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Chemical Recycling of Polymethacrylates Synthesized by RAFT Polymerization

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[§]SCS-DSM Award for the best poster in Polymers, Colloids & Interfaces

Abstract: Reversing controlled radical polymerization and regenerating the monomer has been a long-standing challenge for fundamental research and practical applications. Herein, we report a highly efficient depolymerization method for various polymethacrylates synthesized by reversible addition-fragmentation chain-transfer (RAFT) polymerization. The depolymerization process, which does not require any catalyst, exhibits near-quantitative conversions of up to 92%. The key aspect of our approach is the utilization of the high end-group fidelity of RAFT polymers to generate chain-end radicals at 120 °C. These radicals trigger a rapid unzipping of the polymethacrylates. The depolymerization product can be utilized to either reconstruct the linear polymer or create an entirely new insoluble gel that can also be subjected to depolymerization. Our depolymerization strategy offers a promising route towards the development of sustainable and efficient recycling methods for complex polymer materials.

Keywords: Chemical recycling · Depolymerization · Polymethacrylates · RAFT polymerization



Hyun Suk Wang received his B.Eng. and M.Eng. in Chemical & Biological Engineering from Korea University, Korea, where he worked on the self-assembly of block copolymers in thin films. In 2019, after a 7-month research internship at the Faculty of Pharmaceutical Sciences in Monash University, Australia, he joined the group of Prof. Athina Anastasaki at ETH Zurich. There, he is working on developing

mild depolymerization strategies for chemical recycling of plastics.

1. Introduction

1.1 Reversible Deactivation Radical Polymerization (RDRP)

Reversible deactivation radical polymerization (RDRP) is an advanced form of radical polymerization that enables the synthesis of well-defined polymers with controlled molecular weight, molecular weight distribution (*i.e.* dispersity), and architecture.^[1–5] As the name implies, RDRP relies on an efficient deactivation–activation equilibrium of propagating polymer chains (Fig. 1). Polymers that are synthesized by RDRP contain a chemical moiety at the chain terminus, widely referred to as an ‘end-group’. This end-group can be reactivated using various methods (*e.g.* a catalyst, exogenous radical, light, *etc.*) and allow either a post-synthetic end-group modification or a chain-extension when further monomer is added, the latter one leading to the formation of block copolymers. This is why materials synthesized by RDRP are referred to as ‘living’ polymers.

1.2 Reversible Addition-fragmentation Chain-transfer (RAFT) Polymerization

Reversible addition-fragmentation chain-transfer (RAFT) polymerization is one of the most widely used RDRP methodol-

ogy and arguably the most versatile.^[6–9] RAFT polymerization relies on the degenerative chain-transfer of propagating polymer chains as the deactivation mechanism. Ultimately, polymers synthesized by RAFT polymerization contain a chain-transfer agent (CTA), typically a thiocarbonylthio group, as the end-group.

1.3 Depolymerization of Polymethacrylates

Polymethacrylates are known to have a moderate ceiling temperature, which is the temperature at which the rate of polymerization and depolymerization are equal and thus there is no net reaction.^[10,11] Above the ceiling temperature, a net depolymerization is expected to occur. However, it is important to emphasize that these thermodynamics are relevant to an active polymer (*i.e.* a polymeric radical), not inactive (‘dead’) chains. For example, the ceiling temperature of an active poly(methyl methacrylate) (PMMA) radical in bulk is reported to be ~200 °C but in order to depolymerize commercially available PMMA, an excess of 300 °C is required as extra energy is needed to form the polymeric radical.^[11] Not only is this energy-inefficient, but also increases the probability of side reactions.

2. Depolymerization of PMMA Synthesized by RAFT Polymerization

Recently, we reported the near-quantitative depolymerization of bulky and non-bulky RAFT-polymethacrylates at 120 °C.^[12,13] The key to this methodology was to enable the formation of chain-end radicals in solution and drive the reaction equilibrium toward the regeneration of monomer by a combination of dilution and heat. PMMA was first synthesized *via* RAFT polymerization using 2-cyano-2-propyl dithiobenzoate as the RAFT agent, resulting in a dithiobenzoate-terminated PMMA (PMMA-DTB). The purified polymer was then dissolved in 1,4-dioxane at a repeat unit concentration of 5 mM and the solution was deoxygenated by bubbling with N₂ for 15 min. The solution was then heated to 120 °C in an oil bath to commence the depolymerization. After 15 min, vinyl proton peaks corresponding to the monomer MMA were visible by ¹H NMR analysis, alongside a decrease in the polymer backbone protons (Fig. 2). Later samples showed an increase in the intensity of the monomer signals and a decrease of

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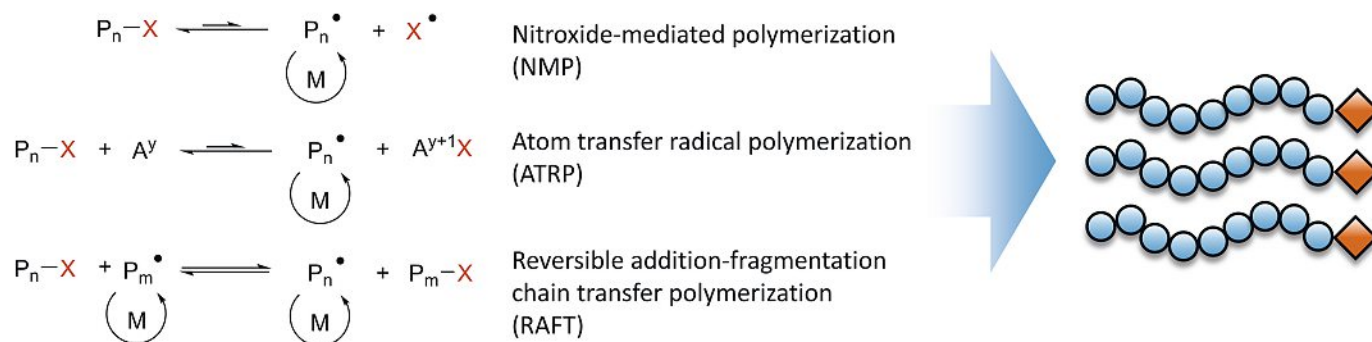


Fig. 1. Schematic of three of the most widely used RDRP techniques: nitroxide-mediated polymerization, atom transfer radical polymerization, and reversible addition-fragmentation chain-transfer polymerization.

the polymer signals, reaching a plateau when 86% conversion was reached. Furthermore, analysis of the reaction by size-exclusion chromatography (SEC) showed a decrease in the signal of the polymer peaks, indicating a decrease in the mass of polymer. In summary, these results demonstrated an efficient depolymerization of PMMA at low temperatures (120 °C versus >300 °C) via the reactivation of the CTA end-group.

3. Depolymerization of RAFT-Polymethacrylates

The scope of the depolymerization methodology was not limited to a single monomer, MMA, but also applicable to various polymethacrylates including those with various functional groups. Polymethacrylates with oligoethylene glycol, alkyl, aromatic, amine, fluorine, and hydroxyl functionalities underwent successful depolymerization into their original monomers (Fig.

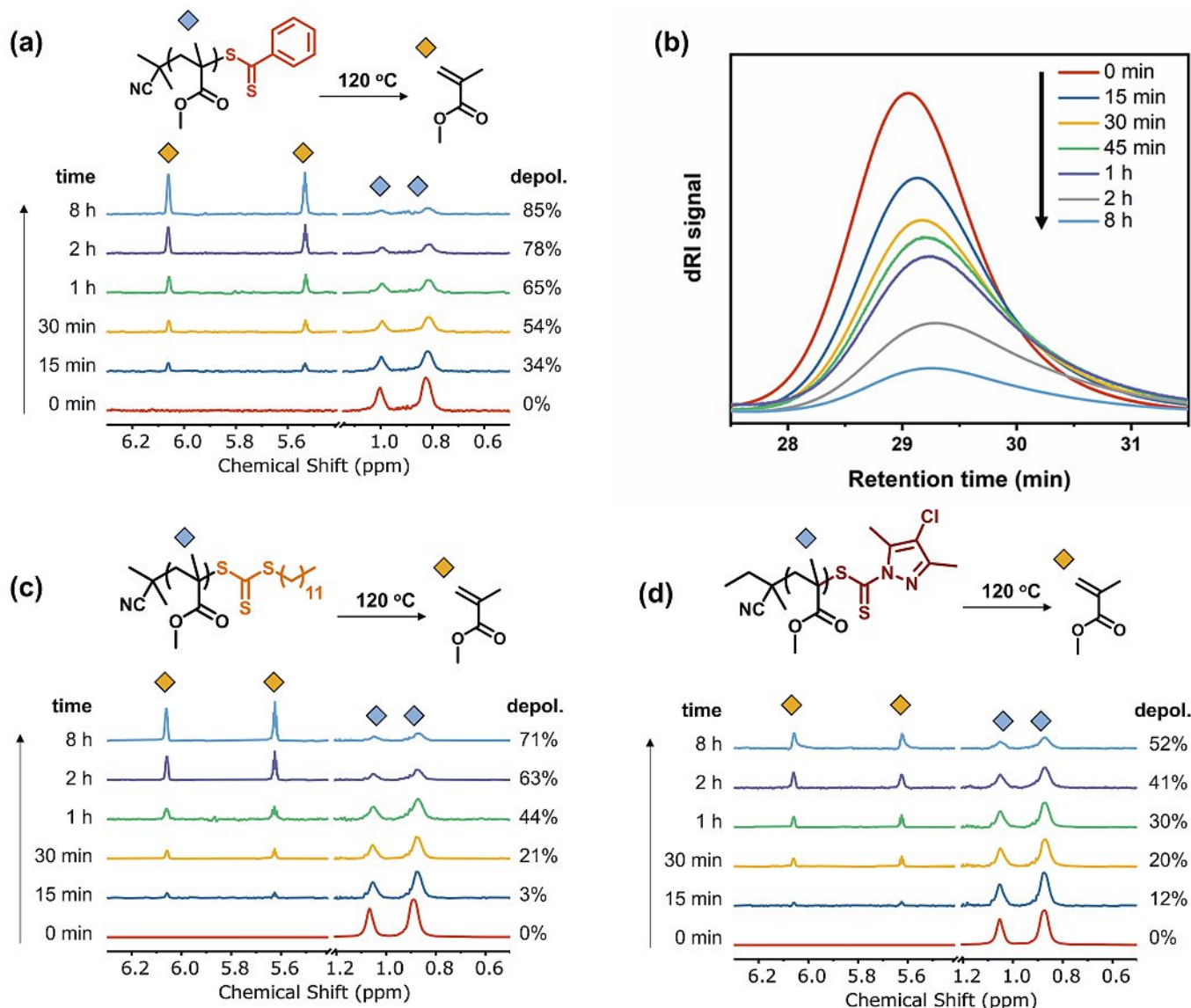


Fig. 2. (a) ^1H NMR spectra and (b) SEC traces of the depolymerization of dithiobenzoate-terminated PMMA. (a) was adapted from ref. [12] and (b) was adapted from ref. [13]. (c) ^1H NMR spectra of the depolymerization of trithiocarbonate-terminated PMMA and (d) pyrazole carbodithioate. Figures were adapted from ref. [13].

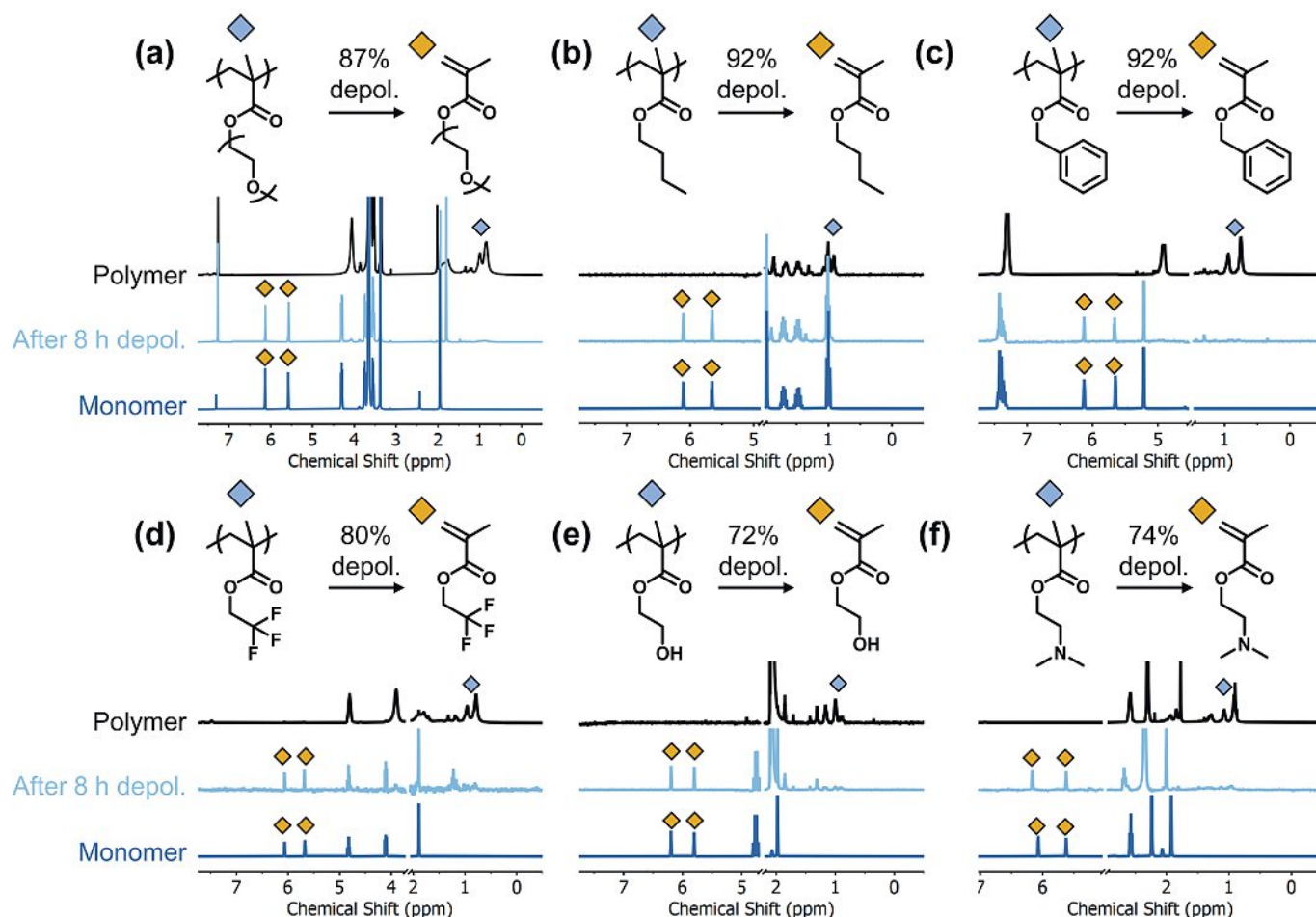


Fig. 3. ^1H NMR spectrum of the polymer, reaction mixture after depolymerization, and the original monomer for various polymethacrylates terminated by a dithiobenzoate end-group. Figure was adapted from ref. [12].

3). Notably, poly(*n*-butyl methacrylate) and poly(benzyl methacrylate) could be depolymerized to 92% monomer.

4. The Effect of the End-group

The scope of the end-group was also not limited to the dithiobenzoate end-group. PMMA samples terminated by a trithiocarbonate (TTC) and 4-chloro-3,5-dimethyl 1H-pyrazole-1-carbodithioate (pyrazoleCD) were both able to undergo depolymerization under identical conditions (5 mM of repeat unit in dioxane at 120 °C), indicating an efficient formation of chain-end radicals (Fig 2). However, a noticeable difference in the depolymerization conversion was observed between PMMA-DTB, PMMA-TTC, and PMMA-pyrazoleCD, with conversion increasing in the order pyrazoleCD < TTC < DTB. The reason behind the difference is currently unclear but most likely attributed to the fact that different RAFT end-groups have varying C–S bond strengths that connect that end-group to the polymer chain. The livingness of the chains (*i.e.* the fraction of polymers that contain the end-group) was concluded to be an insignificant factor as chain-extension experiments showed >94% livingness for PMMA-pyrazoleCD which showed only 52% depolymerized.

5. Depolymerization of Thermally Unstable Polymethacrylates

The low temperatures required for the depolymerization of RAFT-polymethacrylates opened an avenue to depolymerize polymers with thermally unstable side-chains. A prime example of a polymethacrylate with a thermally unstable side-chain is poly(*tert*-butyl methacrylate) whose *tert*-butyl group is prone to undergo elimination at >200 °C to form poly(methacrylic acid)

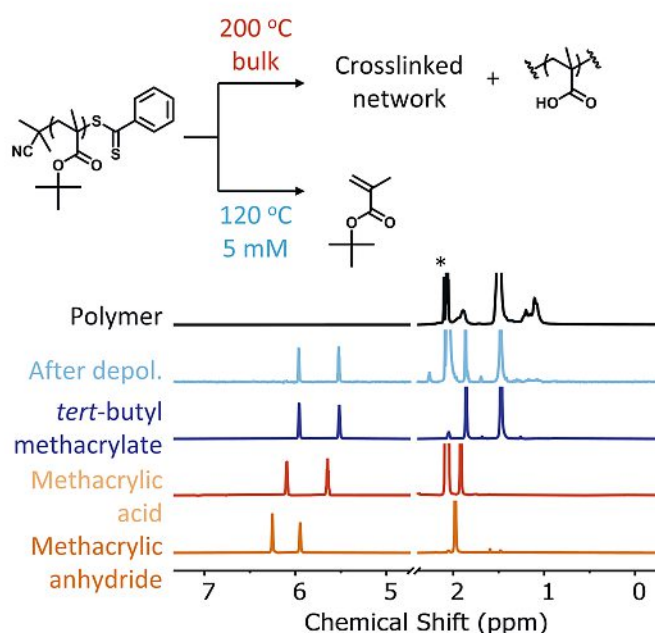


Fig. 4. Depolymerization of dithiobenzoate-terminated poly(*tert*-butyl methacrylate), a thermally unstable polymer, to regenerate *tert*-butyl methacrylate. Figure was adapted from ref. [13].

and isobutylene. Thus, conventional pyrolysis is unsuitable for the regeneration of *tert*-butyl methacrylate. Depolymerization of dithiobenzoate-terminated poly(*tert*-butyl methacrylate) at 120 °C

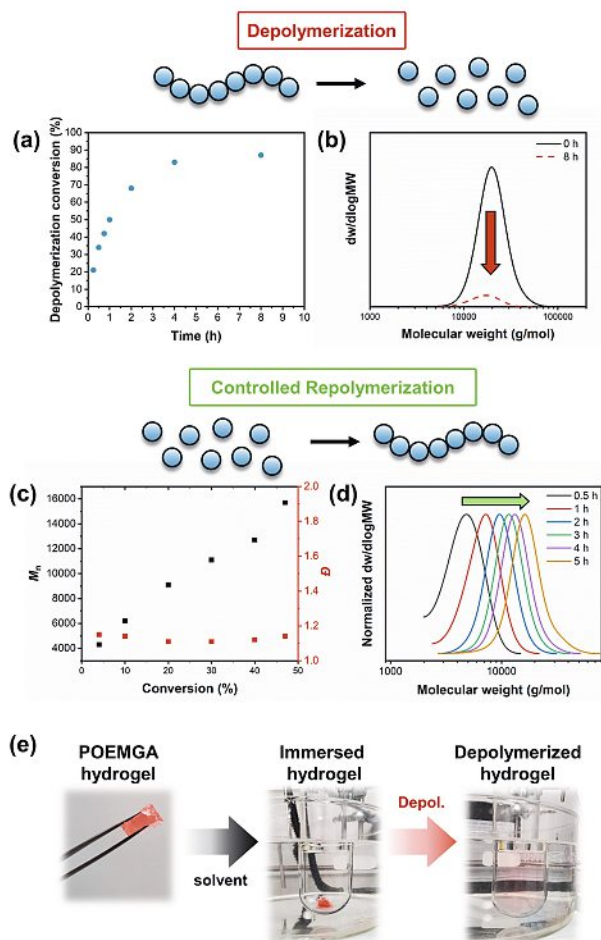


Fig. 5. (a, b) Depolymerization of dithiobenzoate-terminated poly(oligo(ethylene glycol) methyl ether methacrylate) and (c, d) repolymerization with the recycled RAFT agent. (e) Depolymerization of a poly(oligo(ethylene glycol) methyl ether methacrylate) hydrogel. Figure was adapted from ref. [12].

in dioxane yielded pure tert-butyl methacrylate, marking the first thermal regeneration of the monomer (Fig. 4).^[13]

6. Recycling of the RAFT Agent

An important question for the depolymerization of RAFT-polymethacrylates was whether the end-group CTA could also be recycled for subsequent RAFT polymerizations. This was an especially important matter as the RAFT agent is the most expensive reagent in a RAFT polymerization. It was found that a sufficient amount of the end-group could be reused after depolymerization, demonstrated by the RAFT re-polymerization of poly(oligo(ethylene glycol) methyl ether methacrylate) which yielded a controlled polymerization with low dispersity and a linear relationship between M_n and monomer conversion (Fig. 5a–d). Further studies to identify the precise amount of retrieved RAFT agent are currently undergoing in our laboratories.

7. Depolymerization of Insoluble Hydrogels

Many polymers used in everyday life are cross-linked to enhance their mechanical properties and chemical stability. A disadvantage of cross-linked materials is that they are insoluble in a solvent and thus hard to process. As the RAFT-based depolymerization was based on homogeneous solution chemistry, a remaining question was whether depolymerization is possible for insoluble network polymers. To this end, a hydrogel consisting of poly(oligo(ethylene glycol) methyl ether methacrylate) and its analogue dimethacrylate crosslinker was synthesized by RAFT

polymerization and a heterogeneous depolymerization was attempted. Pleasingly, the solution became homogeneous after 4 h (Fig 5e), indicating a disintegration of polymer networks, and ¹H NMR analysis showed the regeneration of both monomers.

8. Conclusion

In conclusion, we have developed a mild depolymerization methodology for polymethacrylates synthesized by RAFT polymerization. This strategy is applicable to various polymethacrylates, including those with thermally unstable side-chains. A variety of end-groups are compatible with this approach and can be recycled after a depolymerization cycle. Finally, insoluble network polymers could also be depolymerized, further expanding the versatility of this RAFT-based depolymerization. Other strategies that aid the depolymerization of RAFT-polymethacrylates through external stimuli including light are also actively being investigated.^[14,15]

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