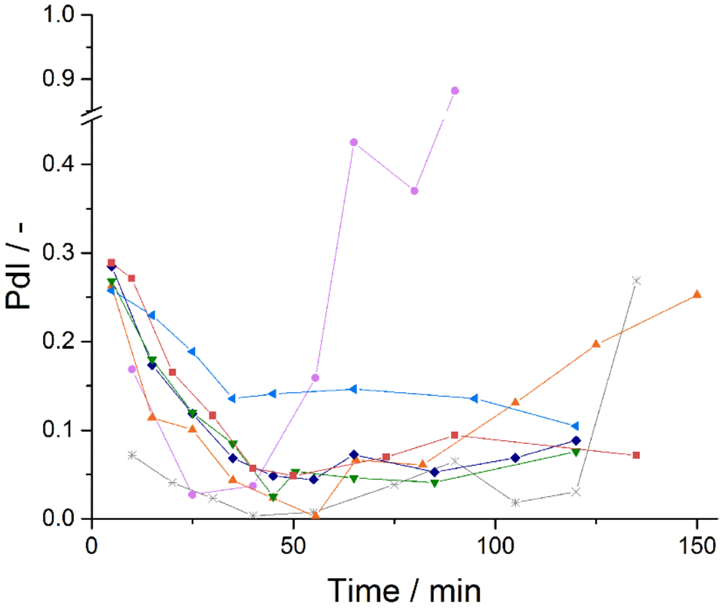

Figure S7. Variation of the particle size dispersity (*PdI*) with time for the Pickering emulsion polymerization of MMA in the presence of different SiO_2-to-monomer contents (SiO_2/M w/w). SiO_2/M = 0.00 (grey), 0.10 (pink), 0.50 (orange), 0.75 (dark blue), 1.00 (green), 1.50 (red), 2.00 (light blue) w/w.

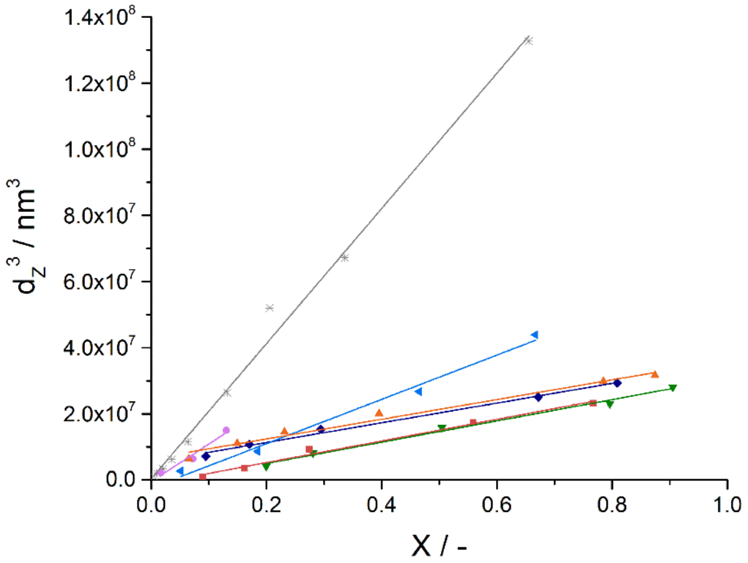

Figure S8. Graph showing the third dependence of the latex particle diameter according to DLS (d_Z^3) with monomer conversion (X). Here the experimental points not used for the interpolation are hidden. SiO_2/M = 0.00 (grey), 0.10 (pink), 0.50 (orange), 0.75 (dark blue), 1.00 (green), 1.50 (red), 2.00 (light blue) w/w.

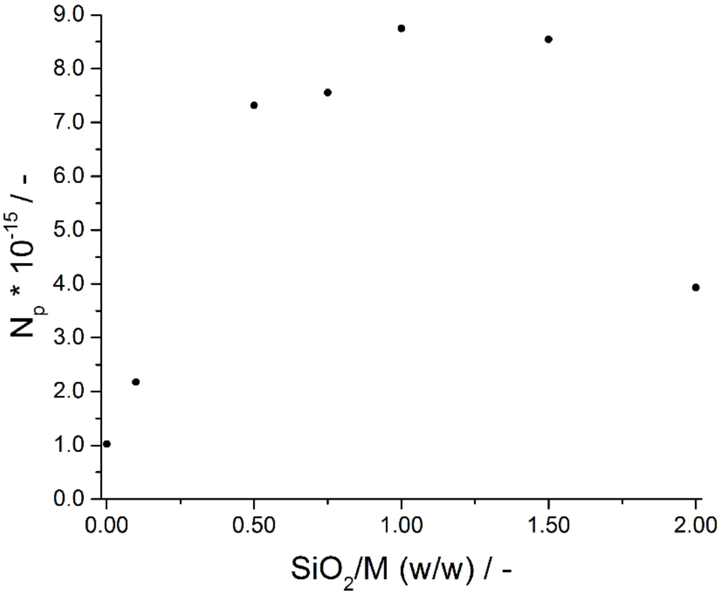

Figure S9. Number of nucleated particles (N_p) for the Pickering emulsion polymerization of MMA in the presence of nanosilica.

Derivation of equation 8

The parameter f was defined as the ratio between the total surface area of silica and latex (nanocomposite) particles at a given time t, $SA_{SiO_2,t}$ and $SA_{L,t}$:

(1)
$$f = \frac{SA_{SiO_2,t}}{SA_{L,t}} = \frac{SA_{SiO_2,0} - SA_{SiO_2,ads}}{\pi d_{L,t}{}^2 N_{L,t}}$$

where $SA_{SiO_2,0}$ and $SA_{SiO_2,ads}$ are respectively the surface area of the initial silica and the one adsorbed at the latex (nanocomposite) particles; $N_{L,t}$ is the number of nucleated latex particles at the time t; $d_{L,t}$ is the average diameter of these particles according to dynamic light scattering.

From equation 1, the two silica surface areas can be written as the product of the surface area of a single silica nanoparticle, SA_{SiO_2}, and the total number of silica particles N_{SiO_2}.

(2)
$$f = \frac{SA_{SiO_2}\left(N_{SiO_2,0} - N_{SiO_2,ads}\right)}{\pi d_{L,t}^{\;2}\left(\dfrac{m_{M,0}X_t}{\rho_p V_{latex.part,t}}\right)}$$

where the number of latex nucleated particles at a time *t*, $N_{L,t}$ was calculated from the initial monomer mass $m_{M,0}$, the polymer density ρ_p and the volume of the polymer phase of one latex nanocomposite particle at time *t*, $V_{latex.part,t}$.

An expression for $N_{SiO_2,ads}$ was developed from an equation previously derived to predict the amount of silica nanoparticles in suspension at a given time *t* in Pickering emulsion polymerization[1]. $N_{SiO_2,0}$ can be expressed using the volume of a single silica nanoparticle $V_{SiO_2.part,t}$, similarly to what was done with $N_{L,t}$.

(3)
$$f = \frac{\pi d_{SiO_2}^{\;2}\left(\dfrac{m_{SiO_2,0}}{\rho_{SiO_2}V_{SiO_2.part,t}} - \dfrac{6m_{M,0}X_t}{d_{SiO_2}^{\;2}\rho_p P\beta d_{L,t}}\right)}{\pi d_{L,t}^{\;2}\left(\dfrac{m_{M,0}X_t}{\rho_p V_{latex.part,t}}\right)}$$

where $m_{SiO_2,0}$ is the initial silica mass and ρ_{SiO_2} is its density; d_{SiO_2} is the average silica diameter measured with SEM; P is a packing parameter and β is a correction factor to account for the nonsmooth nature of the raspberry-type particles and the use of the hydrodynamic diameters instead of the actual ones.

From equation 3, $V_{SiO_2.part,t}$ and $V_{latex.part,t}$ can be substituted from the respective particles diameters. The volume of the polymer phase of one latex particle at time t was calculated from

$d_{L,t}$ by correcting for the diameter of the silica shell (assumed to be equal to d_{SiO_2}, in the case of spheres half embedded on the surface).

(4)
$$f = \frac{\pi d_{SiO_2}{}^2 \left(\frac{6 m_{SiO_2,0}}{\pi \rho_{SiO_2} d_{SiO_2}{}^3} - \frac{6 m_{M,0} X_t}{d_{SiO_2}{}^2 \rho_p P \beta d_{L,t}} \right)}{\pi d_{L,t}{}^2 \left(\frac{6 m_{M,0} X_t}{\pi \rho_p \left(d_{L,t} - d_{SiO_2} \right)^3} \right)}$$

The mathematical rearrangement of equation 4 brings to equation 5, that is equivalent to equation 8 from the main paper text.

(5)
$$f = \frac{m_{SiO_2,0} \rho_p \left(d_{L,t} - d_{SiO_2} \right)^3}{m_{M,0} X_t \rho_{SiO_2} d_{SiO_2} d_{L,t}{}^2} - \frac{\pi \left(d_{L,t} - d_{SiO_2} \right)^2}{d_{L,t}{}^2 P \beta}$$

REFERENCES

(1) Colard, C. A. L.; Teixeira, R. F. A.; Bon, S. A. F. *Langmuir* **2010**, *26* (29), 7915–7921.