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Methacrylic Block Copolymers by Sulfur Free RAFT (SF RAFT) Free Radical Emulsion Polymerisation

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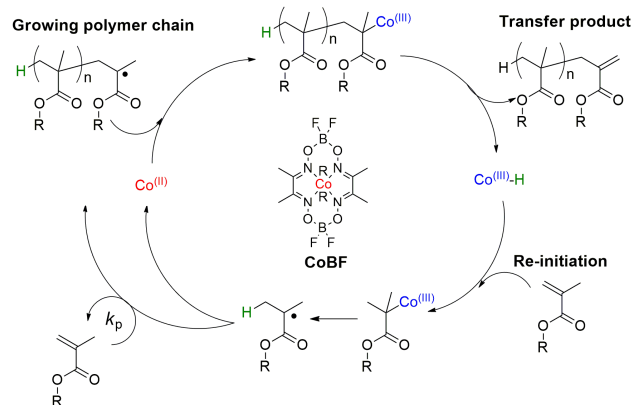
We demonstrate the use of sulfur free reversible addition-fragmentation chain transfer polymerisation (RAFT) as a versatile tool for the controlled synthesis of methacrylic block and comb-like copolymers. Sulfur free RAFT (SF-RAFT) utilises vinyl terminated macromonomers obtained *via* catalytic chain transfer polymerisation (CCTP) of methacrylates as a chain transfer agent (CTA), and thus precluding adverse aspects of the RAFT such as toxicity of dithioesters. We have synthesised a range of narrow dispersity block copolymers ($\bar{D} < 1.2$) and comb-like macromolecules by employing emulsion polymerisation allowing for the preparation of relatively large quantities (~50 g) of the above mentioned copolymers promptly and straightforwardly. Copolymers were characterised using ^1H NMR, size exclusion chromatography (SEC), thermogravimetric analysis (TGA) and matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF-MS) techniques.

Introduction

Developments to control free radical polymerisation^{1,2} have led to the discovery of new polymerisation methods over the last three decades. Nitroxide-mediated polymerisation (NMP),^{3,4} atom transfer radical polymerisation (ATRP),^{5,6} (RAFT),⁷ single electron transfer polymerisation “living” radical polymerisation (SET-LRP)⁸ are well-known approaches to synthesise a variety of polymeric structures using modified free radical polymerisation in a controlled manner, tuning their molecular weights, composition and architectures. Other processes, for example catalytic chain transfer polymerisation, CCTP,^{9,10} have been designed to effectively reduce the molecular weight of produced polymers by introducing novel chain transfer agents, but not to necessary control their constitution and structure.

CCTP, as mediated by a family of low spin cobalt(II)/cobalt(III) compounds, represents the most efficient chain transfer agents for methacrylates by several orders of magnitude. Certain low spin cobalt(II) macrocycles can abstract a hydrogen atom from a propagating polymethacrylic radical to give a Co(III)-H intermediate and an oligomer with terminal vinyl group. The mechanism is interesting and it is noted that the low spin Co(III) d^6 configuration is relatively inert undergoing

ligand-exchange reactions very slowly due to the full t_{2g} shell (see Scheme 1). This process is well documented and has been exploited commercially by a range of companies in a range of coatings applications.^{9,11-22} The catalysts are extremely active and the purpose of the BF_2 groups is to form the macrocycle giving excellent hydrolytic stability even at pH as low as 2 and temperatures close to 100 °C.²³ The chain transfer activity is much less pronounced for monomers which do not contain α -methyl groups such as acrylates and styrenics as the products would then contain an internal double bond and formation is less favoured for both steric and electronic reasons.



Scheme 1. The mechanism of CCTP.

The organic/polymeric product from the reaction is a contains terminal unsaturation “a macromonomer” with the vinyl group α to an electron withdrawing ester group. Moad, Rizzardo and Thang reported in 1996 that these ω -unsaturated methacrylic oligomers exhibited chain transfer activity towards MMA

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polymerizations.²⁴ The transfer constants were found to have some chain length dependence with the dimer a less effective chain transfer agent than the trimer or higher macromonomers with no polymerization retardation observed. This characteristic of these macromonomers allowed for their successful utilisation in the fabrication of well-defined block copolymers,^{25,26} telechelic^{27,28} and star-shaped macromolecules.²⁹ The mechanism proceeds *via* chain transfer to macromonomer followed by a fragmentation to give a macroradical, as derived from the macromonomer, which is able to initiate a second monomer (monomer B) leading to block copolymers. The propagating polymer, now propagating *via* monomer B addition, has competing chain transfer to residual macromonomer in a further addition-fragmentation process similar to RAFT as mediated by S containing chain transfer agents.^{25,30-31} It is noted that this same research group discovered sulfur based RAFT fairly soon after first reporting this sulphur free process^{25,26}. The resulting product from the addition-fragmentation is an AB block copolymer with a single terminal monomer B with residual unsaturation which can re-enter the polymerisation resulting in chain growth of block B in a process which is very similar to traditional RAFT. This proposed mechanism was verified by Haddleton and co-workers whereby a pure MMA tetramer was used as a chain transfer agent with d^8 -MMA to give d^8 MMA₁MMA_x, d^8 MMA₃MMA_x, d^8 MMA₄MMA_x but an absence of d^8 MMA₂MMA_x as shown by MALDI-TOF MS.³ The process is a simple free radical chain transfer process and as such has all of the attributes of free radical polymerisation. In particular, free radical polymerisation lends itself to many processes including emulsion polymerisation.

The ability to use most controlled radical polymerisation systems (NMRP, RAFT and ATRP) under effective emulsion conditions has proved to be somewhat problematic. There has been some excellent work reported by Hawket³⁵⁻³⁷ and a comprehensive review by Perrier and Zetterlund.³⁸ This gave us the inspiration to revisit this elegant and inspiring work from CSIRO, and DuPont, from 1995 that pre dates the well-known sulfur based RAFT to see how it compares given its neglect and almost absence from the literature.^{18,19} We have recently reported the use of SF-RAFT to make sequence controlled polymers with up to 20 blocks.³⁹ Herein, we report a single stage synthesis of simple AB block and comb-shaped copolymers employing CCTP under emulsion polymerisation conditions followed by a second monomer addition. Azo-initiators were employed to obtain macromonomers which were subsequently reacted with a persulfate initiator to destroy cobalt catalyst thus preventing further CCTP and allowing for the addition-fragmentation process to give A-B block copolymers, or comb-shaped structures, depending on the added monomers. An optimised synthesis of macromonomers which led to fabrication of block copolymers with dispersities as low as < 1.2 is also presented. The limits of sulphur-free RAFT under emulsion polymerisation conditions were studied using a variety of monomers. Finally, the formation of comb-shaped structures was investigated with an eye to control their composition and architecture.

Results and Discussion

Synthesis of Macromonomers under Emulsion Polymerisation Conditions

Successful synthesis of macromonomer latexes depends on the CTA efficiency during emulsion CCTP.⁴⁰⁻⁴⁴ In considering the heterogeneous nature of emulsion polymerisation, the partition ratio (K_p) of CTA's between a monomer and water needs to be considered. A free movement and distribution of catalyst between the aqueous and organic phase is required as it allows preservation of the CTA efficiency constant throughout the polymerisation. To select an appropriate catalyst and monomer, the hydrophilicity of both components is considered. Emulsion polymerisation requires a certain solubility of monomers in the aqueous phase, and therefore highly hydrophobic monomers (e.g. lauryl methacrylate) cannot be successfully polymerised. The catalyst solubility in water also plays a significant role. For instance, tetra-phenyl-cobaloxime boron fluoride (CoPhBF) is insoluble in water regardless of monomers used, resulting in a lack of CTA in the latex particles which form the loci of polymerisation in biphasic systems. According to available data a combination of CoBF/methyl methacrylate (MMA) is very effective in emulsion CCTP, whilst more hydrophobic monomers and catalysts give inferior performance.⁴⁰ An increasing hydrophobicity of monomers forces the relatively hydrophilic CoBF to distribute mainly in the aqueous phase, whilst CoPhBF does not partition even in the case of MMA, Table S1.

The activity of CoBF in emulsion CCTP also depends on the glass transition temperature (T_g) of latex particles.^{40-43,45} In order to maintain an efficient chain transfer rate, the T_g should be below the reaction temperature allowing for the catalyst to diffuse into the particles without hindrance. The reaction is controlled by a monomer feed that keeps the instantaneous conversion at approximately 50% resulting in the T_g of the particle to be below the reaction temperature thus allowing for mobility between the phases.

Semi-batch monomer-rich conditions of emulsion CCTP were proved to be the most effective to synthesise macromonomers in a controlled and reproducible manner.^{40-42,45,46} Considering aforementioned aspects of emulsion CCTP we synthesised poly(methyl methacrylate) (PMMA) macromonomers by varying the concentration of CoBF as well as PMMA in absence of the catalyst, Table 1. The reaction with 41 ppm of CoBF allowed reduction of the number average molecular weight (M_n) of PMMA from 93000 to 4800 g mol⁻¹ and the dispersity index (\mathcal{D}) from 2.0 to 1.7. Further increase of the CoBF concentration resulted in lower M_n values of PMMA macromonomers retaining comparable \mathcal{D} indices, Figures S1-S4. The lower conversion of the monomer observed for reactions with higher catalyst concentrations is typical for CCTP.^{10,46,47} A decrease of polymerisation rate (R_p) is a complex phenomenon which cannot exclusively be defined by higher termination rates, but requires a wider view on mechanistic aspects of CCTP.^{48,49} In emulsion CCTP this effect is less pronounced, which results in relatively high monomer

conversions without affecting the performance of the chain transfer.

Table 1. Data for emulsion CCTP of MMA under the conditions described in the Experimental Section

Run	CoBF, ppm	Conversion, %	M_n^{NMR} g mol ⁻¹	M_n^{SEC} g mol ⁻¹	M_w g mol ⁻¹	\mathcal{D}
1	0	>99	-	93000	186000	2.00
2	41.2	>99	3600	4800	8200	1.70
3	82.4	>99	2600	2900	4900	1.69
4	123.6	96	1800	2000	3400	1.70
5	164.8	81	1100	1400	2400	1.78
6	206.0	75	800	1000	1800	1.80

However, the decrease of R_p does have an impact on the molecular weight distribution (MWD) of the macromonomers giving a small but significant low-molecular weight shoulder to SEC traces. To study this phenomenon, we measured the temperature of the reaction every two seconds by employing a computer controlled thermosensor integrated into the reactor. The acquired exotherms revealed a clear difference between polymerisations carried out in absence and presence of CoBF (Figure 1A). In both cases the reactor jacket temperature was constant throughout the reaction time, and the increase of the reactor contents temperature is strictly related to the exothermic nature of polymerisation. Without CTA the temperature starts to increase immediately upon monomer addition ($t = 0$), whilst in presence of CoBF the temperature drops slightly within first 5 minutes and then starts a slow growth. The temperature drop can be explained by a high chain transfer activity of the catalyst resulting in higher termination rates. Thus, the rates of initiation (R_i) and termination (R_t) are not subject to the steady-state approximation, when equilibrium is shifted to R_t and predominantly short chains are produced. Since R_p is proportional to the square root of initiator concentration (*viz.* initiator decomposition rates), and hence depends on R_i , a higher reaction temperature can counterbalance the effect of CTA on the steady-state equilibrium. This in turn means that even a reduced heat of polymerisation observed for CCTP will eventually equilibrate R_i and R_t resulting in a two-stage polymerisation; before and after the steady-state approximation. In terms of MWD, the synthesised polymer should have a bimodal distribution, which was observed as the low-molecular weight shoulder (Figure 1B, red line). In contrast, the MWD of free radical PMMA (Figure 1B, black line) has a normal distribution, which led us to hypothesise that a controlled overhear regime could eliminate the bimodal distribution of macromonomers obtained *via* emulsion CCTP. We found that a gradual temperature increase (~ 1 °C min⁻¹) during the first seven minutes after monomer addition gives

macromonomers where SEC analysis showed a near Gaussian distribution (Figure 1B, green line). The importance of normally distributed macromonomers for production of block and comb-like copolymers will be discussed in the following sections.

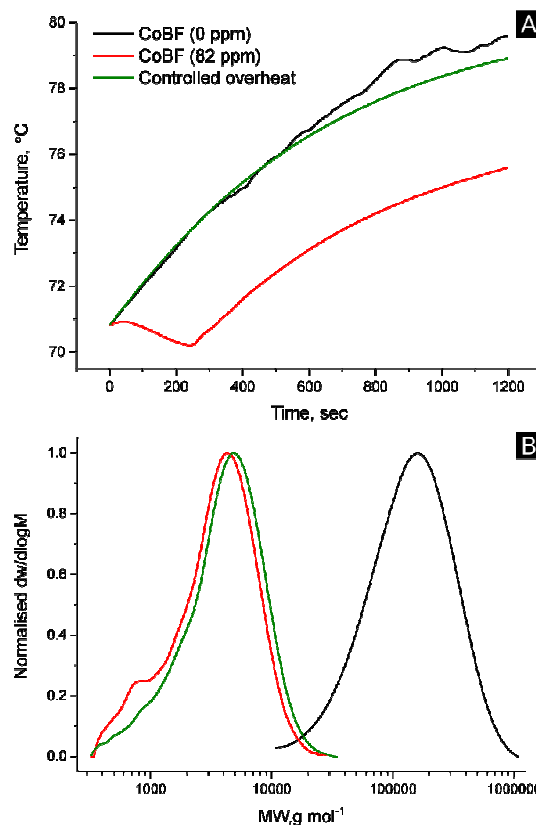


Figure 1. Comparative thermal and SEC data for polymers synthesised in absence and presence of CoBF. (A) online temperature measurements. (B) SEC traces of obtained polymers.

The chain transfer activity of CoBF can be determined by applying the Mayo equation (Eq. 1).⁵⁰ It is important to realise that the obtained chain transfer constant is not absolute, as not all molecules of CoBF are involved in emulsion CCTP due to the above-mentioned reasons and MMA/CoBF solutions are fed into the reactor. Nonetheless, the Mayo equation provides an effective chain transfer constant (C_S^E) of CoBF in emulsion CCTP, which is an informative parameter.

$$\frac{1}{DP_n} = \frac{1}{DP_{n,0}} + C_S^E \left(\frac{CTA}{M} \right) \quad \text{Equation 1}$$

The number average degrees of polymerisation in presence of the catalyst (DP_n) and absence ($DP_{n,0}$) of PMMA were estimated using M_n values obtained *via* SEC analysis. Equation 1 allows for the construction of a pseudo-Mayo plot determining C_S^E by measuring a slope of the graph (Figure 2). C_S^E for CoBF = 463 which is significantly higher than the chain transfer constant of mercaptans (~ 1), which are typical CTA's in emulsion polymerisations. It must be noted that the

estimated C_s^E is lower in comparison to the previously published data^{40–42,51} for emulsion CCTP and is explained by lower catalyst purity.

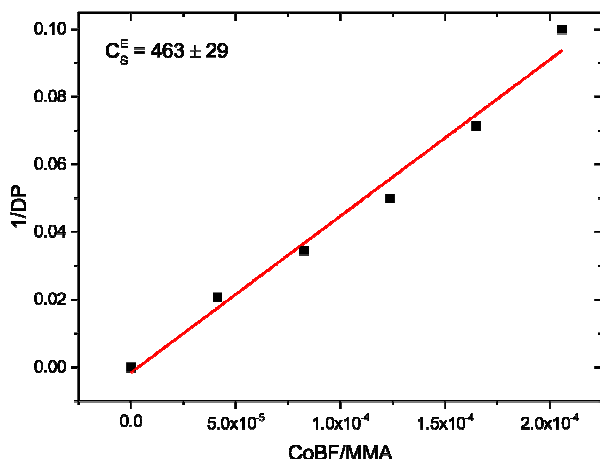


Figure 2. Pseudo-Mayo plot for CoBF-mediated emulsion polymerisations.

The mechanism of CCTP implies the preparation of vinyl-terminated polymer chains (macromonomers), which can be subsequently employed to produce block or comb-like copolymers (Figure 3). An effective post-polymerisation of macromonomers in many respects depends on the vinyl end-group fidelity. This parameter can straightforwardly be estimated by ^1H NMR. Depending upon their location, methoxy groups of PMMA macromonomer have a different chemical shift, and therefore allowing quantification of the end group fidelity. Thus, the terminal methoxy group (Figure S5, peak “b”, δ 3.69 ppm) is shifted in comparison to the main-chain methoxy groups (Figure S5, peak “c”, δ 3.60 ppm). On integrating the vinyl peaks (Figure S5, peak “a”) with respect to the terminal methoxy group, we found that >99% of PMMA chains from this process are vinyl terminated.

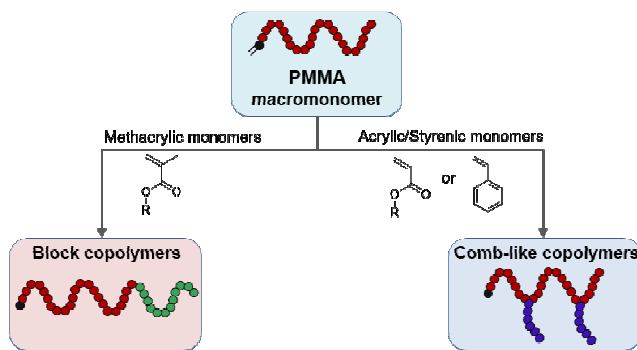


Figure 3. Synthesis of block or comb-like polymers *via* sulphur free RAFT.

A further valid method to estimate the amount of vinyl terminated polymer chains is the use of thermal degradation analysis (TGA). In the absence of a chain transfer agent MMA polymerises under free radical conditions with termination by combination and/or disproportionation. PMMA with different saturated, unsaturated (vinyl terminated) and head-to-head

terminated chains show distinct thermal degradation.⁵² In CCTP chain transfer dominates over other possible termination mechanisms, resulting in unsaturated chains, but cannot exclude the formation of head-to-head linkages between polymer chains. Kashiwagi *et al.* reported that weak unsaturated and head-to-head linkages can be distinguished by means of TGA,⁵³ but further investigations questioned these conclusions.^{54–56} Nevertheless, different decomposition temperatures of the saturated (360 °C)^{56,57} and vinyl terminated (275 °C)^{54–56} chains allow a direct determination of the percentage of the above mentioned species in synthesised polymers. We found that the free radical PMMA (Table 1, entry 1) consists of 16.9% unsaturated chains, while PMMA macromonomers (Table 1, entries 2–6) are 95–97% vinyl terminated. We also discovered that despite previously published results,⁵⁴ it is possible to differentiate head-to-head linkages from the unsaturated chains by employing TGA. A significant weight loss occurs below 200 °C (Figure 4), which is indicative for head-to-head linkages, according to Kashiwagi *et al.*⁵³ At 178 °C free radical PMMA lost 7.2% of the initial mass, while PMMA macromonomer (Table 1, entry 3) 3.9%. Correlation of the TGA curves with an unambiguously saturated PMMA, shows that decomposition occurs only at 380 °C verifying TGA as a robust method to calculate the end group fidelity. The first derivatives of the TGA traces (dashed lines) reveal a clearer difference between analysed polymers in terms of their thermal stability.

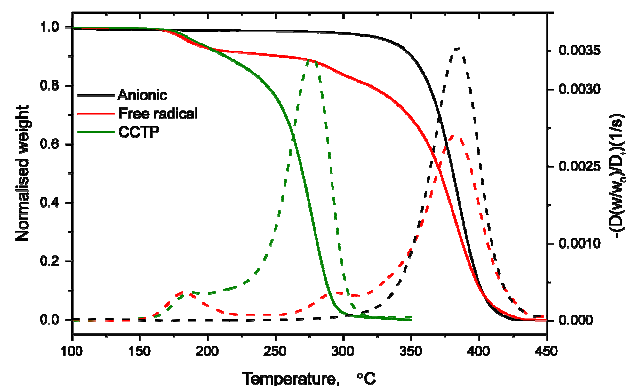


Figure 4. Thermal stability of PMMA obtained by anionic, free radical and catalytic chain transfer polymerisations.

MALDI-ToF-MS analysis also confirmed high end group fidelity of macromonomers obtained *via* emulsion CCTP. The dominant role of Co^{III} in the chain transfer and subsequent initiation by hydrogen atoms transferred from $\text{Co}^{\text{III}}\text{-H}$ (Scheme 1) produces macromonomers with a protic α -chain and vinyl ω -chain ends⁵⁸, Figure 5.

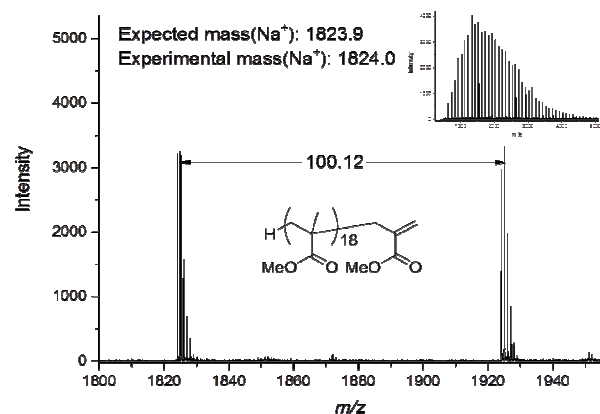
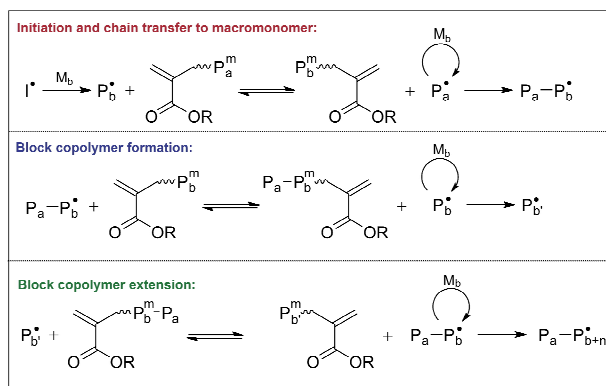


Figure 5. Expanded MALDI-ToF-MS spectra of PMMA macromonomer between $DP=18$ and 19 verifies high vinyl end-group fidelity.

Thus, emulsion CCTP is an excellent method to synthesise macromonomers achieving a significant reduction in molecular weight, retaining high conversions and introducing the functional end group to the polymer chains.

Synthesis of Block Copolymers

The mechanism for the synthesis of homo and diblock copolymers in SF-RAFT is outlined in Scheme 2 and occurs *via* the following major steps: (i) initiation; (ii) chain transfer to macromonomer; (iii) block copolymer formation.^{25,26} The reaction starts with an inception of propagating radicals (P_b^*) in the system after a normal free radical initiation. These radicals subsequently transfer to a macromonomer (P_a^m), forming an intermediate low reactive radicals (addition), which then undergo the β -scission reaction (fragmentation). As a consequence of the addition-fragmentation chain transfer, the majority of the initial macromonomer chains become new propagating radicals (P_a^*) by losing the vinyl terminated ω -chain end, whilst added radicals transform into a macromonomer (P_b^m) by gaining it. The new radicals add monomer b producing propagating block copolymer chains ($P_a-P_b^*$). These chains further transfer to the newly formed macromonomer, which results in the formation of the block copolymer macromonomer ($P_a-P_b^m$). At this stage, the reaction is being reversed to the initial state, with the only difference that macromonomer is now the block copolymer. Subsequent addition of the monomer leads to the block copolymer chain extension *via* the same addition-fragmentation route described above. Considering the mechanism of SF-RAFT, a decisive role of macromonomer, *i.e.* aforementioned end group fidelity, becomes apparent.



Scheme 2. Mechanism of sulfur free RAFT.⁴⁰

Since most of the block copolymers presented in this study were obtained via the semi-batch seeded emulsion polymerisation, colloidal and interfacial phenomena should also be considered to obtain a more complete understanding. The first point to consider is that macromonomer is dispersed in an aqueous medium in form of hydrophobic polymer nanoparticles. The addition of the second monomer, which is also hydrophobic, transforms solid *nanoparticles* into monomer-swollen colloids, turning each of them in the independent locus of copolymerisation. This means that most likely only one radical can exist per particle,⁵⁹ forcing the propagating chains to terminate predominantly transfer to macromonomer. In contrast to solution polymerisation, this compartmentalisation effect reduces the probability of bimolecular termination allowing for simultaneous growth of all chains, resulting in a better controlled MWD of the final product. The second important feature is that these seeded emulsion polymerisations proceed under monomer-starved conditions maintaining high monomer conversion rates (>85-95%) throughout the reaction. As a result, the ratio of macromonomer to added monomer is always favoured to the first one, which again increases the likelihood of successful chain transfer and subsequent block copolymer formation. Alongside high end group fidelity of macromonomers these phenomena are key to the successful synthesis of block copolymers *via* SF-RAFT. This is primarily due to the relatively low chain transfer activity of macromonomers, which in turn demands specific conditions to increase it to give the desired effect.^{27,28,33}

Taking into account an ability of macromonomers to undergo the β -scission reaction (fragmentation) depending on their chain length and ester group of employed monomer, the chain transfer constant (C_S^E) of the employed macromonomer is a subject of interest.^{24,28,33,60-63} Assuming that macromonomers are CTA's in SF-RAFT, the C_S^E can be estimated using a pseudo-Mayo plot method.⁴⁰⁻⁴² As in the case with CoBF, this method allows determination of an effective constant C_S^E rather than an absolute value. We found a value of 0.87 (Figure 6), C_S^E of the employed macromonomer is comparable to widely used sulfur-based CTA's (mercaptans). Moad *et al.* previously reported that C_S^E of a PMMA macromonomer ($M_n = 2300$ g.mol⁻¹) is 0.22, which is four times lower than the value obtained herein.²⁴ This can be explained by the different

methods of copolymerisation used. Bulk polymerisation used by Moad and co-workers is arguably less effective in terms of favouring the chain transfer over the propagation, whilst the compartmentalisation occurring in emulsion polymerisation increases the probability of chain transfer success.

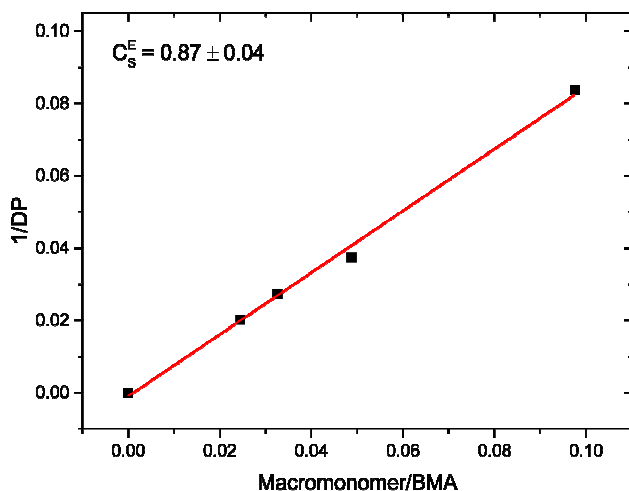


Figure 6. Pseudo-Mayo plot for macromonomer mediated SF-RAFT. M_n^{SEC} of the utilised macromonomer is 2900 g mol^{-1} .

Macromonomer latexes obtained by emulsion CCTP retain performance for at least 6 months after synthesis, providing an opportunity to store them and use on demand. Despite this, we found that a continuous one-pot fabrication of block copolymers is a more efficient approach. Firstly, the reactor contents remain under oxygen-free conditions and at an appropriate temperature to carry out the copolymerisation immediately after the macromonomer production. Secondly, the deoxygenation of latexes compromises their colloidal stability, since polymer nanoparticles can cover nitrogen bubbles,^{64–67} in essence inducing coagulation. Unless stated otherwise, we utilised the one-pot approach to fabricate a variety of block copolymers, producing a macromonomer and subsequently extending it with a second monomer, Table 2, Figures S6–S13.

Table 2. Data for the obtained block copolymers under conditions described in the Experimental Section*

Run	2 nd monomer	Conversion, %	M_n^{NMR} , g mol^{-1}	M_n^{SEC} , g mol^{-1}	\bar{D}
1	MMA	>99	9300	10000	1.28
2	EMA	>99	10200	11000	1.17
3	n-BMA	>99	9600	10000	1.14
4	i-BMA	>99	8900	9500	1.17
5	t-BMA	>99	7700	8500	1.42
6	EHMA	>99	8600	9000	1.15
7	LMA	60	3700	4200	1.50
8	BzMA	>99	8900	9500	1.20
9	IBMA	>99	4600	5200	3.00

*For all reactions macromonomers had $M_n = 2900 \text{ g mol}^{-1}$ and $\bar{D} = 1.69$

** Copolymer was obtained *via* a two-step solution polymerisation in methyl ethyl ketone

A controlled macromonomer chain growth was confirmed by SEC analysis. Macromonomer chains grow accordingly to the molar equivalents of added monomer (Figure 7B), which results in a predicted chain extension from 2900 to ~10000 Da. Also, SEC analysis reveals the importance of monomodal MWD of the macromonomers with regards to the dispersity of the final product. Bimodal MWD would result in a simultaneous chain growth of both populations of macromonomer chains thus broadening the SEC chromatograms of the obtained copolymers. The utilisation of normally distributed macromonomers allow for the synthesis of relatively narrow disperse copolymers (Figure 7A).

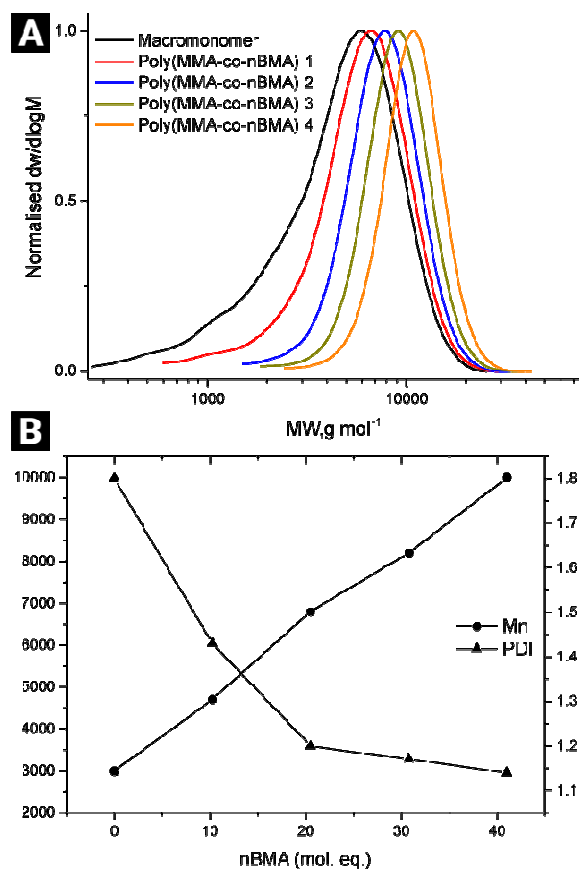


Figure 7. (A) SEC chromatograms of synthesised block copolymers PMMA-co-PBMA and (B) Evolution of M_n and \mathcal{D} versus the molar equivalents of added monomer

By a consideration of the dominant role of the vinyl ω -chain end of macromonomers in the SF-RAFT mechanism the final DP_n of block copolymers can be estimated using equation 2:^{25,26}

$$DP_n = \frac{\text{moles of added monomer}}{\text{moles of macromonomer}} + DP_n^m \quad \text{Equation 2}$$

where DP_n^m is the degree of polymerisation of the macromonomer

Krstina *et al.* mentioned that this equation is correct for ideal conditions, when the total concentration of macromonomer stays constant throughout the reaction.^{25,26} Monomer-starved seeded emulsion polymerisation complies perfectly to this scenario. The obtained experimental data confirms that Equation 2 is valid within the analytical error margin.

However, very hydrophobic monomers (e.g. LMA and IBMA) cannot successfully be applied, due to the peculiarities of the biphasic polymerisation method. These highly hydrophobic monomers are virtually insoluble in water they are unable to diffuse to the macromonomer particles to enable initiation of the chain transfer process. This semi-batch approach allows for chain extension in the early stages of copolymerisation, as a relatively low amount of added monomer is partially swelling

macromonomer particles (Table 2, entries 7 and 9, Figures S11 and S13). Further monomer addition induces a complete separation of the monomer phase from the latex, preventing an efficient inflow of monomer to the macromonomer particles. Monomers which are feasible for emulsion polymerisation and soluble in water by more than 1 wt% limit the \mathcal{D} -index in a range of 1.5 - 1.3. A lower solubility allows synthesis of block copolymers which are more narrowly distributed ($\mathcal{D} \leq 1.2$) Table S2.

From the mechanism of SF-RAFT successful chain transfer to macromonomer would give a vinyl ω -chain end and the terminal methoxy group will appear in the ¹H NMR spectrum regardless equivalents of an added monomer. Secondly, the ratio of characteristic groups must change accordingly to the molar amount of an added monomer. Figure 8 illustrates these aspects of SF-RAFT, taking the copolymerisation of EMA with PMMA macromonomer as an excellent example. Thus, the vinyl (peaks "a", δ 6.30 and δ 5.4 ppm) and terminal methoxy groups (peaks "c", δ 3.69 ppm) are present in the spectra of block copolymers, while the area of the ethoxy group of EMA (peaks "b", δ 3.95 ppm) increases relative to the methoxy group of the macromonomer (peaks "d", δ 3.60 ppm).

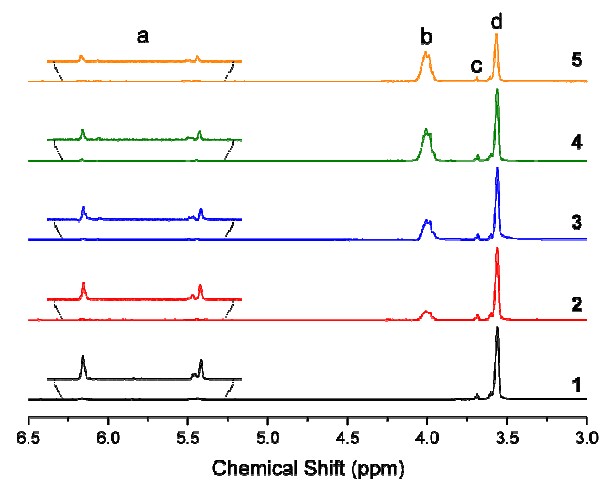


Figure 8. ¹H NMR spectra of block copolymers (2-5) produced by copolymerisation of PMMA macromonomer with EMA. (1) $M_n = 2600 \text{ g}\cdot\text{mol}^{-1}$. (2) $M_n = 4000 \text{ g}\cdot\text{mol}^{-1}$, 13 mol. eq. of EMA. (3) $M_n = 5500 \text{ g}\cdot\text{mol}^{-1}$, 26 mol. eq. of EMA. (4) $M_n = 7200 \text{ g}\cdot\text{mol}^{-1}$, 40 mol. eq. of EMA. (5) $M_n = 9100 \text{ g}\cdot\text{mol}^{-1}$, 54 mol. eq. of EMA.

The TGA/DSC evaluation also sheds light on the mechanism and block copolymer composition of the obtained block copolymers. Since the block copolymers are chain extended macromonomers they should have the same thermogravimetric properties as pure macromonomers, Scheme 2. We found that block copolymers decompose at $\sim 275 \text{ }^\circ\text{C}$, verifying the SF-RAFT mechanism as a controlled growth of initial chains, mediated by the reactive ω -chain end and thermally degrading *via* the same "unzipping"⁵³ mechanism observed for homo-macromonomers (Figure 9).

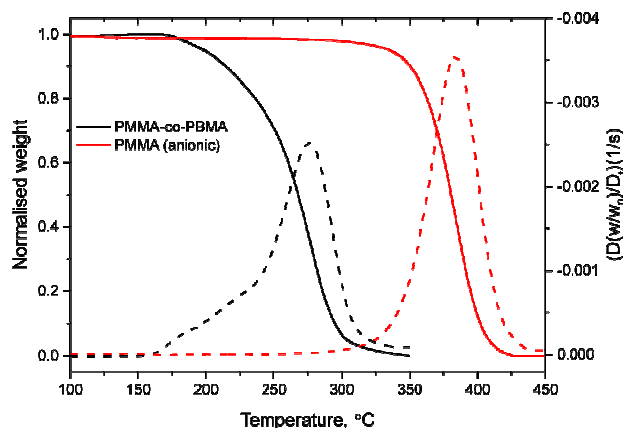


Figure 9. TGA/DSC chromatograms of PMMA-co-PBMA copolymer. Black dashed trace represents the T_d of block copolymer in comparison to PMMA synthesised via anionic polymerization (red dashed trace). The solid black trace represents the T_g of the block copolymer versus the amount of added monomer.

It is evident from the results that SF-RAFT has all of the features of controlled reversible-deactivation polymerisation.^{7,68} All chains grow simultaneously and their lifetime is equal to reaction duration, since the vinyl group is always present at the ω -chain end, as well as narrow MWD of the synthesised polymers.

Synthesis of Comb-like Copolymers

In addition to the synthesis of block copolymers, the products of CCTP can be used as macromonomers allow for the fabrication of comb-like structures by switching from methacrylic to acrylic monomers for the second addition.⁶⁹⁻⁷⁰ In this case chain transfer does not occur due the absence of α -methyl group, and macromonomers primarily copolymerise with a propagating acrylic radical. This results in the formation of comb-like copolymers with an acrylic backbone and macromonomer "teeth". To compare the effect of different monomers on the structure of produced copolymers, we employed butyl acrylate (BA) and styrene (St) as an alternative to BMA and BzMA using the same experimental conditions. An inequality of obtained products is directly observable by using the SEC analysis. For instance, BMA allows synthesis of a narrowly distributed block copolymer, while a polymer obtained by adding BA have a much broader distribution (see Figure 10). This is typical for branched polymer structures, for example for comb-like copolymers.⁷¹

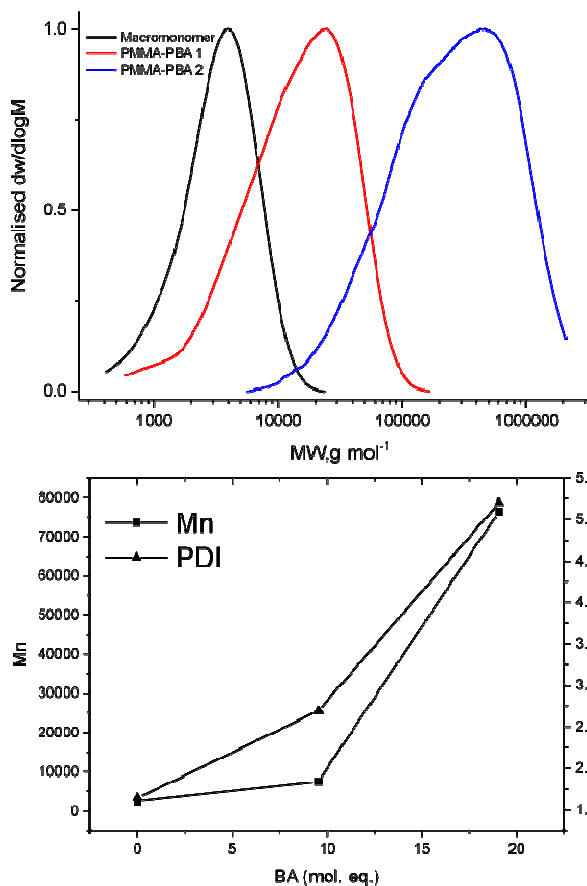


Figure 10. SEC chromatogram of PMMA-PBA comb-like copolymers.

An addition of more equivalents of BA led to a formation of crosslinked polymer gel. This allowed us to assume that depending on amounts of added monomers, fabricated polymers can exhibit various structural properties. To study an influence of acrylic monomers on the structure of comb-like copolymers, we applied a triple detection SEC analysis using a universal calibration. This method allows distinguishing molecular structures of polymers by applying the Mark-Houwink equation (Eq. 3).⁷¹⁻⁷⁶

$$[\eta] = KM^\alpha \quad \text{Equation 3}$$

where $[\eta]$ is the intrinsic viscosity, K and α - Mark-Houwink parameters.

The Mark-Houwink plots of the comb-like copolymers appear bicurved indicating that their molecular structure/shape is not uniform across the MWD (Figure 11). An evolution of comb-like copolymers architecture is seen by the change of the α constant as a function of MW. Initial α parameters are below the range of branched structures displaying values characteristic for star polymers, Figure 11. However, with increasing molecular weight the α constant changes from 0.16 to 0.59 (Figure 11A), indicating to a shift from star-shaped structures to linear coils.

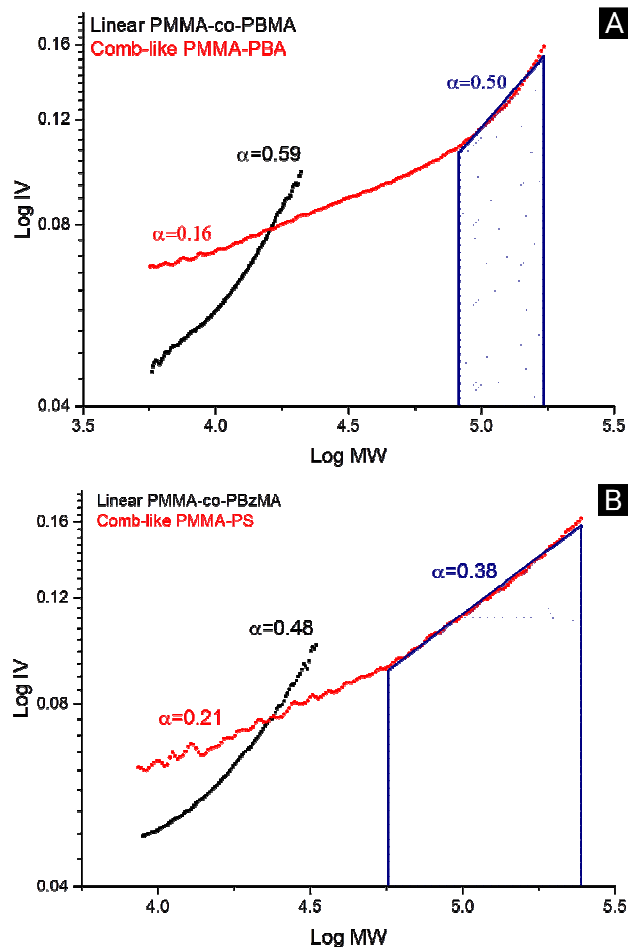
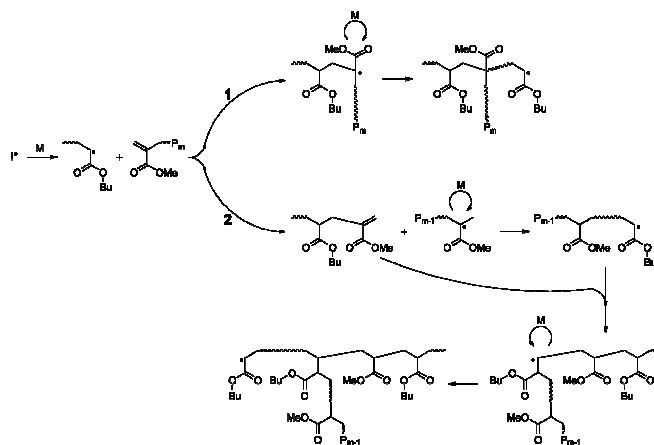


Figure 11. Mark-Houwink plots of block and comb-like copolymers produced *via* SF-RAFT. (A) PMMA-co-PBMA vs. PMMA-PBA. (B) PMMA-co-PBzMA vs. PMMA-PS.

This transformation is explained by the total consumption of macromonomer, when the whole system switches to a single monomer polymerisation. This in turn means that the initially formed comb-like copolymer eventually gains a “tail” formed by an added monomer. The aforementioned cross-linking, which was observed only for BA, also indicates the presence of the “tail”, due to the “backbiting” phenomenon typical for acrylic monomers. In the case of styrene, additional monomer amounts solely growing the main chain, while BA radicals can abstract from the backbone, creating cross-linked networks. The low α values observed for comb-like copolymers at the initial stages of copolymerisation, correspond to previously published data.⁷⁷ The ratio of macromonomer to propagating chains, which is favoured to the first one under monomer-starved conditions, resulting in densely packed comb-like copolymers exhibiting properties of star-shaped polymer chains ($\alpha < 0.33$).

The absence of α -methyl group implies a virtual infeasibility of the addition-fragmentation chain transfer (AFCT) in the case of copolymerisation of methacrylic macromonomers with an

acrylic monomer at temperatures ≤ 90 °C. However, Yamada and co-workers demonstrated that the AFCT mechanism cannot be excluded from consideration.^{78,79} Considering this factor, Heuts and Smeets. proposed a mechanism of comb-shaped polymers synthesis which differs from the generally accepted “backbone-teeth” model (Scheme 3, approach 1).⁴⁹ This mechanism includes following stages: (1) AFCT of propagating acrylic radicals to macromonomer; (2) copolymerisation of the newly formed methacrylic chains with acrylic radicals; (3) copolymerisation of chains obtained during stages 1 and 2 (Scheme 3, approach 2).



Scheme 3. Copolymerisation mechanisms of PMMA macromonomers with butyl acrylate resulting in fabrication of comb-like structures.

In order to define the mechanism, NMR studies were employed. If approach 1 is likely to be the case, five equivalents of added acrylic monomer would exclude the signals of vinyl and terminal methoxy groups of macromonomers, due to their irreversible consumption. Approach 2 demands more equivalents of acrylic monomer, since the AFCT is occurring and functional groups are consumed only at stage 3 of the above-mentioned mechanism. We found that the Heuts and Smeets concept is more suitable to describe the synthesis of comb-like copolymers under the conditions of SF-RAFT. After addition of five equivalents of an acrylic monomer, vinyl groups (peaks “a”) and terminal methoxy groups (peak “c”) are detectable, Figure S14.

Conclusions

In this study, the synthesis of block and comb-like copolymers employing the emulsion SF-RAFT approach has been investigated in detail. Optimised conditions of macromonomer synthesis which allowed for the fabrication of methacrylic block copolymers is presented. It is shown it is possible to produce a variety of well-defined block copolymers, considering peculiarities of emulsion polymerisation, such as hydrophobicity of monomers. The mechanistic aspects of comb-shaped copolymers synthesis and their architectures were also identified. The generally accepted “backbone-teeth” model is not suitable for the description of the mechanism,

since acrylic monomer undergo the AFCT even at relatively low temperatures. Depending on the amount of added acrylic monomer, comb-like copolymers can structurally vary from densely packed to “match-like” objects having a “tail” of linear chain attached to a comb “head”. This represents an excellent versatile and scalable method to produce narrow molecular weight distribution methacrylic block copolymers.

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Notes and references

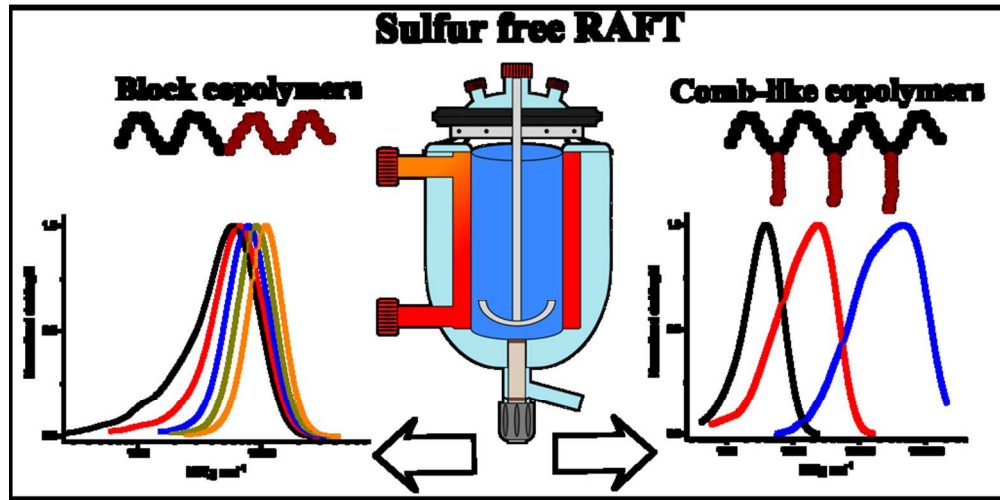
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