Supporting Information

Fundamentals of chemical incorporation of ionic monomers onto polymer colloids: Paving the way for surfactant-free waterborne dispersions

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1) Reaction in the aqueous phase

The material balance for NaSS (A) in the aqueous phase is

$$\frac{dA}{dt} = -\left(kp_{AA} P_A M_A + kp_{BA} P_B M_A\right)[R]_w$$

(S1)

where A and B are the amounts of NaSS and comonomer in the aqueous phase, kp_{ij} the propagation rate coefficient between radical i and monomer j, M_i the number of moles of monomer i, $[R]_w$ the concentration of radicals in the aqueous phase and P_i the probability of having a radical terminated in monomer i given by

$$P_A = \frac{kp_{BA} M_A}{kp_{BA} M_A + kp_{AB} M_B} \quad ; \quad P_B = 1 - P_A$$

(S2)

Equation S2 shows that as M_B increases P_A decreases and P_B increases. Therefore the condition for an increase in the NaSS consumption as M_B increases is that $kp_{BA} > kp_{AA}$.

The reactivity ratios were calculated using the Alfrey and Price Q-e scheme [1] using the Q and e values given in Table S1.

Table S1. Q and e values

	Q	e
NaSS [2]	2.0	-0.4
MMA[1]	0.78	0.4
EMA [1]	0.76	0.17
BMA [1]	0.82	0.28
2HEA [3]	0.75	0.65
MA [1]	0.45	0.64
EA [1]	0.41	0.55
BA [1]	0.38	0.85
S [1]	1.0	-0.8

Table S2 presents the reactivity ratios of NaSS with different comonomers. It can be seen that in all cases $r_1>1$ and $r_2<1$. Taking into account that the homopolymerization rate coefficient of styrenic monomer is substantially lower than those of the (meth)acrylates [4], kp_{BA} is greater than kp_{AA} for the methacrylate and acrylate monomers. Therefore, NaSS consumption increases as M_B increases.

Table S2. Estimated reactivity ratios of NaSS with different monomers.

Monomer 1	Monomer 2	r1	r2
NaSS	MMA	1.862	0.283
	EMA	2.095	0.345
	BMA	1.858	0.339
	2HEA	1.752	0.190
	MA	2.932	0.116
	EA	3.336	0.122
	BA	3.192	0.066
	S	2.347	0.363

2) Conversion of NaSS by ^{1}H-NMR

To quantify the amount of unreacted NaSS in the final latexes, DMF was used as a reference. DMF gives an intense amide hydrogen peak around 7.8 ppm. A set of mixtures were prepared by mixing 10 µL of 142.5 mM DMF reference solution with 5-70 µL of 48.5 mM or 100-500 µL of 0.370 mM NaSS solution directly in NMR tubes. Then, 50 µL D_2O was introduced to each tube, the total volumes of the mixtures were adjusted to 560 µL with ultra pure water. From ^{1}H-NMR spectra of the mixtures, the absolute areas for singlet amide peak of DMF at 7.80 ppm and vinyl hydrogen doublets of NaSS appearing at 5.85 and 5.90 ppm were calculated. The calibration curve was obtained by plotting the ratio of these absolute areas against the ratio of NaSS weight to the moles of DMF (Fig. S1). By using the calibration curve, the amount of unreacted NaSS in the latexes could be calculated. For that, 500 µL of latex, 10 µL of DMF reference solution and 50 µL D_2O is introduced into the NMR tube. The ratio of the areas of the peaks of interest is calculated from the spectrum and the corresponding weight of unreacted NaSS in the sample can be determined by the calibration curve.
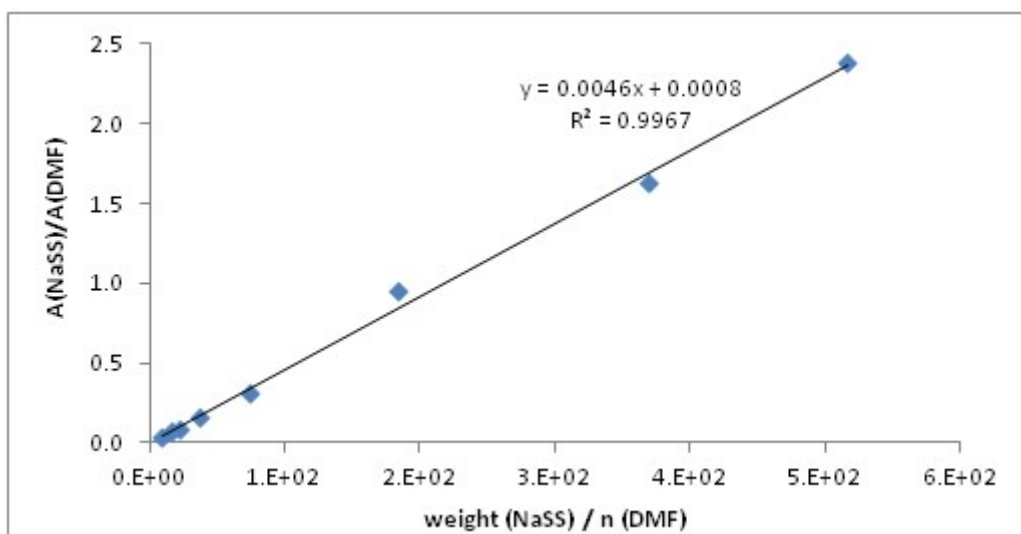
Figure S1. Calibration curve used for quantification of unreacted NaSS in the final latexes

References

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