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Bulk depolymerization of PMMA using difunctional pyromellitic or monofunctional phthalimidic ATRP initiators

Ferdinando De Luca Bossa, Gorkem Yilmaz, Carlo Gericke, Krzysztof Matyjaszewski *

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, United States

ABSTRACT

This study presents a new approach for enhancing the depolymerization efficiency of poly(methyl methacrylate) (PMMA) by incorporating multiple depolymerization sites within the polymer chains. Four distinct PMMA polymers were synthesized, each bearing different combinations of phthalimide ester and chloride, or bromide functionalities placed in specific positions in the polymer chain. The polymers were prepared by atom transfer radical polymerization. Increasing the number of activation sites enhanced the depolymerization yield. Experiments conducted under reduced pressure in bulk revealed depolymerization yields ranging from 73 % to 86 % achieved within 30 min at 220 °C. Thermogravimetric analysis performed on polymers with four different molecular weights demonstrated the efficiency of this approach also for polymers with higher molecular weights. A similar strategy was also performed on crosslinked networks by incorporating activatable pyromellitic moieties to reach 85 % of depolymerization yield. This strategy demonstrates the potential for efficient depolymerization of PMMA at relatively low catalyst loadings and temperatures, offering promising prospects for sustainable polymer recycling processes.

1. Introduction

Growing environmental concerns require reducing carbon footprints while improving sustainability. Consequently, the chemical recycling of synthetic polymers has become increasingly important. This attention arises from the prospect of recovering the monomer, opening the door to its reuse in re-producing the original polymers, or forming entirely novel materials [1–3]. The major drawback of depolymerization processes is associated with the requirement of high temperatures for both thermodynamic and kinetic reasons [4–10]. The thermodynamic parameters are related to ceiling temperatures (T_c), above which depolymerization is favored, and equilibrium monomer concentration, $[M]_{eq}$, below which the depolymerization should be quantitative. However, this requires the presence of an active species responsible for polymerization/depolymerisation [4]. Incorporating labile functional groups at polymer chain ends or in the backbone could overcome this limitation and allow depolymerizations at lower temperatures. This should generate reactive species and can reverse polymerization toward the monomer formation. Reversible deactivation radical polymerization (RDRP) processes provide control over molecular weight, dispersity and chain-end functionality. Among the RDRP techniques, atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT) polymerization have been widely used for synthesizing tailor-made well-defined polymers [11–15]. Both the α- and ω- chain ends are predetermined by the initiator structure. Activated alkyl halides are used as initiators in ATRP, which leads to an alkyl group at the α-chain end and the halide moiety at the ω-chain end. The carbon-halogen bond is activated by a catalyst, which is usually a transition metal complex in its lower oxidation state that is reversibly oxidized upon halogen abstraction. Activators are typically Cu(I)/L complexes, whereas the deactivators are the higher oxidation state counterparts, X-Cu(II)/L (L being typically multidentate amines).

Once the active species is generated, the polymerization/depolymerization equilibrium is established. Thus, increasing the temperature and removing the monomers from the reaction mixture should push the equilibrium toward depolymerization.

Recent advances in depolymerization focused on developing efficient systems to carry out depolymerizations at higher polymer concentrations, lower temperatures, and shorter reaction times. The initial depolymerization studies of poly(methyl methacrylate) (PMMA), with terminal chlorine chain end functionality and a ruthenium catalyst, exhibited a 24 % efficiency at 120 °C [16]. In contrast, depolymerization processes of poly(*n*-butyl methacrylate) (PBMA) with terminal chlorine chain-end groups (at a concentration of 750 mM repeating units (RU)) (8 wt% In solvent), performed with a $CuCl_2$/tris(2-pyridyl methyl)amine (TPMA) catalyst at 170 °C, proceeded with a much higher 67 % yield [17]. Subsequently, the depolymerization of ω-chloro functional PBMA and PMMA (with a concentration of [RU] = 700 mM), mediated by iron

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* Corresponding author.
E-mail address: matyjaszewski@cmu.edu (K. Matyjaszewski).
@MatyPolymerLab (K. Matyjaszewski)

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chloride salts and iron powder at 170 °C, resulted in a 70 % depolymerization yields within 20 min [18]. The RAFT technique was also used for depolymerization, and up to 92 % yield was reached at 120 °C but under highly diluted conditions [19]. Using light [20,21] and a photocatalyst, such as eosin Y [22] or ZnTTP [23] reduced the reaction temperature and accelerated the process. Photoinduced depolymerization afforded the temporal control of the process by switching the light on and off, both in Fe-based ATRP [24] and RAFT [25]. Recent studies reported bulk depolymerization of PMMA and PBMA in the temperature range between 150 and 230 °C [26–30]. The depolymerization of end-unsaturated polymethacrylates in bulk at 220 °C reached 84 % conversion [27]. Depolymerization under reduced pressure to ensure continuous monomer removal resulted in up to 84 % yields within 15 min using a copper catalyst [26]. PMMA containing a thermolabile phthalimide ester at the α chain-end and a trithiocarbonate as a RAFT agent group at the ω chain end afforded 92 % of depolymerization at 220 °C in 1 h [28]. When the RAFT moiety was substituted by ATRP Br-chain end, the yield was lower because Br-chain ends participated in the lactonization and loss of active chain ends [17]. On the contrary, since chloride is a poorer leaving group than bromide, higher yields of depolymerizations were attained due to diminished lactonization [17]. Incorporation of *N*-acyloxy phthalimide groups at the side chain by copolymerizing methyl methacrylate with 1,3-dioxoisoindolin-2-yl methacrylate generated radicals at the backbone, leading to β-scission followed by depolymerization, yielding up to 90 % monomer [29]. Recently, synthesis of PMMA featuring two distinct depolymerization sites was reported [31]. The depolymerization processes were conducted in two modes: from the core to the chain ends and from the chain ends to the core (Scheme 1).

The efficiencies of these processes were 5 to 25 % higher than those achieved through mono-triggered depolymerization, with variations depending on the molecular weight of the PMMA. These reactions were performed under high dilution to reduce the contribution of side reactions.

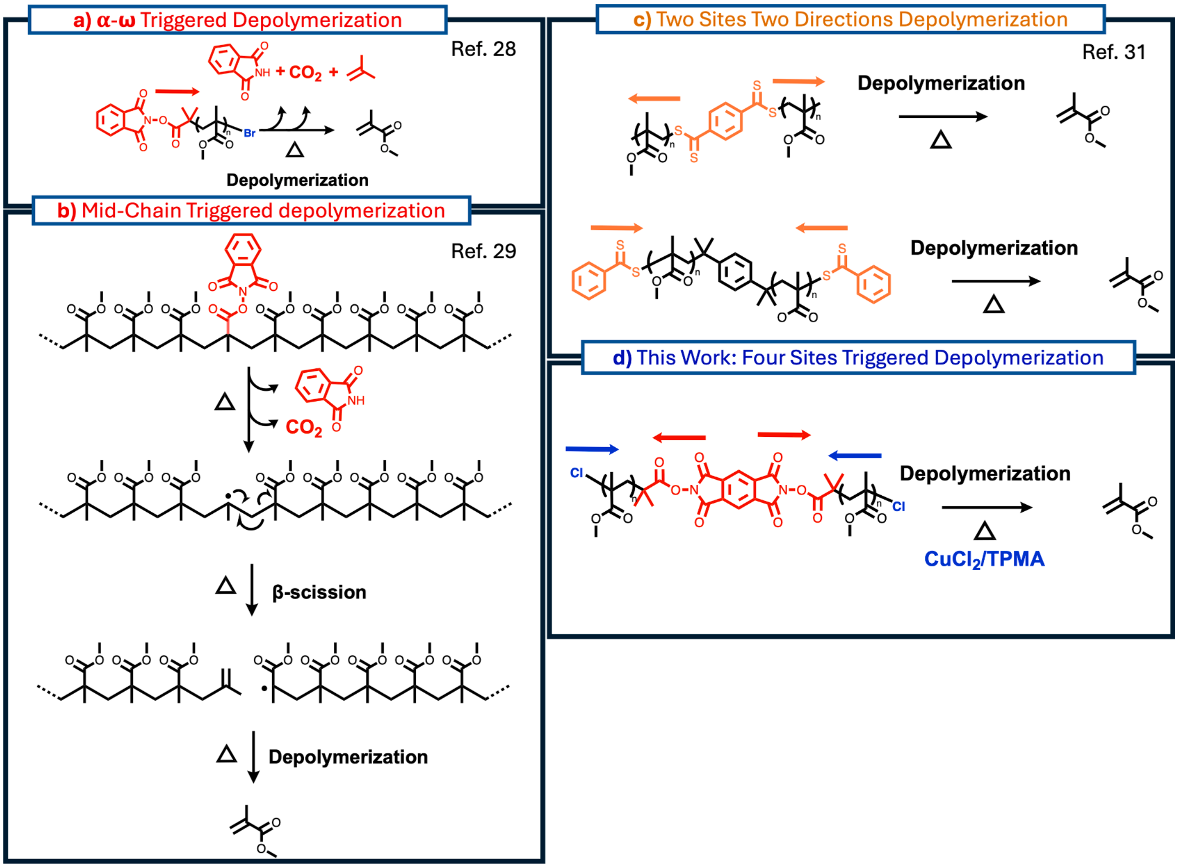
In this study, we present a novel strategy utilizing PMMA polymers with four distinct depolymerization sites, conducted in bulk. For this purpose, various initiators were employed (see Figs. S1–S4) alongside PMMA polymers containing:

i) two pyromellitic imide ester groups in the middle of the polymer chain and two tertiary chloride groups at the ω-chain-ends – 4 active sites (PM-PMMA-Cl_2) ii) α-phthalimide and ω- -2 active sites (Phth-PMMA-Cl), iii) two ω-chlorides (EG-PMMA-Cl_2) were synthesized; iv) network (PM-PMMA-Gel) with pyromellitic moieties as crosslinkers was also prepared by free radical polymerization to test network degradation under depolymerization conditions. Thus, more active sites were incorporated into the polymers to increase the depolymerization yield. Halogen groups at the ω-chain ends required $CuCl_2$/TPMA precatalyst for radical generation, whereas phthalimide and pyromellitic ester moieties formed radicals by homolytic thermal cleavage of the N-O bond at ca. 230 °C.

2. Results and discussion

The polymers were synthesized by SARA ATRP using CuX_2/TPMA and Cu(0) [32,33]. The choice of solvent for the reaction was critical due to the reactive nature of the phthalimide-activated ester moiety. Polymerizations in dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) lead to bimodal polymer distributions, probably due to the chemical instability of the initiator (see Figs. S5 and S6; NMR analyses). Polymerizations in acetonitrile (MeCN) lead to polymers with narrow molecular weight distributions. It should be noted that the comproportionation of Cu(II) and Cu(0) occurs more rapidly and Cu(I) displays an enhanced stability in MeCN [33].

High-resolution thermogravimetric analysis (HR-TGA, with a



Scheme 1. Summary of the previous literature reports and a new approach with 4 depolymerization sites.

dynamic heating rate, staring at 10 °C/min and slowing down while detecting a mass loss) were performed to characterize the stability of the polymers at elevated temperatures. Polymers with no thermolabile functionality (EG-PMMA-Cl_2), nor defects in the backbone started decompositions above ~350 °C [34]. In contrast, polymers bearing thermolabile moieties (PM-PMMA-Cl_2 and Phth-PMMA-X) showed decompositions at lower temperatures (Fig. 1a). Specifically, PM-PMMA-Cl_2 underwent degradation with an onset temperature of 220 °C, demonstrating the advantage of pyromellitic moiety. Notably, both polymers reached similar depolymerization yields (ca 75 %) through *N*-acyloxy group activation.

The HR-TGA of the polymers in the presence of the Cu catalyst (X-Cu^{II}/TPMA, 0.055 eq with respect to chain ends) was then performed. Both depolymerization modes were observed in the thermograms of Cl-terminated polymers, with an onset of 180 °C for ω- Cl activations and 240 °C for α- Imide activations (Fig. 1b).

The Cu/L catalyst could activate/decompose Phth and PM moieties at lower temperatures which could explain why the depolymerization obtained from the activated ester in the absence of catalyst accounted for 70 % depolymerization in the range of ca. 250 °C but only for 10–20 % in the presence of Cu/L (Fig. 1b) [35].

Next, a vacuum distillation setup was used for depolymerization on a preparative scale (0.5 g of PMMA). Since the glass transition temperature of PMMA is lower than the depolymerization temperatures (220 °C), the reactions were carried out in bulk without any solvent. A round bottom flask was charged with PMMA and $CuCl_2$/TPMA in an oil bath at 220 °C without deoxygenation. The generated MMA was collected in a pre-cooled receiving flask under reduced pressure (2–3 mbar). Table 1 shows the depolymerization yields for different PMMA samples after 30 min. The molecular weights of the polymer with different initiators were monitored by GPC before and after the depolymerization. The molecular weight of PMMA containing the pyromellitic-based initiator was reduced by half after the vacuum distillation, confirming that the initiator was degraded and the polymeric chain was chopped by half (Fig. S25).

The depolymerization results obtained under the vacuum distillations align with the HR TGA analyses. Remarkably, PM moiety leads to higher depolymerization yields in the absence of the catalyst (27 %). Cu-catalysts increased the yields. Previously, we demonstrated that ω-chloro terminated PMMA could be depolymerized with a yield of 73 % at 230 °C using 0.22 eq $CuCl_2$/TPMA [26]. EG-PMMA-Cl_2, with Cl-groups at the α- and ω-chain ends reached a similar depolymerization yield (70.5 %), requiring less Cu catalyst (0.055 eq with respect to the chain ends) due to the increased number of activation sites. When the *N*-acyloxy moiety (Phth-PMMA-Cl) was used as the reactive α- group, the yield increased to 86 %, demonstrating the improved efficiency of this method. PM-PMMA-Cl_2, which has four possible activation sites, two central α-PM sites and two terminal ω- Cl sites, depolymerized in a yield of 73 % with high monomer recovery (83 %).

Table 1
Depolymerization of PMMA structures at 220 °C, for 30 min, and 2–3 mbar.

Polymer	CuX_2/ TPMA (X, eq)	Yield (%)[a]	MMA recovered (%)[b]	Molecular Weight, M_n, $Đ$
EG-PMMA-Cl_2	Cl, 0055	70.5	87.4	10,700; 1.24
Phth-PMMA-Br	–	13	68.3	5,200; 1.08
Phth-PMMA-Br	Br, 0055	50	53	5,200; 1.08
Phth-PMMA-Cl	–	12	65	11,900; 1.23
Phth-PMMA-Cl	Cl, 0055	86	76	11,900; 1.23
PM-PMMA-Cl_2	–	27	79	7,900; 1.22
PM-PMMA-Cl_2	Cl, 0055	73	83	7,900; 1.22

[a] (Mass loss/Polymer Mass) × 100 [b] (Recovered MMA mass)/Mass loss × 100.

Then, the effect of 4 depolymerization sites on the depolymerization of PMMA with different molecular weights was studied. Polymers with DP = 50, 150, 350, and 800 were synthesized using conditions similar to those discussed before (Figs. S16–S24, Tables S1 and S2). HR-TGAs revealed that in the absence of the catalyst, the depolymerization of PM-PMMA-Cl_2 was more efficient than that of Phth-PMMA-Cl at lower DP (Fig. 2a). However, for polymers with higher DP = 350 and 800, the depolymerization of Phth-PMMA-Cl was more efficient. Moreover, when $CuCl_2$/TPMA was added, better depolymerization was obtained with PM moiety at higher DP (Fig. 2b and c).

Crosslinked networks are important thermosetting materials that are difficult to recycle. Therefore, their depolymerization is essential [19]. To demonstrate the depolymerizability of PMMA networks, a degradable crosslinker was synthesized by reacting *N,N'*-dihydroxypyromellitic diimide with methacryloyl chloride (Fig. S7). Then, the crosslinker was copolymerized with MMA by conventional radical polymerization to form the PM-PMMA-Gel (Fig. 3a and SI). HR-TGA demonstrated that PM-PMMA-Gel without the presence of any solvent or catalyst depolymerized in a range of temperature between 220 °C and 250 °C with a remarkable 85 % yield (Fig. 3b). This confirmed the possibility of recycling networks by incorporating activatable moieties into their structures.

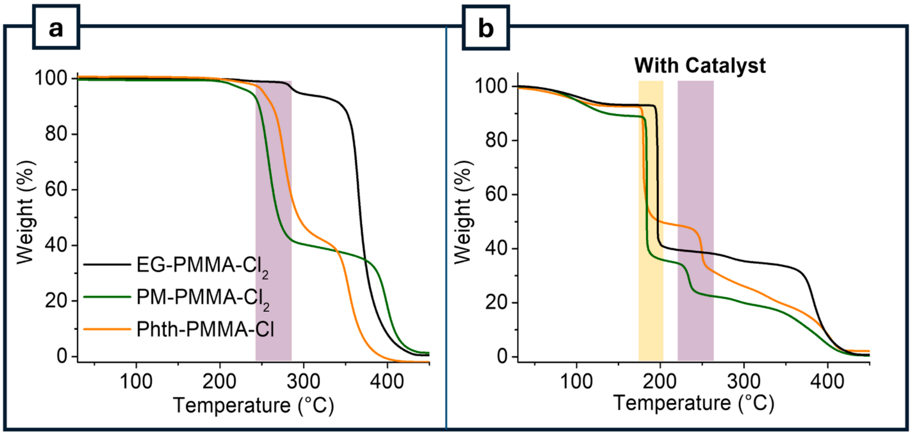


Fig. 1. a) HR-TGA of EG-PMMA-Cl_2, PM-PMMA-Cl_2, and Phth-PMMA-Cl. b) HR-TGA analyses of the polymers in the presence of (Cl-Cu^{II}/TPMA 0.055 eq with respect to Cl). (HR-TGA conditions: dynamic heating rate of 10 °C/min under N_2 flow).

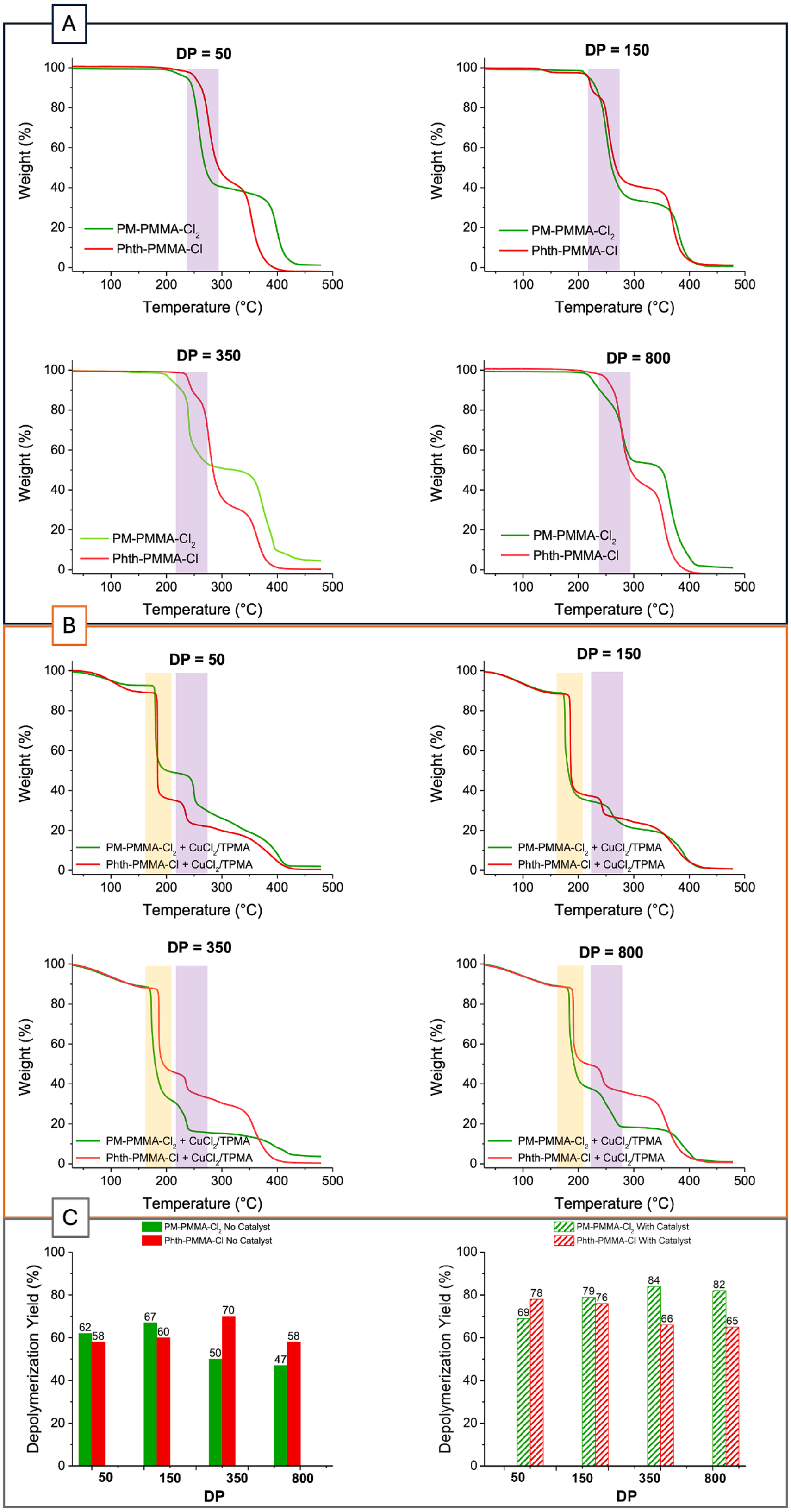


Fig. 2. Thermogravimetric analysis (TGA) of the PMMAs with different molecular weights. a) without catalyst, b) with catalyst ($CuCl_2$/TPMA 0.055 eq to chain end (s), c) summary of the results from TGAs.

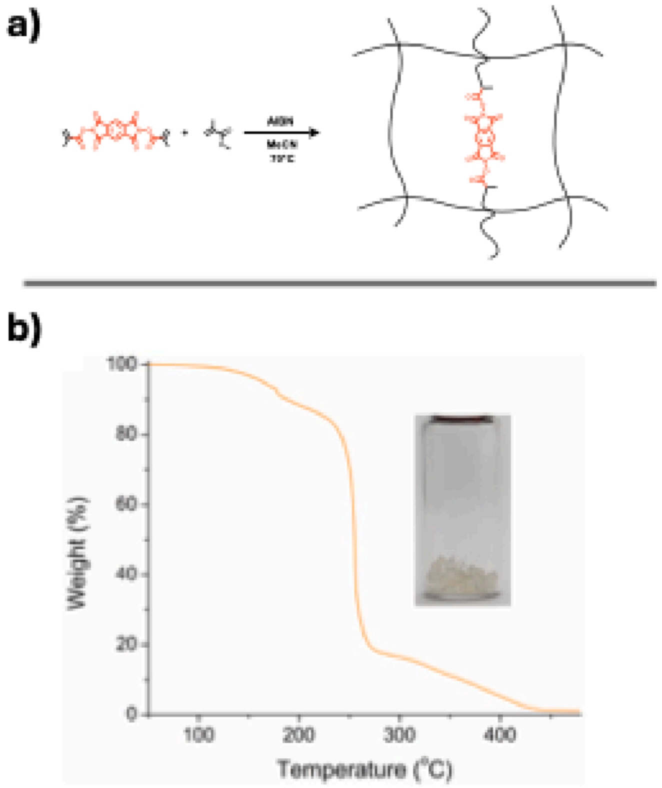


Fig. 3. Preparation of the crosslinked gel, PM-PMMA Gel (a), and its HR-TGA analysis (b) (HR-TGA conditions: dynamic heating rate of 10 °C/min under N_2 flow).

3. Conclusions

This study presents an approach to enhance the chemical recycling of PMMA by increasing the number of active sites within the polymer. By incorporating thermolabile moieties, such as pyromellitic imide esters and phthalimide functionalities, alongside ω-terminal halide groups, significant improvements in depolymerization efficiency were achieved. Polymers with multiple activation sites demonstrated high depolymerization yields (73–86 %) and relatively rapid monomer recovery under bulk conditions at 220 °C within 30 min, even with low catalyst loadings. Crosslinked PMMA networks with PM-based dimethacrylate crosslinkers were also successfully depolymerized, achieving yields of 85 %, showing the potential for recycling thermosetting materials. Molecular weight analysis revealed that higher molecular weight polymers particularly benefited from the catalytic systems and multiple activation sites.

These findings demonstrate a scalable, efficient strategy for polymer depolymerization under mild conditions, offering a promising solution to the challenges of polymer sustainability. Future work could focus on scaling the process, applying the method to other polymers, designing advanced catalysts to further reduce reaction temperatures, and assessing the environmental and economic implications of this approach. This research highlights the potential for chemically recyclable materials to bridge the gap between performance and sustainability, providing new opportunities for advancing polymer recycling technologies.

CRediT authorship contribution statement

Ferdinando De Luca Bossa: Writing – original draft, Formal analysis, Data curation, Conceptualization. **Gorkem Yilmaz:** Writing – review & editing. **Carlo Gericke:** Data curation. **Krzysztof Matyjaszewski:** Writing – original draft, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [K Matyjaszewski reports a relationship with National Science Foundation that includes: funding grants. The other authors declare no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper].

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Highlights: ATRP allows the synthesis of Polymers with retained chain end functionality useful to efficiently generate active chains for depolymerization at lower temperatures.

Chemical recycling to monomer or Depolymerization is a selective process that allows to minimize or eliminate the side reactions during a depolymerization process.

Bulk Depolymerization makes the process industrially relevant in terms of sustainability, safety, and economically. It implies the performance of a depolymerization without the use of any solvent during the process.

Networks are important class of materials employed in many applications. They are difficult to recycle or depolymeriza because they are crosslinked.

Network depolymerization was possible because of the use of degradable crosslinker which triggered the depolymerization in bulk above 220 °C.

Activated Esters.

Activated Esters Stability.

Appendix A. Supplementary data

NMRs, GPCs, TGA, and experimental procedures are reported in the supporting information. Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2024.113646.

Data availability

Data will be made available on request.

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