

# **Hydrophilic MacroRAFT-Mediated Emulsion Polymerization: Synthesis of Latexes for Crosslinked and Surfactant-Free Films**

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## **SUPPORTING INFORMATION**

## Analytical techniques

*Nuclear magnetic resonance (NMR).* For the synthesis of the macroRAFT agents, MAA conversion was determined by  $^1\text{H}$  NMR spectroscopy in  $\text{D}_2\text{O}$  at room temperature (Bruker DRX 300) by the relative integration of the protons of the internal reference (1,3,5-trioxane) at 5.1 ppm and the vinylic protons of MAA at 5.6 and 6.0 ppm.

*Viscosity measurements.* The viscosity of latexes was measured using a RFS III rheometer with a Couette geometry (Rheometric Scientific). The measurements were performed on 12 g of latex at 25 °C at a shear rate of 200  $\text{s}^{-1}$ .

*Size exclusion chromatography (SEC-THF).* Size exclusion chromatography (SEC) measurements were performed in tetrahydrofuran (THF) at 40 °C at a flow rate of 1  $\text{mL min}^{-1}$ . Before analysis, polymers were modified by methylation of the carboxylic acid groups using trimethylsilyl diazomethane.<sup>1</sup> They were analyzed at a concentration of 4  $\text{mg mL}^{-1}$  after filtration through a 0.45  $\mu\text{m}$  pore-size membrane. The separation was carried out on three columns from Malvern Instruments [PLgel Olexis Guard (300  $\times$  7.5 mm)]. The setup (Viscotek TDA305) was equipped with a refractive index (RI) detector ( $\lambda = 670 \text{ nm}$ ). The number-average molar mass ( $M_n$ ), the weight-average molar mass ( $M_w$ ) and the dispersity ( $\mathcal{D} = M_w/M_n$ ) were derived from the RI signal by a calibration curve based on poly(methyl methacrylate) standards (PMMA from Polymer Laboratories).

*Dynamic light scattering (DLS).* The particle size (z-average diameter,  $D_z$ ) and the dispersity of highly diluted samples (PDI) were measured by dynamic light scattering (NanoZS from Malvern Instruments) at 25 °C. The data were collected at 173° using the fully automatic mode of the Zetasizer system, and depending on the size distribution, either the monomodal cumulant analysis or the CONTIN analysis was performed.

*Tensiometry.* Surface tension ( $\gamma$ ) measurements were carried out with a Krüss tensiometer

thermostated at 25 °C, on 25 mL samples. The aqueous macroRAFT solution or the latex was stirred for 15 min to reach the equilibrium temperature and the surface tension was measured using the Wilhelmy plate method.

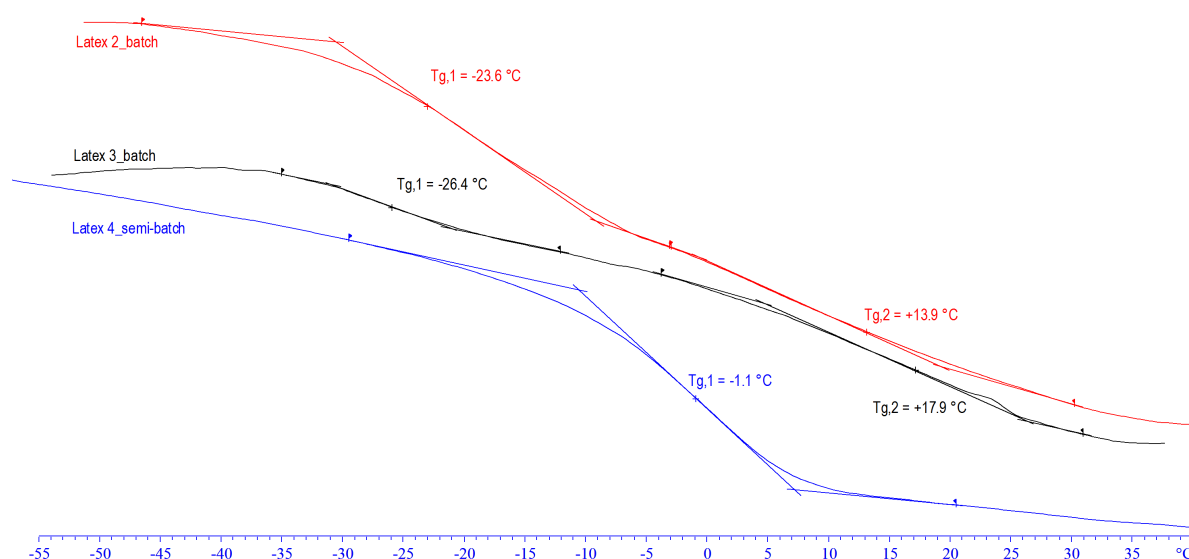
*Differential scanning calorimetry (DSC).* Thermal characterizations were performed with a differential scanning calorimeter, Mettler Toledo DSC 1, equipped with an auto-sampler and a 120 thermocouples sensor. The temperature and the heat flow of the equipment were calibrated with indium standard. All samples were accurately weighed (around 10 mg) and sealed in aluminum pans. They were heated from -70 °C to +120 °C at 20 °C min<sup>-1</sup> with an empty aluminum pan as reference. Two successive heating and cooling were performed and only the second run was considered. Dry nitrogen with a flow rate set at 30 mL min<sup>-1</sup> was used as the purge gas. The glass transition temperature ( $T_g$ ) was measured at the midpoint. The STARe thermal analysis software was used for the calculation.

*pH measurements.* The pH values of the aqueous solutions were measured with a Mettler Toledo SevenEasy pH-meter using a InLab Routine Pro electrode. For the latexes, an InLab Science Pro electrode was used. The electrodes were calibrated with buffer solutions from Mettler Toledo (pH 4.01, 7.00 and 10.00).

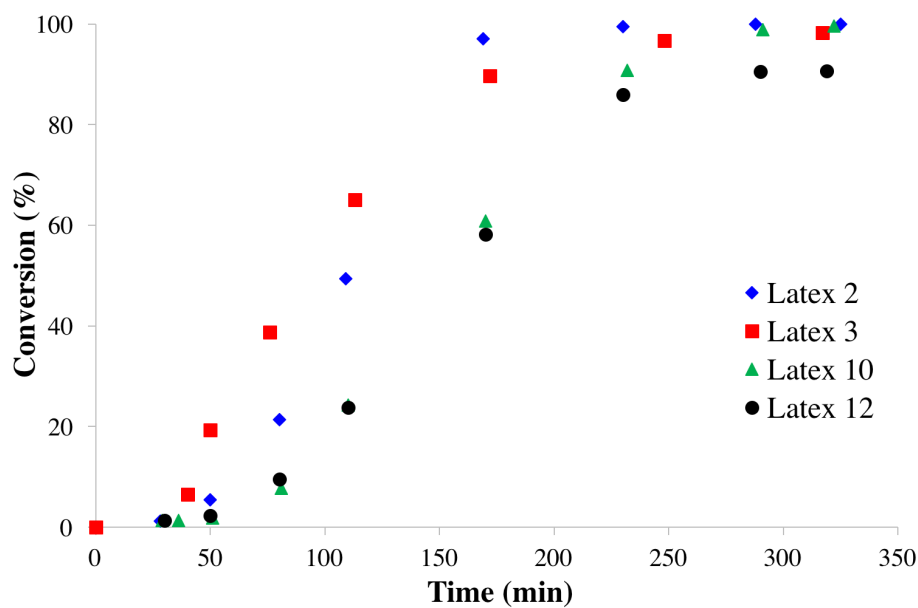
**Table S1.** Properties of some surfactant-free latexes prepared in the presence of PMAA<sub>2k</sub> macroRAFT agent.

Latex	Monomers <sup>a</sup>	wt% macroRAFT <sup>b</sup>	$M_n$ (kg mol <sup>-1</sup> ) / $\bar{D}$ <sup>c</sup>	Viscosity <sup>d</sup> (cP)	Film <sup>e</sup>
2	BA/MMA (60/40)	1.5	111.0 / 3.2	17	T
3	BA/MMA (60/40)	1.0	168.8 / 3.0	8	T
4 <sup>f</sup>	BA/MMA (60/40)	1.0	n.d.	n.d.	T
5	BA/S (55/45)	1.0	n.d.	n.d.	O
6	BA/S (55/45)	0.75	n.d.	84	O
7	BA/S/MMA (60/25/15)	0.75	n.d.	n.d.	T+O
8	BA/S/MMA (60/15/25)	0.75	n.d.	n.d.	T
9	BA/S/MMA (60/15/25)	1.0	n.d.	n.d.	T
10	BA/S/MMA (60/15/25)	1.5	95.5 / 3.2	55	T
11	BA/S/MMA (60/10/30)	1.0	n.d.	n.d.	T
12	BA/S/MMA (60/10/30)	1.5	89.7 / 3.4	37	T

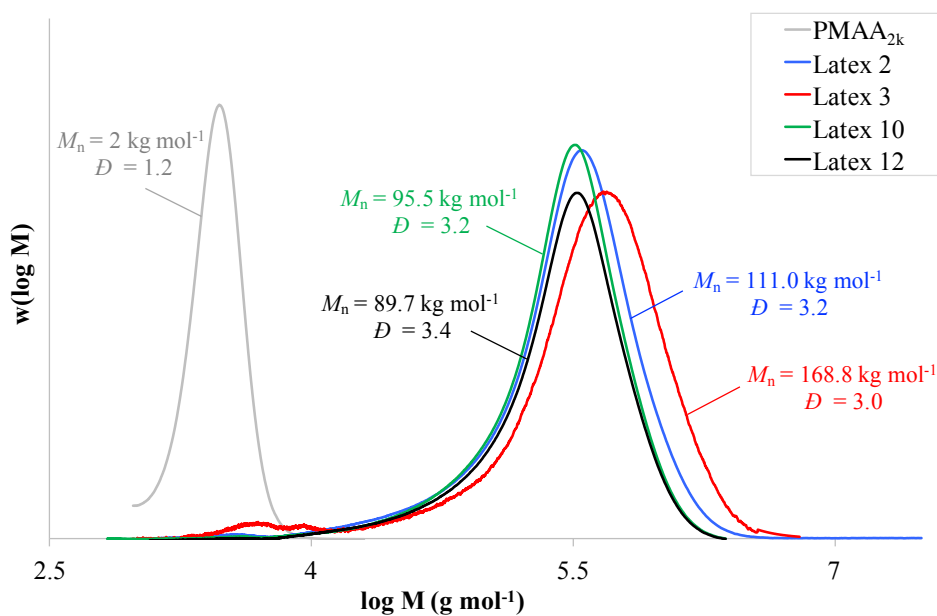
All the experiments were performed at 70 °C, using 2 mmol L<sup>-1</sup> of APS. <sup>a</sup> Composition of the initial mixture of hydrophobic monomers - Weight fractions are given in brackets. <sup>b</sup> With respect to the monomers. <sup>c</sup> Number-average molar mass and dispersity determined by SEC-THF. <sup>d</sup> Viscosity determined at 200 s<sup>-1</sup>. <sup>e</sup> T stands for transparent and O for opaque. <sup>f</sup> Semi-batch experiment.



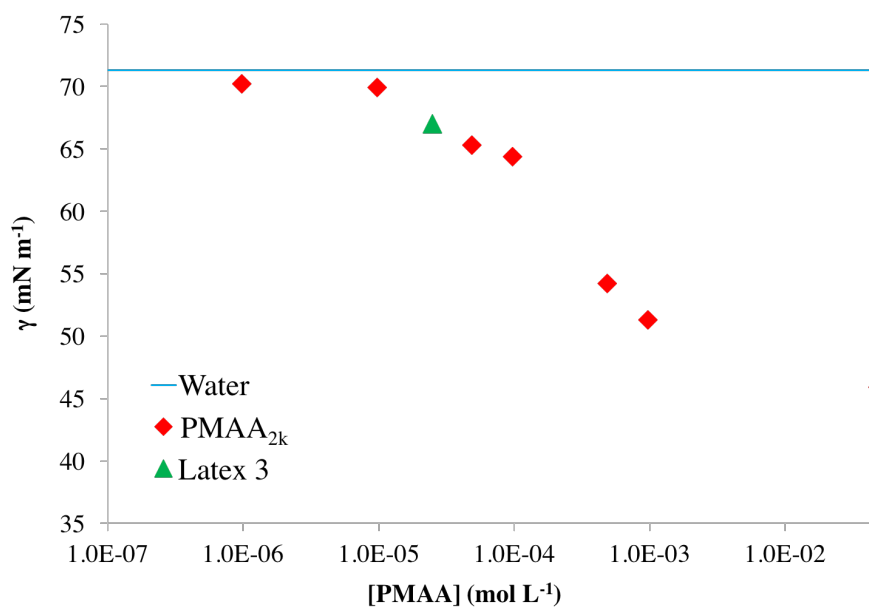
**Figure S1.** DSC curves of Latex 2, Latex 3 and Latex 4 (see Table S1 for more information on these samples).



**Figure S2.** Kinetics of the emulsion polymerizations of Latex 2, Latex 3, Latex 10 and Latex 12. (See Table S1 for more information on these samples.)












**Figure S3:** Size exclusion chromatograms of PMAA<sub>2k</sub>, Latex 2, Latex 3, Latex 10 and Latex 12 (see Table S1 for more information on these samples).



**Figure S4.** Surface tension ( $\gamma$ ) measurements for Latex 3, compared to that of water and various concentrations of aqueous solutions of the macroRAFT agent PMAA<sub>2k</sub>.

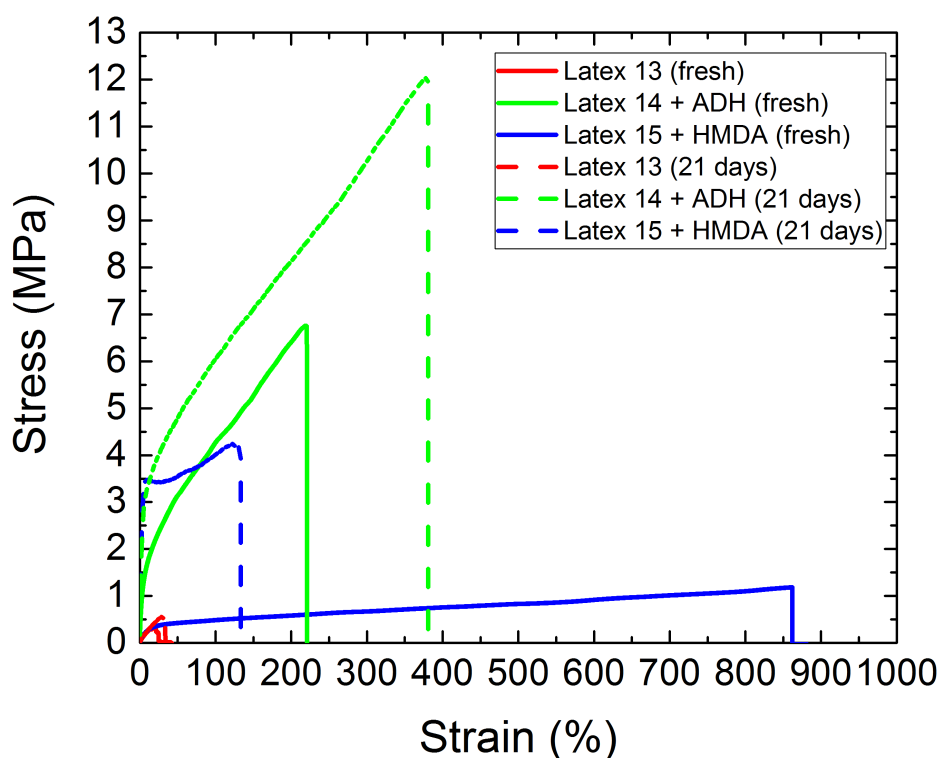
**Table S2.** Visual stability test of Latex 3 at 50 °C

	Day 0	Week 1					Week 2	Week 3	Week 4
		Day 1	Day 2	Day 3	Day 6	Day 7			
pH	7.0	-	-	-	-	-	-	-	7.0
Viscosity (cP)	9	-	-	-	-	-	-	-	9
Particle size ( $D_z$ , nm) / $\sigma$	204 / 0.03	-	-	-	-	-	-	-	197 / 0.02
Sedimentation?	No	No	No	No	No	No	No	No	No
Separation into layers?	No	No	No	No	No	No	No	No	No
Appearance									
Comments	-	Skin forming at the interface	Presence of a skin	Presence of a skin	Presence of a skin	Presence of a skin	Presence of a skin	Presence of a skin	Presence of a skin

**Table S3.** Properties of the surfactant-free and (self-)crosslinking latexes prepared in the presence of 1 wt% of PMAA<sub>2k</sub> macroRAFT agent.

Latex	Functional comonomer	Monomers <sup>a</sup>	Viscosity <sup>b</sup> (cP)	Film Appearance <sup>c</sup>	Gel fraction <sup>d</sup> (%)
13	BuDA	BA/MMA/BuDA (59.0/39.3/1.7)	10	T	96.9
14	DAAm	BA/MMA/DAAm (57.5/38.5/4.0)	23	T	100.0 <sup>e</sup>
15	AAEM	BA/MMA/AAEM (57.5/38.5/4.0)	10	T	100.0 <sup>e</sup>

All the experiments were performed at 70 °C, using 2 mmol L<sup>-1</sup> of APS and 1 wt% of macroRAFT. The pH was initially adjusted to 7 by addition of a 1M NaOH solution. <sup>a</sup> Composition of the initial mixture of hydrophobic monomers. Weight fractions are given in brackets. <sup>b</sup> Viscosity determined at 200 s<sup>-1</sup>. <sup>c</sup> T stands for transparent. <sup>d</sup> Gel fraction determined by Soxhlet extraction in THF. <sup>e</sup> After ADH/HMDA addition.

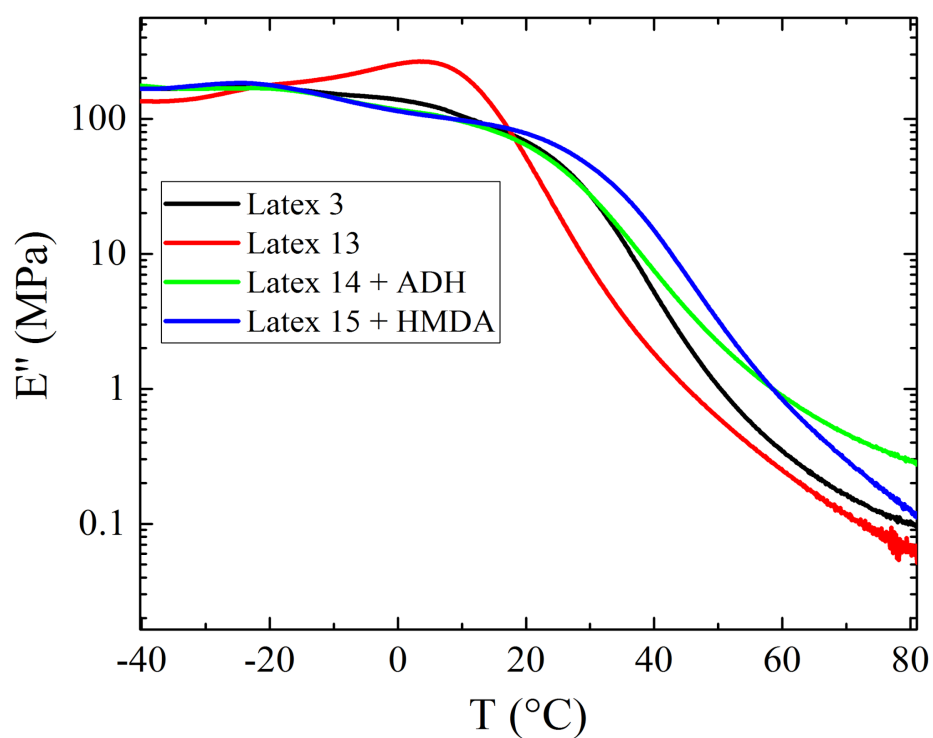


**Figure S5.** Representative large-strain deformation data from latex films with different cross-linking functionalities. Solid lines show data from films that were formed immediately after the crosslinker (ADH or HMDA) was added to the wet latex (14 (green line) and 15 (blue line), respectively). For comparison, data from films that were formed 21 days after adding the crosslinker are also shown (dashed line). Films from Latex 13 (red line), which was internally crosslinked with BuDA, were analyzed in two separate trials at the same times as the crosslinking latexes.



**Table S4.** Mechanical properties of latex films with different cross-linking functionalities (film-formed 21 days after mixing latex and crosslinker)

Latex	Young's modulus (+/-error) (MPa)	Tensile strength (+/-error) (MPa)	Strain at failure (+/-error) (%)	Yield point (+/-error) (MPa)
13	7.55 (2.9)	0.62 (0.22)	33 (8)	-
14 + ADH	94.12 (6.92)	10.17 (0.28)	348 (52)	2.23 (0.4)
15 + HMDA	98.55 (31.08)	3.99 (1.33)	154 (46)	2.52 (0.76)



**Figure S6.** Loss modulus ( $E''$ ) for four latexes, as are identified in the legend. (See Tables 1, 2 and 3 for more information on these samples).

## References

1. Couvreur, L.; Lefay, C.; Belleney, J.; Charleux, B.; Guerret, O.; Magnet, S., First Nitroxide-Mediated Controlled Free-Radical Polymerization of Acrylic Acid. *Macromolecules* **2003**, *36*, 8260-8267.