Electronic Supplementary Material (ESI) for Polymer Chemistry.

Nitroxide-mediated polymerization-induced self-assembly of amphiphilic block copolymers with a pH/temperature dual sensitive stabilizer block

X. G. Qiao,[1,2] P-Y. Dugas,[1] B. Charleux,[1] M. Lansalot,[1] E. Bourgeat-Lami[1*]

[1] Univ Lyon, Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5265, Chemistry, Catalysis, Polymers and Processes (C2P2), 43 Bvd. du 11 Nov. 1918, F-69616 Villeurbanne, France.

[2] College of Chemistry and Chemical Engineering, and Henan Key laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang 471934, China.

SUPPORTING INFORMATION

Synthesis of comb-like P(PEOMA$_{300}$-*co*-MAA-*co*-S)-SG1 macroinitiators. A mixture of monomers (PEOMA, MAA and S), SG1 and DMSO was stirred in an erlenmeyer flask and deoxygenated by nitrogen bubbling for 20 min at room temperature. The BlocBuilder® alkoxyamine initiator was added and nitrogen was bubbled for 10 additional minutes. The mixture was then introduced into a three-neck round-bottom flask (50 mL) and heated to 80 °C. The time zero of the reaction was triggered at 75 °C. Samples were periodically withdrawn to follow monomer conversion by using proton NMR. All the corresponding experiments and results for this kinetic analysis are given in Table 1. Then, the polymerizations were reproduced on a larger scale in a 500 mL three-neck round-bottom flask to get a larger amount of polymer to be used as macroinitiator in emulsion polymerization experiments. The reaction was carried out for 1 h and the final products were dried under vacuum after precipitation in diethyl ether before analysis.

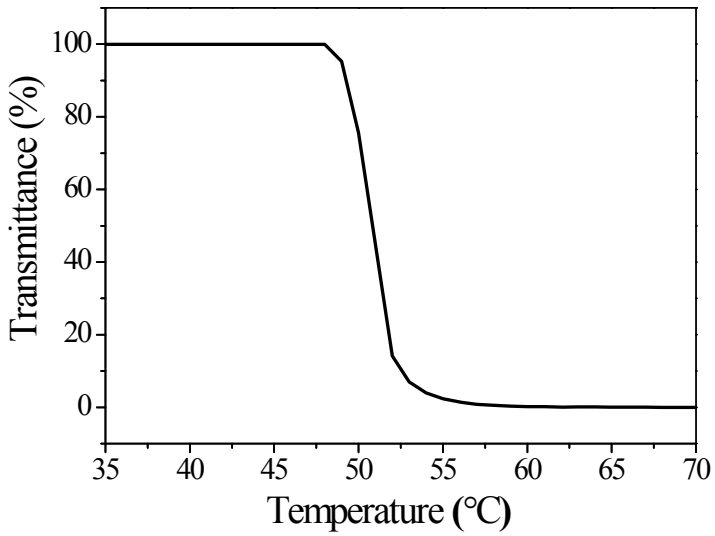

Figure S1. Plot of transmittance as a function of temperature (heating rate = 1 °C min^{-1}) for an aqueous solution (0.5 wt%, pH = 4) of the P($PEOMA_{300}$-*co*-S)-SG1 macroinitiator (Ma0, M_n = 12 100 g mol^{-1}, M_w/M_n = 1.17, Table 2) as measured by UV/Vis spectroscopy at 500 nm [1]. The cloud point was defined as the temperature corresponding to 50% transmittance and was found to be equal to 51 °C. Data extracted from Ref. [1]

Figure S2. Picture of Ma3 in water at pH = 6.1 (left) and pH = 4.4 (right) showing that while Ma3 is fully water soluble above pH 6, it is completely insoluble at low pH in agreement with previous literature.[2]

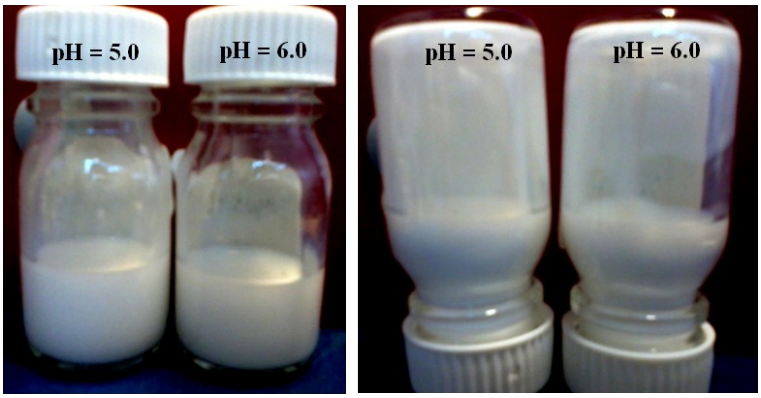

Figure S3. Pictures of the final latexes obtained at different pH values. pH = 5.0 (E4) and pH = 6.0 (E5).

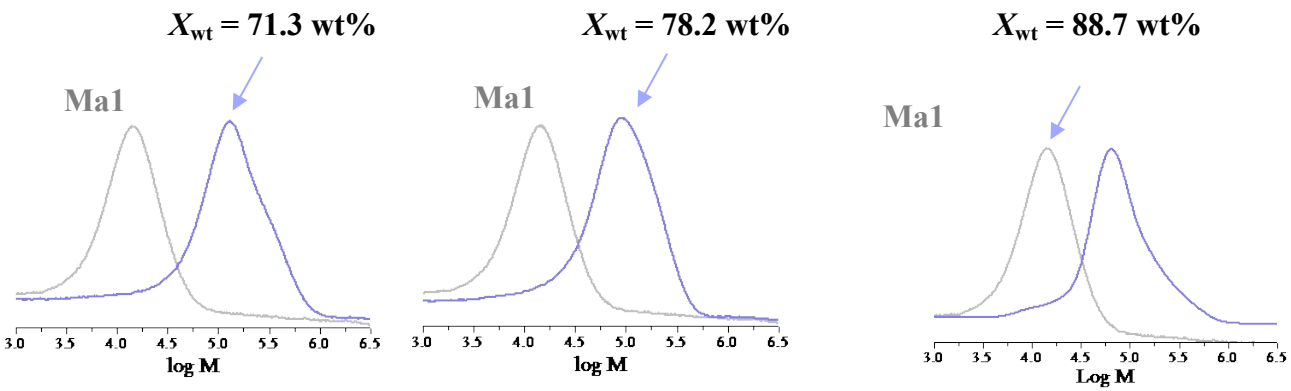

Figure S4. Size exclusion chromatograms (SEC in THF, PMMA calibration) of the final P(PEOMA$_{300}$-*co*-MAA-*co*-S)-*b*-P(BMA-*co*-S) copolymers obtained by surfactant-free emulsion polymerization of BMA and S for increasing Ma1 concentrations at pH 7.5. A) E1: 2.6 mM, B) E2: 5.2 mM and C) E3: 9.1 mM (Table 3).

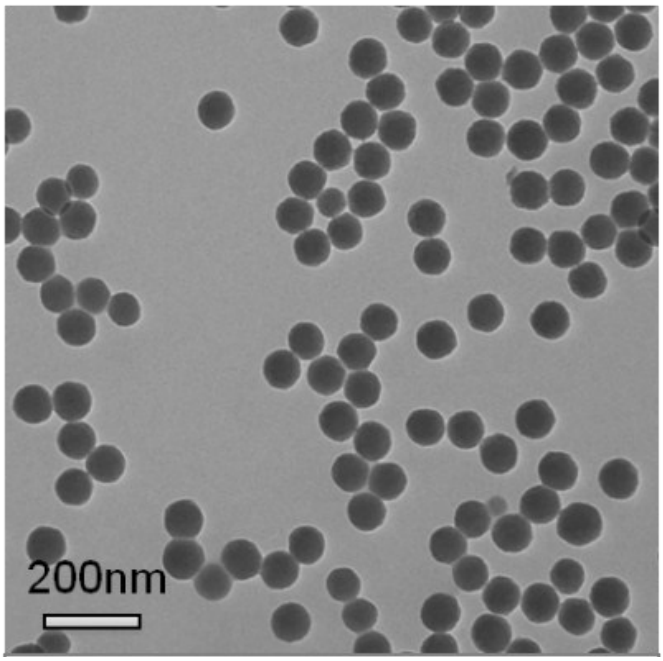

Figure S5. TEM image of the Klebosol 30N50 silica particles (D_n TEM = 77 nm).

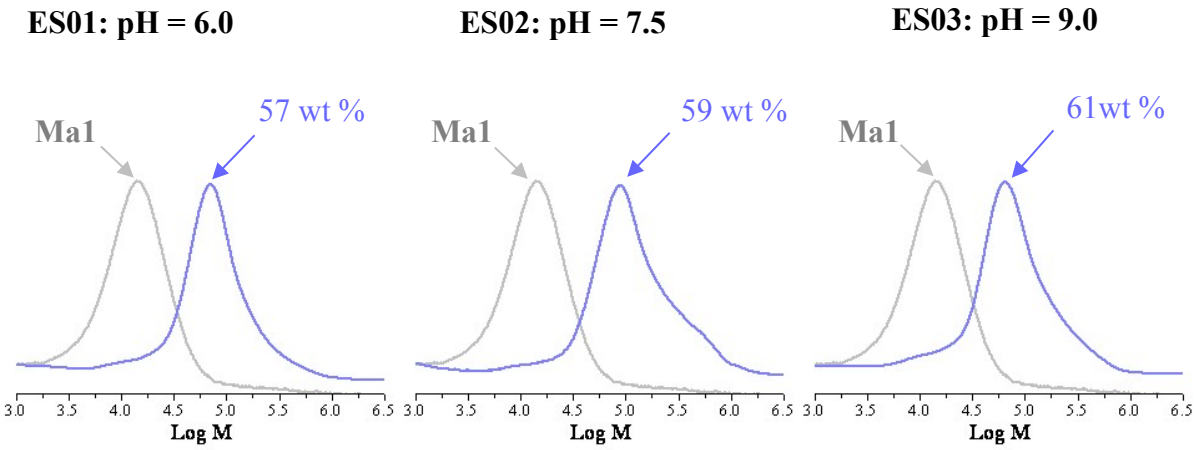

Figure S6. Size exclusion chromatograms (SEC in THF, PMMA calibration) of the final P(PEOMA$_{300}$-*co*-MAA-*co*-S)-*b*-P(BMA-*co*-S) copolymers obtained by surfactant-free emulsion polymerization of BMA and S in the presence of 77 nm diameter silica particles using Ma1 as macroinitiator for different pH values (ES01, ES02 and ES03, respectively). See Table 4 for experimental details.

REFERENCES

1. Qiao, X. G.; Lansalot, M.; Bourgeat-Lami, E.; Charleux, B., Nitroxide-Mediated Polymerization-Induced Self-Assembly of Poly(poly(ethylene oxide) methyl ether methacrylate-co-styrene)-b-poly(n-butyl methacrylate-co-styrene) Amphiphilic Block Copolymers. *Macromolecules* **2013,** *46*, 4285-4295.
2. Jones, J. A.; Novo, N.; Flagler, K.; Pagnucco, C. D.; Carew, S.; Cheong, C.; Kong, X. Z.; Burke, N. A. D.; Stöver, H. D. H., Thermoresponsive copolymers of methacrylic acid and poly(ethylene glycol) methyl ether methacrylate. *J. Polym. Sci. Part A: Polym. Chem.* **2005,** *43*, 6095-6104.