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Mechanochemically Promoted Functionalization of Postconsumer Poly(Methyl Methacrylate) and Poly(α-Methylstyrene) for Bulk Depolymerization

*James B. Young[+], Sofia L. Goodrich[+], James A. Lovely, Madison E. Ross, Jared I. Bowman, Rhys W. Hughes, and Brent S. Sumerlin**

Abstract: We describe a methodology of post-polymerization functionalization to enable subsequent bulk depolymerization to monomer by utilizing mechanochemical macro-radical generation. By harnessing ultrasonic chain-scission in the presence of *N*-hydroxyphthalimide methacrylate (PhthMA), we successfully chain-end functionalize polymers to promote subsequent depolymerization in bulk, achieving up to 82 % depolymerization of poly(methyl methacrylate) (PMMA) and poly(α-methylstyrene) (PAMS) within 30 min. This method of depolymerization yields a high-purity monomer that can be repolymerized. Moreover, as compared to the most common methods of depolymerization, this work is most efficient with ultra-high molecular weight (UHMW) polymers, establishing a method with the potential to address highly persistent, non-degradable all-carbon backbone plastic materials. Lastly, we demonstrate the expansion of this depolymerization method to commercial cell cast PMMA, achieving high degrees of depolymerization from post-consumer waste. This work is the first demonstration of applying PhthMA-promoted depolymerization strategies in homopolymer PMMA and PAMS prepared by conventional polymerization methods.

Introduction

Reversible-deactivation radical polymerization (RDRP) techniques have grown remarkably over the past two decades, establishing themselves as critical tools within polymer chemistry. These methodologies have prompted researchers to achieve previously unattainable polymer molecular weights, compositions, and morphologies.[1] A critical feature of RDRP is the high degree of chain-end fidelity granted by specific techniques such as atom-transfer radical polymerization (ATRP) and reversible addition-fragmentation chain-transfer (RAFT) polymerization, which retain a terminal alkyl halide and thiocarbonylthio chain-transfer agent (CTA), respectively.[2] The chain ends imparted by RDRP techniques are essential for achieving an equilibrium between dormant and active chains, thereby affording control of polymer molecular weight and dispersity. The retention of the end group imparts a "living" character to the polymer, enabling subsequent chain extension to afford a block copolymer. These end-groups also serve as functional handles for end-group modification and, most recently, to initiate high degrees of depolymerization.[3]

Initial work on RDRP chain-end-initiated depolymerization focused on metal-catalyzed ATRP methodologies to drive depropagation at elevated temperatures under dilute conditions with polymethacrylates.[4] Similarly, thiocarbonylthio-terminated polymethacrylates can undergo chain-end reactivation for catalyst-free depolymerizations at mild temperatures (≤120 °C) under dilute conditions (≤10 mM).[5] Our group and Anastasaki's further demonstrated that accelerated depolymerization occurs in the presence of light with a wide variety of thiocarbonylthio-terminated poly(methyl methacrylate)s (PMMA).[6] Aimed at innovating more sustainable depolymerization methodologies, a variety of solvent-free depolymerization strategies have been developed for PMMA, all hinging on thermally labile end-groups that produce active backbone radicals capable of unzipping to monomer.[7] Key to the approach reported by our group was the use of an α-end *N*-hydroxyphthalimide ester capable of undergoing decarboxylation-initiated depolymerization at elevated temperatures (>200 °C) to achieve up to 92 % depolymerization when accompanied by an ω-end trithiocarbonate. This bulk approach allows for gram-scale depolymerizations in a solvent- and catalyst-free manner, potentially enabling efficient depolymerization methodologies that are industrially relevant. However, all these examples of chain-end-initiated depolymerization have relied on the pre-installation of triggerable chain ends by RDRP methods.

Our group recently demonstrated that incorporating *N*-hydroxyphthalimide ester methacrylate (PhthMA) as a comonomer can achieve up to 96 % depolymerization of PMMA at ~180 °C.[8] This approach is particularly promising in that installing the depolymerization triggers as pendent

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groups precludes the need for end-group control and overcomes the requirement for controlled polymerization methods to access PMMA capable of efficient depolymerization under mild conditions.[9] However, while this strategy allowed depolymerizable PMMA to be prepared by conventional radical polymerization, it still requires the degradable nature of the polymer to be considered *a priori*, ensuring that depolymerization triggers were installed during synthesis.[10]

The Stache group recently demonstrated a method to circumvent the need for synthesizing polymers primed for depolymerization using quantum dots in postconsumer plastic to drive macromolecular chain-scission and subsequent depolymerization via a photothermal route.[11] We reasoned that another viable route to chemically recycle post-consumer PMMA is to utilize macro-radical generation from mechanochemical processes to functionalize polymers for depolymerization. Mechanochemistry is a powerful tool for harnessing mechanical energy to promote unprecedented or even thermodynamically unfavorable chemical transformations.[12] Mechanochemistry has been readily adopted for its synthetic capabilities because in many cases it can eliminate the need for heating or adding solvent, catalysts, or exogenous initiators.[13]

Mechanochemistry (e.g., ball-mill grinding (BMG) and ultrasonication) is utilized for macromolecular transformations that can be productive (e.g., polymerization or functionalization) or destructive (e.g., chain degradation).[13–14] Chains above a limiting molecular weight experience chain scission under applied stress. Recent reports have utilized BMG and ultrasound with reactive additives, such as strong bases or enzymes, to depolymerize natural and synthetic plastics.[12,15] Balema and co-workers partially depolymerized (7 wt %) polystyrene with BMG, relying solely on the macroradicals formed by chain-scission to initiate depolymerization.[16] Subsequent work achieved moderate degrees of depolymerization (64 %) of bulk poly(α-methylstyrene) (PAMS) under mild BMG conditions.[17]

We drew inspiration from Qiao, Schmidt-Naake, and Yagci's work, where ultrasound was exploited to cleave PMMA in the presence of small molecules (4-hydroxy-2,2,6,6- tetramethylpiperidine-1-oxyl and copper chloride, respectively) to generate chain-end functionalized macro-CTAs suitable for subsequent chain extension with RDRP methods.[18] Ultrasound ($f > 20$ kHz) induces the expansion and contraction of gas bubbles in response to pressure oscillations.[19] When the external pressure surpasses the internal pressure, these cavitation bubbles implode, creating localized hot spots ($T \geq 5000$ K) and shear forces to facilitate molecular pyrolysis and polymer chain scission, respectively. Interestingly, low-frequency sonication can also lead to efficient chain scission while minimizing side reactions that occur via pyrolysis at higher frequencies.[20]

Herein, we demonstrate the ability to mechanochemically install terminal depolymerization triggers onto pre-existing polymers by harnessing low-frequency ultrasound (Figure 1). Depolymerization of the resulting polymers can be triggered by heating under non-equilibrium conditions at temperatures as low as 153 and 170 °C for PAMS and PMMA, respectively. This approach broadens the applicability of decarboxylation-promoted depolymerization, as it does not require depolymerization triggers to be incorporated during polymer synthesis, and, counterintuitively, leads to an enhanced ability to depolymerize at higher molecular weights.

Results and Discussion

We sought to develop a post-polymerization modification method suitable for various commercially produced methacrylate polymers. We hypothesized that mechanochemical polymer chain-scission could be leveraged to form macroradicals in the presence of an activated ester monomer to

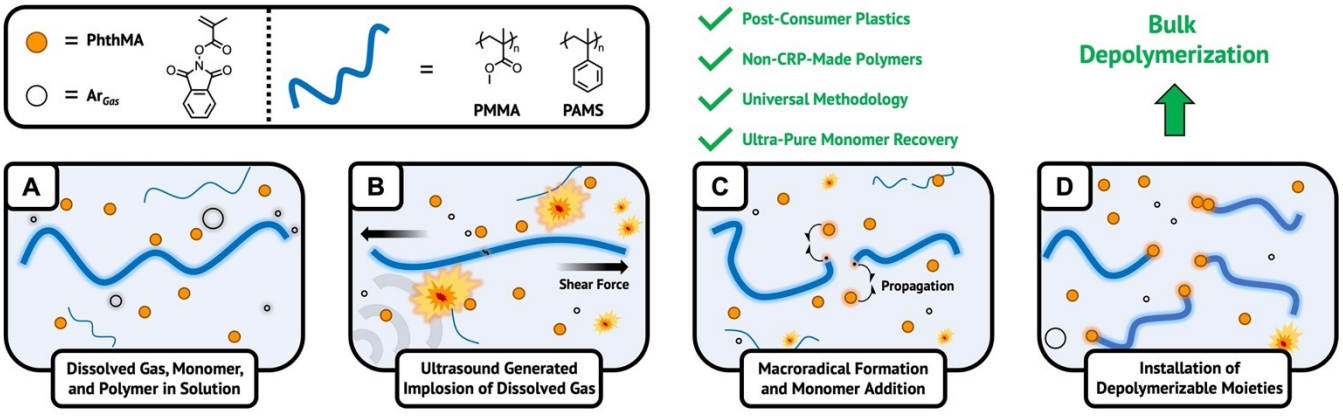

Figure 1. N
(A) (B)
(C)
(D)

install moieties that can trigger depolymerization at the newly exposed end groups. Provided this route of functionalization is efficient, the resulting functionalized polymer could undergo bulk depolymerization via a thermally triggered decarboxylation process.

To understand the mechanochemical chain scission of PMMA under low-frequency sonication (f = 40 kHz), we analyzed the decrease in molecular weight of PMMA (M_n = 1,800 kg/mol) synthesized via conventional radical polymerization throughout sonication at various concentrations in 1,4-dioxane (Figure S1). We found that as the concentration of polymer increased from 1–10 mg/mL, longer sonication times were needed to approach the limiting lower molecular weight, a common phenomenon observed when polymer chains are no longer large enough to undergo macromolecular chain-scission (Figures 2A, B and S2–3).[21] Higher concentrations of polymer (e.g., 15 mg/mL) reduced the efficiency of mechanochemical chain-scission, even at longer sonication times, as increased solution viscosity dampens mechanochemical implosions and prevents chain scission (Figure S3).[21] As such, subsequent studies were conducted at a polymer concentration of 10 mg/mL. At this concentration, significant chain cleavage occurred within just 1 h (1800 kg/mol to 230 kg/mol), with a plateau eventually being reached at 87 kg/mol after 4 h (Figure 2A). Dispersity also reduced with decreasing molecular weight, coinciding with other reports of sonication-promoted mid-chain scission (Figure 2B).[22] Interestingly, the T_{95} of sonicated PMMA increased by approximately 70 °C, potentially suggesting the weaker head-to-head linkages that inevitably form by combination during conventional radical polymerization were preferentially broken during sonication (Figure S4). With these data, we set out to study the effect of adding PhthMA during sonication to determine the extent of bulk depolymerization the resulting products could undergo after functionalization.

PMMA was sonicated in the presence of PhthMA at 0.25, 0.5, and 1 mol % with respect to MMA monomer units (Figure 3A). While monomer addition was not visible by NMR spectroscopy, size-exclusion chromatography with UV/Vis detection (SEC-UV/Vis) at 305 nm confirmed the presence of PhthMA on the polymer chains after sonication (Figure S5 and S6). The depolymerization of the resulting PhthMA-functionalized PMMA was investigated by thermogravimetric analysis (TGA) to determine the temperature at which 5 % of the initial mass was lost (T_{95}). Notably, the T_{95} of functionalized PMMA decreased significantly with increasing incorporation of PhthMA during sonication (Figure 3B, C). In the absence of PhthMA, the sonicated PMMA exhibited a T_{95} as high as 349 °C, while just 0.25 mol % PhthMA decreased the T_{95} by almost 100 °C to 255 °C. By increasing the concentration of PhthMA to 1 mol %, the T_{95} was depressed to as low as 170 °C. This relationship shows that functionalization efficiency increases with increasing PhthMA concentration during sonication.

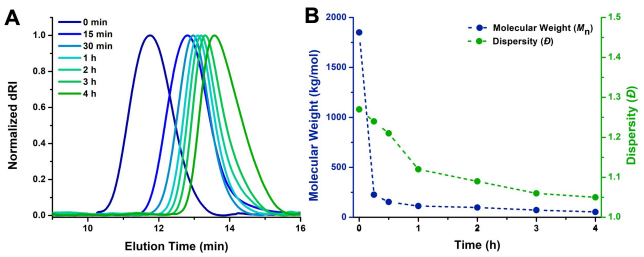

Fig 2 (A) M = (B)

We observed a direct relationship between the concentration of PhthMA added during sonication and depolymerization efficiency. An isothermal hold at 290 °C for 2 h was used to determine the extent of depolymerization achievable after sonication under each condition (Figure 3D). PMMA sonicated in the absence of PhthMA exhibited < 1 % mass loss. With 1 mol % PhthMA being present during sonication, the resulting polymer demonstrated 81 % depolymerization, suggesting the introduction of terminal PhthMA units is essential for triggering depolymerization. Interestingly, sonication in the presence of 2 mol % PhthMA did not result in a further increase in depolymerization efficiency (Figure S7). This mechanochemical approach also showed high purity of the recovered MMA at temperatures as low as 181 °C, as evidenced by tandem TGA-mass-spectrometry (TGA-MS), an observation consistent with our previous reports of side-chain-initiated and chain-end-initiated depolymerization utilizing phthalimide esters (Figure 4).[7a,8]

There is some degree of uncertainty with respect to the end groups of the polymer that forms during the sonication of PMMA in the presence of PhthMA. The high molecular weight required for efficient chain cleavage by sonication precludes the typical characterization methods that might provide insight into the efficiency of functionalization and offer evidence of alternative byproducts. The macroradicals formed mechanochemically could undergo a variety of side reactions before adding to PhthMA, including recombination, disproportionation, or abstraction of hydrogen from another species present during the reaction (e.g., solvent). Alternatively, it is known that dioxane can form radicals during sonication, and these radicals may terminate with the sonication-generated PMMA radicals before addition to PhthMA.[23] Similarly, assuming the majority of cleaved chains add to at least one PhthMA, these same reaction possibilities exist, giving rise to considerable uncertainty with respect to the exact identity of the end groups after mechanochemical treatment. However, given that sonication in the absence of PhthMA exhibits negligible depolymerization, it is reasonable to conclude that PhthMA plays a crucial role in promoting depolymerization, presumably by enabling subsequent decarboxylation and unzipping at elevated temperatures.

A potentially counterintuitive result of the depolymerization triggers being incorporated via chain scission is that higher molecular weight PMMA resulted in greater extents of depolymerization compared to lower molecular weights. For example, while sonication of PMMA of 200 kg/mol led to 61 % depolymerization after having been sonicated in the

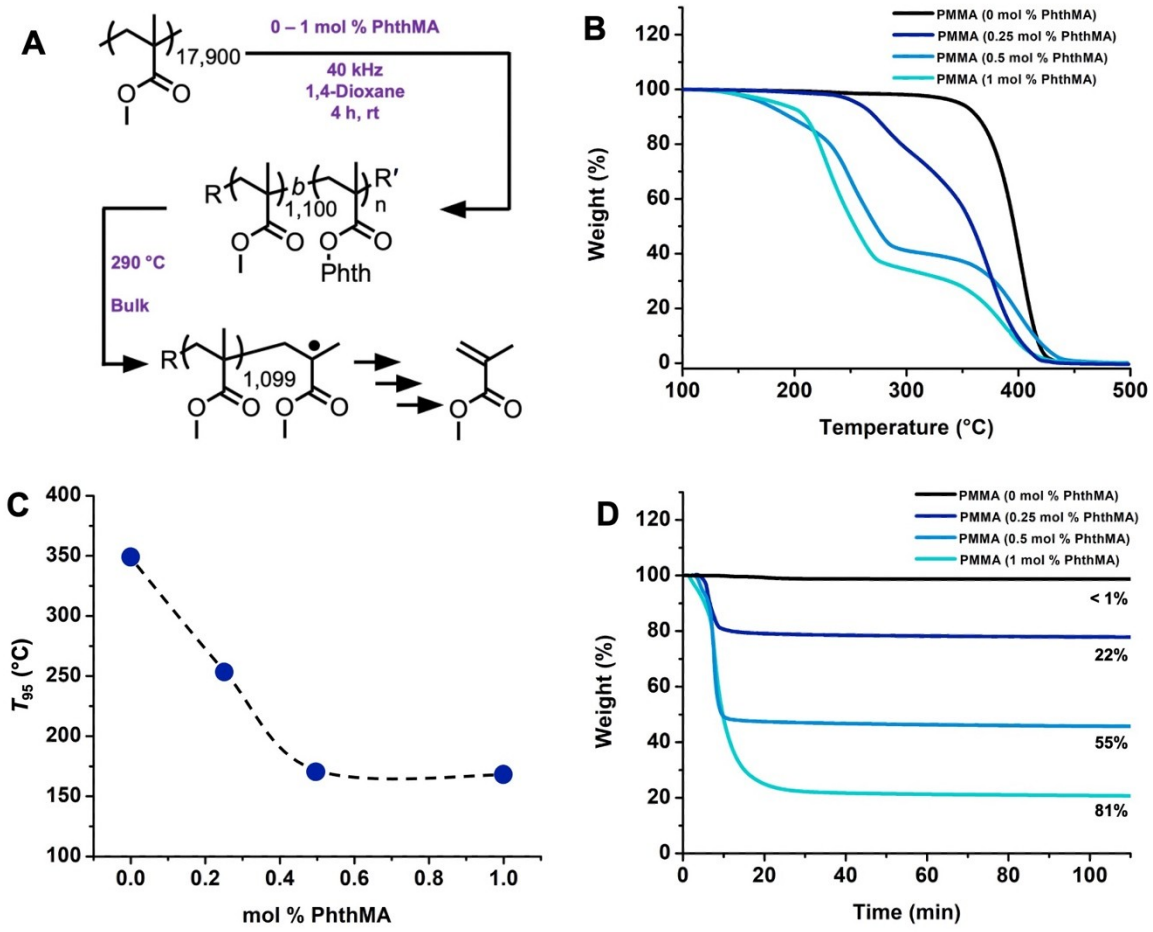

Fig. 3. (A) (B) (C) (D)

presence of 1 % PhthMA, PMMA of 1,800 kg/mol treated in the same manner resulted in 81 % depolymerization (Figure 3D, S8). We attribute this observation to a higher degree of PhthMA functionalization with increasing molecular weight due to the larger number of mechanochemical chain-scission events expected per chain. Indeed, this is different from most reports of chain end-initiated depolymerization in that higher molecular weight starting materials generally lead to lower extents of depolymerization.[5c,7a] For example, this methodology achieves a 68 % increase in depolymerization efficiency compared to our previously reported phthalimide-ester chain-end-initiated depolymerization of PMMA (~100 kg/mol) (48 %).[7a] Moreover, while most recent reports of chain end-initiated depolymerization of PMMA have relied on polymer synthesis via RDRP methods, we propose that the approach reported here can be extended to PMMA produced by conventional radical polymerization (see below), which is generally higher in molecular weight and does not contain the readily cleavable end groups afforded by controlled polymerization techniques.

Next, we sought to expand our sonication methodology to other polymers susceptible to depolymerization at moderate temperatures.[24] Sonication of PAMS of $M_n = 900$ kg/mol for 4 h resulted in ~10 fold reduction in chain length to $M_n =$ 96 kg/mol (Figure 5A, S9 and S10). SEC-UV/Vis detection at 305 nm confirmed the presence of PhthMA on the chains after sonication (Figure S11). Depolymerization analysis of the resulting polymer by TGA showed that the T_{95} of PAMS was reduced by over 135 °C, from 289 to 153 °C, as the concentration of PhthMA during sonication was increased from 0–1 mol % (Figure 5 B, C). Isothermal holds at 220 °C demonstrated increased degrees of depolymerization with increasing PhthMA content (Figure 4D). For example, only 2 % depolymerization was observed under these conditions for PAMS that had been sonicated in the absence of PhthMA, while 80 % depolymerization was observed for PAMS sonicated in the presence of 1 mol % PhthMA.

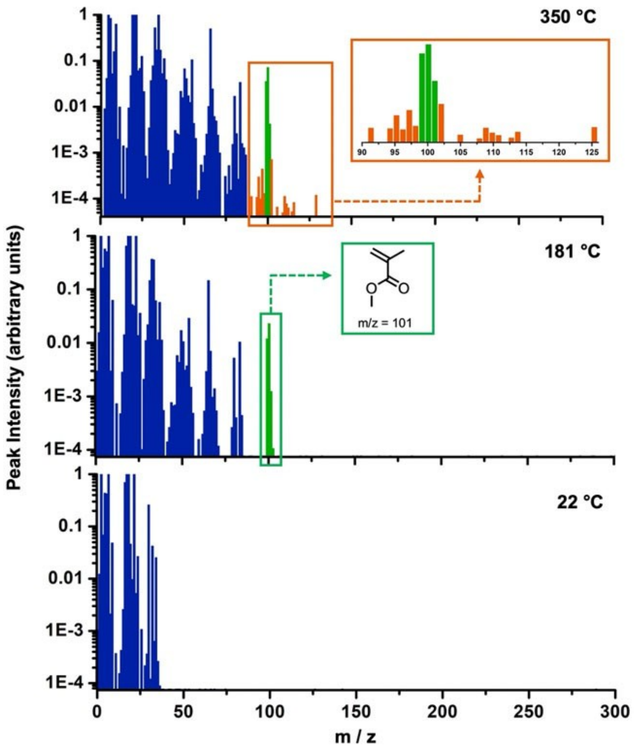

Figure 4.

TGA-MS allowed for the characterization of depolymerization degradation byproducts at various temperatures (Figure 6A). Maintaining a low depolymerization temperature was critical to achieving high purity of the recovered AMS monomer. For example, at higher temperatures (> 300 °C), small molecule byproducts (m/z = 208 and 281) were detected by MS in addition to the desired AMS monomer (m/z = 118); however, reducing the depolymerization temperature to 220 °C eliminated these undesired side products. These findings emphasize the utility of methods that serve to enhance bulk depolymerization efficiency at moderate temperatures (Figure 6B, S12). Indeed, the AMS collected by depolymerization at 200 °C was repolymerized anionically to generate well-defined PAMS (Figure 6C).

To demonstrate the versatility of this sonochemical approach for the installation of depolymerization triggers, we extended the methodology to post-consumer cell-cast PMMA. A sheet of commercial PMMA was broken up into small pieces and left to dissolve overnight in 1,4-dioxane for subsequent characterization (Figure 7A). The sample was found to have M_n = 560 kg/mol, = 1.56 (Figure S13). Upon sonication in the presence of 1 mol % PhthMA for 4 h, a significant reduction in molecular weight and narrowing of dispersity was observed (M_n = 110 kg/mol, = 1.06) (Figure 7B). The resulting PMMA exhibited 76 % depolymerization under an isothermal hold at 290 °C via TGA, compared to just 12 % depolymerization for the virgin PMMA (Figure 7C, S14). The reduced extent of depolymerization is potentially attributable to the low molecular shoulder present in the commercial PMMA, representing a fraction of chains below the critical degree of polymerization necessary for chain cleavage, although additives could also play a role. Nonetheless, the monomer collected during depolymerization at T ≤ 290 °C was highly pure (Figure S14), a potential benefit over typical PMMA depolymerization approaches that rely on temperatures ranging from 400-500 °C, suggesting the combination of mechanochemistry and low-temperature reversion to monomer may represent a path forward toward increasing life-cycle circularity of existing polymer waste.[25]

Conclusion

These results present an advancement in the field of chemical recycling, addressing the challenge of depolymerizing vinyl polymers such as PMMA. By employing mechanochemical macro-radical generation via low-frequency ultrasound, we demonstrated an efficient post-polymerization functionalization technique to facilitate bulk depolymerization. This approach is particularly effective for ultra-high molecular weight polymers, achieving up to 82 % depolymerization of PMMA within 30 min. The high-purity monomer that results from this process may offer a sustainable pathway for repolymerization towards a more circular economy for plastics.

The application of PhthMA as a functionalizing agent enables depolymerization of commercially synthesized polymers without the need for installing depolymerization triggers *a priori*, thereby addressing a challenge in the recycling of post-consumer plastic waste. The successful depolymerization of commercial PMMA further signifies the potential applicability of this approach to real-world scenarios. This work may allow expansion of depolymerization strategies to a variety of polymer types beyond PMMA and PAMS, and future research will focus on enhancing the efficiency of functionalization, understanding the mechanism of chain-end and mid-chain cleavage in greater detail, and expanding the applicability of this method to a wider range of polymers. Sonication serves only as a model method for leveraging mechanochemistry for installation of depolymerization triggers. In principle, the concept of chain scission and subsequent addition of the resulting radical to a monomer containing a triggerable unit can be extended to other approaches of mechanochemistry (e.g., shear during extrusion, ball milling).

Through continued development, this general approach could play a pivotal role in enabling the recycling of polymers that are currently challenging to depolymerize, thereby paving the way for their reintroduction into the manufacturing cycle and reducing the dependence on virgin resources.

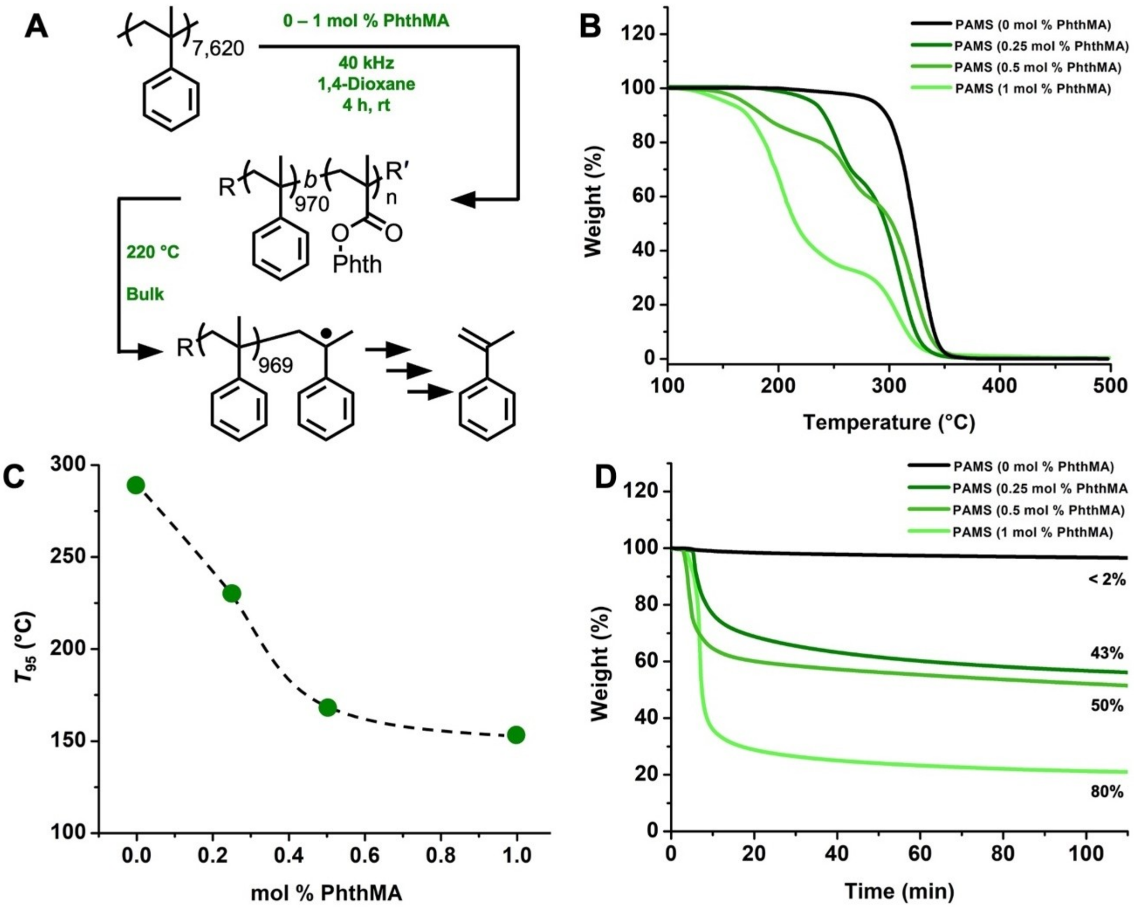

Figure 5. (A) (B) ° ° (C) ° (D)

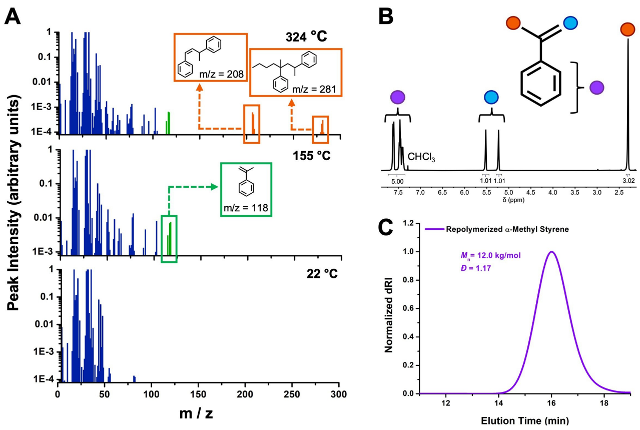

Figure 6. (A) ° (B) ° (C)

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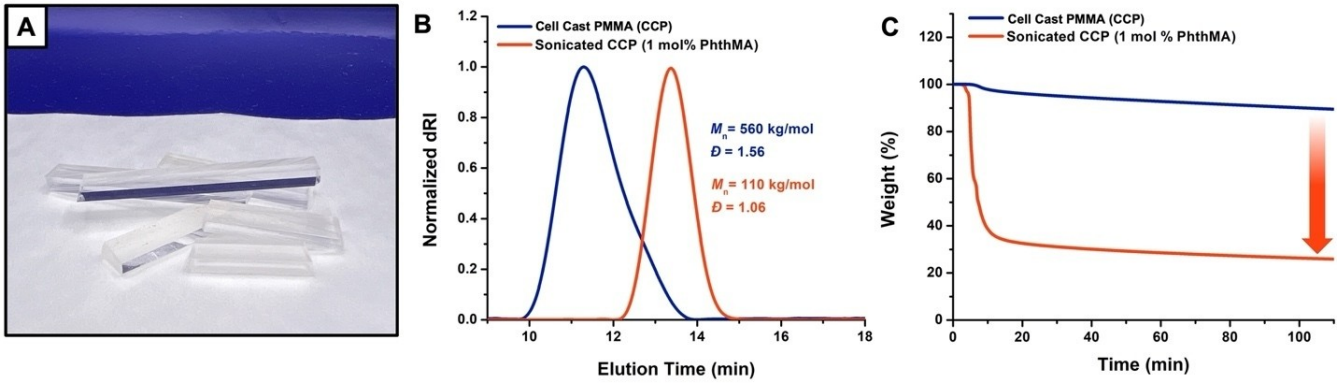
Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: · ·



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