Supporting Information to:

Poly(ethylene glycol)-b-poly(vinyl acetate) block copolymer particles of various morphologies via RAFT/MADIX aqueous emulsion PISA

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Table of contents

- 1. Preparation and characterization of PEG-X macroCTA
- 2. SEC analyses of samples withdrawn during MADIX-mediated emulsion polymerizations of VAc performed in the presence of PEG-X, with a solids content of 10 wt% (A1-A6 in Table 1) and additional TEM images for A5 and A6
- 3. SEC analyses of samples withdrawn during MADIX-mediated emulsion polymerizations of VAc performed in the presence of PEG-X, with a solids content of 15 wt% (B1-B3 in Table 1)
- 4. Particle size distribution for spherical particles (A2, A3, B1)

1. Preparation and characterization of PEG-X macroCTA



Figure S1. Two-step synthesis of PEG-X starting from commercial PEG-OH



Figure S2. ¹H NMR spectra of PEG-X and its precursor PEG-Br and commercial PEG-OH (CDCl₃, 256 scans).



Figure S3. ¹³C NMR of the PEG-X (CDCl₃, 4096 scans)



Figure S4. Normalized SEC traces for PEG-X according to the RI detector (red line) and the UV detector set at 270 nm (blue line).

2. <u>SEC analyses of samples withdrawn during MADIX-mediated emulsion</u> polymerizations of VAc performed in the presence of PEG-X, with a solids content of <u>10 wt% (A1-A6 in Table 1)</u> and additional TEM images for A5 and A6



Figure S5. Normalized SEC traces for latex A1 (DP_{target} = 51, Table 1) at 81% conversion according to the RI detector (red straight line) and the UV detector set at 270 nm (blue dashed line).



Figure S6. PEG-X mediated VAc emulsion polymerization - entry A2 ($DP_{target} = 62$, Table 1). Left: SEC traces for samples withdrawn during the polymerization. Right: Normalized SEC traces at 95% conversion according to the RI detector (red line) and the UV detector set at 270 nm (blue line).



Figure S7. SEC traces for samples withdrawn during PEG-X mediated VAc emulsion polymerization - entry A3 ($DP_{target} = 75$, Table 1).



Figure S8. SEC traces for samples withdrawn during PEG-X mediated VAc emulsion polymerization - entry A4 ($DP_{target} = 100$, Table 1).



Figure S9. PEG-X mediated VAc emulsion polymerization - entry A5 (DP_{target} = 152, Table 1). Left: SEC traces for samples withdrawn during PEG-X mediated VAc emulsion polymerization. Right: Normalized SEC traces at 98% conversion according to the RI detector (red line) and the UV detector set at 270 nm (blue line).



Figure S10. PEG-X mediated VAc emulsion polymerization - entry A6 (DP_{target} = 199, Table 1). Left: SEC traces for samples withdrawn during PEG-X mediated VAc emulsion polymerization. Right: Normalized SEC traces at 93% conversion according to the RI detector (red line) and the UV detector set at 270 nm (blue line).



Figure S11. Additional cryo-TEM images of the crude latexes A5 and A6 (Table 1)

3. <u>SEC analyses of samples withdrawn during MADIX-mediated emulsion</u> polymerizations of VAc performed in the presence of PEG-X, with a solids content of <u>15 wt% (B1-B3 in Table 1)</u>



Figure S12. a) SEC traces for samples withdrawn during PEG-X mediated VAc emulsion polymerization - entry B1 (DP_{target} = 51, Table 1). b) Corresponding evolution of the number-average molar masses M_n (plain squares) and dispersity ($D = M_w/M_n$, hollow squares) upon VAc conversion.



Figure S13. Normalized SEC traces at 95% conversion according to the RI detector (red line) and the UV detector set at 270 nm (blue line) - entry B1 (DP_{target} = 51, Table 1).



Figure S14. a) SEC traces for samples withdrawn during PEG-X mediated VAc emulsion polymerization - entry B2 (DP_{target} = 76, Table 1). b) Corresponding evolution of the number-average molar masses M_n (plain squares) and dispersity ($D = M_w/M_n$, hollow squares) upon VAc conversion.



Figure S15. Normalized SEC traces at 97% conversion according to the RI detector (red line) and the UV detector set at 270 nm (blue line) - entry B2 (DP_{target} = 76, Table 1).



Figure S16. a) SEC traces for samples withdrawn during PEG-X mediated VAc emulsion polymerization - entry B3 (DP_{target} = 100, Table 1). b) Corresponding evolution of the number-average molar masses M_n (plain squares) and dispersity ($\partial = M_w/M_n$, hollow squares) upon VAc conversion.

4. Particles size distribution for spherical particles



Figure S17. Particle size distribution based on the cryo-TEM images for the spherical particles in the crude latexes A2, A3 and B1 (Table 1).



Figure S18. Left: intensity-size distribution and right: number-size distribution for latex B1 (Table 1). Results were obtained by DLS through distribution analysis. The mean diameter for the smaller population is : $D_1 = 25.5$ nm according to the intensity-size distribution.