Electronic Supplementary Material (ESI) for Polymer Chemistry.

Surfactant-free synthesis of layered double hydroxide-armored latex particles

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Effect of MAA on LDH particles size

A series of experiments was carried out to demonstrate that MAA can effectively interact with the LDH platelets and promote their aggregation. The MAA concentration was varied such as to cover the range of HEMA molar concentration used in the Pickering emulsion polymerization experiments, which are reminded on top of Table S1. The results show that the LDH particles size increases with increasing the MAA concentration supporting the assumption of MAA interaction with the LDH sheets.

Table S1. Effect of the addition of MMA on LDH particles size

Run	/	H02	H04
HEMA (wt%)[a]	0	40	80
HEMA (mol%)[b]	0	0.4	0.8
Control experiments			
MAA (wt%)[a]	0	38.3	77.5
MAA (mol%)[b]	0	0.4	0.9
$Z_{av.}$ (nm)[c]	70	128.9	361
PdI[c]	0.27	0.25	0.95

[a]Weight and [b] Mole percentages based on the amount LDH. [c] Determined by DLS

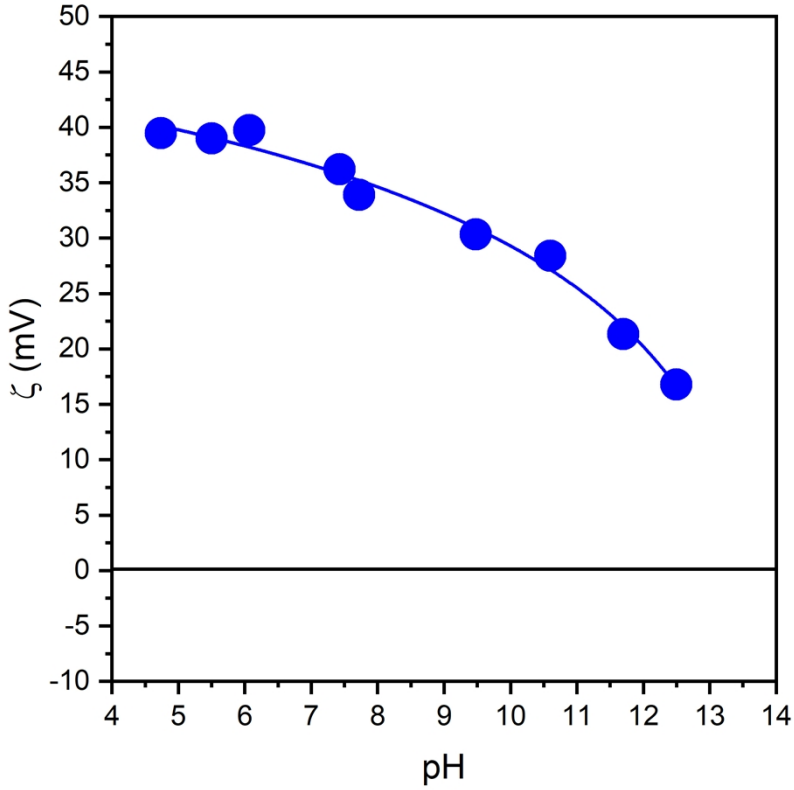

Figure S1. Zeta potential values of the MgAL LDH particles as a function of pH.

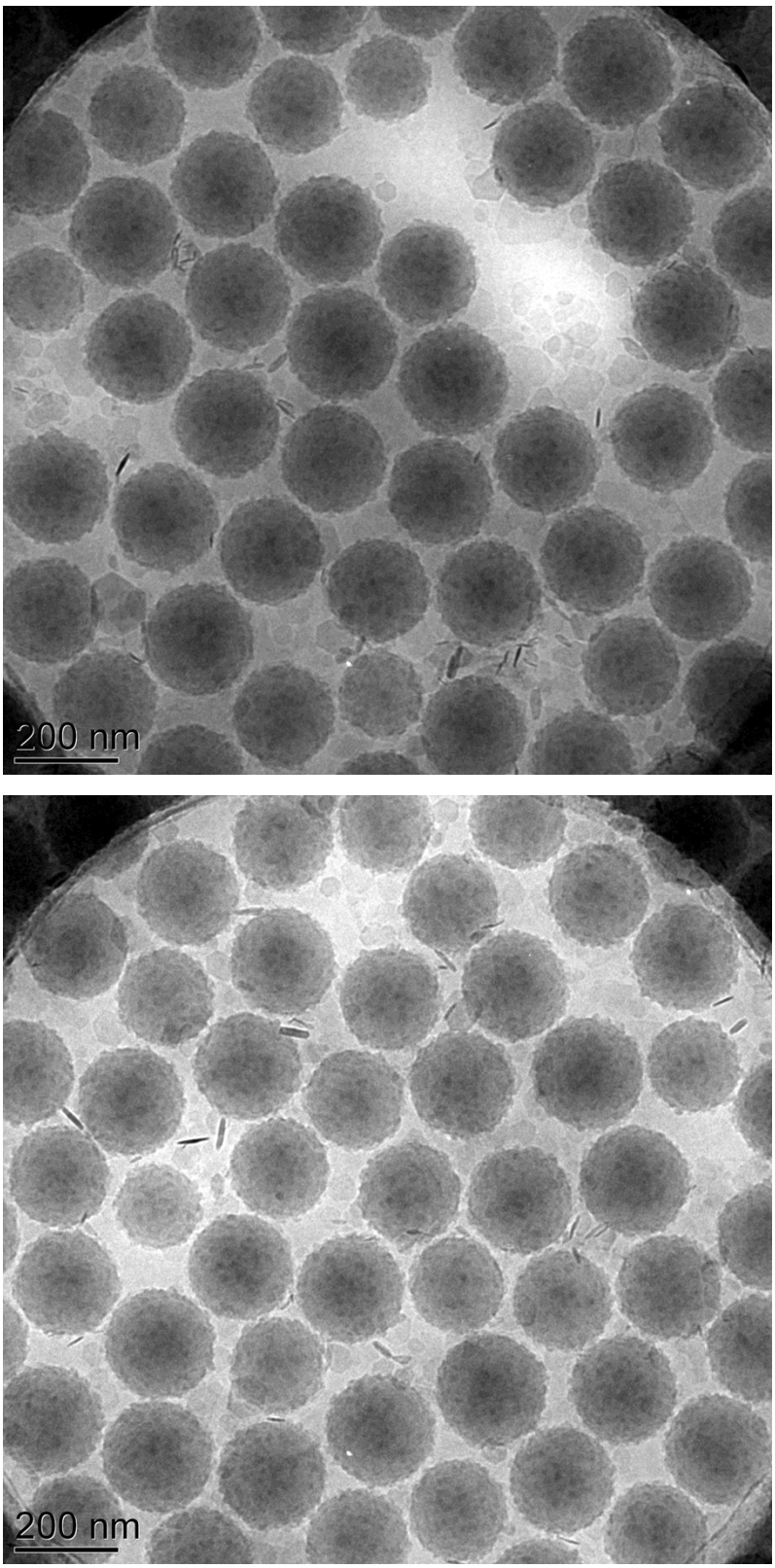

Figure S2. Cryo-TEM images of the particles obtained from blends of LDH platelets and the surfactant-free latex synthesized in the presence of HEMA (H01 in Table 1) in the same proportion as in H04 (Table 1).

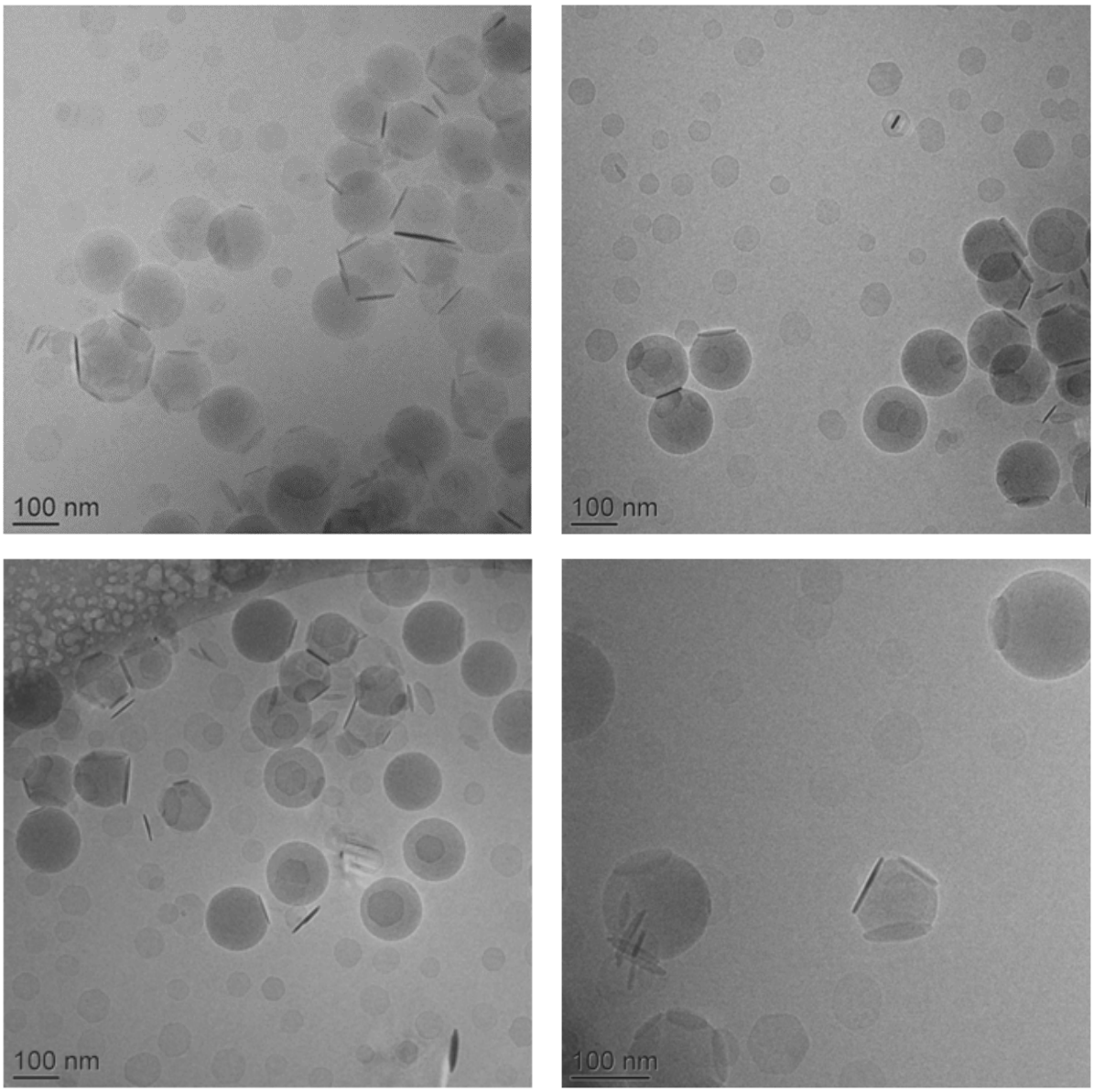

Figure S3. Cryo-TEM images of LDH-armored latex particles obtained by Pickering emulsion copolymerization of St and MMA (80/20 wt/wt) in the presence of 10 wt% of LDH (M02 in Table 2).

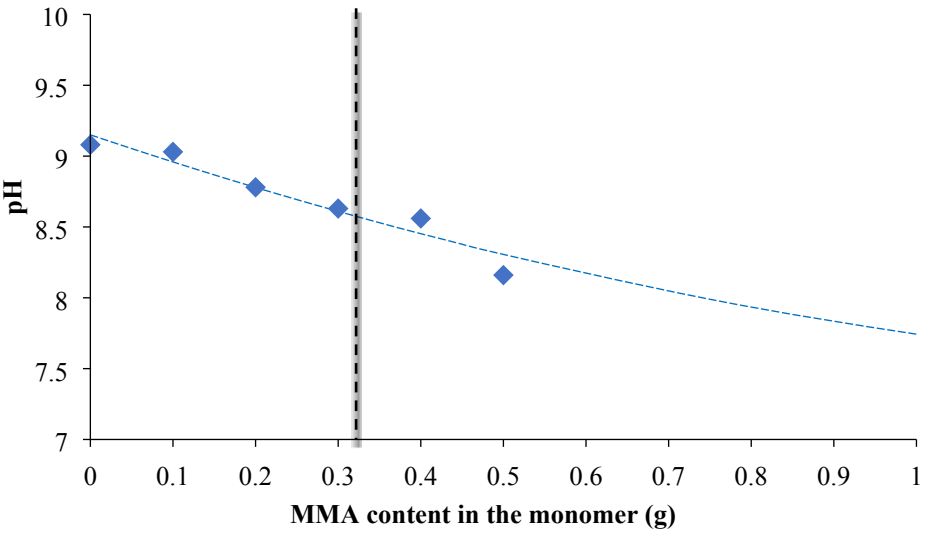

Figure S4. Effect of MMA content on the pH value of the final latex suspensions for 10 wt% of LDH (M01 to M06 in Table 2).

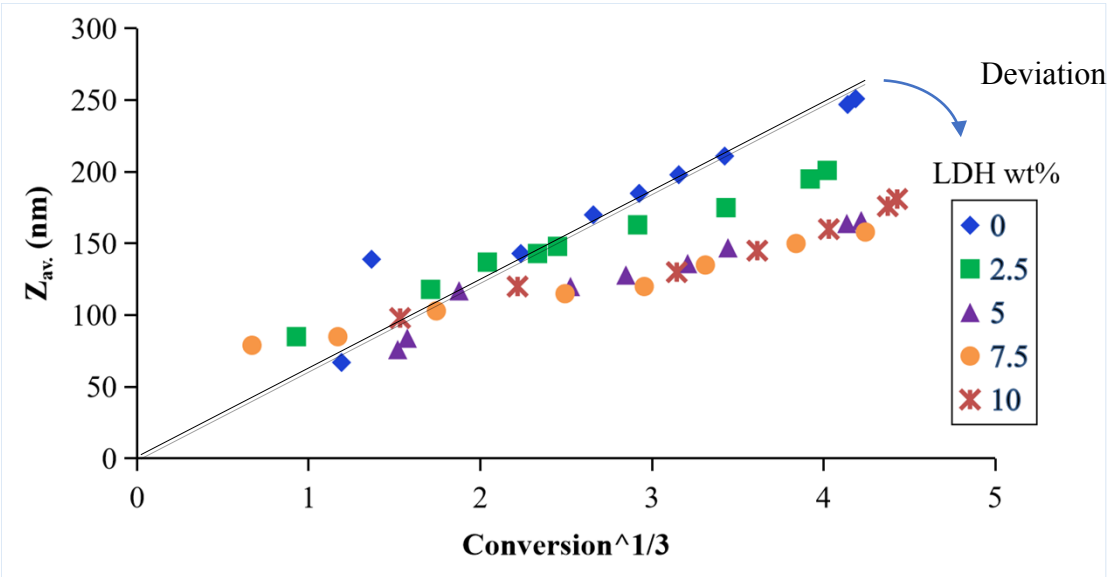

Figure S5. Evolution of the average particle diameter versus the cube root of monomer conversion during Pickering emulsion copolymerization of St and MMA (80/20 wt/wt) for increasing LDH contents (see Table 3 for details).

Estimation of the latex surface coverage by LDH platelets

The percentage of latex surface coverage by the LDH platelets was determined as reported in the literature, from the ratio of the total effective surface area provided by the LDH discs to the total surface area of the latex particles according to:

$$Cov.(\%) = \frac{N_{LDH}\, S_{LDH}}{N_{latex}\, S_{latex}} \times 100 \qquad (S1)$$

with : N_{LDH} the number of LDH platelets, S_{LDH} the area occupied by one LDH disc assuming a 2D square lateral packing, N_{latex}, the number of latex particles, and S_{latex} the area of one latex particle.

$$N_{LDH} = 4\frac{m_{LDH}}{\rho_{LDH}\, \pi\, D_{LDH}^{2}\, h} \qquad (S2) \qquad S_{LDH} = D_{LDH}^{2} \qquad (S3)$$

$$N_{latex} = 6\frac{m_{latex}}{\rho_{latex}\, \pi\, D_{latex}^{3}} \qquad (S4) \qquad S_{latex} = \pi\, D_{latex}^{2} \qquad (S5)$$

with : m_{LDH} (g): mass of the LDH platelets,

D_{LDH} (nm): diameter of the LDH discs,

h (nm): height of a platelet,

ρ_{LDH} (g cm^{-3}) LDH density,

m_{latex} : mass of the polymer taking into account the conversion,

D_{latex} (nm): diameter of the latex particles as determined by TEM, and

ρ_{latex} (g cm^{-3}): polymer density.

Introducing equations S2, S3, S4 and S5 into equation S1, it comes:

$$Cov.\,(\%) = \frac{4\, m_{LDH}\, \rho_{latex} D_{latex}}{6\, \pi\, \rho_{LDH}\, h\, m_{latex}} \times 100 \qquad \text{(S6)}$$

The following values were used for the calculation:

h_{LDH} = 10 nm (as determined by AFM)

ρ_{LDH} = 2 g cm^{-3}

ρ_{PSty} = 1.06 g cm^{-3}

ρ_{PMMA} = 1.18 g cm^{-3}

ρ_{PHEMA} = 1.15 g cm^{-3}

The results are reported in Tables S2 and S3.

Table S2. Estimated values of the latex surface coverage by LDH platelets for various amounts of auxiliary comonomer and increasing LDH contents.

	HEMA series					**MMA series**					
	H02	H03	H04	H06	H07	M01	M02	M03	M08	M09	M10
LDH (wt%)[a]	10	10	10	2.5	5	10	10	10	2.5	5	7.5
Comonomer (wt%)[a]	4	6	8	8	8	10	20	30	20	20	20
[NaCl] (mM)	0	0	0	0	0	0	0	0	0	0	0
Coverage (%)	18.1	18.5	24.5	4.4	7.5	17.5	16.1	14.4	7.6	10.8	14.9

[a] wt% based on total monomers

Table S3. Estimated values of the latex surface coverage by LDH platelets for Pickering emulsion copolymerization of St and MMA (90/10 wt/wt) in the presence of 10 wt% of MgAl-LDH and increasing salt concentrations.

	Effect of NaCl			
	M01	M11	M12	M13
LDH (wt%)[a]	10	10	10	10
Comonomer (wt%)[a]	10	10	10	10
[NaCl] (mM)	0	2	10	50
Coverage (%)	17.5	33.0	48.6	102.5

[a] wt% based on total monomers

As seen in Table S2, the estimated surface coverages are not in good agreement with the TEM observations. Indeed, they are very low overall (lower than typically 20%) whatever the HEMA, MMA or LDH contents, although TEM analyses suggest higher surface coverages, which raises questions about the validity of the calculation method. There are a number of possible reasons for this discrepancy. First, the calculation is based on the assumptions that: i) the polymer/water interface is "fully" covered, (ii) the polymer particles and the solid LDH sheets are uniform in size and fully dispersed in water, and (iii) the dimensions of the LDH platelets are negligible with respect to the size of the armored latex particles. The latter assumption ignores however curvature and thus geometrical constraints and is thus likely non valid. Indeed, it was shown that LDH forms aggregates in the presence of HEMA while the latex particles size is of the same order of magnitude as the diameter of the LDH discs, which may both invalidate the calculation. At last, we used the thickness determined by AFM that is an average value and a small variation in thickness may result in a large difference in surface coverage.

The results reported in Table S3 seem to be however in better agreement with the visual observations and indicate that the surface coverage increases with increasing the salt concentration.