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Efficient catalytic depolymerization of high-molecular-weight PMMA under low-temperature and high-concentration conditions

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To help alleviate resource waste and environmental pollution from discarded poly(methyl methacrylate) (PMMA), we demonstrate facile synthesis and efficient catalytic depolymerization of high-molecular-weight PMMA. A small fraction of C–Me bonds are replaced with catalytically activatable C–Cl bonds via free radical copolymerization of MMA with readily available methyl α -chloroacrylate. Leveraging low-temperature efficient catalysis by Cu(0), the synthesized polymers achieve high recyclability while maintaining ideal intrinsic properties. For PMMA with M_n exceeding 300 kg mol^{−1} (380–1010 kg mol^{−1}), Cu(0)-catalyzed depolymerizations attain the highest reported depolymerization efficiency (~90% in 4 hours) at a temperature well below 200 °C (160 °C) and high concentrations ([MMA unit]₀ = 400–8800 mM). The recovered MMA monomer can be effectively repolymerized into a polymer with molecular weight and properties comparable to those of the polymer synthesized from a virgin monomer, and both catalysts and solvents used in this approach exhibit potential for recyclability.

Green foundation

1. This work advances green chemistry by enabling facile synthesis and efficient depolymerization of high-molecular-weight PMMA with ideal intrinsic properties under mild conditions. The simple Cu(0)-catalyzed depolymerization approach reduces reliance on high temperatures/high dilution (large volumes of solvent) and resolves the dilemma of balancing thermal stability vs. recyclability, promoting plastic recycling and boosting sustainable high-performance material circulation.
2. For PMMA with M_n exceeding 300 kg mol^{−1} (380–1010 kg mol^{−1}), the Cu(0)-catalyzed depolymerizations in this work attain the highest reported depolymerization efficiency (~90% in 4 hours) at a temperature well below 200 °C (160 °C) and high concentrations ([MMA unit]₀ = 400–8800 mM).
3. Further research could make it greener by investigating Cu(0) catalyst recycling, exploring greener catalysts, lowering temperatures, and enhancing monomer recovery yield.

Introduction

Vinyl polymers synthesized *via* chain-growth polymerization are prized for structural durability from their carbon-based backbones but face recycling challenges due to C–C bond stability.^{1–4} As a premier thermoplastic material, PMMA has emerged as a vital glass alternative in the aerospace and construction industries, boasting an annual global production volume of 4 million tons. However, less than 10% of PMMA waste is recycled annually.^{5,6} Conventional depolymerization

via pyrolysis (400–500 °C) faces challenges in achieving high monomer purity due to undesired radical side reactions. While pyrolytic depolymerization of PMMA has achieved a 98% yield and over 97% purity of recovered MMA through improved reactor designs such as fluidized bed and laboratory fixed-bed reactors,^{7,8} even minor impurities generated during pyrolysis act as chain transfer agents during the repolymerization of recovered MMA *via* radical polymerization. This significantly reduces the molecular weight of the repolymerized product. Yoshida, E. made an improvement and recovered MMA with 95% purity and 87% yield under vacuum pyrolysis at 1 mmHg and 420 °C.⁹ Compared to PMMA produced from the original MMA monomer, the polymer obtained from recycled MMA still exhibits a lower molecular weight and a broader molecular weight distribution. Consequently, high-temperature pyrolysis might not only lead to higher total energy input due to the significant sensible heat required for

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heating materials and the energy needed to compensate for system heat losses, but it also places greater demands on both equipment and energy sources. More importantly, the excessively high temperatures lead to the production of numerous “harmful” impurities. These challenges have prompted researchers to explore the use of polymers with active chain ends, prepared *via* controlled radical polymerization (CRP), which enable the recycling of PMMA through chain-end-initiated depolymerization under milder conditions. Pioneering Ru-catalyzed depolymerization of ATRP-synthesized PMMA was reported by Ouchi *et al.*,¹⁰ and Fe/Cu catalysts achieved ~75% depolymerization conversion at 170–230 °C, as reported by Matyjaszewski *et al.*^{11–14} Research groups including those of Anastasaki,^{15–19} Gramlich,²⁰ and Sumerlin²¹ achieved 70–86% depolymerization conversion for RAFT-derived PMMA at 100–120 °C, yet required high dilutions (~5 mM [MMA unit]₀).²² These methods demand CRP-synthesized PMMA with preserved chain-end functionality, often sacrificing polymerization conversion and molecular weight. In addition, the studies showed that the efficiency decreased significantly when depolymerizing high molecular weight PMMA.¹⁵ Therefore, the M_n of the end-functionalized PMMA used in the abovementioned studies usually does not exceed 6 kg mol⁻¹, or even as low as 2.5 kg mol⁻¹. This is significantly lower than the molecular weight range (10⁵–10⁶ g mol⁻¹) of practically applied PMMA, which is conventionally synthesized *via* free radical polymerization.

Recent breakthroughs have been achieved in depolymerizing high-molecular-weight PMMA ($M_n \geq 100$ kg mol⁻¹). Early strat-

egies relied on pre-incorporating thermally labile sites during synthesis (Fig. 1a): Sumerlin *et al.* achieved 65% and 48% depolymerization conversions at 250 °C (bulk) for 100 kg mol⁻¹ and 980 kg mol⁻¹ PMMA, respectively, *via* difunctional α/ω -end activation;²³ Diao *et al.* attained 48–91% depolymerization conversion for 360–1200 kg mol⁻¹ polymers at 200 °C under highly diluted conditions (14 mM [MMA unit]₀) through in-chain fragile monomer unit activation (α -methylstyrene analogs);²⁴ Sumerlin's alternative approach using labile pendent groups yielded >90% depolymerization conversion at 290 °C (bulk) for 100–2300 kg mol⁻¹ PMMA.²⁵ More recently, the post-introduction of thermally labile sites onto existing PMMA demonstrated enhanced practicality (Fig. 1b): Sumerlin's chain-end/side-group post-functionalization achieved 60–80% depolymerization conversion at 290 °C (bulk) for 100–1800 kg mol⁻¹ PMMA;^{26,27} Anastasaki's method attained ~98% depolymerization of 60–1600 kg mol⁻¹ PMMA in chlorinated solvents, requiring near-UV light (415 nm), a prolonged reaction time (48 h), and high dilution (10 mM [MMA unit]₀).²⁸

The above-mentioned advances in the depolymerization of high-molecular-weight PMMA are remarkable. The independence from catalysts undoubtedly simplifies the reaction system and reduces costs. However, thermally triggered depolymerization strategies usually still require high temperatures (250–290 °C); otherwise, highly dilute systems (10–14 mM [MMA units]₀) and long reaction times (16–48 h) are needed to achieve high depolymerization conversion (>70%). Moreover, they struggle to balance the thermal stability and thermo-depo-

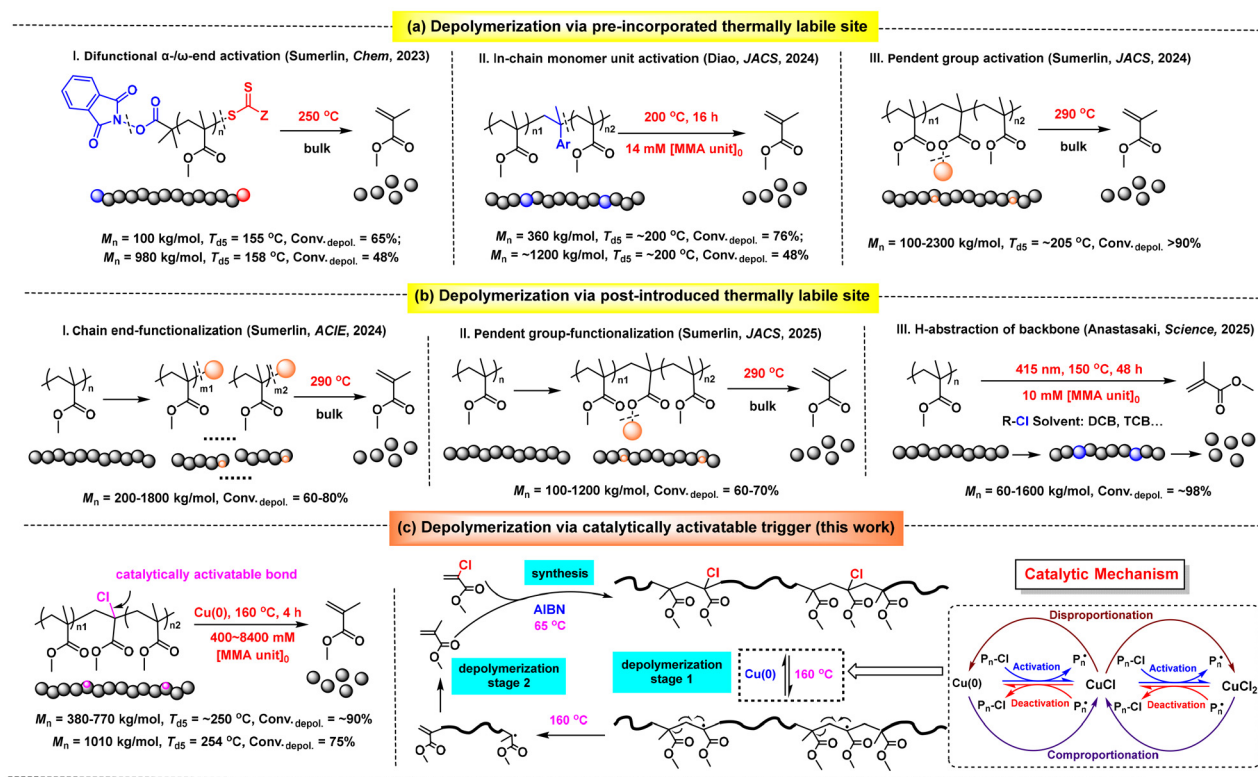


Fig. 1 Strategies for the depolymerization of high-molecular-weight PMMA.

lymerizability of materials. In contrast, controlled depolymerization through a catalytic response mechanism offers potential for achieving efficient depolymerization under milder conditions and alleviating the dilemma of the thermal stability and thermo-depolymerizability of materials. As aforementioned, Matyjaszewski's chain end-atom transfer (AT) activation using Fe/Cu catalysts was only applied to low-molecular-weight PMMA ($M_n < 6.0 \text{ kg mol}^{-1}$). Our²⁹ and Ouchi's groups,³⁰ respectively, degraded PMMA with "in-chain" C-Cl bonds synthesized by ATRP and RAFT polymerization into fragments through main chain-AT catalytic activation. Admittedly, depolymerizing PMMA to recover its monomer is more valuable in applications and better aligned with the principles of sustainable green chemistry. However, monomer regeneration from catalytic depolymerization of high-molecular-weight PMMA has never been attained. In this work, we employed a simple Cu(0) catalyst^{31,32} to catalytically activate main-chain C-Cl at lower temperatures (Fig. 1c). The efficient depolymerization under mild conditions breaks through the limitations of molecular weight and polymer concentration, achieving high depolymerization conversions of ~90% within 4 h at a temperature well below 200 °C (160 °C) for PMMA with high M_n ranging from 380 kg mol^{-1} to 1010 kg mol^{-1} under high [MMA unit]₀ conditions of 400–8800 mM. Furthermore, the polymer synthesis does not rely on CRP, enabling the facile production of PMMA with excellent depolymerizability and inherent properties comparable to or even superior to those of commercial PMMA.

Results and discussion

Synthesis of C-Cl bond-containing PMMA with various molecular weights and excellent thermodynamic properties

First, a series of C-Cl bond-containing PMMAs with M_n ranging from 40.8 to 1010 kg mol^{-1} were synthesized by copo-

lymerizing MMA with adamantyl α -chloroacrylate (2-ADCA) or methyl α -chloroacrylate (MCA) at 65 °C using AIBN as the initiator (Table 1 and Table S1). Due to the higher reactivity of chlorinated monomers compared to MMA,³⁰ their incorporation ratio (5–14 mol%) in the copolymer consistently exceeded the initial feed ratio (2–9 mol%). These copolymers exhibit excellent thermal stability, with 5% and 40% weight-loss temperatures (T_{d5} and T_{d40}) of 248–260 °C and 376–403 °C, respectively. They also demonstrate high glass transition temperatures ($T_g = 121$ –129 °C), exceeding that of commercial PMMA (117 °C). These results indicate that the synthesized C-Cl bond-containing PMMA possesses thermodynamic properties comparable to or even superior to those of commercial PMMA.

Effects of catalysts and reaction conditions on depolymerization

We dissolved PMMA₃₅₈-2-ADCA_{20.5} in DMSO and conducted the depolymerization at 120 °C for 10 h in a sealed Schlenk tube filled with argon. By setting [MMA unit]₀ as 439 mM, the effect of the catalytic system was investigated (Fig. 3a, Table S3). The depolymerization system was analysed *via* ¹H NMR to determine the depolymerization conversion (Conv._{depol.}) based on the decrease in the integral area of MMA units relative to that of the internal standard (mesitylene). See the SI for the detailed calculation method. Using the SARA ATRP catalyst (side-armed bisoxazoline (SaBOX)/CuBr₂/Cu(0)^{33–39}), AT-mediated C-Cl activation achieved 19% depolymerization conversion. By removing CuBr₂ and using SaBOX/Cu(0) as the catalyst, the depolymerization conversion increased significantly to 29%. Replacing SaBOX with other classic ligands (dNbpy, PMDETA) decreased the depolymerization conversion. Unexpectedly, without adding a ligand and using only Cu(0) as the catalyst, a higher depolymerization conversion of 35% was obtained. In contrast, using catalysts

Table 1 Catalytic depolymerization of C-Cl bond-containing PMMA

Run ^a	Polymer	M_n (kg mol^{-1})	D	T_g (°C)	T_{d5} (°C)	T_{d40} (°C)	[MMA unit] ₀ (mM)	Conv. _{depol.} ^e (%)	Yield _{MMA} ^f (%)
1	PMMA ₃₅₈ -2-ADCA _{20.5}	40.8	1.8	129	250	376	439	64	95
2	PMMA ₄₅₇ -Cl	46.0	1.1	127	311	377	489	0	—
3	PMMA ₇₅ -Cl	7.70	1.2	110	—	—	487	4	—
4	PMMA ₃₇₈ -MCA _{28.2}	41.2	2.0	124	251	393	459	65	95
5	PMMA ₃₇₈ -MCA _{28.2}	41.2	2.0	124	251	393	459	69	91
6	PMMA ₅₃₄ -MCA _{29.3}	57.0	1.8	121	249	380	468	63	98
7	PMMA ₃₉₇ -MCA _{50.5}	41.5	1.9	127	255	403	418	60	98
8	PMMA ₃₄₂₃ -MCA ₃₂₆	382	2.2	127	260	399	448	74	>99
9	PMMA ₆₇₀₈ -MCA ₈₁₆	771	1.7	124	248	394	435	74	99
10 ^b	PMMA ₆₇₀₈ -MCA ₈₁₆	771	1.7	124	248	394	1740	77	>99
11 ^b	PMMA ₈₈₅₁ -MCA ₁₀₂₈	1010	1.6	124	255	388	1753	77	91
12 ^b	PMMA ₈₈₅₁ -MCA ₁₀₂₈	1010	1.6	124	255	388	8763	66	86
13 ^{a,c}	PMMA ₃₄₂₃ -MCA ₃₂₆	382	2.2	127	260	399	448	91	—
14 ^{a,c}	PMMA ₆₇₀₈ -MCA ₈₁₆	771	1.7	121	248	393	435	87	87
15 ^{c,d}	PMMA ₉₈₂ -MCA ₁₀₆	111	2.3	130	251	393	435	75	93

^a $m_{\text{polymer}} = 100$ –120 mg, $m_{\text{Cu(0) powder}} = 17.8$ mg, 160 °C, using DMSO as the solvent, 10 h for runs 1–4, 4 h for runs 5–15. ^b $m_{\text{polymer}} = 40$ –50 mg, $m_{\text{Cu(0) powder}} = 8.9$ mg. ^c Depolymerization for 1 h at 160 °C and removing the MMA monomer under vacuum at 30 °C for 0.5 h in a repetitive manner for four cycles. ^d $m_{\text{polymer}} = 2.5$ g, $m_{\text{Cu(0) powder}} = 445$ mg. ^e The depolymerization conversion measured by ¹H NMR as the decrease in MMA units relative to mesitylene as the internal standard. ^f Fraction of the obtained MMA monomer based on the loss of MMA units.



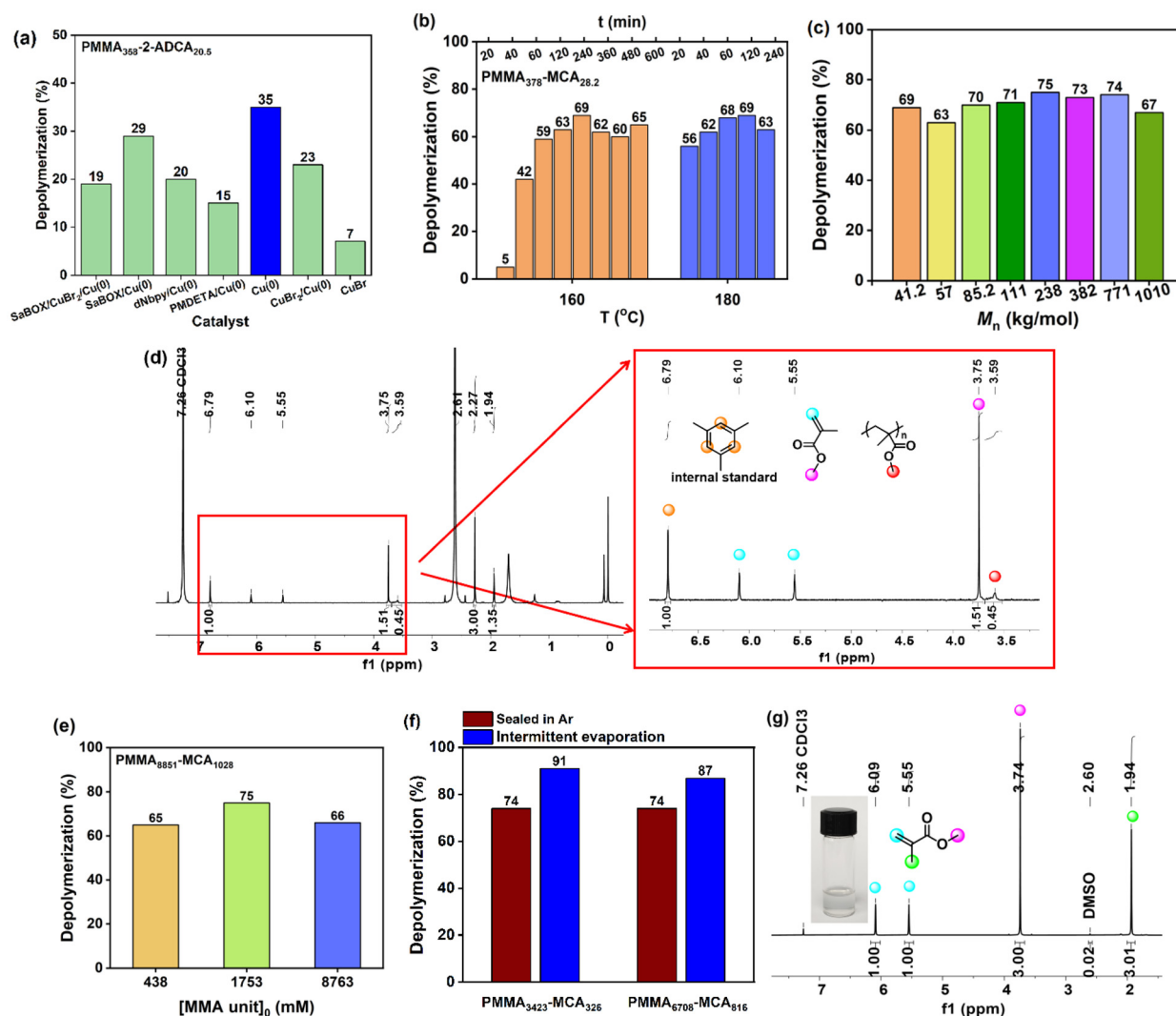


Fig. 3 Catalytic depolymerization of C–Cl bond-containing PMMA. Effect of (a) catalyst, (b) time, (c) polymer molecular weight, (e) polymer concentration, and (f) operational procedure on the final depolymerization conversion. Quantitative ¹H NMR spectra of a typical (d) depolymerization system (run 10, Table 1, 40 mg polymer, 25 μ L mesitylene) and (g) a separated monomer from a gram-scale depolymerization system.

for the typical AT mechanism such as CuBr₂/Cu(0) or CuBr gave depolymerization conversions of only 23% and 7%, respectively. These results indicate that activating C–Cl simply using Cu(0) as the catalyst is more favourable for the depolymerization of C–Cl bond-containing PMMA than complex AT catalytic systems. Increasing the amount of Cu(0) further improved the depolymerization conversion to 40%, while Fe(0) could not catalyse depolymerization under the same conditions. Temperature also influenced depolymerization. At 65 °C, no monomer formation was observed. When the temperature increased to 100 °C, the depolymerization conversion was only 7%. Upon elevation from 120 °C to 160 °C, the depolymerization conversion substantially improved from 40% to 62% (Table S4). Solvent selection also demonstrated notable impacts on depolymerization efficiency. When using tetraethylene glycol dimethyl ether (TEGDME), tetramethylene sulfone (TMS), *N*-methylpyrrolidone (NMP), γ -valerolactone

(GVL), or 1,2,4-trichlorobenzene (TCB) as the solvent, the depolymerization conversion remained limited to 6–19%. Only when employing tetramethylene sulfoxide (TMSO), another sulfoxide solvent, was a relatively high depolymerization conversion (53%) achieved (Table S4). This observation aligns with DMSO's established role as an optimal solvent for Cu(0)-catalysed CRP, where disproportionation is crucial.³¹ DMSO's high polarity, coordination capability, and solvation power synergistically enable highly efficient catalytic cycling *via* promoting efficient disproportionation of Cu(i)X and enhancing dispersion of Cu(0) nanoparticles. We further validated these effects through UV-vis spectroscopy studies examining how temperature, ligands, and solvents influence CuBr disproportionation—with results directly correlating with the depolymerization outcomes (Fig. S4).

In addition to the depolymerization conversion, the yield of MMA monomer (Yield_{MMA}) in the depolymerization system

was calculated *via* ^1H NMR, defined as the fraction of yielded MMA monomer relative to the loss of MMA units. The quantity of generated MMA monomer was determined based on the integral area ratio of MMA monomer to the internal standard (mesitylene). See the SI for the detailed calculation method. Using DMSO as the solvent and Cu(0) as the catalyst, depolymerization of PMMA₃₅₈-2-ADCA_{20.5} ($[\text{MMA unit}]_0 = 439 \text{ mM}$) gave a depolymerization conversion of 64% and an MMA yield of 95% after 10 h at 160 °C, indicating a negligible side reaction (Table 1, run 1). In contrast, PMMA₄₅₇-Cl bearing a C-Cl chain end, synthesized *via* ATRP with comparable molecular weight and thermodynamic properties, showed no depolymerization under identical conditions (run 2). PMMA₇₅-Cl ($M_n = 7.7 \text{ kg mol}^{-1}$) with a T_g of 110 °C achieved only a 4% Conv._{depol.} (run 3). These results highlight the distinct advantages of the C-Cl bond-containing PMMA in terms of high molecular weight, efficient catalytic depolymerization capability, and superior thermodynamic properties. The copolymer PMMA₃₇₈-MCA_{28.2}, synthesized using MCA as a comonomer, exhibits molecular weight, composition, and thermodynamic properties similar to those of PMMA₃₅₈-2-ADCA_{20.5}. It achieved a Conv._{depol.} of 65% and Yield_{MMA} of 95% after 10 h (run 4), consistent with the depolymerization results of PMMA₃₅₈-2-ADCA_{20.5}. The influence of depolymerization time was investigated (Fig. 3b). At 160 °C, almost no monomer was generated within 20 min, while a Conv._{depol.} of 42% was attained after 40 min. Extending the reaction time to 4 h gradually increased the conversion to 69%. However, further prolonging the time to 10 h resulted in a declining trend in conversion. When the temperature was raised to 180 °C, PMMA₃₇₈-MCA_{28.2} depolymerized more rapidly, achieving a conversion of 56% within 20 min. Nevertheless, after monitoring the reaction for 4 h, the maximum conversion did not exceed the result observed at 160 °C. Notably, when the number of MMA or MCA units in the polymer chain was increased (*e.g.*, PMMA₅₃₄-MCA_{29.3} or MMA₃₉₇-MCA_{50.5}), the depolymerization results in 4 h were similar to that of PMMA₃₇₈-MCA_{28.2} (runs 6–7).

Depolymerization of high molecular weight polymers

PMMA₃₄₂₃-MCA₃₂₆ and PMMA₆₇₀₈-MCA₈₁₆, with M_n of 382 and 771 kg mol^{-1} , respectively, both exhibit excellent thermodynamic properties ($T_g > 120$ °C, $T_{d5} \sim 250$ °C, $T_{d40} > 390$ °C). These polymers achieved high Conv._{depol.} of 74% with Yield_{MMA} of $\geq 99\%$ after 4 h at 160 °C (runs 8–9). For PMMA₆₇₀₈-MCA₈₁₆, even when increasing the $[\text{MMA unit}]_0$ from 435 mM to 1740 mM, the conversion remained remarkably high at 77%, with Yield_{MMA} of $> 99\%$ (run 10). The quantitative ^1H NMR spectrum of the system after the depolymerization reaction is shown in Fig. 3d. Similarly, PMMA₈₈₅₁-MCA₁₀₂₈ with a higher molecular weight ($M_n = 1010 \text{ kg mol}^{-1}$) demonstrated a 77% depolymerization conversion and 91% MMA yield under highly concentrated conditions ($[\text{MMA unit}]_0 = 1753 \text{ mM}$) (run 11). Further increasing the $[\text{MMA unit}]_0$ to 8763 mM (using only 0.05 mL of DMSO to dissolve 50 mg of polymer), the Conv._{depol.} reached 66% within 4 h (run 12).

When the depolymerization was performed in a sealed system, the monomer remained in the system throughout the process, and the polymerization–depolymerization equilibrium limited the maximum depolymerization conversion. To overcome this limitation, we adopted an approach where the generated monomer was intermittently separated from the system, thereby shifting the equilibrium toward depolymerization. Specifically, the polymer was depolymerized at 160 °C for 1 h, rapidly cooled to 30 °C, and the monomers were evacuated under vacuum for 0.5 h; this cycle was repeated four times. The reaction device is shown in Fig. S5. With $[\text{MMA unit}]_0 = 435 \text{ mM}$, the depolymerization conversion of PMMA₃₄₂₃-MCA₃₂₆ increased from 73% (under sealed conditions) to 91% (Fig. 3f). Similarly, PMMA₆₇₀₈-MCA₈₁₆ achieved an improved depolymerization conversion of 87% with an MMA yield of 87% (run 14). The slightly lower Yield_{MMA} compared to sealed systems is primarily attributed to a small fraction of generated monomers being retained in the apparatus. Furthermore, a gram-scale depolymerization reaction was conducted *via* intermittent distillation, achieving a depolymerization conversion of 75% and a monomer yield of 93% (run 15). The high-purity monomer ($> 99.7 \text{ wt}\%$) can be conveniently separated from the depolymerization system *via* simple distillation, with only trace amounts of DMSO present (Fig. 3g). Theoretically, such a low content of DMSO ($< 0.3 \text{ wt}\%$), a commonly used solvent, will not have a significant impact on the repolymerization of the recovered monomer. And the experimental results confirmed this speculation. When the recovered MMA was copolymerized with MCA, the molecular weight and the properties of the obtained copolymer were comparable to those of the copolymer prepared using virgin MMA monomer (Table S5).

These experimental results demonstrate that the catalytic depolymerization of the C-Cl bond-containing PMMA is not constrained by molecular weight (Fig. 3c) or polymer concentration (Fig. 3e). Benefiting from the low-temperature efficient Cu(0)-catalysed activation, for PMMA with M_n exceeding 300 kg mol^{-1} and excellent thermodynamic performance, we achieved the highest depolymerization efficiency ($\sim 90\%$ in 4 h) reported to date under mild and high-concentration conditions well below 200 °C ($T = 160$ °C, $[\text{MMA unit}]_0 = 400\text{--}8800 \text{ mM}$). Moreover, the recycled MMA monomer can be effectively repolymerized, demonstrating performance comparable to that of virgin MMA.

Recyclability of the catalyst and the entire depolymerization system (including the catalyst and solvent)

When copper powder was used as the catalyst under the standard reaction conditions of the sealed system outlined in Table 1, PMMA₁₆₆₁-MCA₂₄₆ exhibited a depolymerization conversion of 73% after 4 hours (Table S6). Replacing the high-surface-area copper powder with easily recoverable copper gauze under the same conditions resulted in a similar conversion of 68%. After the reaction, the copper gauze was immersed in concentrated hydrochloric acid, regaining its metallic luster within seconds. It was then rinsed with purified water and dried. The recycled copper gauze was reused as the



catalyst with a recovery rate of 99.7%, yielding comparable depolymerization conversion in the second cycle. These findings indicate the recyclability potential of the Cu(0) catalyst.

In addition to catalyst recycling, we further investigated the recyclability of the entire depolymerization system (including both the catalyst and solvent). Under similar sealed-system reaction conditions (180 °C, 2 h) as described in Table 1, the depolymerization conversion for PMMA₃₇₈-MCA_{28.2} was 54% (Table S6). After the reaction, the monomer was removed, and 100 mg of fresh polymer was added to the same reaction tube for the subsequent depolymerization cycle. The depolymerization conversions for the second and third cycles were 59% and 67%, respectively. These results preliminarily suggest the potential of the entire depolymerization system (including the catalyst and solvent) for recycling and reuse.

Depolymerization mechanism

The molecular weight of the residual polymer during depolymerization was monitored (Fig. S6). Within 20 min, minimal monomer production (5%) contrasted with significant molecular weight reduction (M_p 114 → 81.4 kg mol⁻¹), demonstrating dominant backbone scission. By 40 min, M_p further decreased to 18.0 kg mol⁻¹ with 42% Conv._{depol.}. After 2 h, the conversion reached 63% without significant molecular weight changes. These results suggest a two-stage catalytic depolymerization process: backbone scission to “living” low-molecular-weight fragments with radical termini, followed by chain-end depolymerization of these fragments into MMA monomers (Fig. 1c). This process initiates with the crucial role of the α -chloro group: first, Cu(0) acts as an electron donor, transferring an electron to the α -chloro group (C-Cl bond), and this induces heterolytic cleavage, generating a backbone carbon radical and CuCl. Subsequently, the backbone radical initiates β -scission of adjacent C-C bonds, producing fragments with a terminal vinyl group and a radical. Polar solvent (DMSO) promotes disproportionation of CuCl (2CuCl → Cu(0) + CuCl₂), regenerating the Cu(0) catalyst. This establishes a catalytic cycle that sustains a high concentration of active Cu(0) species. Finally, radical chain ends trigger instantaneous unzipping depolymerization with the release of monomers. Thus, the α -chloro group (C-Cl bond) serves as the core initiation site for the depolymerization process, playing a decisive role in generating backbone carbon radicals and driving subsequent chain cleavage and monomer release.

During the late stage, the molecular weight of the residual polymer remained virtually unchanged. This should be related to the loss of active ends of some polymers mainly *via* lactonization of the chain-end (Scheme S1),^{12,15} which was confirmed by the variation of the infrared spectra of the remaining polymers during the depolymerization of PMMA₃₇₈-MCA_{28.2} (Fig. S7). As the depolymerization proceeds, the newly emerged carbonyl signal at approximately 1784 cm⁻¹ can be attributed to lactonization at the chain end.^{12,15} This reaction leads to the loss of terminal functionality, thereby terminating depolymerization of the polymer chain and limiting the overall depolymerization conversion. However, the result that high-purity

(>99.7 wt%) MMA monomer containing only trace amounts of DMSO solvent could be obtained through simple distillation indicates that the lactonization reaction does not compromise the monomer's purity. The formation of the lactonization product was further supported by mass spectrometry analysis of the residual polymer (Fig. S8). Matyjaszewski *et al.* previously reported that low-molecular-weight (10³–10⁴ g mol⁻¹) poly(methacrylate)s with a halogen terminus readily undergo lactonization with loss of active chain ends under thermally catalyzed depolymerization conditions. Related literature provides detailed qualitative studies of this process also primarily

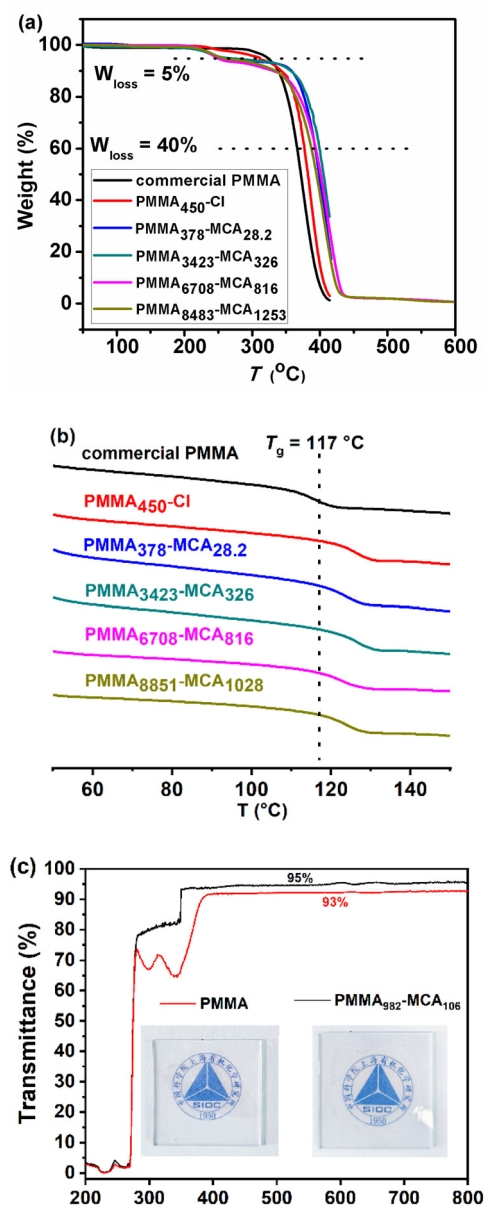


Fig. 2 (a) TGA and (b) DSC curves of commercial PMMA, ATRP-PMMA and C-Cl bond-containing PMMA. (c) Appearance and UV-vis transmittance spectra of solvent-cast films of commercial PMMA and PMMA₉₈₂-MCA₁₀₆ with similar molecular weights.

via infrared spectroscopy.^{12,15,40} The second stage of the depolymerization of high-molecular-weight PMMA in this work, where the “living” low-molecular-weight fragments are depolymerized into MMA monomer from the active chain end, is similar to the catalyzed depolymerization of low-molecular-weight PMMA with a halogen terminus reported by Matyjaszewski *et al.* Therefore, lactonization occurred during the second depolymerization stage as well.

As inferred from the proposed mechanism (Fig. 1c), the complete depolymerization of MMA structural units in the “living” low-molecular-weight fragments generated in the first stage ultimately yields an acrylate vinyl radical, which needs to be captured by a Cl radical to form the MCA monomer (Fig. S9a). However, DFT calculations indicate that the formation of the acrylate vinyl radical is both thermodynamically and kinetically much less favourable compared to the formation of the methacrylate alkyl radical released after the prior unzipping depolymerization steps (Fig. S9b). This should be the reason why the MCA monomer was not detected in our depolymerization system.

Optical transparency and reactivity of C–Cl bond-containing PMMA

In addition to thermodynamic performance (Fig. 2), the recyclable PMMA/MCA copolymers exhibit excellent optical transparency (95% UV-vis transmittance) and a colourless appearance comparable to commercial PMMA (Fig. 2c). The copolymers of MMA with MCA also function as reactive polymers for grafting applications: using PMMA₅₃₅–MCA₄₃ as an ATRP macroinitiator at ambient temperature achieved full methyl acrylate (MA) conversion in 17 h, yielding an MMA/MA copolymer with MALS-detected molecular weight ($M_{n,LS} = 85.7 \text{ kg mol}^{-1}$) nearly doubling RI values ($M_{n,RI} = 46.7 \text{ kg mol}^{-1}$)—a disparity confirming branched topology (Fig. S10a). Besides, the rms conformation curve of grafted copolymer PMMA₅₃₅–MCA₄₃–graft-PMA is below that of linear PMMA₅₃₅–MCA₄₃ with a lower slope (Fig. S10b), further verifying the branched topology. A single diffusion coefficient in DOSY NMR (Fig. S10c) validated uniform graft copolymer formation. Therefore, these C–Cl-containing PMMA materials combine commercial-grade performance with enhanced functionality: superior catalytic depolymerizability under mild conditions and serving as high-value reactive polymers to prepare topology-tunable hybrids.

Conclusions

In summary, we have developed a strategy for the facile synthesis and catalytic depolymerization of high-molecular-weight PMMA, in which a small portion of C–Me bonds are substituted with catalytically activatable C–Cl bonds through radical copolymerization of MMA with MCA. The polymer synthesis does not rely on CRP, enabling facile production of PMMA with exceptional depolymerizability and intrinsic properties comparable to or even superior to commercial PMMA. Leveraging the efficient Cu(0)-catalyzed activation of C–Cl

bonds, the depolymerization at a temperature well below 200 °C (160 °C) overcomes molecular weight and concentration limitations.

This work successfully depolymerized PMMA with M_n as high as 1010 kg mol^{-1} while maintaining a high conversion of 75%–90%. In contrast, some literature methods (such as those reported by Sumerlin and Diao) exhibit a decline in conversion to below 50% when M_n reaches the million-level. The applicable molecular weight (M_n) for the catalytic depolymerization of halogen-terminated PMMA reported by Matyjaszewski *et al.* usually does not exceed 6 kg mol^{-1} . Moreover, our method operates efficiently at high concentrations of 400–8400 mM [MMA unit]₀, significantly exceeding the 10–14 mM levels reported by Diao and Anastasaki *et al.*, and requires shorter reaction times, suggesting its greater potential for practical applications. The catalytic depolymerization temperature in this work is only 160 °C, considerably lower than the 250–290 °C required in Sumerlin *et al.*'s work that relies entirely on thermal activation. This method has the potential to lower energy consumption, eliminate the need for sophisticated equipment, and suppress undesirable side reactions that occur under harsh, high-temperature conditions. Furthermore, compared to the “depolymerization *via* pre-incorporated thermally labile site” strategy adopted by Sumerlin and Diao *et al.*, the polymers used in this study exhibit superior thermal stability. This results in an optimal balance among operability, efficiency, intrinsic material properties, and depolymerization performance for high-molecular-weight PMMA. Preliminary experimental results also indicate that both the solvent and catalyst used in the depolymerization process show potential for recyclability.

Compared to conventional high-temperature pyrolysis conducted at 400–500 °C, the low-temperature catalytic depolymerization in this work, despite potentially requiring a longer reaction time, operates at a significantly lower temperature of only 160 °C. This substantially reduces the energy required to heat and maintain the reaction system at the target temperature while also lowering the demand for advanced equipment, thereby diminishing the embedded energy consumption associated with equipment manufacturing. Furthermore, the process generates fewer “harmful” impurities and the recovered MMA monomer can be effectively repolymerized into a polymer with molecular weight and properties comparable to those of the polymer synthesized from a virgin monomer, which reduces the energy burden associated with subsequent separation and purification. Although catalysts and solvents are used in this approach, both exhibit potential for recyclability. Additionally, the method effectively suppresses random chain scission and side reactions, resulting in minimal gaseous waste streams. In contrast, high-temperature pyrolysis tends to produce solid char and complex gaseous by-products, increasing both separation challenges and environmental impacts. Therefore, from the standpoint of energy consumption and waste generation, the “low-temperature catalytic depolymerization” strategy presented in this work shows promise as a more sustainable and environmentally friendly pathway for the green chemical recycling of PMMA.



This work highlights the prospect of catalytic methodologies—simple yet highly efficient—to enable the replacement of conventional commodity materials with high-performance polymers that can be easily reverted to their monomers, thereby advancing the establishment of a green circular economy through chemical processes. However, it must be acknowledged that the current method still requires a reaction duration of several hours and relies on the use of an organic solvent and a catalyst. Our future research will aim to enhance depolymerization efficiency and catalyst recyclability, reduce solvent consumption, and even achieve depolymerization under bulk conditions. Further efforts will focus on enabling low-temperature, highly efficient catalytic depolymerization of commercial-grade PMMA.

Author contributions

Y. M.: investigation, data curation, and validation. X.-M. Y.: investigation, data curation, and validation. H.-N. S.: investigation. J.-F. L.: investigation. X.-Y. W.: conceptualization, methodology, writing – original draft, and writing – review & editing. Y. T.: conceptualization, methodology, supervision, and writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5gc04143k>.

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References

- 1 C. Jehanno, J. W. Alty, M. Roosen, S. De Meester, A. P. Dove, E. Y.-X. Chen, F. A. Leibfarth and H. Sardon, Critical advances and future opportunities in upcycling commodity polymers, *Nature*, 2022, **603**, 803.
- 2 X.-Y. Wang, Y.-S. Gao and Y. Tang, Sustainable developments in polyolefin chemistry: Progress, challenges, and outlook, *Prog. Polym. Sci.*, 2023, **143**, 101713.
- 3 G. Xu, H. Jiang, M. Stapelberg, J. Zhou, M. Liu, Q.-J. Li, Y. Cao, R. Gao, M. Cai, J. Qiao, M. S. Galanek, W. Fan, W. Xue, B. Marelli, M. Zhu and J. Li, Self-Perpetuating Carbon Foam Microwave Plasma Conversion of Hydrocarbon Wastes into Useful Fuels and Chemicals, *Environ. Sci. Technol.*, 2021, **55**(9), 6239.
- 4 F. Zhang, M. Zeng, R. D. Yappert, J. Sun, Y.-H. Lee, A. M. LaPointe, B. Peters, M. M. Abu-Omar and S. L. Scott, Polyethylene upcycling to long-chain alkylaromatics by tandem hydrogenolysis/aromatization, *Science*, 2020, **370**, 437.
- 5 X.-M. Yang, X.-Y. Wang and Y. Tang, The Chemical Recovery of PMMA into Monomer, *Chem. – Eur. J.*, 2025, **31**, e202404030.
- 6 J. De Tommaso and J.-L. Dubois, Risk Analysis on PMMA Recycling Economics, *Polymers*, 2021, **13**(16), 2724.
- 7 B.-S. Kang, S. G. Kim and J.-S. Kim, Thermal degradation of poly(methyl methacrylate) polymers: Kinetics and recovery of monomers using a fluidized bed reactor, *J. Anal. Appl. Pyrolysis*, 2008, **81**, 7.
- 8 D. S. Achilias, Chemical recycling of poly(methyl methacrylate) by pyrolysis. Potential use of the liquid fraction as a raw material for the reproduction of the polymer, *Eur. Polym. J.*, 2007, **43**, 2564.
- 9 E. Yoshida, High-purity monomer recovery from commercial engineering plastics by vacuum pyrolysis depolymerization, *RSC Sustainability*, 2024, **2**, 3909.
- 10 Y. Sano, T. Konishi, M. Sawamoto and M. Ouchi, Controlled radical depolymerization of chlorine-capped PMMA via reversible activation of the terminal group by ruthenium catalyst, *Eur. Polym. J.*, 2019, **120**, 109181.
- 11 M. R. Martinez, S. Dadashi-Silab, F. Lorandi, Y. Zhao and K. Matyjaszewski, Depolymerization of P(PDMS₁₁MA) Bottlebrushes via Atom Transfer Radical Polymerization with Activator Regeneration, *Macromolecules*, 2021, **54**(12), 5526.
- 12 M. R. Martinez, F. De Luca Bossa, M. Olszewski and K. Matyjaszewski, Copper(II) Chloride/Tris(2-pyridylmethyl) amine-Catalyzed Depolymerization of Poly(*n*-butyl methacrylate), *Macromolecules*, 2022, **55**(1), 78.
- 13 M. R. Martinez, D. Schild, F. De Luca Bossa and K. Matyjaszewski, Depolymerization of Polymethacrylates by Iron ATRP, *Macromolecules*, 2022, **55**(23), 10590.
- 14 F. De Luca Bossa, G. Yilmaz and K. Matyjaszewski, Fast Bulk Depolymerization of Polymethacrylates by ATRP, *ACS Macro Lett.*, 2023, **12**(8), 1173.
- 15 H. S. Wang, N. P. Truong, G. R. Jones and A. Anastasaki, Investigating the Effect of End-Group, Molecular Weight, and Solvents on the Catalyst-Free Depolymerization of RAFT Polymers: Possibility to Reverse the Polymerization of Heat-Sensitive Polymers, *ACS Macro Lett.*, 2022, **11**(10), 1212.
- 16 H. S. Wang, N. P. Truong, Z. Pei, M. L. Coote and A. Anastasaki, Reversing RAFT Polymerization: Near-Quantitative Monomer Generation Via a Catalyst-Free



- Depolymerization Approach, *J. Am. Chem. Soc.*, 2022, **144**(10), 4678.
- 17 R. Whitfield, G. R. Jones, N. P. Truong, L. E. Manring and A. Anastasaki, Solvent-Free Chemical Recycling of Polymethacrylates made by ATRP and RAFT polymerization: High-Yielding Depolymerization at Low Temperatures, *Angew. Chem., Int. Ed.*, 2023, **62**, e202309116.
 - 18 H. S. Wang, K. Parkatzidis, T. Junkers, N. P. Truong and A. Anastasaki, Controlled radical depolymerization: Structural differentiation and molecular weight control, *Chem*, 2024, **10**(1), 388.
 - 19 V. Bellotti, K. Parkatzidis, H. S. Wang, N. De Alwis Watuthanthrige, M. Orfano, A. Monguzzi, N. P. Truong, R. Simonutti and A. Anastasaki, Light-accelerated depolymerization catalyzed by Eosin Y, *Polym. Chem.*, 2023, **14**, 253.
 - 20 M. J. Flanders and W. M. Gramlich, Reversible-addition fragmentation chain transfer (RAFT) mediated depolymerization of brush polymers, *Polym. Chem.*, 2018, **9**, 2328.
 - 21 J. B. Young, J. I. Bowman, C. B. Eades, A. J. Wong and B. S. Sumerlin, Photoassisted Radical Depolymerization, *ACS Macro Lett.*, 2022, **11**(12), 1390.
 - 22 K. S. C. Jäger, G. D. Ammini, P.-J. Voort, P. Subramanian, A. Kumar, A. Anastasaki and T. Junkers, Accelerated Continuous Flow Depolymerization of Poly(Methyl Methacrylate), *J. Am. Chem. Soc.*, 2025, **147**(1), 594.
 - 23 J. B. Young, R. W. Hughes, A. M. Tamura, L. S. Bailey, K. A. Stewart and B. S. Sumerlin, Bulk depolymerization of poly(methyl methacrylate) via chain-end initiation for catalyst-free reversion to monomer, *Chem*, 2023, **9**(9), 2669.
 - 24 M. T. Chin, T. Yang, K. P. Quirion, C. Lian, P. Liu, J. He and T. Diao, Implementing a Doping Approach for Poly(methyl methacrylate) Recycling in a Circular Economy, *J. Am. Chem. Soc.*, 2024, **146**(9), 5786.
 - 25 R. W. Hughes, M. E. Lott, I. S. Zastrow, J. B. Young, T. Maity and B. S. Sumerlin, Bulk Depolymerization of Methacrylate Polymers via Pendent Group Activation, *J. Am. Chem. Soc.*, 2024, **146**(9), 6217.
 - 26 J. B. Young, S. L. Goodrich, J. A. Lovely, M. E. Ross, J. I. Bowman, R. W. Hughes and B. S. Sumerlin, Mechanochemically Promoted Functionalization of Postconsumer Poly(Methyl Methacrylate) and Poly(α -Methylstyrene) for Bulk Depolymerization, *Angew. Chem., Int. Ed.*, 2024, **63**, e202408592.
 - 27 R. W. Hughes, T. Maity, T. Sergeant, A. H. Balzer, I. S. Zastrow, M. S. Patel, L. M. Baker, P. M. Keown, L. T. J. Korley and B. S. Sumerlin, Retrofitting PMMA with a Thermal Trigger for Efficient Depolymerization, *J. Am. Chem. Soc.*, 2025, **147**(23), 19485.
 - 28 H. S. Wang, M. Agrachev, H. Kim, N. P. Truong, T.-L. Choi, G. Jeschke and A. Anastasaki, Visible light-triggered depolymerization of commercial polymethacrylates, *Science*, 2025, **387**, 874.
 - 29 Y. Ma, Y.-N. Zhao, X.-M. Yang, J.-F. Li, X.-Y. Wang and Y. Tang, SaBOX/Copper-Catalyzed Synthesis, Degradation, and Upcycling of a PMMA-Based Copolymer, *Macromolecules*, 2023, **56**(17), 7032.
 - 30 T. Kimura, K. Kuroda, H. Kubota and M. Ouchi, Metal-Catalyzed Switching Degradation of Vinyl Polymers via Introduction of an "In-Chain" Carbon-Halogen Bond as the Trigger, *ACS Macro Lett.*, 2021, **10**(12), 1535.
 - 31 N. Zhang, S. R. Samanta, B. M. Rosen and V. Percec, Single Electron Transfer in Radical Ion and Radical-Mediated Organic, Materials and Polymer Synthesis, *Chem. Rev.*, 2014, **114**(11), 5848.
 - 32 D. Konkolewicz, Y. Wang, M. Zhong, P. Kryszewski, A. A. Isse, A. Gennaro and K. Matyjaszewski, Single Electron Transfer in Radical Ion and Radical-Mediated Organic, Materials and Polymer Synthesis, *Macromolecules*, 2013, **46**, 8749.
 - 33 Z.-H. Chen, X.-Y. Wang, X.-L. Sun, J.-F. Li, B.-H. Zhu and Y. Tang, Highly Efficient Atom Transfer Radical Polymerization System Based on the SaBOX/Copper Catalyst, *Macromolecules*, 2019, **52**, 9792.
 - 34 Z.-H. Chen, Y. Ma, X.-Y. Wang, X.-L. Sun, J.-F. Li, B.-H. Zhu and Y. Tang, Winning Strategy for Iron-Based ATRP Using In Situ Generated Iodine as a Regulator, *ACS Catal.*, 2020, **10**, 14127.
 - 35 X.-Y. Wang, X.-L. Sun, F. Wang and Y. Tang, SaBOX/Copper Catalysts for Highly Syndio-Specific Atom Transfer Radical Polymerization of Methyl Methacrylate, *ACS Catal.*, 2017, **7**, 4692.
 - 36 S. Schaubach, X.-Y. Wang, J.-F. Li, X.-L. Sun, S. R. Wang and Y. Tang, Yb(NTf₂)₃/HFIP induced high isotacticity in atom transfer radical polymerization of methyl methacrylate, *Polym. Chem.*, 2018, **9**, 4711.
 - 37 X.-Y. Wang, Z.-H. Chen, X.-L. Sun and Y. Tang, Low temperature effect on ATRP of styrene and substituted styrenes enabled by SaBOX ligand, *Polymer*, 2019, **178**, 121630.
 - 38 Y. Ma, H.-M. Yang, Z.-H. Chen, Y.-N. Li, J.-F. Li, X.-L. Sun, X.-Y. Wang and Y. Tang, Highly branched polymethacrylates prepared efficiently: brancher-directed topology and application performance, *Polym. Chem.*, 2021, **12**, 6606.
 - 39 Y.-N. Li, X.-Y. Wang and Y. Tang, The Regulation of Stereoselectivity in Radical Polymerization, *Acta Chim. Sin.*, 2024, **82**, 213.
 - 40 M. R. Martinez, D. Schild, F. De Luca Bossa and K. Matyjaszewski, Depolymerization of Polymethacrylates by Iron ATRP, *Macromolecules*, 2022, **55**, 10590.

