

Chemical Recycling of Bromine-Terminated Polymers Synthesized by ATRP

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General procedures

Synthesis of PBzMA-Br by photoinduced iron-catalyzed ATRP

In a 30 mL glass vial, equipped with a stirring bar, 17.4 mg of FeBr₃ (0.06 mmol, 0.1 eq.) and 19.0 mg (0.06 mmol, 0.1 eq.) were dissolved in anisole (5 mL). The solution was sonicated for 2 minutes to fully solubilize the catalyst. This resulted in a dark orange solution. Next, 5 mL of benzyl methacrylate (BzMA) (29.5 mmol, 50 eq.) and 103.3 μ L of ethyl α -bromophenyl acetate (EBPA) (0.6 mmol, 1 eq.) were added. The vial was sealed with a rubber septum and deoxygenated via nitrogen purging for 20 minutes. Following deoxygenation, the vial was placed in a homemade LED light box (48 W, λ = 465 nm (\pm 5 nm)) emitting blue light and left to polymerize under constant stirring. After 1.5 hours the reaction was stopped by removing the vial from the blue light and opening it to air. ¹H NMR and SEC samples were taken, and purification was performed by diluting the reaction mixture in acetone and passing it through a column of basic alumina to remove any remaining catalyst. The solution was then precipitated in cold methanol 3 times. The purified polymer was dried in vacuo for 2 days and was analyzed via ¹H NMR to confirm its purity and SEC to measure its final molecular weight and dispersity.

Chain extension of PBzMA-Br by photoinduced iron catalyzed ATRP

In a 6 mL glass vial, equipped with a stirring bar, 0.99 mg of FeBr₃ (0.003 mmol, 0.2 eq.) and 1.07 mg of TBABr (0.003 mmol, 0.2 eq.) were dissolved in 545 μ L of anisole. Next, 103.9 mg of the PBzMA-Br (0.017 mmol, 1 eq.) were weighed and placed in the vial. It was subsequently stirred for 5 minutes until total dissolution had occurred. Lastly, 545 μ L of BzMA (3.33 mmol, 200 eq.) were introduced into the vial and it was degassed by nitrogen purging for 20 minutes. The reaction was then placed under blue light and left to react under constant stirring for 2.5 hours. To stop the reaction, the vial was opened to air prior to ¹H NMR and SEC analysis.

Kinetic analysis

A scaled-up reaction as described in previous procedure, was performed in an identical way with double of each reagent (2 mL of solvent). Aliquots were taken under

nitrogen blanket with nitrogen sparged needles at designated intervals (0, 20, 40, 50, 60, 70, 80, 90 and 180 seconds) for ^1H NMR and SEC analysis.

General procedure for depolymerization of PBzMA-Br with $\text{FeBr}_3/\text{TBABr}$

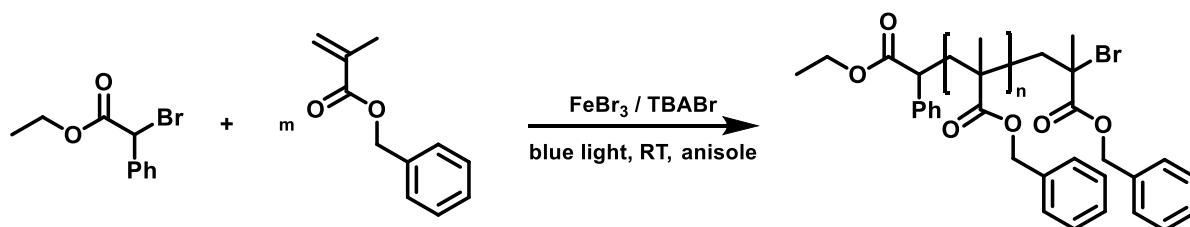
The FeBr_3 stock solution was prepared by dissolving 3 mg (1.02×10^{-5} mol, 1 eq.) of FeBr_3 in TEGDME, using the same procedure as previously described.

General procedure for dark depolymerization of PBzMA-Br

The same procedure as described in $\text{FeBr}_2/\text{TBABr}$ catalyzed depolymerization was followed. All vials and tubes were covered in aluminum foil in order to prevent any exposure to room light.

Additional characterization data

Polymer synthesis



Scheme S1: Schematic representation of polymerization of BzMA via photoinduced iron-catalyzed ATRP under the following conditions: [BzMA]:[EBPA]:[FeBr₃]:[TBABr] = 50:1:0.1:0.1 in anisole (1:1 monomer to solvent ratio) at room temperature under blue light for 1.5 hours. Conversion was measured by ¹H NMR to be 68%.

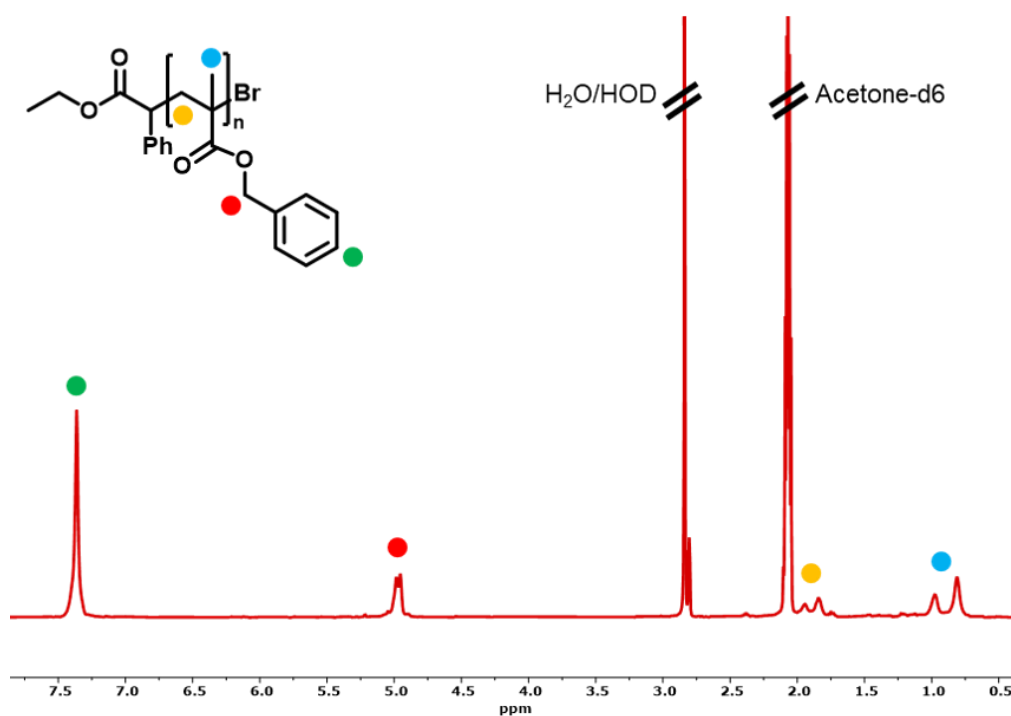


Figure S1: ¹H NMR spectrum of purified PBzMA-Br obtained by photoinduced iron-catalyzed ATRP, under the following conditions: [BzMA]:[EBPA]:[FeBr₃]:[TBABr] = 50:1:0.1:0.1 in anisole (1:1 monomer to solvent ratio) at room temperature under blue light.

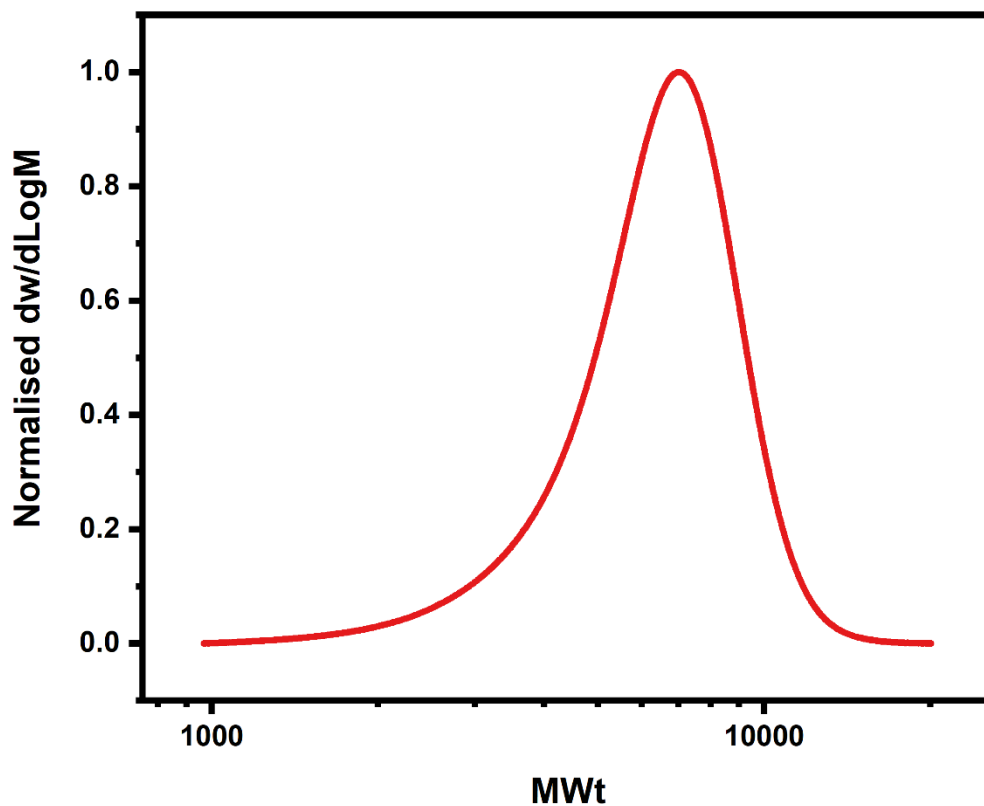


Figure S2: SEC trace of purified PBzMA-Br obtained by photoinduced iron-catalyzed ATRP, under the following conditions: [BzMA]:[EBPA]:[FeBr₃]:[TBABr] = 50:1:0.1:0.1 in anisole (1:1 monomer to solvent ratio) at room temperature under blue light. The molecular weight was measured to be 6000 and the dispersity was 1.14.

Depolymerization of PBzMA-Br in TEGDME

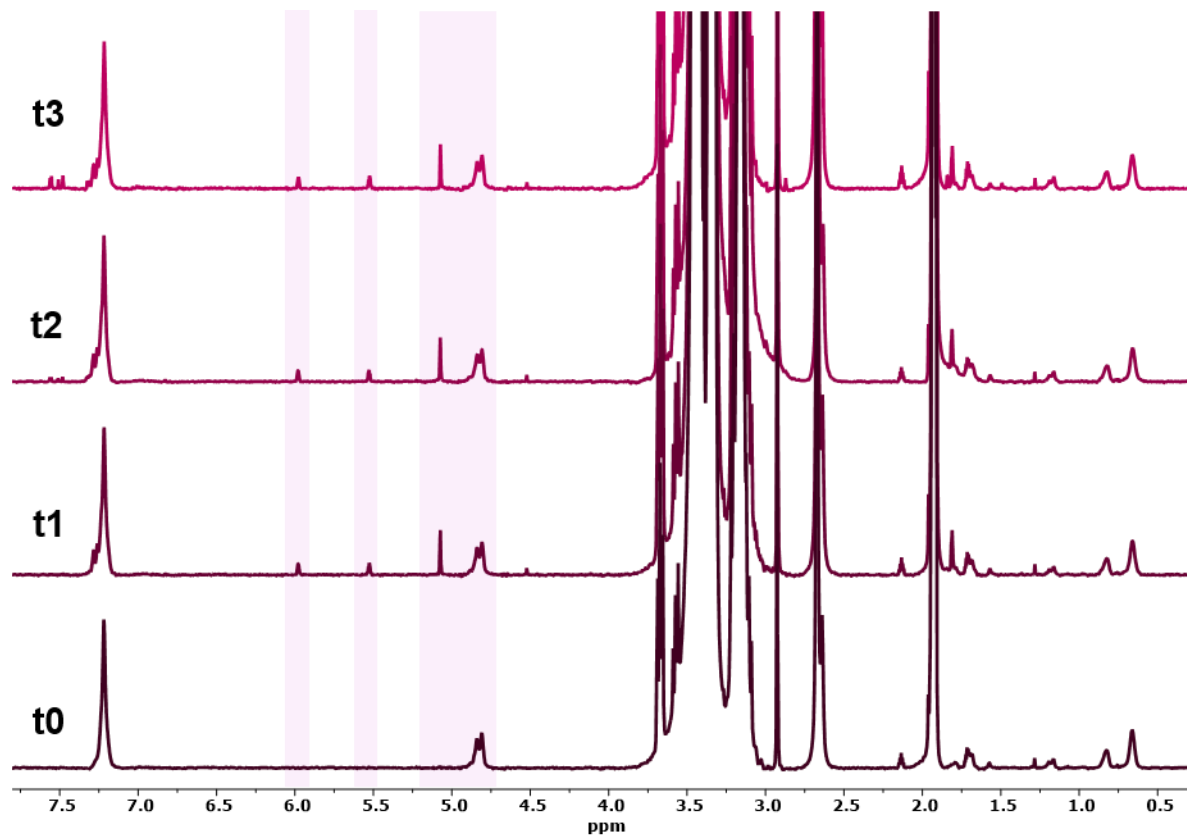


Figure S3: ¹H NMR spectra for the depolymerization of PBzMA-Br with 0 eq. TBABr (1:4:0) in TEGDME. Samples were taken after 0, 5, 15 and 60 minutes. The depolymerization conversion was calculated on comparison of the integrals of the monomeric vinyl peaks (5.66 – 6.13 ppm) and combined -CH₂ polymer and monomer peaks (4.96 – 5.22 ppm). These are highlighted in pink.

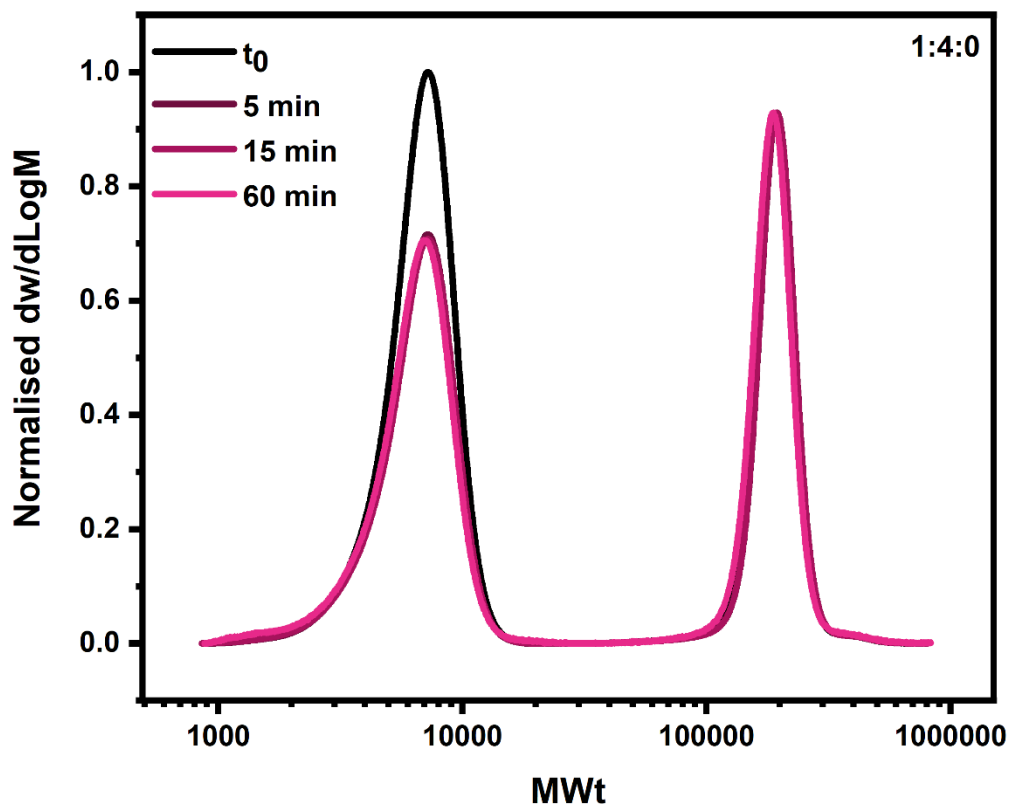


Figure S4: SEC traces for the depolymerization of PBzMA-Br with 0 eq. TBABr (1:4:0) in TEGDME. Samples were taken after 0, 5, 15 and 60 minutes. PS-H ($M_n = 180000$, $D = 1.05$) was used as an internal standard. The conversion was calculated by comparison of the constant PS-H peak area compared to the decreasing peak area of the PBzMA-Br.

Livingness quantification

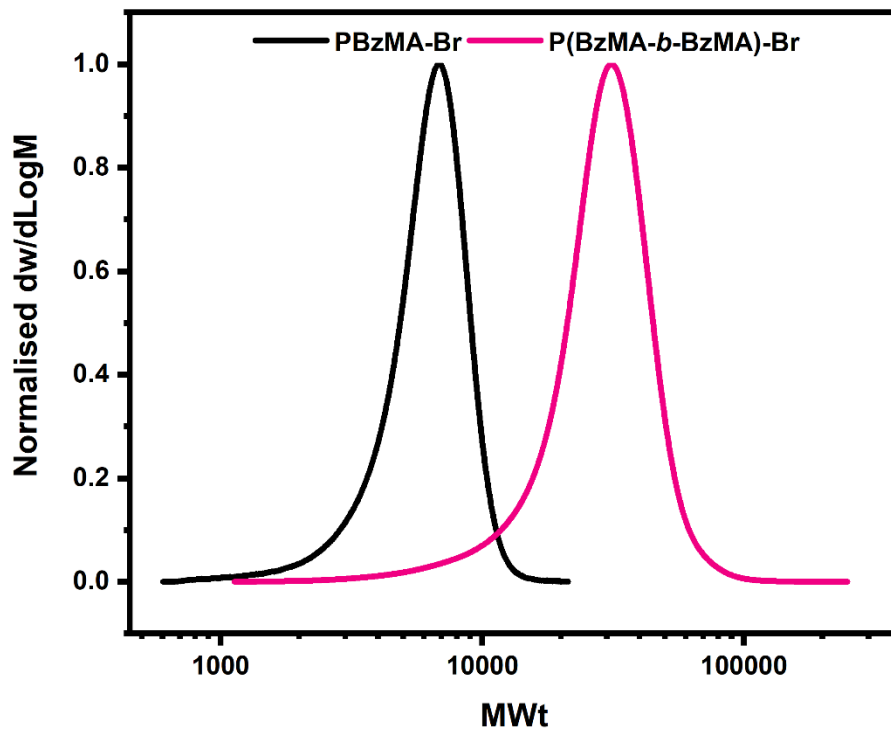


Figure S5: SEC traces of the PBzMA-Br and its chain extension with BzMA under the following conditions: [BzMA]:[PBzMA-Br]:[FeBr₃]:[TBABr] = 200:1:0.2:0.2 in anisole (1:1 monomer to solvent ratio) at room temperature under blue light. The molecular weight was measured to be 24100 and the dispersity was 1.31.

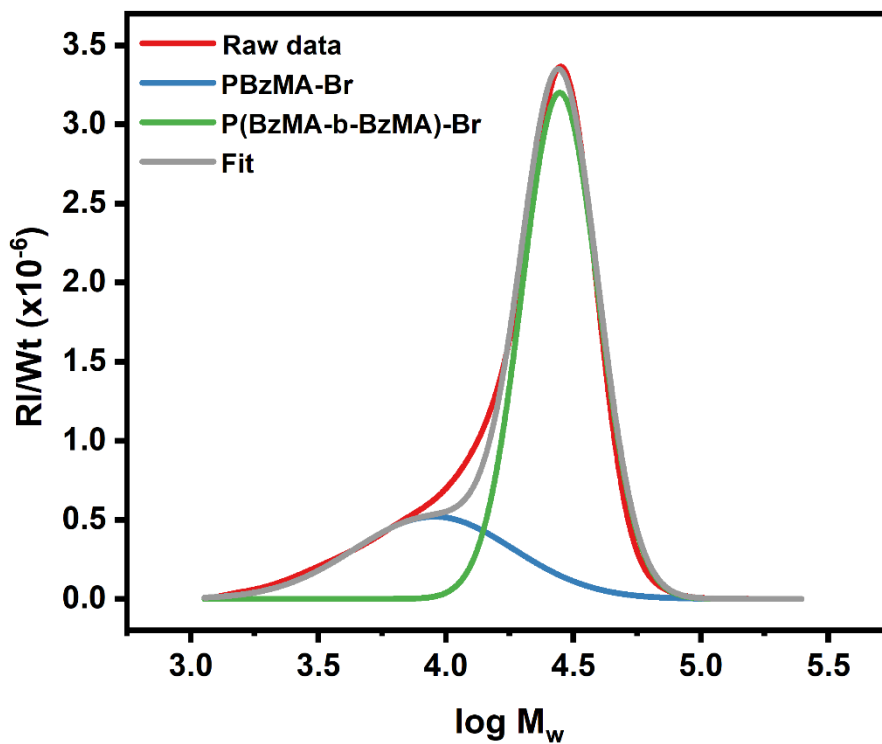


Figure S6: Deconvoluted SEC traces of the chain extended PBzMA-Br to quantify livingness. The livingness was calculated by comparison of the integration area of the extended P(BzMA-bBzMA)-Br versus the unreacted PBzMA-Br, based on the methodology reported by Wooley et al.¹

Depolymerization of PBzMA-Br in TEGDME with FeBr₂/TBABr

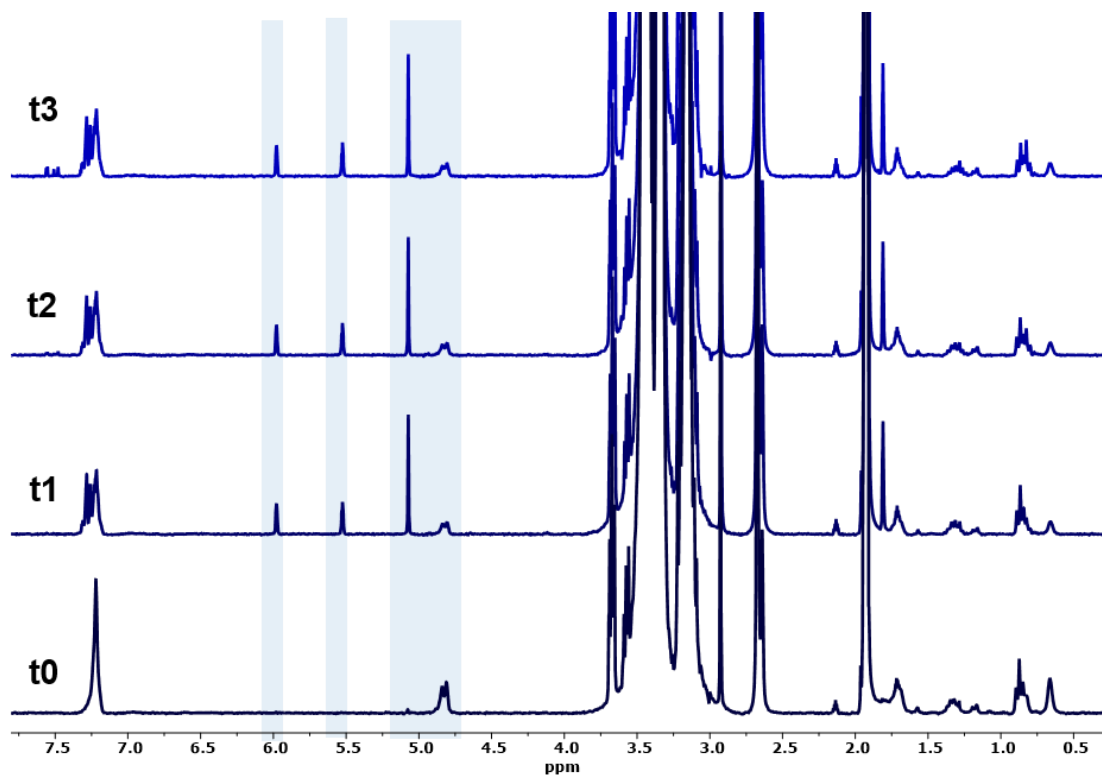


Figure S7: ¹H NMR spectra for the depolymerization of PBzMA-Br with 4 eq. TBABr (1:4:0) in TEGDME. Samples were taken after 0, 5, 15 and 60 minutes. The depolymerization conversion was calculated on comparison of the integrals of the monomeric vinyl peaks (5.66 – 6.13 ppm) and combined -CH₂ polymer and monomer peaks (4.96 – 5.22 ppm). These are highlighted in blue.

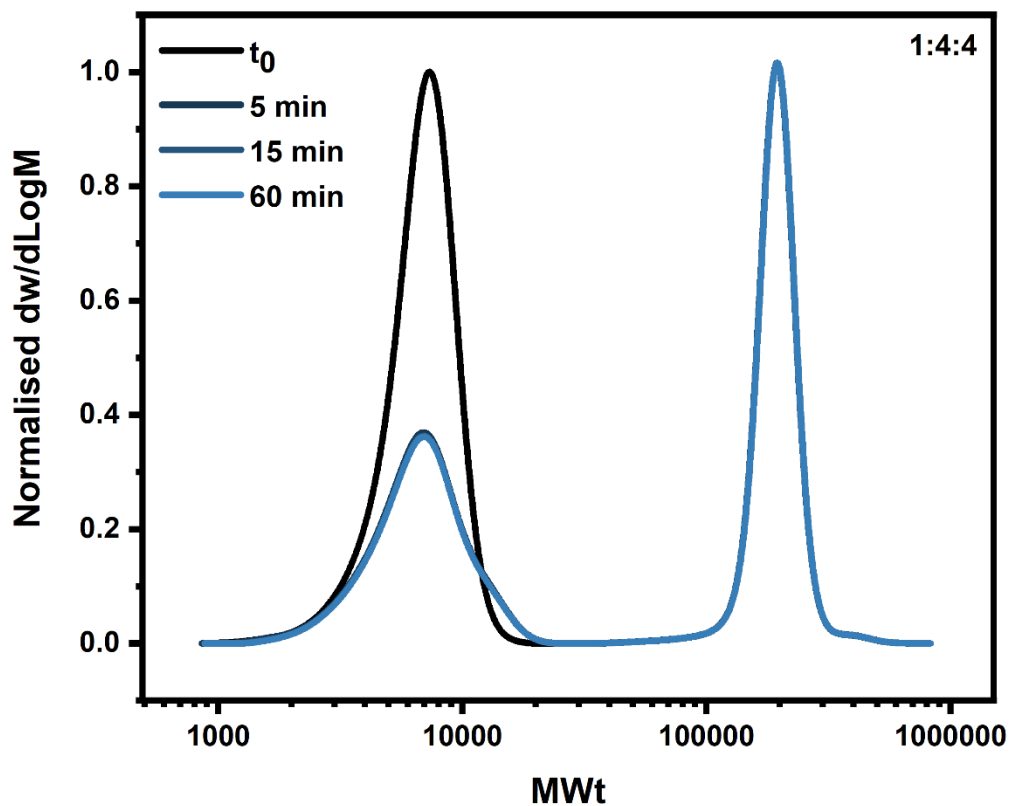


Figure S8: SEC traces for the depolymerization of PBzMA-Br with 4 eq. TBABr (1:4:4) in TEGDME. Samples were taken after 0, 5, 15 and 60 minutes. PS-H ($M_n = 180000$, $\bar{D} = 1.05$) was used as an internal standard. The conversion was calculated by comparison of the constant PS-H peak area compared to the decreasing peak area of the PBzMA-Br.

Table S1: The effect of TBABr addition on the depolymerization of PBzMA-Br in TEGDME.

Entry	[P]:[FeBr ₂]:TBABr	Time (min)	Depol.(%) ^a (NMR)	Depol. (%) efficiency	Depol.(%) ^b (SEC)	M _n (SEC) ^c	Đ ^c
1		0	0	0	0	6100	1.14
2	1:4:0	5	20	24	24	5900	1.15
3		15	18	21	25	5900	1.15
4		60	18	21	27	5500	1.19
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5		0	0	0	0	6200	1.13
6	1:4:4	5	49	58	49	5800	1.23
7		15	48	56	50	5900	1.22
8		60	45	53	51	5900	1.21

^[a]Extent of depolymerization at various timepoints during the reaction. This was obtained by ¹H NMR and

^[b]SEC. ^[c]SEC analysis was used to acquire the molecular weight and the dispersity values.

Depolymerization of PBzMA-Br in various solvents

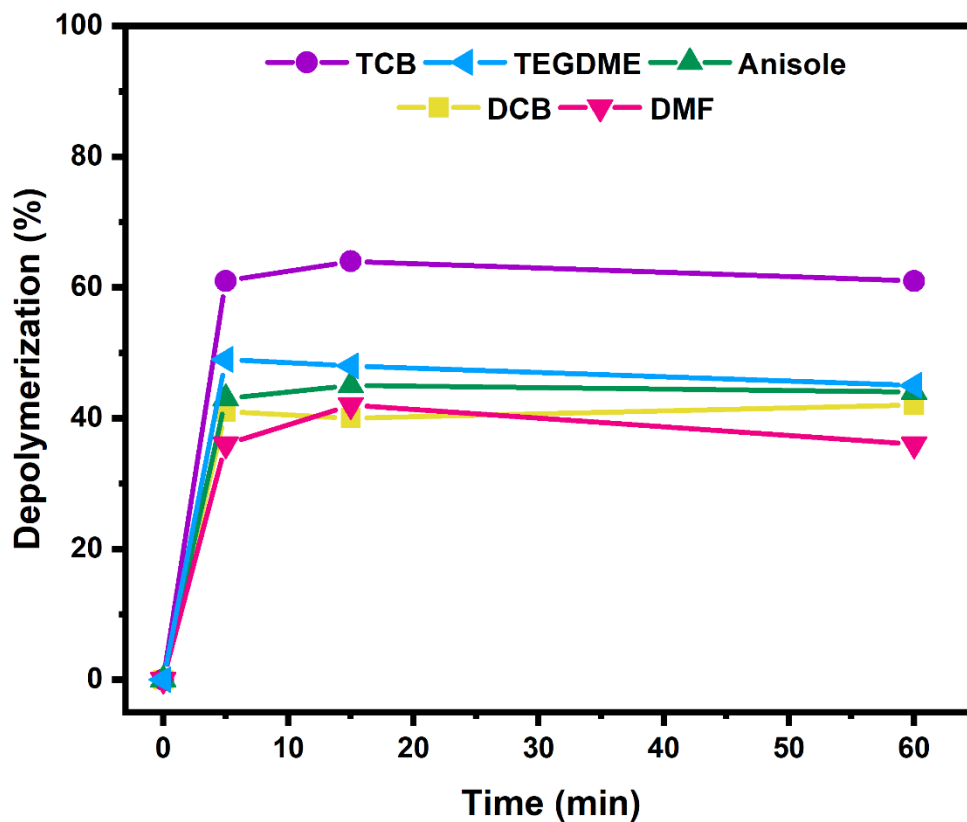


Figure S9: ^1H NMR data illustrating the effect of solvent on the depolymerization of PBzMA-Br.

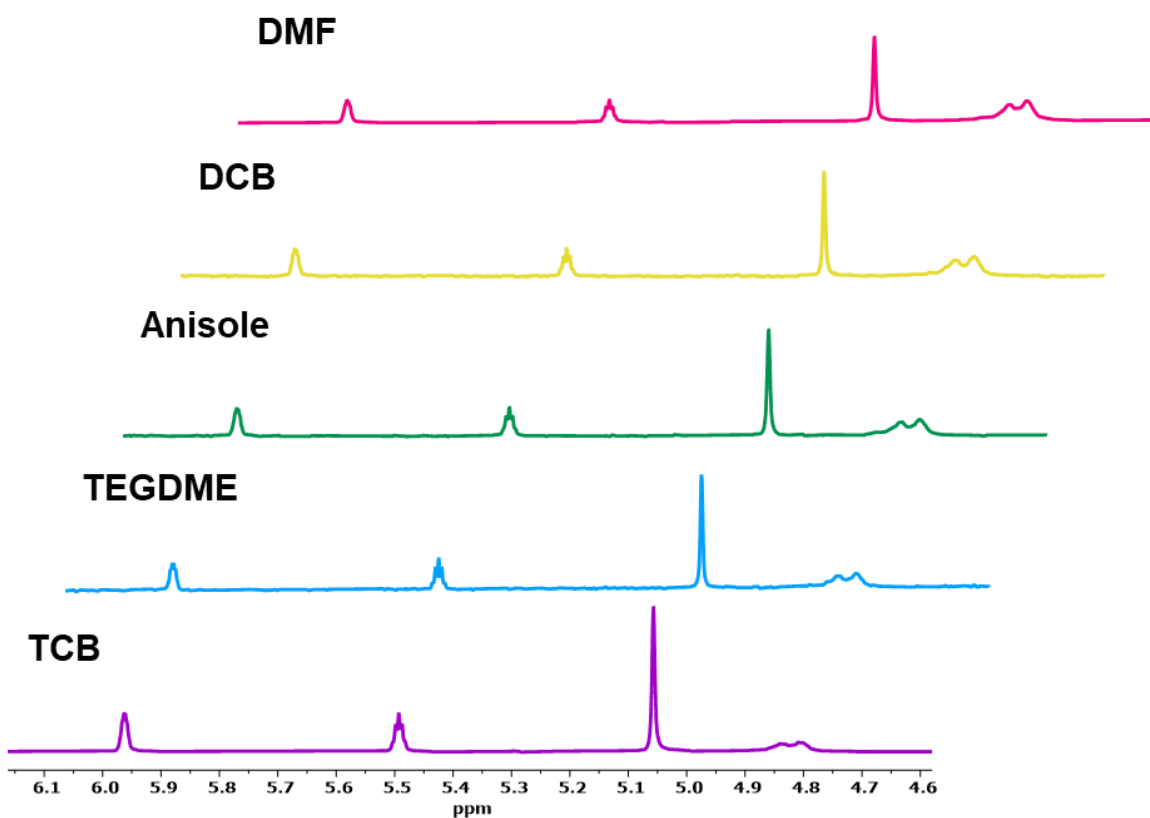


Figure S10: ¹H NMR spectra for the depolymerization of PBzMA-Br with 4 eq. TBABr (1:4:4) in different solvents. Samples were taken in 60 min. The depolymerization conversion was calculated on comparison of the integrals of the monomeric vinyl peaks (5.66 – 6.13 ppm) and combined -CH₂ polymer and monomer peaks (4.96 – 5.22 ppm).

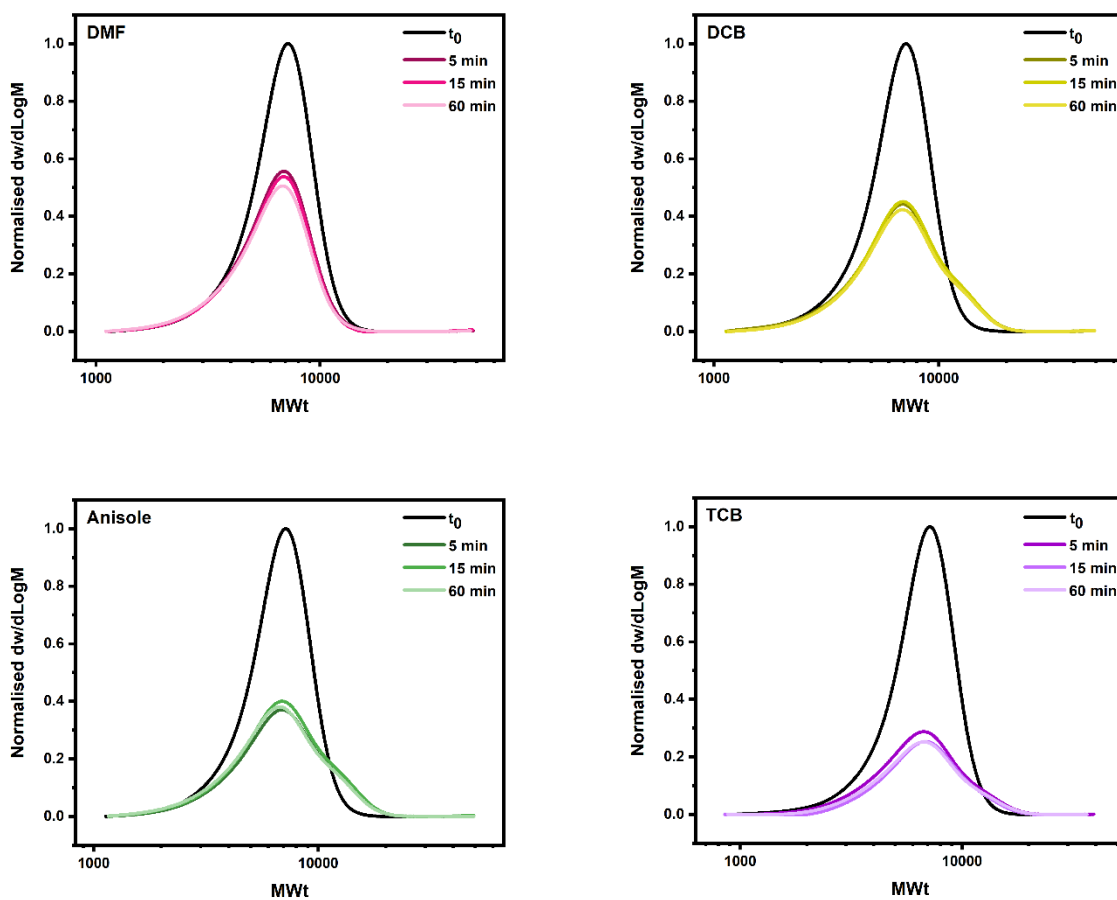


Figure S11: SEC traces for the depolymerization of PBzMA-Br with 4 eq. TBABr (1:4:4) in different solvents. Samples taken after 5, 15 and 60 minutes. PS-H was used as an internal standard for the conversion calculation.

Table S2: The effect of solvent on the depolymerization of PBzMA-Br.

Entry	Solvent	Time (min)	Depol. (%) ^a (NMR)	Depol. (%) efficiency	Depol. (%) ^b (SEC)	M_n^c (SEC)	\mathcal{D}^c
1		0	0	0	0	6000	1.14
2	DCB	5	41	48	39	5900	1.25
3		15	40	47	39	6000	1.22
4		60	42	49	43	6000	1.23
5		0	0	0	0	6000	1.13
6	Anisole	5	43	51	48	5900	1.24
7		15	45	53	44	5900	1.24
8		60	44	52	47	5700	1.25
9		0	0	0	0	6000	1.13
10	DMF	5	36	42	37	5500	1.16
11		15	42	49	41	5500	1.16
12		60	36	42	41	5400	1.17
13		0	0	0	0	6000	1.14
14	TCB	5	61	72	65	5400	1.25
15		15	64	75	69	5400	1.24
16		60	61	72	67	5400	1.25

^[a]Extent of depolymerization at various timepoints during the reaction. This was obtained by ¹H NMR and ^[b]SEC. ^[c]SEC analysis was used to acquire the molecular weight and the dispersity values. All reactions were conducted under the following conditions: [P-Br]:[FeBr₂]:[TBABr] = 1:4:4.

Effect of FeBr_2 , $\text{FeBr}_2/\text{TBABr}$ and TBABr concentration on the depolymerization of PBzMA-Br

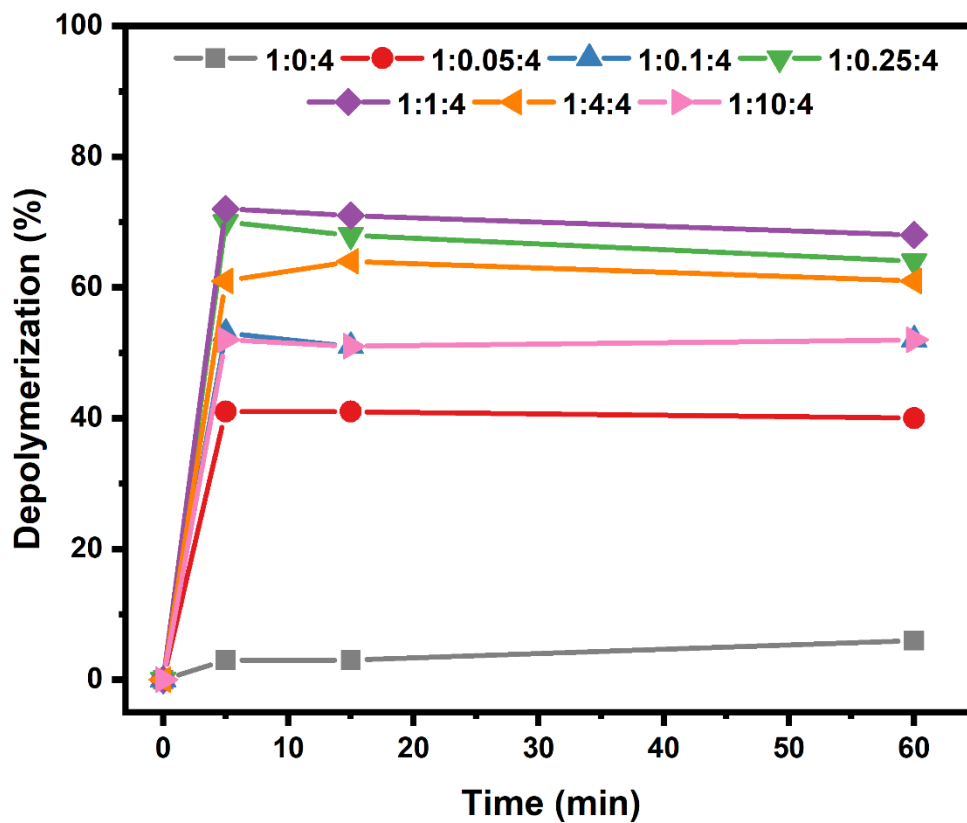


Figure S12: ^1H NMR data illustrating the effect of FeBr_2 concentration (1:X:4) on the depolymerization of PBzMA-Br.

Table S3: The effect of FeBr₂ concentration (1:X:4) on the depolymerization of PBzMA-Br.

Entry	[P-Br]:[FeBr ₂]:[TBABr]	Depol.(%) ^a (NMR)	Depol. (%) efficiency	Depol.(%) ^b (SEC)	<i>M</i> _n (SEC) ^c	<i>D</i> ^c
1	1:10:4	52	61	56	5000	1.30
2	1:4:4	61	72	65	5400	1.25
3	1:1:4	72	85	73	4500	1.30
4	1:0.25:4	70	82	66	4700	1.26
5	1:0.10:4	53	62	54	5100	1.14
6	1:0.05:4	41	48	38	5600	1.16
7	1:0:4	3	4	9	5800	1.15

^[a] Extent of depolymerization at 5 minutes during the reaction. This was obtained by ¹H NMR and ^[b]SEC.

^[c]SEC analysis was used to acquire the molecular weight and the dispersity values. All reactions were conducted in TCB.

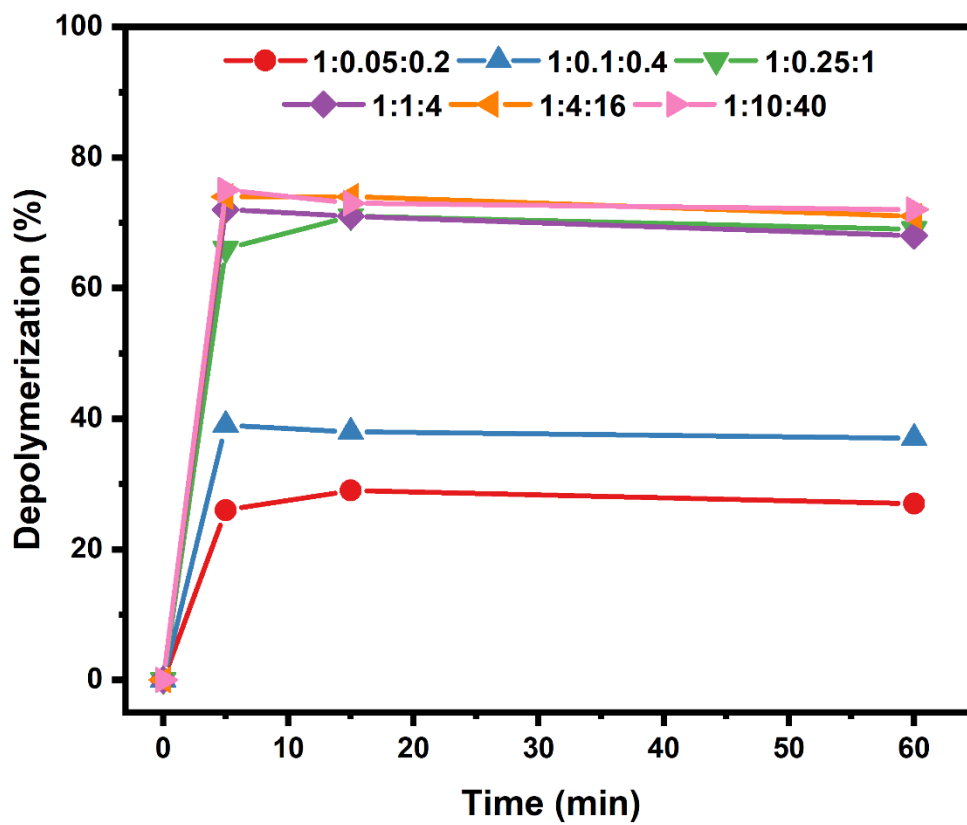


Figure S13: ¹H NMR data illustrating the effect of FeBr₂/TBABr concentration (1:X:4X) on the depolymerization of PBzMA-Br.

Table S4: The effect of FeBr₂/TBABr concentration (1:X:4X) on the depolymerization of PBzMA-Br.

Entry	[P-Br]:[FeBr ₂]:[TBABr]	Depol. ^a (%) (NMR)	Depol. (%) efficiency	Depol. ^b (%) (SEC)	<i>M_n</i> ^c (SEC)	<i>D</i> ^c
1	1:10:40	75	88	77	5300	1.12
2	1:4:16	74	87	80	5400	1.14
3	1:1:4	72	85	73	4500	1.30
4	1:0.25:1	66	78	72	4900	1.22
5	1:0.1:0.4	39	46	38	5000	1.19
6	1:0.05:0.2	26	31	26	5400	1.15

^[a] Extent of depolymerization at 5 minutes during the reaction. This was obtained by ¹H NMR and ^[b]SEC.

^[c]SEC analysis was used to acquire the molecular weight and the dispersity values. All reactions were conducted in TCB.

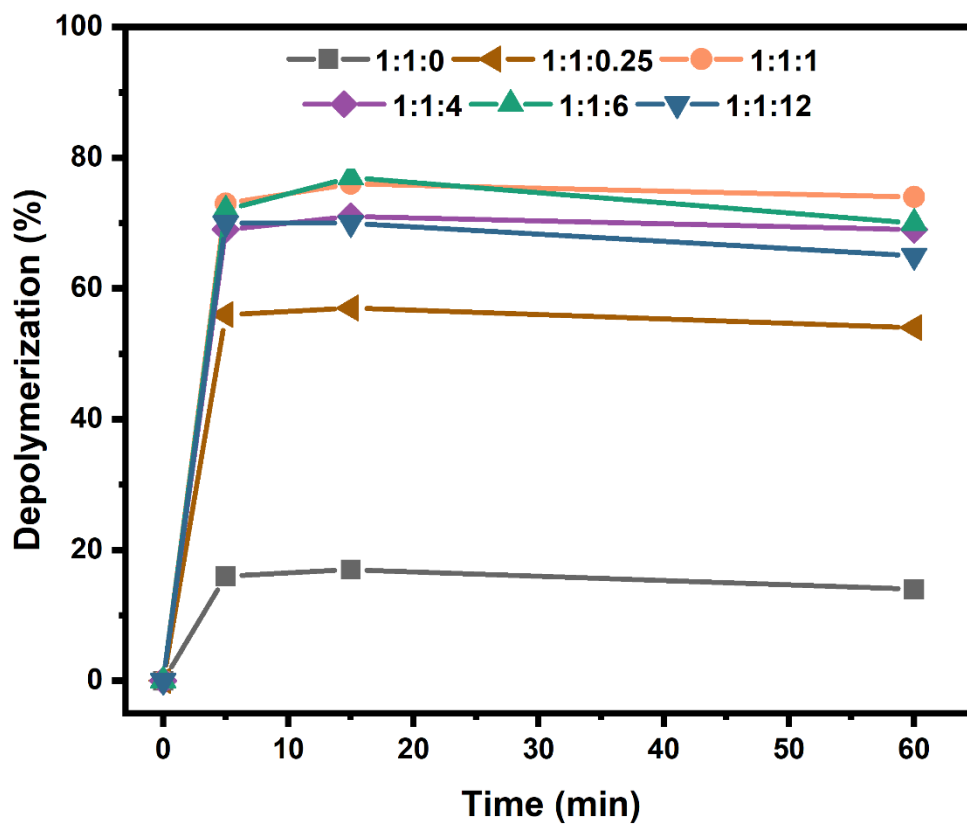


Figure S14: ^1H NMR data illustrating the effect of TBABr concentration (1:1:X) on the depolymerization of PBzMA-Br.

Table S5: The effect of FeBr₂/TBABr concentration (1:1:X) on the depolymerization of PBzMA-Br.

Entry	[P-Br]:[FeBr ₂]:[TBABr]	Depol.(%) ^a (NMR)	Depol. (%) efficiency	Depol.(%) ^b (SEC)	<i>M</i> _n (SEC) ^c	<i>D</i> ^c
1	1:1:12	70	82	69	4600	1.17
2	1:1:6	72	85	73	4700	1.21
3	1:1:4	72	85	73	4500	1.30
4	1:1:1	73	86	75	4300	1.24
5	1:1:0.25	56	66	57	4500	1.21
6	1:1:0	16	19	19	5400	1.16

^[a] Extent of depolymerization at 5 minutes during the reaction. This was obtained by ¹H NMR and ^[b]SEC.

^[c]SEC analysis was used to acquire the molecular weight and the dispersity values. All reactions were conducted in TCB.

Depolymerization kinetics of PBzMA-Br

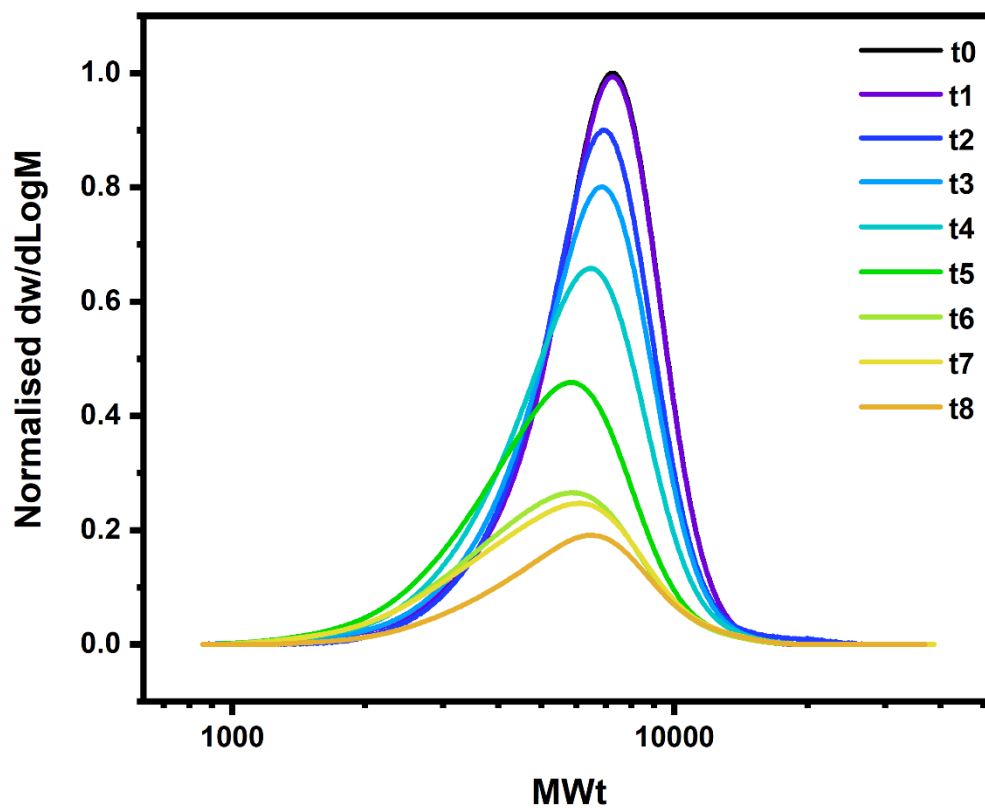


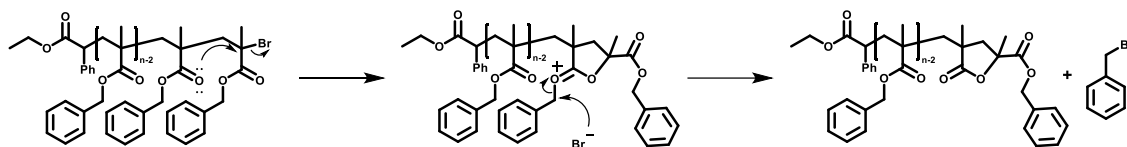
Figure S15: SEC traces for the depolymerization kinetics of PBzMA-Br under the optimized conditions (P-Br:FeBr₂:TBABr = 1:1:1). PS-H was used as an internal standard for the conversion calculation.

Table S6: Detailed depolymerization kinetics of PBzMA-Br under the optimized conditions (P-Br:FeBr₂:TBABr = 1:1:1).

Entry	Time (s)	Depol. ^a (%) (NMR)	Depol. (%) efficiency	Depol. ^b (%) (SEC)	<i>M_n</i> ^c (SEC)	<i>D</i> ^c
1	0	0	0	0	6000	1.14
2	20	3	4	0	6000	1.14
3	40	6	7	0	6000	1.13
4	50	14	16	2	5600	1.15
5	60	26	31	10	5200	1.17
6	70	41	48	12	4500	1.25
7	80	56	66	56	4500	1.23
8	90	62	73	58	4600	1.24
9	180	73	86	71	5200	1.19

^[a] Extent of depolymerization at designated timepoints during the reaction. This was obtained by ¹H NMR and ^[b]SEC. ^[c]SEC analysis was used to acquire the molecular weight and the dispersity values. All reactions were conducted in TCB.

Lactonization Study



Scheme S2: The mechanism for the lactonization of poly(benzyl methacrylate) prepared by ATRP. The product of this side reaction is benzyl bromide.

Table S7: ¹H NMR and SEC data illustrating the background effect of lactonization on the depolymerization of PBzMA-Br.

Entry	[PBzMA-Br]:[FeBr ₂]:[TBABr] ^a	Time (min)	Depol. (%) (NMR) ^b	<i>M</i> _n (SEC) ^c	<i>D</i>
1		5	7	5700	1.12
2	1:0:0	15	6	5700	1.13
3	1:0:0	5	0	5700	1.14
4	+0:1:1	15	25	5700	1.13

^aReactions were performed at 170 °C in the absence of catalyst for 5 minutes prior to either no addition of catalyst (entry 2) or the addition of catalyst (entry 4). ^bExtent of depolymerization at designated timepoints during the reaction as obtained by ¹H NMR. ^cSEC analysis was used to acquire the molecular weight and the dispersity values.

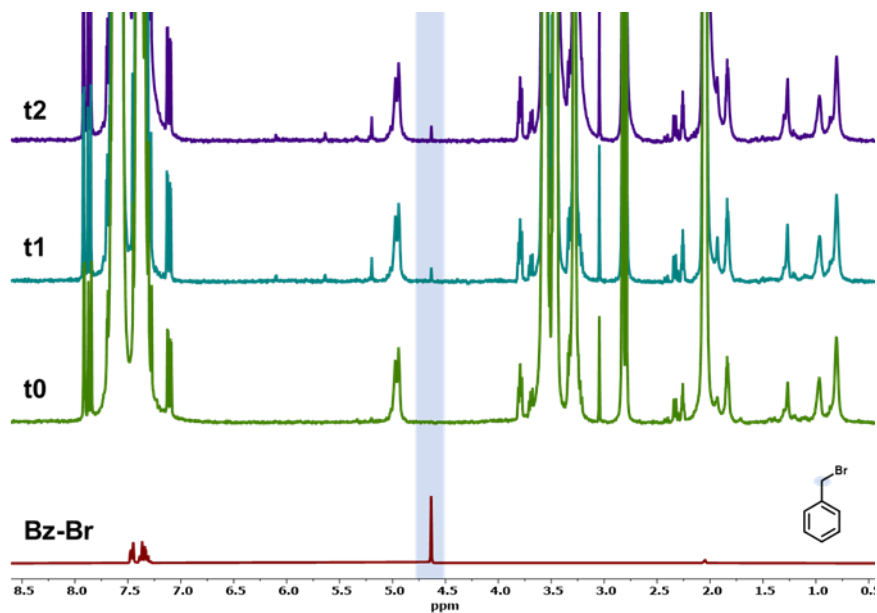


Figure S16: ¹H NMR data for the depolymerization of PBzMA-Br in the absence of catalyst. The formation of benzyl bromide (4.66 ppm) is evidence that lactonization occurs within 5 minutes (t1) resulting in a loss of bromine end-groups and therefore is a competitive process for all the depolymerization reactions.

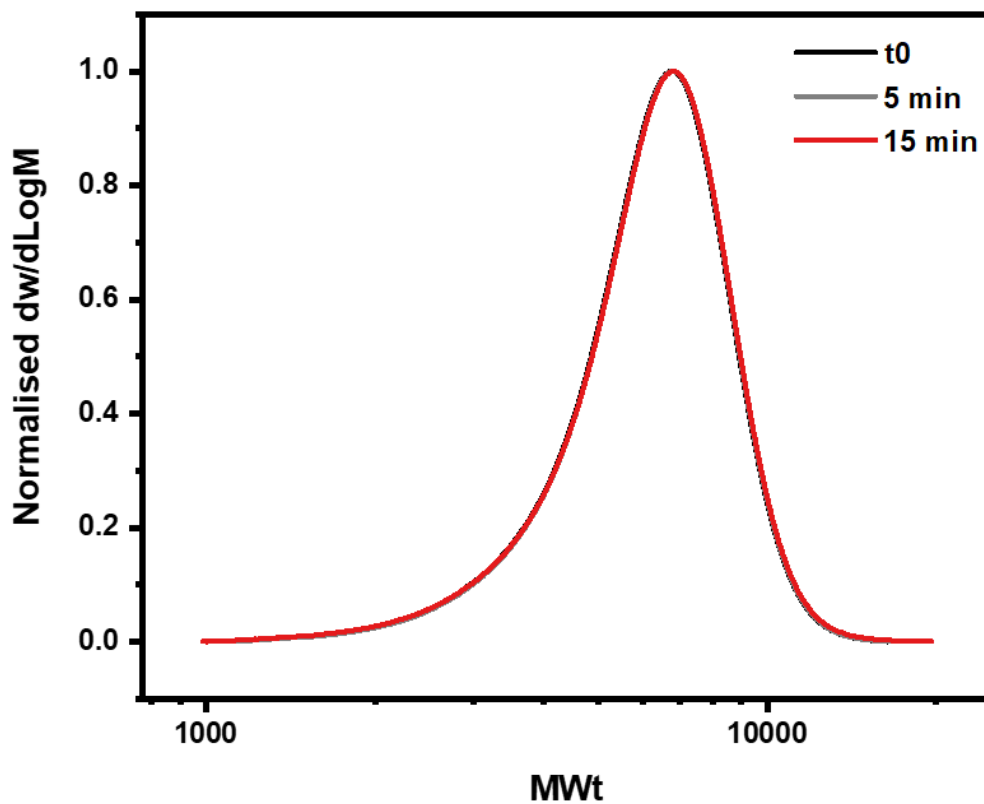


Figure S17: SEC analysis for the depolymerization of PBzMA-Br in the absence of catalyst. There is no change in the molecular weight distribution, suggesting lactonization is the only side reaction over 15 minutes. These chromatograms correspond to the experiments in Figure S16.

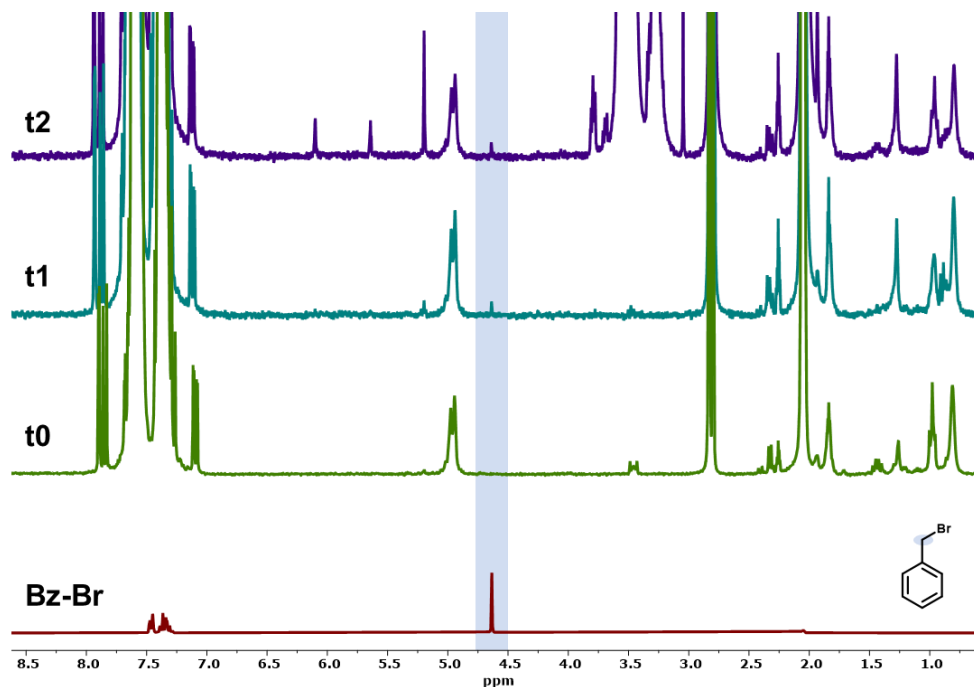


Figure S18: ¹H NMR data for the depolymerization of PBzMA-Br in the absence of catalyst. The formation of benzyl bromide (4.66 ppm) is evidence that lactonization occurs within 5 minutes (t1). The subsequent addition of FeBr₂ resulted in just 25% of depolymerization after 15 minutes (t2), further demonstrating the loss of bromine functionality. This compares to 73% depolymerization which was achieved if the catalyst was added to the reaction at time zero.

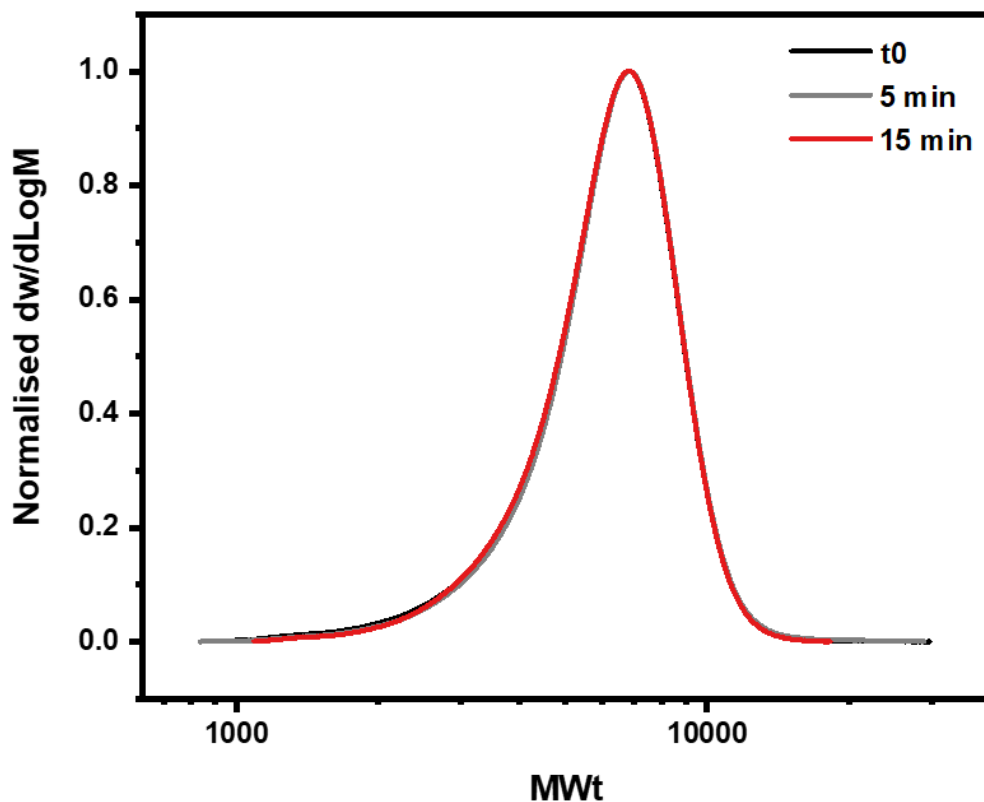


Figure S19: SEC analysis for the depolymerization of PBzMA-Br after the reaction was kept at 170 °C for 5 minutes in the absence of catalyst and FeBr₂ was subsequently added. There is no change in the molecular weight distribution, suggesting that termination is not happening under these conditions and that lactonization is the only side reaction. These chromatograms correspond to the experiments in Figure S18.

Expanding the scope of PBzMA-Br depolymerization

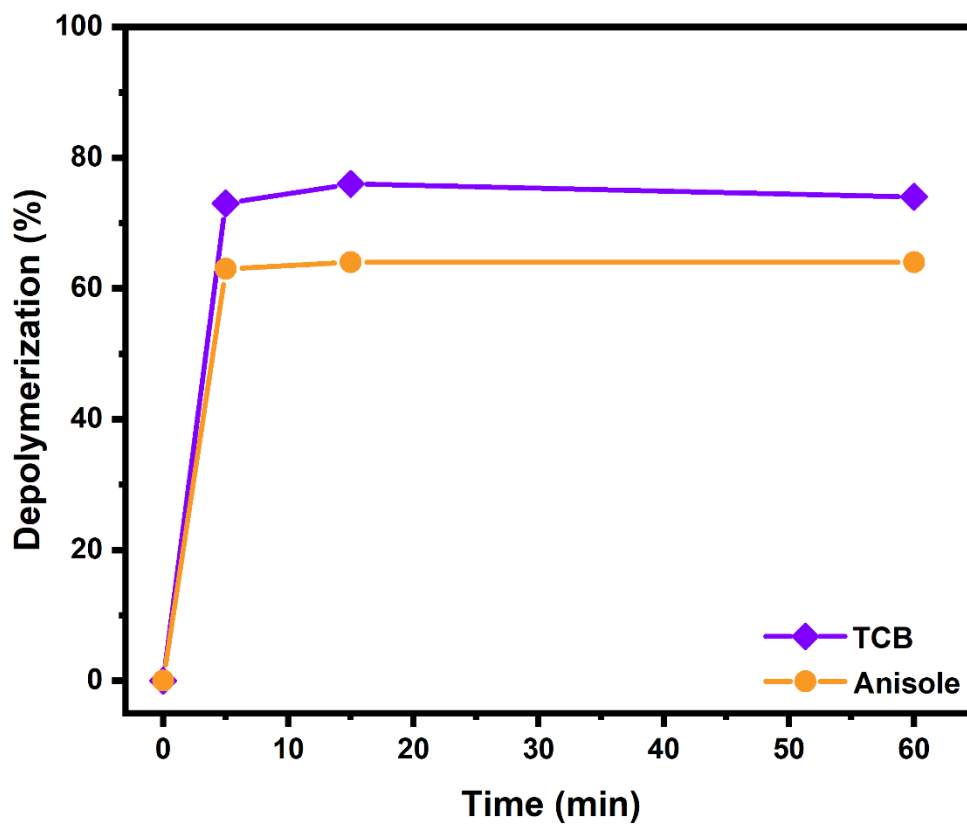


Figure S20: ^1H NMR data illustrating the effect of solvent on the depolymerization of PBzMA-Br under the optimized conditions (P-Br:FeBr₂:TBABr = 1:1:1).

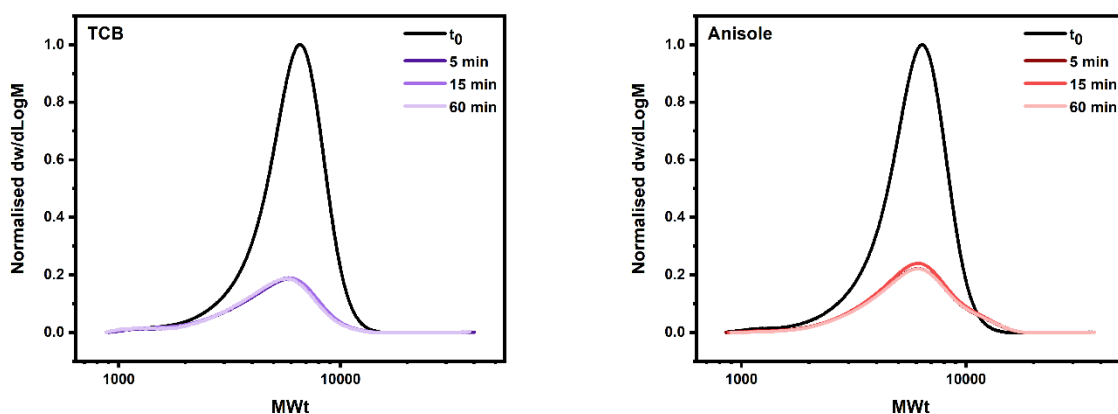


Figure S21: SEC traces for the depolymerization of PBzMA-Br under the optimized conditions (P-Br:FeBr₂:TBABr = 1:1:1) in different solvents. Samples taken after 5, 15 and 60 minutes. PS-H was used as an internal standard for the conversion calculation. under optimal conditions, at various timepoints.

Table S8: The effect of the solvent on the depolymerization of PBzMA-Br under the optimized conditions (P-Br:FeBr₂:TBABr = 1:1:1).

Entry	Solvent	Time (min)	Depol.(%) ^a (NMR)	Depol. (%) efficiency	Depol.(%) ^b (SEC)	M_n (SEC) ^c	\bar{D}^c
1		0	0	0	0	5500	1.13
2	TCB	5	73	86	75	4300	1.24
3		15	76	89	75	4200	1.26
4		60	74	87	77	4100	1.25
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5		0	0	0	0	5400	1.12
6	Anisole	5	63	74	68	4900	1.24
7		15	64	75	67	5100	1.22
8		60	64	75	69	5100	1.22

^[a]Extent of depolymerization at various timepoints during the reaction. This was obtained by ¹H NMR and

^[b]SEC. ^[c]SEC analysis was used to acquire the molecular weight and the dispersity values.

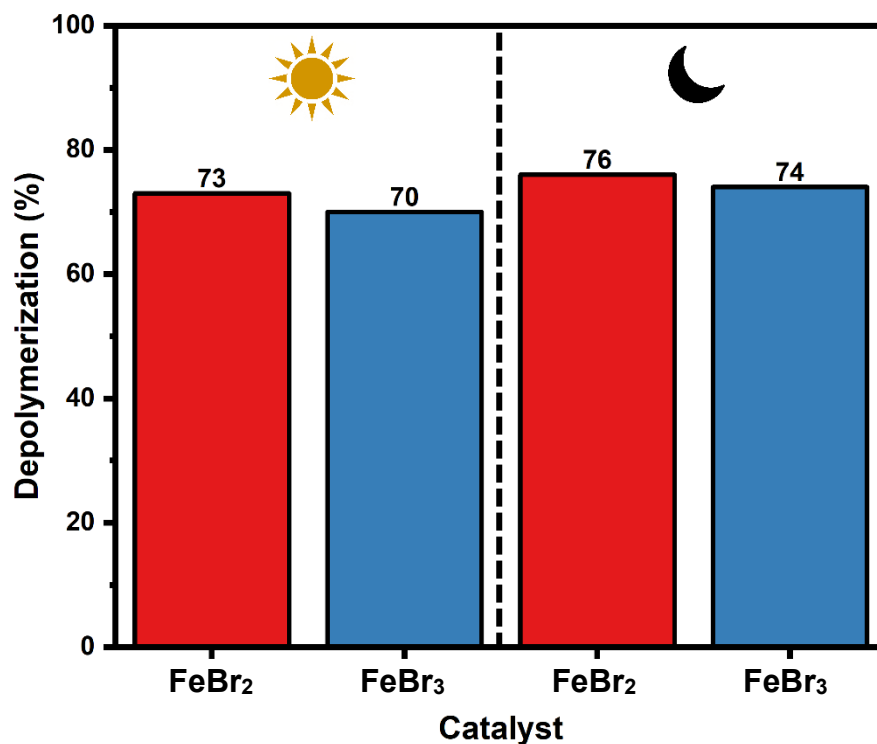


Figure S22: The effect of the metal salt on the depolymerization of PBzMA-Br. Reactions were performed under the optimized conditions (P-Br:FeBr_x:TBABr = 1:1:1) in light and in dark. Conversions were calculated by ¹H NMR.

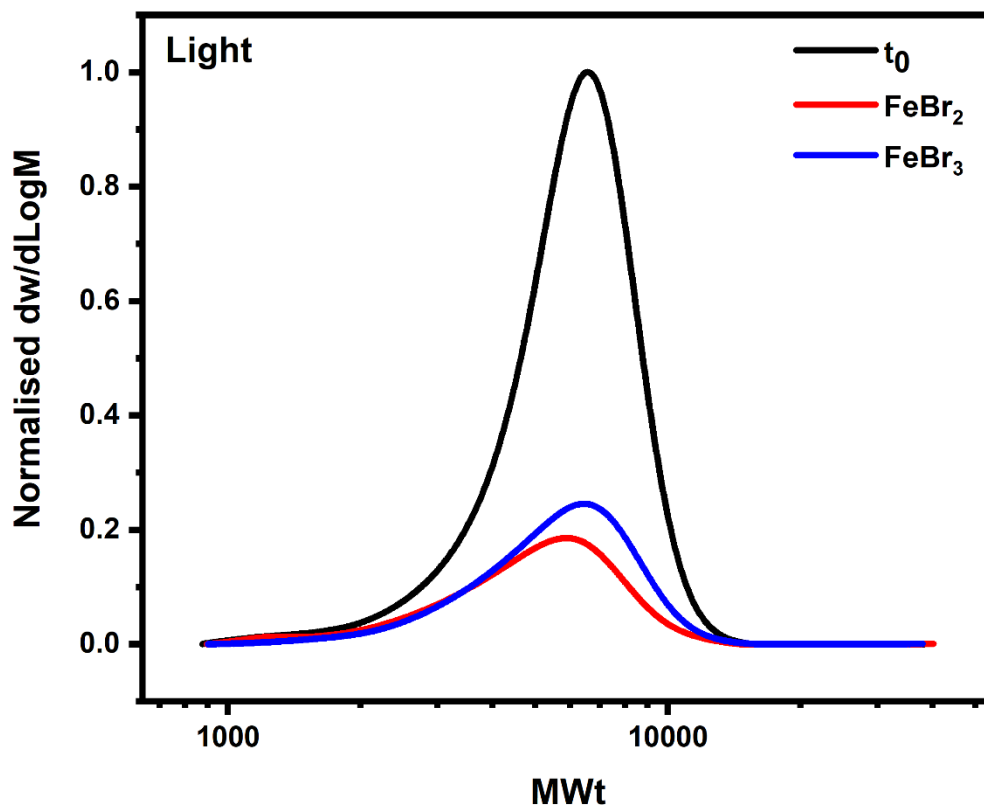


Figure S23: SEC traces for the depolymerization of PBzMA-Br under the optimized conditions (P-Br:FeBr_x:TBABr = 1:1:1) in light, taken after 5 minutes. PS-H was used as an internal standard for the conversion calculation.

Table S9: Depolymerization conversion of PBzMA-Br with different metal salts, in light.

Entry	Catalyst	Depol.(%) ^a (NMR)	Depol. (%) efficiency	Depol.(%) ^b (SEC)	M_n (SEC) ^c	\mathcal{D} ^c
1	FeBr ₂	73	86	75	4300	1.24
2	FeBr ₃	70	82	71	4900	1.19

^[a] Extent of depolymerization at 5 minutes of reaction. This was obtained by ¹H NMR and ^[b]SEC. ^[c]SEC analysis was used to acquire the molecular weight and the dispersity values. All reactions were conducted in TCB under the optimized conditions (P-Br:FeBr_x:TBABr = 1:1:1).

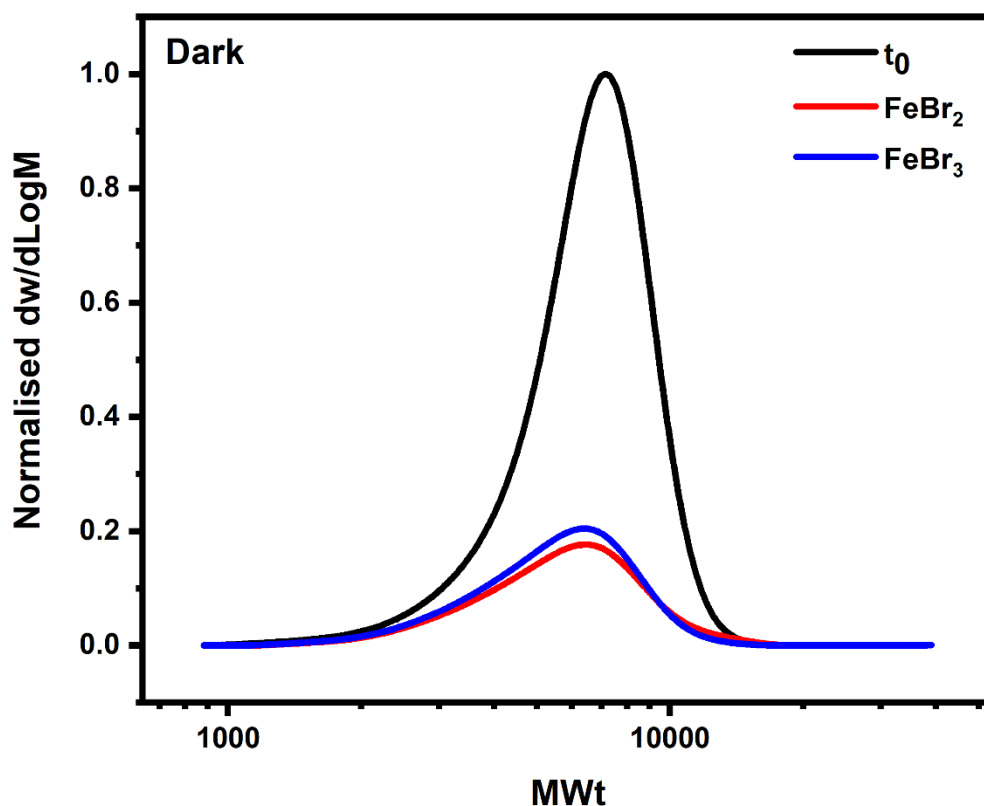


Figure S24: SEC traces for the depolymerization of PBzMA-Br under the optimized conditions (P-Br:FeBr_x:TBABr = 1:1:1) in dark, taken after 5 minutes. PS-H was used as an internal standard for the conversion calculation.

Table S10: Depolymerization conversion of PBzMA-Br with metal salts, in dark conditions.

Entry	Catalyst	Depol.(%) ^a (NMR)	Depol. (%) efficiency	Depol.(%) ^b (SEC)	M_n (SEC) ^c	\mathcal{D} ^c
1	FeBr ₂	76	89	76	5100	1.20
2	FeBr ₃	74	87	73	4900	1.18

^[a] Extent of depolymerization at 5 minutes of reaction. This was obtained by ¹H NMR and ^[b]SEC. ^[c]SEC analysis was used to acquire the molecular weight and the dispersity values. All reactions were conducted in TCB under the optimized conditions (P-Br:FeBr_x:TBABr = 1:1:1).

References

1. J. W. Bartels, S. I. Cauët, P. L. Billings, L. Y. Lin, J. Zhu, C. Fidge, D. J. Pochan and K. L. Wooley, *Macromolecules*, 2010, **43**, 7128-7138.