

# Bulk Depolymerization of PMMA 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 ultra-high 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 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 and high-performance polymethacrylate materials, holding great potential for various applications in polymer science.

The increase in demand of plastic materials has led to concomitant increase in plastic waste.<sup>1</sup> Despite the increased production of plastic materials, current recycling methods lag behind the rate at which the polymers are made.<sup>2</sup> 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.<sup>3,4</sup> Thermomechanical recycling often results in a reduction in the molecular weight and mechanical properties of the recycled polymer.<sup>5,6</sup> 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 re-polymerized to afford new polymeric materials with identical or enhanced mechanical properties, providing an appealing approach to address the chemical circularity of polymers.<sup>7</sup>

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,<sup>8–10</sup> degradation of vinyl-based polymers remains a formidable challenge due to their robust all-carbon backbones.<sup>11</sup> Efforts to impart degradability have centered around the incorporation of ester, thioester, and disulfide bonds within the polymer backbone.<sup>12–16</sup> Alternatively, the incorporation of monomers that can be triggered to generate main chain radicals allows efficient degradation of polymer backbones via  $\beta$ -scission.<sup>17–21</sup> 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.<sup>21</sup> The PhthMA unit can accept an electron from a single electron donor which induces a cascade reaction, liberating CO<sub>2</sub> and generating a backbone radical which can cleave the polymer backbone via  $\beta$ -scission.<sup>21–25</sup>

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.<sup>26</sup> PMMA is primarily used as glass substitutes in the aircraft and automotive industries but is also used in orthopedics and dentistry.<sup>26,27</sup> 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 2027.<sup>28</sup> 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.<sup>29</sup> However, the high-temperature requirement results in a variety of undesired byproducts along with MMA.<sup>30</sup>

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.<sup>31–35</sup> 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.<sup>34</sup> 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.<sup>36,37</sup> 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.<sup>32,33,35</sup> Anastasaki and coworkers 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.<sup>38,39</sup> 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 have allowed for high extents of depolymerization at significantly lower temperatures than industrially used, affording highly pure MMA for new materials. Anastasaki and coworkers demonstrated that the depolymerization of PMMA synthesized by RAFT polymerization and ATRP could be depolymerized with high efficiencies in a two-step catalytic process.<sup>40</sup> Matyjaszewski and coworkers 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.<sup>41</sup> We reported the bulk depolymerization of PMMA in a one-step, catalyst-free approach, achieved through the thermolysis of labile  $\alpha$ - and  $\omega$ -chain-ends which afforded high extents of depolymerization to MMA.<sup>42</sup> 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 a *N*-hydroxyphthalimide ester on the  $\alpha$ -end and a trithiocarbonate on the  $\omega$ -end. By analyzing the thermogravimetric analysis (TGA) data, we attributed 60% depolymerization to initiation from the  $\alpha$ -end *N*-hydroxyphthalimide ester and 30% depolymerization from the  $\omega$ -end trithiocarbonate.

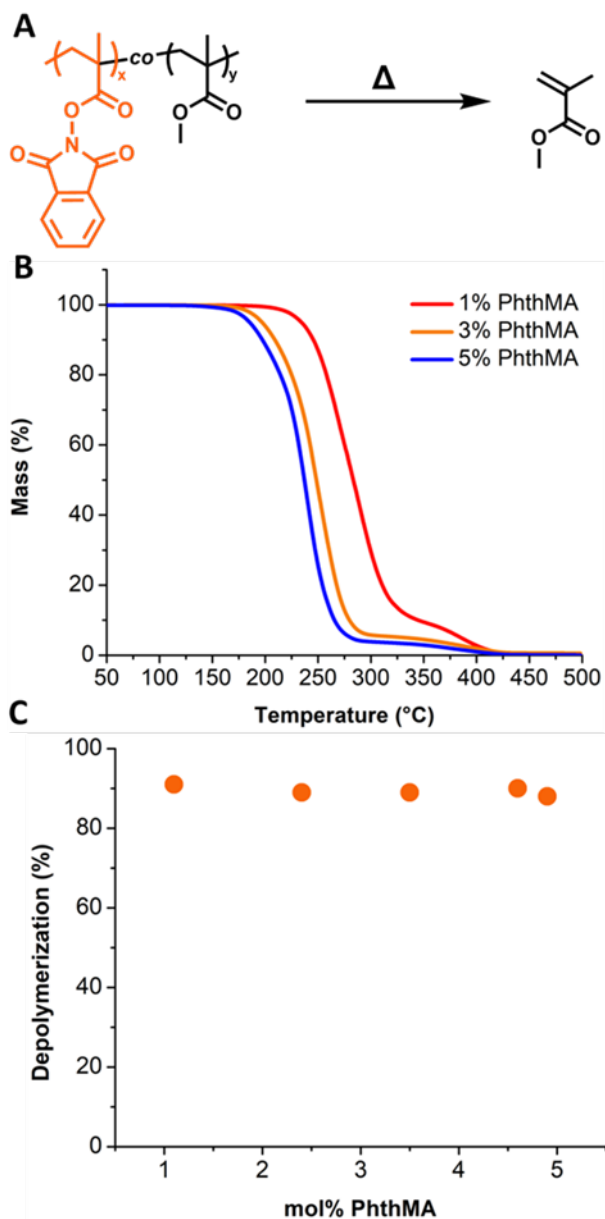
Despite the current reports on the depolymerization of PMMA providing great advances in the field, the approaches are reliant on RDRP methods to allow for efficient depolymerization through their thermolytically labile chain-ends. As a result, the polymers are often colored or require catalysts for efficient 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.<sup>42,43</sup> 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.<sup>44</sup> 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 dimethylsulfoxide (DMSO), employing azobisisobutyronitrile (AIBN) as the initiator. 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 (Figure 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 <sup>1</sup>H NMR spectroscopy (Figure S29–S31). The polymers ranged in molecular weight between 60–80 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<sub>95</sub> of the polymers differed based on the incorporation of PhthMA, with higher incorporations resulting in lower T<sub>95</sub> values. The highest T<sub>95</sub> of 234 °C was observed for the P(PhthMA-*co*-MMA)<sub>1%</sub> and the lowest T<sub>95</sub> of 185 °C for P(PhthMA-*co*-MMA)<sub>5%</sub> (Figure 1B).

Averaging the T<sub>95</sub> of the P(PhthMA-*co*-MMA) copolymers containing 1, 3 and 5 mol% PhthMA resulted in an averaged T<sub>95</sub> of 205 °C, roughly 170 °C lower than PMMA homopolymers synthesized via anionic or conventional radical polymerization methods.<sup>30</sup> 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)<sub>5%</sub>. 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 the P(PhthMA-*co*-MMA) copolymers, with as little as 1% incorporation of PhthMA achieving ~90% depolymerization (Figure 1A–C).

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 that correspond to monomer were observed; however, after increasing the temperature to 220 °C, molecular ion signals for MMA were present (Figure S47, S48). To provide insight into the mechanism of depolymerization, select ion fragments were tracked over time. The ion peak corresponding to CO<sub>2</sub> 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 S49). 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  $\beta$ -scission of the backbone radical (Figure S49).

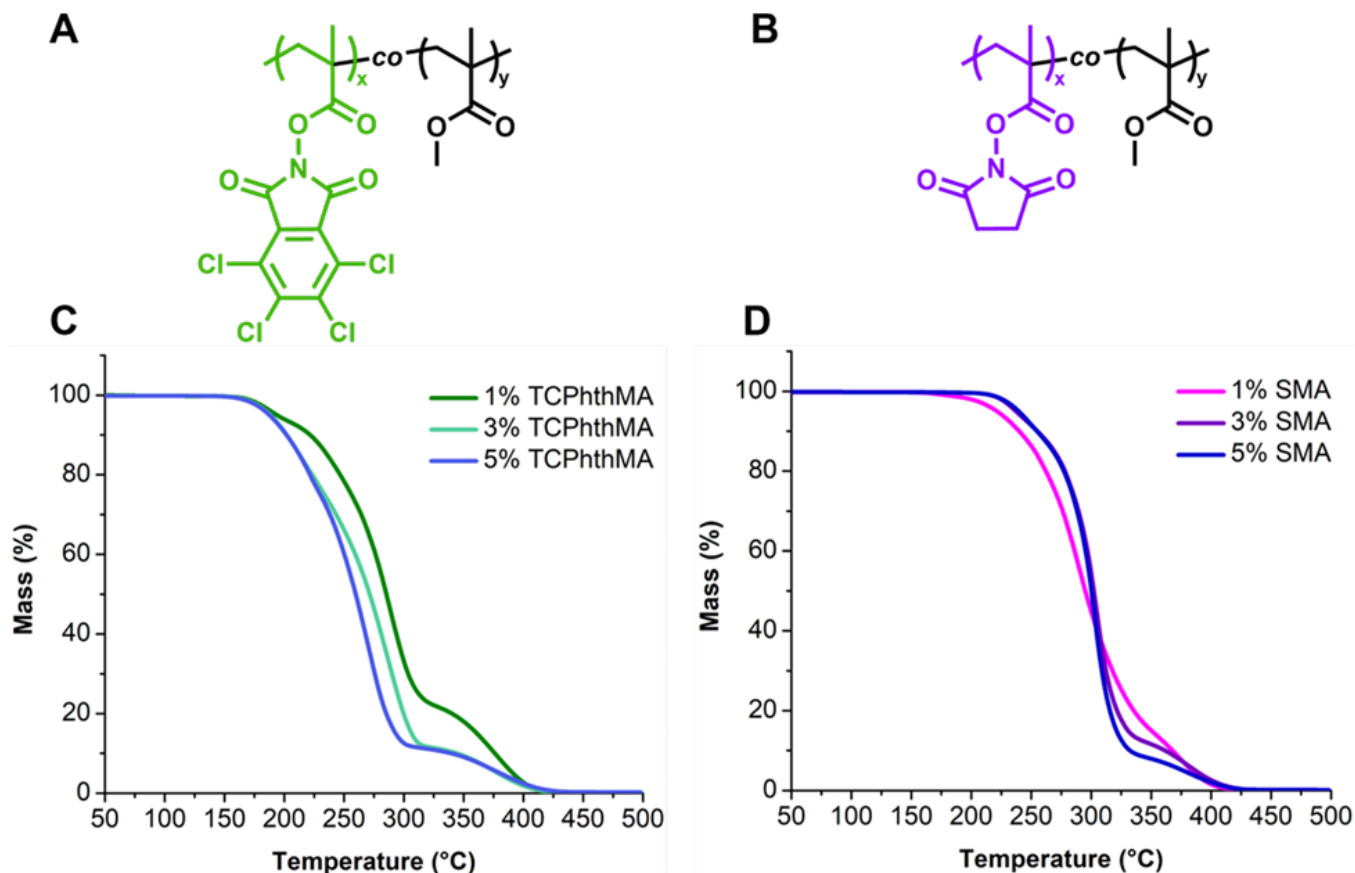


**Figure 1.** (A) Reaction scheme for the depolymerization of PMMA copolymers. (B) Thermogravimetric traces of the PMMA copolymers. (C) Extent of depolymerization vs. mol% incorporation of *N*-(methacryloxy)phthalimide. Values for extent of depolymerization were obtained from isothermal hold data at 290 °C for 2 h (Figure S44–S46).

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 of depolymerization by changing the ester that acts as the radical trigger. *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 (Figure S1–S4). Varying ratios of TCPhthMA were copolymerized with MMA by conventional radical polymerization to produce P(TCPhthMA-*co*-MMA) copolymers. The incorporation of TCPhthMA was estimated from the feed ratio of TCPhthMA to MMA due to the absence of distinguishing <sup>1</sup>H NMR signals in the resulting copolymer. After purification, the synthesized copolymers of varying composition were of similar molecular weight, ranging from 60–80 kg/mol (Figure S12–S17). Gratifyingly, the  $T_{95}$  for the P(TCPhthMA-*co*-MMA)<sub>1%</sub> was reduced by 40 °C to 194 °C compared to the P(PhthMA-*co*-MMA)<sub>1%</sub>. 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. 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%) (Figure S50–S52).

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 also 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 180–220 °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 (Figure S18–S23). The incorporations of SMA were determined by <sup>1</sup>H NMR spectroscopy by comparing the methylene protons of SMA to those of the methyl ester of PMMA (Figure S32–S34). Gratifyingly the averaged  $T_{95}$  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 extents of depolymerization were also high for the P(SMA-*co*-MMA) copolymers with up to 85% depolymerization achievable (Figure S53–S55). 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



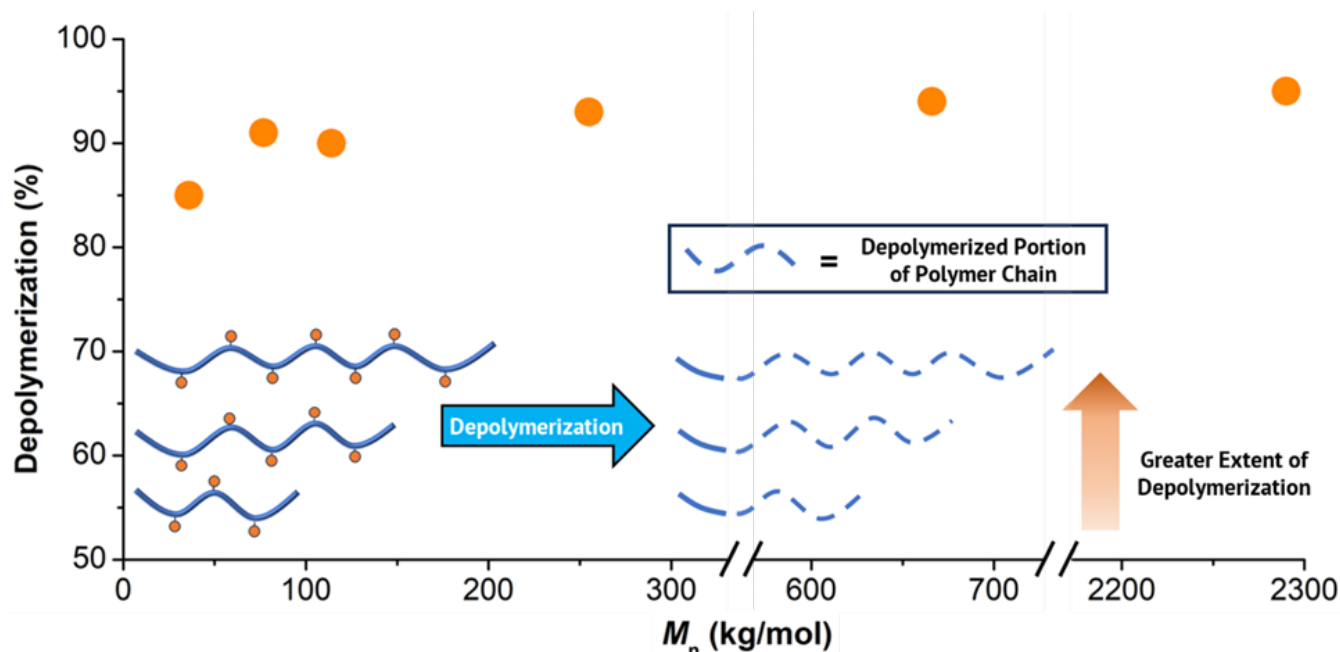
**Figure 2.** (A) P(TCPhtMA-*co*-MMA) and (B) P(SMA-*co*-MMA) structures. Thermogravimetric analysis (TGA) traces of the (C) P(TCPhtMA-*co*-MMA) and (D) P(SMA-*co*-MMA) copolymers with varying incorporations of the depolymerization triggerable comonomers.

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)<sub>5%</sub> copolymer which equates to 85% depolymerization (Figure S56–S58). 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.

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.<sup>42,43</sup> 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)<sub>1%</sub> of varying molecular weights were synthesized by conventional radical polymerization by tuning the amount of radical initiator (Figure S24–S28, S35–S39). UHMW copolymers<sup>45–51</sup> 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 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.<sup>42</sup> 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).

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). Solutions of the P(PhthMA-*co*-MMA) and P(TCPhtMA-*co*-MMA) copolymers demonstrated no absorbance at wavelengths within the visible range and only absorbance between 250–365 nm attributable to the  $\pi$ - $\pi^*$  transitions of the aromatic rings, while a slight absorbance was also observed at 425 nm for the P(TCPhtMA-*co*-MMA) copolymer. The P(SMA-*co*-MMA) copolymer demonstrated no absorbance between 200–600 nm.



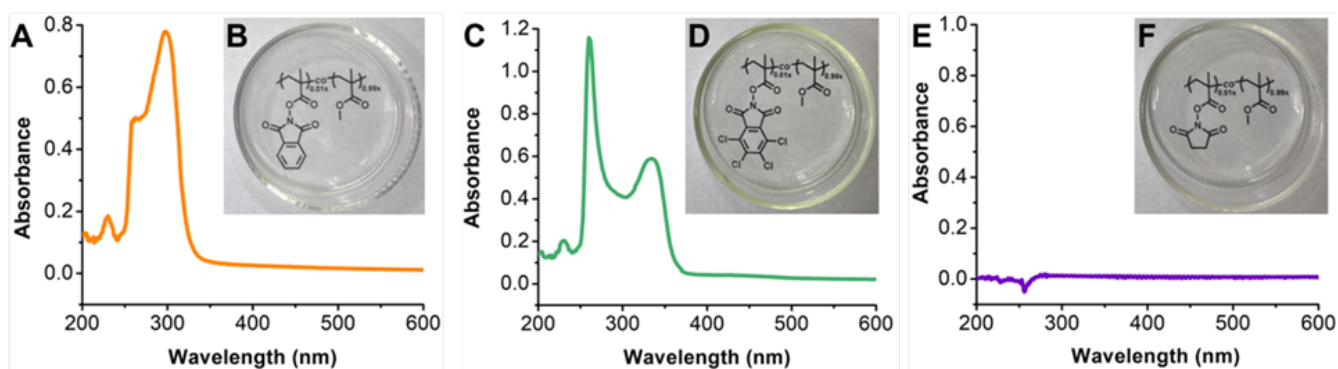
**Figure 3.** Extent of depolymerization vs. number average molecular weight ( $M_n$ ) for the P(PhthMA-*co*-MMA)<sub>1%</sub> copolymers.

Thin films of P(PhthMA-*co*-MMA)<sub>1%</sub>, P(TCPhthMA-*co*-MMA)<sub>1%</sub>, and P(SMA-*co*-MMA)<sub>1%</sub> 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)<sub>1%</sub> and the P(SMA-*co*-MMA)<sub>1%</sub> thin films are colorless like that of unfunctionalized PMMA (Figure 4B, F). From a top-down view of P(TCPhthMA-*co*-MMA)<sub>1%</sub> 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 S40B). These results provide promise for these polymer materials to be used as optical materials.

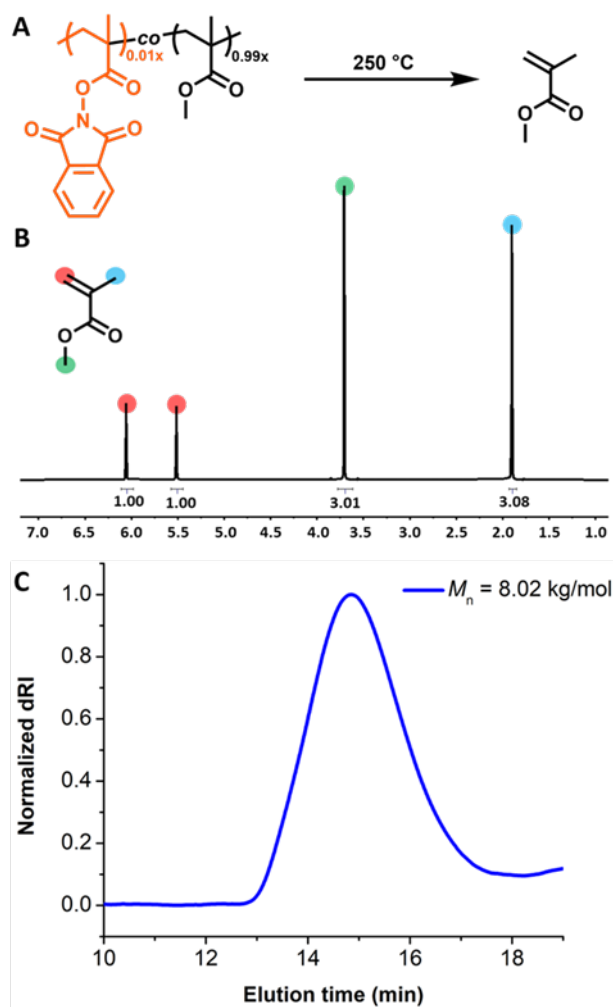
We aimed to demonstrate that MMA could be recovered from the bulk depolymerization and simultaneous distillation of the copolymers (Figure 5A). Solid P(PhthMA-*co*-MMA)<sub>1%</sub> was added to a round bottom flask equipped with a distillation apparatus, and the polymer was heated to 250 °C in a sand bath under vacuum (Figure S41A). After depolymerization, a colorless liquid was obtained in the collection flask (Figure S41B).

The <sup>1</sup>H NMR spectrum of the colorless liquid confirmed its identity as MMA with no discernable byproducts observed (Figure 5B). This depolymerization methodology afforded 81% recovery of the theoretical mass of MMA.

The recovered MMA was used for polymerization to synthesize P(PhthMA-*co*-MMA)<sub>1%</sub>, demonstrating the potential chemical circularity of this depolymerization methodology (Figure S42). After reaction completion, 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 <sup>1</sup>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 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 5C). The <sup>1</sup>H NMR spectrum of the polymer byproduct demonstrated peaks that correspond to PMMA. Alkenyl proton peaks were observed between 4.7–4.9 ppm, which are consistent with depolymerization being initiated after β-scission (Figure S43).<sup>21,52</sup>

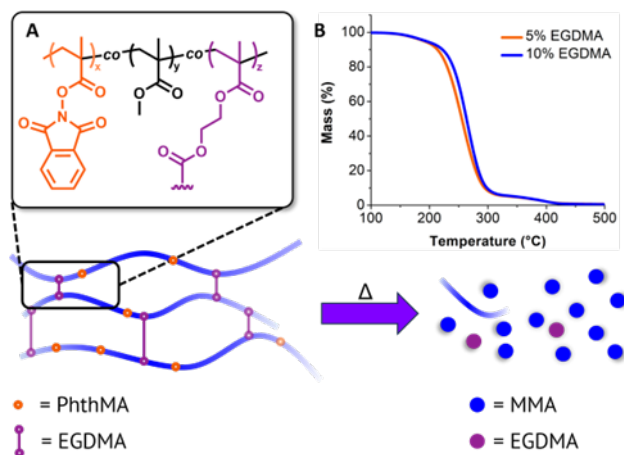


**Figure 4.** UV-Vis spectra of (A) P(PhthMA-*co*-MMA)<sub>5%</sub>, (C) P(TCPhthMA-*co*-MMA)<sub>5%</sub>, and (E) P(SMA-*co*-MMA)<sub>5%</sub>. Top-down view of (B) P(PhthMA-*co*-MMA)<sub>1%</sub>, (D) P(TCPhthMA-*co*-MMA)<sub>1%</sub>, and (F) P(SMA-*co*-MMA)<sub>1%</sub> films.



**Figure 5.** (A) Reaction scheme for the bulk depolymerization of P(PhthMA-*co*-MMA). (B)  $^1\text{H}$  NMR spectrum of the 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 were explored. This is potentially important since crosslinked 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%). Depolymerization of the polymethacrylate networks reached high extents of mass loss (>95%) when subjected to an isothermal hold at 290 °C for 2 h (Figure S59, S60). The extent of mass loss was independent of the amount of EGDMA added. Given that EGDMA is a dimethacrylate crosslinker, the independence of the incorporation of EGDMA on the mass loss can be rationalized by depolymerization occurring across both ends of the dimethacrylate crosslinker. This result is promising since the recycling of thermoset polymers is limited.



**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 crosslinker.

In conclusion, we have demonstrated an efficient method to prepare depolymerizable PMMA by conventional radical polymerization. The incorporation of *N*-hydroxy phthalimide/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/living polymerization techniques.

## ASSOCIATED CONTENT

Materials, instrumentation, synthetic procedures, and additional characterization including polymerization kinetics, GPC data, and NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>

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## Notes

Any additional relevant notes should be placed here.

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