

Solvent-Free Chemical Recycling of Polymers made by ATRP and RAFT polymerization: High-Yielding Depolymerization at Low Temperatures

Richard Whitfield^a, Glen R. Jones^a, Nghia. P. Truong^a, Lewis E. Manring^b, Athina Anastasaki^{a,*}

^aLaboratory for Polymeric Materials, Department of Materials, ETH Zürich, Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland.

^b1346 Manitou Rd., Santa Barbara, CA 93101.

Abstract

Although controlled radical polymerization is an excellent tool to make precision polymeric materials, reversal of the process to retrieve the starting monomer is far less explored despite the significance of chemical recycling. Current depolymerization approaches typically require elevated temperatures (>350 °C), high dilutions in specific solvents (typically 0.1-25 mM polymer concentrations), and/or expensive catalysts. Here, we report that RAFT-synthesized polymers can undergo a low-temperature solvent-free depolymerization back to monomer thanks to the partial *in-situ* transformation of the RAFT end-group to macromonomer. To aid a more complete depolymerization, we performed a facile and quantitative end-group modification strategy with the modified RAFT polymers exhibiting significantly higher depolymerization conversions (~90%) at comparable temperatures. The end-group transformation was applied to polymers synthesized by ATRP triggering an efficient low-temperature bulk depolymerization (~90% of monomer regeneration) with an onset at 150 °C, in contrast to previous reports where depolymerization could only be triggered at much higher temperatures (> 350 °C). The versatility of the methodology was demonstrated by a scalable depolymerization (~10 g of starting polymer) retrieving 84% yield of the starting monomer intact which could be subsequently used for further polymerization. This work presents a new low-energy approach for depolymerizing controlled radical polymers and creates many future opportunities as high-yielding, solvent-free and scalable depolymerization methods are sought.

Introduction

The development of controlled radical polymerization (CRP) methods, and in particular atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization, has revolutionized polymer science, as well-defined vinyl polymers can be prepared under mild conditions with unprecedented control over molecular weight, molecular weight distribution, architecture and composition.¹⁻⁸ The unparalleled success of these techniques lies in their ability to preserve the end-group fidelity of the vast majority of polymer chains, which not only helps to maintain control over the polymerization, but also allows a plethora of complex materials to be prepared.⁹⁻¹³ However, while polymer

chemists have focused almost exclusively on developing the synthesis, very limited reports exist on reversing the process, i.e. achieving depolymerization by chemically breaking down polymers back into their starting monomers, which can then be repolymerized into virgin-like materials.¹⁴⁻¹⁸ Although excellent degradation strategies have been widely developed, these approaches focus on breaking down the polymer into small molecules rather than retrieving the starting monomer.¹⁹⁻²⁴ Instead, chemical recycling is essential if we are going to make polymers more sustainable, reduce waste and prevent their continued accumulation in the environment.²⁵⁻²⁸

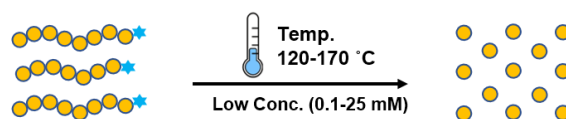
Achieving depolymerization of vinyl polymers is particularly challenging, as the carbon-carbon bonds that form the polymer backbone have extremely high thermal stability.²⁹ Nevertheless, remarkable achievements have emerged recently with the development of solution-based depolymerization methods for polymers made by CRP.¹⁸ Seminal work from the group of Ouchi illustrated that in the presence of a ruthenium catalyst, it was possible to depolymerize poly(methyl methacrylate) (PMMA) obtained from ATRP.³⁰ Matyjaszewski and coworkers very impressively illustrated that both copper and iron catalysts could be exploited to depolymerize a wide-range of methacrylate polymers, obtaining around 70% of the original monomer at temperatures as low as 170 °C.³¹⁻³³ In addition, polymers obtained from RAFT polymerization have been depolymerized by our laboratory and those of Gramlich and Sumerlin.³⁴⁻³⁸ Notably, these methods have been developed to recover as much as 90% of the original monomer at temperatures as low as 120 °C, or even at 100 °C in the presence of UV or blue light irradiation.³⁴⁻³⁸

Despite the aforementioned outstanding results, the vast majority of current approaches operate best in specific solvents, such as dioxane, while significantly lower depolymerization conversions are reported in alternate media, thus limiting the scope of depolymerizable materials.³⁵⁻³⁸ In addition, very high polymer dilutions (i.e. 0.1 mM polymer concentration or 5 mM repeat unit concentration) are typically essential to favour a successful depolymerization.³⁵⁻³⁸ When higher polymer concentrations have been employed (i.e. 12-25 mM polymer concentration or 100-750 mM repeat unit concentration), higher temperatures were required (e.g. 170 °C) in conjunction with significant amounts of copper or iron ATRP catalysts.³¹⁻³³ As such, a scalable and both catalyst and solvent-free (i.e. bulk) approach to depolymerize ATRP and RAFT materials would be highly beneficial and could potentially attract considerable attention from both academia and industry. However, to date current reports require high temperatures to facilitate repeat unit scission events to achieve high depolymerization conversions.^{32, 33, 39-41} In terms of RAFT polymers, previous work by Moad and coworkers showed the possibility of degradation at high temperatures (>300 °C).³⁹ Although the focus of this work was to study the thermolysis of the RAFT end-groups, rather

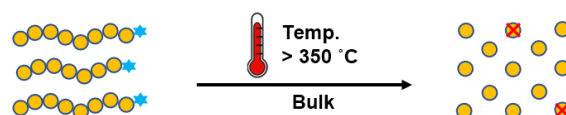
than to promote depolymerization, it provided important preliminary evidence that macromonomer formation is possible at elevated temperatures.³⁹⁻⁴³ For ATRP polymers, high temperatures were also required for depropagating radicals to be generated and lactonization was cited as the primary side reaction preventing depolymerization at lower temperatures.^{32, 33, 44} As such, in both cases the bulk depolymerization of either RAFT or ATRP materials at lower temperatures was not possible. Inspired by previous work by Moad and coworkers we envisaged that macromonomer formation, either produced *in-situ* or through a facile end-group modification strategy, could promote the chain-end low temperature bulk depolymerization of both RAFT and ATRP polymers while significantly minimizing the contribution from scission events.^{39, 43, 45}

In this work, we first trigger the solvent-free depolymerization of RAFT polymers at 210 °C and provide unambiguous evidence that the partial macromonomer formation is primarily responsible for the high depolymerization conversions obtained. Through an efficient chain-end depolymerization approach at lower temperatures, high temperature scission events and side reactions can be avoided, therefore suppressing monomer waste (i.e. sacrificial monomer that is essential to trigger scission) and recovering high amounts of pristine monomer.⁴⁶⁻⁵⁴ To aid a more complete macromonomer formation, we then performed a facile and near quantitative post-polymerization modification of the ATRP and RAFT polymers to macromonomers. The modified polymers were subsequently successfully depolymerized resulting in up to 90% monomer regeneration at temperatures as low as 220 °C. The potential to scale up the developed methodology was also attempted to exemplify the robustness of our approach.

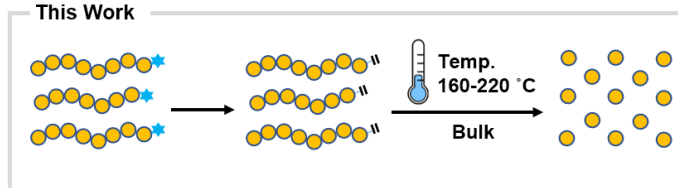
A Solution Depolymerization Approaches



B Bulk Depolymerization Approaches



This Work



Scheme 1: Depolymerization approaches for polymers obtained by controlled radical polymerization. Advantages and disadvantages of these methods are illustrated.

Results and Discussion

To investigate the bulk depolymerization of ATRP and RAFT polymers, PMMA was synthesized by photoATRP and thermal RAFT polymerization, respectively, followed by rigorous precipitation to remove residual monomer.⁵⁵⁻⁵⁸ The purified polymers exhibited comparable molecular weights and dispersity (Figure S1-5), thus allowing for a fair comparison between their depolymerization profiles, as recorded by thermogravimetric analysis (TGA, Figure S6). For the ATRP polymer, the main onset of depolymerization was observed at temperatures just above 350 °C, with 400 °C required for complete weight loss of the polymer (Figure 1a, blue traces). It is noted that a very small amount of depolymerization was possible at lower temperatures as evidenced by ¹H nuclear magnetic resonance (NMR) spectroscopy and TGA but the vast majority of the polymer chains did not depolymerize until very high temperatures had been reached (Figures 1a-1b, blue). The high temperatures required here suggest that the polymer synthesized by ATRP can only depolymerize once side group or backbone scission events had occurred, with repeat unit degradation essential in generating the backbone radicals that will partially unzip the polymer chain.^{47, 59, 60} To verify this hypothesis, the depolymerization of a polymer without reactive or labile end-groups (prepared by anionic polymerization), was also studied as a reference (Figures 1a-1b, green). Under otherwise identical conditions, significant weight loss only occurred at temperatures higher than 350 °C, with no monomer detected by ¹H NMR when a sample was taken at 220 °C. Altogether, these results suggest that the main depolymerization mechanism for both ATRP and anionic polymers is nearly identical, and although ATRP materials may still generate a small amount of monomer at lower temperatures, the carbon-bromide bond is not sufficiently thermally labile to trigger an efficient depolymerization.

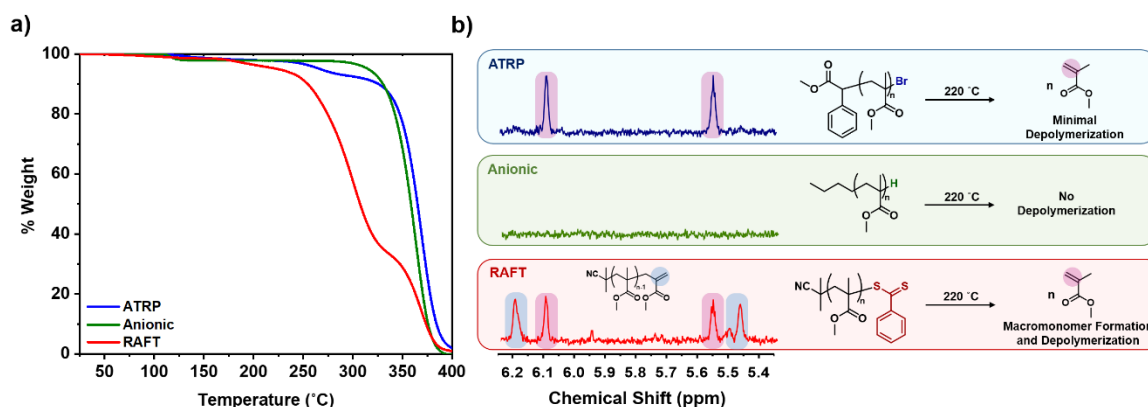


Figure 1: The depolymerization of PMMA prepared by ATRP, RAFT and anionic polymerization. In a), TGA traces are presented to illustrate the depolymerization profile of

these various polymers. Experiments were performed with a heating rate of 1 °C per minute. In b) zoomed in ¹H NMR spectra of each polymer's vinyl region are shown after heating to 220 °C. MMA monomer and macromonomer peaks are highlighted in purple and orange, respectively. Schemes are shown to illustrate the relative extent of low-temperature depolymerization after heating these polymers to 220 °C.

In stark contrast, the depolymerization of the RAFT polymer presented a completely different profile (Figures 1a-1b, red). Initial weight loss was recorded at ~200 °C followed by a significant reduction in weight commencing at 250 °C while approximately 50% of depolymerization took place by 300 °C. This contrasts previous reports where all depolymerization occurred at temperatures greater than 300 °C.³⁹ We attributed this difference to the slower heating rate used for our experiments (1 °C/minute vs 5 or 10 °C/minute) resulting in either a change in the depolymerization pathway or allowing more time for suitable depropagating radicals to form (Figure S7). The significantly lower onset for the RAFT polymer (100 °C earlier than its anionic counterpart) was hypothesized to be due to a rapid unzipping chain-end depolymerization reaction, rather than random scission events. To further investigate our hypothesis, samples were taken periodically throughout the RAFT depolymerization and were subsequently analyzed by both size exclusion chromatography (SEC) and ¹H NMR spectroscopy. On measuring SEC from a sample obtained at 220 °C, a 95% decrease in the polymer signal was observed in the UV detector, illustrating that the RAFT agent had been near-quantitatively degraded (Figures S8-S10). Upon analysis of the same sample by ¹H NMR, a significant amount of recovered monomer was detected, accompanied by an additional set of distinctive vinyl peaks at 5.45 and 6.20 ppm attributed to macromonomer formation. This was in line with previous reports proposing Chugaev elimination as a potential end-group degradation pathway (Scheme S1, Figure 1).^{39, 41} In total, ¹H NMR showed that 65% of the polymer chains had converted to macromonomer which closely matched the percentage of weight loss in TGA by 325 °C (66%), thus suggesting that the macromonomer formation may be responsible for the observed lower temperature depolymerization of RAFT polymers (Figure 1, red). To provide further evidence, we subsequently sampled the reaction at 325 °C (the temperature at which low temperature depolymerization ceased) and ¹H NMR confirmed the complete consumption of the macromonomer (Figure S11). In addition, SEC analysis from the sample obtained at 325 °C showed that the shape of the molecular weight distribution was nearly identical to the starting polymer, thus further validating our hypothesis of a lower temperature rapid chain-end radical unzipping (Figure S12). Should side-group scission have been involved, a clear decrease in M_n would instead be expected, and as we also see in the case of the anionic polymer a lower M_n was obtained (7400 vs 9400) accompanied with an increase in dispersity (1.25 vs 1.09)

when sampling at 360 °C (Figure S13).⁵⁰ This difference is because the backbone radical formed after side-group scission is only capable of depolymerizing in one direction, so the remainder of the chain is thermally stable until further scission events have occurred (Scheme S2). In the case of the RAFT polymer, the remaining one third of polymer chains underwent weight loss at much higher temperatures (350 °C), similar to those at which the anionic and ATRP polymer depolymerized, thus illustrating that high-temperature repeat unit scission was essential to achieve high depolymerization conversions in all cases (Figure S14).

Considering the importance of the macromonomer formation, we envisaged that by converting the ATRP and RAFT polymer end-groups to double bonds, we could potentially trigger a more efficient bulk depolymerization. The advantages of such transformation would be to (i) enhance the depolymerization conversion, (ii) retrieve pristine monomer by avoiding scission events and (iii) significantly lower the bulk depolymerization temperature. To explore the feasibility and the benefits of this scenario, we sought a polymerization method whereby macromonomer would be the sole polymerization product. Inspired by previous work from Manring and coworkers, our attention was directed to catalytic chain transfer polymerization, a method which can in principle result in highly pure PMMA macromonomer.^{45, 61-64} To maximize the macromonomer formation, we utilized CoBF (bis[(difluoroboryl)dimethylglyoximato]cobalt(II)) as the catalytic chain transfer agent and synthesized a well-defined PMMA ($M_n = 4100$, $\mathcal{D} = 1.26$ after purification) exhibiting nearly quantitative end-group fidelity (i.e. macromonomer formation), as indicated by both SEC and MALDI-ToF-MS (Figures S15-17). The purified PMMA was then subjected to our previously optimized depolymerization conditions. Consistent with previous work,⁴⁵ the depolymerization onset occurred at 150 °C with weight loss evidenced in the TGA chromatogram and ¹H NMR clearly demonstrating monomer regeneration (Figures 2a & S18). This is a much lower onset temperature than the polymers prepared by RAFT, ATRP and anionic polymerization, with depolymerization observed at temperatures 200 °C lower than of the anionic and ATRP polymers and actually ~50 °C lower than that of the RAFT polymer. Following the early onset, rapid depolymerization was evident as the temperature exceeded 220 °C and a total of 92% of depolymerization was reached by 260 °C (Figure 2a). This acceleration of the depolymerization was attributed to the more rapid removal of the monomer produced at these elevated temperatures. When comparing the depolymerization of the CCTP macromonomer to the polymers prepared by the other methods, the temperature required to achieve 90% depolymerization was reduced by more than 125 °C in all cases (Figure 2b).

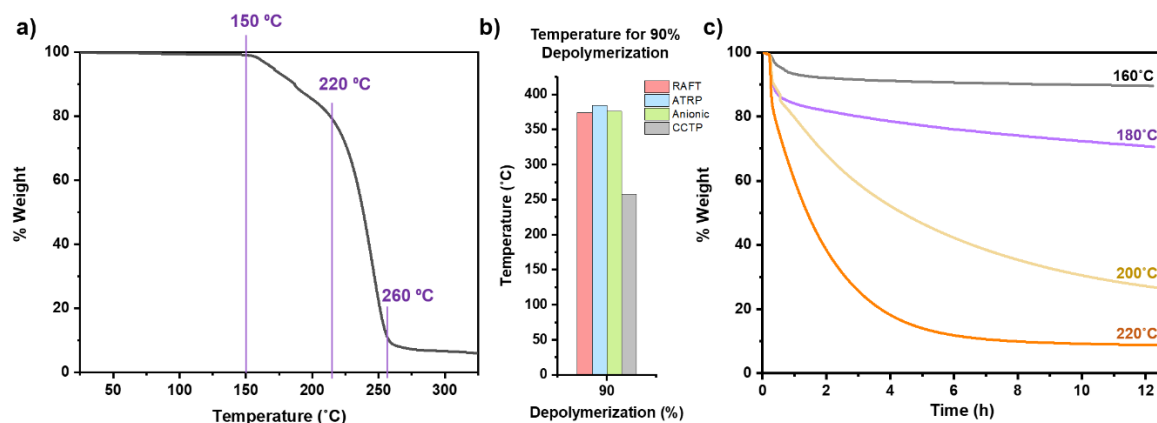


Figure 2: The depolymerization of PMMA obtained by CCTP. In a) a TGA trace is presented, which illustrates the depolymerization profile of this polymer. Experiments were performed with a heating rate of 1 °C per minute. The onsets of slow and rapid depolymerization and the temperature at which low-temperature depolymerization is complete are illustrated in purple. In b) a bar chart compares the temperatures at which 90% depolymerization is achieved for polymers obtained from various methods. In c), TGA traces are presented, which illustrates the depolymerization profile of this polymer, when the temperature was increased by 10 °C/minute and then maintained at various temperatures for 12 hours.

To further lower the depolymerization temperature, a series of isothermal experiments were performed where rather than continuously heating the polymer, the polymer was heated to a specific temperature, which was maintained for a selected period of time. These experiments allow us to observe the maximum possible depolymerization at any given temperature. The first isothermal experiment of the CCTP polymer at 160 °C (Figure 2c, black) resulted in approximately 10% of mass loss after 12 hours and subsequent experiments at 180 °C, 200 °C and 220 °C, gave rise to 30%, 73% and 91% of depolymerization respectively (Figure 2c, purple, yellow & orange & Figure S19). These data illustrate that a near-quantitative bulk depolymerization can be achieved at temperatures as low as 220 °C. However, thus far, all depolymerization reactions had been performed in a TGA, with very small quantities of polymer (~7 mg) and the purity of the obtained monomer had not been assessed. A bulk vacuum distillation experiment was performed by heating 0.5 grams of polymer to 220 °C. Notably, just over 87% mass loss was observed in just 4 hours with over 0.4 g of monomer obtained (408 mg), an impressive 81.6% yield. Importantly, on ¹H NMR analysis, methyl methacrylate monomer was clearly observed in very high purity (Figure S20). The high purity of the recovered monomer was attributed to the lower temperature depolymerization whereby the contribution from scission events had been presumably eliminated.

Collectively, these experiments highlight that if we can successfully convert ATRP and RAFT polymers to macromonomers, a much lower depolymerization temperature could be employed (Figure 3a). In addition, another advantage of this approach would be the possibility to obtain pristine monomer while suppressing the side reactions that occur at much higher temperatures. Such transformation would also create the prospect of depolymerizing a far wider range of materials with controlled molecular weights, dispersity and architecture.⁶⁵⁻⁶⁷ To modify the ATRP bromine end-group, MMA monomer, ATRP photocatalyst and CoBF were added together with PMMA-Br in anisole with the following ratio: [PMMA]:[MMA]:[AIBN]:[CoBF] of 1:5:0.08:0.15 and the mixture was left to stir overnight under blue light irradiation. ¹H NMR analysis confirmed a near-quantitative macromonomer formation (>90%) and the purified polymer was subsequently subjected to depolymerization (Figure S21). TGA revealed an onset of depolymerization at 160 °C for the modified ATRP polymer, a remarkably lower onset when compared to the Br-terminated analogue which required temperatures higher than 350 °C to record a significant extent of depolymerization. A near-quantitative depolymerization was achieved at 270 °C with depolymerization conversions exceeding 90% (Figure 3b). The key to the success of this approach is the vinyl end-group installed by the successful transformation to macromonomer. Thanks to this transformation, monomer is generated at very low (for bulk depolymerization) temperatures and is constantly removed from the reaction as a gas, preventing the equilibrium monomer concentration from being reached and allowing depolymerization to proceed to high conversions, at temperatures below the ceiling temperature. By having a consistent end-group on all the polymer chains, not only can we generate all the monomer from a given polymer chain, we can also generate monomer from almost all of the chains, thus allowing high overall yields to be obtained. This depolymerization approach is therefore far more energy efficient to perform, not only avoiding the necessity for high temperature scission reactions to trigger monomer generation, but also circumventing the requirement of high polymer dilutions to lower the ceiling temperature and prevent the equilibrium monomer concentration from being surpassed.⁶⁸⁻⁷⁰ Importantly, the reaction could be conducted without solvent or catalyst, instead with just the polymer as the only component, so is therefore very simple to carry out, avoiding the need to optimize reaction conditions. To summarize, through an efficient macromonomer transformation strategy, ATRP polymers were shown to depolymerize in bulk at significantly lower temperatures.

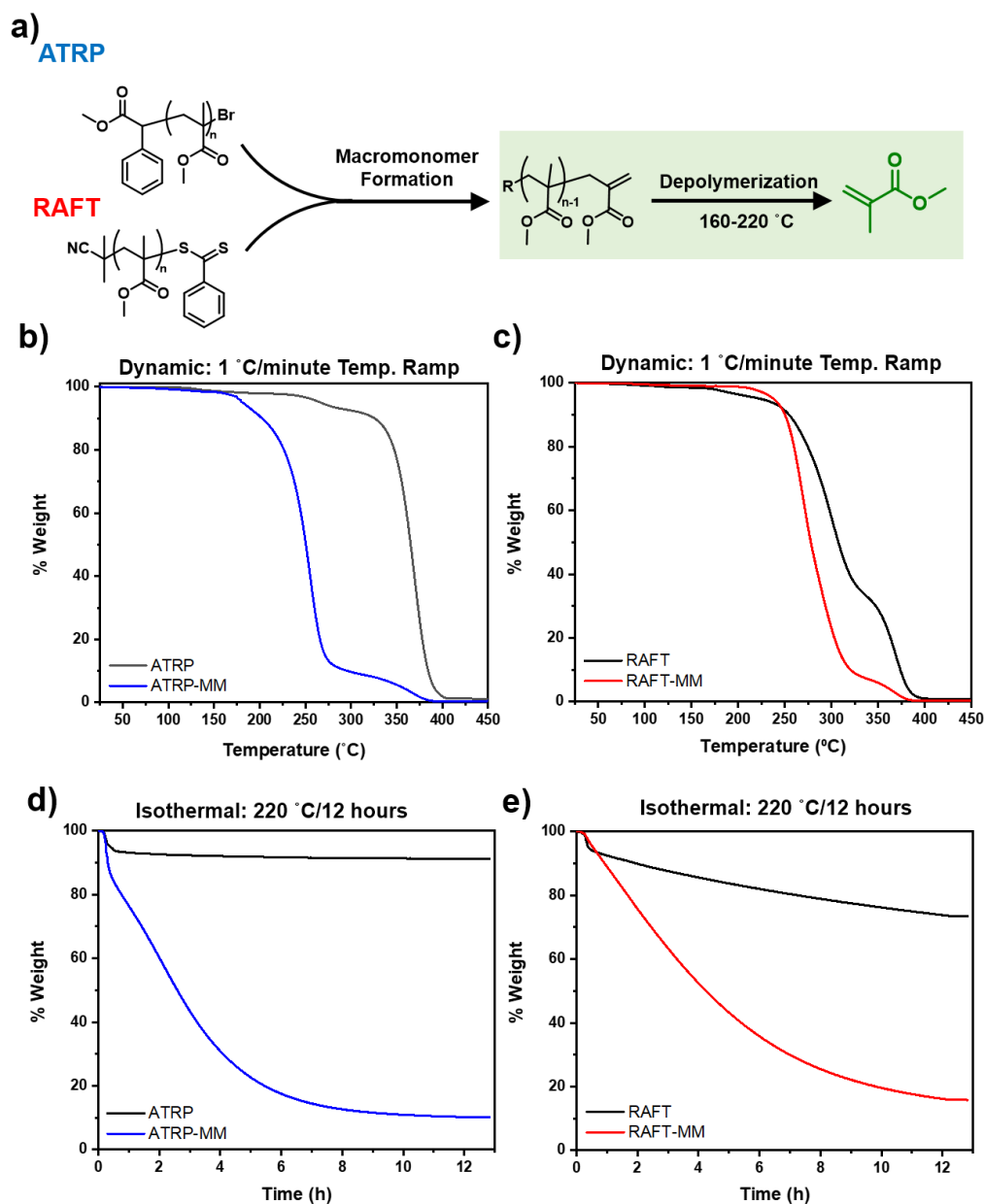


Figure 3: The effect of converting ATRP (left panels) and RAFT (right panels) polymers to macromonomer on the extent of their respective depolymerization. In a) a scheme illustrates the formation of macromonomer and the subsequent depolymerization. In b) and c) TGA traces are presented with experiments performed using a heating rate of 1 °C per minute, and in d) and e) TGA traces are presented with experiments performed at a constant temperature of 220 °C for 12 hours after heating at 10 °C/minute.

Considering the success of these experiments, we envisaged that we could further leverage this macromonomer transformation strategy to also lower the depolymerization temperatures of RAFT-synthesized polymers. By following a similar transformation strategy with the ATRP analogues, the end-group of PMMA produced by RAFT polymerization was

modified under the optimal reaction conditions: [PMMA]:[MMA]:[AIBN]:[CoBF] of 1:5:0.08:0.15 at 80 °C in acetonitrile achieving approximately 90% of macromonomer formation (Figures S22-S23).⁷¹ Similarly, after purification, a depolymerization experiment was performed (Figures 3c). Interestingly, the RAFT macromonomer had a much faster depolymerization than the original RAFT polymer. In addition, higher depolymerization conversions at lower temperatures could also be achieved with 90% weight loss for the RAFT macromonomer as opposed to 66% weight loss for the RAFT polymer. The difference in rate was attributed to the additional step required to form the macromonomer for the initial RAFT polymer, the presence of degraded thiol species in the depolymerization mixture or the occurrence of a potential side reaction, i.e. backbiting or radical chain transfer. These side reactions could be of particular importance, as one-third of the original RAFT polymer chains did not form macromonomer on heating, but instead formed a thermally stable end-group and only depolymerized through a much higher temperature side group or backbone triggered scission pathway. Instead, by converting the RAFT polymer to macromonomer, this side-reaction was avoided, thus resulting in a lower temperature depolymerization and up to 90% of depolymerization conversion. Isothermal experiments for both the ATRP and RAFT derived macromonomers were subsequently conducted (Figures 3d-e). After 12 hours at 220 °C, 85-90% depolymerization of the macromonomers could be achieved in both cases. This compares favourably to both of the precursor polymers, where it was only possible to achieve 8% and 27% under otherwise identical conditions, further emphasizing the success of our approach. To achieve more than 90% depolymerization either a gradual temperature ramp to 260 °C is required, or the temperature can be reduced to 220 °C when longer reaction times are utilized. Together, these temperatures are significantly lower than those reported for repeat unit scission so in both cases there is a vast improvement in comparison to their unmodified precursors, where around 400 °C was required to achieve full depolymerization.

Finally, a further advantage of bulk depolymerization that we wanted to fully exploit is the ability to scale up the reactions (Figure 4a) and obtain pristine monomer considering that scission events can be eliminated at our lower depolymerization temperatures. A particularly challenging task for solution approaches is the low concentrations at which they are performed, for example, to successfully depolymerize 5g of polymer at 5mM repeat unit concentration, 10 litres of solvent would be required.³⁵ This makes the scale-up of these depolymerization processes unfeasible. Alternative scalable approaches in bulk, have only been reported at temperatures greater than 400 °C.⁴⁶⁻⁴⁹ To address this, a higher scale vacuum distillation at 220 °C was performed starting with a 10 g of an ATRP-derived macromonomer (Figures 4b-d & S24-26). After 4 h of reaction, 8.4 g of monomer could be regenerated (84% yield) and the retrieved MMA was obtained in a high purity. The collected monomer was then

employed, without any further purification, to synthesize another batch of both ATRP and RAFT polymer with controlled molecular weight and dispersity, further illustrating the closed-loop nature of our approach (Figures 4c-d & S27). Together this exemplifies the success of our strategy, with low-temperature high scale depolymerization being attainable, while generating monomer in high yields.

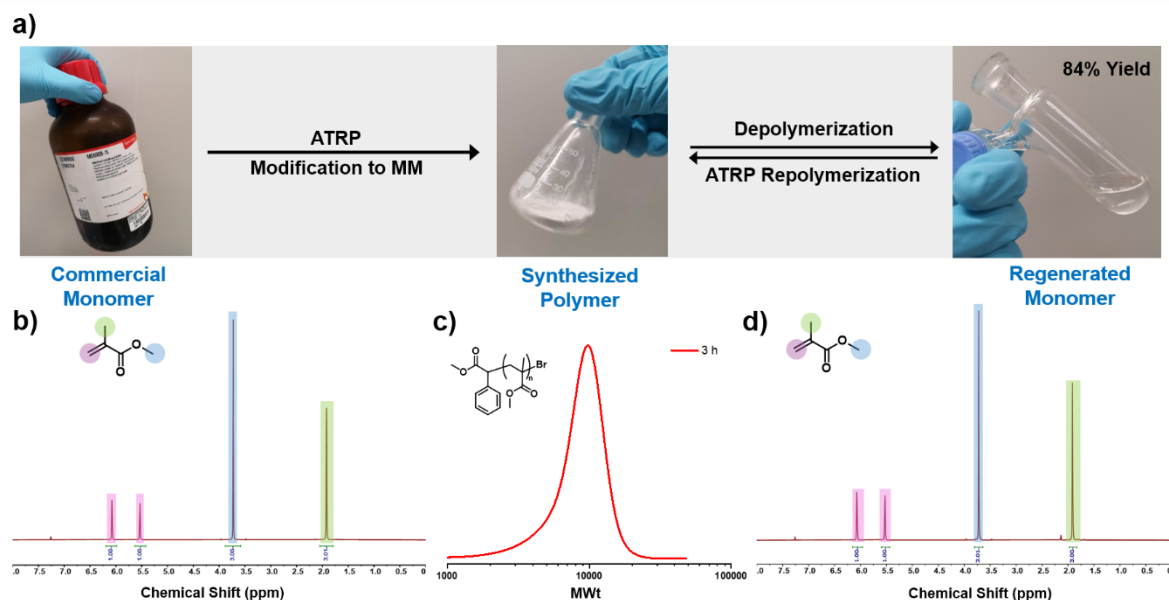


Figure 4: The closed-loop and scalable depolymerization of PMMA obtained from ATRP. In a), photographs show the commercial monomer being polymerized and modified into macromonomer, followed by the depolymerization of this polymer regenerating the starting monomer. In b), a ^1H NMR spectrum of commercial monomer is presented, in c) SEC chromatogram illustrating a polymer produced from regenerated monomer, and in d) a ^1H NMR of regenerated monomer is shown.

Conclusions

In this work we showed that through an efficient end-group modification strategy, polymers synthesized by either ATRP or RAFT polymerizations can undergo a low temperature bulk depolymerization with onset temperatures at as low as 150 °C. Notably, very high depolymerization conversions exceeding 90% could be achieved within a short time-scale. Our approach proceeds in the complete absence of solvents, without requiring additional catalysts or components and can regenerate high purity monomer in a very high yield. Scalability of our methodology via vacuum distillation up to 10 g was also demonstrated thus highlighting the robustness of this strategy. The recovered pristine monomer was subsequently employed for another polymerization cycle resulting in the synthesis of a well-defined polymer with low dispersity. This is a potentially important step in developing scalable

and more energy efficient depolymerization and generates many future new research directions for chemical recycling.

Acknowledgments

A.A. gratefully acknowledges ETH Zurich (Switzerland) and the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (DEPO: Grant No. 949219) for financial support. N.P.T. acknowledges the award of a DECRA Fellowship from the ARC (DE180100076). We acknowledge Professor Markus Niederberger and Ms. Aina Perappadan (Laboratory for Multifunctional Materials) for access to the TGA instrument, and Dr. Louis Bertschi and Mr. Daniel Wirz (MoBias) for access to the MALDI-ToF Mass Spectrometer.

Conflicts of Interest

The authors declare no competing interests.

References

1. N. Corrigan, K. Jung, G. Moad, C. J. Hawker, K. Matyjaszewski and C. Boyer, *Prog. Polym. Sci.*, 2020, **111**, 101311.
2. J.-S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, 1995, **117**, 5614-5615.
3. J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 1998, **31**, 5559-5562.
4. S. Perrier, *Macromolecules*, 2017, **50**, 7433-7447.
5. F. Lorandi, M. Fantin and K. Matyjaszewski, *J. Am. Chem. Soc.*, 2022, **144**, 15413-15430.
6. R. Whitfield, N. P. Truong, D. Messmer, K. Parkatzidis, M. Rolland and A. Anastasaki, *Chem. Sci.*, 2019, **10**, 8724-8734.
7. C. Barner-Kowollik, *Handbook of RAFT polymerization*, John Wiley & Sons, Weinheim, Germany, 2008.
8. D. A. Shipp, J.-L. Wang and K. Matyjaszewski, *Macromolecules*, 1998, **31**, 8005-8008.
9. K. Parkatzidis, H. S. Wang, N. P. Truong and A. Anastasaki, *Chem*, 2020, **6**, 1575-1588.
10. G. Polymeropoulos, G. Zapsas, K. Ntetsikas, P. Bilalis, Y. Gnanou and N. Hadjichristidis, *Macromolecules*, 2017, **50**, 1253-1290.
11. L. Barner, T. P. Davis, M. H. Stenzel and C. Barner-Kowollik, *Macromol. Rapid Commun.*, 2007, **28**, 539-559.
12. M.-N. Antonopoulou, R. Whitfield, N. P. Truong, D. Wyers, S. Harrison, T. Junkers and A. Anastasaki, *Nat. Chem.*, 2022, **14**, 304-312.
13. H. Dau, G. R. Jones, E. Tsogtgerel, D. Nguyen, A. Keyes, Y.-S. Liu, H. Rauf, E. Ordonez, V. Puchelle and H. Basbug Alhan, *Chem. Rev.*, 2022, **122**, 14471-14553.
14. G. W. Coates and Y. D. Getzler, *Nat. Rev. Mater.*, 2020, **5**, 501-516.
15. M. Hong and E. Y.-X. Chen, *Green Chem.*, 2017, **19**, 3692-3706.
16. R. Chinthapalli, P. Skoczinski, M. Carus, W. Baltus, D. de Guzman, H. Käß, A. Raschka and J. Ravenstijn, *Ind. Biotechnol.*, 2019, **15**, 237-241.
17. Y. Miao, A. von Jouanne and A. Yokochi, *Polymers*, 2021, **13**, 449.
18. M. R. Martinez and K. Matyjaszewski, *CCS Chemistry*, 2022, 1-36.
19. F. Bennet, G. Hart-Smith, T. Gruending, T. P. Davis, P. J. Barker and C. Barner-Kowollik, *Macromol. Chem. Phys.*, 2010, **211**, 1083-1097.
20. F. Fleischhaker, A. P. Haehnel, A. M. Misske, M. Blanchot, S. Haremza and C. Barner-Kowollik, *Macromol. Chem. Phys.*, 2014, **215**, 1192-1200.
21. A. H. Soeriyadi, V. Trouillet, F. Bennet, M. Bruns, M. R. Whittaker, C. Boyer, P. J. Barker, T. P. Davis and C. Barner-Kowollik, *J. Polym. Sci. Pol. Chem.*, 2012, **50**, 1801-1811.

22. S. Kobben, A. Ethirajan and T. Junkers, *J. Polym. Sci. Pol. Chem.*, 2014, **52**, 1633-1641.
23. A. Adili, A. B. Korpusik, D. Seidel and B. S. Sumerlin, *Angew. Chem. Int. Ed.*, 2022, **61**, e202209085.
24. J. B. Garrison, R. W. Hughes and B. S. Sumerlin, *ACS Macro Lett.*, 2022, **11**, 441-446.
25. R. Geyer, in *Plastic waste and recycling*, Elsevier, 2020, pp. 13-32.
26. R. Geyer, J. R. Jambeck and K. L. Law, *Sci. Adv.*, 2017, **3**, e1700782.
27. S. C. I. E. C. I. E. i. E. Defruyt, *Field Actions Sci. Rep.*, 2019, 78-81.
28. G. Moad and D. H. Solomon, *Sustainability*, 2021, **13**, 8218.
29. E. Van Artsdalen, *J. Chem. Phys.*, 1942, **10**, 653-653.
30. Y. Sano, T. Konishi, M. Sawamoto and M. Ouchi, *Eur. Polym. J.*, 2019, **120**, 109181.
31. M. R. Martinez, S. Dadashi-Silab, F. Lorandi, Y. Zhao and K. Matyjaszewski, *Macromolecules*, 2021, **54**, 5526-5538.
32. M. R. Martinez, F. De Luca Bossa, M. Olszewski and K. Matyjaszewski, *Macromolecules*, 2022, **55**, 78-87.
33. M. R. Martinez, D. Schild, F. De Luca Bossa and K. Matyjaszewski, *Macromolecules*, 2022.
34. M. J. Flanders and W. M. Gramlich, *Polym. Chem.*, 2018, **9**, 2328-2335.
35. H. S. Wang, N. P. Truong, Z. Pei, M. L. Coote and A. Anastasaki, *J. Am. Chem. Soc.*, 2022, **144**, 4678-4684.
36. H. S. Wang, N. P. Truong, G. R. Jones and A. Anastasaki, *ACS Macro Lett.*, 2022, **11**, 1212-1216.
37. J. B. Young, J. I. Bowman, C. B. Eades, A. J. Wong and B. S. Sumerlin, *ACS Macro Lett.*, 2022, **11**, 1390-1395.
38. V. Bellotti, K. Parkatzidis, H. S. Wang, N. D. A. Watuthanthrige, M. Orfano, A. Monguzzi, N. P. Truong, R. Simonutti and A. Anastasaki, *Polym. Chem.*, 2023, **14**, 253-258.
39. B. Chong, G. Moad, E. Rizzardo, M. Skidmore and S. H. Thang, *Aust. J. Chem.*, 2006, **59**, 755-762.
40. M. Z. Bekanova, N. K. Neumolotov, A. D. Jablanović, A. V. Plutalova, E. V. Chernikova and Y. V. Kudryavtsev, *Polym. Degrad. Stab.*, 2019, **164**, 18-27.
41. A. Postma, T. P. Davis, G. Moad and M. Shea, *Macromolecules*, 2005, **38**, 5371-5374.
42. S. J. Stace, C. M. Fellows, G. Moad and D. J. Keddie, *Macromol. Rapid Commun.*, 2018, **39**, 1800228.
43. G. Moad, E. Rizzardo and S. H. Thang, *Polym. Int.*, 2011, **60**, 9-25.
44. C. Borman, A. Jackson, A. Bunn, A. Cutter and D. Irvine, *Polymer*, 2000, **41**, 6015-6020.
45. L. E. Manring, *Macromolecules*, 1989, **22**, 2673-2677.
46. T. Faravelli, M. Pinciroli, F. Pisano, G. Bozzano, M. Dente and E. Ranzi, *J. Anal. Appl. Pyrolysis*, 2001, **60**, 103-121.
47. L. E. Manring, *Macromolecules*, 1991, **24**, 3304-3309.
48. W. Kaminsky and J. Franck, *J. Anal. Appl. Pyrolysis*, 1991, **19**, 311-318.
49. L. S. Diaz-Silvarrey, K. Zhang and A. N. Phan, *Green Chem.*, 2018, **20**, 1813-1823.
50. L. E. Manring, *Macromolecules*, 1988, **21**, 528-530.
51. Z. Czech, K. Agnieszka, P. Ragańska and A. Antosik, *J. Therm. Anal. Calorim.*, 2015, **119**, 1157-1161.
52. A. Monroy-Alonso, A. Ordaz-Quintero, J. C. Ramirez and E. Saldívar-Guerra, *Polymers*, 2021, **14**, 160.
53. R. A. Gilsdorf, M. A. Nicki and E. Y.-X. Chen, *Polym. Chem.*, 2020, **11**, 4942-4950.
54. T. Junkers and C. Barner-Kowollik, *J. Polym. Sci. Pol. Chem.*, 2008, **46**, 7585-7605.
55. G. Moad, E. Rizzardo and S. H. Thang, *Acc. Chem. Res.*, 2008, **41**, 1133-1142.
56. D. Konkolewicz, K. Schröder, J. Buback, S. Bernhard and K. Matyjaszewski, *ACS Macro Lett.*, 2012, **1**, 1219-1223.
57. S. Dadashi-Silab, X. Pan and K. Matyjaszewski, *Macromolecules*, 2017, **50**, 7967-7977.
58. C. Barner-Kowollik, M. Buback, B. Charleux, M. L. Coote, M. Drache, T. Fukuda, A. Goto, B. Klumperman, A. B. Lowe and J. B. Mcleary, *J. Polym. Sci. Pol. Chem.*, 2006, **44**, 5809-5831.
59. C. B. Godiya, S. Gabrielli, S. Materazzi, M. S. Pianesi, N. Stefanini and E. Marcantoni, *J. Environ. Manage.*, 2019, **231**, 1012-1020.
60. T. Kashiwagi, A. Inabi and A. Hamins, *Polym. Degrad. Stab.*, 1989, **26**, 161-184.
61. J. P. Heuts and N. M. Smeets, *Polym. Chem.*, 2011, **2**, 2407-2423.
62. D. M. Haddleton, D. R. Maloney, K. G. Suddaby, A. V. Muir and S. N. Richards, *Macromo. Symp.*, 1996, **111**, 37-46.
63. A. H. Janowicz, *Journal*, 1987, U.S. Patent 4,694,054.
64. S. Yamago, E. Kayahara and H. Yamada, *React. Funct. Polym.* 2009, **69**, 416-423.

65. N. P. Truong, G. R. Jones, K. G. Bradford, D. Konkolewicz and A. Anastasaki, *Nat. Rev. Chem.*, 2021, **5**, 859-869.
66. R. Whitfield, K. Parkatzidis, N. P. Truong, T. Junkers and A. Anastasaki, *Chem*, 2020, **6**, 1340-1352.
67. R. Whitfield, K. Parkatzidis, M. Rolland, N. P. Truong and A. Anastasaki, *Angew. Chem. Int. Ed.*, 2019, **58**, 13323-13328.
68. R. Snow and F. Frey, *J. Am. Chem. Soc.*, 1943, **65**, 2417-2418.
69. S. Penczek and K. Kaluzynski, *Thermodynamic and kinetic polymerizability*, 2012, **4**, 5-20.
70. D. Grant and S. Bywater, *J. Chem. Soc. Faraday Trans.*, 1963, **59**, 2105-2112.
71. A. H. Soeriyadi, C. Boyer, J. Burns, C. R. Becer, M. R. Whittaker, D. M. Haddleton and T. P. Davis, *Chem. Commun.*, 2010, **46**, 6338-6340.