Reversible-addition fragmentation chain transfer (RAFT) mediated depolymerization of brush polymers

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Brush polymers synthesized by reversible-addition fragmentation chain transfer (RAFT) polymerization underwent depolymerization when heated in the absence of initiator. The depolymerizations followed pseudo first order kinetics and reached significant monomer concentrations (ca. 30 mM). RAFT polymerizations confirmed that depolymerizations reached thermodynamic equilibrium and the thermodynamic parameters of polymerization were independent of macromonomer molecular weight. Depolymerized polymers still had active terminal RAFT agents that could reinitiate polymerization, confirming that depolymerization was a thermodynamically driven and mediated by the RAFT agent.

Introduction

Synthesis of dense brush or bottlebrush block polymers is of significant interest in materials science as these materials can enable technologies such as photonic crystals,[1,2] drug delivery,[3,4] and complex nanoscale composites.[5,6,7] Polymerization techniques that give significant control over these polymerizations, enabling complex copolymer structures and end-group functionality, are required.[8] Ring-opening metathesis polymerization (ROMP) of high ring strain macromonomers (e.g. norbornenes) can produce brush polymers quickly,[9] yield narrow dispersity (Đ), straightforwardly enable brush block polymers,[10] is functional group tolerant,[11,12] and is seen by many as a preferred method to synthesize these polymers with high molecular weight macromonomers in a "grafting-through" approach. Controlled radical polymerizations such as atom transfer radical polymerization (ATRP) and reversible-addition fragmentation chain transfer (RAFT) polymerizations have been described to lack sufficient reactivity to polymerize such macromonomers reliably.[13] Nevertheless, brush polymers are routinely synthesized by the "grafting through" methodology using polymerization methods such as RAFT and are often targeted due to the wide variety of macromonomers commercially available, functional group tolerance, and possible post-polymerization modifications.[14] Understanding the kinetics and thermodynamics of the RAFT polymerization of these macromonomers is of the upmost importance to yield the desired molecular structure in a controlled fashion.

Of the possible radical polymerizable macromonomer functionalities, the methacrylate group is commonly used due to its ease of a "grafting through" synthesis, commercial availability, and reactivity. For example, commercially available oligo-ethylene glycol methacrylates (OEGMAs) are well-studied macromonomers that are often used as a water soluble component for RAFT polymers[15,16] and as a result much is known about their polymerization behaviour under various conditions.[17,18] Another commercially available macromonomer is methacrylate-terminated oligo-dimethylsiloxane (ODMSMA), which has been used for anti-biofouling coatings[19,20] and graft copolymers.[21] As compared to OEGMA, less is known about ODMSMA's polymerization under various conditions, necessitating understanding how these conditions affect the polymerization control and ultimate coating applications as graft or brush copolymers.

To this end, we synthesized poly(ODMSMA) (PODMSMA) using RAFT polymerization under various conditions and aimed to explore how it could be incorporated into amphiphilic block copolymers as anti-biofouling coatings. When trying to create block polymers, we discovered that when dilute solutions of PODMSMA were heated, ODMSMA monomer was produced. The initial hypothesis was that by purifying the original polymer and reinitiating the RAFT polymerization process, the ODMSMA7 depolymerized to reach its equilibrium monomer concentration ($[M]_{eq}$) under the dilute polymerization conditions. To test this hypothesis and understand the origin of the observed depolymerization phenomenon, RAFT depolymerizations and polymerizations of methacrylate terminated macromonomers were studied. Furthermore, we determined the entropy and enthalpy of these polymerizations to understand the driving force for the significant observed unpolymerized macromonomer present. We also demonstrated that this depolymerization phenomenon is enabled by the RAFT chain transfer agent (CTA) chain end, indicating that this observed depolymerization could have significant effects on other RAFT polymerizations.

Results and Discussion

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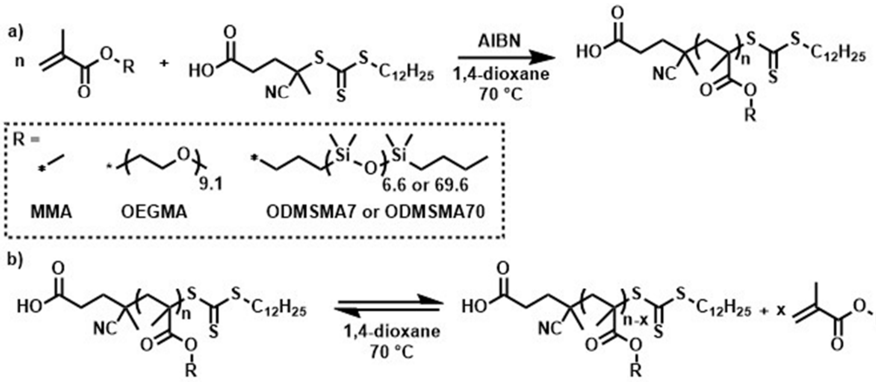

Scheme 1: A) RAFT polymerization method for methacrylate macromonomers. Polymerizations were typically run at 25:1:0.2 ratio of monomer to CTA to AIBN at 70 °C to about 80 – 90% monomer conversion. B) Polymerization and depolymerization equilibrium due to heating at 70 °C.

The pilot study involved synthesizing block copolymers of ODMSMA and a methacrylate functionalized fluorescein (FMA, see ESI Scheme S1) monomer to create a fluorescent polymer, enabling study of brush polymer coating stability on surfaces using fluorescence imaging. ODMSMA with 6.6 repeat units (RUs) was polymerized by the RAFT polymerization process shown in Scheme 1a to yield PODMSMA7. The PODMSMA7 was purified by precipitation to remove the macromonomer and then polymerization of FMA was initiated with PODMSMA7 acting as a macroCTA for the block polymerization (see ESI). Analysis of the crude reaction mixture by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy indicated that FMA did not appreciably polymerize, but even more interestingly, the concentration of ODMSMA7 increased (Figure S1) as compared to the purified polymer. This repeatable result suggested that ODMSMA7 monomer was being produced from the polymer through a depolymerization that yielded individual ODMSMA7 monomers.

Controlled depolymerizations of PODMSMA7 and poly(oligo-ethylene glycol methacrylate) (POEGMA) were conducted to study the kinetics of the depolymerization phenomenon observed. These two polymers were selected to give two polymers with disparate polarities. To enable this study, PODMSMA7 was synthesized by RAFT polymerization using an ODMSMA macromonomer with 6.6 RU of dimethylsiloxane (confirmed by ^{1}H NMR spectroscopy, Figure S2) and the RAFT CTA 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTP) (Figure S3), which was synthesized following a previously reported method.[22] Using 2,2′-azobis(2-methylpropionitrile) (AIBN) as the initiator (25:1:0.2 ODMSMA7:CDTP:AIBN) at 70 °C in 1,4-dioxane, yielded PODMSMA7 with 22 RU of the macromonomer (see ESI, Figure S4 and S5). Additionally, the molar ratio of monomer to initiator could be varied to create ODMSMA7 polymers with 48 and 89 RUs (see ESI Figure S5). Using the same CTA, initiator, and ratios, OEGMA macromonomer with 9.1 RU of ethylene glycol (confirmed by ^{1}H NMR spectroscopy, Figure S6) was polymerized to yield POEGMA with 21 RU of the macromonomer (see ESI, Figure S7 and S8). These polymers were then used to study depolymerization behaviour.

The depolymerization rate and equilibrium were explored by controlled depolymerization reactions using the shortest ODMSMA7 and OEGMA polymers (22 and 21 RU, respectively) due to solubility issues with the higher molecular weight polymers. These polymers were first thoroughly purified through precipitation to remove all monomer and remaining AIBN initiator before they were dissolved in 1,4-dioxane at a 0.1 M concentration of the

Table 1 Measured and calculated kinetic and thermodynamic values for the depolymerization and polymerization of methacrylate monomers

Monomer	$[M]_{eq,d}$ [a] (mM)	$[M]_{eq,p}$ [b] (mM)	$k_{app,d}$ [c] (x 10^{-5} s^{-1})	$k_{app,p}$ [d] (x 10^{-5} s^{-1})	ΔH_p [e] (kJ mol^{-1})	ΔS_p [f] (J mol^{-1} K^{-1})
OEGMA	27 ± 2	27 ± 1	1.8 ± 0.2	3.8 ± 0.2	-43 ± 2	-95 ± 5
ODMSMA7	28 ± 1	33 ± 2	3.4 ± 0.1	2.2 ± 0.1	-44 ± 2	-97 ± 5
ODMSMA70	-	23 ± 1	-	2.9 ± 0.2	-46 ± 1	-103 ± 4
MMA	-	27 ± 7	-	2.9 ± 0.6	-	-

[a]Equilibrium monomer concentration from depolymerization. [b]Equilibrium monomer concentration from polymerization. [c]Apparent rate constant for depolymerization. [d]Apparent rate constant for polymerization. [e]Standard state enthalpy of polymerization. [f]Standard state entropy of polymerization. – indicates not measured.‡

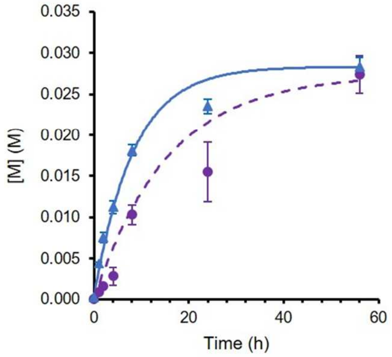

Fig. 1 Released monomer concentration ([M]) as a function of heating time for 22 RU PODMSMA7 (blue triangles) and 21 RU POEGMA (purple circles) at 70 °C in 1,4-dioxane at 0.1 M initial RU concentration. No external radical initiator was added. Monomer concentration measured by ^{1}H NMR spectroscopy. Error bars are one standard deviation with n ≥ 3 replications. Also plotted are theoretical monomer profiles for the depolymerization of PODMSMA7 (solid) and POEGMA (dashed) assuming equilibrium kinetics for a controlled depolymerization and apparent rate constants derived from the first 8 h of polymerization (see ESI).

macromonomer RU and heated air-free in sealed ampules, to avoid solvent loss, at 70 °C (see ESI). No external radical initiator was added to these solutions to explore whether depolymerization was due to thermal degradation alone. The solvent 1,4-dioxane was selected as it is commonly used for RAFT polymerization at 70 °C for these monomers.[23] An ampule was removed for each data point, cooled, and analysed by ^{1}H NMR spectroscopy (Figure S9 and S10) to determine the amount of monomer liberated from the polymer as a function of time (Figure 1). Size exclusion chromatography (SEC) confirmed progressing depolymerization as the polymer shifted to higher elution volume with heating time (Figure S11).

Both PODMSMA7 and POEGMA generated free monomer while heated in the absence of radical initiator to give a concentration that plateaued around 56 h, which was characteristic of reaching an equilibrium monomer concentration. Whether this observed process fit equilibrium depolymerization behaviour was probed by fitting data to Equation 1 which describes monomer concentration as a function of time for an equilibrium polymerization:

$$\ln\left(\frac{[M]_{eq}-[M]_0}{[M]_{eq}-[M]_t}\right)=k_{app}t \qquad \text{Equation 1}$$

where $[M]_{eq}$ is the equilibrium monomer concentration, $[M]_0$ is the initial monomer concentration, $[M]_t$ is the monomer concentration at a particular time, and k_{app} is the apparent rate constant (see ESI for derivation). Using this linearized equation, the initial rate (first 8 h) was fit to calculate apparent rate constants (see Figures S12 and S13) for both the depolymerization ($k_{app,d}$) of PODMSMA7 and POEGMA to be 3.4 x 10^{-5} and 1.8 x 10^{-5} s^{-1}, respectively (Table 1). These results indicate that ODMSMA7 depolymerizes faster, but at a similar order of magnitude as compared to the OEGMA under these conditions. Using these $k_{app,d}$ values and the measured $[M]_{eq}$ of depolymerization ($[M]_{eq,d}$, Table 1), theoretical curves were calculated as presented in Figure 1 that traced the data with outlying points for each polymer. Since the curve fit early in the polymerization and reached the plateau, likely the observed plateau at 56 h was due to reaching the equilibrium monomer concentration. Heating of higher molecular weight PODMSMA7 polymers (48 and 89 RUs) also led to depolymerization, demonstrating that depolymerization is independent of molecular mass (see ESI, Figures S14 and S15), which is consistent with an equilibrium driving force for depolymerization. Furthermore, the similar $[M]_{eq,d}$ values for both POEGMA and PODMSMA7 (27 versus 28 mM), strongly suggested that the same equilibrium driving forces were in play for both polymers to depolymerize without exogenous radical initiator. If these depolymerizations were reaching equilibrium, we hypothesized that polymerization of the monomers should also reach the same concentrations seen in Figure 1. To test this hypothesis, the monomers were polymerized to equilibrium.

RAFT polymerizations of ODMSMA7 and OEGMA were conducted to determine whether thermodynamic polymerization behaviour was driving the depolymerization and whether equilibrium was reached for the depolymerization of the respective polymers. After 56 h of polymerization at 70 °C with an initial monomer concentration of 0.1 M (25:1:0.2 monomer:CDTP:AIBN molar ratio), ODMSMA7 and OEGMA reached polymerization equilibrium monomer concentrations ($[M]_{eq,p}$) of 33 and 27 mM, respectively (Table 1, Figure 2a). These values are near or equal to the depolymerization equilibrium monomer values ($[M]_{eq,d}$) with the same total initial monomer (RU in polymer or macromonomer in solution) present, confirming that depolymerization reached an equilibrium monomer concentration likely dictated by the thermodynamics of the polymerization. A possible cause of the reduced monomer conversion, instead of equilibrium, could have been due to full AIBN consumption after 56 h since the half-life of AIBN is approximately 8 h at 70 °C in 1,4-dioxane.[24] To test this hypothesis, ODMSMA7 was RAFT polymerized as above for 56 h, reaching an $[M]_{eq,p}$ of 34 ± 1 mM, and then cooled to terminate the reaction. More AIBN was added to the polymerization to reach a 0.2 molar ratio of RAFT agent to AIBN as in the initial polymerization, and then the solution was heated at 70 °C for an additional 24 h. This 80 h data point yielded an $[M]_{eq,p}$ of 26 ± 1 mM, which is slightly less than the original RAFT polymerization of ODMSMA7, but nearly the same value as the $[M]_{eq,d}$ of PODMSMA7 (28 ± 1 mM, Table 1) (Figure S16). This additional monomer consumption suggests that under the conditions tested polymerization equilibrium may not have been reached at 56 h; however, since the additional polymerization time led to a $[M]_{eq,p}$ nearly that of depolymerization, we confirmed that equilibrium was indeed being reached during depolymerization. Perhaps the most significant finding is that regardless of whether external initiator was added as in polymerization or not added as with depolymerization, the same

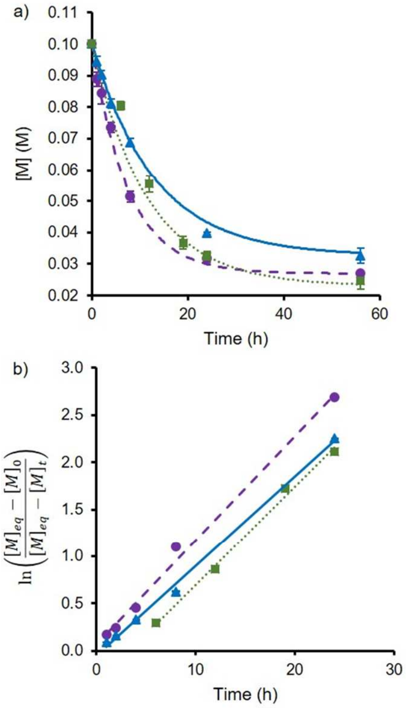

Fig. 2 A) Monomer concentration for the RAFT polymerization of ODMSMA7 (6.6 RU DMS macromonomer, blue triangles), ODMSMA70 (69.6 RU DMS macromonomer, green squares), and OEGMA (9.1 RU of EO, purple circles) as a function of polymerization time at 70 °C in 1,4-dioxane with a starting monomer concentration of 0.1 M (initial 25:1:0.2 monomer:CDTP:AIBN molar ratio). Also plotted are theoretical monomer profiles for the polymerization of ODMSMA7 (solid), ODMSMA70 (dotted) and OEGMA (dashed) assuming equilibrium kinetics for a controlled polymerization and rate constants derived from the first 8 h of polymerization. Monomer concentration measured by ^{1}H NMR spectroscopy. Error bars are one standard deviation with n ≥ 3 replications. Note: OEGMA and PODMSMA70 24 h points coincide. B) Data from A linearized according to equation 1 out to 24 h. Best fit linear lines are given for each polymerization. Note: error bars (one standard deviation) are given, but some are small enough that they are not visible under marker.

final monomer concentrations were reached. These results confirm that complete consumption of radical generating species is not the cause for the observed plateau in monomer concentration. Rather, such a plateau is directly attributable to reaching the equilibrium monomer concentration. Interestingly, these $[M]_{eq}$ values from both polymerization and depolymerization at 70 °C are several times greater than expected for methyl methacrylate (4 mM), which has an analogous polymerizable group.[25]

We hypothesized that the increased steric bulk of the macromonomers affected the thermodynamic properties of polymerization, leading to measurable $[M]_{eq}$ values. To test this hypothesis, a ODMSMA macromonomer with 69.6 RUs (ODMSMA70) was polymerized and analysed under the same conditions. This polymerization yielded an $[M]_{eq,p}$ value of 23 mM (Table 1, Figure 2a), analogous to the values obtained to the two other macromonomers, indicating that macromonomer length did not significantly affect equilibrium thermodynamics. ODMSMA70 polymerization times longer than 56 h confirmed that equilibrium was achieved at 56 h as evidenced by the monomer concentration plateau (Figure S17). Methyl methacrylate (MMA) was polymerized under the same conditions (Figure S18), reaching a $[M]_{eq,p}$ of 27 mM (Table 1). Since this value was nominally the same as all other monomers polymerized, the observed $[M]_{eq}$ values are likely inherent to polymerizing the methacrylate group under these conditions and not a function of the pendent group off the ester. The discrepancy with the expected value of MMA is likely due to the fact that the literature reported thermodynamic constants are for the bulk polymerization of MMA, while our polymerizations were all conducted in 1,4-dioxane under reduced pressure due to our ampule sealing method. Our different conditions (i.e. polarity and pressure) could have affected the enthalpy and entropy of polymerization slightly, leading to the $[M]_{eq}$ values observed. Additionally, the RAFT CTA that controls the polymerization may have some unforeseen effect upon the thermodynamics of polymerization.

Comparison of the polymerization kinetics confirmed that all monomers behaved similarly regardless of the pendent group (Figure 2B). All three macromonomers had similar $k_{app,p}$ values as evidenced by the nearly parallel behaviour when linearized as given in Figure 2B. Additionally, the $k_{app,p}$ for MMA agrees with the macromonomers (Table 1, Figure S19), confirming that the pendent groups do not significantly affect polymerization kinetics. Such a result is consistent with the RAFT CTA controlling the kinetics of the polymerization as the equilibrium between free propagating radical and dormant radical typically dictates the rate of polymerization for RAFT polymerizations.[26,27] Previous studies of MMA polymerization with the CDTP agent have demonstrated that it controls the polymerization rate, which supports the RAFT agent mediated $k_{app,p}$ observed.[28] Interestingly, the $k_{app,d}$ values for the depolymerization of POEGMA and PODMSMA7 are the same order of magnitude as the $k_{app,p}$ values, which suggests that the RAFT CTA at the chain end mediated the rate of depolymerization as well. This result is particularly interesting, as the depolymerizations were performed without external initiator, while polymerizations had AIBN added. The added initiator for the polymerization could be expected to significantly increase the $k_{app,p}$ above the $k_{app,d}$ as the availability of propagating radicals is expected to be higher; however, it appears that the RAFT CTA activation-deactivation equilibrium significantly reduces propagating radical concentration whether external initiator is added or not, yielding minimal propagating centres, and thus similar k_{app} values.

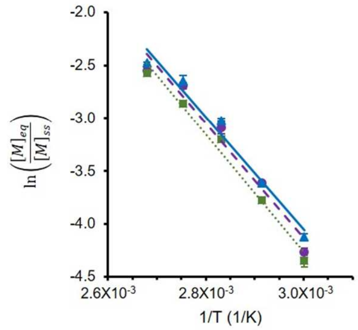

Fig. 3 Comparison of equilibrium polymerization behaviour using a van't Hoff analysis plot for the RAFT polymerization of ODMSMA7 (blue triangles), ODMSMA70 (green squares), and OEGMA (purple circles) for polymerizations from 60 – 100 °C in 1,4-dioxane and at 0.1 M starting monomer concentration (initial 25:1:0.2 monomer:CDTP:AIBN molar ratio). $[M]_{eq}$ was measured at 56 – 96 h of polymerization and $[M]_{ss}$ was assumed to be 1 M. Linear fits are given for ODMSMA7 (solid), ODMSMA70 (dotted), and OEGMA (dashed). Error bars are one standard deviation with n ≥ 3

Confirmation that all three macromonomers examined had similar behaviour came from determining the thermodynamic parameters of the polymerizations. To estimate these parameters, polymerizations with each monomer were run at different temperatures until reaching equilibrium. A van't Hoff analysis was conducted utilizing equation 2:

$$\ln\left(\frac{[M]_{eq}}{[M]_{ss}}\right) = \frac{\Delta H_p}{RT} - \frac{\Delta S_p}{R} \qquad \text{Equation 2}$$

where ΔH_p and ΔS_p are the standard enthalpy and entropy of polymerization, respectively, T is the temperature at which the polymerization was run, and $[M]_{ss}$ is the standard state monomer concentration, which was assumed to be 1 M for these analyses. These $[M]_{eq}$ were plotted as a function of inverse temperature for the three monomers, giving trends that fell on top of each other (Figure 3). Calculation of the standard enthalpy and entropy of polymerization for these macromonomers gave essentially the same values (Table 1), which is consistent with these macromonomers having the same $[M]_{eq}$ at 70 °C. Interestingly, both the enthalpy and entropy of polymerization were more positive than the reported values for MMA.[25] This discrepancy may be due to the polymerization in 1,4-dioxane as opposed to the bulk polymerization conditions that the original MMA measurements were made under. Additionally, the polymerizations were performed under reduced pressure due to the method used to seal the ampules. This reduced pressure changes the standard state that these polymerizations were performed under as compared to previous measurements. This effect is not unheard of as other radical polymerizations have demonstrated that lower pressures give higher $[M]_{eq}$ values.[29,30] Nevertheless, the results confirmed that all macromonomers behaved the same under these conditions and that the observed depolymerization phenomenon was a result of the polymerization thermodynamics being more unfavourable for polymerization under these conditions.

Though experiments confirmed that the thermodynamics of the monomer polymerization were driving depolymerizations to $[M]_{eq}$, we explored the mechanism that initiated this depolymerization since no external radical initiators were added. Thermal depolymerization of polymers synthesized by RAFT polymerization have been reported to typically follow a mechanism where the CTA degrades initiating the process.[31,32] Such degradation events have been reported at significantly higher temperatures than observed in this study and do not reinitiate as should be possible for a controlled depolymerization process if the RAFT CTA is retained.[33,34] To elucidate the mechanism in our system, a 22 RU PODMSMA7 was heated at a 0.1 M concentration of RUs for 56 h in 1,4-dioxane without an external radical generating species, resulting in a decrease of 5.5 RU as indicated by ^{1}H NMR spectroscopy (Figure S20) and confirmed by SEC (Figure 4) with a shift to higher elution volume. More RUs could be lost from the polymer due to depolymerization of PODMSMA7 as observed by SEC when depolymerization was performed at a RU concentration equal to that of $[M]_{eq,d}$ (Figure S21), indicating that by selecting the right concentration and time, molecular weights could be targeted through depolymerization.

To probe the fidelity of the terminal RAFT CTA, UV-Vis was performed on the 22 RU PODMSMA7 polymer before and after depolymerization (Figure S22) to measure any decrease in the absorbance of the terminal RAFT CTA which would be consistent with its degradation. The UV-Vis data indicated that only a 5.1% decrease in the absorbance signal was observed after 56 h, which is consistent with insignificant degradation of the CTA. Dispersity of the polymer after depolymerization increased slightly from 1.17 to 1.18, which correlates to a persistent equilibrium during heating, leading to a mixing of monomers about chain ends and a broadening of the distribution in addition to possible irreversible termination events. These results suggested that the CTA was still intact at the end of the polymer chain after depolymerization, which contrasts with previous studies.[31,32]

Since the RAFT CTA end group appeared intact, the chain ends were hypothesized to be still available to reinitiate polymerization. To test this, ODMSMA7 monomer (0.5 M) and AIBN (1:0.2 CDTP:AIBN molar ratio) were added to the depolymerized 22 RU PODMSMA7 and polymerized for 16 h. SEC of the reinitiated polymerization (Figure 4) confirmed the re-initiation of RAFT polymerization off the depolymerized polymer as the SEC curve shifted to a lower elution volume (M_n = 114 kg/mol). Furthermore, the SEC peak corresponding to the original depolymerized polymer was not present, indicating complete initiation. The dispersity did increase somewhat (1.43 versus 1.18) suggesting that some irreversible termination did occur, but this may be a result of running the polymerization to high monomer conversion (95%) and not due the depolymerized polymer. These experiments confirmed that the cause of the observed depolymerizations without an external radical initiator was not due to RAFT CTA degradation, but was instead a result of the inherent equilibrium monomer concentration of these monomers, which is consistent with the RAFT equilibrium being present during heating without radical initiator.

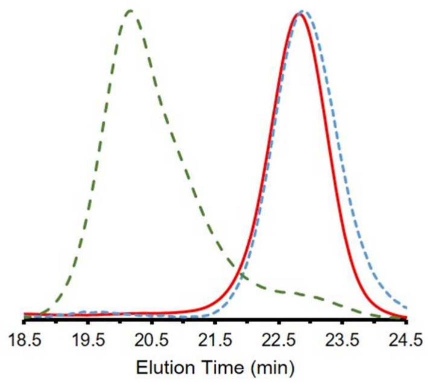

Fig. 4 Normalized SEC elution curves of 22 RU PODMSMA7 (red solid line, Đ = 1.17, Mn = 19.2 kg/mol), 22 RU PODMSMA7 heated at 0.1 M concentration of RUs in 1,4-dioxane at 70 °C for 56 h (blue dotted line, Đ = 1.18, Mn = 16.8 kg/mol), and polymer formed through the re-initiation of the depolymerized polymer at 0.5 M ODMSMA7 in 1,4-dioxane and AIBN at 70 °C for 16 h (green dashed line, Đ = 1.43, Mn = 114 kg/mol).

Since the RAFT CTA terminus is retained and the depolymerized polymers have a low dispersity, the depolymerization process is likely a controlled depolymerization process mediated by the RAFT CTA at the end of the polymer chain. Initiation of the RAFT equilibrium typically requires the addition of a thermal radical initiator which was not needed for these depolymerizations; however, several other radical generating reactions are possible. Initiator-free, low temperature RAFT polymerization and RAFT CTA removal from polymers has been demonstrated using zero valent transition metals catalysing these radical processes through metal oxidation.[35,36,37] The RAFT CTA degradation observed in these processes is different than the CTA retention in our study, suggesting that metal contamination does not catalyse the observed depolymerization. Conversely, radicals can be generated from monomers and polymers upon heating as evidenced by high temperature initiator-free, conventional radical polymerizations of acrylates and methacrylates that occur through a self-initiation process[38,39,40] and reports of lower temperature polymerizations (80 °C) self-initiating.[41] Recent reports of light initiated RAFT polymerizations using trithiocarbonate CTAs,[42] even with just ambient light,[43] also provide a mechanism for the activation of the RAFT CTA end group and subsequent depolymerization since these samples were not completely shielded from light. Even low levels of peroxides present in the 1,4-dioxane could initiate this depolymerization process.[44] Any one or a combination of these proposed processes could initiate the observed depolymerization and such depolymerization may likely be a concern for any methacrylate RAFT polymer when heated even to modest temperatures.

Several additional depolymerizations were run to determine which of these aforementioned radical generating mechanisms were responsible for initiating depolymerization. Heating ODMSMA7 RAFT polymers in tetrahydrofuran (THF) and xylenes for 60 h at 70 °C yielded depolymerization as evidenced by monomer generation in ^{1}H NMR spectra and SEC elution curves shifting to higher elution volumes (see ESI, Figures S23 – S25). Though THF does generate peroxides when exposed to oxygen as 1,4-dioxane does, xylenes do not, suggesting that a peroxide generating solvent is not a requirement to initiate depolymerization under these conditions. Similarly, heating ODMSMA7 RAFT polymers in 1,4-dioxane at 70 °C while the ampules were covered in foil to block ambient light, yielded observed depolymerization (Figure S26). This result suggests that light is not a requirement for radical generation to initiate depolymerization. Since depolymerization did not require 1,4-dioxane and light, these could be ruled out as the only source of radicals for initiation.

To further explore the mechanism that initiated the depolymerization without addition of radical initiator, PODMSMA7 was heated in the presence of butylated hydroxytoluene (BHT). BHT was expected to trap radicals produced in the solution or off the polymer prior to their possible reaction with the RAFT CTA, inhibiting depolymerization. If the RAFT CTA were undergoing homolytic cleavage between the sulphur-carbon bond that connects the RAFT CTA to the polymer chain due to its thermal degradation, a radical centre would be produced on the polymer chain end, enabling depolymerization before BHT could trap the produced radical. Released monomer concentration measured by ^{1}H NMR spectroscopy was constant for the first 24 h, consistent with BHT inhibiting depolymerization (Fig. 5). Subsequent measurements at 56 and 120 h yielded increased free monomer, indicating that depolymerization had begun. SEC elution curves of representative samples at these later times (Figure S27) showed a decrease in polymer molar mass. These results confirmed that BHT could inhibit depolymerization, supporting a radical generation mechanism not due to the homolytic cleavage of the RAFT CTA at the polymer end. Moreover, since depolymerization had an induction period with BHT present, the study suggests that radicals are continuously produced during heating such that once BHT is sufficiently consumed, the radicals can initiate depolymerization. This result is consistent with a radical producing species at significantly higher concentrations than the RAFT CTA, leaving only the solvent or polymer as the potential source of radicals upon heating. Since all solvents investigated initiated depolymerization without an added radical generating species, likely the radical production occurs from the polymer chain; however, since the radical concentration required for RAFT polymerizations can be extremely low, any source of radicals produced by thermolysis may initiate this depolymerization process. Since radicals are continuously produced upon heating, if a radical trap like BHT is used to prevent this depolymerization, its concentration should be selected carefully to ensure sufficient inhibitor is present.

Additionally, the observed depolymerization phenomenon and higher than expected equilibrium monomer concentration bring to light some considerations for polymer scientists that aim to create brush type polymers using RAFT polymerization. First, like a ceiling temperature (T_c) exists for radical polymerizations, a ceiling macromonomer molecular weight (M_{cmm}) exists for radical polymerizations where macromonomer molecular weights above the M_{cmm} will not have polymerization take place. This M_{cmm} exists when the polymerization is under bulk conditions of the macromonomer and the molecular weight of the macromonomer is such that the concentration of polymerizable end groups is the equilibrium monomer concentration at those conditions. For example, for the OEGMA and ODMSMA macromonomers in our study (at 70 °C) M_{cmm} are 40 and 29 kg/mol, respectively (see ESI). These M_{cmm} are significantly larger than even the ODMSMA70 used in this study, which yielded narrow dispersity polymers (Figure S28). However, polymerizations have used macromonomers approaching these M_{cmm} values, which would suffer significant equilibrium polymerization issues while attempting bottle brush RAFT polymerization.[45,46,47] Such an effect will be amplified at higher temperatures, necessitating careful design of bottle brush macromonomers and conditions for RAFT polymerization.

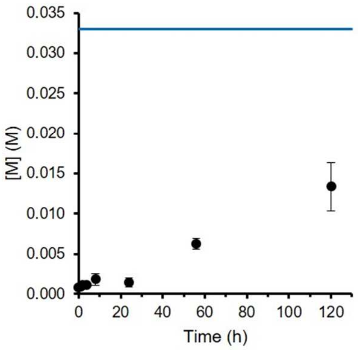

Fig. 5 Released monomer concentration ([M]) of 22 RU PODMSMA7 heated with BHT at a 0.2 molar ratio to RAFT CTA (without an external radical initiator) in 1,4-dioxane at 70 °C as a function of time (black circles). Error bars are one standard deviation with n ≥ 3 replications. The blue solid line indicates the $[M]_{eq}$ measured for PODMSMA7 at 56 h (33 mM).

A second consideration is that the polymerization conditions beyond temperature do appear to significantly affect the thermodynamics of RAFT polymerization as evidenced by the discrepancy between our measured entropy and enthalpy values and those reported for other methacrylate polymerizations. The polymerizations were run under reduced pressure (vapour pressure of 1,4-dioxane at 70 °C = 0.35 bar) due to running them in evacuated and sealed ampules. Higher pressure polymerizations and solvent selection could be used to reduce the $[M]_{eq}$ for these polymerizations much like that observed for ATRP and mitigate the effects of depolymerization.[30] Moreover, different solvents may also affect the generation of in situ radicals that activate the observed RAFT depolymerization and should be considered.

Conclusions

In conclusion, we demonstrated that RAFT polymers retaining a trithiocarbonate CTA end-group depolymerized to the monomer’s inherent equilibrium monomer concentration without adding radical initiator and without the RAFT CTA degrading. The observed $[\boldsymbol{M}]_{\boldsymbol{eq}}$ for these methacrylate monomers was significantly higher than expected (ca. 30 mM versus 4 mM), leading to a noticeable change in molecular weight during depolymerization. The calculated entropy and enthalpy of polymerization values were the same for all macromonomers regardless of chain length or chain type, indicating that equilibrium was dictated by the polymerizable methacrylate end group. The thermodynamic parameters suggested that the monomers were more resistant to polymerization than expected, which was likely due to the low pressure that these polymerizations were performed under. Depolymerization was found to retain the RAFT CTA such that polymerization could be reinitiated, confirming that ambient radicals in the reaction mixture initiate the depolymerization process. Depolymerization experiments without an exogenous radical generating species and under different conditions confirmed that 1,4-dioxane was not required for depolymerization and that thermolytic cleavage of bonds within the polymer continuously generated radicals to initiate activity of the RAFT CTA and depolymerization upon heating. These conclusions underscore the need to carefully select polymerization conditions (beyond temperature) to avoid significant equilibrium effects during polymerization and that simply heating RAFT CTA terminated polymers can lead to measurable monomer loss and significant molecular weight reduction if macromonomers are used.

Conflicts of interest

There are no conflicts to declare

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Notes and references

‡ A ODMSMA70 $[M]_{eq,d}$ value was not reported because its polymer had limited solubility in 1,4-dioxane at room temperature, leading to high variability. Not all MMA values were reported because the gravimetric measurement of remaining monomer was prohibitively time consuming (ca. 2 weeks per sample).

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TOC Graphic

Brush polymers synthesized by reversible-addition fragmentation chain transfer (RAFT) polymerization undergo controlled depolymerization when heated as dictated by polymerization thermodynamics.