Exploitation of the nanoreactor concept for efficient synthesis of multiblock copolymers via macroRAFT-mediated emulsion polymerization

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ABSTRACT: Multiblock copolymers are a new class of polymeric materials with a range of potential applications. We report here a strategy for the synthesis of multiblock copolymers based on methacrylates. Reversible addition-fragmentation chain transfer (RAFT) polymerization is implemented as an emulsion polymerization to generate seed particles as nanoreactors, which can subsequently be employed in sequential RAFT emulsion polymerizations. The segregation effect allowed synthesis of a high molar mass (>100,000 g.mol^{-1}) decablock homopolymer at high polymerization rate to an extent not previously achieved. A heptablock copolymer containing seven different 100 unit blocks was also successfully prepared, demonstrating how the strategy can be employed to precisely control the polymer composition at a level hitherto not accessible in environmentally friendly aqueous emulsion polymerization. Importantly, the methodology is a batch process without any intermediate purification steps, thus rendering industrial scale up more feasible.

The promise of manufacturing new materials with a wide range of unique properties has made the synthesis of multiblock copolymers an important focal point in polymer chemistry in recent years.[1-7] Multiblock copolymers are composed of three or more covalently linked polymer segments, manifesting distinct and oftentimes exploitable chemical and physical properties in comparison to their constituent segments. The customization of such polymers by way of block sequence, segment length and monomer functional groups has attracted significant interest in a number of fields, *e.g.* advanced materials[8] and microelectronics.[3, 9]

Since the pioneering work in 2011,[1] reversible deactivation radical polymerization (RDRP) has been extensively employed for the synthesis of multiblock copolymers. Gody *et al.*[2, 10-12] reported a one-pot strategy to synthesize acrylamide-based multiblock copolymer comprising up to 20 blocks via sequential reversible addition-fragmentation chain transfer (RAFT) polymerizations. The degree of livingness, *i.e.* the number fraction of chains possessing a RAFT ω-end group, was demonstrated to be a key parameter for synthesis of well-defined multiblock copolymers;[10] only the living chains can be extended in each consecutive polymerization step. In an ideal RAFT process, dead chains are generated only via bimolecular termination of propagating radicals. Considering that each radical eventually partakes in termination, and given that the number of radicals generated from initiator decomposition during the polymerization is approximately known, a maximum degree of livingness can be readily predicted. One faces a trade-off between high polymerization rate and high livingness – the higher the initiator concentration, the faster the polymerization but the lower the livingness. The loss of livingness associated with the higher initiator concentration can only be partially compensated for by the shorter polymerization time. Moreover, an increase in target degree of polymerization (DP) leads to a loss in livingness as a consequence of a reduction in the number of living chains (less RAFT agent gives higher degree of polymerization). As a consequence, the synthesis of a multiblock copolymer composed of low k_p monomers such as methacrylates[13-16] is particularly challenging. A solution to this issue has been recently proposed by our group,[17] whereby the segregation effect[18-20] in heterogeneous systems can be exploited. It was demonstrated that the livingness can be improved when conducting RAFT in miniemulsion due to the enhanced polymerization rate relative to the corresponding bulk system. This strategy was exploited for the synthesis of a triblock copolymer exhibiting high MW (M_n = 94,000 gmol^{-1}; $Đ$ = 1.48) via miniemulsion polymerization. By contrast, the corresponding synthesis under homogeneous conditions (bulk/solution) would be next to impossible due to the low rate of polymerization. MacroRAFT-mediated

emulsion polymerization[21] has previously been demonstrated to be highly suitable for synthesis of ultrahigh molecular weight polystyrene[22-23] and gradient copolymers,[24] as well as diblock copolymers.[25] Engelis *et al.*[5, 26] reported a strategy to synthesize multiblock copolymer (up to 21 blocks) via "sulfur-free" RAFT emulsion polymerization. The key point in their work was however the use of slow feed of monomer into the system via syringe pump, thus ensuring a low monomer concentration, which is crucial to render a methacrylate macromonomer system "living" by decreasing the number of monomer units added per activation/deactivation cycle.[27-30]

In our recent work,[31] we demonstrated how RAFT emulsion polymerization can be successfully employed for the synthesis of complex multiblock copolymer structures. The use of this strategy in nano-engineering was illustrated by the preparation of multilayered polymer nanoparticles. The elaborate morphology was accessible due to linkage of five consecutive blocks of chemically incompatible copolymers (pentablock copolymer), which results in microphase separation within the particle. However, the final multiblock copolymers exhibited broad molecular weight distributions (MWDs) ($Đ$ = 1.7~2.1), which can be associated with some inevitable loss of livingness affecting the block formation efficiency.

Herein we report a successful strategy (Figure 1A) in which the nanoreactor concept has been exploited to provide access to high molecular weight multiblock copolymers comprising low k_p monomers within relatively short periods of time, thus significantly advancing the potential of this methodology from a materials synthesis perspective. An amphiphilic macroRAFT was used as both stabiliser and chain transfer agent in the emulsion polymerization

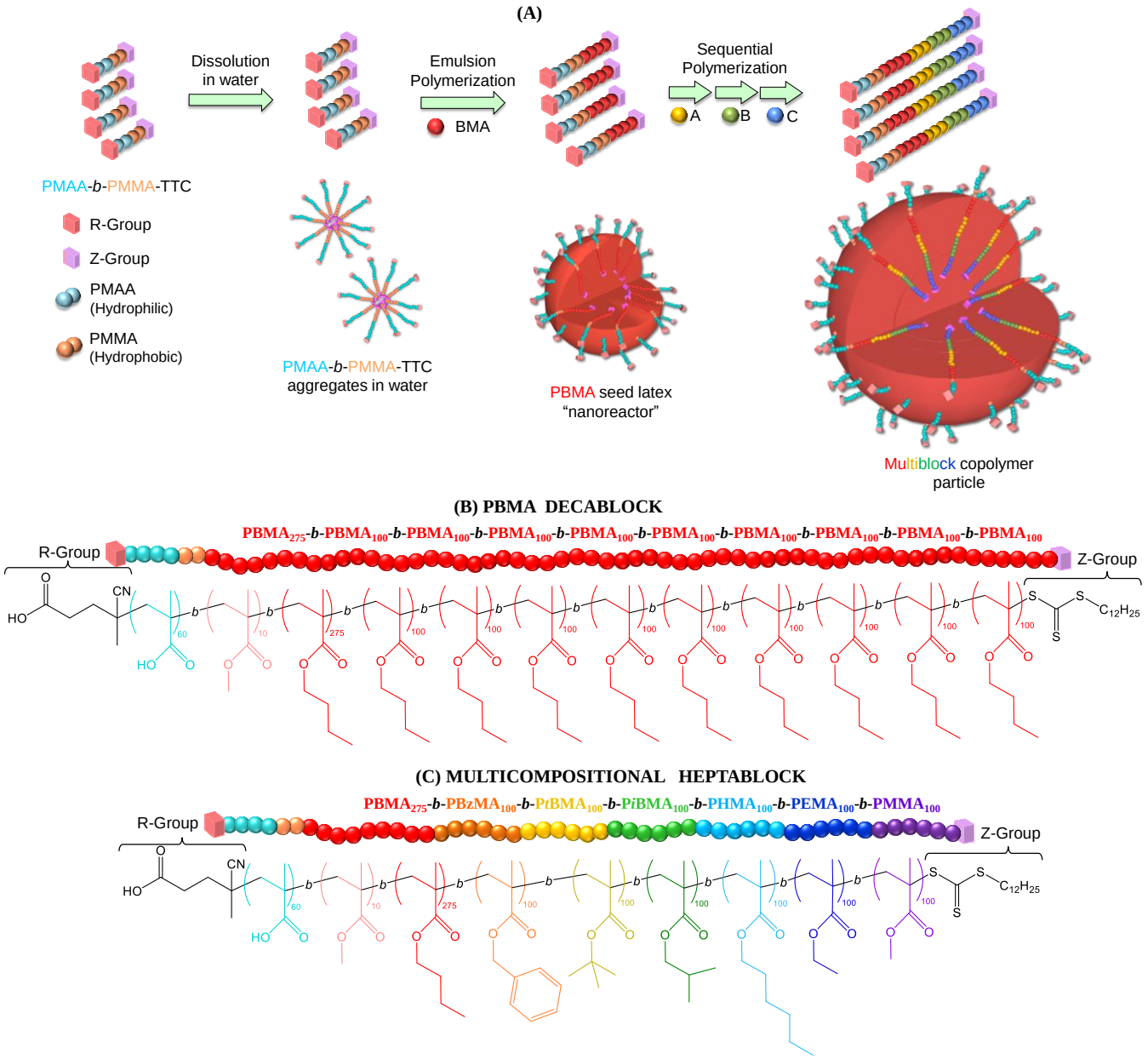


Figure 1. (A) Synthesis of multiblock copolymers via sequential RAFT emulsion polymerization. (B) Structures of PBMA decablock homopolymer and (C) multicompositional heptablock copolymer (PBMA$_{275}$-*b*-PBzMA$_{100}$-*b*-P*t*BMA$_{100}$-*b*-P*i*BMA$_{100}$-*b*-PHMA$_{100}$-*b*-PEMA$_{100}$-*b*-PMMA$_{100}$).

of butyl methacrylate (BMA) leading to formation of polymer particles. The resulting polymer particles act as "nanoreactors" in the subsequent sequential emulsion polymerizations in a compartmentalized system, allowing the synthesis of high M_n polymers (158,100 $gmol^{-1}$) in only 6.5 h. The versatility of the process was highlighted by the preparation of a multicompositional multiblock copolymer composed of 7 blocks of different monomers exhibiting high degree of polymerization per block (DP = 100). It is noteworthy that such high DP values are typically not targeted in multiblock copolymer syntheses, and most examples of multiblock copolymers prepared by RDRP are limited to three or four different monomer types in the polymer composition.[1, 26, 32-33] It is important to emphasize that all emulsion polymerizations were conducted in batch without monomer feed strategies, *i.e.* all monomer was added in one shot prior to each polymerization step.

The amphiphilic poly(methacrylic acid)-*b*-poly(methyl methacrylate) macroRAFT agents were synthesized via one-pot solution polymerization in dioxane ($PMAA_{62}$-*b*-$PMMA_{11}$-TTC, detailed experimental conditions, ^1H NMR and SEC data in Supplementary Information) following a methodology reported elsewhere.[34] This amphiphilic macroRAFT was used in the emulsion polymerization of BMA based on the experimental conditions in Table SI 3 (results in Table 1). This is a crucial aspect of our strategy, because nucleation occurs during this step, generating the particles that will be acting as nanoreactors in the subsequent multiblock copolymer synthesis. However, prior to the synthesis of complex multiblock structures, the system was optimized as outlined in **Figure 2**. The macroRAFT concentration was the first parameter studied (10.8, 19.2 and 28.9 gL^{-1} corresponding to targeted DPs of 755, 410 and 275 (Exp 1-3, respectively, Table 1 and Table SI 3) while keeping the ratio [RAFT]/[I] (I = the initiator KPS) at 14 and the polymer content at 18% (wt% monomer relative to total). High polymerization rates were observed in all systems with the polymerizations being completed in less than 1 h (conversion-time and particle size data in Figure SI3). Also, by increasing the concentration of macroRAFT (thereby targeting a lower DP), lower dispersity was obtained for the final polymer (Table 1; Figure SI4). Consequently, the highest concentration of macroRAFT, 28.9gL^{-1} (target DP = 275; Exp 3, Table 1), was selected for multiblock copolymer synthesis (it may be difficult to use higher macroRAFT concentrations than this due to water solubility issues).

The ratio of RAFT to initiator was subsequently investigated. As the emulsion polymerization constitutes a compartmentalized system, a low concentration of initiator could be employed while still achieving high polymerization rate due to the rate enhancing effect of segregation of propagating radicals in particles.[17-20] The use of [RAFT]/[I] = 14 and 29 led to high conversion in less than 90 min (Figure SI5) despite this being a methacrylate-based system (low k_p monomer) (Exp 3-4 in Table 1). However, for the system with the lowest initiator concentration ([RAFT]/[I] = 58, Exp 5, Table 1), the conversion was limited to 77%. On the other hand, for the system with the highest initiator concentration ([RAFT]/[I] = 14, Exp 3 in Table 1), the theoretical degree of livingness was the lowest (92.6% according to Eq. SI3, Table 1). In addition narrower MWD (Figure SI4 and SI6) and lower dispersities were obtained for [RAFT]/[I] = 29 (Exp 4, $Đ$ = 1.19, Table 1) compared to the experiment performed with the higher initiator concentration ($Đ$ = 1.25, Exp 3). Considering the above, the

Table 1 – Experimental conditions and results for the synthesis of PBMA particles and multiblock copolymers via emulsion polymerization mediated by $PMAA_{62}$-*b*-$PMMA_{11}$-TTC. See also Figure 2 and SI for further details.

Exp.	X (%)/ t (min)	$M_{n,theo}$	$M_{n,exp}$/ $Đ$	Z_{av} (nm)/ PDI	L (%)
1st step – MacroRAFT concentration					
1	87/75	99,800	73,500/1.49	97/0.06	92.4
2	98/75	63,700	51,400/1.31	86/0.05	92.7
3	96/60	43,800	42,800/1.25	75/0.08	92.6
1st step – [RAFT]/[I] ratio					
4	99/60	45,100	44,700/1.19	86/0.04	93.6
5	77/60	39,900	-	102/0.22	93.9
1st step – Monomer					
6	92/30	54,600	47500/1.43	78/0.05	93.7
7	96/60	32,700	45700/2.52	115/0.13	93.7
Multiblock Copolymers					
8	99/375	171,100	146,400/1.59	137/0.01	90.7
9	99/375	173,200	158,100/1.47	151/0.01	92.1
10	96/375	132,800	75,250/1.44	135/0.03	92.4

T = 80°C; SC (Solids Content) ≈ 20%. KPS was used as initiator. X = Overall conversion; L = Livingness. Full experimental details are available in SI.

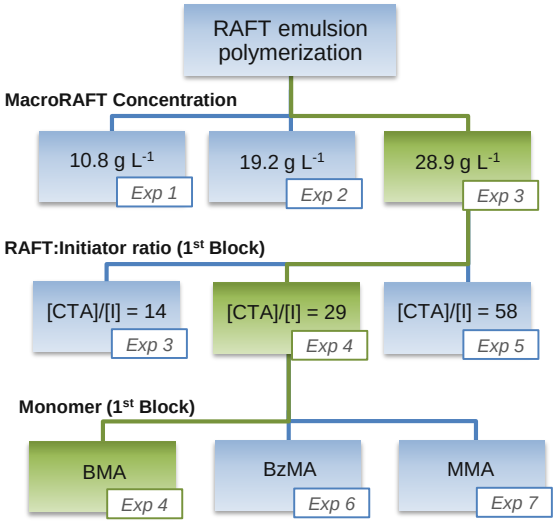
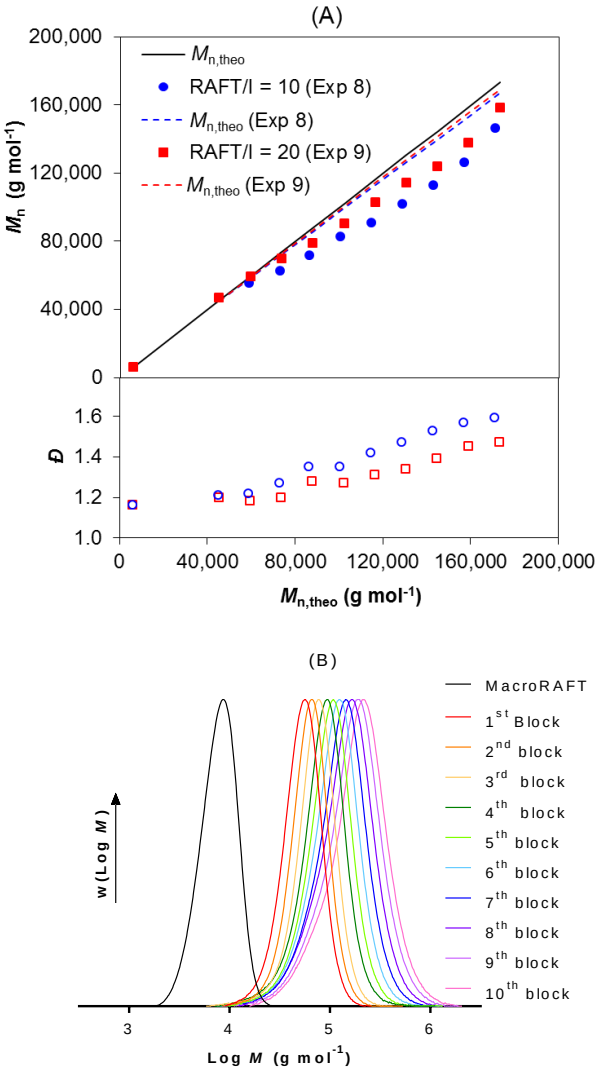


Figure 2. Scheme outlining experimental optimization strategy for synthesis of PBMA particles ("nanoreactors") via macroRAFT-mediated emulsion polymerization using $PMAA_{62}$-*b*-$PMMA_{11}$-TTC as macroRAFT agent.

system with the intermediate initiator concentration (Exp 4, Table 1 and SI3) appeared most suitable as it offers both sufficiently high polymerization rate (99% conversion in 1 h) and high livingness (93.6%).

The versatility of the system was subsequently explored using the different monomers BMA, benzyl methacrylate (BzMA) and methyl methacrylate (MMA) (Exp 4, 6 and 7 in Table 1, respectively). Methacrylates were chosen both due to their industrial significance and relatively low k_p values. Using the conditions selected above in regards to macroRAFT concentration (target DP) and initiator concentration (Figure 2), all polymerizations reached full conversion in less than 1 h (Figure SI7). However, the final PMMA latex exhibited significant flocculation, bimodal MWDs (Figure SI8) and $Đ$ = 2.52 (Exp 7, Table 1), presumably caused by homogenous nucleation due to the relatively high water solubility of MMA. In the case of BMA and BzMA, significantly higher $Đ$ was obtained for the BzMA system compared to the BMA system ($Đ$ = 1.43 and 1.19, respectively (Table 1), SEC-traces in Figure SI 6 and SI 8). This can presumably be at least partly ascribed to the higher value of k_p for BzMA (3150 and 1540 $Lmol^{-1}s^{-1}$ for BzMA and BMA, respectively),[35-36] which would lead to a lower chain transfer constant ($C_{tr} = k_{tr}/k_p$, where k_{tr} is the rate constant for chain transfer).[37-38] A lower value of C_{tr} means that more monomer units are added to each chain per activation/deactivation cycle, resulting in a broader MWD.[38] BMA was chosen for the preparation of our nanoreactors despite the somewhat longer polymerization time because of the lower dispersity of the generated polymer.

Having established the conditions for the synthesis of the nanoreactors, we turned our attention to multiblock copolymer synthesis. A PBMA decablock homopolymer was initially prepared as a model system (Figure 1B). PBMA latex particles (nanoreactors) were synthesized in a scaled-up experiment using a 300 mL double jacket reactor (Figure SI 9) following the optimized conditions of Exp 4 (Table 1). This emulsion polymerization was conducted for 90 min at 80ºC leading to full BMA conversion (X = 99.1%, entry Block 1 of Exp 8 in Table SI 4). Initiator (KPS) solution, BMA and water (detailed recipe in Table SI 4) were then added to the reactor and polymerization was performed for 45 min for the synthesis of the second block. Eight sequential seeded emulsion polymerizations of 30 min each were subsequently carried out by addition of only BMA and water (no initiator was added for blocks 3-10). The target DP of 100 units was fixed for each block (from 2nd to 10th block) except for the first block (275 units). The [RAFT]/[I] ratio was initially fixed at 10 (Exp 8, Table 1 and Table SI 4) and near full conversion was obtained after each cycle of polymerization (X_{av} = 99.0%, Figure SI10 and Table SI 4). THF-SEC analysis revealed the expected shifts of the main peak towards higher molecular weight (**Figure 3**B) indicating the successful synthesis of decablock homopolymer. However, some broadening was observed for the last blocks leading to a gradual increase in $Đ$ (**Figure 3**A and B), which can be ascribed to the inevitable loss of livingness associated with the process. In a second experiment (Exp 9, Table 1 and Table SI5), the initiator concentration was reduced to [RAFT]/[I] = 20. Despite this low initiator concentration, near full conversion was obtained for each block (X_{av} = 99.0, Table SI 5 and Figure SI 11) in only 30 min for each polymerization cycle. Furthermore, the SEC-traces of **Figure 3**C demonstrate the successful preparation of decablock copolymer with a no-



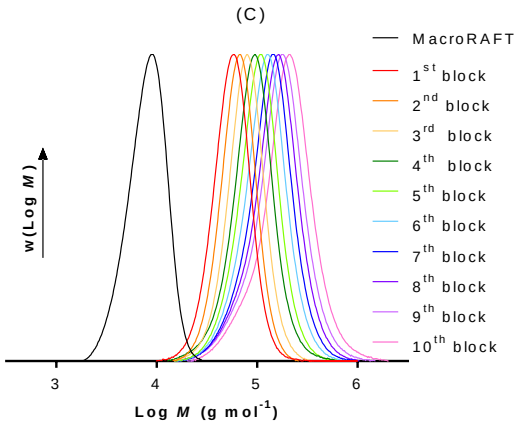
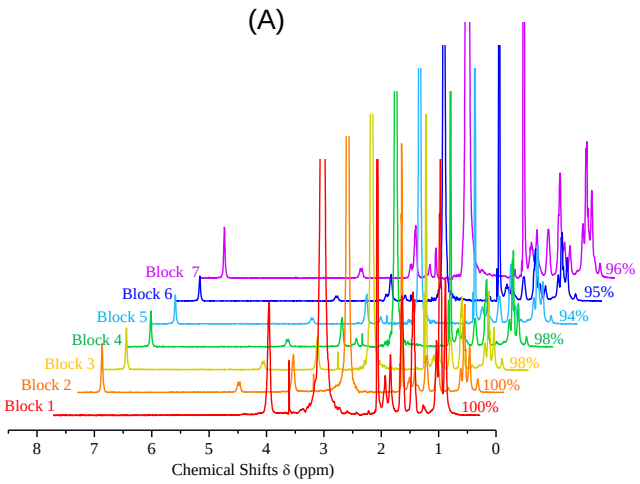


Figure 3. SEC-THF results for PBMA decablock homopolymer synthesized by sequential RAFT emulsion polymerization using RAFT/I ratios of 10 and 20. (A) M_n (filled symbols) and $Đ$ (open symbols) after each polymerization cycle for decablock homopolymer syntheses. The straight line represents the theoretical evolution of M_n. The dashed line represents $M_{n,theo}$ considering chains derived from initiator (f = 0.2) using Eq. SI2. MWDs of the systems using [RAFT]/[I] of (B) 10 and (C) 20 (Exp 8 and 9, respectively, in Table SI4 and SI5).

table reduction in low molecular weight tailing (Exp 8, **Figure 3**B, overlay of SEC-traces for the 5th and 10th blocks in Figure SI12) resulting in lower $Đ$ (**Figure 3**A). Overall, this is a remarkable result which demonstrates that by exploiting the segregation effect, it is possible to synthesize decablock homopolymer using low k_p monomers with high molecular weight and relatively low dispersity (M_n = 158,100 and $Đ$ = 1.47) exhibiting high degree of livingness (92.1%) in only 6.5 h. The final mass of latex was 94.16 g with a solids content (by mass) of 20%, corresponding to a dry polymer weight of 18.79 g.

The ultimate allure of high-order multiblock copolymers lies with the myriad of novel materials that are accessible. To illustrate the scope of our methodology, we endeavoured to prepare a heptablock copolymer composed of seven different monomers: BMA, BzMA, *tert*-butyl methacrylate (*t*BMA), *iso*-butyl methacrylate (*i*BMA), hexyl methacrylate (HMA), ethyl methacrylate (EMA) and MMA (Figure 1C). This multicompositional multiblock copolymer was synthesized using a similar strategy to that employed in the decablock homopolymer synthesis above. The same seed latex was employed, composed of 275 units of BMA. Six different monomers, as listed above, were used for the subsequent polymerization cycles (Exp 10, Table SI 6). The target DP for each block was kept at 100 units (except for the first block; 275 units) and the [RAFT]/[I] ratio at 20. Near full conversion was obtained for each block (Figure 4A) and the ^{1}H NMR peaks of the different polymer segments could be clearly observed after each polymerization cycle (Figure SI 13) indicating the successful synthesis of the multicompositional multiblock. The MWDs shifted towards higher MW (Figure 4C) after each cycle of polymerization (Figure 4B), indicating the successful formation of the heptablock copolymer. This impressive result demonstrates how this nanoreactor strategy can be successfully employed for the synthesis of multicompositional multiblock copolymer composed of seven different blocks each based on a different monomer and a relatively high DP of 100 units per block (the blocks originating from the macroRAFT, PMAA and PMMA, are not considered in the block count due to their relatively short lengths).

The synthesis of multiblock copolymers requires each polymerization step to proceed with a high degree of end-group fidelity; this has in the past required sacrifices in terms of polymerization rate and narrow ranges of viable molecular weights towards shorter chains. The fact that a combination of high polymerization rate, molecular weight, conversion and low dispersity was achieved in the present work carries significant implications for the synthesis of multiblock copolymer comprising low k_p monomers such as methacrylates and styrene. We have herein demonstrated that by exploiting the nanoreactor concept that is characteristic of emulsion polymerization under our conditions, the successful synthesis of decablock BMA homopolymer exhibiting high molecular weight (M_n = 158,100 gmol^{-1} and $Đ$ = 1.47) can be achieved in only 6.5 h. A high molecular weight multicompositional heptablock copolymer (PBMA$_{275}$-*b*-PBzMA$_{100}$-*b*-P*t*BMA$_{100}$-*b*-P*i*BMA$_{100}$-*b*-PHMA$_{100}$-*b*-PEMA$_{100}$-*b*-PMMA$_{100}$) was also prepared, further demonstrating the high potential of the reported strategy for synthesis of novel materials based on a variety of industrially significant methacrylates. It is also important to point out that this strategy is considered environmentally friendly (water used as solvent). The synthesis also features no intermediate purification steps, good colloidal stability, very high monomer conversion, low RAFT agent concentrations (high molecular weight polymer targeted), and is a series of batch processes with no continuous monomer feed strategies. These are all requirements if the process is to be applied on industrial scales.



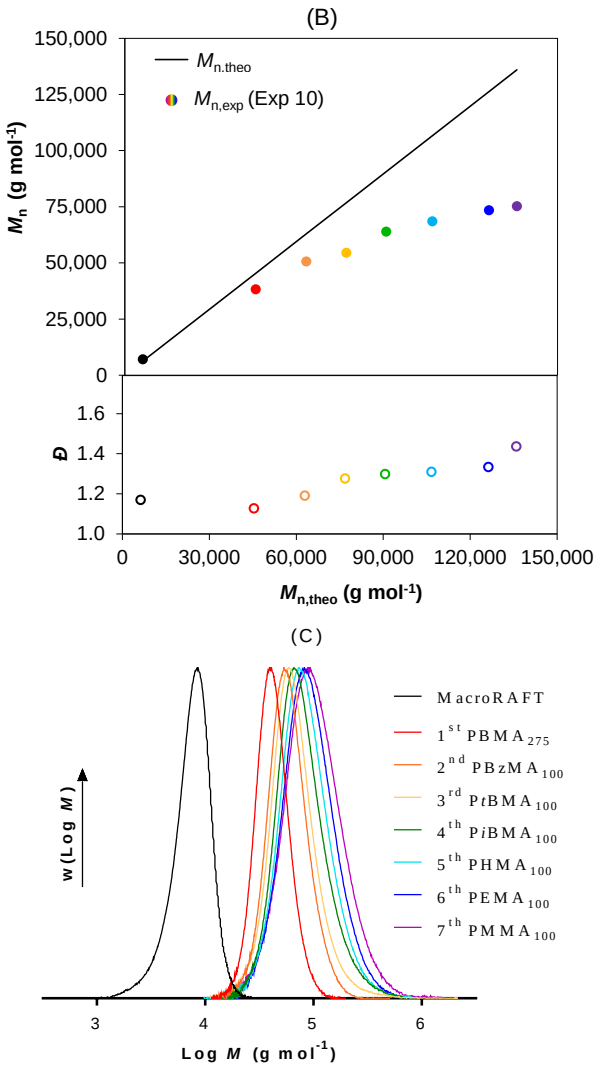


Figure 4. (A) ^{1}H NMR spectra for sequential RAFT emulsion polymerization for synthesis multicompositional heptablock copolymer (Exp 10, Table SI 6) showing the monomer conversion for each block. (B) M_n (filled symbols) and $Đ$ (open symbols) determined by SEC-THF after each polymerization cycle for multiblock copolymer syntheses and its respective (C) MWDs for each block (Exp 10, Table SI6).

ASSOCIATED CONTENT

Supporting Information. Detailed experimental description, conversion *vs* time plots, DLS results, additional SEC, TEM and NMR results are presented in Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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