Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Laponite-based colloidal nanocomposites prepared by RAFT-mediated surfactant-free emulsion polymerization: the role of non-ionic and anionic macroRAFT polymers on stability and morphology control

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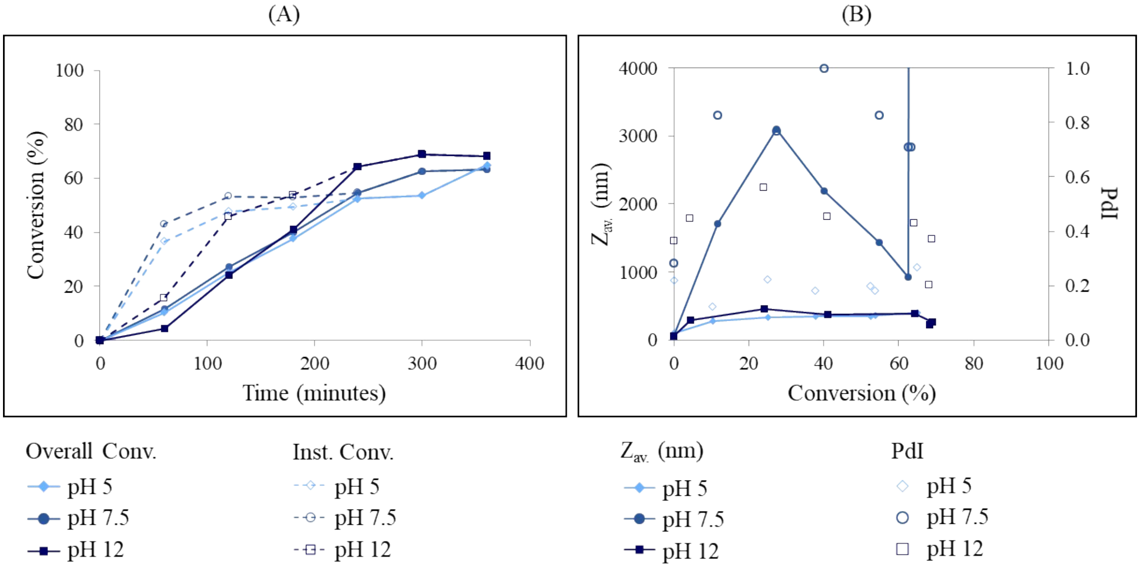

Figure S1 – Effect of pH on the evolutions of: (A) overall monomer conversion (full line) and instantaneous conversion (dashed line) with time and (B) average hydrodynamic diameters and PdI with conversion during the synthesis of P(MMA-*co*-BA)/Laponite nanocomposite latexes by RAFT-mediated surfactant-free emulsion polymerization using PAA_{40}-TTC macroRAFT agent (M1) at different pHs, i.e. pH = 5.0 (R1A); pH = 7.5 (R1B) and pH = 12.0 (R1C).

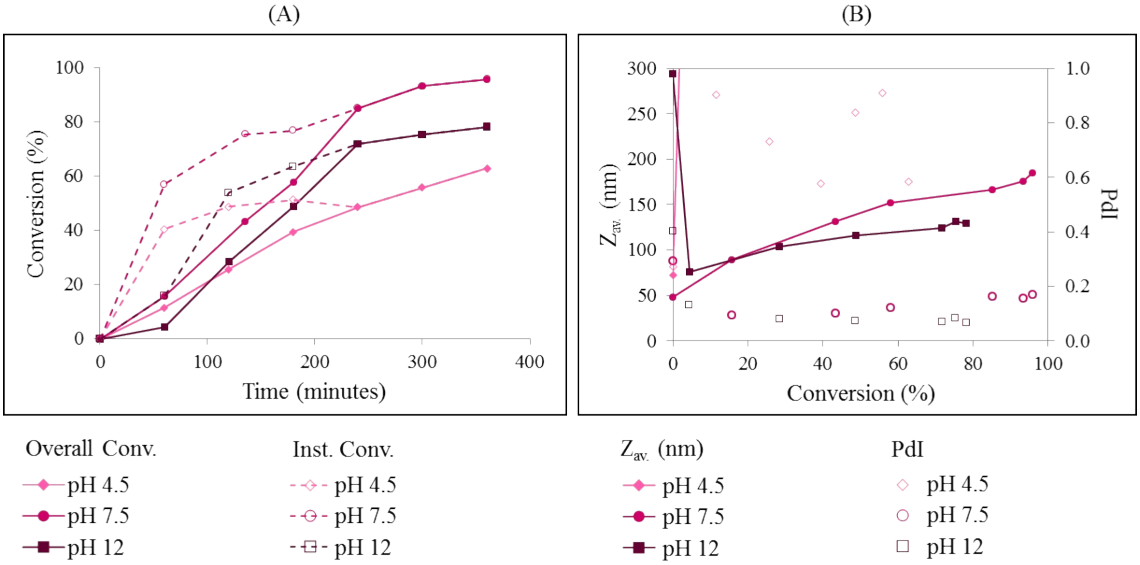

Figure S2 – Effect of pH on the evolutions of: (A) overall monomer conversion (full line) and instantaneous conversion (dashed line) with time, and (B) average hydrodynamic diameters and PdI with conversion during the synthesis of P(MMA-*co*-BA)/Laponite nanocomposite latexes by RAFT-mediated surfactant-free emulsion polymerization using PEG_{45}-*b*-PAA_{42}-TTC macroRAFT agent (M2) at different pHs, i.e. pH = 4.5 (R2A); pH = 7.5 (R2B) and pH = 12.0 (R2C).

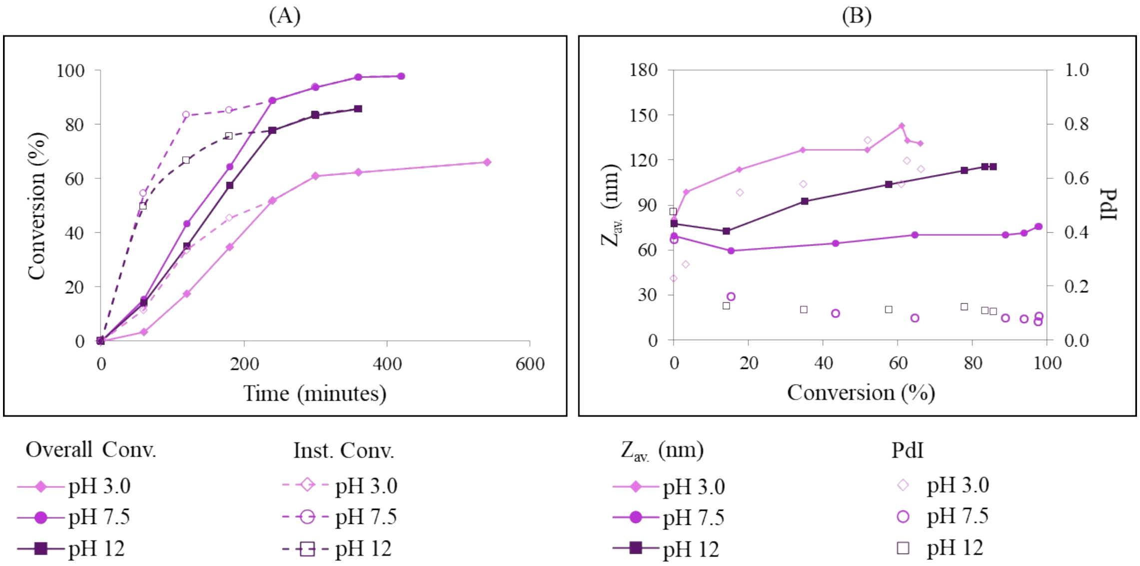

Figure S3 – Effect of pH on the evolutions of: (A) overall monomer conversion (full line) and instantaneous conversion (dashed line) with time and (B) average hydrodynamic diameters and PdI with conversion during the synthesis of P(MMA-*co*-BA)/Laponite nanocomposite latex by RAFT-mediated surfactant-free emulsion polymerization using PAA_{40}-*b*-$PPEGA_4$-TTC macroRAFT agent (M3) at different pHs, i.e. pH = 3.0 (R3A); pH = 7.5 (R3B) and pH = 12.0 (R3C).

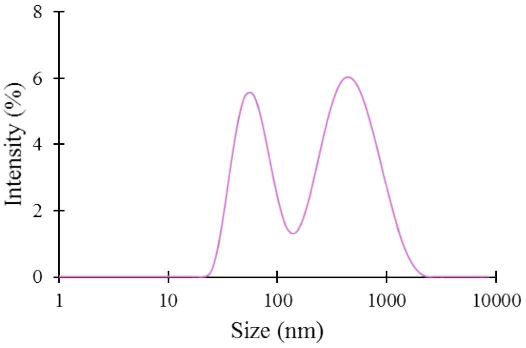

Figure S4. Size distribution by intensity of P(MMA-*co*-BA)/Laponite nanocomposite latexes synthesized by RAFT-mediated surfactant-free emulsion polymerization using PAA_{40}-*b*-$PPEGA_4$-TTC macroRAFT agent (M3) at pH 3.0 (R3A).

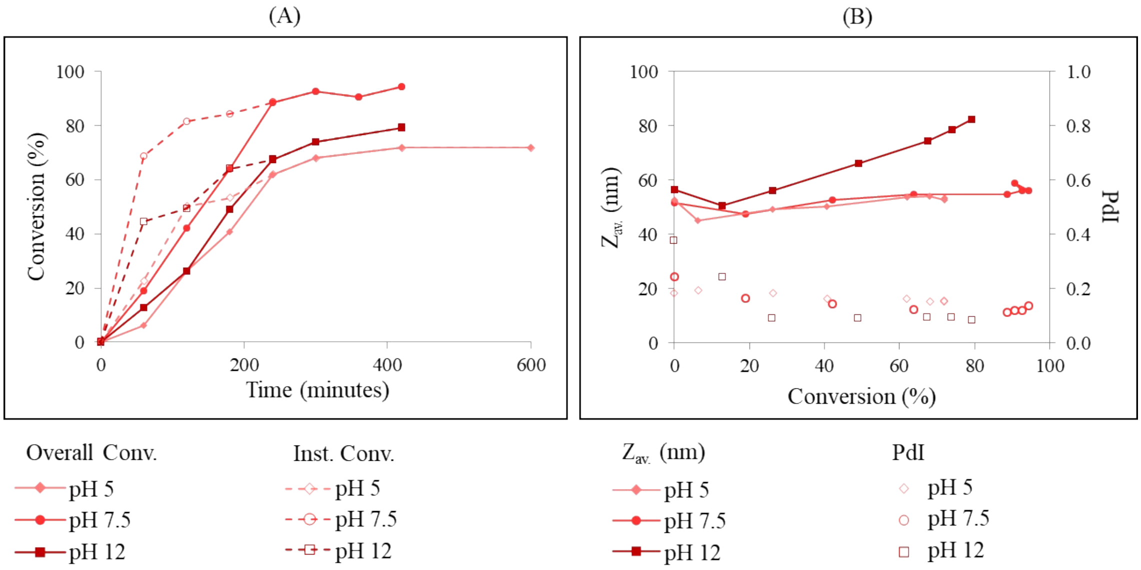

Figure S5 – Effect of pH on the evolutions of: (A) overall monomer conversion (full line) and instantaneous conversion (dashed line) with time and (B) average hydrodynamic diameters and PdI with conversion during the synthesis of P(MMA-*co*-BA)/Laponite nanocomposite latex by RAFT-mediated surfactant-free emulsion polymerization using PAA_{40}-*b*-P($PEGA_6$-*co*-BA_4)-TTC macroRAFT agent (M4) at different pHs, i.e. pH = 5.0 (R4A); pH = 7.5 (R4B) and pH = 12.0 (R4C).

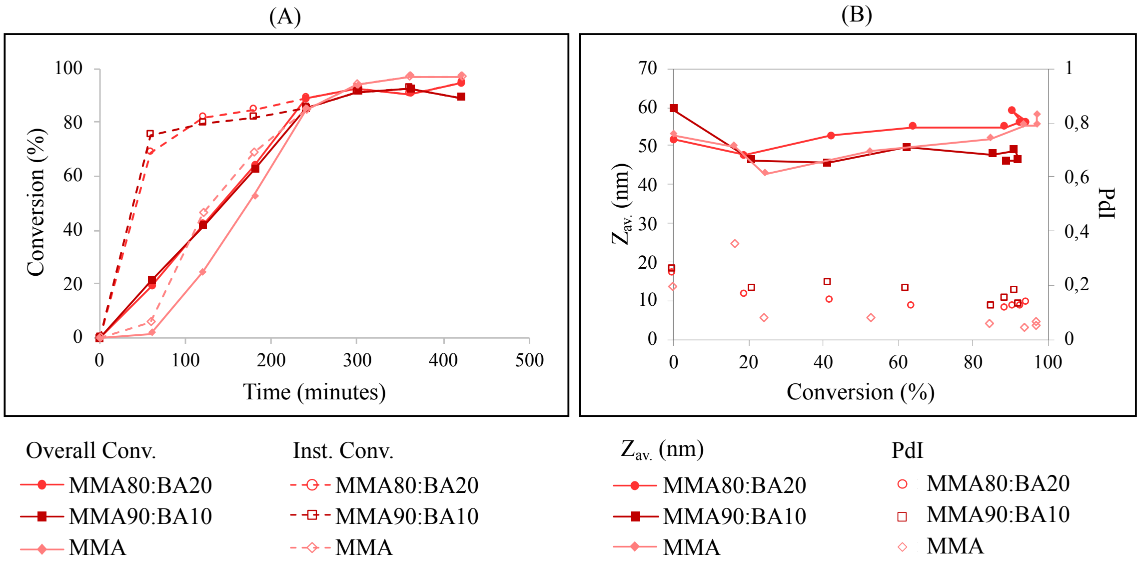

Figure S6 – (A) Evolution of overall monomer conversion (full line) and instantaneous conversion (dashed line) with time and (B) evolution of the average hydrodynamic diameters and PdI with conversion during the synthesis of polymer/Laponite nanocomposite latex by RAFT-mediated surfactant-free emulsion polymerization using PAA_{40}-*b*-P($PEGA_6$-*co*-BA_4)-TTC macroRAFT agent (M4) with different molar ratios of monomers MMA and BA, i.e. MMA:BA 80:20 (R4B); MMA:BA 90:10 (R4D) and pure MMA (R4E).

The polymerization of pure MMA (R4E) presented an induction period. Generally related to the nucleation mechanism, induction periods may correspond to the first chain transfer reactions necessary for the copolymer to self-assemble in water (right after the hydrophobic block has reached a sufficient length). One factor that may have led to this phenomenon during polymerization with MMA is the high hydrophilicity of the monomer, which increases the critical length of the hydrophobic block necessary for the self-assembly process, retarding the nucleation of particles. In this scenario, it is possible that the self-assembly process involves block copolymers grown from the clay surface with block copolymers formed in water. In addition, the induction period shows that polymerization with MMA does not start during the first 60 minutes and so there is no competitive homogenous nucleation. Having this in mind, another factor that should be considered is that the initialization period[1] in the presence of MMA can be significantly longer than for the equivalent reactions in the presence of MMA and BA. So, before being able to properly grow, all the PAA_{40}-*b*-P($PEGA_6$-*co*-BA_4)-TTC chains should add at least one BA unit. And upon fragmentation of the intermediate macroradical PMMA-S-$C^{\bullet}$(S-C_3H_5)-S-M4, preferentially the methacrylate moieties will be released (as they are more stable than the polyacrylate $M4^{\bullet}$ species) and so extension of M4 by a PMMA segment may need more time to be accomplished (as the BA units help the fragmentation to occur more efficiently). In addition, the synthesis of hybrid latexes with pure MMA presented lower instantaneous conversions. It is known that, besides forming droplets (which compete for adsorption of macroRAFT stabilizers and Laponite platelets), accumulated monomer might act as plasticizer and decrease the T_g of the polymer shell, which is undesirable in the present work.

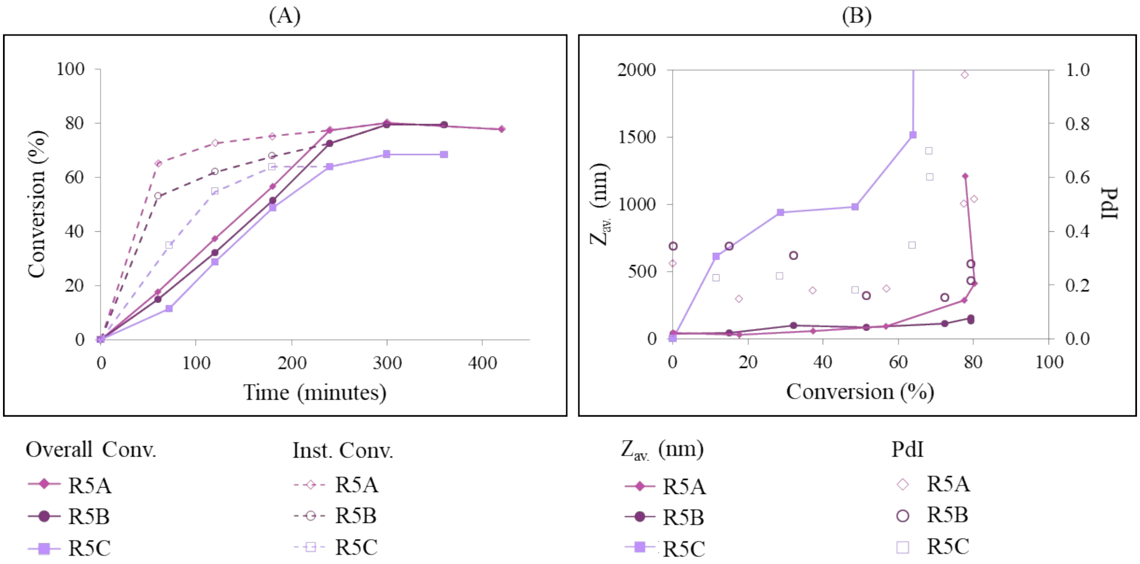

Figure S7 – (A) Evolution of overall monomer conversion (full line) and instantaneous conversion (dashed line) with time and (B) evolution of the average hydrodynamic diameters and PdI with conversion during the synthesis of P(MMA-*co*-BA)/Laponite nanocomposite latex (MMA:BA = 90:10 wt ratio) by RAFT-mediated surfactant-free emulsion polymerization using P(PEGA$_5$-*co*-BA$_3$)-TTC macroRAFT agent (M5) for experiments R5A, R5B (with five-minute sonication process, at 30% amplitude) and R5C (blank, without Laponite).

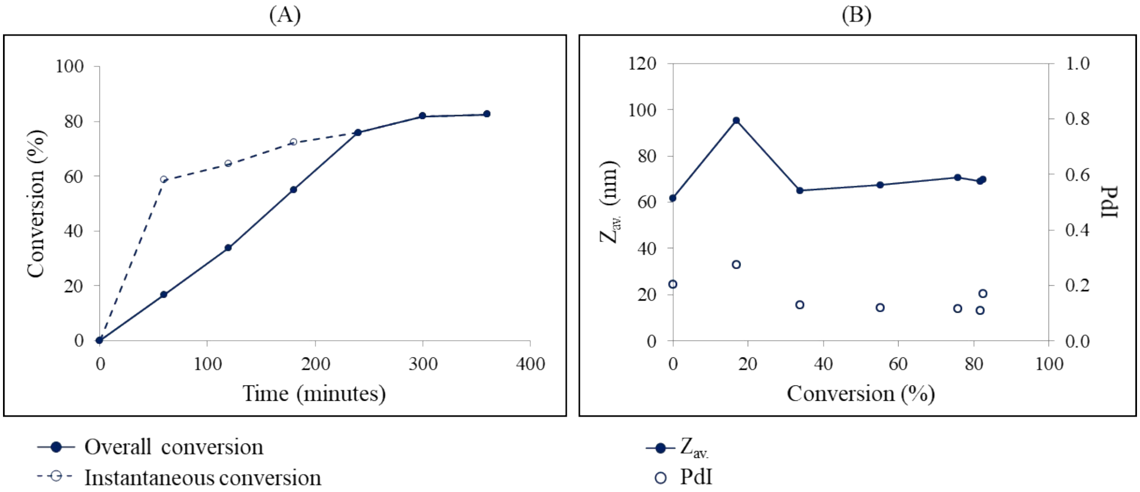

Figure S8. (A) Evolution of overall monomer conversion (full line) and instantaneous conversion (dashed line) with time and (B) evolution of the average hydrodynamic diameters and PdI with conversion during the synthesis of P(MMA-*co*-BA)/Laponite nanocomposite latex (MMA:BA = 90:10 wt ration) by surfactant-free RAFT-mediated emulsion polymerization using 2.2 mM of P(AA$_{16}$-*co*-BA$_{16}$)-TTC macroRAFT agent (M6) at pH 7.5 (R6).

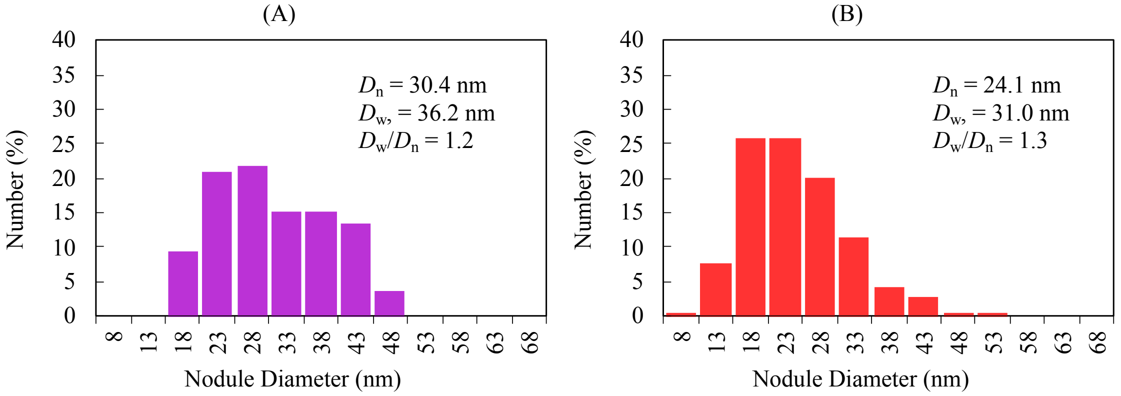

Figure S9. Particle size distribution by number histograms of P(MMA-*co*-BA)/Laponite nanocomposite latexes synthesized by RAFT-mediated surfactant-free emulsion polymerization using (A) PAA_{40}-*b*-$PPEGA_4$-TTC macroRAFT agent (M3) at pH 7.5 (R3B) and (B) PAA_{40}-*b*-P($PEGA_6$-*co*-BA_4)-TTC macroRAFT agent (M4) at pH 7.5 (R4B).

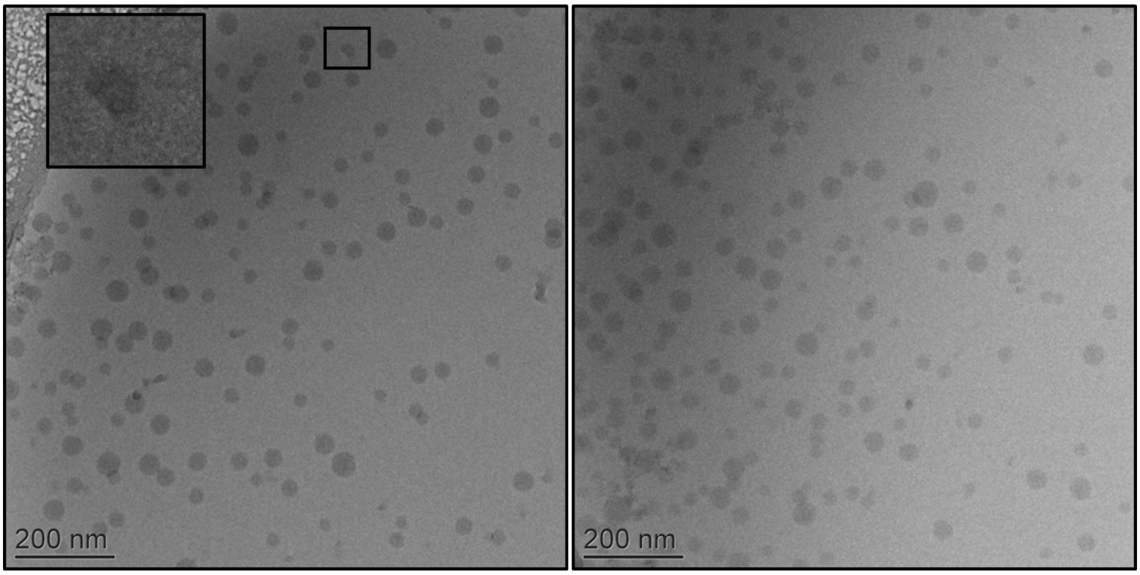

Figure S10. Cryo-TEM images of hybrid particles obtained by the copolymerization of MMA:BA 80:20, at 80 ºC, in the presence of 2.2 mM of macroRAFT agent PAA_{40}-*b*-$PPEGA_4$-TTC (M3) and 5 g L^{-1} of Laponite at pH 7.5 (R3B).

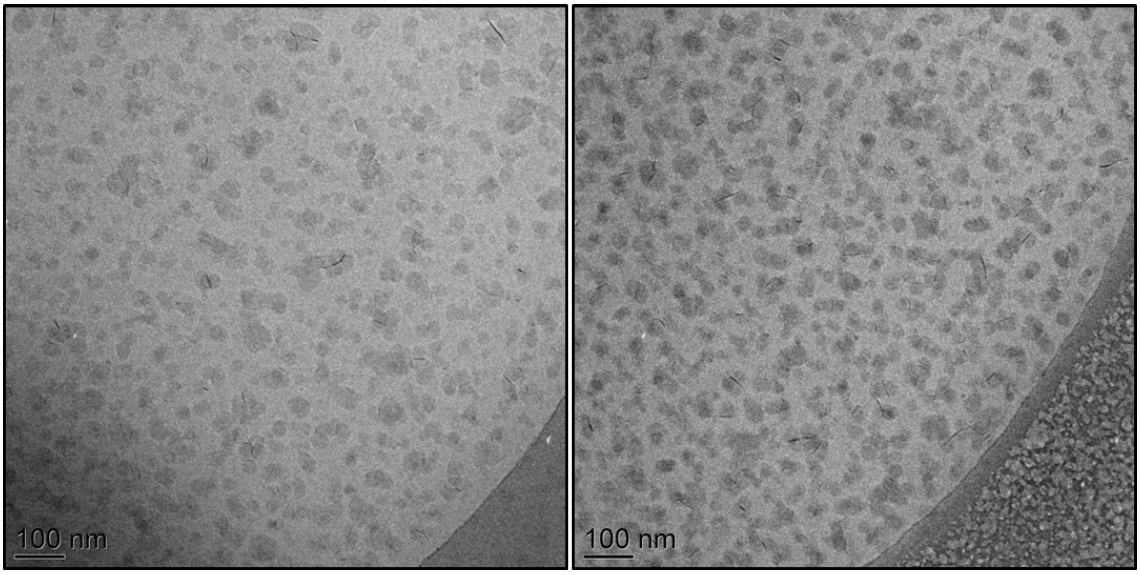

Figure S11. Cryo-TEM images of hybrid particles obtained by the copolymerization of MMA:BA 90:10, at 80 ºC, in the presence of 2.2 mM of macroRAFT agent P(AA_{16}-*co*-BA_{16})-TTC (M6) and 5 g L^{-1} of Laponite at pH 7.5 (R6).

1. J. B. McLeary, F. M. Calitz, J. M. McKenzie, M. P. Tonge, R. D. Sanderson and B. Klumperman, *Macromolecules*, 2005, **38**, 3151-3161.