

# Synthesis of high solids content low surfactant/polymer ratio nanolatexes

## Supporting Information

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The z-average particle size of the polymeric nanoparticles was measured by dynamic light scattering using a Zetasizer Nano ZS apparatus (Malvern Instruments). For this measurement, about 1 mL of the latex was placed in a vial and the reaction was immediately quenched with a drop of a 1wt% aqueous solution of hydroquinone. Before the analysis, the samples were diluted until 0.4wt % with deionized water in order to avoid multiple scattering. The value was obtained from the average of two repeated measurements. The number of particles ( $N_p$ ) was calculated from the z-average diameter of the particles, the overall conversion, and the amount of the monomer added to the reactor, namely, assuming that in the highly diluted latex the monomer (if present) was in aqueous phase.

Particle size distributions were obtained from transmission electron microscopy micrographs (Philips CM200). For this measurement, latex samples were diluted until 0.0075 % solids and stained with 0.5% aqueous solution of phosphotungstic acid. A drop of the stained sample was placed on copper grids covered with formvar and the grid was dried overnight. The particle size distributions were determined on representative sample micrographs of around 500 particles and were analysed using ImageJ software (version 1.46r) from United States National Institutes of Health (NIH). The number ( $\overline{d_n}$ ), the volume ( $\overline{d_v}$ ) and the weight ( $\overline{d_w}$ ) average particle diameters, as well as the polydispersity index (PDI) were calculated from the particle size distribution and are defined as:

$$\overline{d_n} = \frac{\sum n_i d_i}{\sum n_i} \quad (1)$$

$$dp_v = \left( \frac{\sum n_i \times d_i^3}{\sum n_i} \right)^{1/3} \quad (2)$$

$$\overline{d_w} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (3)$$

$$PDI = \frac{\overline{d_w}}{\overline{d_n}} \quad (4)$$

where  $n_i$  is the number of particle of diameter  $d_i$ .

The CMC of the surfactants was determined by means of the surface tension measurements using a Du Noüy ring (KSV Sigma 70, KSV Instruments Ltd.). The same equipment was used to estimate the parking area,  $a_s$ , of the surfactant on poly(methyl methacrylate) latex by titrating a diluted latex with a solution of surfactant until micelles appeared in the system.

$$a_s = \frac{10^{16}}{N_A \Gamma_1} (\text{\AA}^2/\text{molecule}) \quad (5)$$

where  $N_A$  is Avogadro's number and  $\Gamma_1$  is the surface concentration given by

$$\Gamma_1 = \frac{\Delta C V}{A_s m} (\text{mol}/\text{cm}^2) \quad (6)$$

where  $V$  is the volume of the liquid phase (L),  $A_s$  is the surface area of the latex ( $\text{cm}^2$ ),  $m$  is the mass of solid adsorbent,  $\Delta C = \text{CMC}_p - \text{CMC}$ , where CMC is the concentration of surfactant at the point at which micelles appeared in the diluted latex, and CMC is the critical micelle concentration.

Molecular weights were determined by size exclusion chromatography (SEC, Waters). The setting consisted of a pump Waters model 510, three columns in series (Styragel HR2, HR4 and HR6; with a pore size from  $1 \times 10^2$  to  $1 \times 10^6$  \AA), an RI detector (Waters 2410), at  $35^\circ\text{C}$  and using tetrahydrofuran (THF) as eluent.