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Synthesis of Ultra-High Molecular Weight ABA Triblock Copolymers via Aqueous RAFT-mediated Gel Polymerisation, End Group Modifications and Chain Coupling

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The synthesis of ultra-high molecular weight (UHMW) polymers using reversible deactivation radical polymerisation techniques remains a challenge and has only been the centre of attention in a limited number of studies. Although UHMW was achieved in these researches, the complexity in architecture has mainly been focused on linear homopolymers and AB diblock copolymers. We hereby report a new pathway to synthesise UHMW ABA triblock copolymers using a combination of reversible addition-fragmentation chain transfer (RAFT) polymerisation, end group modification by aminolysis and chain coupling. A simple aqueous RAFT-mediated gel polymerisation technique was initially employed to synthesise high molecular weight AB diblock copolymers with low dispersities ($D < 1.50$). The use of said gel polymerisation method in combination with a redox initiation system allowed for the rapid chain propagation of water soluble monomers under a low reaction temperature of 20°C. These polymers were subsequently treated by aminolysis to convert the chain end into thiol functionality, which spontaneously coupled under oxidative condition to form disulfide bridge between the AB diblock copolymers to produce the final UHMW ABA triblock copolymers ($M_{n,SEC} > 1,000 \text{ kg mol}^{-1}$; $D < 1.70$).

Introduction

Reversible deactivation radical polymerization (RDRP) has gained tremendous interest from the polymer research community as it can produce polymers with precise molecular weight, diverse architectures and narrow dispersity. However, the design and synthesis of ultra-high molecular weight (UHMW) polymers ($M_n > 500 \text{ kg mol}^{-1}$) using RDRP techniques remain a challenge and have only been reported in a few isolated studies.¹⁻³ UHMW polymers are extensively used in many industrial applications, including but not limited to oil recovery, hydraulic fracturing, mining and minerals processing, paper production, wastewater treatment and biotechnology.^{1,4}

Well-defined UHMW polymers have previously been synthesised by atom transfer radical polymerisation (ATRP),⁵⁻¹¹ single-electron transfer living radical polymerisation (SET-LRP),¹²⁻¹⁴ and reversible addition-fragmentation chain transfer (RAFT)^{1-3,11,15-17} polymerisation. However, the methodologies employed to synthesise these polymers often required the use of environmentally unfriendly organic solvents, metal catalysts or high reaction pressures. For instance, pressures of up to 9 kbar were used by both Arita *et al.*⁸ and Rzyayev *et al.*¹⁵ to

synthesise well-controlled poly(methyl methacrylate) with M_n up to 3,600 kg mol^{-1} . Mueller *et al.*⁹ was able to synthesise polystyrene with M_n of 1,030 kg mol^{-1} under a pressure of 6 kbar. Well-defined polyacrylonitrile with M_n of 1,030 kg mol^{-1} was synthesised by Huang *et al.*¹⁰ within just 2 hours under a pressure of 5 kbar. Some recent studies however reported the synthesis of well-defined UHMW acrylamido-based polymers via fast and simple aqueous RAFT polymerisations without the need for high pressure nor metal catalyst.¹⁻³ Read *et al.*¹ were able to produce acrylamido-based polymers with molecular weights of 1,000 kg mol^{-1} by utilising gel polymerisation conditions and redox initiation pair ammonium persulfate (APS) and sodium formaldehyde sulfoxylate (SFS). Gel polymerisation is a type of homogeneous aqueous polymerisation process that utilises high monomer concentration in combination with an optimised initiation profile that would favour fast reaction kinetics at low temperatures. At this high monomer concentration, the reaction mixture rapidly typically forms a non-covalent gel throughout the polymerisation, and hence the name.^{1,18} Another study conducted by Carmean *et al.*² pushed the limit further by utilising photopolymerisation to produce poly(dimethylacrylamide) with a molecular weight of 8,570 kg mol^{-1} , which is the highest value reported to-date.

Although UHMWs were attained in these studies, the complexity in architecture has primarily been homopolymers, statistical copolymers, and AB diblock copolymers. Read *et al.*¹ reported the synthesis of an AB diblock copolymer ($M_n = 1,020 \text{ kg mol}^{-1}$) where the A and B blocks were derived from *N*-isopropylacrylamide (NIPAM) and dimethylacrylamide (DMA), respectively. Carmean *et al.*² were able to produce another AB

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diblock copolymer with higher molecular weight ($M_n = 2,670 \text{ kg mol}^{-1}$), where both blocks were derived from DMA. To the best of our knowledge, only one recent study conducted by Despax *et al.*³ has reported the synthesis of ABA triblock copolymers polymerised from DMA and NIPAM but the molecular weight of the polymers was only up to 500 kg mol^{-1} . Therefore, the ability to develop different polymers with advanced architectures and higher molecular weight ($M_n > 1,000 \text{ kg mol}^{-1}$) could potentially give rise to a whole new class of materials with unique properties.² This next stage of development in well-controlled UHMW polymers could be achieved by exploiting the end group removal and modification process of RAFT polymers.

The conversion of a thiocarbonylthio group into a thiol in the presence of nucleophiles or ionic reducing agents is one of the most widely reported techniques of end group modification for RAFT polymers.¹⁹ Thiol-terminated polymers can subsequently undergo spontaneous disulfide coupling under oxidative environment.²⁰ Primary or secondary amines are most commonly used for this, in a process referred to as aminolysis.²¹ The formation of disulfide linkages by chain coupling could be exploited to design and synthesise UHMW polymers with complex architectures such as ABA triblock, star-shaped and hyperbranched structures. Disulfide linkages also have high resistance towards moisture, ozone, weathering, as well as oil and organic solvents.²² In addition, the disulfide linkages formed can be cleaved in the presence of reducing agents such as zinc dust and acetic acid, or tris(2-carboxyethyl)phosphine.¹⁹ The high tolerance in harsh conditions as well as cleavable feature of these disulfide linkages could provide to be advantageous in a multitude of industrial applications.

In this work, we have synthesised a series of UHMW water-soluble ABA triblock copolymers where the A and B blocks were derived from acrylic acid (AA) and acrylamide (AM), respectively. Copolymers based on AA and AM have many uses in industries that are also in alignment to those that employ UHMW polymers. Some examples include agriculture, wastewater treatment, mining, oil drilling, cosmetics, personal care, paints and detergents.²³ In addition, the electrolytic nature of AA in well-defined block copolymers can be tuned at different pH and ionic strength to allow for desirable amphiphilic properties.²⁴ We employed a water-soluble monofunctional trithiocarbonate chain transfer agent (CTA), 3-(((1-carboxyethyl)thio)carbonothioyl)thio)propanoic acid (CETCTP), in combination with gel polymerisation conditions and an ammonium persulfate and sodium formaldehyde sulfoxylate redox initiating system (APS/SFS) to synthesise the initial AB diblock copolymers. Poor blocking efficiency was observed when RAFT polymerisation was initially used to incorporate the third A block into the polymer chain. Therefore, this problem was addressed with a simple aminolysis and chain end coupling stage using *n*-butylamine, where the AB diblock copolymers were converted into the desired UHMW ABA triblock copolymers with molecular weight above $1,000 \text{ kg mol}^{-1}$. These ABA triblock copolymers are the first of their kinds with such high molecular weights and low dispersities.

Experimental Section

Materials

Acrylic acid (AA, Aldrich, 99%) was pre-treated with basic aluminium oxide (Acros Organics) to remove the radical inhibitor monomethyl ether hydroquinone prior to use. Acrylamide (AM, Sigma, 99%), 3-(((1-carboxyethyl)thio)carbonothioyl)thio)propanoic acid (CETCTP, Boron Molecular, 90%), ammonium persulfate (APS, Sigma-Aldrich, 98%), sodium formaldehyde sulfoxylate dihydrate (SFS, Aldrich, 98%), *n*-butylamine (Sigma-Aldrich, 99.5%), sodium hydroxide (Merck, 99%), sodium nitrate (Merck, 99.9%), sodium bicarbonate (Merck, 99.9%), *N,N*-dimethylformamide (DMF, Ajax FineChem, 99.9%), water (deionised and Milli-Q grades), deuterium oxide (Merck, 99.9%) were used as received without further purification.

General procedure for the RAFT polymerisation of AA or AM

In a typical RAFT polymerisation experiment, an 8M aqueous solution of AA or AM, the required amount of the CTA and water was initially charged in an ampule (refer to the ESI). DMF (0.3 mL) was also added into the reaction mixture as an internal standard. The polymerisation mixture was then deoxygenated by argon bubbling for 30 minutes, and maintained at 20°C using a thermostated water bath. Stock solutions of APS and SFS were prepared accordingly and deoxygenated in the same manner. Once the deoxygenation process was completed, the required amount of APS was carefully injected into the ampule and the reaction was further bubbled with argon for another 5 minutes. This was immediately followed by the injection of SFS in an equimolar amount relative to APS (refer to the ESI), and another 5 minutes of argon bubbling was applied. The reaction was left to proceed under a flow of argon for 24 hours. At this point, the monomer conversion was analysed by ¹H NMR spectroscopy by comparing the disappearance of one of the monomer's vinyl peaks (dd, 1H, 5.80-6.00 ppm) with respect to DMF (s, 1H, 7.95 ppm). The polymer was then purified by dialysis and freeze-dried to give a yellow or white powder. Once dried, the molecular weight and dispersity were measured by size exclusion chromatography (SEC).

General procedure for the aminolysis reactions

In a typical aminolysis experiment, 50 mg of the AB diblock copolymer was dissolved in 10 mL of water. If required, the pH of the solution was adjusted to approximately 8 using 0.1 M sodium hydroxide solutions. The solution was bubbled with oxygen gas for 30 minutes to promote an oxidative environment. This was followed by the injection of the optimal amount of *n*-butylamine (refer to the ESI). The reaction was stirred and maintained at 50°C in a closed system for where the molecular weight and dispersity were directly monitored by SEC throughout 24 hours. For UV-Vis measurements, the aminolysis reactions were repeated until the right reaction time was reached, and the final polymer was separated from the excess *n*-butylamine by dialysis and freeze-dried to give a yellow/white powder.

Field Code Changed

Purification and freeze-drying of the polymer samples

The synthesised polymers were purified using a SnakeSkin regenerated cellulose dialysis tubing with a molecular weight cut-off at 3.5 kg mol⁻¹. Once purified, the polymers were freeze-dried using a Labconco FreeZone Benchtop Freeze Dry system.

Nuclear magnetic resonance (NMR) spectroscopy

¹H NMR spectra were measured and recorded at 400 MHz using a Bruker DRX 400 spectrometer in deuterium oxide (D₂O).

Size exclusion chromatography (SEC)

Molecular weight and dispersity measurements were performed on a Tosoh High Performance EcoSEC HLC-8320GPC System, which comprised of an autosampler, a vacuum degasser, a dual flow pumping unit, a Bryce-type refractive index (RI) detector, a UV detector set at 280 nm, a TSKgel SuperH-RC reference column, and three TSKgel PW_{XL} columns (TSKgel G5000PW_{XL}, TSKgel G6000PW_{XL} and TSKgel MPW_{XL}) connected in series. The analytical columns were calibrated with a series of polyacrylic acid (PAA) standards ranging from 106 g mol⁻¹ to 1,520 kg mol⁻¹. The eluent used was deionised water with 0.1 M NaNO₃ and 0.1 M NaHCO₃ (pH ≈ 8.3) at 40°C and at a flow rate of 1.0 mL/min.

UV-Vis spectroscopy

All UV-Vis measurements were performed on a Shimadzu UV-1800 UV Spectrophotometer.

Determination of monomer conversion

The monomer conversion (C) was calculated from ¹H NMR data using Eqn. 1:

$$\text{Conversion (p)} = \frac{[M]_0 - [M]_t}{[M]_0} = \frac{f M_0 - f M_t}{f M_0} \quad (1)$$

where [M]₀ and [M]_t are the concentrations of the monomer at time 0 and time t, respectively; and $\int M_0$ and $\int M_t$ are the corrected integral (based on DMF) for a vinyl proton (5.70 ppm) of the monomer at time 0 and time t, respectively.

Calculation for the theoretical molecular weight ($M_{n,th}$)

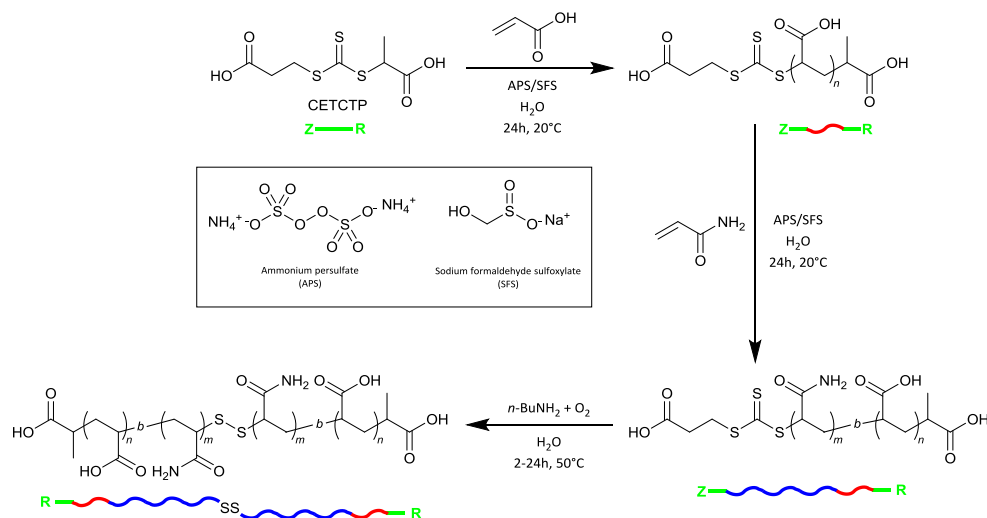
The theoretical number-average molecular weight ($M_{n,th}$) of the polymers were determined using Eqn. (2):

$$M_{n,th} = \frac{[M]_0}{[CTA]_0} \times p \times M_M + M_{CTA} \quad (2)$$

where [M]₀ and [CTA]₀ are the initial concentrations of the monomer and the CTA in mol L⁻¹, respectively; **p is the monomer conversion as determined by Eqn. 1**, and M_M and M_{CTA} are the molecular weights of the monomer and the CTA in g mol⁻¹, respectively.

Results and Discussion**Initial screening experiments for the synthesis of the A block**

The synthesis of the UHMW ABA triblock copolymers was performed in three main steps: initial synthesis of the A block by polymerisation of AA, formation of the B block by chain



Scheme 1 Overall reaction strategy for the synthesis of UHMW ABA triblock copolymers using sequential RAFT-mediated gel polymerisation of AA and AM monomers, and subsequently the end group modification of the thiocarbonylthio functionality via aminolysis. The RAFT polymerisations were performed in water at 20°C with APS and SFS acting as the redox initiation pair. The aminolysis process were also performed in water at 50°C with *n*-butylamine being employed as the nucleophilic reagent.

extension with AM, and lastly the aminolysis of the AB diblock copolymers using nucleophilic *n*-butylamine (Scheme 1). Prior to the synthesis of the A blocks, a series of screening experiments were conducted to determine the polymerisation conditions that would allow for optimal growth in molecular weight whilst also maintaining an adequate control over the dispersity. There are several factors that could affect the outcome of the polymerisation, including but not limited to the type and concentration of the monomer, the type of RAFT agent, the redox initiation system, temperature, pressure, time, ratio between the RAFT agent and the initiators, and ratio between the oxidant and reductant initiators pair.^{25–28} These screening tests have the potential to reveal certain trends in the data, and therefore possibly allow the optimal conditions to be identified.

CETCTP,²⁹ a trithiocarbonate RAFT agent, was selected as the CTA due to its water-solubility and compatibility with AA and AM.^{25–34} High monomer concentrations will favour fast reaction kinetics and optimised initiation in the gel polymerisation process and therefore the initial concentration of the monomers was maintained at approximately 33 wt%.^{1,35,36} This initial screening test involved the polymerisation of AA, targeting a molecular weight of 200 kg mol⁻¹, at two different reaction temperatures (10°C and 20°C) and six different ratios of CETCTP to the redox initiators (ranging from 4:1:1 to 20:1:1, maintaining an equimolar ratio between APS and SFS). The molecular weights and dispersities of the polymers obtained were assessed by SEC after 24 hours of polymerisation, and compared for determination of the optimal reaction temperature and the [CETCTP]:[APS]:[SFS] ratio (Fig. 1).

The data obtained from SEC indicated that polymerisations conducted at a temperature of 20°C resulted in higher molecular weight compared to those at 10°C. Consequently, these molecular weights are closer to the targeted value of 200 kg mol⁻¹. The highest molecular weight was obtained at a [CETCTP]:[APS]:[SFS] ratio of 6:1:1. Low dispersities ($D < 1.20$) were obtained for all polymerisations from this screening test, which indicated good control across the range of the

Fig. 1 SEC data obtained from the screening polymerisations of AA, targeted a molecular weight of 200 kg mol⁻¹, conducted at two reaction temperatures (10°C and 20°C) and six [CETCTP]:[APS]:[SFS] ratios (ranging from 4:1:1 to 20:1:1) for 24 hours. [CETCTP]:[APS]:[SFS] ratios employed. Another trend was observed where the dispersity decreased as the [CETCTP]:[APS]:[SFS] ratio increased. This was attributed to lower flux of radicals and hence better control over the molecular weight distribution of the polymers was observed.³⁷ However, this decrease in the initiators concentration also led to a drop in molecular weight due to slower polymerisation kinetics.^{36,37} Therefore a reaction temperature of 20°C and a [CETCTP]:[APS]:[SFS] ratio of 6:1:1 were chosen as the optimal conditions for the synthesis of the initial A blocks.

Synthesis of the A blocks by polymerisation of AA

Once the optimal conditions for the synthesis of the initial A blocks were established, the polymerisations of AA were performed with eight different target molecular weights (Table 1). Polymers **A1** to **A5** were intended to have molecular weights ranging from 10–50 kg mol⁻¹ with an increment of 10 kg mol⁻¹, while subsequent polymers had a higher increment of 50 kg mol⁻¹ up until a target value of 200 kg mol⁻¹ for polymer **A8**. The purpose of synthesising the A blocks with varying molecular weights was to determine the effect of this on the efficiency of the subsequent chain extension and chain coupling stages.

From the ¹H NMR data, high monomer conversions (74–85%) were obtained for all of the eight reactions listed in Table 1. Lower monomer conversion was achieved for polymers with smaller target molecular weights (polymers **A1** to **A3**). This was attributed to the retardation in reaction kinetics due to elevated concentration of CETCTP.^{25,38} As expected, these conversions were shown to have a direct correlation with the resultant molecular weights. The molecular weight values obtained by SEC for all eight A blocks were in close agreement with the theoretical molecular weights. In addition, the dispersities of these polymers remained below 1.20 which were in agreement with the results obtained in the screening test. Therefore, no further optimisation was required for this step.

The SEC traces of all eight polymers (Fig. 2a) were monomodal, which further proved that the polymerisations were well controlled under the optimal reaction conditions selected. Linear growth in molecular weight was also observed as the reaction progressed. An example of this linear relationship between the molecular weight and the monomer conversion is shown Fig. 2b, for the RAFT polymerisation of AA, targeting a molecular weight of 50 kg mol⁻¹. These polymers were directly purified by dialysis and freeze dried prior to use as the macro-CTA for the next RAFT polymerisation stage.

Optimisation and synthesis of the AB diblock copolymers

The second stage involves the chain extension of the A blocks described in Table 1 with AM to form a series of UHMW AB diblock copolymers. The reaction conditions required for this process were not established yet and thus further screening

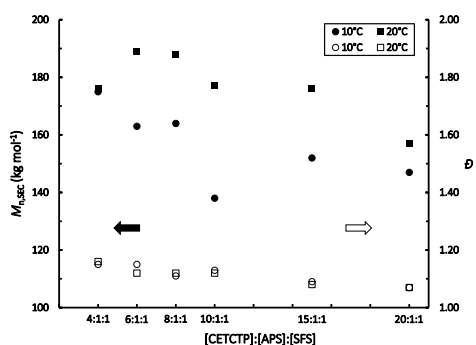


Table 1 Summary of ^1H NMR and SEC data obtained for the synthesis of the initial A blocks polymerised from AA.

Entry	$\text{DP}_{\text{target}}^{\text{a}}$	Monomer conversion (%) ^b	$M_{n,\text{th}}^{\text{c}}$ (kg mol ⁻¹)	$M_{n,\text{SEC}}^{\text{d}}$ (kg mol ⁻¹)	D^{e}
A1	139	74	7.67	5.21	1.18
A2	278	74	15.1	11.8	1.17
A3	416	79	23.9	20.9	1.18
A4	555	84	33.8	33.9	1.17
A5	694	83	41.8	45.7	1.16
A6	1,390	84	84.4	84.8	1.14
A7	2,080	80	120	118	1.15
A8	2,780	85	171	173	1.14

^a Polymerisations were performed with an initial AA concentration of 4.63 mol L⁻¹ and a [CETCP]:[APS]:[SFS] ratio of 6:1:1 at 20°C for 24 hours (refer to ESI). ^b Monomer conversion was determined by ^1H NMR spectroscopy with DMF as an internal standard using Eqn. 1 (refer to Experimental Section). ^c Theoretical molecular weight was calculated using Eqn. 2 (refer to Experimental Section). ^d Molecular weight data was determined using aqueous SEC calibrated with PAA standards (refer to Experimental Section).

reactions were required in order to achieve optimum molecular weight growth and maintain a low dispersity. It was desired to synthesise the final UHMW ABA triblock copolymers with molecular weight of 1,000 kg mol⁻¹. Therefore the main objective of these screening reactions was to determine the optimal conditions to synthesise the AB diblock copolymers with molecular weights higher than 500 kg mol⁻¹, whilst also maintaining low dispersities. In addition, it was hypothesised that each macro-CTA would exhibit different characteristics with regards to chain conformation, steric hindrance and viscosity, which would affect the reaction kinetics. Therefore, performing an array of reaction conditions would prove to be beneficial. Consequently, polymers **A1** to **A8** were subjected to RAFT polymerisations at 20°C for 24 hours with an initial [Macro-CTA]:[APS]:[SFS] ratio of 6:1:1, with the varying factor being the initial monomer to macro-CTA ratio, or targeted degree of polymerisation ($\text{DP}_{\text{target}}$). Three different ratios ranging from 28,100 to 56,300 were initially targeted (Table 5-6 in ESI).

The SEC data for this set of polymerisations showed several trends (refer to the ESI for the comprehensive results obtained by ^1H NMR and SEC). There was a decrease in the molecular

weight of the AB diblock copolymers as higher molecular weight macro-CTA was used. However, a drop in the dispersity of the polymer was also observed. In addition, the overall molecular weight generally increased with a higher $\text{DP}_{\text{target}}$. This increment was at times insignificant even with a two-fold elevation in the $\text{DP}_{\text{target}}$. These results demonstrated that there was a limitation on the degree of chain growth based on the length of the macro-CTA. This was clearly evidenced by the significant drop in monomer conversion with a higher molecular weight macro-CTA. For instance, at a $\text{DP}_{\text{target}}$ of 28,100, the monomer conversion dropped from 77% to 16% when macro-CTA **A1** and **A8** were employed, respectively (Table 5 in ESI). A similar decline was also observed in the other $\text{DP}_{\text{target}}$.

PAA and its derivatives contain several carboxylic acid functionalities that can partially dissociate in water. The conformational change of these polyelectrolytes in solution remains complex and depends on several factors.³⁹ PAA has been shown to exhibit conformational changes based on the pH at high molecular weight ($M_n > 16.5$ kg mol⁻¹).⁴⁰ Below this molecular weight, PAA maintains an extended coil conformation despite changes in the pH. A transformation from

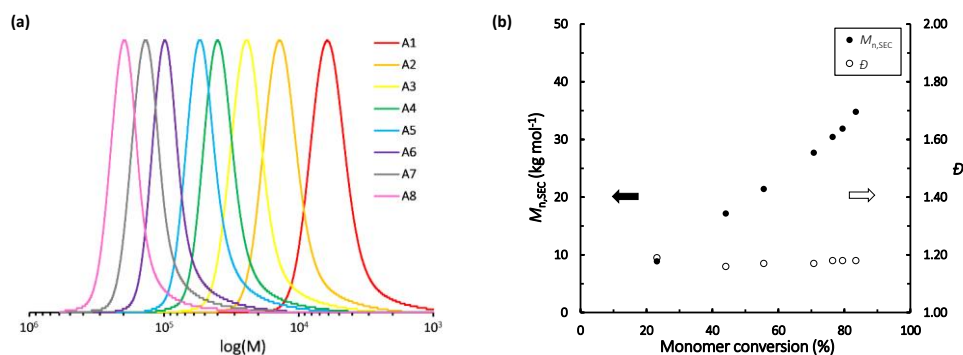


Fig. 2 (a) Overlay of SEC chromatograms for polymers **A1** to **A8** obtained from the polymerisation of AA with target molecular weights ranging from 10 to 200 kg mol⁻¹; (b) example plot showing a linear growth in the measured molecular weight data for the RAFT polymerisation of AA, targeting a molecular weight of 50 kg mol⁻¹.

an extended coil to a condensed globular structure would further cause steric hindrance at the active chain end, particularly for long chain polymers.⁴¹ In addition to this, the hydrophobic or hydrophilic interactions between the carboxyl groups on the PAA chains and other polymer chains can significantly alter the overall conformation.³⁹ For instance, hydrogen bonding between the carboxyl groups on the A block and the amide groups on the B block, as well as AM in solution could significantly reduce the polymer conformation into a globular aggregate. This effect would be more significant with higher molecular weight PAA due to larger quantity of carboxyl groups. Therefore, macro-CTAs of PAA with longer chain length are more susceptible to kinetics retardation. These macro-CTAs also possess higher viscosity with longer chain length. High viscosity also correlates with the reduction in random termination as it is a diffusion-controlled process.⁴² With longer chain length, the drastic drop in segmental and translational diffusion rates result in a reduction in the chain-chain interaction, and hence a deceleration in the termination process.² Consequently, this effect possibly contributed to the drop in the dispersity when higher molecular weight macro-CTAs was used.

Five well-controlled AB diblock copolymers (AB1 to AB5) were initially synthesised from five different macro-CTAs (polymers A1 to A5, respectively) (Table 2). This was achieved under different DP_{target} and the resultant molecular weights of these polymers ranged from approximately 500 to 550 kg mol^{-1} ($\bar{D} < 1.50$). As for the AB diblock copolymers produced from macro-CTAs A6 to A7, the final molecular weights were inadequate for the subsequent aminolysis stage ($M_{n,\text{SEC}} < 500 \text{ kg mol}^{-1}$), even with a high DP_{target} of 56,300 (Table 6 in ESI). From previous screening polymerisation results, there was typically a trade-off between the molecular weight and the dispersity based on the variation in the [CTA]:[APS]:[SFS] ratios. Higher molecular weight was often obtained when lower [CTA]:[APS]:[SFS] ratio (i.e. higher flux of radicals) was used. However, broader molecular weight distribution also coincides with this trend, and vice versa. Consequently, further polymerisations were conducted with polymers A6 to A8 as the macro-CTA. This time, the DP_{target} was increased to 70,300, and the [Macro-

CTA]:[APS]:[SFS] ratio was decreased to approximately 5:1:1. As expected, the combination of higher targeted chain length and higher flux of radicals facilitated the successful synthesis of the AB diblock copolymers AB6 to AB8 (Table 2). The molecular weights of these polymers varied from approximately 582 to 641 kg mol^{-1} and thus were deemed to be satisfactory for aminolysis. The large discrepancies between the theoretical molecular weight and the SEC result could be explained by the calibration method employed for this study. The structural difference between the PAA calibration standards and the AB diblock copolymers would lead to dissimilar hydrodynamic volume in solution, and hence different retention time. In addition, the hydrogen bondings between the carboxyl and the amide groups would reduce the polymer chain into a condensed globular structure, which consequently lower the resultant molecular weight. Although these analytical SEC columns are catered towards the analysis of UHMW polymers, the SEC analysis of polyelectrolytes such as these AB diblock copolymers is difficult due to the complexity in conformational changes. Therefore the numerical values obtained for the molecular weights of these AB diblock copolymers and subsequent ABA triblock copolymers should only be used as a guide to understand the changes in the molecular weight after aminolysis and chain coupling.

Synthesis of the UHMW ABA triblock copolymers

An initial control experiment was performed using only RAFT polymerisation for the second chain extension step from AA to form an UHMW ABA triblock copolymer. The purpose of this reaction was to determine the blocking efficiency of this second chain extension stage, particularly when an UHMW macro-CTA is employed. A similar derivative to polymer AB-1 ($M_n = 626 \text{ kg mol}^{-1}$, $\bar{D} = 1.46$) was used as the macro-CTA for this polymerisation with a DP_{target} of approximately 31,300 and a [Macro-CTA]:[APS]:[SFS] ratio of 6:1:1 (refer to Table 3 in ESI). Poor chain growth was observed where the final monomer conversion and molecular weight were 4% and 566 kg mol^{-1} ($\bar{D} = 1.80$), respectively. The final molecular weight after chain extension was lower due to a broader molecular weight

Table 2 Summary of optimised ^1H NMR and SEC data for the formation of the B blocks by chain extension with AM.

Entry	Macro-CTA	$M_{n,\text{SEC}}$ of Macro-CTA		[Macro-CTA]:[APS]:[SFS] ^a	Monomer conversion ^b (%)	$M_{n,\text{th}}^c$ (kg mol^{-1})	$M_{n,\text{SEC}}^d$ (kg mol^{-1})	\bar{D}^d
		(kg mol^{-1})	DP_{target}^e					
AB1	A1	5.21	28,100	6:1:1	77	1,540	557	1.49
AB2	A2	11.8	42,200	6:1:1	67	2,020	542	1.44
AB3	A3	20.9	42,200	6:1:1	70	2,120	502	1.39
AB4	A4	33.9	56,300	6:1:1	55	2,230	537	1.32
AB5	A5	45.7	56,300	6:1:1	51	2,090	513	1.21
AB6	A6	84.8	70,300	5:1:1	48	2,480	602	1.50
AB7	A7	118	70,300	5:1:1	40	2,120	641	1.36
AB8	A8	173	70,300	5:1:1	27	1,520	582	1.23

^a Polymerisations were performed with an initial AM concentration of 4.69 mol L^{-1} at 20°C for 24 hours (refer to ESI). ^b Monomer conversion was determined by ^1H NMR spectroscopy with DMF as an internal standard using Eqn. 1 (refer to Experimental Section). ^c Theoretical molecular weight was calculated using Eqn. 2 (refer to Experimental Section). ^d Molecular weight data was determined using aqueous SEC calibrated with PAA standards (refer to Experimental Section).

distribution, which indicated poor control over the polymerisation. In addition, a large fraction of monomer remained unreacted and thus the use of only RAFT polymerisation to synthesise UHMW ABA triblock copolymers in this study was considered to be unsatisfactory. To overcome this problem, aminolysis and chain coupling were employed as an alternative.

The final stage involved the aminolysis of the eight AB diblock copolymers by *n*-butylamine. This would allow for the spontaneous coupling of the modified thiol groups under oxidative conditions to form the desired UHMW ABA triblock copolymers. Polymer **AB1** was initially subjected to several aminolysis reactions to determine the most optimal conditions required. Factors such as the quantity and structure of the nucleophilic reagent, solvent nature, temperature, and concentration of the initial polymer have significant influences on the reaction rates.⁴³ *N*-butylamine was chosen as the aminolysis reagent due to its miscibility with water. Two initial AB diblock copolymer concentrations were employed, 0.5 and 1.0 wt%. Previous aminolysis reactions typically employ a 5–20 fold molar excess of *n*-butylamine to thiocarbonylthio end groups.^{44–48} However, initial trials indicated that these ratios were insufficient, where the molecular weight remained the same after aminolysis. This was possibly attributed to the long polymer chain of the AB diblock copolymers restricting the nucleophilic attack particularly with minimal presence of *n*-butylamine. Therefore, three different excess ratios ranging from 2,000 to 200,000 fold of *n*-butylamine were employed. These reactions were monitored using SEC for 24 hours and compared against one another (refer to the ESI for the detailed plots showing molecular weight growth of polymer **AB1** under different aminolysis conditions).

The SEC data showed a distinctive growth in the molecular weight when comparing different excess ratios of *n*-butylamine. Higher ratio corresponded to larger growth in molecular weight and vice versa. However, the dispersity of these polymers also increased as the reaction progressed. As for the two different initial AB diblock copolymer concentrations used, greater growth in molecular weight was obtained for the lower concentration. Therefore the most optimal ratio of *n*-butylamine to thiocarbonylthio functionality was determined to

be 20,000 with an initial polymer concentration of 0.5 wt%. After 6 hours of aminolysis, the molecular weight of polymer **AB1** increased from 557 to 1,050 kg mol^{-1} (polymer **ABA1**), with a corresponding dispersity increase from 1.49 to 1.67 (**Error! Reference source not found.**). The same condition was applied to polymers **AB2** to **AB8** (refer to ESI for the SEC data). As expected, the molecular weights and dispersities of all seven AB diblock copolymers increased as the reactions progressed. However, the growth in molecular weights was generally observed to be smaller for polymers with longer A block, and vice versa. For instance, the molecular weight of polymer **AB8** increased to only 662 kg mol^{-1} after 6 hours, which was significantly less than the growth observed in polymer **AB1**. From this set of reactions, two more satisfactory ABA triblock copolymers (**ABA2** and **ABA3**) were obtained at reaction times of 8 and 12 hours, respectively (**Error! Reference source not found.**). *N*-butylamine is a weak organic base which would interact with the carboxylic acid functionalities on the polymer chain of the AB diblock copolymers. This consequently could reduce the desired interaction between *n*-butylamine and the thiocarbonylthio group, resulted in lower molecular weight growth as observed with longer A block.

To counteract this problem, the aminolysis procedures with a 20,000-fold excess of *n*-butylamine were reattempted at the same reaction conditions, with a higher pH (approximately 8.0) compared to their unadjusted original pH of 4.0–4.5. The interaction between primary and secondary amines with thiocarbonylthio groups is significantly dependent on the solution pH. The rate of aminolysis should increase with an increase in the pH.⁴⁹ Consequently, the quantity of *n*-butylamine required for the aminolysis of the AB diblock copolymers could possibly be reduced with an addition of a base, such as sodium hydroxide. However, the SEC data obtained for the aminolysis at pH 8 indicated otherwise. The molecular weight growth for all eight AB diblock copolymers were relatively lower compared to when the reactions were performed at lower pH (Table 8 in ESI). In addition, as the reaction progressed, the dispersity of these polymers increased at larger increments at higher pH, which led to a drop in the M_n from the initial increase by the 24 hours mark. The molecular

Table 3 Summary of the aminolysis conditions employed in the synthesis of the final UHMW ABA triblock copolymers.

Entry	AB Diblock Copolymer	$M_{n,SEC}$ of AB Diblock Copolymer (kg mol ⁻¹) ^a	[BuNH ₂]:[C=S] ^a	[BuNH ₂]:[COOH] ^b	Reaction time (h)	$M_{n,SEC}$ (kg mol ⁻¹) ^c	\bar{D}^c
ABA1	AB1	557	20,000:1	278:1	6	1,050	1.67
ABA2	AB2	542	20,000:1	122:1	8	1,010	1.68
ABA3	AB3	502	20,000:1	69:1	12	1,000	1.67
ABA4	AB4	537	131,000:1	278:1	6	1,050	1.59
ABA5	AB5	513	176,000:1	278:1	24	967	1.53
ABA6	AB6	602	654,000:1	556:1	2	1,170	1.59
ABA7	AB7	641	911,000:1	556:1	4	1,210	1.49
ABA8	AB8	582	1,330,000:1	556:1	24	1,000	1.46

^a Molar excess ratio of *n*-butylamine to thiocarbonylthio groups. ^b Molar excess ratio of *n*-butylamine to the carboxylic acid functionalities on polymer chain of the AB diblock copolymers. ^c Molecular weight data was determined using aqueous SEC calibrated with PAA standards (refer to Experimental Section).

weights of these polymers did not reach a target value of 1,000 kg mol⁻¹ at any stage during the reaction. The hydrolytic stability of thiocarbonylthio groups is compromised at high pH due to the large energy difference between the C=O and the C=S functionalities (180 kJ mol⁻¹).^{49,50} This would lead to the loss of the active terminal group and thus inhibiting both the aminolysis and chain coupling processes. Partial hydrolysis of the thiocarbonylthio functionality on the polymer chains was suspected to be the reason for the slow molecular weight growth and the increase in dispersity. Although the rate of aminolysis was elevated with higher pH, this was negated with a corresponding increase in hydrolysis rate, which was also exacerbated at a high reaction temperature of 50°C. Therefore the increase in the solution pH to decrease the amount of *n*-butylamine was unsuitable.

The next solution was to increase the amount of *n*-butylamine such that the ratio between amine and carboxyl groups is 278:1 (Table 9 in ESI). This value corresponds to the base to acid ratio employed in the aminolysis of polymer **AB1**. At this ratio, polymers **AB4** and **AB5** were successfully converted to polymers **ABA4** and **ABA5** after 6 and 24 hours, respectively (**Error! Reference source not found.**). This ratio was then doubled to 556:1 for the remaining three AB diblock copolymers to allow for faster and larger growth in molecular weight (Table 10 in ESI). Consequently, polymers **ABA6** to **ABA8** were successfully produced after 2, 4 and 24 hours of aminolysis, respectively (**Error! Reference source not found.**). The steady increase in the dispersity of all eight AB diblock copolymers as the reaction progressed could be explained by the presence of unreacted polymer chains, leading to a broader distribution as the molecular weight increased over time. In addition to this, the presence of pre-existing dead polymer chains and inactive AB diblock copolymers due to hydrolysis could also contribute to this broadening effect. However, the fraction of these polymer chains is considered to be insignificant compared to the fraction of ABA triblock copolymers produced in this step. This was

evaluated by the molecular weight distribution obtained by SEC, as well as UV-vis measurements.

An example overlay of the SEC traces for polymers **A1**, **AB1** and **ABA1** is shown in Fig. 3a showing distinctive changes in the molecular weight throughout the three main reaction stages (refer to the ESI for the SEC chromatograms of the remaining polymers reported in this study). UV-Vis measurements were also performed on the polymer samples before and after the aminolysis process. Fig. 3b shows a typical UV-vis spectrum of the AB diblock copolymer and the corresponding ABA triblock copolymer. In this example, polymer **AB1** has a strong absorbance at approximately 300–310 nm which is attributed to the presence of the thiocarbonylthio group.²¹ After the aminolysis process, the reduction of this peak was observed for polymer **ABA1**. Similar UV-Vis measurements were obtained for the remaining AB diblock and ABA triblock copolymers.

Conclusions

The synthesis of eight different UHMW ABA triblock copolymers were performed successfully in three separate reaction stages. The first stage involved the RAFT-mediated gel polymerisation of AA to form eight different A blocks with $M_{n,SEC}$ ranging from 5.21 to 173 kg mol⁻¹ ($D < 1.20$). These polymers were subsequently used as the macro-CTA for the second stage which involved the formation of the B blocks by chain extension from AM. The molecular weight of the macro-CTA had a significant impact on the growth of the B block. Under the same reaction condition, less efficient chain extension of the B block was observed for macro-CTAs with higher molecular weight. Therefore, combinations of different DP_{target} and [Macro-CTA]:[APS]:[SFS] ratios were employed for different macro-CTA to promote better chain extension efficiency. Consequently, eight AB diblock copolymers were synthesised with satisfactory molecular weight ($M_{n,SEC} > 500$ kg mol⁻¹) whilst dispersities

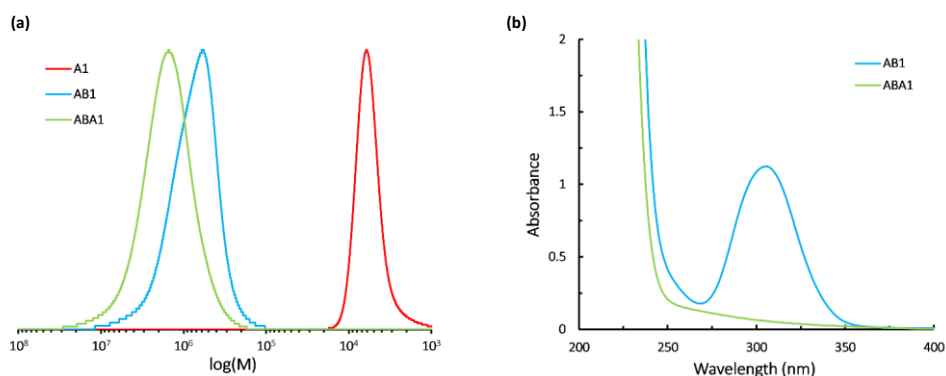


Fig. 3 (a) An example overlay of SEC chromatograms showing changes in molecular weight for polymers **A1**, **AB1** and **ABA1**; (b) typical UV-Vis spectrum showing the changes in the absorbance of the thiocarbonylthio peak before and after the aminolysis process.

remained relatively low ($D < 1.50$). The final stage involved the aminolysis of the AB diblock copolymers. This process converted the terminal thiocarbonylthio groups into thiols, which spontaneously coupled to form the UHMW ABA triblock copolymers. This coupling process was more challenging with respect to the size of the A block. Polymers with longer A block had slower molecular weight growth and this was attributed to the unfavourable interaction between *n*-butylamine and the carboxylic acid functionalities. Consequently, different optimal concentrations of *n*-butylamine was utilised to successfully synthesise the desired UHMW ABA triblock polymers, with $M_{n,sec}$ ranging from 967 to 1,210 $kg\ mol^{-1}$ ($D < 1.70$).

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