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Looped flow RAFT polymerization for multiblock copolymer synthesis

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Agnès Kuroki^a, Ivan Martinez-Botella^b, Christian H. Hornung^b, Liam Martin^a, Elizabeth G. Williams^b, Katherine E. S. Locock^b, Matthias Hartlieb^a, Sébastien Perrier^{*a, c}

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A looped flow process was designed for the synthesis of well-defined multiblock copolymers using Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization. The reaction conditions were optimized to reach high conversions whilst maintaining a high end-group fidelity. The loop set-up proved to be a flexible, robust and time-efficient process for scaling-up multiblock copolymers.

Industrial screening of block copolymer libraries has recently received increasing interest,¹ therefore simpler processes for the synthesis of highly-defined polymer-libraries are required as demonstrated with the success of the automated synthesizer for the one-pot synthesis of quasiblock copolymers by Haven and co-workers.² Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization is an extremely robust and versatile Reversible-Deactivation Radical Polymerization (RDRP) technique and may be used to readily obtain polymers of defined molecular weight with narrow molecular weight distributions^{3,4,5} for a range of monomer families. Furthermore, developments in RDRP methods now allow for greater control over the monomer distribution along the polymer backbone⁶ which can have an interesting influence over the physico-chemical properties of the resulting polymers.⁷ Multiblock copolymers may now be prepared *via* RAFT using a one-pot iterative addition process through careful optimization of polymerisation conditions to achieve quantitative monomer conversion whilst maintaining high end-group fidelity.^{6,8} With such time and resource-efficiency, complex multiblock copolymer architectures are becoming increasingly accessible and offer enormous potential for industrial applications.

However, the scale-up of solution polymerizations is generally undermined with issues concerning temperature control,⁹

hence affecting end-group fidelity and the properties of the polymers obtained.¹⁰

Emulsion polymerization generally allow for lower viscosities and possess superior temperature control compared to solution polymerizations, offering potential for scalability.¹¹ RAFT emulsion polymerization was employed by Engelis *et al.*¹² to prepare well-defined polymethacrylate multiblock copolymers on multi-gram scales.¹³

Polymerization in continuous flow is another alternative to traditional solution polymerization in batch. Tubular reactors are advantageous due to their excellent heat transfer and the ability to readily maintain homogeneity, possessing potential for up-scaling with reproducibility.^{14,15}

Therefore, Russum¹⁶ and co-workers compared a mini-emulsion RAFT polymerization performed via a continuous flow process with a batch equivalent. However, higher polydispersities were observed with reactions in a tubular reactor as compared to the batch process.¹⁷ This difference was explained by the distribution of residence time of the particles of the emulsion. Therefore, homogeneous polymerizations might be more adapted than emulsion polymerizations for continuous flow processes. Additionally, homogeneous polymerizations are far less limited in terms of polymerizable monomers compared to heterogeneous systems.¹²

The first homogeneous continuous flow RAFT polymerization was performed by Diehl and co-workers¹⁸ to obtain polyNIPAm. The increased kinetics of flow reactions compared to the batch process was explained by a more uniform heating. Hornung *et al.*¹⁹ also used a continuous flow process to synthesise diblock copolymers²⁰ with solution-phase RAFT polymerization, adapting the reaction conditions in order to keep a low viscosity throughout the reactions. By connecting two reactors in series, diblock copolymers were obtained on a 2 gram scale without purification between blocks. However, there appeared to be reduced control of the polymerization with a low molecular weight tail observed on the GPC traces after chain extension.

^a Department of Chemistry, University of Warwick, Coventry, UK

^b CSIRO Manufacturing, Clayton, Victoria, Australia

^c Faculty of Pharmacy and Pharmaceutical Sciences, Monash University, 381 Royal Parade, Parkville, Victoria 3052, Australia

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Junkers and co-workers demonstrated the use of homogenous RAFT in continuous flow using a micro-reactor to prepare a poly(acrylate) multiblock copolymer (up to five blocks).²¹ However, a final yield of 100 mg with a molecular weight distribution of 1.46 and the need for a work-up between each chain extension make this method less amenable to scale-up. Looped processes have previously been used and optimised at an industrial scale for the production of polymers by free radical polymerization in a slurry-liquid phase^{22,23} as well as in emulsion.²⁴ The set-up was chosen as it allows a higher polymer concentration compared to a batch process,²⁵ hence increasing the productivity. However, this process has not yet been applied to a controlled radical polymerization to the best of our knowledge.

The present work aims to show that the loop set-up allows the synthesis of highly defined multiblock copolymers using materials which are commercially available and of relatively low costs in order to comply with industrial requirements.

Acrylamide monomers were chosen for the design of the multiblock copolymers since these monomers are associated with a high propagation rate coefficient (k_p) which allow short polymerization times, and mean that low $[I]_0$ can be used to achieve full conversion.²⁶ They can also be polymerized at high temperature as they are not sensitive to side reactions of chain transfer. In addition many useful acrylamide monomers are water soluble allowing for aqueous solution polymerization, which enhances their k_p ,²⁷ and importantly permits the use of the water soluble azoinitiator VA-044 which possesses a high decomposition rate coefficient (k_d) with a 10 hour half-life of 44 °C (in water). The use of an azo-initiator with such a high k_d results in rapid generation of radicals at temperatures above 60 °C allowing for short polymerization times. However, the overall number of radicals generated is kept low by limiting the concentration of azo-initiator in solution in order to retain a high fraction of ω -functional chains throughout the polymerization.²⁶

The choice of Chain Transfer Agent (CTA) is also a key parameter for the design of multiblock copolymers since the control of the

polymerization is strongly dependent on the structure of the CTA. Trithiocarbonate RAFT agents with a secondary R group have exhibit a good control over the polymerization of acrylamide and acrylate monomers.^{6,8,26} In addition, the induction period of the polymerization can be reduced by choosing a secondary R group. Furthermore, 3-(((1-carboxyethyl)thio)carbonothioyl)thio)propanoic acid (BM1429) was selected because it is water soluble, hence compatible with the mostly aqueous system which was designed. Dioxane was added (20 % in volume) to the mixture in order to keep the polymers in solution. The synthesis in both flow and batch processes have been optimised to achieve high monomer conversions, circumventing the need for purification steps between each chain extension, limiting the work-up and simplifying the process.

The set-up of the automated loop reactor was designed, as a proof of concept, based on a standard continuous flow set-up with a single reactor coil of 10 mL. However, the reactions may be further scaled-up by increasing the volume of the coil. The main feature of the system is the loop pump (which will be referred to as pump B) which recirculates the reaction mixture into the coil. As the volume contained in the reactor coil (10 mL) is much higher as compared to the rest of the loop (1.5 mL) and due to the high flow rate used (5 mL min^{-1}), the residence time outside the reactor coil is negligible in terms of variations in the temperature. All tubing used is made of stainless steel to limit the permeation of air into the system which would interfere with the polymerization. Another key element is the use of three-way valves to isolate defined parts of the circuit depending on the stage of the reaction. The various options are illustrated in Fig. 1 with the relevant sections of the set-up highlighted throughout the stages.

The operational procedure for the synthesis of multiblock copolymers is divided into three steps. After filling the set-up with solvent prior to any operation, the monomer solution is loaded using pump A, with pump B being switched off as shown

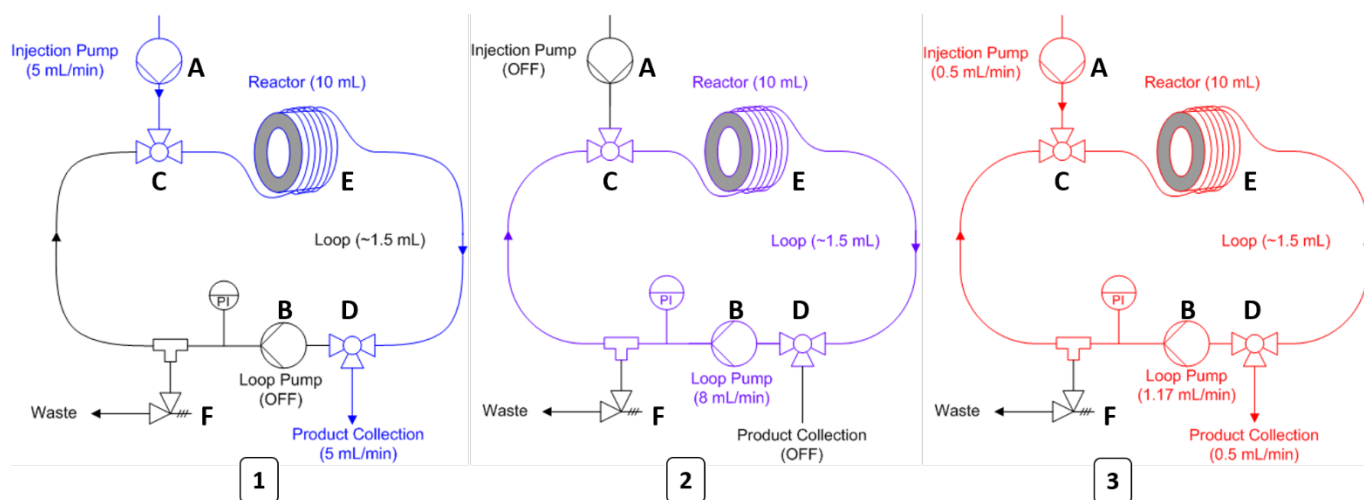


Figure 1. The different stages of the loop process: loading (1), loop circulation (2), injection of the following monomer (3).

on Fig. 1-1. Upon closure of the valves C and D, pump A and the waste collection section are isolated from the loop so the reaction mixture can then be homogenised by letting the solution circulate through the set-up at a high flow rate using pump B, with pump A turned off (Fig. 1-2). The polymerization will accelerate as it reaches the targeted temperature. When the reaction reaches completion, both valves are opened and the next monomer is introduced as shown on Fig. 1-3, whilst a sample is collected for analysis. The loop is closed after the loading is complete to return to the set-up described by Fig. 1-2 and the chain extension can take place. The last two steps are repeated as many times as targeted number of blocks requires. At the end of the reaction of the final block, both valves are opened and the entire set-up is flushed with solvent to collect the product through valve D. Pump A was cleaned between each chain extension by purging with solvent to remove any residual monomer from the previous block.

The entire set-up was monitored using pressure sensors and a pressure relief valve was introduced as an outlet in case system pressure exceeded safe levels due to an increase in the viscosity of the reaction mixture or to a blockage.

Each polymerization was performed at 70 °C in order to give a high rate of radical generation with VA-044, allowing the polymerization time for each block to be reduced to 2 h (\approx 95 % VA-044 consumed under these conditions). A triblock copolymer with a degree of polymerization (DP) of 20 for each block and two hexablock copolymers with blocks of DP 10 each were synthesized using two different processes. The reaction conditions were firstly optimized for the loop set-up, then adapted for a batch process.

Limitations in flow reactions are mainly associated with potential blockages in the coil due to precipitation of the polymer or as a result of excessive viscosity of the reaction

mixture, leading to a pressure build-up. Because polyacrylamides generally have a high glass transition temperature, characterized by a rapid increase in viscosity during polymerization, the solvent system chosen as well as the concentration and the temperature of the reaction mixture, is of particular importance in order to maintain a relatively low viscosity. The reaction conditions were thus optimised in the loop set-up in order to achieve high polymer concentrations whilst avoiding a blockage.

The loop set-up was optimized after several runs. The back pressure regulator (referred to as F in Figure 1) played a major role in maintaining a pressure difference between the inlet and the outlet of pump B when the set-up functioned as a loop (step described in Fig. 1-2). Pump B requires a back pressure in order to operate and circulate the polymer solution through the system whilst the new monomer solution is added when the viscosity is relatively low. Nevertheless, as the polymerization(s) proceed, the viscosity of the solution increases and eventually the pressure applied by the back pressure regulator becomes too high for pump B to operate. When the viscosity of the solution reaches this point, typically observed from the third chain extension, the regulator is removed since the pressure of the solution is high enough for pump B to function without it.

The loading of the monomer solution for each block was of particular interest as it could affect the control on the chain extension. Indeed, the final molecular weight distribution is closely related to the homogeneity of the content in the loop. For this reason, the monomer stock solution was loaded at a flow rate of 0.5 mL min⁻¹ whilst simultaneously circulating the previous block at 1.15 mL min⁻¹. Indeed, the monomer solution would not have mixed with the solution of macroCTA if the

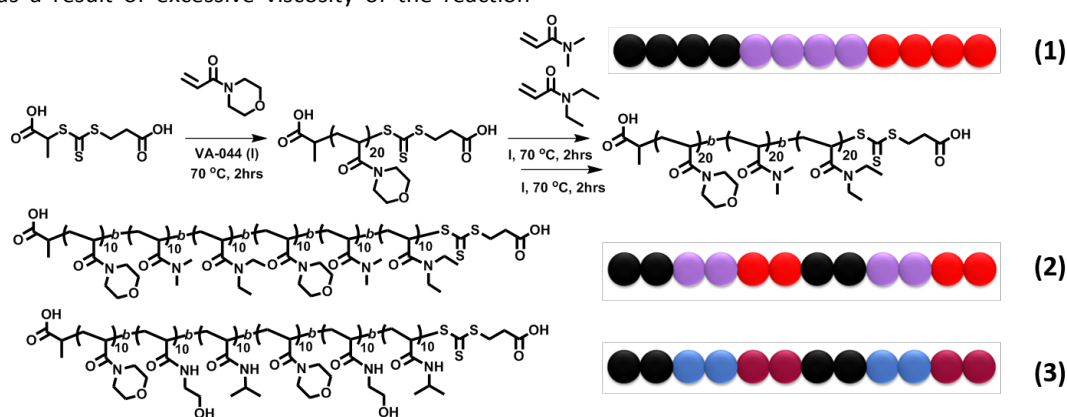


Figure 2 Scheme for the one-pot sequential-addition polymerization of pNAM₂₀-*b*-pDMAM₂₀-*b*-pDEAM₂₀ (1), pNAM₁₀-*b*-pDMAM₁₀-*b*-pDEAM₁₀-*b*-pNAM₁₀-*b*-pDMAM₁₀-*b*-pDEAM₁₀ (2), pNAM₁₀-*b*-pHEAM₁₀-*b*-NIPAM₁₀-*b*-pNAM₁₀-*b*-pHEAM₁₀-*b*-pNIPAM₁₀ (3), see Table 1, S1 and S2 for experimental conditions.

latter had not been circulated during the injection of the monomer solution. The circulation within the loop after injection would have allowed the two solutions to mix eventually but free radical polymerization of the monomer

could have occurred prior to any mixing. Potential free radical polymerization of the additional monomer can also be limited by maintaining the temperature of the reactor coil at room temperature until the homogeneity of the mixture was

ensured by circulation of the polymer solution for 5 minutes after monomer injection.

Firstly, an ABC triblock copolymer was synthesized in the looped reactor, composed of pNAM₂₀-*b*-pDMAM₂₀-*b*-pDEAm₂₀ (Fig. 2-1). According to the ¹H NMR analysis (Fig. S1-1), near-quantitative monomer conversion (>98 %) was achieved for each block while SEC shows a clear shift towards higher molecular weight (maintaining narrow molecular weight distributions) with each successful extensions (Fig. S2-1). However, the viscosity of the solution became too high after the third block and further chain extensions could not be carried out in the tubular reactor. Therefore, shorter blocks were synthesized to attempt additional chain extensions. Subsequently, we chose to target a lower DP for each block (DP of 10) in order to conduct a higher number of chain extensions. By targeting blocks of DP 10 each, a hexablock (ABCABC) of pNAM₁₀-*b*-pDMAM₁₀-*b*-pDEAm₁₀-*b*-pNAM₁₀-*b*-pDMAM₁₀-*b*-pDEAm₁₀ (Fig. 2-2) was successfully obtained (Fig. 3-1). Again, full conversion was obtained for each block (> 98 %) as determined by ¹H NMR (Fig. S3-1). This synthesis was completed in 12 hours, spread over 2 days, by producing 3 blocks per day. The polymer solution was left at room temperature in the loop overnight without having the pump operating. Another hexablock (ABCABC) was synthesized using different monomers pNAM₁₀-*b*-pHEAm₁₀-*b*-NIPAm₁₀-*b*-pNAM₁₀-*b*-pHEAm₁₀-*b*-pNIPAm₁₀ (Fig. 2-3). The process was completed over 12 hours as well, within 3 days with the synthesis of 2 blocks a day. Near-quantitative conversion was obtained with each polymerization (with the exception of block 3, 94 % by ¹H NMR, Fig. S4-1). However, this may be considered acceptable given the low DP targeted. Chain

extensions could be carried out after leaving the macroCTA solution in the loop overnight in both cases, demonstrating the robustness and the impermeability to air of the set-up, hence the potential to conduct multiblock copolymers synthesis over the course of several days if required.

Similarly, the triblock and both hexablock copolymers were synthesized in batch in order to compare the polymers obtained those from the loop system. The monomer concentration could be increased as compared to equivalent reaction in flow since the viscosity does not affect the process as strongly. High conversions were achieved as evidenced by ¹H NMR (Fig. S1-2, S3-2 and S4-2), SEC shows clear shift to high molecular weight (Fig. 3-2, S2-2 and S5-2).

The main difference between the loop and the batch processes was the scale at which the polymerizations were performed: 1.5 g of the triblock was yielded with the loop set-up, compared to 0.4 g obtained in batch. Similarly, the two hexablocks were obtained at a scale of over 3 grams using flow and under a gram with batch. Interestingly, the scale-up of the synthesis of multiblock copolymers in the loop set-up did not affect the dispersity of the polymers. Indeed, according to the SEC chromatograms (Fig. 3, S1 and S2), the molecular weight distribution of the three multiblock copolymers had a low dispersity for both processes ($\mathcal{D} \leq 1.12$ with flow and $\mathcal{D} \leq 1.18$ with batch, Table 1, S1 and S2). A high molecular weight shoulder was observed on the polymers obtained with the tubular reactor, as well as the hexablock with NAM, DMAM and DEAm in batch. This could be attributed to side reactions such as chain transfer or termination by combination.

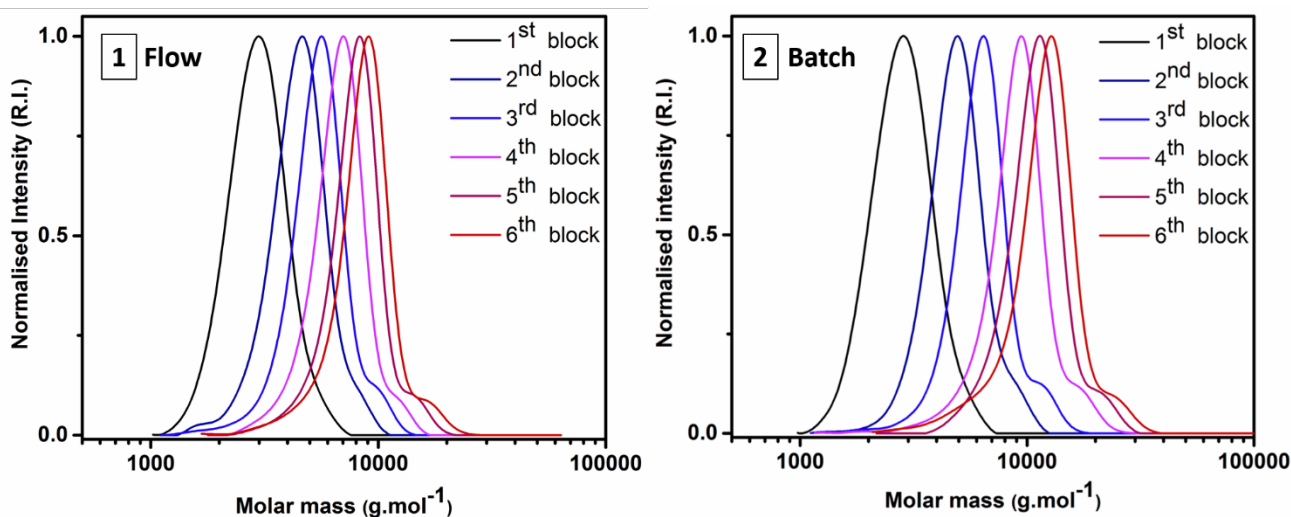


Figure 3 DMF-SEC chromatograms for successive chain extensions of pNAM₁₀-*b*-pDMAM₁₀-*b*-pDEAm₁₀-*b*-pNAM₁₀-*b*-pDMAM₁₀-*b*-pDEAm₁₀ in batch (1) and in loop (2), see Table 1 for experimental conditions.

Although the dispersities of the polymers obtained with both systems are similar, the average molecular weight is lower for those which were synthesized in the loop set-up according to the SEC data (Table 1, S1 and S2). By improving the precision

of the flow rate at which the monomers are introduced, the accuracy of the targeted DP could be further optimized.

As the concentrations used in the flow process were optimized to be relatively high, a high livingness of the polymer chains could be maintained with both processes, which is key for the

synthesis of well-defined multiblock copolymers (see Table S3 for polymer concentration).

Using a tubular reactor helped maintaining good control over the temperature of the reaction mixture when scaling-up whereas the temperature profile cannot be controlled as precisely at large scale using round bottom flasks.⁹ The scale can be further increased by choosing a reactor coil with a larger volume whilst maintaining the characteristics of the final product. In addition, because the heat transfer is optimized with tubular reactors, the heating and cooling of the reaction mixture is more efficient than in batch,⁹ shortening the duration of the overall polymerization process.

Although tubular loop reactors have been explored for free radical polymerization processes, their potential for the synthesis of multiblock copolymers has been overlooked so far. There are several advantages in using a looped system for the scale-up of multiblock copolymers over a continuous flow system. Primarily, there are fewer steps in the process since there is no loading and unloading of the macroCTA from the reactor coil needed between chain extensions. Equipment costs are also kept low since only a single reactor is required instead of several blocks in sequence. Furthermore, the

homogeneity of the reaction mixture was further improved compared to continuous flow polymerizations for which the homogeneity strictly relies on the simultaneous loading of the new monomer solution with the solution containing the previous block. All the chain extensions were successful using the loop set-up, highlighting the difference in homogeneity with previous block copolymer synthesis in tubular reactors.²⁰ In addition, the looped system offers flexibility in polymerization time, in contrast to continuous flow polymerization, which is limited by a finite residence time (dictated by coil volume and flow rate). As the stainless steel tubing is impermeable to air, the reaction mixture can be left overnight without affecting the polymerization, as demonstrated by the successful chain extensions.

Our work demonstrates a facile scale-up of the synthesis of highly defined multiblock copolymers using a looped polymerization process. The process was shown to be flexible, robust and time-efficient whilst maintaining good control over the polymerization as attested by the low dispersity and the high livingness of the obtained polymers.

Process	Block	$[I]_0$ (mol.L ⁻¹)	$[(m)CTA]^{[a]}$ (mol.L ⁻¹)	$[M]_0$ (mol.L ⁻¹)	Monomer conversion ^[b] (%)	$M_{n,th}^{[c]}$ (g.mol ⁻¹)	$M_{n,SEC}^{[d]}$ (g.mol ⁻¹)	$\mathcal{D}^{[d]}$	$L_{th}^{[e]}$ (%)
Flow	1 st	$2.7 \cdot 10^{-3}$	0.27	3.0	99	1700	2800	1.09	99.0
	2 nd	$1.1 \cdot 10^{-3}$	0.23	2.1	98	2700	4200	1.10	98.5
	3 rd	$0.9 \cdot 10^{-3}$	0.17	1.6	99	3900	5200	1.10	98.0
	4 th	$1.0 \cdot 10^{-3}$	0.12	1.1	99	5300	6400	1.09	97.0
	5 th	$1.0 \cdot 10^{-3}$	0.08	0.8	99	6300	7600	1.09	96.0
	6 th	$1.0 \cdot 10^{-3}$	0.07	0.6	99	7570	8100	1.11	94.6
Batch	1 st	$1.9 \cdot 10^{-3}$	0.30	2.7	98	1700	2700	1.10	99.4
	2 nd	$1.0 \cdot 10^{-3}$	0.21	2.3	> 99	2800	4600	1.10	99.0
	3 rd	$1.0 \cdot 10^{-3}$	0.16	1.7	> 99	3900	6000	1.11	98.3
	4 th	$1.0 \cdot 10^{-3}$	0.11	1.2	99	5400	8500	1.12	97.5
	5 th	$1.0 \cdot 10^{-3}$	0.08	0.8	98	6500	10400	1.10	96.4
	6 th	$1.0 \cdot 10^{-3}$	0.06	0.7	99	7600	11000	1.15	94.8

[a] Concentration of CTA for the first block and macroCTA for the following blocks [b] Determined by ¹H NMR and is based on the initial ratio of CTA to monomer as detailed in the experimental method; [c] Theoretical molecular weight calculated from equation 1 (SI); [d] Determined by SEC/RI in DMF using PMMA as molecular weight standards; [e] Theoretical estimation of the cumulated fraction of living chains calculated using Equation 2.

Table 1 Experimental conditions and characterisation data for the synthesis of the hexablock pNAM₁₀-b-pDMA₁₀-b-pDEAm₁₀-b-pNAM₁₀-b-pDMA₁₀-b-pDEAm₁₀ in loop and batch.

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