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# Sequence-controlled methacrylic multiblock copolymers: expanding the scope of sulfur-free RAFT

Nikolaos G. Engelis<sup>†</sup>, Athina Anastasaki<sup>\*†</sup>, Richard Whitfield, Glen R. Jones, Evelina Liarou, Vasiliki

Nikolaou, Gabit Nurumbetov and David M. Haddleton<sup>\*</sup>

University of Warwick, Chemistry Department, Library road, CV4 7AL, Coventry, United Kingdom.

<sup>†</sup>These authors contributed equally to this work.

## Abstract

Sulfur-free reversible addition fragmentation transfer polymerization (SF-RAFT) in emulsion allows access to the synthesis of sequence-controlled methacrylic multiblock copolymers. Herein, we expand the scope of sulfur-free RAFT emulsion polymerization by utilizing four different macrochain transfer agents (mCTA) to mediate the synthesis of diblocks and sequence-controlled methacrylic multiblock copolymers. Upon varying the reaction conditions (e.g. altering the type of catalyst and catalyst concentration), poly(methyl methacrylate) (pMMA), poly(butyl methacrylate) (pBMA), poly(ethyl methacrylate) (pEMA) and poly(benzyl methacrylate) (pBzMA) of a similar  $M_n$  ( $\sim 4,300 \text{ g mol}^{-1}$ ) were successfully synthesized via catalytic chain transfer polymerization (CCTP) in emulsion. The capability of these mCTAs to act as macroinitiators was investigated through the synthesis of “*in situ*” diblock copolymers demonstrating excellent control over the molar masses. Under optimized conditions, pEMA, pBzMA and pBMA mCTAs were then employed for the synthesis of deca and hexablock multiblock copolymers with varying degrees of polymerization ( $DP_n=10-50$  per block,  $M_{n, \text{total}}=7,000-55,000 \text{ g mol}^{-1}$ ) yielding well-defined complex materials with controlled molecular weights, quantitative conversions (>99%) and low dispersities ( $\mathcal{D} \sim 1.2$ ) without the need for sulfur or transition metal reagents.

## Introduction

Nature is capable of achieving a high level of sequence control in the synthesis of natural polymers such as DNA and proteins. In contrast, synthetic chemists are currently far away from replicating this precision.<sup>1</sup> Solid-state peptide synthesis (Merrifield synthesis) remains a benchmark towards this target providing a reliable method for the synthesis of precisely controlled macromolecules.<sup>2</sup> However, this strategy is time consuming, challenging to scale up and is also limited to lower molar masses and as such alternative strategies have also been explored. It is also noted that a distribution of masses within a polymeric material is often the most desirable property. Single monomer insertion,<sup>3-6</sup> tandem monomer addition and modification,<sup>7, 8</sup> kinetic control,<sup>9, 10</sup> segregating templating,<sup>11, 12</sup> selected reactivities,<sup>13</sup> sequential growth on soluble polymer supports and discrete oligomers strategies have successfully been developed although also suffer from related issues (e.g. limited to low molecular weight oligomers).<sup>14-18</sup>

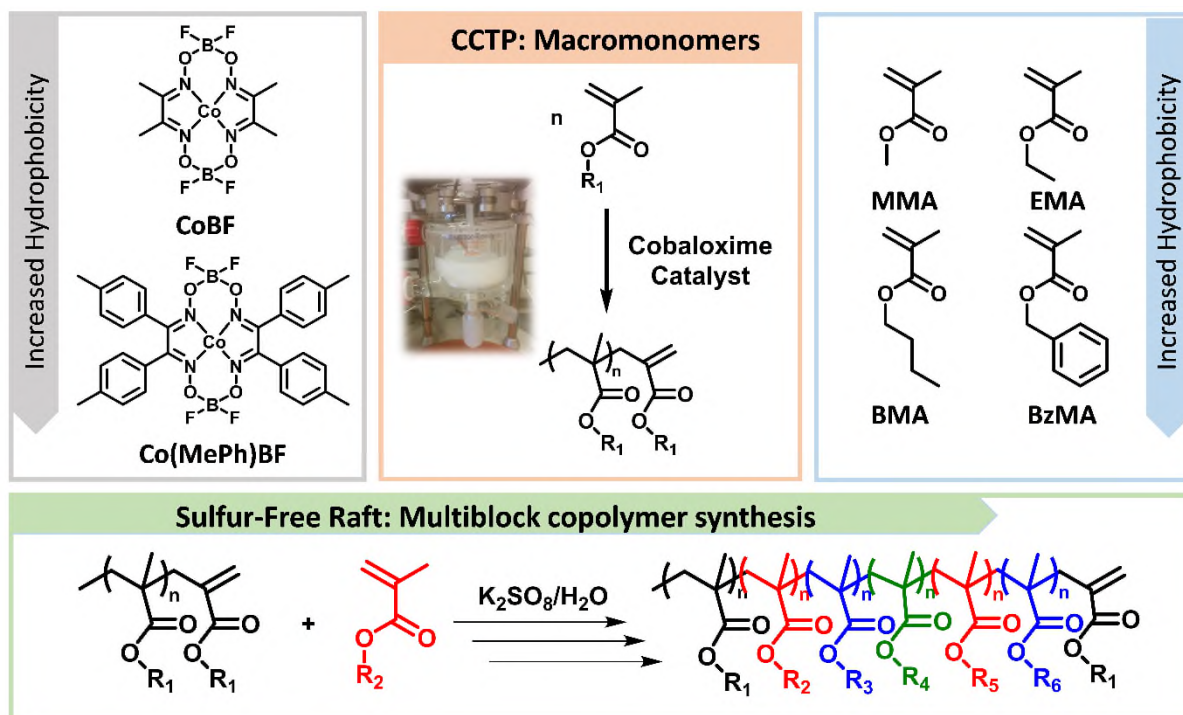
In contrast, sequence-controlled multiblock copolymers obtained through controlled polymerization strategies offer a scalable and faster alternative allowing access to higher molecular weight materials with a wide range of functionalities.<sup>1, 11, 19, 20</sup> Whittaker and co-workers reported the first example of one pot sequence-controlled acrylic multiblocks via Cu(0)-wire reversible deactivation radical polymerization (RDRP).<sup>21</sup> The same group subsequently expanded the scope to include the synthesis of higher molecular weight and star sequence-controlled multiblock copolymers.<sup>22, 23</sup> Subsequently, Haddleton, Junkers and co-workers introduced sequence-controlled multiblocks mediated by a light-mediated copper polymerization.<sup>24-26</sup> Finally, a novel approach exploiting the disproportionation of CuBr/Me<sub>6</sub>Tren in water was employed to confer control over the synthesis of acrylamide based multiblock copolymers.<sup>27</sup> Aside from copper, traditional reversible addition-fragmentation transfer (RAFT) polymerization has been employed by Perrier and co-workers yielding an impressive icosablock copolymer consisting of various acrylamides.<sup>28-31</sup> Very fast reaction rates could be maintained throughout the sequential monomer additions helped by the high

propagation rate constant of acrylamides. However, all these approaches suffer from two main limitations. The first one is their incapability to polymerize low  $k_p$  monomer families such as methacrylates; this monomer category exhibits much slower polymerization rates than acrylamides or acrylics, and is susceptible to more side reactions.<sup>32-36</sup> The second drawback is that the final multiblock copolymers are often contaminated by either copper or sulphur residues which can induce undesired odour and potential toxicity in the final materials and thus require time-consuming and relatively expensive purification methods or post-polymerization modification strategies. Other limitations of these techniques include somewhat high dispersity values, significant side reactions when water is employed as the reaction medium,<sup>37</sup> slow polymerization rates and non-quantitative conversions throughout the sequential monomer additions.<sup>38-40, 22</sup>

Recently, our group reported the sequence-controlled methacrylic multiblock copolymers via a sulphur-free RAFT (SF-RAFT) emulsion polymerization strategy.<sup>41</sup> CCTP in emulsion was initially employed to synthesize poly(methyl methacrylate) (PMMA) macromonomers/mCTAs bearing a vinyl group at the  $\omega$ -terminus. This macromonomer was subsequently used as a mCTA to mediate the controlled polymerization of methacrylates thanks to the susceptibility of the vinyl  $\omega$ -end group to undergo radical addition resulting in the formation of a macromonomer-ended polymer radical which can undergo  $\beta$ -scission (addition/fragmentation).<sup>42</sup> The latter reaction leads to a tertiary radical generated via fragmentation of the adduct product.<sup>43</sup> Subsequently, a new macromonomer/mCTA is formed through combination of the initial growing radical with the vinyl end group of the initial macromonomer. Importantly, the newly formed vinyl terminated polymer can act as a CTA following the same reaction mechanism. Thus, the combination of CCTP and sulfur-free RAFT allowed access to the scalable synthesis of sequence-controlled methacrylic multiblock copolymers while maintaining very fast polymerization rates ( $\sim$  2-3 h per block), quantitative conversions ( $>99\%$ ) and low dispersity values (typically  $\bar{D} < 1.3$ ) for the entire process.

However, only pMMA of  $M_n \sim 2,000 \text{ g mol}^{-1}$  was used as the macromonomer/mCTA in this work.

Herein, we expand the scope of SF-RAFT emulsion polymerization by synthesizing four different macromonomers with a terminal vinyl group, pMMA, pEMA, pBMA and pBzMA of comparable  $M_n$  ( $\sim 4,000 \text{ g mol}^{-1}$ ) via CCTP. Their capability to act as efficient chain transfer agents is investigated through the synthesis of diblocks and sequence-controlled multiblock copolymers (Fig 1). Macromonomers of higher  $M_n$  are also be reported and compared with lower  $M_n$  analogues with the goal of revealing the potential and the limitations of this system.



**Figure 1.** Schematic diagram showing the concept of the synthesis of sequence-controlled multiblock copolymers by the use of macromonomers as macro chain transfer agents (CTA). Catalyst type and concentration are optimized as to provide macromonomers of the desired  $M_n$  which subsequently serve as CTA in the free radical polymerization of methacrylic monomers.

## Results and Discussion

### Synthesis of macromonomers/macro chain transfer agents

Our initial target was to obtain various macromonomers of comparable  $M_n$  in order to assess their capability to act as successful chain transfer agents. As previous studies focused on  $M_n \sim 2,000 \text{ g mol}^{-1}$  or even lower (e.g. dimers/trimers),<sup>45</sup> we decided to target a constant  $M_n$  of  $\sim 4,000 \text{ g mol}^{-1}$  for all targeted macromonomers, namely pMMA, pEMA, pBMA and pBzMA. In our recent publication, sequence-controlled methacrylic multiblock copolymers using pMMA macromonomer ( $M_n \sim 2,000 \text{ g mol}^{-1}$ ) were successfully demonstrated. In order to achieve such low molecular weight pMMA, high concentrations of bis[(difluoroboryl)dimethylglyoximato]cobalt(II) (CoBF) (104 ppm) were required.<sup>41</sup> In agreement with our previous report, all macromonomers were synthesized in a double-jacketed reactor (supplied with a temperature detector and overhead stirrer) *via* CCTP emulsion polymerization. For the case of pMMA, lower concentration of CoBF was essential (42 ppm, Supplementary Table 1, entry 1, Supplementary Fig 1) in order to achieve  $M_n \sim 4,300 \text{ g mol}^{-1}$ . The presence of the  $\omega$ -end group vinyl protons was confirmed by both  $^1\text{H NMR}$  and MALDI-ToF-MS (Supplementary Fig 2), the latter showing a major polymer peak distribution identified as pMMA chains with a proton  $\alpha$ -chain end, thus confirming that initiation *via* H-transfer from  $\text{Co}^{\text{III}}$  complex is the dominant mode of initiation, as suggested by the mechanism of CCTP (Supplementary Fig 3). Under otherwise identical conditions (42 ppm of CoBF) the polymerization of EMA was then attempted. However, a rather higher  $M_n$  was obtained ( $M_n \sim 7,000 \text{ g mol}^{-1}$ , Supplementary Table 2, entry 1). In order to address this, higher concentrations of catalyst were investigated. It was found that 65 ppm of CoBF allowed access to pEMA of  $M_n \sim 4,300 \text{ g mol}^{-1}$  (Supplementary Table 1, entry 2, Supplementary Fig 4-5). These differences in catalyst concentration required to achieve comparable molecular weights can be attributed to the partition coefficient ( $m_{\text{Co}}$ ), which is equal to the ratio of the catalyst concentration in the dispersed phase (monomer) to that in the aqueous phase ( $m_{\text{Co}} = [\text{Co}]_{\text{disp}}/[\text{Co}]_{\text{aq}}$ ) and differs for each monomer.<sup>46</sup> The catalyst needs to be present at the loci of polymerization and thus mass

transport of the catalyst between continuous and dispersed phase is required.<sup>47</sup> Although CoBF proved to be a very efficient catalyst for the polymerization of MMA and EMA, it is insoluble in BMA and BzMA (in concentrations higher than 60 ppm). In order to circumvent this, the more hydrophobic catalyst bis[(difluoroboryl) dimethylphenylglyoximato]cobalt(II) (Co(MePh)BF) was used in place of CoBF (Figure 1). Under optimized conditions, pBMA and pBzMA macromonomers (Supplementary Tables 3-4, Supplementary Fig 7, 9) of  $M_n \sim 4,200$  g mol<sup>-1</sup> and 4,400 g mol<sup>-1</sup> were synthesized. For all macromonomers synthesized, <sup>1</sup>H NMR analysis confirmed full monomer conversion (>99%) and the existence of the vinyl group at the  $\omega$ -chain end. MALDI-ToF-MS also showed very high end group fidelity for all macromonomers confirming the successful synthesis (Supplementary Fig 6, 8). Finally, dynamic light scattering (DLS) was additionally employed showing that the particle size mainly depends on the nature of the polymer targeted rather than the final  $M_n$ . It is noted, that latexes generated upon the polymerization of BMA consisted of considerably smaller particles as opposed to the other three monomers studied.

### **Synthesis of methacrylic diblock copolymers using PMMA, PEMA, PBMA and PBzMA as macromonomers/macro chain transfer agents**

After obtaining different macromonomers of comparable  $M_n$  the next step was to assess their capability to mediate the polymerization of methacrylates. BMA was selected and kinetics in the presence of pMMA were initially conducted targeting  $DP_n=80$  (monomer : CTA=1:80). Samples were periodically taken from the reaction mixture and SEC showed a gradual decrease of the dispersity from 1.55 (dispersity of pMMA macromonomer prior to BMA addition) to  $\mathcal{D} \sim 1.17$  for the final diblock copolymer (Supplementary Table 5, Supplementary Fig 10). In a similar vein, pBMA macromonomer was also employed to polymerize BMA with the kinetics exhibiting virtually identical behaviour and SEC showing a clear shift to higher molecular weights and constantly decreasing dispersities (Supplementary Table 6, Supplementary Fig 11). It is noted that although macromonomers of higher  $M_n$  than in previous reports were used, the “living” characteristics of the system could be maintained and low

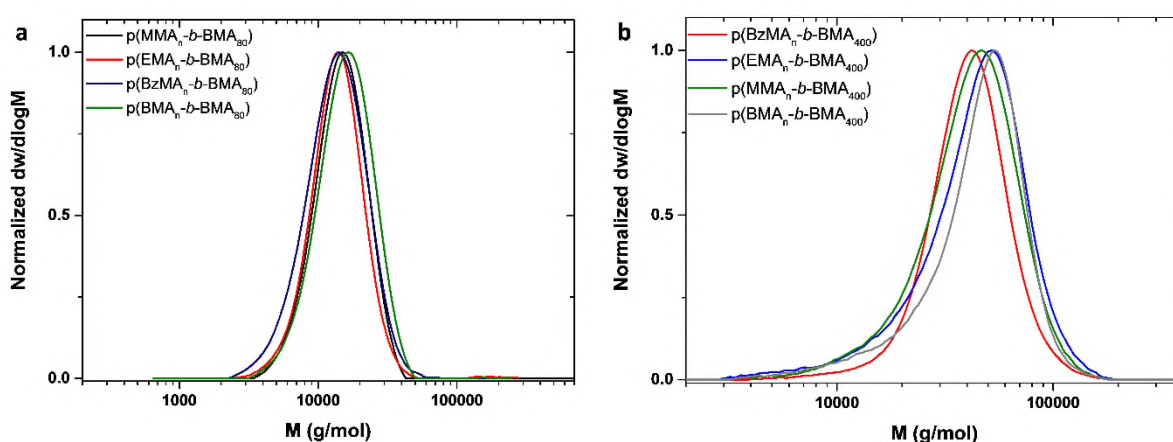
dispersity diblock copolymers were achieved. Having demonstrated a similar kinetic behaviour for two different macromonomers, pEMA and pBzMA (Supplementary Table 7) were also employed targeting  $DP_n=80$ . All tested macromonomers were capable to successfully mediate the polymerization of BMA yielding nearly identical diblock copolymers (Figure 2a) with low dispersity values ( $<1.28$ ) and reasonable agreement between theoretical and experimental molar masses (Table 1). In particular, when pMMA and pEMA macromonomers were employed, diblock copolymers with a final dispersity of 1.23 and 1.20 respectively were obtained. For the case of pBMA and pBzMA slightly higher dispersities were achieved ( $\bar{D} \sim 1.27$ ) (Table 1). To further probe the potential of the macromonomers in maintaining control for higher molecular weights a more challenging diblock was targeted, aiming for  $DP_n=400$  of BMA. Despite the higher targeted molecular weight, all macromonomers yielded well-controlled polymers with dispersities as low as 1.17 and  $M_n \sim 60,000 \text{ g mol}^{-1}$  (Figure 2b, Supplementary Table 8). Thus, it was concluded that regardless the type of the macromonomer used, SF-RAFT emulsion polymerization was unaffected allowing access to well-defined diblock copolymers. Importantly, in all cases, full monomer conversion could be achieved ( $>99\%$ ) suggesting that these macromonomers could be potentially used for more complex targets such as sequence-controlled multiblock copolymers. It is also worth mentioning that although deionized water was used for the aforementioned experiments, tap water appeared to be equally efficient and no compromise over the dispersity or the control over the polymerization was observed further highlighting the robustness of this system (Supplementary Table 9, Supplementary Fig. 15).

**Table 1.** Synthesis and characterisation data for the diblock copolymers ( $DP_n=80$ ) synthesized by the use of different CTAs

Entry	Employed CTA	Conv. <sup>a</sup> (%)	$DP_n^b$ H-NMR	$M_n^b$ <sub>H-NMR</sub> (g mol <sup>-1</sup> )	$M_n$ <sub>SEC</sub> (g mol <sup>-1</sup> )	$\bar{D}$	Size <sup>c</sup> (nm)	PSD
1	pMMA	>99	84	16,200	12,800	1.23	148	0.041
2	pEMA	>99	82	16,000	12,300	1.20	157	0.044
3	pBzMA	>99	71	14,500	11,600	1.28	489	0.078
4	pBMA	>99	82	15,900	13,500	1.27	77	0.026



[a]: Conversion was measured by diluting the polymer latex with a mixture of deuterated solvents (chloroform/acetone=3/2) [b]:  $DP_n$  and  $M_n$  by  $^1H$ -NMR were measured by dissolving the isolated polymer in deuterated chloroform [c]: Polymer particle size, expressed as hydrodynamic diameter, measured by DLS

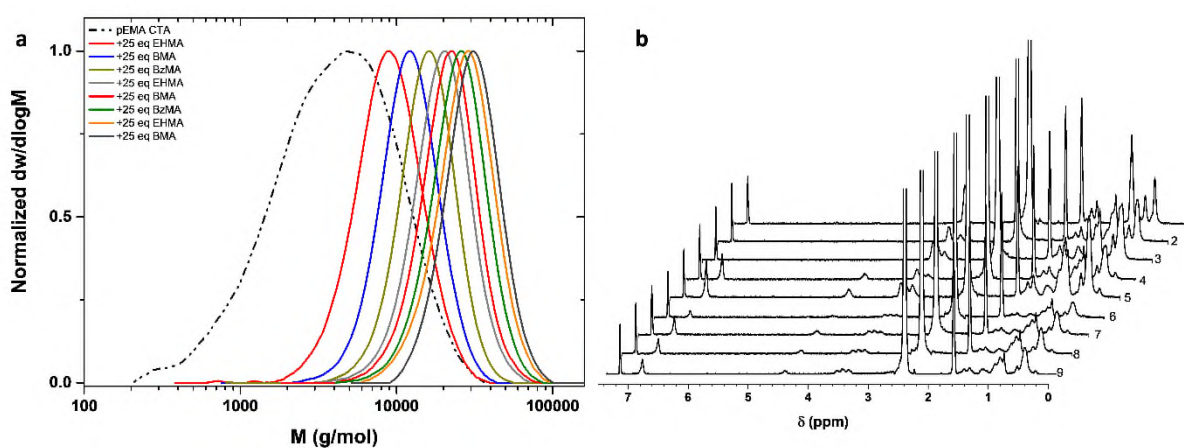


**Figure 2.** a) SEC traces of molecular weight distributions for the diblock macromonomers formed by different CTAs ( $DP_n=80$  BMA) b) SEC traces of molecular weight distributions for the diblock macromonomers formed by different CTAs ( $DP_n=400$  BMA)

### Synthesis of sequence-controlled methacrylic copolymers using pMMA, pEMA, pBMA and pBzMA as macromonomers/chain transfer agents

The pBMA macromonomer ( $M_n=4,300 \text{ g mol}^{-1}$ ,  $\mathcal{D} \sim 1.91$ ) was subsequently used as a chain-transfer agent to facilitate the synthesis of multiblock copolymers, employing an initial ratio of  $[CTA]:[monomer]:[initiator] = 1:10:0.03$  and each block was designed to be  $DP_n=10$ . It is important to highlight that lower molecular weights were not targeted in order to limit the proportion of missing blocks (percentage of defective chains) in the final multiblock copolymer, which should be as low as possible according to Harrisson, Perrier and co-workers.<sup>48</sup> Upon

completion of the monomer addition (BzMA) to the reaction mixture, the reaction was allowed to proceed for one hour to ensure quantitative or near-quantitative conversion. Indeed,  $^1\text{H}$  NMR spectroscopy confirmed very high conversion (>99%, Supplementary Fig 16) while SEC showed a shift to higher molecular weights (Supplementary Fig 17). BMA was subsequently added and when full conversion was reached a third monomer 2-ethylhexyl methacrylate (EHMA) was then injected in the reaction mixture. This one pot sequential addition was repeated ten times resulting in an undecablock copolymer (including the CTA) with  $M_n \sim 20,200 \text{ g mol}^{-1}$  and a final dispersity of 1.29 (Supplementary Tables 10-11). Throughout all the monomer additions, the SEC distributions were monomodal, while  $^1\text{H}$  NMR indicated full monomer conversion prior to the addition of the next block. Despite multiple chain extensions control over the molecular weight was maintained throughout, highlighting the capacity of pBMA to act as a very efficient chain transfer agents under sulfur-free RAFT emulsion polymerization.



**Figure 3.** a) SEC traces of consecutive monomer additions for the preparation of the nonablock copolymer ( $DP_n=25$  per block) utilizing pEMA macromonomer as CTA b)  $^1\text{H}$ -NMR spectra for consecutive cycles during synthesis of the nonablock copolymer (values to the right indicate the number of sequential monomer additions carried out prior to collection of the spectrum)

Upon using pEMA ( $M_n=4,300 \text{ g mol}^{-1}$ ,  $\mathcal{D} \sim 1.9$ ) as the macromonomer, a higher targeted  $DP_n$  was attempted ( $DP_n=25$  per block). Following addition of the first monomer, a significant decrease in the dispersity was observed ( $\mathcal{D} \sim 1.24$ ) and the polymerization reached very high monomers conversions ( $>99\%$ , Fig 3b) in less than two hours. After this time period, a second monomer was added resulting in a further reduction on the dispersity ( $\mathcal{D} \sim 1.20$ ). The sequential inclusion of various monomers finally yielded a nonablock copolymer (including the CTA) with a dispersity as low as 1.19 and a final  $M_n \sim 28,200 \text{ g mol}^{-1}$  (Fig 3a, Supplementary Tables 12-13). SEC confirmed complete shifts to higher molecular weights throughout the monomer additions with the dispersity values being kept  $< 1.2$  for the vast majority of the monomer additions which is a remarkable achievement for such a complex multiblock structure.

Finally, pBzMA was selected as the macromonomer ( $M_n=4,400 \text{ g mol}^{-1}$ ,  $\mathcal{D} \sim 1.78$ ). As high molecular weight multiblock copolymers could be of a potential interest for a wide range of applications, including self-assembly in bulk and in solution, the technique was pushed to reach its limits by targeting  $DP_n=50$  per block. Remarkably, and despite the increased size of block, a well-defined octablock copolymer (or nonablock including the CTA) could be obtained achieving  $M_n \sim 30,000 \text{ g mol}^{-1}$  and a dispersity of 1.28 for the final multiblock copolymer (Supplementary Tables 14-15, Supplementary Fig 18-19). From this data, it is apparent that pBzMA can successfully mediate the synthesis of well-controlled multiblock copolymers.

### **Limitations of sulfur-free RAFT emulsion polymerization**

We were also interested in exploring the limitations of this system. In our original publication, pMMA of  $M_n \sim 2000 \text{ g mol}^{-1}$  was employed and the dispersity was as low as  $\sim 1.12$  after 4 monomer additions.<sup>41</sup> In this work, we employed pMMA of higher  $M_n$  as CTA and as such a pMMA of  $M_n$  of  $11,700 \text{ g mol}^{-1}$  was synthesized (Supplementary Table 16). However, upon three monomer additions, a broad bimodal polymer peak distribution was observed by SEC with the final dispersity being  $\sim 2.4$ , which is an indication of an uncontrolled process

(Supplementary Table 17, Supplementary Fig 20). Thus, pMMA of this  $M_n$  is not recommended to be used as a CTA to facilitate the synthesis of multiblock copolymers. In order to further confirm this limitation, two pBMA macromonomers were also compared. In the previous section, pBMA of  $M_n \sim 4,300 \text{ g mol}^{-1}$  was successfully synthesized and subsequently used as CTA for the undecablock copolymer mentioned above. After four monomer additions the dispersity of the pentablock copolymer was  $\sim 1.30$  (Supplementary Table 11). However, when a pBMA of a higher  $M_n$  ( $\sim 7,200 \text{ g mol}^{-1}$ ) was employed instead, after the same number of additions a broader molecular weight distribution was observed ( $D \sim 1.45$ , Supplementary Fig 21, Supplementary Tables 18-19). Therefore, it is apparent that upon gradually increasing the molecular weight of the CTA, a compromise of control over the molecular distribution takes place as the number of chains with vinyl  $\omega$ -end-group is reduced as a result of conventional free radical termination events. Apart from MMA, EMA, BzMA and BMA, different types of monomers were considered. Extremely hydrophobic monomers such as lauryl methacrylate (LMA) or isobutyl methacrylate (iBMA) are known for not being able to be successfully applied in emulsion polymerization.<sup>49</sup> Nevertheless, the polymerization of iBMA ( $DP_n=80$ ) in the presence of a pMMA CTA produced a diblock copolymer with a dispersity broader than that obtained when BMA was polymerized ( $1.26 > 1.23$ , Supplementary Tables 20, Supplementary Fig 22). However, by SEC analysis, a shoulder towards lower molecular weight is evidenced. Thus, such monomers are not ideal to polymerize under our current conditions. Moreover, polymerization of trifluoroethyl methacrylate (TFEMA) was also attempted. Notably, due to the low boiling point of this monomer ( $59 \text{ }^\circ\text{C}$ ), the reaction took place at a temperature lower than usually ( $55 < 80 \text{ }^\circ\text{C}$ ). Although no phase separation was observed, SEC analysis suggests that TFEMA did not polymerize as there was no clear shift on the SEC trace (Supplementary Fig 23, Supplementary Table 21). Although this appears to be the current limitation of this approach, studies within the group are currently conducted aiming to allow access to the synthesis of a broader range of materials. However, this will be the subject of a forthcoming publication.

## Conclusions

In summary, the scope of sequence-controlled methacrylic multiblock copolymers via sulfur-free RAFT was expanded to include a range of chain transfer agents including pMMA, pEMA, pBMA and pBzMA. The synthesis of the macromonomers was successful by either changing the catalyst type and/or optimizing the catalyst concentration. Subsequently all macromonomers were shown to efficiently catalyse the synthesis of sequence-controlled methacrylic multiblock copolymers consisting of both lower and higher targeted degrees of polymerization per block. Importantly, all multiblocks were synthesized in one pot *via* sequential monomer additions achieving very high monomer conversions and narrow molar mass distributions. In addition, both lower and higher  $M_n$  macromonomers were employed for the synthesis of complex multiblocks with the lower  $M_n$  ones achieving much higher efficiency thus highlighting the potential and the limitations of this system.

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