Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

High solids content nitroxide mediated miniemulsion polymerization of *n*-butyl methacrylate

*Nicholas Ballard,[1] Miren Aguirre,[1] Alexandre Simula,[1] Jose R. Leiza,[1] Steven van Es,[1,2] and José M. Asua[1]**

[1] POLYMAT and Kimika Aplikatua Saila, University of the Basque Country UPV/EHU, Joxe Mari Korta Zentroa, Tolosa Hiribidea 72, 20018, Donostia/San Sebastián, Spain

[2] Dispoltec BV, PO Box 331, 6160 AH Geleen, The Netherlands

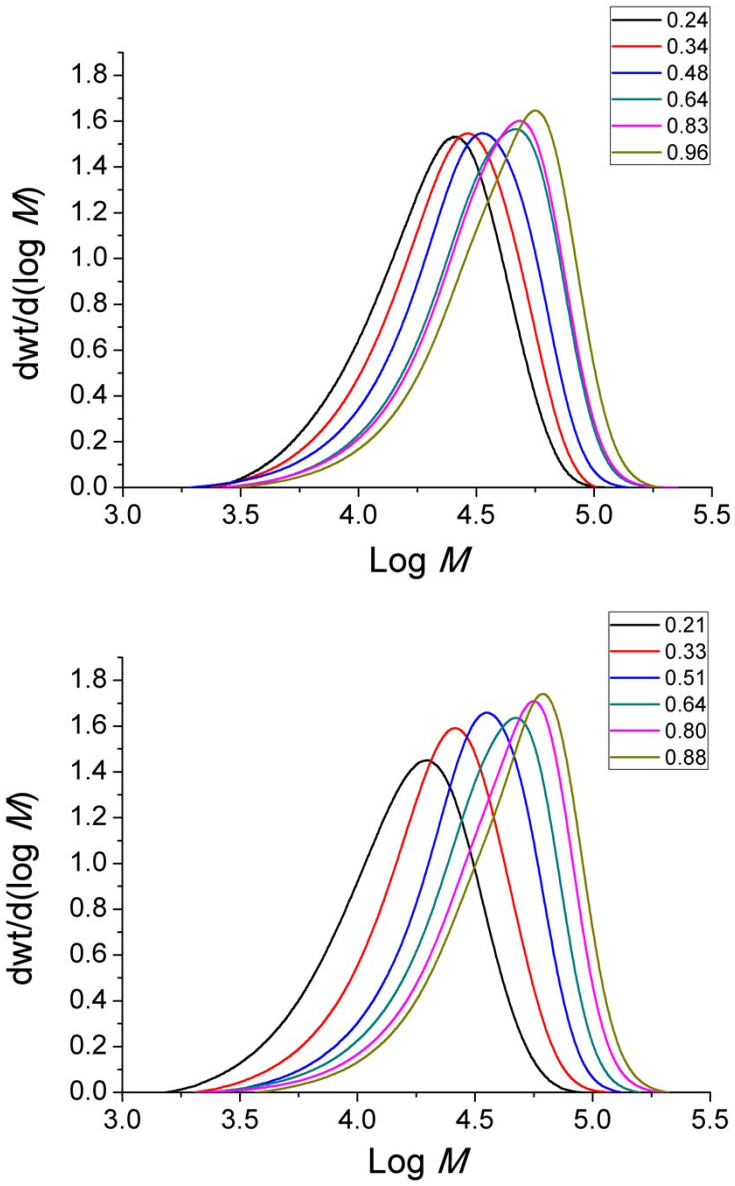

Figure S1 Evolution of MWD with conversion [BMA] / [AAm] = 200 in bulk (top, Run 1) and in miniemulsion (bottom, Run 2). The conversion at each point is shown in the figure legend.

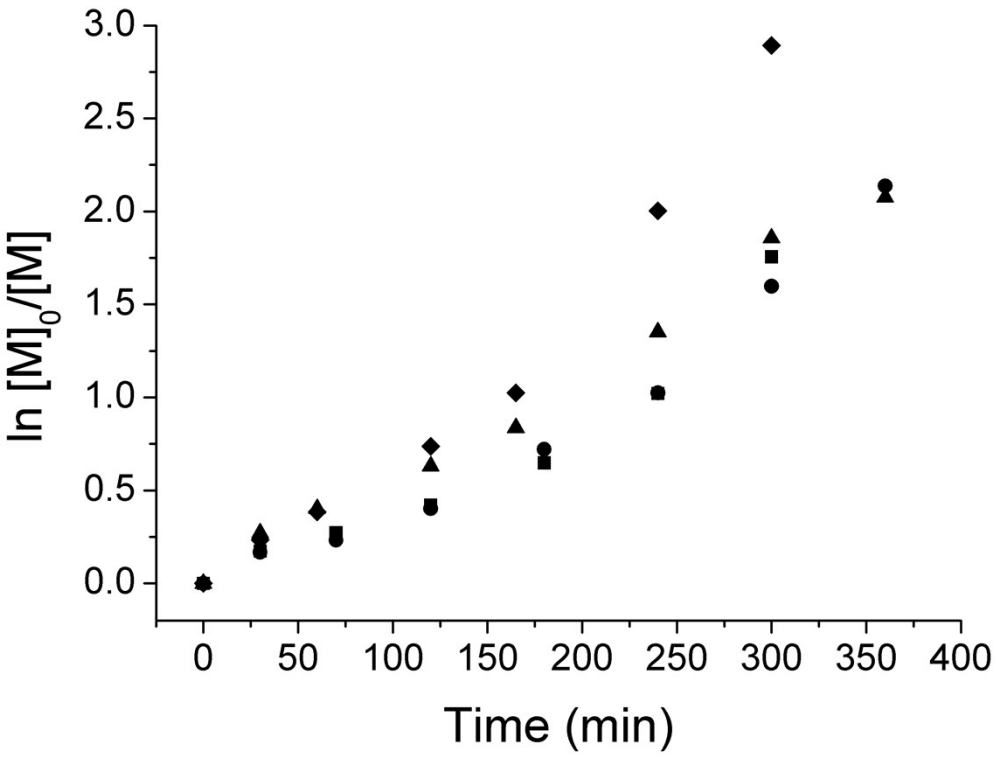

Figure S2 First-order kinetic plot with varying surfactant concentration in miniemulsion polymerization of BMA. Bulk polymerization (Run 1, squares), 0.45 wbm Dowfax (Run 2, diamonds), 2.25 wbm Dowfax (Run 3, circles) and 4.5 wbm Dowfax. (Run 4, triangles). [BMA] / [AAm] = 200.

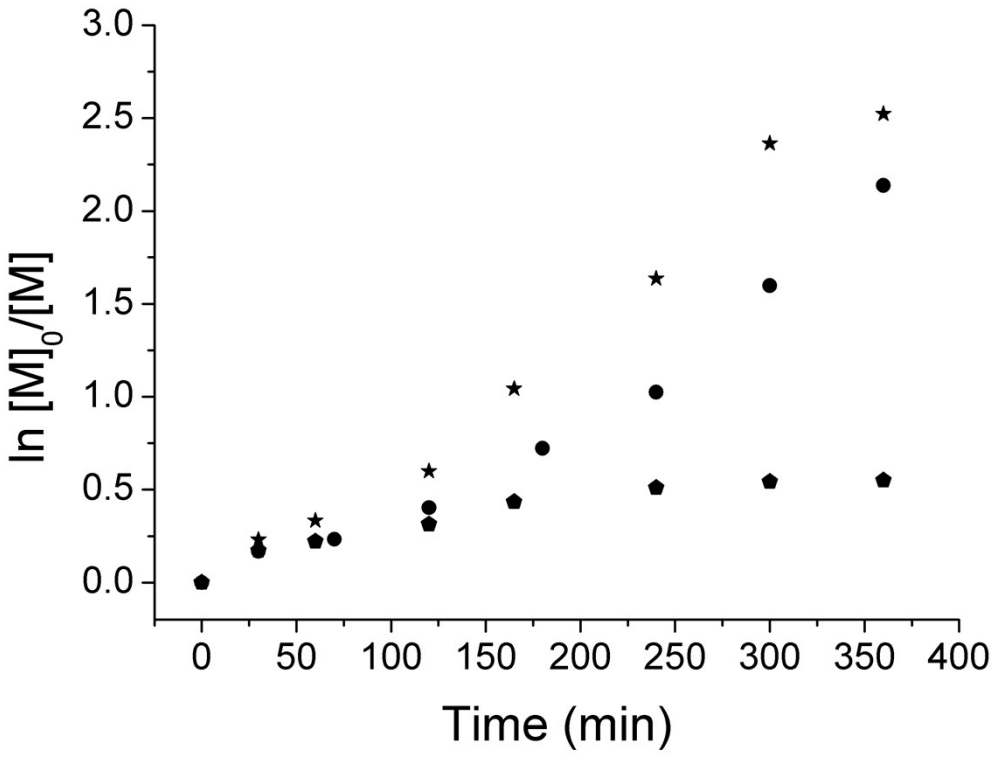

Figure S3 First-order kinetic plot with varying alkoxyamine concentration in miniemulsion polymerization of BMA. [BMA] / [AAm] = 100 (Run 5, stars), [BMA] / [AAm] = 200 (Run 3, circles) and [BMA] / [AAm] = 400 (Run 6, pentagons).

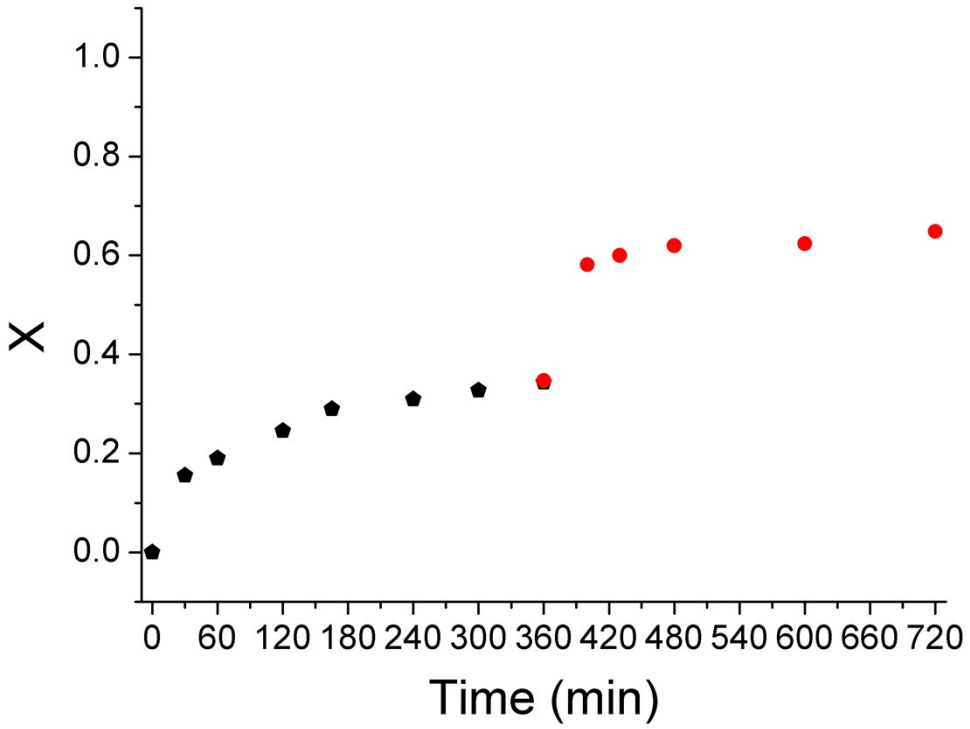

Figure S4 Evolution of conversion on kinetics of miniemulsion polymerization of BMA (left) with [BMA] / [AAm] = 400 (Run 6, pentagons). After 6 h the reaction was cooled to 20 °C and left stirring overnight. The following day the reaction was heated to 90 °C and 5 mL of an aqueous solution of ascorbic acid (1.65 mg/mL) was added (red circles).

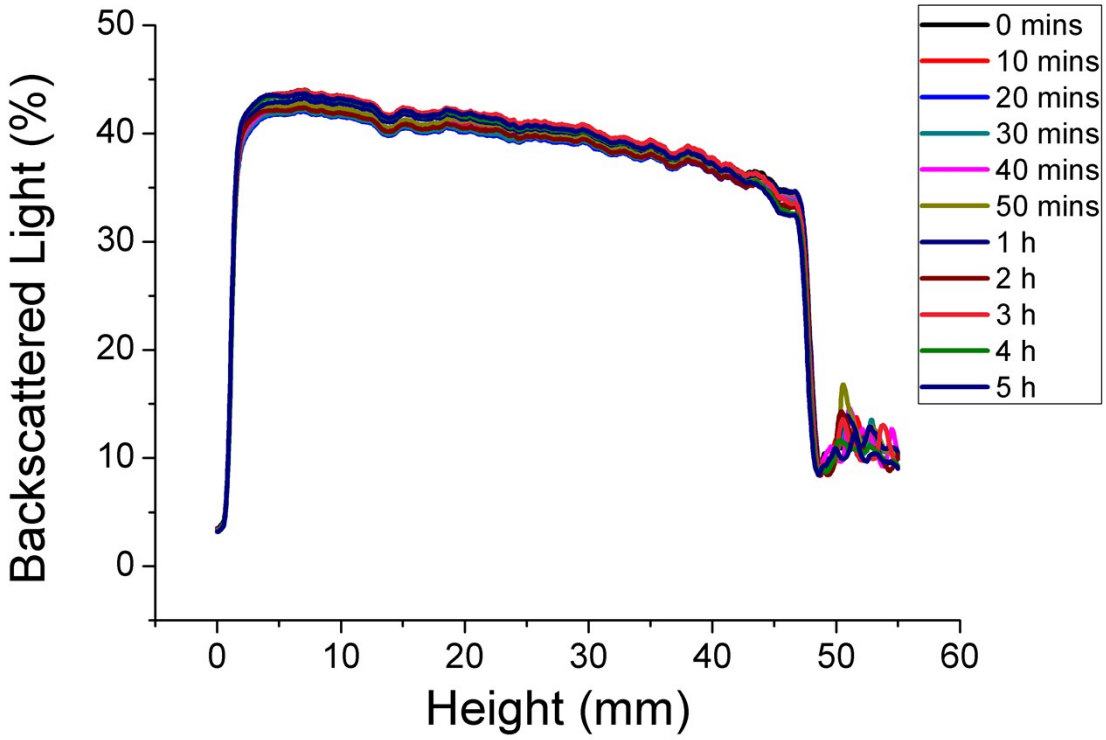

Figure S5 Evolution with time of backscattered light intensity as a function of height of the reaction vessel at 60 °C for a 52 wt % miniemulsion made according to the formulation used in Run 8.

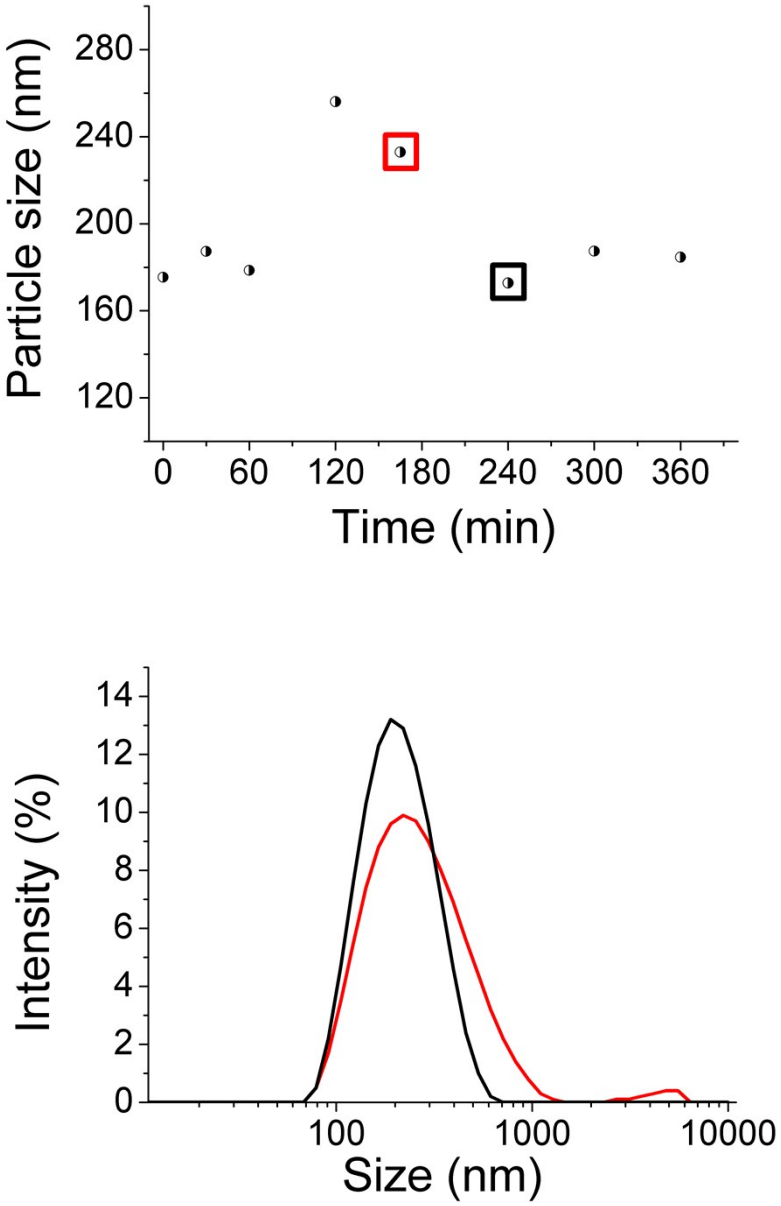

Figure S6 Number and intensity particle size distributions obtained by DLS of selected samples from Run 8 (50 wt% BMA). The two samples taken are at t = 170 min (red) and t = 240 min (black) and are highlighted in the upper part of the figure which shows the evolution of the *z*-average particle size with time.

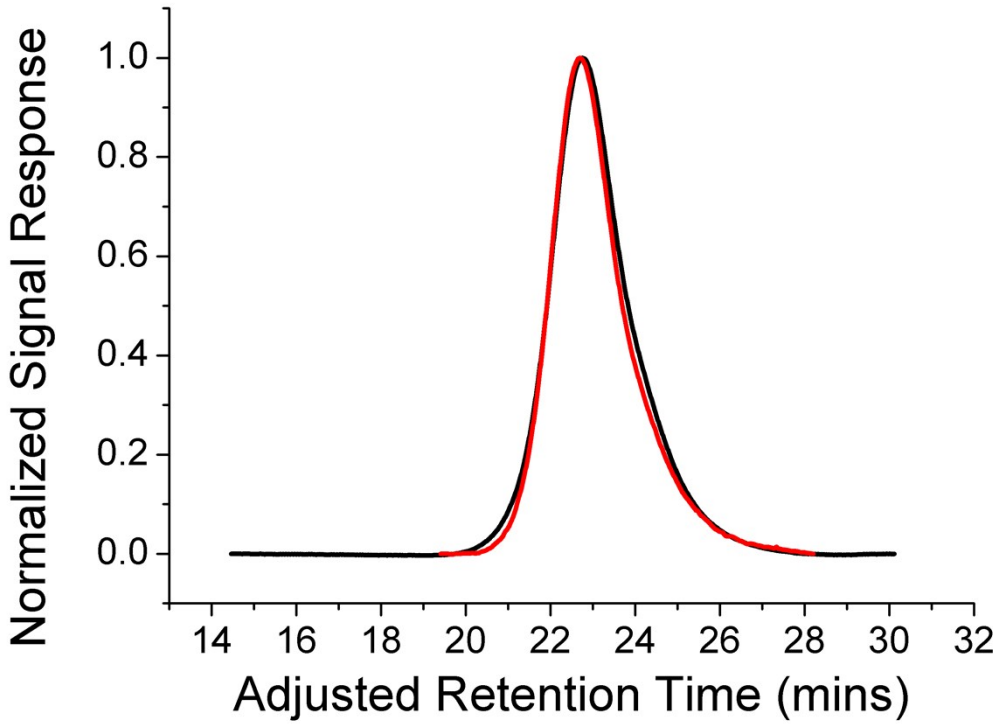

Figure S7 Signal detector response in the SEC chromatogram of chain extended poly(n-butyl methacrylate) with benzyl methacrylate using a UV detector (red) or a differential refractive index detector (black). The UV signal from the alkoxyamine end groups is low (essentially no signal is observed when using only butyl methacrylate) and thus the UV signal can be judged to come exclusively from the benzyl methacrylate units. Note: the retention time is adjusted to account for the time delay between the two detectors.