



# Polymerisable surfactants for polymethacrylates using catalytic chain transfer polymerisation (CCTP) combined with sulfur free-RAFT in emulsion polymerisation

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## ABSTRACT

Statistical copolymers of methacrylic acid and methyl methacrylate were synthesised via free radical catalytic chain transfer polymerisation (CCTP) in emulsion to form a hydrophilic emulsifier/surfactant. The vinyl-terminated oligomers were in turn utilised as chain transfer agents, with no further purification, for the formation of diblock copolymers with butyl and methyl methacrylate which constitutes the emulsifier via sulfur-free reversible addition-fragmentation chain transfer polymerisation (SF-RAFT). In turn these polymers were solubilized with various concentrations of ammonium hydroxide and utilised in the surfactant-free emulsion polymerization of butyl methacrylate using persulfate initiators, which also stabilized the polymer particles with observed no coagulation, with solid contents as high as 40%.

## 1. Introduction

Emulsion polymerisation in the absence of added emulsifier, or surfactant, has received significant attention as a technique for synthesising monodisperse spherical particles and clean lattices [1,2]. Emulsion polymerisation is a complex colloidal phenomena with free radical polymerisation occurring with various external factors affecting nucleation, growth and the stabilization of particles. This has been remarkably successful commercially in many applications including coatings, adhesives and in encapsulation technology [2–4]. Although, the nucleation period is typically very short, the formation of particle nuclei throughout the initial stage of the polymerisation plays a fundamental role in determining the final latex particle size and particle size distribution [5–12].

Three major mechanisms for particle nucleation in emulsion polymerization have been proposed to date: *Micellar Nucleation Theory*, originally proposed by Harkins [5,6,13–15] in 1947 Smith [6,8] and Ewart [10,11,14] and modified by Gardon [5,7,8,10–12,16], states that micelles are the principal loci of particle formation is usually understood to be the main nucleation mechanism for the monomers with relatively low water solubility ( $[M]_{aq} < 15 \text{ mmol dm}^{-3}$ ) [5–8,10,13–15,17–19]. Homogeneous nucleation models, proposed by

Fitch [13–15] and Tsai [5,8,15], Priest [5,8,10,12–15] and Roe [8–11,13–15], is considered the primary mechanism for formation of particles in systems with surfactant concentration below the critical micelle concentration CMC, surfactant free polymerisation and formation for the monomers with relatively high water solubility's ( $[M]_{aq} > 170 \text{ mmol dm}^{-3}$ ) [5–8,10–17,19–22]. The third nucleation theory which is significantly less common, is called monomer droplets nucleation mechanism as proposed by Hansen [6,8,13–15] and Ugelstad [6,13], Durlin [5–8,10,11,13–15]. However, this third method occurs very rarely: the cases are in some systems such as chlorobutadiene, which have extremely large spontaneous initiation component, the unique systems of mini-emulsion and micro-emulsion polymerisation, and in some controlled radical systems [7,12,23–26]. Droplet nucleation is the origin of the high molecular weight products [7,8,16,24,26].

When reversible deactivation radical polymerisation (RDRP) methods such as atom transfer radical polymerisation (ATRP), nitroxide mediated polymerization (NMP), single electron transfer living radical polymerisation (SET-LRP) and conventional reversible addition-fragmentation chain transfer polymerisation (RAFT) polymerisation are compared RAFT has been used most successfully under emulsion conditions. There is an excellent review on the use of controlled radical

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methods in dispersed processes [27–30]. Catalytic chain transfer polymerisation (CCTP) in combination with sulfur-free reversible addition–fragmentation chain transfer polymerisation (SF-RAFT) has been shown to be versatile and simple with relatively mild reaction conditions, requiring only parts per million amounts of bis[(difluoroboryl)dimethylglyoximate] cobalt(II), (CoBF) catalyst in the reaction mixture to obtain low molecular weight co-oligomers with vinyl-end group functionality, a wide range of methacrylic monomers can be utilised regardless of the low rate of propagation, tolerance of various functionalities, and is stable at elevated temperatures and low pH [31–41].

The utilisation of either transition metals or sulphur comprising catalysts/chain transfer agents often requires purification methods such as precipitation or dialysis to isolate pure usable products. Furthermore, RAFT or copper mediated techniques are often most suited to acrylic and acrylamide monomers and are often less effective with methacrylates, due to lower rates of propagation [31,32,34–36,39,42–47]. In this current work we utilise statistical copolymers of methacrylic acid and methyl methacrylate, as synthesised via CCTP in emulsion, to form the hydrophilic part of an emulsifier. The vinyl-terminated oligomers were in turn successfully utilised as chain transfer agents for the formation of diblock copolymers of butyl and methyl methacrylate, which constitutes to the hydrophobic part of the emulsifier via (SF-RAFT). In turn these polymers were dissolved with various concentrations of ammonium hydroxide and utilised as polymeric polymerisable surfactants in the subsequent emulsion polymerization of butyl methacrylate using potassium persulfate (KPS) as initiator which also stabilizes the polymer particles with no observable coagulation and solid contents as high as 40%.

## 2. Results and discussion

### 2.1. Synthesis of reactive surfactant via SF-RAFT

We focused on statistical co-oligomers of MMA (85 wt%) and MAA (15 wt%) as prepared using CCTP in emulsion polymerisation with bis[(difluoroboryl)dimethylglyoximate] cobalt(II), (CoBF) as the catalyst, which has been previously reported as an effective CTA for the emulsion CCTP of methacrylates [32,48]. Under these conditions p(MMA<sub>85wt%</sub>-MAA<sub>15wt%</sub>) macromonomers with a range of CoBF concentrations were prepared as previously reported (SI Table 1) [33]. Co-oligomers with 15 wt% MAA and 85 wt% MMA composition were utilised for the synthesis of all of the di-block co-polymers, since higher ratios of incorporated acid in the composition resulted in a small amount of coagulation during polymerisation (approximately 3–8 wt% with respect to the total solid content measured gravimetrically following filtration and drying). At higher acid concentrations (e.g. 35 wt% MAA and 65 wt% MMA) it was not possible to reproducibly achieve very low  $M_n$  polymers with CCTP for reasons that are not fully understood, nevertheless 15% acid content was found to be sufficient for these purposes. Moreover, increasing the acid concentration within the co-oligomers also resulted in an increase in the particle size of the polymers resulting in phase separation ascribed to the particles becoming very hydrophilic and in turn causing water to enter the particles over time giving rise to latex destabilisation, whereas when MAA<sub>15%</sub>-MMA<sub>85%</sub> was used particle sizes < 310 nm were obtained giving stable latex's with long shelf life (stable after 15 months).

The CCTP macromonomers (2) illustrated in Scheme 1 were used as macro-CTAs for the formation of diblock copolymers (3), with a second block consisting of either butyl methacrylate or methyl methacrylate, with a degree of polymerisation (DP) = 10, both block copolymers contained vinyl end groups and acid (MAA) functionality according to <sup>1</sup>H NMR, Fig. 1. The second block comprising the hydrophobic part of the emulsifier, with DP = 10 was selected as a suitable size as when the DP was larger (e.g. DP = 20) it would not fully solubilise with the addition of ammonium hydroxide (NH<sub>4</sub>OH), (4) leaving a pale white dispersion/solution even upon heating to 60 °C. With constant stirring

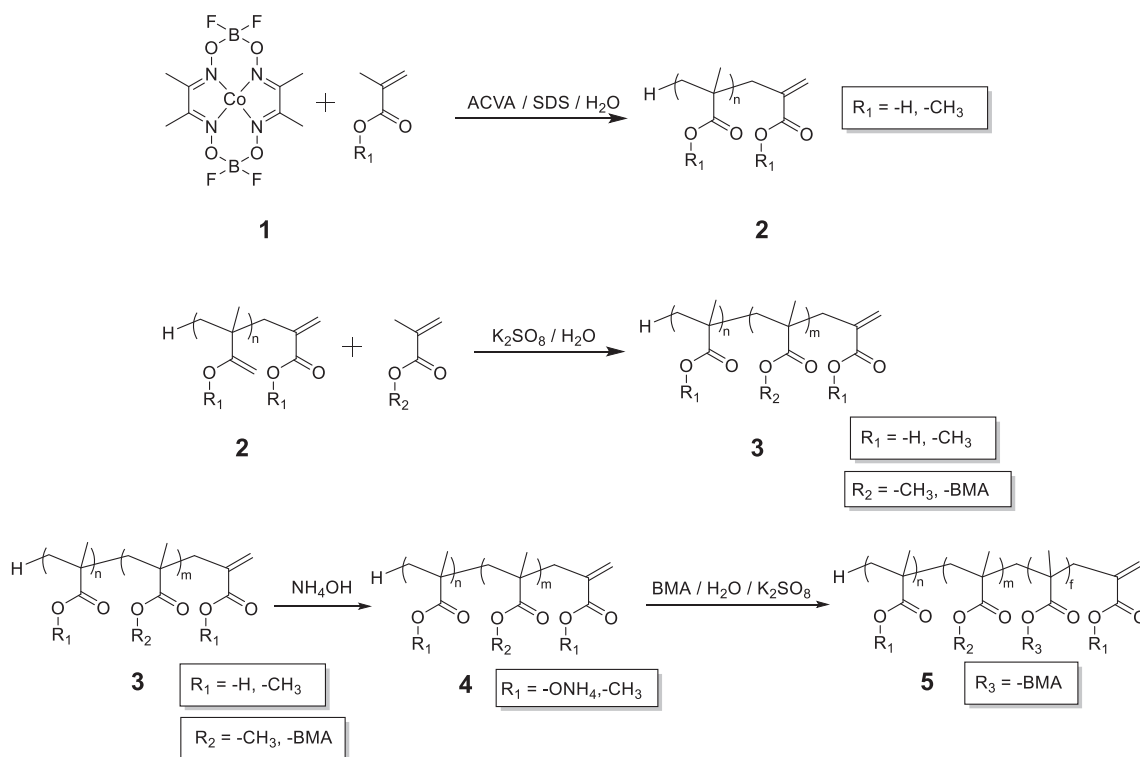
the emulsifier with (DP = 20) completely solubilised and whereas with (DP = 30) upon addition of (NH<sub>4</sub>OH) the latex would remain unchanged (equivalent to the appearance to full fat milk). Upon heating to 60 °C it decolourised slightly changing appearance to pale white solution. In turn, polymeric polymerisable surfactants (4) were subsequently used in emulsion polymerization of butyl methacrylate (5) using potassium persulfate (KPS) as initiator, which also stabilizes the polymer particles with no observable coagulation and solid contents as high as 40%.

### 2.2. Emulsion polymerisation stabilised by polymethacrylate polymerisable surfactants

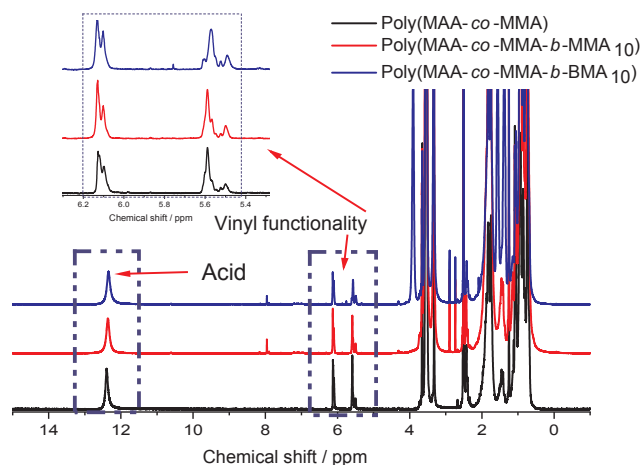
The polymethacrylate-derived surfactants, as described above, were subsequently used as stabilisers for the emulsion polymerisation of butyl methacrylate. All SF-RAFT polymerisations were performed under monomer-starved conditions, such that the polymer particles were not saturated with monomer, but are being polymerised at an instantaneous conversion of 90% or greater [32–34,49,50]. This ensures control of the monomer concentration within the polymer particles. If the reaction were to operate under monomer-flooded conditions, the control over the copolymer composition would be lost [32,33,51].

For all reactions, the [monomer], [initiator] and temperature were kept constant. The temperature was kept > 75 °C, as temperatures < 70 °C are known to reduce the monomer conversion below 100%. This is predominantly due to the formation of macroscopic agglomerates on the reactor wall and on the surface of the overhead stirrer, which in turn reduces the latex yield [11]. Furthermore, it has been previously reported that increasing the temperature decreases the particle size due to increasing decomposition rate of the initiator and increasing monomer solubility in the aqueous phase [11]. Thus, the concentration of the growing chains increases which in turn reduces particle size. However, in these reactions the opposite effect is expected since BMA solubility increases with increase in temperature as a result, the critical chain length increases for the polymer precipitation which may lead larger particles. This was observed for emulsifiers with the hydrophobic moiety consisting of MMA (DP = 10) but not for the series of surfactants containing BMA (DP = 10) as the hydrophobic moiety, which suggest the second effect of temperature is also important in determining the particle size as well as to the principal effect of initiated chain concentration in determining the particle size.

The diblock copolymers of poly(MMA-co-MAA-*b*-BMA<sub>10</sub>) were dissolved in various concentrations of NH<sub>4</sub>OH, referred to with respect to molar equivalence with respect to MAA concentration, and utilised as polymerisable surfactants in place of a conventional surfactant such as SDS. For reaction A' (Fig. 2) post polymerisation with BMA monomer with 0 equivalents of NH<sub>4</sub>OH, both the diblock poly(MMA-co-MAA-*b*-BMA<sub>10</sub>) and subsequent *pseudo* tri-block copolymers resulted in monomodal particles of 614 nm, according to DLS and SEM. Upon dropwise addition, of NH<sub>4</sub>OH to the diblock dispersion of poly(MMA-co-MAA-*b*-BMA<sub>10</sub>) with constant stirring the particle size reduced according to both DLS and SEM. At 0.59 M equivalence of NH<sub>4</sub>OH with respect to MAA reaction B prior to polymerisation with BMA, the latex appeared slightly soluble with the particle size decreasing from 314 nm to 251 nm. SEM, images showed reduction particle size upon 0.59 M equivalence of NH<sub>4</sub>OH and the latex particle went from uniform monomodal particles depicted (Fig. 2: A) to *spongy* less uniform particles (Fig. 2: B) and most of the particles dissolved with NH<sub>4</sub>OH addition and raising of the pH. Upon, free radical polymerization with BMA of the sample with 0.59 M equivalence of NH<sub>4</sub>OH reaction: B' post polymerisation, new particles were formed with small particle size (84 nm) and small number of large particles appeared according to both DLS and SEM. The larger particles (565 nm) are due to the initial particles not completely dissolving in NH<sub>4</sub>OH such that the BMA polymer grows from the dispersed particles. For the reaction with 1.18 M equivalence of NH<sub>4</sub>OH reaction (Fig. 2: C' post polymerisation), prior to the free



**Scheme 1.** Reaction schemes for CCTP and SF-RAFT polymerisation.

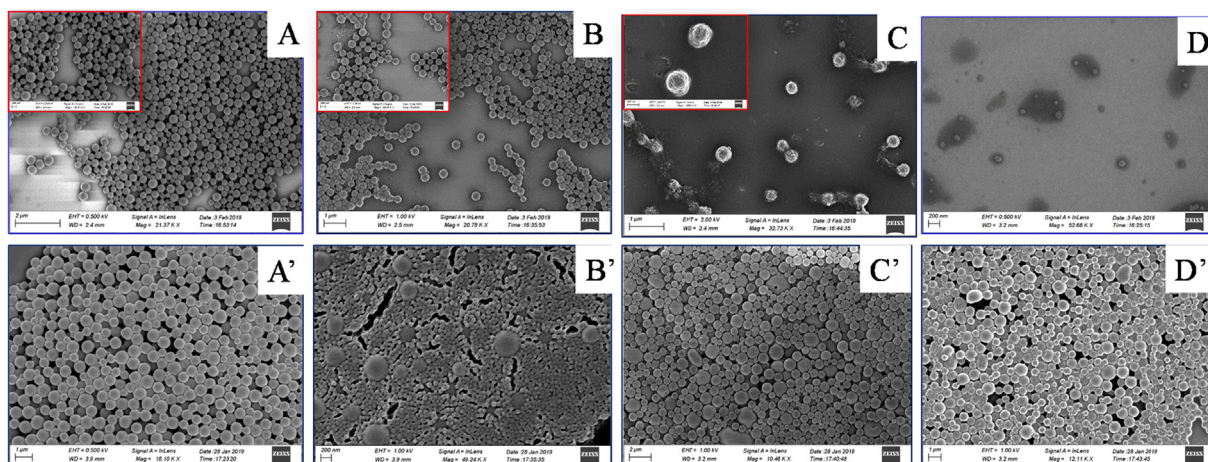


**Fig. 1.** 400 MHz  $^1\text{H}$  NMR in  $d^6$  DMSO of co-oligomer and resulting di-block copolymers.

radical polymerisation with BMA the polymer latex poly(MMA-co-MAA-b-BMA<sub>10</sub>) was visually completely soluble with 1.18 M equivalence of  $\text{NH}_4\text{OH}$ . However, from SEM we observed a small amount of spongy like particles remained prior to the BMA polymerisation (Fig. 2: C). Upon polymerisation with BMA, the SEM showed a few large particles and a majority of the particles uniform in size and the  $\bar{D}$  and PDI both decreased according to SEM and SEC. For the reaction with 1.77 M equivalence of  $\text{NH}_4\text{OH}$  all poly(MMA-co-MAA-b-BMA<sub>10</sub>) was visually completely solubilised prior to the polymerisation with BMA. SEM showed the absence of particles upon addition of  $\text{NH}_4\text{OH}$  (Fig. 2: D). Upon polymerisation with BMA, the particles appeared uniform in size according to SEM (Fig. 2: D' post polymerisation) and DLS showed a significant reduction in PDI (Table 1). Whereas, SEM also showed reduction in  $\bar{D}$ . Furthermore, upon each increase in concentration of  $\text{NH}_4\text{OH}$  and associated increase in the pH results in increasing the half-life of the KPS initiator with the molecular weight of the final

polymers increasing, the  $\bar{D}$  decreased suggesting more radicals' present ensuring sufficient propagation and uniformed particle sizes. For all of the reactions, A' to D' according to  $^1\text{H}$  NMR the  $\omega$ -vinyl end group functionality remained, 6.12–6.09 ppm and 5.58–5.49 ppm respectively (Table 1 and SI figure 1 & 6).

The diblock copolymers, poly(MMA-co-MAA-b-MMA<sub>10</sub>), were dissolved with various amounts of  $\text{NH}_4\text{OH}$ : 0, 0.56, 1.12 and 1.68 M equivalents with respect to MAA and utilized as polymeric substitutes for standard surfactants. All of the latex, prior to any addition of any  $\text{NH}_4\text{OH}$ , appeared as the SEM image E, with particles of uniform size. With no addition of  $\text{NH}_4\text{OH}$ , reaction E' both the SEM and DLS showed a large particle 415 nm compared to the reactions where  $\text{NH}_4\text{OH}$  was added. Furthermore, a general trend was observed that larger particles were formed at d lower pH (Table 2). For the reaction with 0.56 M equivalence of  $\text{NH}_4\text{OH}$  the SEM images prior to reaction showed most of the particles dissolved and some spongy looking particles remained, upon heating it is believed that all the particles dissolved in the  $\text{NH}_4\text{OH}$ , since the solubility of methacrylic containing polymers tends to increase with increase in temperature and upon post polymerisation with BMA (Fig. 3: F') all of the particles obtained were monomodal in contrast to the surfactant with the hydrophobic moiety consisting of BMA (Table 1). Since BMA is more hydrophobic than MMA it is these polymers are less soluble than the MMA containing analogues at higher temperatures, thus some small particles were observed with SEM at low concentrations of  $\text{NH}_4\text{OH}$  (Fig. 2). Furthermore, the SEC data for 0.56 M equivalence showed a general decrease in  $\bar{D}$  and particle size reduced to more than half (186 nm) compared to the reaction with no added  $\text{NH}_4\text{OH}$ . For the reaction with 1.12 and 1.68 M equivalence of  $\text{NH}_4\text{OH}$  with respect to MAA reaction G' and H', showed that prior to the polymerisation SEM images G and H, showed no presence of any particles and all latex was visually also completely soluble in  $\text{NH}_4\text{OH}$ . Upon completion of the reaction, G' with 1.12 M equivalence  $\text{NH}_4\text{OH}$  had particle size of 144 nm according to SEC and H' with 1.68 M equivalence of  $\text{NH}_4\text{OH}$  had particle size = 118 nm and the molecular weights showed a general increase in  $M_n$  with higher concentrations of  $\text{NH}_4\text{OH}$ . SEM, images of products from 1.12 and 1.68 M equivalence of



**Fig. 2.** Latex particles with A being poly(MMA-co-MAA-b-BMA<sub>10</sub>) diblock, B, C and D are poly(MMA-co-MAA-b-BMA<sub>10</sub>) with 0.59, 1.18 and 1.77 M equivalence of NH<sub>4</sub>OH prior to free radical polymerisation with BMA and A', B' C' and D' post polymerisation with BMA monomer to form poly (BMA).

**Table 1**

Data for the formation of poly(MMA-co-MAA-b-BMA<sub>10</sub>) diblock with varied concentration of ammonium hydroxide with post free radical polymerisation of poly (BMA) with varied concentration of ammonium hydroxide.

Reaction	M <sub>n,SEC</sub> /g mol <sup>-1</sup> (THF)	M <sub>w</sub> /g mol <sup>-1</sup>	$\bar{D}$	Particle size/nm	PDI	Prior pH	Post pH
15% MAA & 85% MMA	2200	3700	1.67	–	–	–	2.38
DP-BMA-10	3100	4700	1.50	314	0.099	–	2.23
NH <sub>4</sub> OH (0 equiv.)-A'	18,000	22,400	1.25	644	0.053	2.23	2.19
NH <sub>4</sub> OH (0.59 equiv.)-B'	16,600	25,600	1.54	132	0.283	7.92	4.89
NH <sub>4</sub> OH (1.18 equiv.)-C'	18,500	26,900	1.46	564	0.221	9.19	7.26
NH <sub>4</sub> OH (1.77equiv.)-D'	19,900	27,400	1.38	586	0.088	10.32	7.65

NH<sub>4</sub>OH showed that the particles were uniform in size (Fig. 3: G' and H'). Furthermore 1.68 M equivalents of NH<sub>4</sub>OH, reaction H', showed particles arranged in worm or necklace like aggregates yet maintaining much uniformed particle size. For all of the reactions, E' to G' the according to <sup>1</sup>H NMR the vinyl end group functionality was present at reduced amounts (Table 2 and SI figure 5).

SEC data (Table 3), shows that the average molecular weights decreases with temperature and the  $\bar{D}$  also decreases with increase in temperature at 50 °C with  $\bar{D}$  is 1.66, reducing down to 1.44 at 65 °C, and further decreases to 1.29 at 76 °C and then at 84 °C a slight increase in  $\bar{D}$  is observed to 1.38. Furthermore, at low temperatures some macroscopic coagulum or agglomerates occurred on the reactor wall and on the surface of the overhead stirrer, which in turn reduced the latex yield [11].

From all of the reactions (Tables 1 and 2), the final pH of the latex dropped from the initial pH; this was initially thought to be due to ammonia from the ammonium hydroxide evaporating at higher temperature or/and KPS producing sulphuric acid at higher temperatures. All of the latexes were dissolved in equal molar equivalence (1.68) of ammonium hydroxide solution with respect to MAA, (Table 3). At lower

temperatures there is less significant drop from the initial pH of 9.89 at 50 °C the drop in pH was 7.04 whereas as the temperature increases further a more significant drop in pH was seen: 65 °C, 6.44, 76 °C, 4.85 and finally at 84 °C, 3.44. In order to factor in the significance of temperature on the amount of ammonium hydroxide remaining in solution and [KPS] in aqueous solution the poly(MMA-co-MAA-b-MMA<sub>10</sub>) was dissolved with 1.68 equivalents of ammonium hydroxide and heated for 14 h under nitrogen at 85 °C, the initial pH was 9.89 and the final pH after 14 h was 9.53. Suggesting that the ammonium salt formed from the ammonium hydroxide reacting with poly(MMA-co-MAA-b-MMA<sub>10</sub>) remains as the salt and that KPS may play more important role on pH. The KPS was dissolved in water the initial pH of the deionized water was 5.88 and upon addition of KPS the pH decreased to 3.63, upon heating to 85 °C the pH further decreased to 1.87 after 3 h.

The final reaction (Table 3 & Fig. 4) was carried out with 1.68 equivalence of ammonium hydroxide with respect to MAA: the pH of the KPS dissolved in water was raised to the same pH as the latex (9.53): post polymerisation the pH dropped to 5.99 and  $\bar{D}$  according to SEC increased from 1.29 (Table 3 & Fig. 4) to 1.43 with the particle size decreasing from 118 nm to 58 nm (DLS and SEM). This suggests that at

**Table 2**

Data for the formation of poly(MMA-co-MAA-b-MMA<sub>10</sub>) diblock copolymer with varied concentration of ammonium hydroxide followed by free radical polymerisation of BMA with varied concentration of ammonium hydroxide.

Reaction	M <sub>n,SEC</sub> /g mol <sup>-1</sup> (THF)	M <sub>w</sub> /g mol <sup>-1</sup>	$\bar{D}$	Particle size/nm	PDI	Prior pH	Post pH
15% MAA & 85% MMA	1900	3400	1.75	–	–	–	3.08
DP-MMA-10	3100	4500	1.46	234	0.033	–	2.82
NH <sub>4</sub> OH-0 equiv.-E'	8900	14,000	1.58	415	0.069	2.82	1.89
NH <sub>4</sub> OH-0.56 equiv.-F'	9200	12,300	1.33	186	0.033	6.95	2.95
NH <sub>4</sub> OH-1.12 equiv.-G'	13,900	18,100	1.30	144	0.023	7.66	4.37
NH <sub>4</sub> OH-1.68 equiv.-H'	12,400	16,000	1.29	118	0.044	9.89	4.85



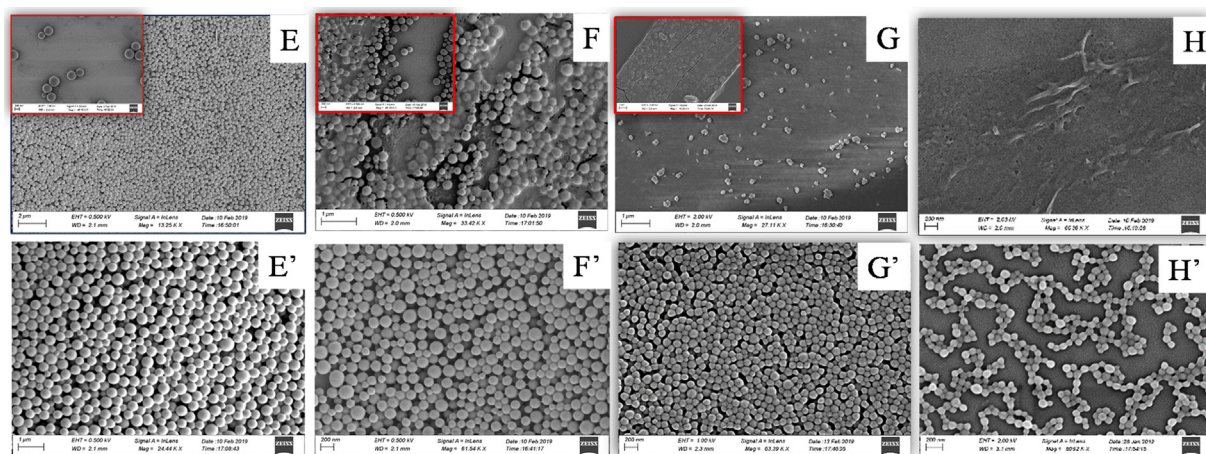


Fig. 3. Formation of poly(MMA-co-MAA-b-MMA<sub>10</sub>) diblock copolymers with varied concentration of ammonium hydroxide with post free radical polymerisation of poly(BMA) with varied concentration of ammonium hydroxide.

higher temperatures KPS still produces some sulphuric acid lowering the pH of the overall reaction. Furthermore, for the reaction of poly(MMA-co-MAA-b-MMA<sub>10</sub>) diblock copolymer with 1.68 equivalents of ammonium hydroxide with respect to MAA followed by post free radical polymerisation with BMA at varied temperatures gave polymers with relatively low  $M_n$ , SEC, with <sup>1</sup>H NMR showing the ω-vinyl end group remaining (Table 3 and SI figure 3) (SI figure 4). The concentration of initiator has two effects on the particle size. Firstly, increasing the KPS concentration increases the concentration of sulfate ions which in turn leads to the stabilisation of particles by achieving smaller particles. Secondly, increasing the concentration of KPS initiator also increases the ionic strength of the aqueous phase, which should result in larger particles. As a result the two opposite effect in theory should compensate each other under the experimental conditions. In (Table 3) the temperatures were varied and the KPS concentration were kept constant. As the temperature increased the particle size's increased (Table 3 & Fig. 4).

These reactions (SI Table: 2): demonstrate that for poly(MMA-co-MAA-b-BMA<sub>10</sub>) dissolved at various concentrations of NH<sub>4</sub>OH followed by post free radical polymerisation of with BMA that the onset of the glass transition temperature, remains relatively the same for all the polymers:  $T_{g, \text{onset}}$  varied between 36 °C ± 3 °C, the  $T_{g, \text{mid}} = 48 \text{ °C} \pm 1 \text{ °C}$  and the  $T_{g, \text{end}} = 61 \text{ °C} \pm 4 \text{ °C}$ . For the reaction with poly(MMA-co-MAA-b-MMA<sub>10</sub>) dissolved in varies concentration of NH<sub>4</sub>OH and then post free radical polymerisation of with BMA monomer we also observed  $T_g$ 's that are similar for all the polymers:  $T_{g, \text{onset}}$  varied between 38 °C ± 5 °C,  $T_{g, \text{mid}} = 50 \text{ °C} \pm 2 \text{ °C}$  and  $T_{g, \text{end}} = 64 \text{ °C} \pm 4 \text{ °C}$ .

The surface zeta potential (SI Table: 3) for poly(MMA-co-MAA-b-BMA<sub>10</sub>) the initial surface zeta potential of the block copolymer was -43 mV, once dissolved at various concentrations of NH<sub>4</sub>OH and with post free radical polymerisation of BMA showed: that for reaction with

generally large particle size reaction A', C' and D' including reaction B' which had combination of large and small particles both according to DLS and SEM has very negative zeta potential  $-63 \pm 8 \text{ mV}$  compared to the polymers poly(MMA-co-MAA-b-MMA<sub>10</sub>). For the reactions with poly(MMA-co-MAA-b-MMA<sub>10</sub>) the starting zeta potential of the block copolymer was -52 mV: once dissolved post free radical polymerisation with BMA monomer were undertaken. The zeta potential for the smaller particles reaction F', G' H' were less negative  $-38 \pm 8 \text{ mV}$ , while for the reaction E' with large particle according to DLS and SEM, had zeta potential  $-70 \pm 7 \text{ mV}$  which is in similar region to the particles utilising poly(MMA-co-MAA-b-BMA<sub>10</sub>) as polymer surfactant substitute. The polymers contain carboxylic acid functionality monomers and the zeta surface potential are all in the region expected for carboxylated latex [33,52,53].

### 3. Conclusion

Lowering of the pH with ammonium hydroxide addition and formation of ammonium salts of poly(MMA-co-MAA-b-BMA<sub>10</sub>) and poly(MMA-co-MAA-b-MMA<sub>10</sub>) resulted in solubilisation to quite low viscosity polymer solutions which were used as a polymerisable surfactants. Subsequent emulsion polymerisation of BMA gave latex's with high solid contents (40%), stable, long shelf lives and generally mono-disperse particles. This is especially true for higher concentrations of NH<sub>4</sub>OH, higher pH, with poly(MMA-co-MAA-b-BMA<sub>10</sub>) utilised as the surfactant. Whereas, with poly(MMA-co-MAA-b-MMA<sub>10</sub>) we achieved monodisperse particles at varies concentration of ammonium hydroxide and was an effective way to control the average particle sizes. We find out that at lower pH's (acidic) the final latex occurred had larger particle size's. This is due to the ionic initiator utilised (KPS) which at higher temperature and acidic pH produces H<sub>2</sub>SO<sub>4</sub> (aq) which lowers the final pH further (more acidic) resulting in larger particle sizes at

Table 3

Formation of poly(MMA-co-MAA-b-MMA<sub>10</sub>) diblock copolymers with 1.68 equivalents of ammonium hydroxide with respect to the MAA with post free radical polymerisation of poly(BMA) at varied temperatures and reaction with latex and KPS dissolved in water having the same pH.

Reaction	$M_{n, \text{SEC}} / \text{g mol}^{-1}$ (THF)	$M_w / \text{g mol}^{-1}$	$D$	Particle size/nm	PDI	Prior pH	Post pH
15% MAA & 85% MMA	1900	3400	1.75	–	–	3.08	–
DP-MMA-10	3100	4500	1.46	234	0.033	2.82	–
50 °C-NH <sub>4</sub> OH-1.68 equiv.	15,400	25,600	1.66	60	0.254	9.57	7.04
65 °C-NH <sub>4</sub> OH-1.68 equiv.	13,700	19,700	1.44	43	0.048	9.62	6.44
76 °C-NH <sub>4</sub> OH-1.68 equiv.	12,400	16,000	1.29	118	0.044	9.53	4.85
84 °C-NH <sub>4</sub> OH-1.68 equiv.	8200	11,300	1.38	195	0.061	9.64	3.44
76 °C-NH <sub>4</sub> OH-1.68 equiv.	12,900	18,400	1.43	58	0.015	9.53	5.99

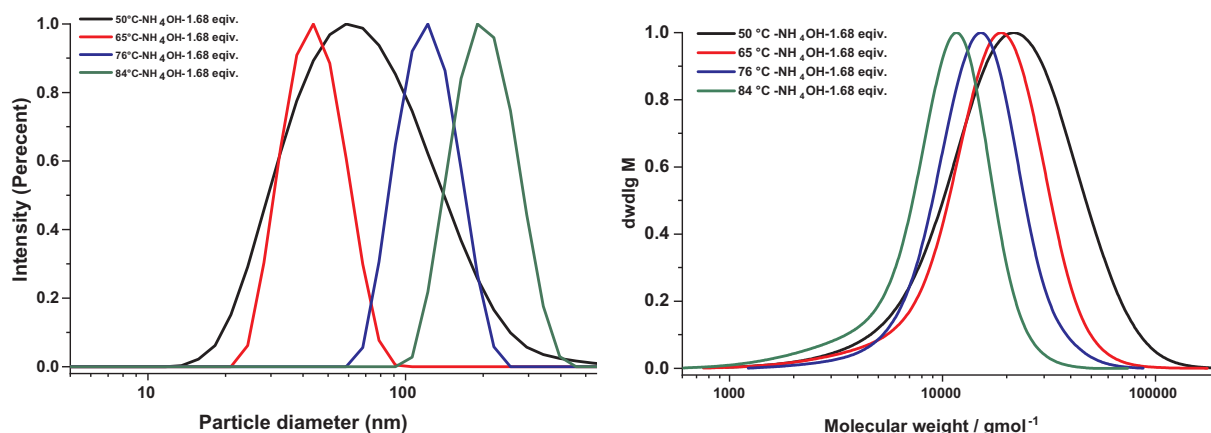


Fig. 4. DLS and GPC data of formation of poly(MMA-co-MAA-b-MMA10) diblock with 1.68 equivalence of ammonium hydroxide with respect to the MAA with post free radical polymerisation of poly(BMA) at varied temperatures.

lower pH's. Furthermore, these latex particles derived from polymerisable surfactants for polymethacrylates opens the possibility for numerous applications in for example, medical diagnostics, adhesives, impact modifiers, as well as in paper and textile coatings.

#### CRediT authorship contribution statement

**Ataulla Shegiwal:** Conceptualization, Data curation, Formal analysis, Project administration, Writing - original draft, Methodology. **Alan M. Wemyss:** Conceptualization, Investigation, Project administration, Formal analysis, Validation. **Evelina Liarou:** Formal analysis, Data curation. **James Town:** Data curation, Formal analysis. **Geogios Patias:** Data curation, Formal analysis. **Christophe J. Atkins:** Data curation, Formal analysis. **Arkadios Marathianos:** Data curation, Formal analysis. **Daniel W. Lester:** Data curation, Formal analysis, Resources. **Spyridon Efstathiou:** Data curation, Formal analysis. **David M. Haddleton:** Supervision, Project administration, Conceptualization, Methodology, Funding acquisition, Writing - review and editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2020.109491>.

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