

Supporting Information

Starch nanoparticles modified with styrene oxide and their use as Pickering stabilizers

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TEM and particle size distribution by DLS of unmodified SNP

The TEM image (**Figure S1a**) and particle size distribution by intensity (**Figure S1b**), number (**Figure S1c**) and volume (**Figure S1d**) obtained from DLS showed that unmodified SNP could be found as individual nanoparticles of about ~14 nm as well as aggregates of ~136 nm.

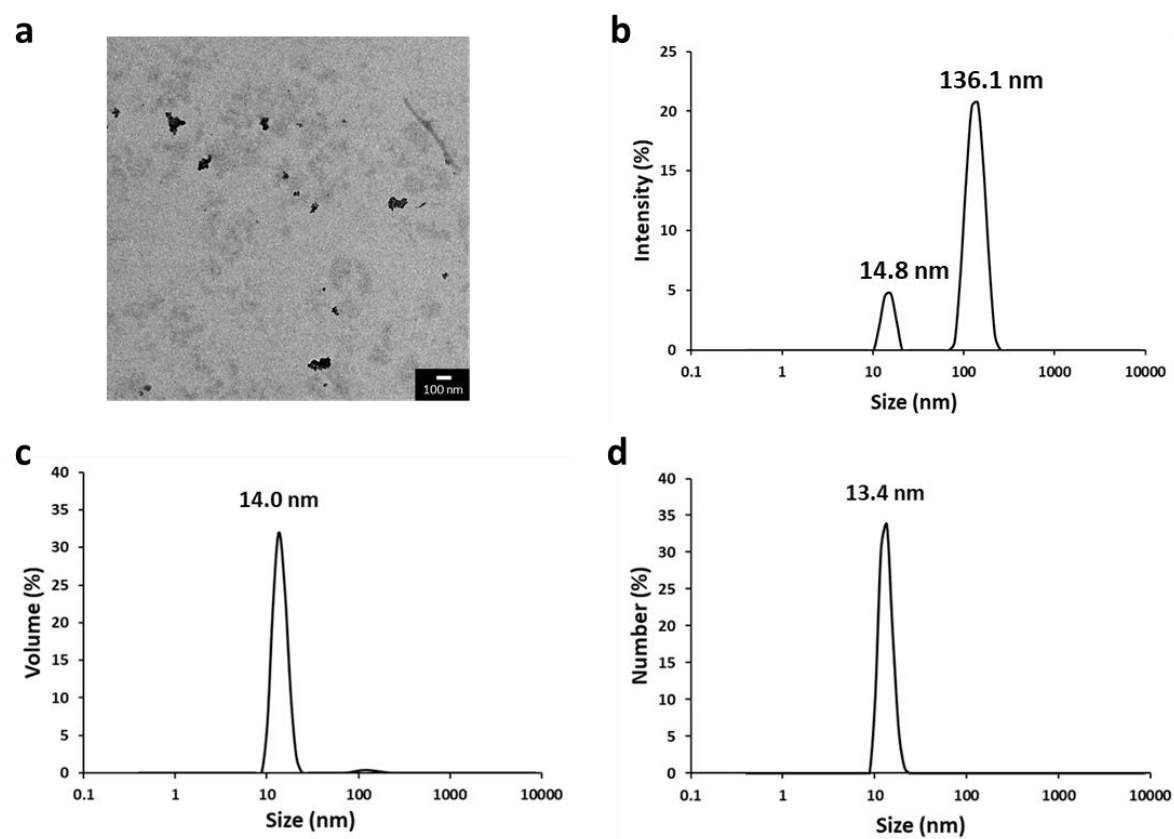


Figure S1: (a) TEM image and particle size distribution by (b) intensity, (c) volume and (d) number from DLS of unmodified SNP.

Preliminary miniemulsion stability tests

In order to prepare the miniemulsion, two approaches were chosen to disperse the oil phase (styrene) in water (or aqueous SNP dispersion): ultra-turrax and sonication. The oil/water ratio was fixed at 1:9 based on weight (1 g of oil phase in 9 g of aqueous phase) corresponding to a miniemulsion of 10 wt% solids content. The dispersions with ultra-turrax approach (20 g) were performed for 5 min at 12,000 rpm; while the dispersions with the sonication approach (10 g) were performed for 5 min at 7 W RMS. **Figure S2** shows the images of the miniemulsions obtained just after the dispersion ($t = 0$ h), as well as the images of the miniemulsions after 5 h ($t = 5$ h) and 24 h ($t = 24$ h). Under the experimental conditions tested, the miniemulsions prepared using the sonication approach were more stable than the miniemulsions prepared with the ultra-turrax approach (phase separation occurring at 5 h). Therefore, the sonication approach was chosen to perform the further investigations in this study.

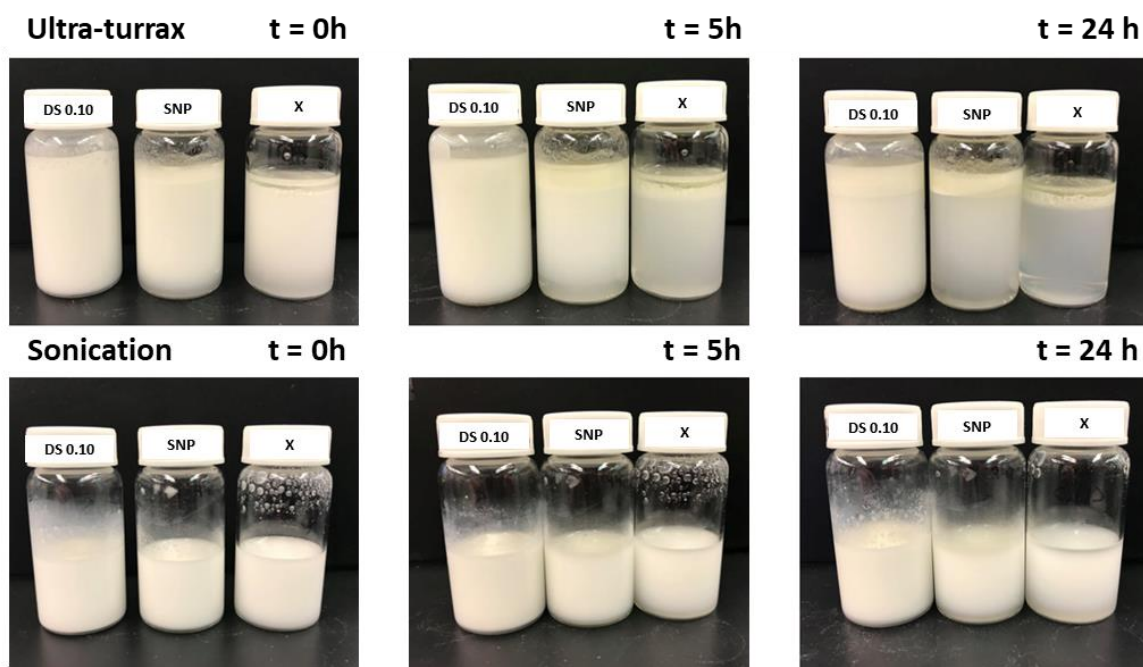


Figure S2. Images of miniemulsions prepared with ultra-turrax (top) and sonication (bottom) approaches at different times. In all images left vials contain SNP-STO (DS 0.10), middle vials contain unmodified SNP and right vials do not contain any Pickering stabilizer (x).

Table S1 shows the preliminary results of miniemulsions prepared using the sonication approach. The miniemulsions were prepared at 1:9 oil/water ratio using unmodified SNP and STO modified SNP (DS 0.05 and 0.10) at two different concentrations: 1.0 and 1.8 wt% SNP based on the oil phase (styrene). The sonication was performed at three different times (1, 3 and 5 minutes) for unmodified SNP. The droplet size of the miniemulsion decreased with the increase of sonication time. Droplets with 1082 nm were obtained when the miniemulsion was sonicated for just 1 min and decreased up to 779 nm when the sonication time was increased to 3 min. When increasing the sonication time from 3 min to 5 min the droplet size did not decrease significantly as it has decreased from 1 min to 3 min. Therefore, the sonication time was set as 3 min for further investigations in this study. With the increase of the DS of the Pickering stabilizers (SNP-STO) a decrease on the droplet size was noticed. The miniemulsion droplet size decreased from 779 nm when using unmodified SNP at 1.0 wt% to 401 nm when using SNP-STO with a DS of 0.10 also at 1.0 wt%. The increase in the concentration of Pickering stabilizer also decrease the size of the miniemulsion monomer droplets. Using the same SNP-STO with DS of 0.10, the droplet size decreased from 401 nm to 311 nm when 1.8 wt% SNP was employed in place of 1.0 wt%.

Table S1. Preliminary miniemulsion (10 wt%) results prepared by sonication approach.

SNP	Sonication time (min)	SNP (wt%)	Droplet size (nm)
unmodified	1	1.0	1082
	3	1.0	779
	5	1.0	710
	3	1.8	678
SNP-STO (DS 0.05)	3	1.0	428
	3	1.8	317
SNP-STO (DS 0.10)	3	1.0	401
	3	1.8	311

Volume and number particle size distributions of unmodified and STO modified SNP

The particle size distributions by number and volume of SNP-STO used as Pickering stabilizers in this study are presented in **Figure S3**. A slight increase in the average particle size is noticed with the increase of the DS.

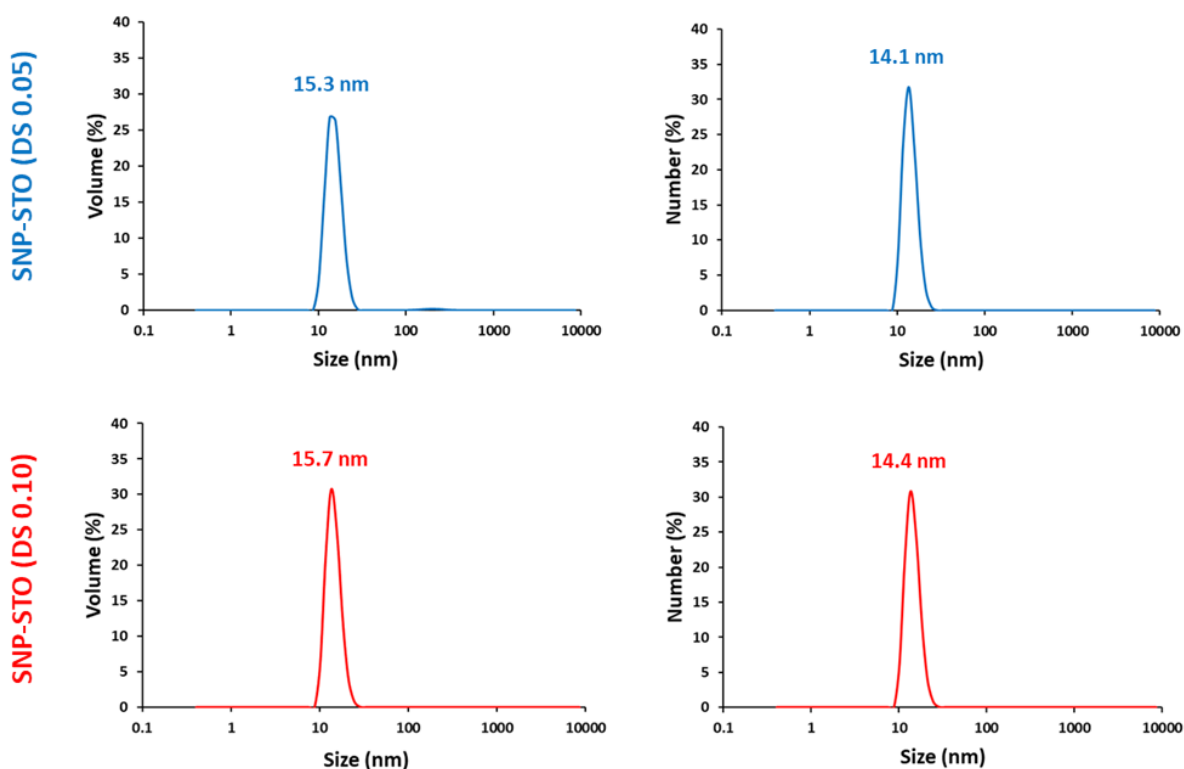


Figure S3: Volume (left) and number (right) particle size distributions of STO modified SNP with DS 0.05 (blue) and DS 0.10 (red).

Additional characterization of the SNP used as Pickering stabilizers

The unmodified and STO modified SNP used as Pickering stabilizers were additionally characterized by FTIR (**Figure S4**), TGA (**Figure S5**) and ζ -potential as a function of pH (**Figure S6**).

FTIR spectra were obtained using a Bruker Alpha FTIR base spectrometer with an attenuated total reflectance (ATR) accessory over 4000-500 cm^{-1} with 24 scans and 4 cm^{-1} of resolution in transmission mode. Overlaid spectra with unmodified and modified SNP are shown in Figure S3. FTIR spectra of unmodified and STO modified SNP are similar since STO does not add any additional signal (such as a carbonyl at 1700 cm^{-1}) to the spectra of modified SNP.

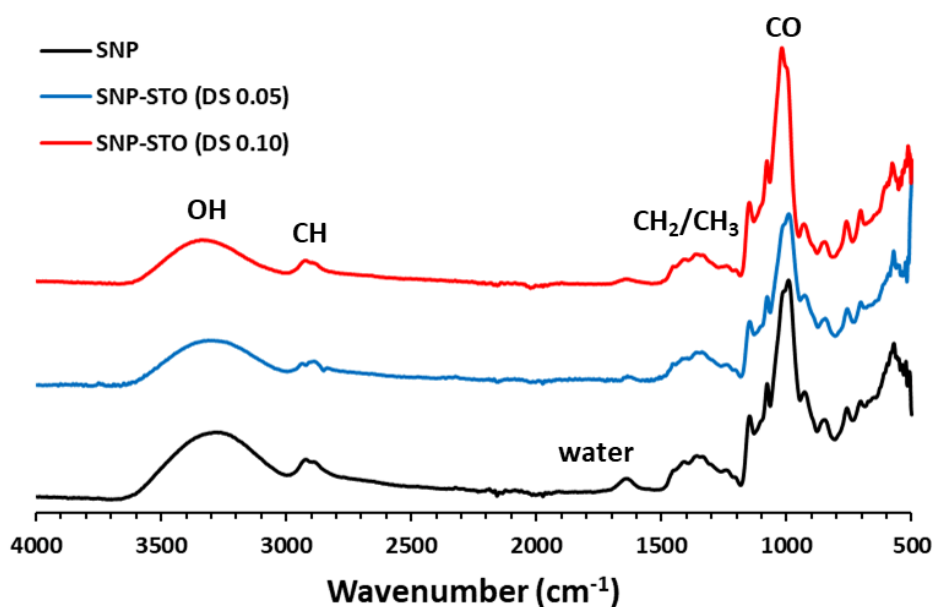


Figure S4: FTIR spectra of unmodified SNP (black) and STO modified SNP with DS 0.05 (blue) and DS 0.10 (red).

Thermogravimetric analysis (TGA) was conducted using a TA Q500 TGA instrument with ramp heating of 10 °C/min from 30 to 600°C and a nitrogen flowrate of 40 mL/h. These results are shown in Figure S4 for unmodified and STO modified SNP. TGA results showed that all materials presented similar degradation profile with only one decomposition loss.

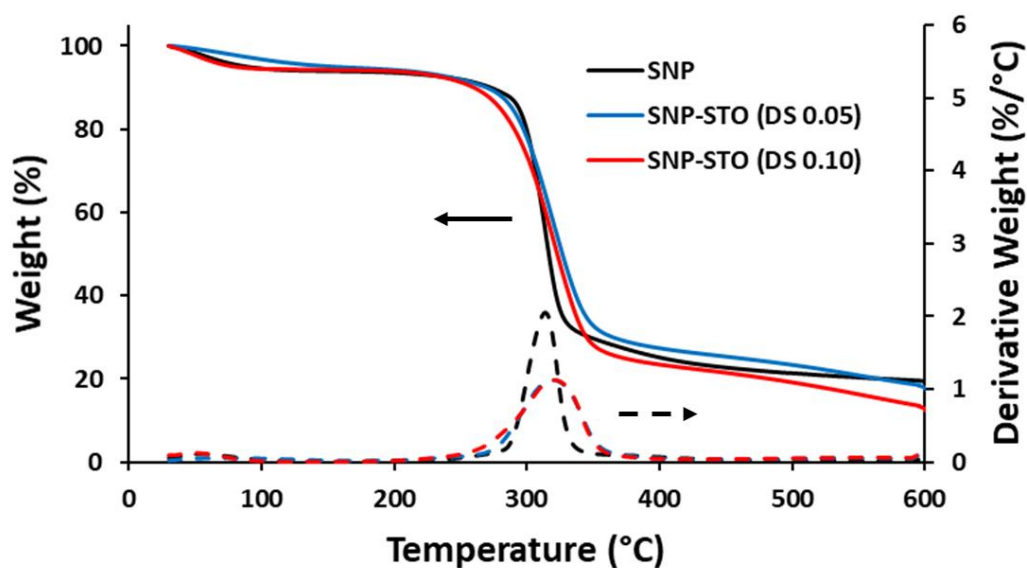


Figure S5: TGA of unmodified SNP (black) and STO modified SNP with DS 0.05 (blue) and DS 0.10 (red).

A DTS1070 disposable folded capillary zeta cell (Malvern Instruments) was used to measure ζ -potential in a ZetasizerNano ZS coupled with a Malvern Multipurpose Titrator (MPT-2). Samples were prepared by dispersing the (modified) SNP in DIW at 1 mg/mL and adjusting the pH to 3.0 with 0.5 M HCl aqueous solution. Titrations were performed from pH 3 to 13 using 0.5 M NaOH aqueous solution at 0.5 pH intervals as shown in Figure S5.

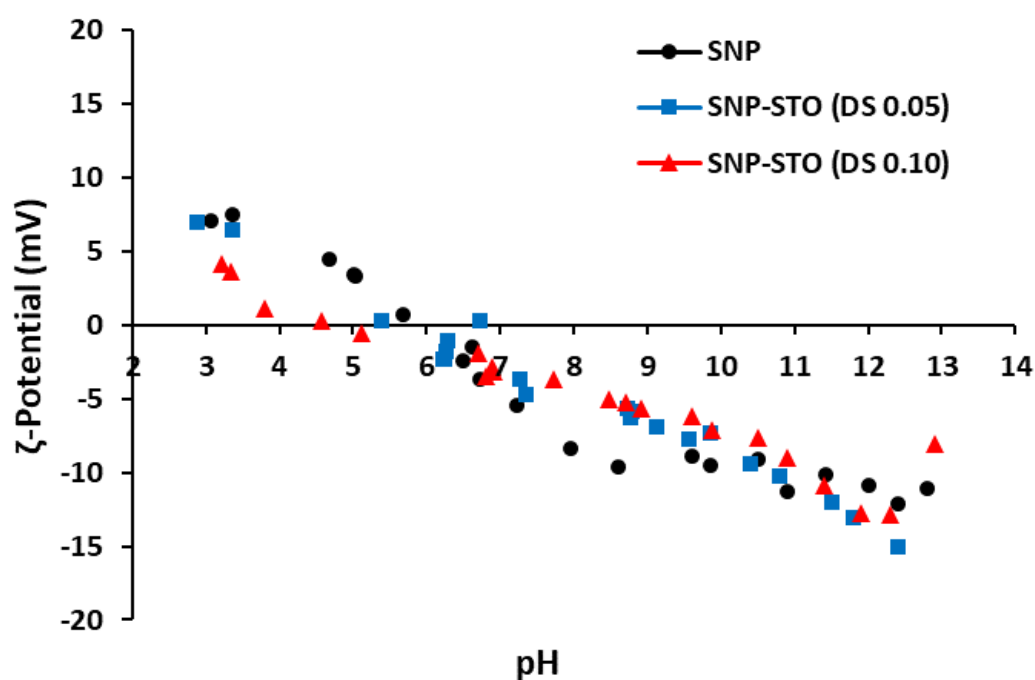


Figure S6: ζ -potential as a function of pH of unmodified SNP (black) and STO modified SNP with DS 0.05 (blue) and DS 0.10 (red).

Characterization of grafted SNP with synthetic polymer

The purified dried samples used for SEM were characterized by FTIR (**Figure S7**) and TGA (**Figure S8**). The purification process must have removed all free SNP not grafted and the drying process must have removed the traces of water from the samples. The presence of a strong band at $3100\text{--}3700\text{ cm}^{-1}$ from the stretching vibration of the O-H bonds on FTIR is attributed to the grafted SNP, as well as the decomposition loss from $240\text{--}360\text{ }^{\circ}\text{C}$ on the TGA of PE-4. The presence of water is dismissed in PE-4 and PE-8 samples since no weight loss was observed from $30\text{--}100\text{ }^{\circ}\text{C}$.

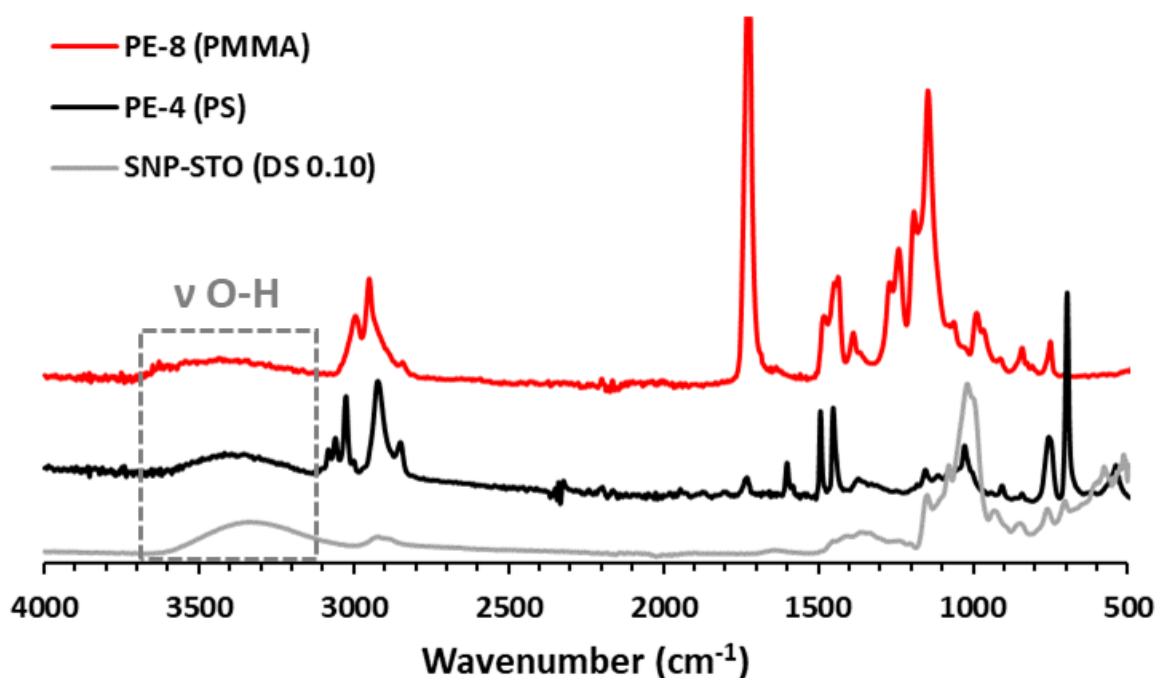


Figure S7: FTIR spectra of PE-8 (PMMA, red), PE-4 (PS, black) and SNP-STO (reference, grey).

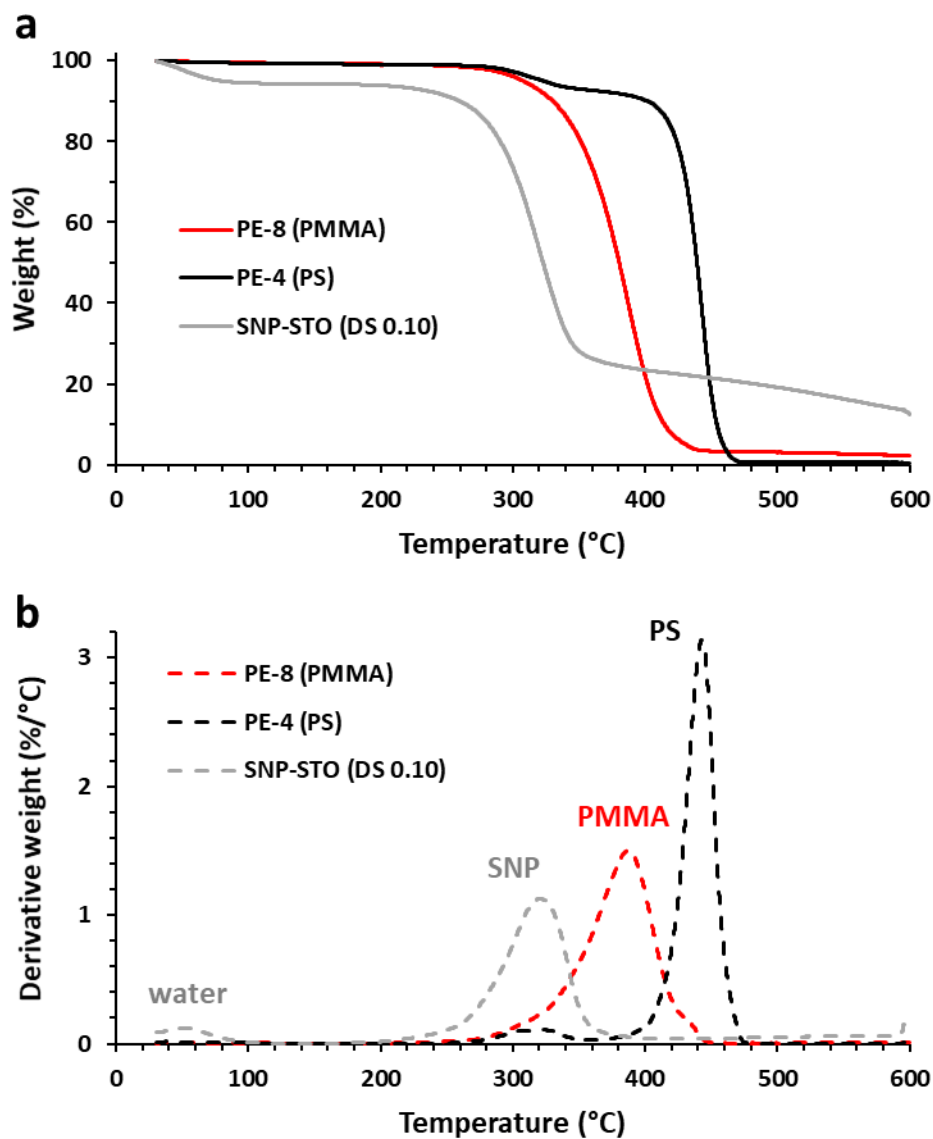


Figure S8: TGA of PE-8 (PMMA, red), PE-4 (PS, black) and SNP-STO (reference, grey): (a) weight and (b) derivative weight as a function of temperature.

PMMA latex stability test with NaCl

Figure S9 shows the evolution of ζ -potential of diluted PMMA latex (PE-8) with different NaCl concentrations (up to 10 mM). **Figures S10, S11 and S12** show the particle size distributions by intensity, volume and number, respectively, of diluted PMMA latex with different NaCl concentrations.

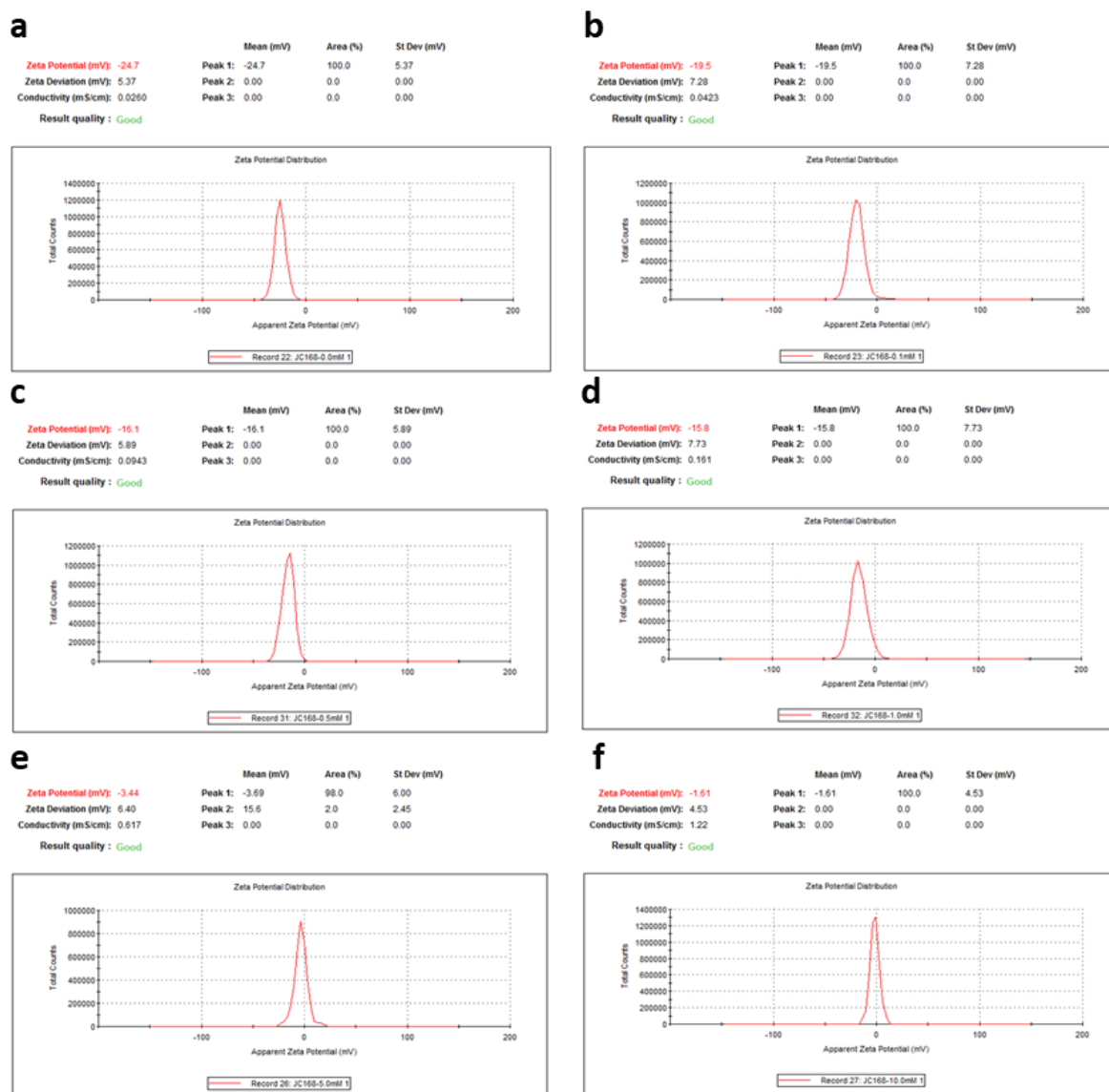


Figure S9: ζ -potential of PE-8 as a function of NaCl concentration: (a) 0 mM, (b) 0.1 mM, (c) 0.5 mM, (d) 1 mM, (e) 5 mM and (f) 10 mM.

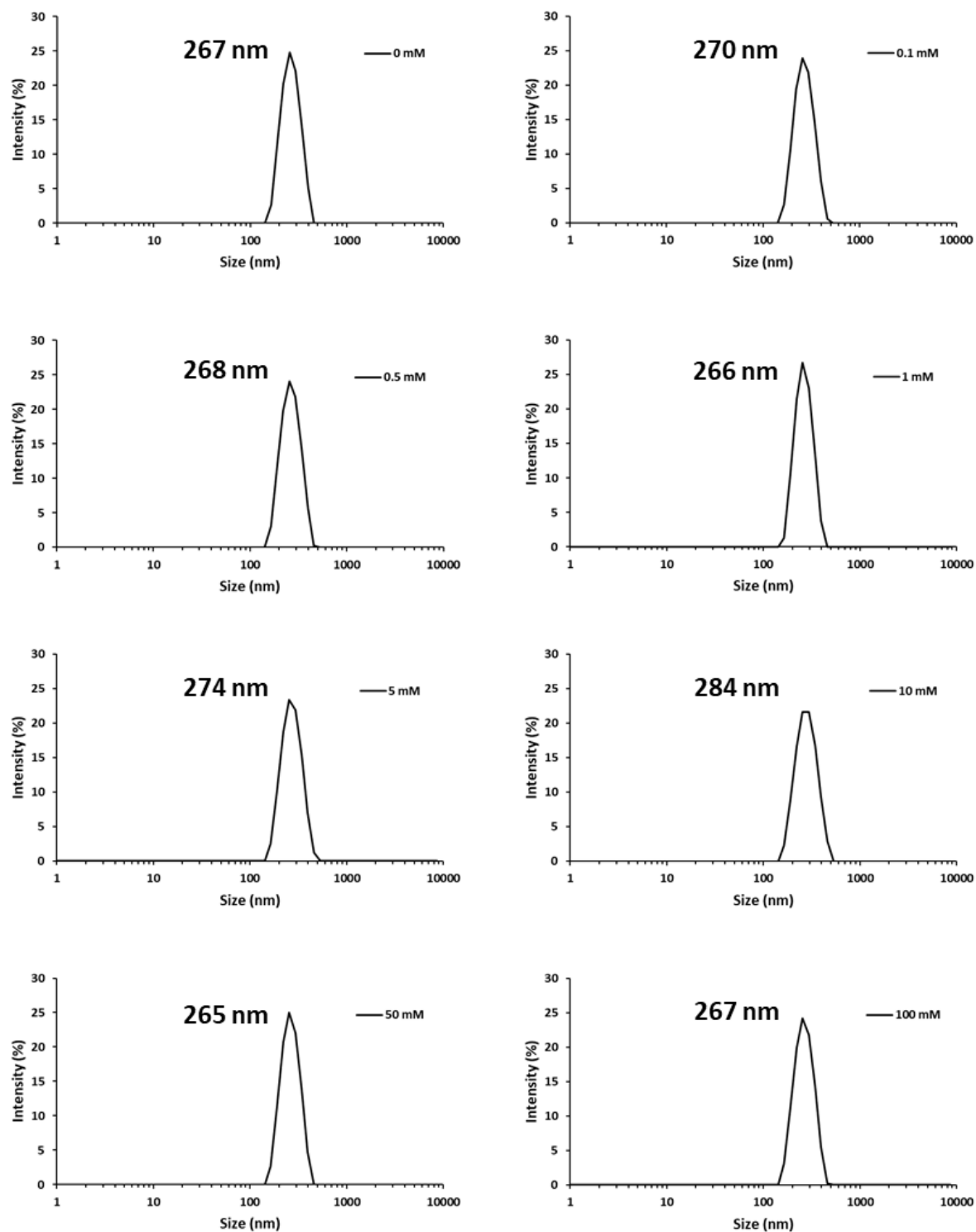


Figure S10: Particle size distribution by intensity of PE-8 as a function of NaCl concentration.

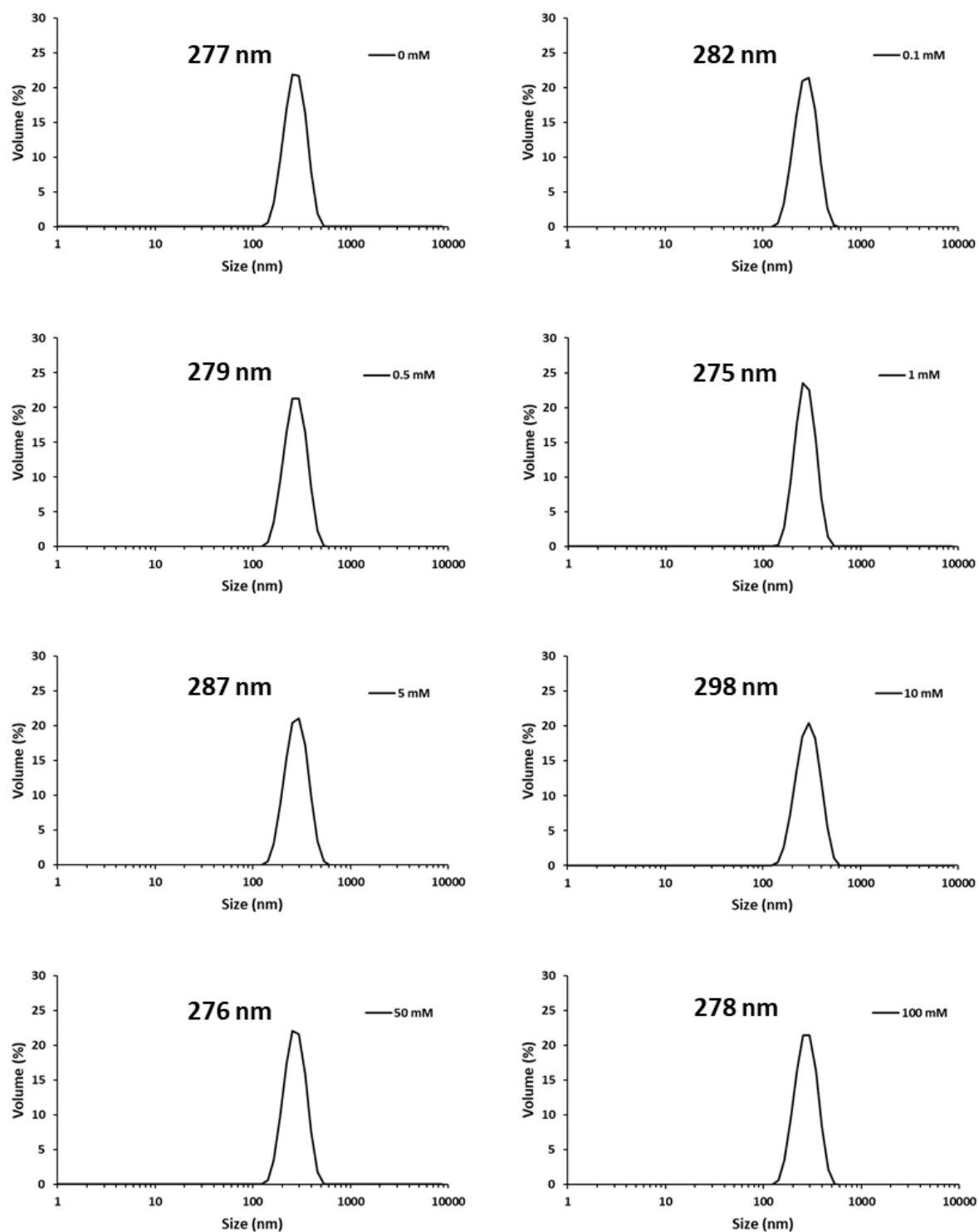


Figure S11: Particle size distribution by volume of PE-8 as a function of NaCl concentration.

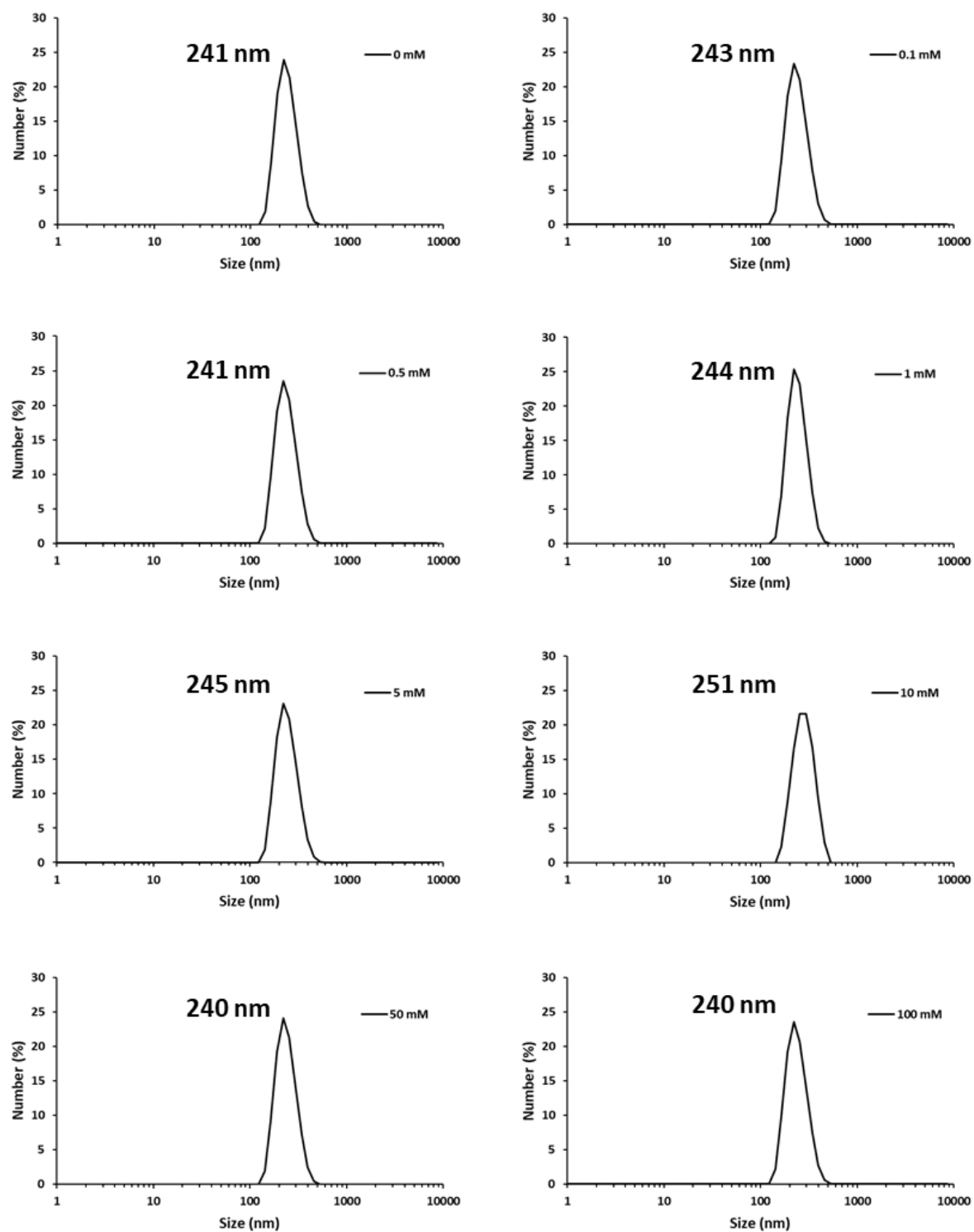


Figure S12: Particle size distribution by number of PE-8 as a function of NaCl concentration.