

Electronic Supplementary Information

Block-Random Copolymer Stabilisers for Semi- batch Emulsion Polymerisation

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Semi-batch Emulsion Polymerization

The sample was polymerised in the absence of salt with 2.5 w/w% of BRC₁. Aggregates are observed in addition to discrete polymer particles because the sample was dry for a few weeks and redispersed into water for TEM purposes. The diameter calculated from TEM is equal to 38.3 ± 3.5 nm based on 150 measurements, calculated with the use of ImageJ software.

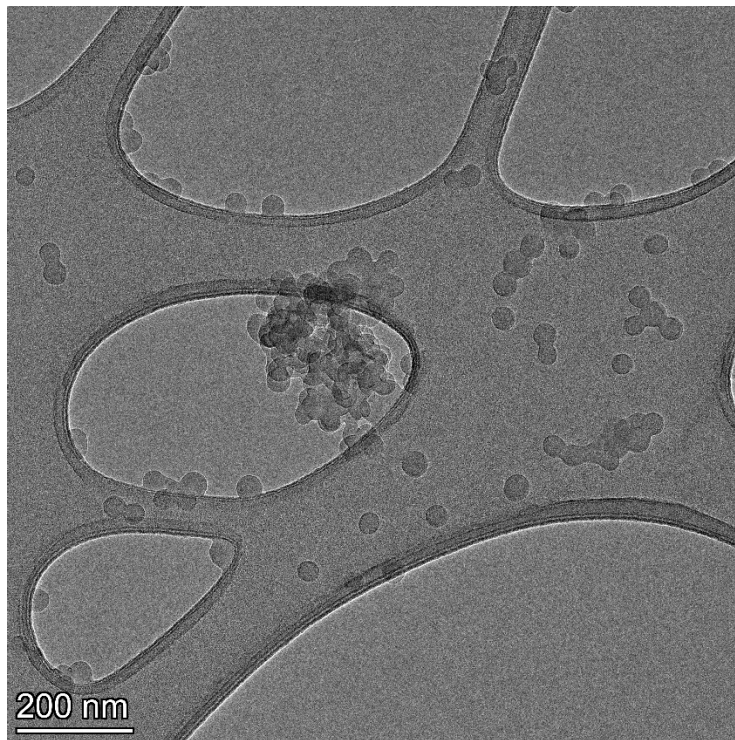


Figure S1. Transmission electronic microscopy (TEM) of a PS latex.

pK_a of BRC₁

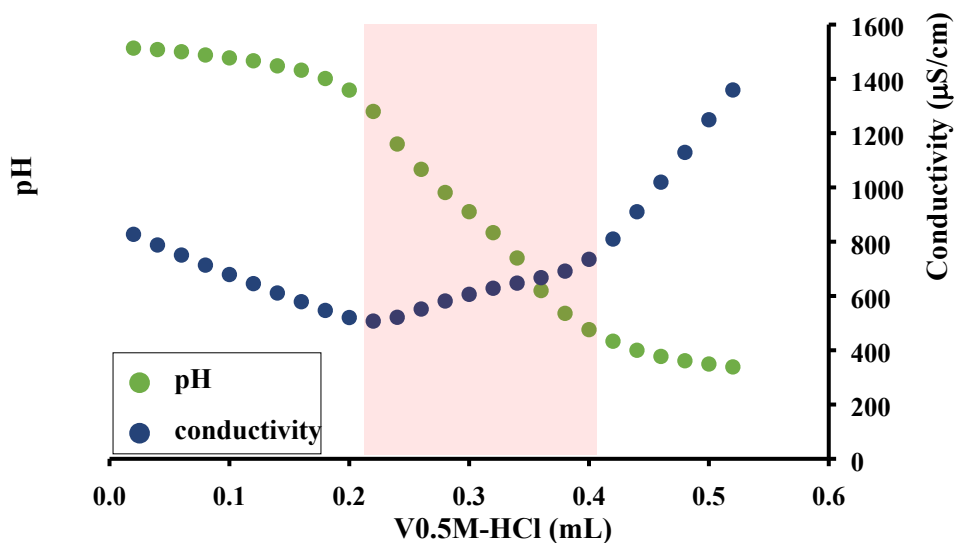


Figure S2. Titration of BRC₁ in at 1 g/L, diluted into pure water. Initial pH is adjusted to ~12 using 1 M NaOH, and 20 µL additions of 0.5 M HCl are added at 45 s intervals. pK_a is estimated as the pH at the midpoint of the middle section (highlighted in red) of the conductivity trace.

Calculation of θ%, the coverage of the particle by acrylic moieties

θ represent the percentage of the surface of the latex which is covered by an acrylic acid molecule and can be calculated with the formula:

$$\theta\% = \frac{DP_{AA} * S_{TPSA}}{a_s} \times 100$$

With DP_{AA} the degree of polymerization of acrylic acid within the chains, S_{TPSA} the topological polar surface area, a constant with a value of 0.373 nm² for acrylic acid and a_s the area stabilized per chain, assuming spherical latex particles and that all the BRC₁ chains are at the interface.

Study of the polymerisation at different pH and ionic strength

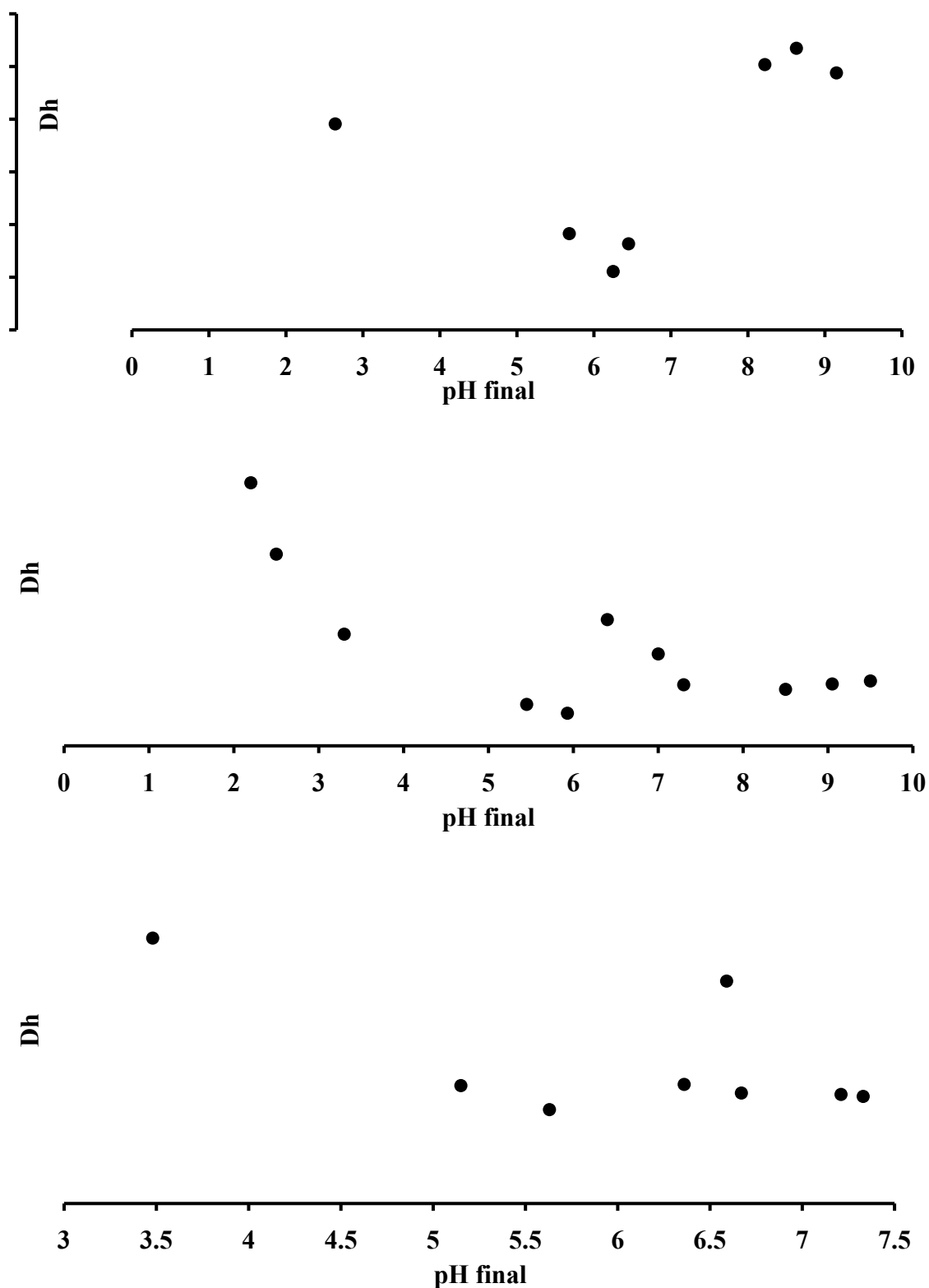


Figure S3: Polystyrene latexes polymerized at various pH in the presence of (a) 0 mM, (b) 25 mM, (c) 50 mM of salt.

Samples were prepared by addition of NaCl, NaOH, HCl, or a combination of two of these salts. Samples were subsequently placed in a sonication bath at room temperature for 2 minutes. For initial $\text{pH} < 7.0$ the samples were turbid before polymerisation. The coagulum of the final latex was minimal ($<1\%$). The initial and final pH, along with the sizes (D_h , D_n) and the PDI are reported in Table S1.

The three experiments show similar trends. An increase in D_h is observed when the pH is decreased from $9 < \text{pH} < 12$ to pH closer to pKa (with $\text{pKa} = 6.5$), reaching a maximum followed by a diminution for final $\text{pH} = \text{pKa}$. This diminution is accentuated in absence of added salt, the enhanced repulsion diminishing the coagulation of the growing latex. The PDI is also maximum for pH around pKa due to the presence of two populations of polymer particles.

Table S1. Characterization of PS latexes stabilized by 5 w/v% of BRC₁ at various initial pH and various salt concentration.

^a Entry	Added Salt (mM)	^b Initial pH _i	^b Final pH _f	^c D _h (nm)	^c D _n (nm)	^c PDI
A ₁	2.0	7.0	2.6	196	140	0.17
A ₂	1.5	7.7	5.7	91	42	0.31
A ₃	0.9	8.3	6.3	55	35	0.23
A ₄	0.3	8.6	6.5	82	31	0.49
A ₅	0.3	9.0	8.6	267	164	0.22
A ₆	1.9	9.5	8.2	252	158	0.16
A ₇	5.4	10.0	9.2	244	188	0.13
B ₁		5.3	2.2	729	732	0.06
B ₂		5.9	2.5	531	510	0.09
B ₃		6.6	3.3	309	267	0.10
B ₄		7.4	5.5	115	80	0.11
B ₅		7.9	5.9	90	58	0.18
B ₆	25.0	8.5	6.4	350	306	0.16
B ₇		9.2	7.0	255	124	0.18
B ₈		9.8	7.3	169	135	0.10
B ₉		10.3	8.5	157	130	0.05
B ₁₀		11.1	9.1	171	138	0.07
B ₁₁		12.4	9.5	180	140	0.09
C ₁		6.8	3.5	400	376	0.02
C ₂		7.5	5.6	142	104	0.11
C ₃		7.7	5.2	178	143	0.09
C ₄	50.0	8.1	6.6	335	95	0.62
C ₅		8.4	6.4	180	130	0.21
C ₆		9.1	6.7	167	147	0.02
C ₇		9.3	7.2	164	144	0.02
C ₈		9.6	7.3	161	136	0.07

^aPolymerization done in 30 mL reactor. ^b initial pH was recorded after adding APS at RT using a pH probe. ^cDetermined using Zetasizer.

The pH effect presented in the paper is not specific of BRC₁ and can be reproduced with other PS-(PS-*r*-PAA) BRCs. A second polymer, BRC₂, was synthesised following the reported procedure.¹ BRC₂ has longer blocks and is more hydrophobic than BRC₁ because of its lower overall acrylic acid content.

Table S2. Characterization of polystyrene-*b*-[polystyrene-*r*-poly(acrylic acid)] block-random copolymers.

Copolymer	Anchor Block			Stabilising Block			Overall		
	DP _{PS} ^a	M _n (g/mol)	Đ	DP _{PS} ^b	DP _{PAA} ^b	mol % AA ^c	M _n ^d (g/mol)	Đ	mol % AA ^c
BRC ₁	25	2600	1.11	50	25	33 %	10,350	1.16	25 %
BRC ₂	37	3800	1.17	67	29	30 %	13,630	1.15	22 %

^a Degree of polymerisation determined from GPC molecular weight.

^b Degree of polymerisation based on ¹H NMR block copolymer composition.

^c Molar percentage of poly(acrylic acid) in copolymer determined by ¹H NMR.

^d M_n for the methylated copolymer, polystyrene-*b*-[poly(methyl acrylate)-*r*-polystyrene], reported as polystyrene equivalent.

BRC₂ (3 grams) was added into pure water (60 mL) at 95°C with the addition of a 1 M NaOH solution until a clear dispersion was reached. 50 mL of the dispersion were used for a semi-batch emulsion polymerisation of styrene. The concentration of initiator, temperature, reaction time, and stirring rate were identical to the experiment presented in the manuscript, 85°C, 3 hours, and 300 rpm, respectively. The total volume of polymerization was fixed at 250 mL with an Oil/Water ratio (O/W) of 20/80 and an initial pH of 7.7.

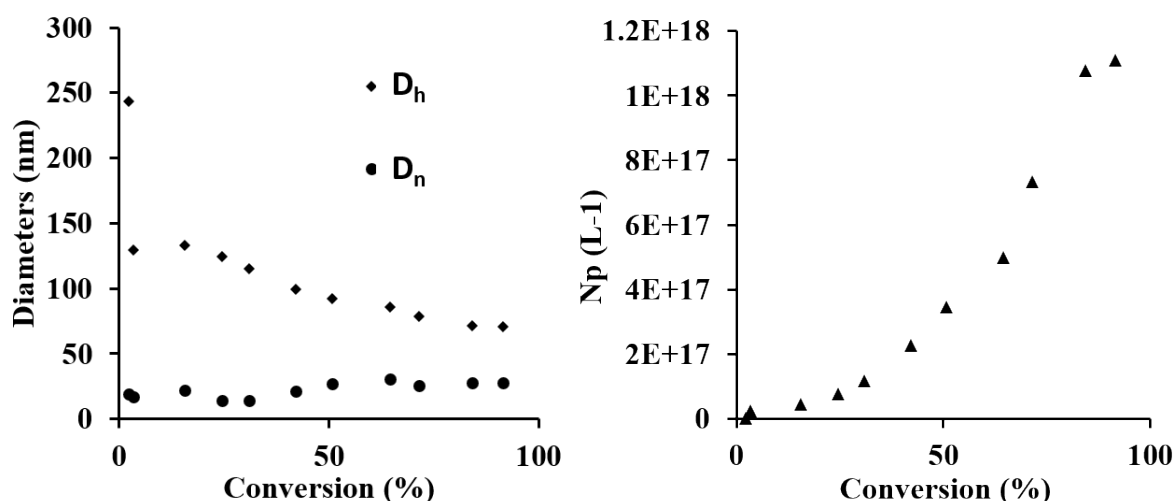


Figure S4: Evolution of D_h (◆), D_n (●), and number of particles of a latex polymerised with a starting pH of 7.7 without addition of salt.

Similar to latexes stabilised by BRC₁, the latex stabilised by BRC₂ undergo a decrease in D_h and a constant value of D_n (20-30 nm) until 100% conversion. Consequently, the number of particles consistently increases, following the samples analyzed in the manuscript. The pH effect is hence also occurring for BRC₂ and is not limited to one specific of BRC.

The morphological change of BRC₁ aggregates in water can be detected in DLS with the increasing signal as the pH decreases. Sixteen dispersions of BRC₁ at 5 g.L⁻¹ were analyzed (Fig. S4) and a clear transition appeared at pH = 8.7 where the count rate increased by a factor of 12.

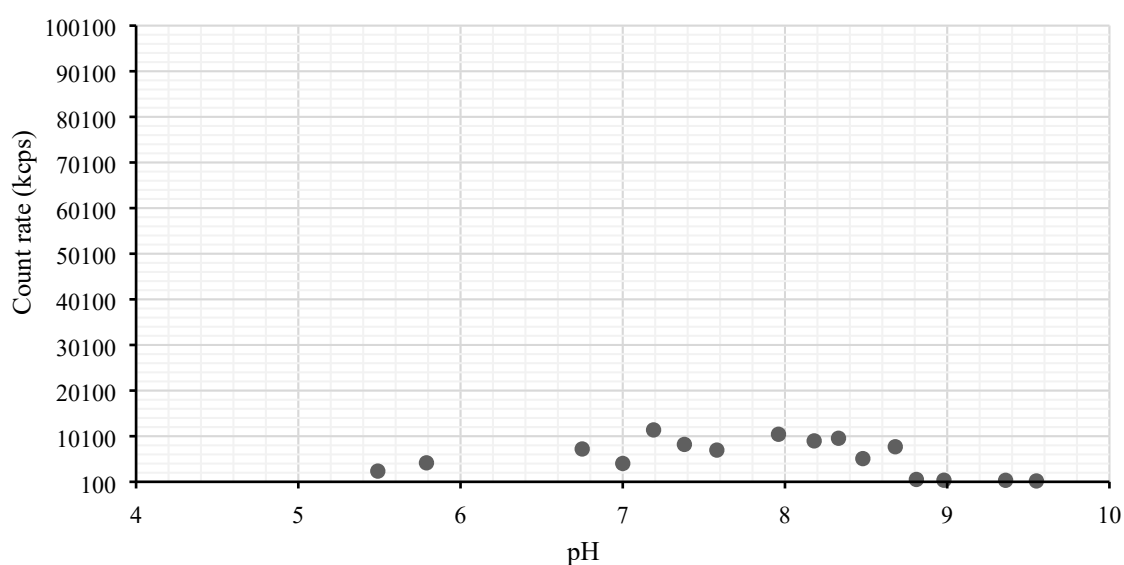


Figure S5: Count rate by DLS plot as function of the pH of a 5 g.L⁻¹ BRC₁ dispersion.

Determination of the populations by sedimentation

Using DLS for the determination of size is fairly accurate when it comes to relatively narrow, monomodal populations. The presence of two or more peaks is a source of error and has to be corrected. To this end, two latexes mixed with a solution of sodium alginate, a creaming agent. After solubilisation in water, the sodium alginate was added to diluted latexes (solid content = 2%), reaching a concentration of 0.3 g.L⁻¹. The latexes were stored 24 h at room temperature before centrifugation and redispersion. Both fractions were analyzed by DLS (Fig. S4) confirming the separation of the two population initially present in the two latexes. The fractions were subsequently dried and the N_p for each population was calculated using Eq. (1).

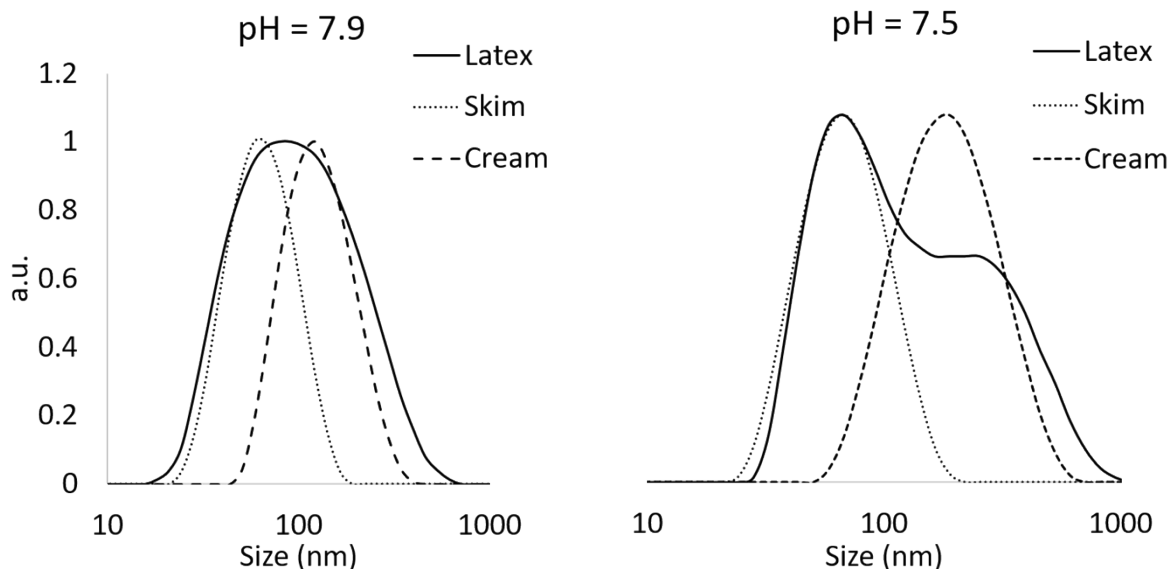


Figure S5: DLS of two polystyrene latexes polymerised at different pH before and after fractional separation with 0.3 g.L^{-1} sodium alginate.

Table S3: D_h and N_p calculation for latexes before and after fractionation by size with the addition of 0.3 g.L^{-1} of sodium alginate

	D_h before (nm)	D_h skim (nm)	D_h cream (nm)	weight % of skim	weight % of cream	N_p before	N_p skim	N_p cream
pH 7.9	81	57	119	71	29	7.2×10^{17}	1.4×10^{18}	6.3×10^{16}
pH 7.5	100	63	170	78	22	2.7×10^{17}	1.3×10^{18}	1.8×10^{16}

Although the quantification of both population was still an estimation, since there were partial overlap of the DLS signals in both case, the number of particle in the skim was similar. For the pH = 7.5 latex, because of the initial pH, closer to pKa and closer to the second order transition observed and described in the manuscript, the number of particles in the cream is three times lower than the pH = 7.9 latex. Closer to this transition, the initial aggregates of BRC₁ were expected to be lower in number, leading to a higher degree of coagulation, hence a wider latex, as verified by this technique.

Rate of polymerisation

The rate of polymerisation is directly related to the number of growing particles in the medium following the equation

$$(S1) \quad R_p = k_p \times [M]_p \times \sum_{i=1}^{\infty} N_i / N_A$$

$k_p[M]_p$ is the molar rate of propagation for a chain radical in a particle, $[M]_p$ is the monomer concentration in a particle, and N_i is the number of polymer particles and N_A the Avogadro number.

In the case of emulsion polymerisation with BRC₁ involving the pH effect, the number of particles is around two orders of magnitude higher than the same emulsion polymerisation started at pH = 9.5. A semi-batch emulsion polymerisation initiated at pH = 8.0 was compared to a batch emulsion polymerisation initiated at pH = 9.5. The feeding time of the semi-batch was set to 1.33 %·min (total time 60 min). As visible on Fig. S5, the rate of polymerisation of the semi-batch experience is over three time higher than the equivalent batch polymerisation, and reach 94 % in 60 min.

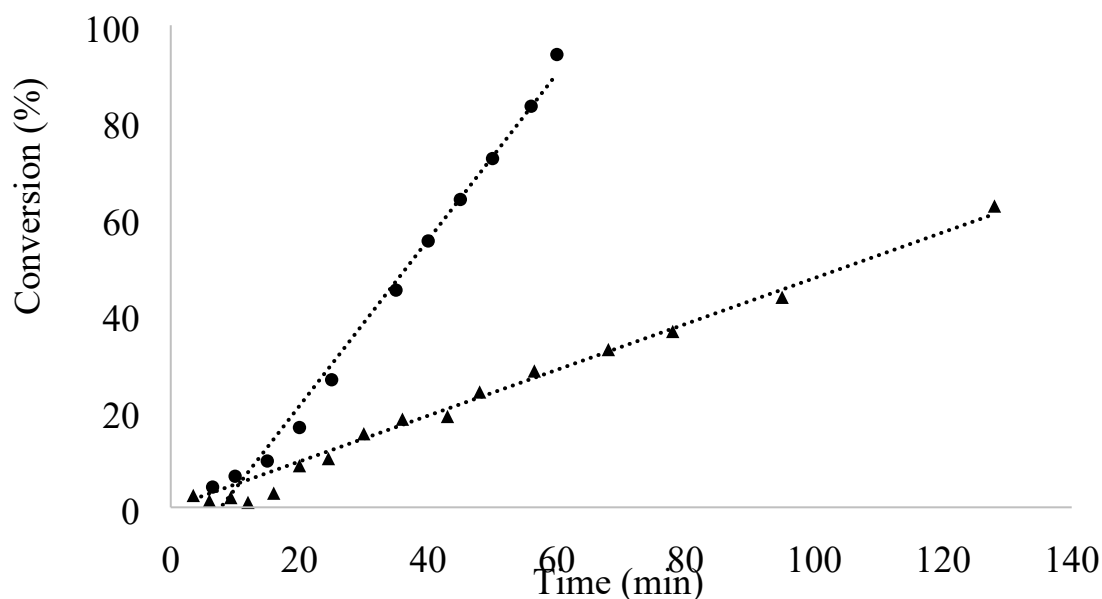


Figure S6: Evolution of the conversion through time for two emulsion polymerisation sample, ● semi-batch initiated at pH 8.0, ▲ batch initiated at pH = 9.5

REFERENCE

1 C. A. Sanders, S. R. George, G. A. Deeter, J. D. Campbell, B. Reck and M. F. Cunningham, *Macromolecules*, 2019, **52**, 4510–4519.