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Reversing RAFT Polymerization: Near-Quantitative Monomer Generation Via a Catalyst-Free Depolymerization Approach

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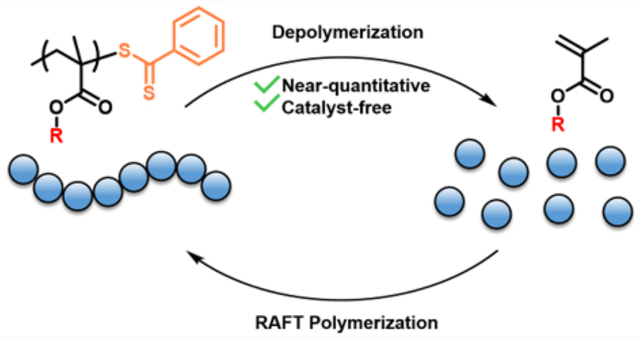
ABSTRACT: The ability to reverse controlled radical polymerization and regenerate the monomer would be highly beneficial for both fundamental research and applications, yet this has remained very challenging to achieve. Herein, we report a near-quantitative (up to 92%) and catalyst-free depolymerization of various linear, bulky, cross-linked, and functional polymethacrylates made by reversible addition−fragmentation chain-transfer (RAFT) polymerization. Key to our approach is to exploit the high end-group fidelity of RAFT polymers to generate chain-end radicals at 120 °C. These radicals trigger a rapid unzipping of both conventional (e.g., poly(methyl methacrylate)) and bulky (e.g., poly(oligo(ethylene glycol) methyl ether methacrylate)) polymers. Importantly, 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. This work expands the potential of polymers made by controlled radical polymerization, pushes the boundaries of depolymerization, offers intriguing mechanistic aspects, and enables new applications.



■ INTRODUCTION

Controlled radical polymerization (CRP), also referred to as reversible deactivation radical polymerization, has innovated the field of polymer science by providing access to well-defined polymers with tunable molecular weight, molar mass distributions, block sequence, and architecture.[1−5] Perhaps the most key feature of CRP is the possibility to synthesize polymers with very high end-group fidelity, which can, in turn, enable the preparation of block copolymers for use in a variety of fields including, among others, polymer self-assembly in bulk and solution.[6−9] Of the CRP strategies, reversible addition−fragmentation chain-transfer (RAFT)[10,11] polymerization and atom transfer radical polymerization (ATRP)[12] are arguably the most versatile and widely utilized methods.[13] The former operates through a degenerative chain transfer process, while the latter goes through a reversible termination mechanism, both of which allow efficient regulation of the equilibrium between active and dormant species and thereby achieve high livingness.[13]

Although such high end-group functionality has been overwhelmingly exploited for chain extensions and block copolymer synthesis in thousands of publications, it has rarely been explored for the polar opposite: reversing controlled radical polymerization and regenerating the monomer. The ability to reverse CRP and regenerate the starting materials would be highly beneficial for fundamental polymer chemistry by revealing unexplored mechanistic aspects and would also significantly expand the pool of potential applications. For instance, regenerating the starting monomer would not only allow the ability to repolymerize the monomer back to the initial polymer but also provide an alternative way to modify the original polymer properties or create an entirely different material (e.g., different composition, molecular weight, dispersity, architecture, etc.) tailored to a different application. This feature can also further facilitate industrial commercialization of CRP materials by offering an important innovation. In fact, IUPAC has recently acknowledged such depolymerization processes as one of the top 10 emerging technologies in chemistry.[14]

The depolymerization of vinyl polymers is, however, not an easy task due to the highly stable carbon−carbon bonds of the backbone.[15,16] Typically, it is challenging to introduce a reactive group (radical) at the end or in the middle of polymer chains to trigger the depolymerization under mild conditions. Current reports on reversing CRP are rather scarce and almost exclusively require the use of a metal catalyst,[17−21] often yield low depolymerization conversions,[18] and are limited to linear[17−19,21] and bulky bottlebrush polymers (Figure

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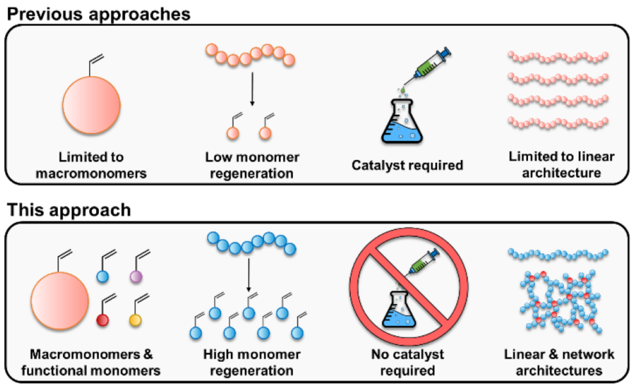

Figure 1. Illustrative comparison of our approach to previous approaches to reversing a controlled radical polymerization.

1).[17−22] For example, Haddleton and co-workers previously described the remarkable depolymerization of water-soluble polymers in the presence of a metal catalyst and dissolved CO_2.[17] However, the depolymerization mechanism was not established, and depolymerization was only feasible in situ following a successful polymerization (i.e., depolymerization of isolated polymers was not demonstrated). In another interesting report by Ouchi's group, a Cl-capped poly(methyl methacrylate) (PMMA) could be depolymerized in the presence of a ruthenium catalyst, yielding relatively moderate depolymerization conversions (e.g., <10%), while side reactions were reported at higher conversions (e.g., 24%).[18] More recently, Matyjaszewski and co-workers enabled the depolymerization of a bottlebrush polymer (i.e., Cl-capped poly(poly(dimethylsiloxane) methacrylate) by utilizing a highly active copper catalyst ($CuCl_2$/tris(2-pyridylmethyl)-amine) at 170 °C.[20] The same group subsequently employed a similar catalytic system to trigger the depolymerization of poly(butyl methacrylate) also at 170 °C.[19] These pioneering reports demonstrate that reversing CRP is possible and have inspired our current contribution. Herein, we report a catalyst-free and near-quantitative (up to 92%) depolymerization methodology for both bulky and nonbulky polymethacrylates as well as insoluble gel-type materials synthesized by RAFT (Figures 1 and 2a).

In a radical polymerization, the Gibbs free energy is usually a negative value ($\Delta G = \Delta H - T\Delta S < 0$, where ΔH is the enthalpy of polymerization, and ΔS is the entropy of polymerization).[23,24] Both ΔH and ΔS are also negative primarily due to the formation of σ bonds from π bonds and a decrease in the degrees of molecular freedom, respectively. The temperature at which $\Delta G = 0$ is the ceiling temperature (T_c).[24−26] Typically, a bulkier polymer side chain leads to a lower T_c due to conformational/steric effects, making the polymerization of macromonomers more difficult.[24,27,28] To trigger depolymerization, we need to address two challenges: (1) to cleave the end groups so as to form radicals and (2) design reaction conditions that favor depropagation[25,29] of those radicals over propagation. With regard to the latter, we note that the ceiling temperature for bulk radical polymerization of conventional, nonbulky polymers such as methyl methacrylate is ~200 °C or more.[24] However, by working under dilute conditions we can favor depropagation over propagation well below the bulk ceiling temperature, because propagation is bimolecular and depropagation is unimolecular (see Table S1). To address more the first challenge, we make use of the relatively weak C−S linkages in the RAFT polymer end group to overcome the energy barrier of forming a chain-end radical that can then undergo depolymerization. Our hypothesis was that the presence of the RAFT polymer end group would allow us to form a chain-end radical and trigger depolymerization of conventional, nonbulky polymers under relatively mild conditions (well below typical depolymerization temperatures of commercial polymers). In contrast, polymers made by free radical polymerization do not have such enabling end groups and thus must overcome a significant energetic barrier to form a polymeric radical that triggers depolymerization.[30,31] Indeed, the depolymerization of PMMA made by free radical polymerization is usually achieved at temperatures above 400 °C, much higher than its bulk ceiling temperature.[30,31] Notably, thermolysis of RAFT-synthesized polymers has been studied as a means to eliminate the RAFT end group. It was shown that, at 180 °C, the trithiocarbonate end group can be, at least partially, eliminated, and the authors proposed a homolytic cleavage mechanism.[32] Instead, dithiobenzoates appeared to be much more stable end groups and could be removed through a proposed concerted elimination process analogous to the Chugaev reaction.[32] Although these experiments were conducted in bulk and focused on removing the RAFT end groups, they indicate that thermally cleaving the RAFT end group is possible. Other studies (also in bulk) suggest that the onset of the RAFT end-group cleavage starts at lower temperatures (e.g., 120 °C).[33] In another report by Stenzel and co-workers, polymethacrylates were heated at 100 °C in solution yielding a 100% alkene-terminated polymer, which was also proposed to be a result of a concerted elimination process.[34] No depolymerization was detected, and the reactions were run at a high polymer concentration (500 mM). In a more recent work by Gramlich's group, brush polymers synthesized by RAFT underwent up to 35% depolymerization at 70 °C prior to reaching an equilibrium, which led to the cessation of the process.[22] The authors concluded that it is important to carefully select polymerization conditions in order to avoid depolymerization during the polymerization of macromonomers. Although the perspective of this work was to draw attention around the polymerization of macromonomers, it inspired our current study.

RESULTS AND DISCUSSION

To initiate our study, a PMMA polymer containing a RAFT end group (i.e., a macro chain-transfer agent (macroCTA)), was first synthesized via RAFT polymerization using 2-cyano-2-propyl dithiobenzoate as the chain transfer agent, yielding a well-defined polymer with narrow molar mass distribution ($Đ$ = 1.13) (Figures S1 & S2, Table S2). To confirm high end-group fidelity, the purified macroCTA was chain-extended with a second monomer (benzyl methacrylate) and 10 mol % azobis(isobutyronitrile) (AIBN) at 70 °C. A clear shift in the size exclusion chromatography (SEC) trace and low dispersity ($Đ$ = 1.07) confirmed the high end-group fidelity of our starting material (Figure S3).

The PMMA macroCTA was then exposed to various depolymerization conditions (deoxygenated by nitrogen sparging) (Figure S4), and after judicious tuning of the reaction parameters, we found that 120 °C and 5 mM of the MMA repeat unit in dioxane (in a typical polymerization, the monomer concentration is ~1 M) is optimal to facilitate an efficient depolymerization reaction (yielding the highest depolymerization rate and the highest depolymerization

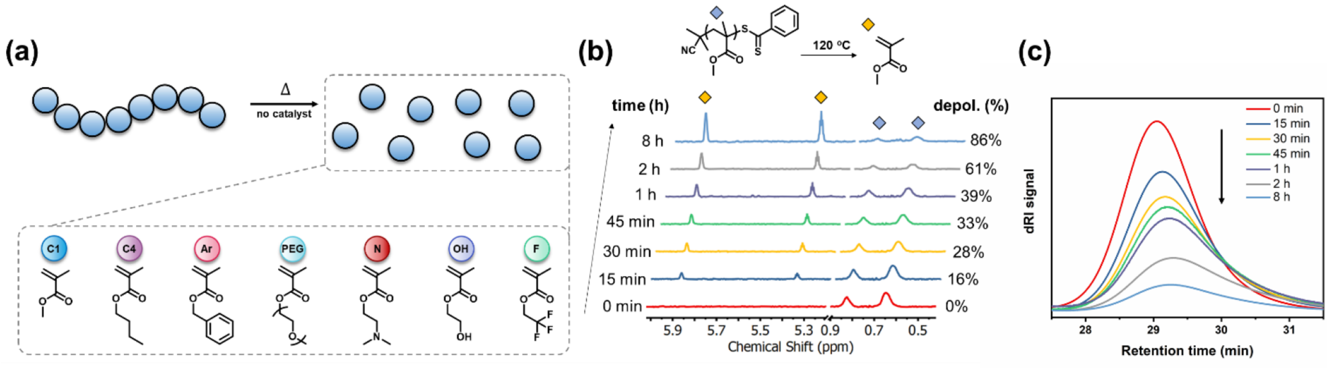

Figure 2. (a) Schematic illustration of reversing RAFT polymerization for various polymethacrylates. (b) ^{1}H NMR spectrum of the depolymerization reaction (5 mM, 120 °C) for PMMA at various time points. The relative increase in the intensity of vinyl signals compared with that of the backbone confirms the regeneration of MMA. (c) Corresponding normalized SEC traces of PMMA during depolymerization. Intensities are normalized to an internal standard to portray the decrease in polymer mass during the reaction.

conversion). In particular, after 15 min, the reaction was sampled, and a ^{1}H NMR analysis showed the unambiguous reappearance of vinylidene peaks corresponding to 16% of depolymerization conversion, thus indicating that the polymerization of PMMA with dithiobenzoate end groups was indeed reversed (Figure 2b). A careful kinetic evaluation showed that the intensity of the vinylidene peaks continued increasing with time, reaching a maximum depolymerization conversion of 86% after 8 h (Figure 2b). A UV−vis analysis showed minor degradation (5%) of the dithiobenzoate chromophore in the reaction after 85% depolymerization (Figure S5). An SEC analysis also confirmed the successful depolymerization of PMMA, as evident by the significant decrease of the intensity of the polymer peak (normalized to an internal control polymer) (Figures 2c & S6). Interestingly, the molar mass distribution did not shift significantly throughout the depolymerization, thus suggesting rapid and complete unzipping of activated polymer chains to regenerate the monomer as well as a lower rate of RAFT relative to that of depropagation (Table S3). To the best of our knowledge, this is the highest reported depolymerization conversion of nonbulky monomers via reversing CRP. It is noted that, when identical conditions to those of the paper by Gramlich and co-workers were employed (70 °C and 28 and 100 mM), negligible depolymerization was observed (<3%) (Table S4), thus highlighting the importance of establishing the right depolymerization conditions. Figure S4 shows that different temperatures and dilutions lead to completely different depolymerization rates and the higher the polymer concentration, the lower the monomer generation as the reaction equilibrium shifts to the formation of polymers. Simple thermodynamic calculations, based on experimental thermodynamic data from the literature, also show that, once the chain-end radicals are formed, the depolymerized material dominates over the starting polymer (10 times higher) at 5 mM and 393 K (Table S1). The equilibrium shifts to the depolymerized material when the temperature is increased and the starting concentration is reduced, which is consistent with our experimental data (Figure S4) and highlights the important role of choosing the right temperature and concentration for achieving high depolymerization conversions. It is also noted that Matyjaszewski's group showed that depolymerization in the presence of a catalyst can proceed at higher concentrations and temperature.[19]

Notably, to recover both the regenerated monomer and solvent, a high-boiling solvent such as dimethyl sulfoxide can be alternatively employed, enabling us to do a fractional distillation of the regenerated MMA and also the dimethyl sulfoxide, recovering both at 99% purity (Figures S7 & S8). Importantly, our depolymerization approach operates in the absence of any catalyst and at significantly lower temperatures compared to polymers synthesized by free radical polymerization. These data further validate our hypothesis and suggest that the RAFT end group is responsible for the efficient depolymerization observed. In contrast, higher temperatures and a copper catalyst were necessary for the depolymerization of a nonbulky ATRP polymer.[19]

To shine a light on the depolymerization mechanism, the PMMA RAFT end group was removed using a previously established protocol[35] in which an excess of AIBN was employed at 70 °C (Figure S9). The dithiobenzoate-free PMMA was then exposed to identical depolymerization conditions. As expected, negligible (<3%) depolymerization could be observed within the same 8 h time frame, thus strongly supporting our initial hypothesis that the RAFT end group is essential to trigger an efficient depolymerization. To further investigate the mechanistic pathway, the radical scavenger 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) was added to the solution (PMMA dissolved in dioxane) prior to depolymerization. In the presence of the radical scavenger, very minimal depolymerization was observed (<5%), thereby indicating that depolymerization occurred via a radical pathway (Figure S10). This is in agreement with the work of Gramlich and co-workers, who observed an induction period in the presence of a radical inhibitor.[22] A key remaining question was to identify the origin of the chain-end radicals, as the reaction was performed in the absence of any known radical-generating species such as AIBN. It has been reported that a chain-end radical can be formed via a photoinduced homolytic cleavage of the RAFT end group from the polymer chain end (i.e., cleaving of the C−S bond).[36−38] To explore the possibility of a thermally induced homolytic cleavage of the RAFT end group, additional experiments were conducted. If this was a viable theory, in the presence of monomer, the macroCTA PMMA would be expected to undergo chain extension at 120 °C in the absence of a free radical initiator. To exclude the possibility of radical generation through the solvent, the chain extension reaction was performed in bulk. When a second monomer (benzyl methacrylate) was added, a

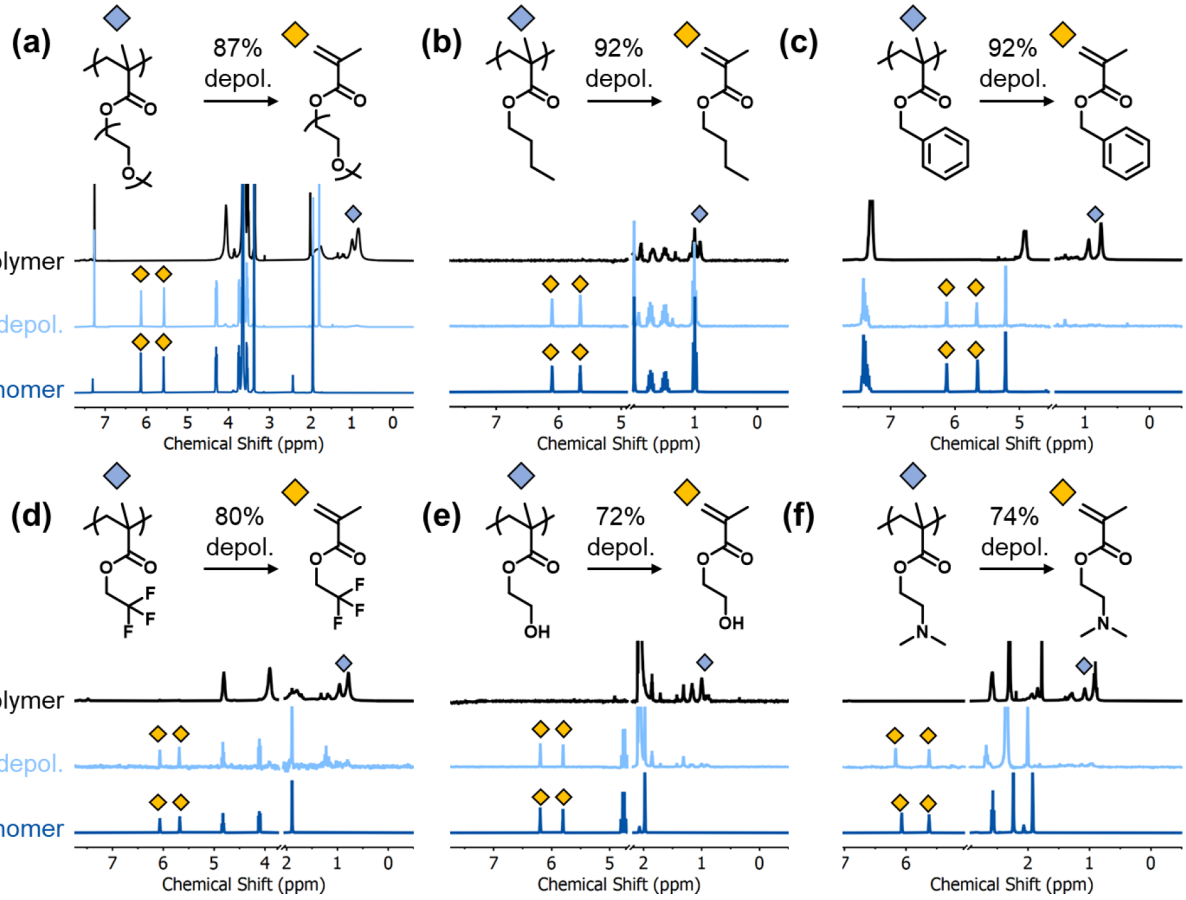

Figure 3. ^{1}H NMR spectrum of the polymer (top spectrum), reaction mixture after depolymerization (middle spectrum), and the original monomer (bottom spectrum) for (a) POEGMA, (b) PBuMA, (c) PBzMA, (d) PTFEMA, (e) PHEMA, and (f) PDMAEMA. Reactions were run in 5 mM concentration and 120 °C for 8 h. Dioxane was used as the solvent in all cases except for PHEMA, for which dimethyl sulfoxide was used.

clear shift to a higher molar mass distribution with low dispersity ($Đ = 1.18$) was evident by SEC (Figure S11). Simply heating up the monomer at 120 °C did not yield to any self-initiated autopolymerization (Figure S12), indicating that no radicals were generated thermally by benzyl methacrylate. Altogether, these results suggest that the chain-end radical was formed via a homolytic C−S cleavage at 120 °C and subsequently triggered the rapid and near-quantitative depolymerization of PMMA. Other pathways that can generate radicals are also feasible and cannot be excluded. For example, although the concerted elimination does not directly involve the formation of radicals, it yields alkene-terminated polymers that may undergo bimolecular autoinitiation[39] to generate chain-end radicals. Alternatively, radicals can also be formed through the solvent, impurities, and/or other routes.

The scope of our depolymerization approach was then extended to a number of other methacrylic polymers synthesized by RAFT polymerization including poly(oligo(ethylene glycol) methyl ether methacrylate) (POEGMA), poly(butyl methacrylate) (PBuMA), and poly(benzyl methacrylate) (PBzMA) (Figures S13−S18). All polymers were successfully depolymerized, achieving 87%, 92%, and 92% conversions, respectively, representing the highest conversion reported to date for any CRP depolymerization strategy (Figure 3). A series of more functional and challenging polymers were also successfully subjected under our optimized depolymerization conditions such as the fluorine-containing poly(trifluoroethyl methacrylate) (PTFEMA), the pH-responsive poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA), and the hydroxyl-functionalized poly(hydroxyethyl methacrylate) (PHEMA) (Figures S19−S24) yielding high percentages of regenerated monomer (Figure 3). We believe that other monomer families such as polyacrylates will be much more challenging to depolymerize due to the interference of midchain radicals as well as the difference in ceiling temperatures.[40] To demonstrate the potential of our methodology to reuse the resulting depolymerization mixture, we chose POEGMA as a model water-soluble polymer, as this is also a promising material for making hydrogels that we will further explore later in the manuscript. POEGMA was first depolymerized to 87% conversion (Figure 4a,b), and the residual polymer was removed via precipitation in diethyl ether/hexane. The supernatant (i.e., depolymerization products excluding the precipitated polymer, Figure S25) was then concentrated and polymerized at 70 °C by adding 10 mol % AIBN. Polymerization proceeded in a controlled manner, with the molar mass distributions gradually shifting to higher molecular weights (linear evolution of M_n with monomer conversion), while very low $Đ$ values (1.11−1.15) were maintained throughout the repolymerization (Figures 4c,d & S26). These data suggest not only that the repolymerization of retrieved mixtures is well-controlled but also that the recycling of both the monomer and CTA is possible.

Last but not least, to probe the potential of this approach for materials application, we performed a double-depolymerization procedure with POEGMA (Figure 4e) with the aim to not

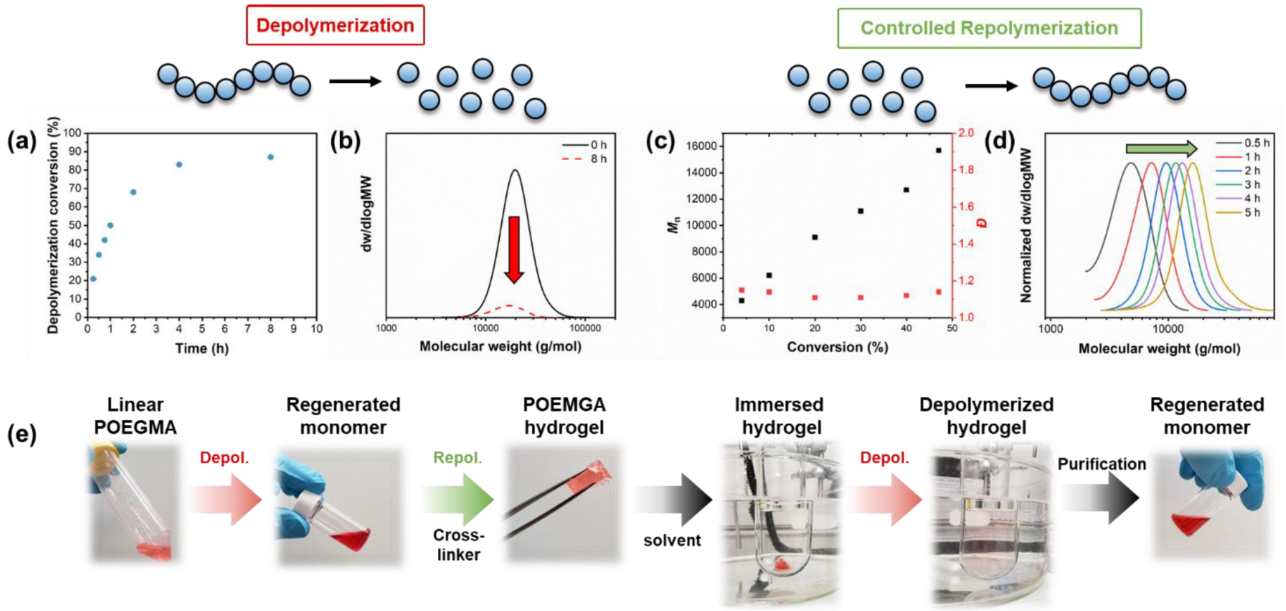

Figure 4. (a) Plot of the monomer conversion during the depolymerization of POEGMA and (b) the normalized SEC trace after 8 h. (c) Evolution of M_n and $Đ$ with conversion during the controlled repolymerization of regenerated OEGMA. (d) SEC traces during controlled repolymerization. (e) Depolymerization and repolymerization steps for synthesizing an entirely new insoluble hydrogel from linear POEGMA, then subsequently depolymerizing the hydrogel to recover the monomers.

only regenerate the monomer twice but also to produce a different material in the process. In the first step, POEGMA was depolymerized to the monomer (87%), and the residual polymer was removed via precipitation in diethyl ether/hexane. The supernatant was concentrated and subsequently polymerized into a hydrogel by adding oligo(ethylene glycol) dimethacrylate (OEGDMA) as a cross-linking comonomer ([OEGMA]/[OEGDMA] = 5:1) (see the Supporting Information for details). The hydrogel was soaked in acetone for 1 d to remove any residual monomer and dried. In the second step, the hydrogel was immersed in dioxane (0.35 g/40 mL), and the solution was bubbled with N_2 and heated to 120 °C. Four hours later, the mixture became a fully homogeneous pink solution, visibly evidencing successful depolymerization even from the gel state. ^{1}H NMR analysis of the homogeneous solution after 12 h showed a depolymerization conversion of 71%, demonstrating the first reversal of CRP for an insoluble gel. The ability to depolymerize insoluble gel-type materials is particularly promising, as it indicates that dissolution of the target material is not a necessity, making this approach applicable to a wider range of materials. To confirm that the dissolution was a consequence of depolymerization and not improved solubility (i.e., that the hydrogel was indeed a fully insoluble network and not merely a high molecular weight branched polymer with limited solubility) we attempted to depolymerize a CTA-cleaved version of the gel (see the Supporting Information, Figure S27). After 12 h, 83 wt % of the gel remained intact (Figure S28), confirming both the networked structure of the gel and the depolymerization-induced dissolution.

■ CONCLUSION

In summary, we report a catalyst-free depolymerization strategy that can be applied to a wide range of linear, bulky, cross-linked, and functional polymethacrylic materials synthesized by RAFT yielding extremely high depolymerization conversions (up to 92%). When the polymethacrylate solutions are heated at 120 °C, chain-end radicals are produced and trigger a rapid depolymerization. By exploiting the high end-group fidelity of RAFT polymers, our method requires a much lower depolymerization temperature than that needed for polymers made by free radical polymerization (e.g., PMMA). Furthermore, the potential to reuse the recovered monomer and turn it into either a similar linear polymer or an entirely new material was also demonstrated.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c00963.

General information, experimental procedures, ^{1}H NMR spectra, SEC traces (PDF)

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Notes

The authors declare no competing financial interest.

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