

Beyond the Chemical Recycling of Polymethacrylates: Depolymerization of Polymethacrylamides

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Abstract: Over the past years, depolymerization has become a focal point of polymer research aiming at improving chemical recycling of various polymer classes. Herein, we present the purely thermal depolymerization of polymethacrylamides made by reversible addition-fragmentation chain-transfer polymerization at temperatures as low as 90 °C. By addition of a free radical initiator, a rapid depolymerization to high conversions was achieved, overcoming end-group degradation that previously led to lower yields. The developed methodology was subsequently applied to a crosslinked hydrogel, which could be effectively reverted back to its monomer, thus highlighting the versatility of our strategy.

Keywords: Depolymerization · Polymethacrylamides



Victoria Lohmann obtained her MSc in Chemistry from ETH Zurich in 2022 working on the synthesis of polymeric nanoparticles in emulsion. She subsequently joined the Laboratory of Sustainable Polymers for her doctoral studies under the supervision of Prof. Athina Anastasaki, where she is researching new ways to chemically recycle vinyl polymers.

1. Introduction

Plastics are an incredibly versatile and highly modifiable material class that has transformed our way of life since their commercial inception in the 20th century. While there are undeniable benefits to continuing to use plastic, the issue of what to do with plastic at the end of its lifecycle remains challenging. As a consequence, only about 9% of plastic waste is currently recycled globally, with about 8 Mt ending up in the oceans every year.^[1] Therefore, it is clear that technological advances are necessary to improve these numbers. Apart from the challenge of properly collecting and sorting plastic waste for recycling, the low recycling quota is a result of the intrinsic limitations associated with mechanical recycling, which is the most common recycling methodology: not all plastics are amenable to mechanical recycling, contaminations and additives accumulate over multiple cycles, the resulting material suffers from thermomechanical degradation, and the new material is limited to the initial properties of the recyclate.^[2] As a result, the recycled materials are commonly mixed with virgin materials or used for lower value applications. One way to overcome many of these limitations is to conduct chemical recycling to monomer (CRM), also called depolymerization, whereby the polymer is broken apart along its backbone. This does not only enable the resyntheses of any desired material from the smallest building block, but also represents an atom-efficient version of chemical recycling, as it is an ideal closed loop.^[3]

For vinyl polymers with all-carbon backbones, this is especially challenging due to the inherent stability of the carbon-carbon bond. At high temperatures, polyolefins, polystyrenes, and polymethacrylates have been reported to revert back to monomer, in the process of pyrolysis, though this typically requires temperatures in excess of 400 °C. However, upon a closer look, it becomes apparent that this higher temperature is not required to thermodynamically achieve depropagation of the polymers like polymethacrylates, but rather to initiate an active species on the chain that can subsequently release the monomer.^[4] If this kinetic barrier to CRM of vinyl polymers was overcome, depolymerization would become feasible under mild conditions.

This was the starting point for depolymerization research in our group. By applying concepts from controlled radical polymerization (CRP), where chain-end functionality is introduced into a polymer to gain control over the molecular-weight distribution, functional end-groups were installed on the polymer. These can be activated under mild conditions to generate a chain-end radical. When a chain-transfer agent was installed on a polymethacrylate *via* reversible addition-fragmentation chain-transfer (RAFT) polymerization, such methacrylates depolymerised to high conversions at 120 °C in dilute solution.^[5] Since this report, depolymerization has been achieved under various reaction conditions, even in bulk without any solvent,^[6] and has also expanded the analytical toolbox for polymers.^[7] Beyond thermally depolymerising, light could also be used as a stimulus for the reaction.^[8] Polymethacrylates could also be depolymerised using transition metal catalysts on halogen-terminated polymers synthesised by atom-transfer radical polymerization (ATRP), employing various external stimuli.^[9] All in all, the past few years of research have proven that such CRP-derived methods are very effective at depolymerising polymethacrylates. However, other polymer classes beyond polymethacrylates remain underexplored. To remedy this, we have looked at other polymer classes that exhibited thermodynamic feasibility for depolymerization under mild conditions. Polymethacrylamides were an interesting polymer class, as they have high theoretical depolymerisability, comparable to their methacrylate counterparts, but had not been as widely reported to depolymerise under higher temperatures as their methacrylate counterparts have. Therefore, we wanted to see if we could move beyond the polymethacrylates.

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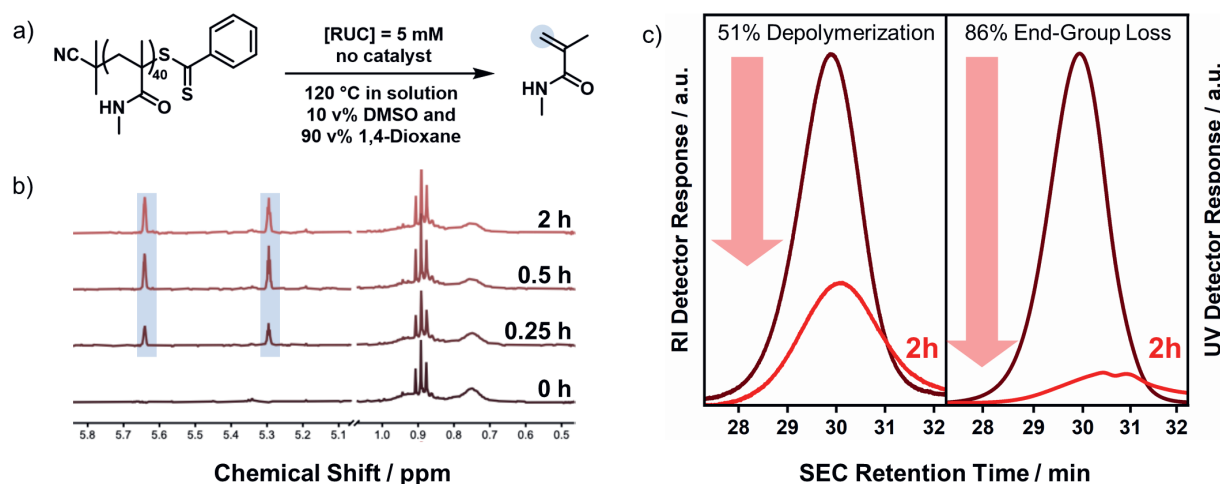


Fig. 1. a) Reaction scheme of the depolymerization of poly(methyl methacrylamide) (PMMAM) under standard conditions. b) ¹H-NMR spectra at various time points during the reaction. c) Size exclusion chromatography (SEC) analysis of polymer before and after depolymerization. Fig. adapted from Ref. [10] with permission, © 2025 The Author(s). *Angewandte Chemie International Edition* published by Wiley-VCH GmbH.

2. Towards Depolymerization of Polymethacrylamides at Low Temperature

In order to attempt the depolymerization of polymethacrylamides, we synthesised poly(methyl methacrylamide) (PMMAM) *via* RAFT polymerization to install a dithiobenzoate chain-transfer agent (CTA) on the chain end.^[10] When the polymer was subsequently heated to 120 °C in a solution of 10 v% DMSO and 90 v% 1,4-dioxane (Fig. 1a), 54% of monomer was regenerated in 2 hours (Fig. 1b), which also corresponded to a similar reduction of polymer concentration in the SEC analysis (Fig. 1c).

Such limited conversion was surprising since methacrylamides were expected to behave comparably to the corresponding methacrylates due to their structural similarity. The corresponding methacrylate depolymerized gradually to high conversion under the same reaction conditions. Additionally, a thermodynamic limitation of the reaction could be excluded.^[10] More detailed kinetic analysis revealed that while the reaction initially proceeded in a rapid fashion, it plateaued off after an hour (Fig. 2). Since a functional chain-end is essential for polymer activation at lower temperatures, our hypothesis was that the polymethacrylamides might suffer from extensive end-group loss *via* a non-radical side reaction, which would prevent further activation and hence depolymerization. Compared to the corresponding methacrylate, a more rapid end-group loss could indeed be observed for the depolymerization of PMMAM (Fig. 1c).

We posited that a much faster activation of the chain-end would outcompete such end-group loss and hence allow for higher depolymerization conversions as well as a faster reaction. In the initial system, the chain-end activation was facilitated by addition of solvent-derived radicals (Fig. 3a).^[11] The addition of 2 equiv. of a free radical initiator (azobis(cyclohexanecarbonitrile), ABCN) to the chain-end, with a relatively high 10-hour half-life temperature, increased the concentration of radicals in the reaction, which indeed led to a faster depolymerization and consequently higher conversion (Fig. 2b). These optimised reaction conditions were then applied to polymethacrylamides with varying pendant groups (phenyl, 2-hydroxypropyl (HPMAM), and isopropyl), which all depolymerised to high conversions (72–86%). Furthermore, polymers bearing trithiocarbonate CTAs could also be successfully depolymerised, demonstrating compatibility with a range of reaction conditions.^[10]

Encouraged by the increased depolymerization rate observed after the addition of a free radical initiator to the reaction, we

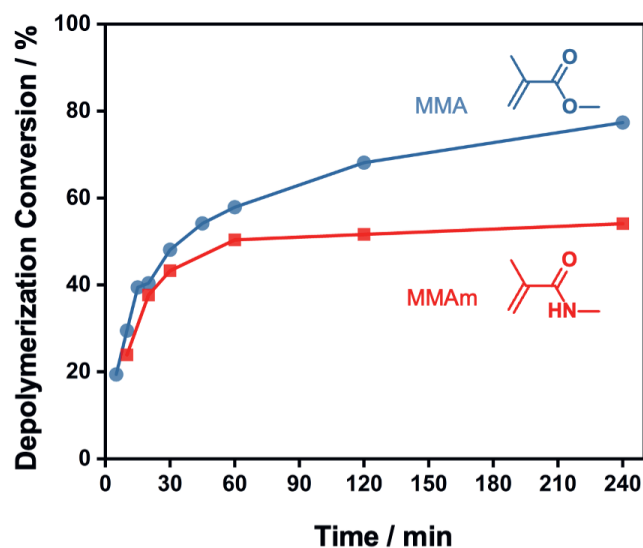


Fig. 2. Kinetic studies of the depolymerization of PMMAM (red) and poly(methyl methacrylate) under identical conditions. Fig. adapted from Ref. [10] with permission, © 2025 The Author(s). *Angewandte Chemie International Edition* published by Wiley-VCH GmbH.

suspected that the reaction was thermodynamically favourable enough to lower the reaction temperature. Consequently, depolymerization was conducted at 90 °C instead of 120 °C, which constituted a significant temperature reduction (Fig. 4). While the lower temperature did reduce the reaction rate, the depolymerization was still able to reach comparable conversions after 1 hour. Since the lower reaction temperature most likely reduced side reactions, this helped to retain polymer livingness and hence preserve overall depolymerization conversion.

Lastly, we sought to apply the depolymerization conditions to a hydrogel, a material, which cannot be mechanically recycled and is a common application for polymethacrylamides. This hydrogel, based on HPMAM crosslinked with poly(ethylene glycol) dimethacrylate, placed in the standard reaction solution at 90 °C together with ABCN, depolymerised, leading to full dissolution caused by disintegration of the crosslinked material within 2 hours of reaction (Fig. 5).

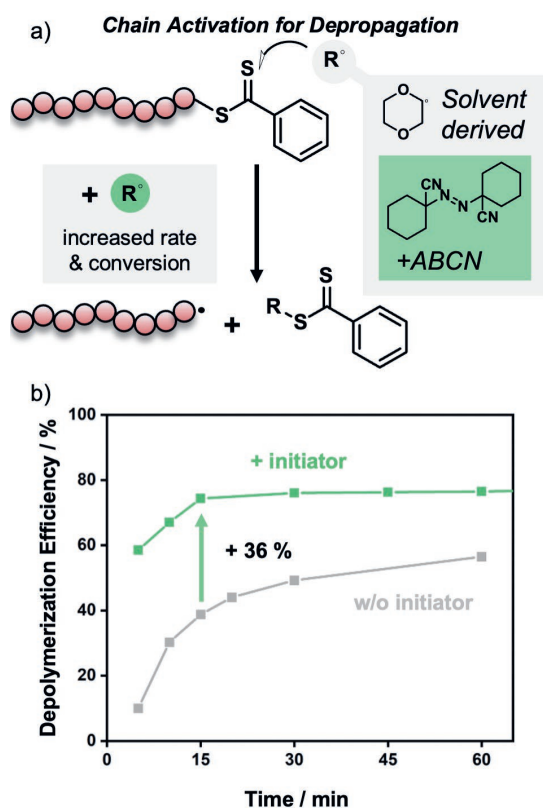


Fig. 3. a) Schematic representation of the chain activation for depolymerization with the solvent-derived radical (grey) and added initiator (azobis(cyclohexanecarbonitrile), ABCN, green). b) Kinetic study of the depolymerization without initiator (grey) and with 2 equiv. of ABCN (green). Fig. adapted from Ref. [10] with permission, © 2025 The Author(s). *Angewandte Chemie International Edition* published by Wiley-VCH GmbH.

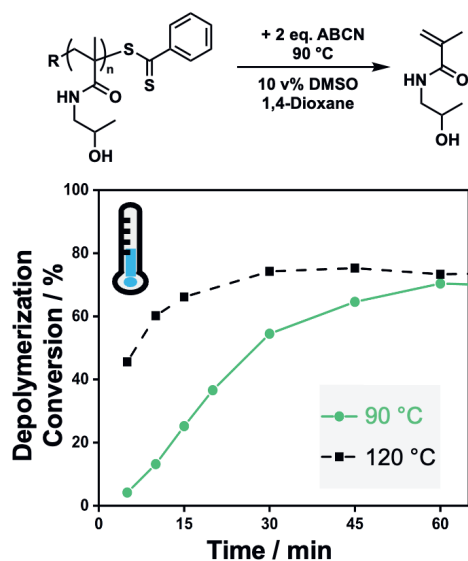


Fig. 4. Depolymerization of poly(2-hydroxypropyl methacrylamide) at 90 °C (green) and 120 °C (black) with 2 equiv. of free radical initiator. Fig. adapted from Ref. [10] with permission, © 2025 The Author(s). *Angewandte Chemie International Edition* published by Wiley-VCH GmbH.

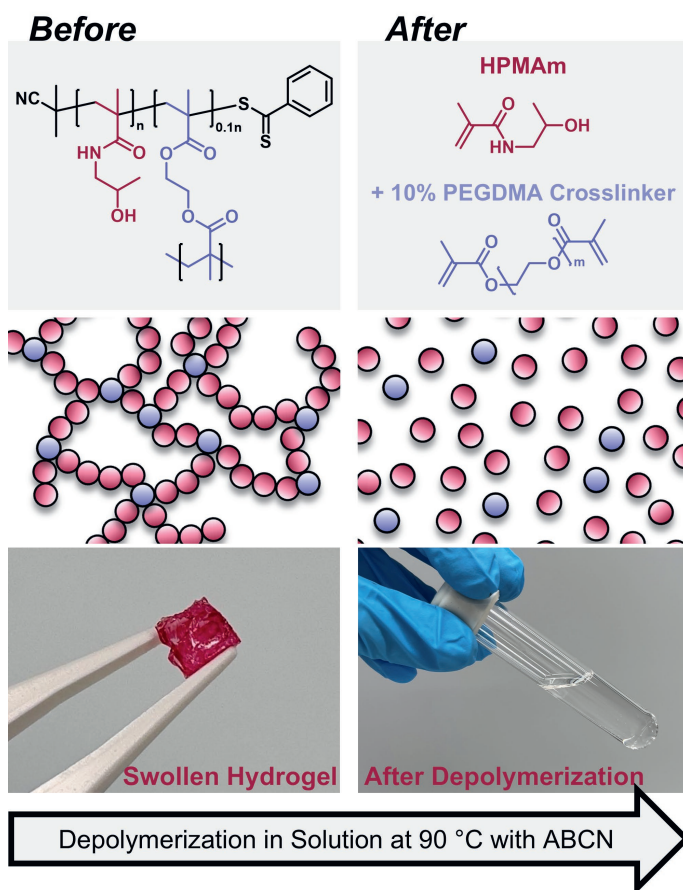


Fig. 5. Depolymerization of a hydrogel made from hydroxypropyl methacrylamide (HPMAM) crosslinked with poly(ethylene glycol) dimethacrylate. Fig. adapted from Ref. [10] with permission, © 2025 The Author(s). *Angewandte Chemie International Edition* published by Wiley-VCH GmbH.

3. Conclusions

Altogether, we developed reaction conditions for the depolymerization of various polymethacrylamides,^[10] which allowed for rapid depolymerization with high conversions. The addition of a free radical initiator was crucial to the process, as it increased the reaction rate, thereby essentially outrunning competing side reactions. The rapid depolymerization then allowed for a temperature reduction to 90 °C. The resulting mild reaction conditions could then be applied to a HPMAM-based hydrogel, which demonstrated the compatibility of the methodology even with heterogeneous materials.

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