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Bulk Depolymerization of Methacrylate Polymers via Pendent Group Activation

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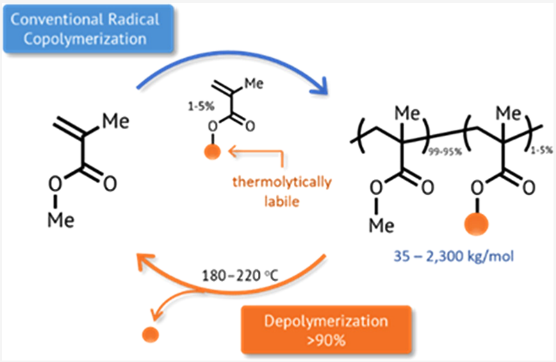
ABSTRACT: In this study, we present an efficient approach for the depolymerization of poly(methyl methacrylate) (PMMA) copolymers synthesized via conventional radical polymerization. By incorporating low mol % phthalimide ester-containing monomers during the polymerization process, colorless and transparent polymers closely resembling unfunctionalized PMMA are obtained, which can achieve >95% reversion to methyl methacrylate (MMA). Notably, our catalyst-free bulk depolymerization method exhibits exceptional efficiency, even for high-molecular-weight polymers, including ultrahigh-molecular-weight (10^6−10^7 g/mol) PMMA, where near-quantitative depolymerization is achieved. Moreover, this approach yields polymer byproducts of significantly lower molecular weight, distinguishing it from bulk depolymerization methods initiated from chain ends. Furthermore, we extend our investigation to polymethacrylate networks, demonstrating high extents of depolymerization. This innovative depolymerization strategy offers promising opportunities for the development of sustainable polymethacrylate materials, holding great potential for various applications in polymer science.



INTRODUCTION

The increase in demand for plastic materials has led to a concomitant increase in plastic waste.[1] Despite the increased production of plastic materials, current recycling methods lag behind the rate at which the polymers are made.[2] Thus, polymer recycling has emerged as a pivotal area of research and innovation. Polymer recycling can be separated into two categories, thermomechanical recycling and chemical recycling.[3,4] Thermomechanical recycling often results in a reduction in the molecular weight and mechanical properties of the recycled polymer.[5,6] On the other hand, chemical recycling is a promising approach to convert polymer into monomer or its precursor forms. The recycled monomer can then be repolymerized to afford new polymeric materials with identical or enhanced mechanical properties, providing an appealing approach to address the chemical circularity of polymers.[7]

While chemical recycling of some commercially relevant polymers such as poly(ethylene terephthalate) (PET) has been achieved through the nucleophilic attack of the ester backbone to yield monomer precursors,[8−10] degradation of vinyl-based polymers remains a formidable challenge due to their robust all-carbon backbones.[11] Efforts to impart degradability have centered around the incorporation of ester, thioester, and disulfide bonds within the polymer backbone.[12−16] Alternatively, the incorporation of monomers that can be triggered to generate main chain radicals allows efficient degradation of polymer backbones via *β*-scission.[17−21] However, many of these methods require catalysts or high dilution with solvent. For example, the inclusion of *N*-hydroxyphthalimide ester-containing monomers such as *N*-(methacryloxy)phthalimide (PhthMA) can lead to direct main chain scission of polymethacrylates.[21] The PhthMA unit can accept an electron from a single electron donor, which induces a cascade reaction, liberating CO_2 and generating a backbone radical that can cleave the polymer backbone via *β*-scission.[21−25]

Poly(methyl methacrylate) (PMMA) is a polymer with an all-carbon backbone produced via chain-growth polymerization. PMMA is a prominent and commercially significant polymer that is lightweight, colorless, and transparent.[26] PMMA is primarily used as glass substitutes in the aircraft and automotive industries but is also used in orthopedics and dentistry.[26,27] The industrial production of PMMA currently resides at >4 million tons per year, with the production of PMMA expected to increase to nearly 6 million tons by

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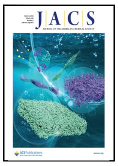

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2027.[28] Industrially, PMMA is synthesized by conventional radical polymerization with molecular weights of 10^5−10^6 g/mol. While PMMA can be recycled by thermomechanical methods, the material properties of the recycled PMMA are often compromised as the material is degraded to lower molecular weight. Alternatively, PMMA can be depolymerized to methyl methacrylate (MMA) by pyrolysis, with high temperatures used to induce C−C bond cleavage of the all-carbon backbone. The high temperatures used (>400 °C) induce random backbone cleavage and unzip the polymer chain, reverting polymer to monomer.[29] However, the high-temperature requirement results in a variety of undesired byproducts along with MMA.[30]

To circumvent the high temperatures needed to depolymerize PMMA, which also result in numerous impurities, recent work has centered around the depolymerization of PMMA synthesized by reversible-deactivation radical polymerization (RDRP) methods.[31−35] Initial work in this area demonstrated that the depolymerization of RDRP-derived polymethacrylates could be achieved efficiently in solution, with high dilutions being used to lower the ceiling temperature of the polymer.[34] Further work on the depolymerization of polymethacrylates derived from reversible addition−fragmentation chain transfer (RAFT) polymerization demonstrated that the depolymerization process could be accelerated when using light in tandem with heat to increase the rate of C−S bond cleavage.[36,37] Concurrently, the Matyjaszewski group reported on a number of methods to depolymerize polymethacrylates synthesized by atom transfer radical polymerization (ATRP) at higher concentrations and temperatures.[32,33,35] Anastasaki and co-workers have also demonstrated that the depolymerization of polymethacrylates can be achieved in a controlled manner by increasing the concentration of thiocarbonylthio moieties in solution to increase the rate of degenerative chain transfer and allow for the uniform depropagation of polymer chains.[38,39] Although the aforementioned routes allow depolymerization of PMMA, the low concentration of polymer (∼0.05 wt %) means that these methods may be difficult to apply on an industrial scale.

To increase the commercial viability of depolymerizing PMMA, bulk depolymerization methodologies of RDRP-made PMMA have recently been reported. The inclusion of labile chain ends such as halogens, thiocarbonylthio, and *N*-hydroxyphthalimide esters has allowed for high extents of depolymerization at significantly lower temperatures than those industrially used, affording highly pure MMA for new materials. Anastasaki and co-workers demonstrated that the depolymerization of PMMA synthesized by RAFT polymerization and ATRP could be depolymerized with high efficiencies in a two-step catalytic process.[40] Matyjaszewski and co-workers also reported on the rapid depolymerization of PMMA synthesized by ATRP by using a copper halide catalyst which activated the carbon−halogen polymer chain end to generate a PMMA macroradical which was then depolymerized.[41] We reported the bulk depolymerization of PMMA in a one-step, catalyst-free approach, achieved through the thermolysis of labile α- and ω-chain ends which afforded high extents of depolymerization to MMA.[42] In the previous report, chain ends inherent to ATRP and RAFT polymerization were investigated, with the highest extents of depolymerization (>90%) achieved with polymers containing an *N*-hydroxyphthalimide ester on the α-end and a trithiocarbonate on the ω-end. By analyzing the thermogravimetric analysis (TGA) data, we attributed 60% depolymerization to initiation from the α-end *N*-hydroxyphthalimide ester and 30% depolymerization from the ω-end trithiocarbonate.

Despite the current reports on the depolymerization of PMMA providing great advances in the field, the approaches are reliant on RDRP methods to allow for efficient depolymerization through their thermolytically labile chain ends. As a result, the polymers are often colored or require catalysts for efficient depolymerization in the bulk. In addition, low extents of depolymerization are achieved at high molecular weights, which is problematic given that high-molecular-weight PMMA is commercially important.[42,43] To further improve the recyclability of PMMA, new depolymerization methodologies that address the drawbacks inherent to depolymerizable PMMA synthesized by RDRP, which may prevent adoption by industry, are required.[44] Herein, we demonstrate a route to synthesize depolymerizable PMMA by conventional radical polymerization. The incorporation of low mol % PhthMA generates backbone radicals at elevated temperatures and affords high extents of depolymerization to generate MMA. This depolymerization methodology is efficient across a broad array of polymer molecular weights with up to 95% depolymerization achievable for higher-molecular-weight polymers at significantly lower temperatures than those industrially used.

■ RESULTS AND DISCUSSION

Poly(*N*-(methacryloxy)phthalimide-*co*-methyl methacrylate) (P(PhthMA-*co*-MMA)) copolymers were synthesized by conventional radical polymerization at 70 °C in dimethyl sulfoxide (DMSO), employing azobis(isobutyronitrile) (AIBN) as the initiator (Figure 1A). The PMMA copolymers were synthesized with varying molar ratios of PhthMA to investigate the effect of different amounts of the radical trigger on the extent of depolymerization (Figures S6−S11). The molar ratios of PhthMA were determined by the integrations of the aromatic protons relative to the methyl ester protons of PMMA by ^{1}H NMR spectroscopy (Figures S31−S33). The polymers ranged in molecular weight between 58 and 80 kg/mol. The TGA traces of the PMMA copolymers showed significant mass loss beginning at 180−200 °C upon heating to 500 °C at a heating rate of 5 °C/min. The T_{95} of the polymers differed based on the incorporation of PhthMA, with higher incorporations resulting in lower T_{95} values. The highest T_{95} of 234 °C was observed for P(PhthMA-*co*-MMA)$_{1\%}$ and the lowest T_{95} of 185 °C for P(PhthMA-*co*-MMA)$_{5\%}$ (Figure 1B). We hypothesize that the lower T_{95} observed at higher PhthMA incorporation is a result of greater mass loss from the thermolysis of PhthMA. In addition, higher incorporations of PhthMA provide more points along the polymer chain from which depolymerization can be initiated.

Averaging the T_{95} of the P(PhthMA-*co*-MMA) copolymers containing 1, 3, and 5 mol % PhthMA resulted in an averaged T_{95} of 205 °C, roughly 170 °C lower than PMMA homopolymers synthesized via anionic polymerization.[30] The inclusion of higher molar ratios of PhthMA resulted in higher mass loss by TGA, with up to 98% mass loss achievable for P(PhthMA-*co*-MMA)$_{5\%}$. To determine the extent of depolymerization of PMMA from TGA, we subtracted the wt % of PhthMA from the total mass loss observed. Gratifyingly, we observe very high extents of depolymerization (∼90%) for all of the P(PhthMA-*co*-MMA) copolymers, with as little as 1% incorporation of PhthMA achieving ∼90% depolymerization

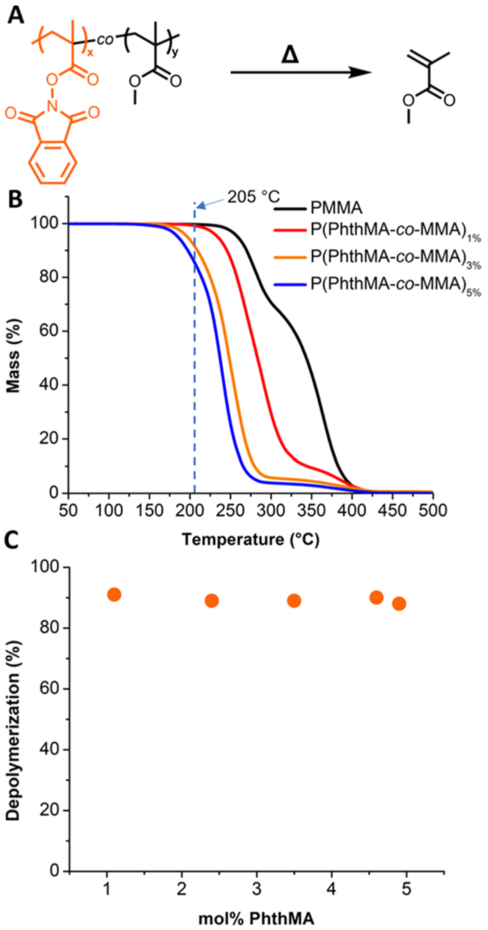

Figure 1. (A) Reaction scheme for the depolymerization of PMMA copolymers. (B) Thermogravimetric traces of the PMMA copolymers; the dashed line indicates averaged T_{95} of the P(PhthMA-*co*-MMA) copolymers. (C) Extent of depolymerization vs mol % incorporation of *N*-(methacryloxy)phthalimide. Values for the extent of depolymerization were obtained from isothermal hold data at 290 °C for 2 h (Figures S51−S55).

(Figures 1A−C and S51−S55). The ~90% depolymerization observed is in close agreement with the theoretical extent of depolymerization of 88% (eqs S1−S6). In comparison, PMMA synthesized by conventional radical polymerization achieved only ~50% depolymerization (Figure S56).

To provide evidence that the mass loss observed by TGA was a result of depolymerization, TGA−tandem mass spectrometry (TGA-MS) was used. At room temperature, no peaks corresponding to monomer were observed; however, after increasing the temperature to 220 °C, molecular ion signals for MMA were present (Figures S57 and S58). To provide insight into the mechanism of depolymerization, select ion fragments were tracked over time. The ion peak corresponding to CO_2 increased after the onset of depolymerization, leading us to believe that depolymerization first proceeds via N−O bond cleavage of the *N*-hydroxyphthalimide ester and decarboxylation of the carboxylate radical to generate a backbone radical (Figure S59). The ion peaks that correspond to MMA also increased after the onset of depolymerization; as such, we attribute the observed reduction in polymer mass primarily to depolymerization following *β*-scission of the backbone radical (Figure S59).

Inspired by the result that pendent group *N*-hydroxyphthalimide esters could efficiently trigger the depolymerization of PMMA at elevated temperatures, we sought to tune the onset temperature of depolymerization by changing the ester that acts as the radical trigger (Figure 2). *N*-(Methacryloxy)-tetrachlorophthalimide (TCPhthMA) was synthesized with the idea that it would result in faster thermolysis and a decrease in the onset temperature of depolymerization due to a weaker N−O bond strength (Figures S1−S4). Varying ratios of TCPhthMA were copolymerized with MMA by conventional radical polymerization to produce P(TCPhthMA-*co*-MMA) copolymers (Figure 2A). The incorporation of TCPhthMA was estimated from the feed ratio of TCPhthMA to MMA due to the absence of distinguishing ^{1}H NMR signals in the resulting copolymer. After purification, the synthesized copolymers of varying compositions were of similar molecular weight, ranging from 60 to 80 kg/mol (Figures S12−S17). Gratifyingly, the averaged T_{95} values were reduced to 190 °C for the P(TCPhthMA-*co*-MMA) copolymers, demonstrating that it is possible to successfully tune the onset temperature of depolymerization (Figure 2C). The TGA profiles of these copolymers exhibited a consistent pattern with higher levels of TCPhthMA correlating with increased mass loss during depolymerization (Figure 2C). High extents of depolymerization were also achieved for these copolymers (~80%) (Figures S60−S62).

Given that it was possible to decrease the onset temperature of depolymerization by the addition of the chlorine atoms to the aromatic ring of the *N*-hydroxyphthalimide ester, we then aimed to increase the onset temperature of depolymerization. Increasing the onset temperature for depolymerization may be an important consideration, given that PMMA is typically processed at temperatures ranging from 180 to 220 °C. We hypothesized that by removing the aromatic ring of the *N*-hydroxyphthalimide ester, the bond strength of the N−O bond would increase and result in higher temperatures required for depolymerization. *N*-(Methacryloxy)succinimide (SMA) (Figure S5) was copolymerized with MMA to produce P(SMA-*co*-MMA) copolymers, using the aforementioned conditions with 1, 3, or 5 mol % SMA (Figures S18−S23). The incorporations of SMA were determined by ^{1}H NMR spectroscopy by comparing the methylene protons of SMA to those of the methyl ester of PMMA (Figures S34−S36). Gratifyingly the average T_{95} of the P(SMA-*co*-MMA) copolymers was increased to 232 °C, nearly 30 °C higher than that of the P(PhthMA-*co*-MMA) copolymers (Figure 2D). The extent of depolymerization was also high for the P(SMA-*co*-MMA) copolymers, with up to 85% depolymerization achievable (Figures S63−S65). Inspired by our result in increasing the T_{95}, we sought to investigate whether the P(SMA-*co*-MMA) copolymers were amenable to heating at 180 °C without inducing depolymerization. To investigate the thermal stability of the P(SMA-*co*-MMA) copolymers, the copolymers were subjected to an isothermal hold at 180 °C for 2 h by TGA. The TGA traces of all P(SMA-*co*-MMA) copolymers showed no mass loss over the 2 h period, while a sequential isothermal hold at 290 °C demonstrated significant mass loss, up to 95% for the P(SMA-*co*-MMA)$_{5\%}$ copolymer which equates to 85% depolymerization (Figures S66−S68). These results suggest that the P(SMA-*co*-MMA) copolymers may be amenable to current industrial PMMA processing conditions, which is attractive to ensure PMMA can be depolymerized intentionally and on command at elevated temperatures and not during processing.

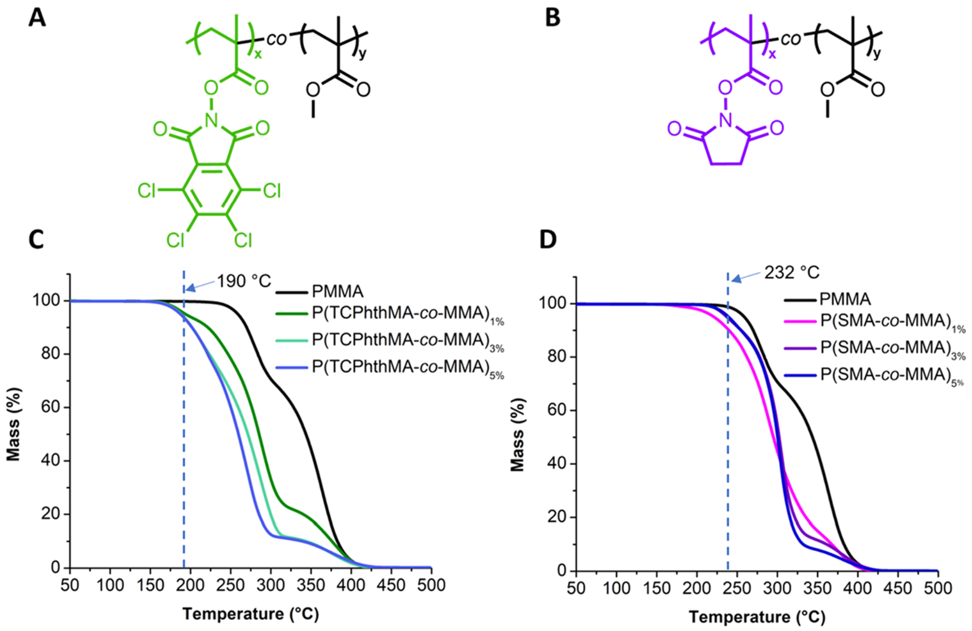

Figure 2. Strucutres of (A) P(TCPhthMA-*co*-MMA) and (B) P(SMA-*co*-MMA). Thermogravimetric analysis (TGA) traces of the (C) P(TCPhthMA-*co*-MMA) and (D) P(SMA-*co*-MMA) copolymers with varying incorporations of the depolymerization triggerable comonomers. Dashed lines indicate averaged T_{95} of the functionalized PMMA copolymers.

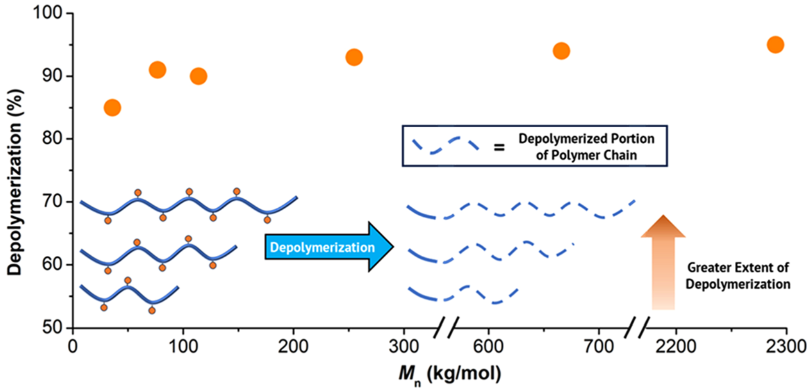

Figure 3. Extent of depolymerization vs number-average molecular weight (M_n) for the P(PhthMA-*co*-MMA)$_{1\%}$ copolymers.

Due to the activated nature of the succinimide ester, the hydrolytic stability of P(SMA-*co*-MMA)$_{1\%}$ was investigated. Gratifyingly after heating the polymer at 60 °C in water for 18 h, no hydrolysis was observed by ^{1}H NMR spectroscopy (Figure S37). We expect that the hydrophobicity of the polymer prevents water from accessing the succinimide ester.

Previous reports on the depolymerization of PMMA using labile chain ends both under dilute and bulk conditions have demonstrated a depolymerization dependence on molecular weight.[42,43] The previously mentioned strategies result in high extents of depolymerization of low molecular weight PMMA but a significant reduction in the extent of depolymerization for higher-molecular-weight polymers. Inspired by our results of achieving high extents of depolymerization for the P(PhthMA-*co*-MMA) copolymers, with molecular weights ~70 kg/mol, we sought to investigate the depolymerization dependence on molecular weight when depolymerization is initiated from the pendent group. To investigate this, P(PhthMA-*co*-MMA)$_{1\%}$ of varying molecular weights were synthesized by conventional radical polymerization by tuning the amount of radical initiator (Figures S25−S29 and S40−S49). Ultrahigh-molecular-weight (UHMW) copolymers[45−51] were synthesized by using very low concentrations of radical initiator to monomer. The synthesized copolymers were subjected to TGA in which an isothermal hold at 290 °C for 2 h was used to determine the mass loss, and the extent of depolymerization was determined after accounting for the wt % of PhthMA within the polymer. High extents of depolymerization were observed for all polymers (>80%) (Figure 3). Interestingly, higher-molecular-weight samples reached greater extents of depolymerization. The depolymerization of high and UHMW polymers yielded >95% depolymerization, which is a 50% increase over chain-end-initiated depolymerization methodologies of polymers of similar molecular weight.[42] We believe the greater extent of depolymerization of higher-molecular-weight polymers is owed to the greater number of PhthMA units per chain, which results in a greater fraction of the polymer chain that can be depolymerized (Figure 3). Inspired by the high extent of depolymerization achieved for the UHMW polymers with 1% PhthMA, we investigated whether a lower loading of PhthMA could be used for efficient reversion to monomer. A PMMA

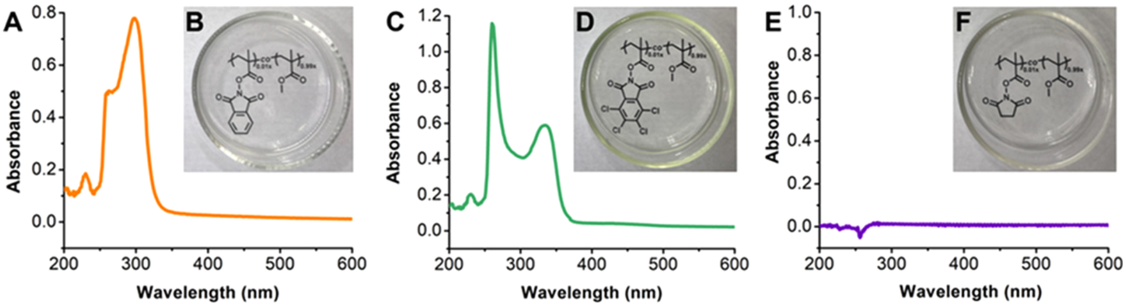

Figure 4. UV−vis spectra of (A) P(PhthMA-*co*-MMA)$_{5\%}$, (C) P(TCPhthMA-*co*-MMA)$_{5\%}$, and (E) P(SMA-*co*-MMA)$_{5\%}$. Top-down views of (B) P(PhthMA-*co*-MMA)$_{1\%}$, (D) P(TCPhthMA-*co*-MMA)$_{1\%}$, and (F) P(SMA-*co*-MMA)$_{1\%}$ films.

copolymer (M_n = 907 kg/mol) was synthesized containing 0.35% PhthMA (Figures S30 and S45). As observed by TGA, ∼93% depolymerization was achieved (Figure S69), demonstrating that for high and UHMW polymers, only very low incorporations of PhthMA are required to achieve high extents of depolymerization.

Given that PMMA is often employed in applications that require colorless materials with high optical clarity, we investigated the optical properties of the depolymerizable copolymers by UV−vis spectroscopy (Figure 4A,C,E). No absorbance was observed for solutions of the P(PhthMA-*co*-MMA) and P(TCPhthMA-*co*-MMA) at wavelengths within the visible range and only absorbance between 250 and 365 nm attributable to the $\pi-\pi^*$ transitions of the aromatic rings, while a slight absorbance was also observed at 425 nm for the P(TCPhthMA-*co*-MMA) copolymer. The P(SMA-*co*-MMA) copolymer demonstrated no absorbance between 200 and 600 nm.

Thin films of P(PhthMA-*co*-MMA)$_{1\%}$, P(TCPhthMA-*co*-MMA)$_{1\%}$, and P(SMA-*co*-MMA)$_{1\%}$ were created by dissolving the polymers in dichloromethane to prepare 10 wt % polymer solutions. The solutions were solvent-cast and allowed to evaporate. The images in Figure 4 demonstrate the high transparency and colorless nature of the synthesized polymers. Both the P(PhthMA-*co*-MMA)$_{1\%}$ and the P(SMA-*co*-MMA)$_{1\%}$ thin films are colorless like that of unfunctionalized PMMA (Figure 4B,F). From a top-down view of P(TCPhthMA-*co*-MMA)$_{1\%}$, the polymer appears both colorless and transparent (Figure 4D); however, from a side-on view of the thin film, a slight green color is observed, which is likely a result of the absorbance of the copolymer at 425 nm (Figure S46B). These results provide promise for these polymer materials to be used as optical materials.

We aimed to demonstrate that MMA could be recovered from bulk depolymerization and simultaneous distillation of the copolymers (Figure 5A). Solid P(PhthMA-*co*-MMA)$_{1\%}$ was added to a round-bottom flask equipped with a distillation apparatus, and the polymer was heated to 250 °C in a sand bath (Figure S47A). After depolymerization, a colorless liquid was obtained in the collection flask (Figure S47B). The ^{1}H NMR spectrum of the colorless liquid confirmed its identity as MMA with no discernible byproducts observed (Figure 5B). This depolymerization methodology afforded an 81% recovery of the theoretical mass of MMA.

The recovered MMA was used for polymerization to synthesize P(PhthMA-*co*-MMA)$_{1\%}$, demonstrating the potential chemical circularity of this depolymerization methodology (Figure S48). After the reaction was completed, a small amount of brown solid was left in the initial round-bottom flask. To determine the identity of the material, the byproduct was analyzed by size exclusion chromatography (SEC) and ^{1}H NMR spectroscopy. Given our hypothesis that β-scission of the polymer backbone precedes depolymerization, low-molecular-weight polymer byproducts are expected. The SEC trace of the residual solid indicated a polymer of low number-average molecular weight (M_n = 8.02 kg/mol), which supports our hypothesis that depolymerization is initiated via the pendent group via β-scission of the polymer backbone (Figure 5A,C). The ^{1}H NMR spectrum of the polymer byproduct demonstrated peaks that correspond to PMMA. Alkenyl proton peaks were observed between 4.7 and 4.9 ppm, which are consistent with depolymerization being initiated after β-scission (Figure S49).[21,52] If higher reversion of polymer to monomer is desired, pyrolysis of the remaining PMMA at high temperatures (>400 °C) is a possibility, although undesired small-molecule byproducts may accompany the additional MMA.

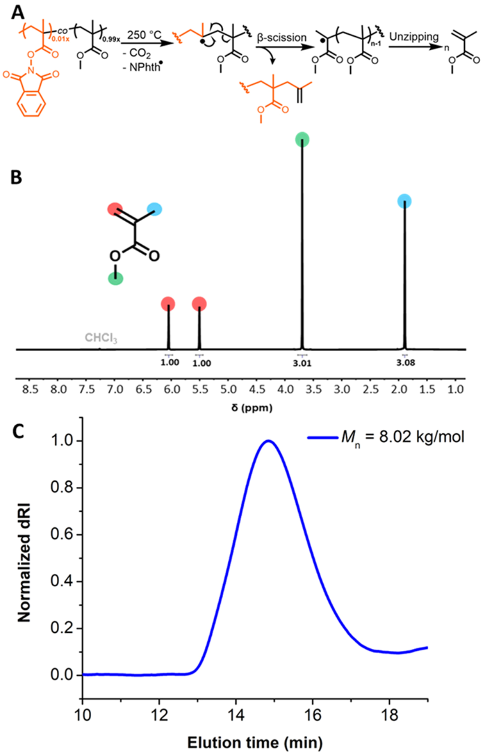

Figure 5. (A) Reaction mechanism for bulk depolymerization of P(PhthMA-*co*-MMA). (B) ^{1}H NMR spectrum of collected MMA. (C) Size exclusion chromatography trace of the polymer byproduct.

To further demonstrate the versatility of the pendent-group approach, depolymerization of polymer networks was explored.

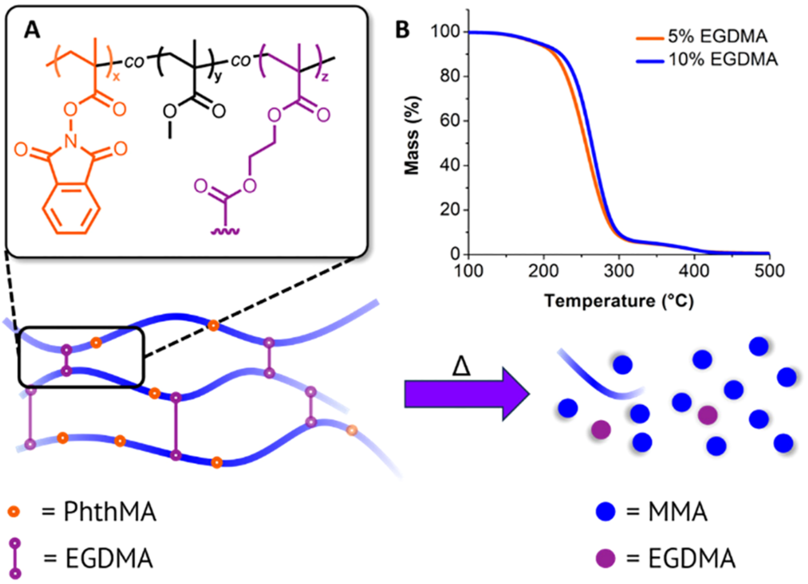

Figure 6. (A) Representation of the bulk depolymerization of P(PhthMA-*co*-MMA-*co*-EGDMA) networks. (B) Thermogravimetric analysis traces of the P(PhthMA-*co*-MMA-*co*-EGDMA) networks with varying incorporations of the dimethacrylate cross-linker.

This is potentially important since cross-linked polymers are typically more difficult to recycle than thermoplastics. Polymethacrylate networks were synthesized from the copolymerization of MMA (85 or 90%), PhthMA (5 mol %), and ethylene glycol dimethacrylate (EGDMA, 5 or 10 mol %) (Figure 6A). Depolymerization of the polymethacrylate networks reached high extents of mass loss (>95%) when subjected to an isothermal hold at 290 °C for 2 h (Figures S70 and S71). The extent of mass loss was independent of the amount of EGDMA added. Given that EDGMA is a dimethacrylate cross-linker, the independence of the incorporation of EGDMA on the mass loss can be rationalized by depolymerization occurring across both ends of the dimethacrylate cross-linker (Figure 6B). The ^{1}H NMR spectrum of the liquid obtained from the bulk distillation of the network containing 10 mol % EDGMA demonstrated that MMA could be recovered (Figure S50). This result is promising since reports of thermoset recycling are limited.[53]

CONCLUSION

In conclusion, we have demonstrated an efficient method to prepare depolymerizable PMMA by conventional radical polymerization. The incorporation of *N*-hydroxyphthalimide/succinimide ester pendent groups, which are thermolytically labile, allows for high extents of depolymerization in the absence of catalysts to generate highly pure MMA. This depolymerization methodology is efficient across a broad range of molecular weights, with near-quantitative reversion to monomer even at UHMW. The T_{95} of the polymers is tunable by modulation of the comonomer incorporation. P(SMA-*co*-MMA) copolymers were thermally stable at 180 °C for 2 h, which is important given that PMMA is often thermally (re)processed at this temperature. Bulk PMMA networks were also able to achieve high extents of depolymerization, setting a precedent for new methods of bulk thermoset recyclability. This approach provides a more facilitated route to chemically recyclable PMMA and does not rely on synthesis by controlled or living polymerization techniques.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.3c14179.

Materials, instrumentation, synthetic procedures, and additional characterization including polymerization kinetics, GPC data, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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