Efficient Catalytic Depolymerization of High-Molecular-Weight PMMA under Low-Temperature and High-Concentration Conditions

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Supplementary General Information

1.1. Materials

Methyl methacrylate (MMA, TCI, 99.8%) and methyl α-chloroacrylate (MCA, TCI, 98%) were distilled with CaH_2 to remove inhibitor and water and stored at -35 ºC in inert atmosphere. 2,2'-Azobis(2-methylpropionitrile) (AIBN, Aladdin, 98%) was recrystallized with ethanol and stored at -35 ºC in inert atmosphere. Ethyl acetate (EA, Titans, AR) was purified by distillation using CaH_2. Ultra-dry dimethyl sulfoxide (DMSO, J&K, 99.9%) was sealed and stored with molecular sieves. 2-admantyl α-chloroacrylate (2-ADCA) was synthesized by reported literature procedures.[1] Other chemicals were used as received and stored at room temperature in inert atmosphere. Cu(0) catalyst specifications: 30 mesh copper gauze woven from 0.15 mm (0.006in) diameter wire (innochem, 99%) or copper powder with the largest particle size of 106 æm (-140 mesh) (Acros, 99%) purified by immersion in conc. HCl for 15 minutes and subsequently rinsed with water and dried prior to use.

1.2. Instrumentation

Nuclear Magnetic Resonance (NMR) Spectroscopy. ^{1}H NMR spectra were recorded by a Bruker 400 MHz spectrometer. Chemical shifts (δ) are given in parts per million (ppm) relative to TMS and referenced to deuterated chloroform (δ^1H 7.26 ppm) at 298 K.

Gel Permeation Chromatography–Multi-Angle Laser Light Scattering (GPC-MALLS) Instrument. GPC-MALLS instrument was equipped with an automatic sampler (Agilent isocratic pump, degasser, sampler), three 300 × 8.0 mm columns (MZ-Gel SDplus 10E3Å 3μm, 4μm and 5μm) and two detectors including with a DAWN EOS multi-angle laser light scattering (MALLS with 18 angles) detector (Wyatt Technology) operating at 658 nm and a T-rEX refractive index detector (Wyatt S6 Technology), and performed in tetrahydrofuran (THF) at 40 °C and a flow rate of 1.0 mL/min.

Differential Scanning Calorimetry (DSC). DSC experiments were carried out on a TA Q2000 DSC. The sample was heated from 40 to 160 ºC at a heating rate of 10 ºC/min under nitrogen atmosphere, followed by cooling to 40 ºC at 10 ºC/min for two cycles. The reported DSC data was collected on the second heating cycle.

Thermogravimetric Analysis (TGA). All TGA experiments were carried out on a TGA Q500 system. The instrument was equilibrated at 40 ºC. For general TGA experiments, the sample was heated up to 420 ºC or 600 ºC at a heating rate of 10 ºC/min under nitrogen atmosphere.

1.3. Characterization

***M*n and Average Composition of PMMAx-RCAy** M_n was calculated by GPC-MALLS instrument using PMMA standards. Average composition of $PMMA_x$-RCA_y was calculated by quantitative ^1H NMR spectra using the following equations.

$$\frac{y}{x}=\frac{I_{\text{MCA unit}}}{I_{\text{MMA unit}}} \text{ or } \frac{3I_{\text{2-ADCA unit}}}{I_{\text{MMA unit}}}$$

$$M_n=M_{MMA}\times x+M_{RCA}\times y$$

Of above equations, $I_{\text{MCA unit}}$, $I_{\text{2-ADCA unit}}$ and $I_{\text{MMA unit}}$ means the integral area of signal peak around 3.70-3.72 ppm, 4.88-4.96 ppm and 3.59 ppm, respectively; M_{MMA} is equal to 100.12 g/mol, and M_{RCA} is equal to 120.53 g/mol for MCA or 240.73 g/mol for 2-ADCA.

Depolymerization Conversion (Conv.depol.) of PMMAx-RCAy and Yield of MMA (YieldMMA) Depolymerization conversion of $PMMA_x$-RCA_y and yield of MMA were determined by the following formulas using mesitylene as the internal standard.

$$Conv._{\text{depol.}}=\frac{n_{\text{MMA unit, bd}}/n_{\text{mesitylene}}-I_{\text{MMA unit, ad}}/I_{\text{mesitylene}}}{n_{\text{MMA unit, bd}}/n_{\text{mesitylene}}}\times 100\%$$

$$Yield_{\text{MMA}}=\frac{I_{\text{MMA monomer, ad}}/I_{\text{mesitylene}}}{n_{\text{MMA unit, bd}}/n_{\text{mesitylene}}-I_{\text{MMA unit, ad}}/I_{\text{mesitylene}}}\times 100\%$$

Of above formulas, “bd” and “ad” means before depolymerization and after depolymerization; $I_{\text{mesitylene}}$ means the integral area of signal peak around 6.79 ppm; $I_{\text{MMA monomer, ad}}$ means the integral area of signal peak around 3.75 ppm; $n_{\text{MMA unit, bd}}$ was determined by the formula below.

$$n_{\text{MMA unit, bd}}=\frac{m_{\text{(co)polymer}}\times x}{M_n}$$

Supplementary Procedures

All feeding processes were performed in an argon-filled glovebox. All polymerization and depolymerization experiments were conducted in a sealed Schlenk flask unless otherwise noted.

General Procedures for Synthesizing $PMMA_x$-RCA_y by Conventional Free Radical Polymerization (FRP). A typical example for synthesis of $PMMA_{378}$-$MCA_{28.2}$ was indicated. In a Schlenk flask, MMA (100 mmol, 10.7 mL), MCA (5 mmol, 0.51 mL) and AIBN (0.4 mmol, 65.7 mg) were dissolved in EA (50 mL). The flask was sealed in an argon-filled glovebox and set in an oil bath at 65 °C. After stirring for the allotted period, a small aliquot was taken and measured by ^{1}H NMR to give the monomer conversions. The residue was poured into 500 mL cold methanol with rapid stirring. The generated white precipitate was filtered and dried overnight in a vacuum oven at 40 °C.

General Procedures for Synthesizing $PMMA_x$-Cl by Atom Transfer Radical Polymerization (ATRP). A typical example for synthesis of $PMMA_{457}$-Cl was indicated. In a Schlenk flask, $CuCl_2$ (0.042 mmol, 5.7 mg), Pentamethyldiethylenetriamine (PMDETA, 0.072 mmol, 15 μL), MMA (19 mmol, 2.0 mL), ethyl α-chlorophenylacetate (ECPA, 0.038 mmol, 6.5 μL) and stannous 2-ethyhexanoate ($Sn(EH)_2$, 0.03mol, 7.5 μL) were dissolved in N,N-dimethylformamide (DMF, 2.0 mL). The flask was sealed in the argon-filled glovebox and set in a heating device at 70 °C. After stirring for the allotted period, a small aliquot was taken and measured by ^{1}H NMR to give the monomer conversions. The residue was diluted by THF and passed through a glass funnel with neutral alumina to remove the metal. The filtrate was concentrated by rotary evaporator and redissolved with THF to obtain about 10 mL solution. The solution was added into 500 mL cold methanol with rapid stirring to form the white precipitate. The polymer was filtered and dried overnight in a vacuum oven at 40 °C.

General Procedures for Depolymerization of $PMMA_x$-RCA_y in a sealed Schlenk Flask. In a 10 mL Schlenk tube equipped a stir bar, Cu powder (0.28 mmol, 17.8 mg), $PMMA_x$-RCA_y (100~120 mg) and DMSO (2 mL) were added and sealed in an argon-filled glovebox. The tube was set in a heating device at 160 °C. After stirring for the allotted period, the tube was transferred into an ice water bath quickly. The system was diluted by chloroform (about 2 mL) and mesitylene (25 μL) as the internal standard was added accurately. Then the tube warmed up to room temperature naturally. A small aliquot was taken and analyzed by quantitative ^{1}H NMR to calculate depolymerization conversions of $PMMA_x$-RCA_y and yield of MMA according to the internal standard.

General Procedures for Depolymerization of $PMMA_x$-RCA_y Through Intermittent Evaporation. In a 100 mL Thick-walled Pressure-resistant Bottle equipped a stir bar, Cu powder (0.28

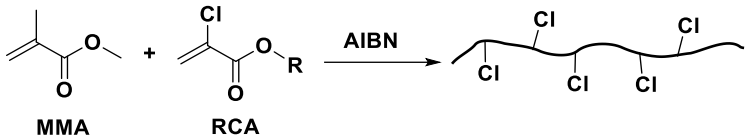
mmol, 17.8 mg), $PMMA_x$-RCA_y (100 mg) and DMSO (2 mL) were added and sealed in an argon-filled glovebox. The flask was cooled at -78 °C and connected with a distillation device equipped with a receiving tube at the inert atmosphere. After pumping for three cycles at -78 °C, the flask was set in a heating device at 160 °C and the system was stirred for the allotted period. Then the flask was cooled quickly to room temperature and MMA was removed to the receiving tube in vacuum for 30 min. The above operation was performed four cycles and the system warmed up to room temperature at the inert atmosphere. The system was stopped by adding acetone (about 2 mL) and mesitylene (25 μL) as the internal standard was added accurately. A small aliquot of the system was taken and analyzed by quantitative ^{1}H NMR to calculate depolymerization conversions of $PMMA_x$-RCA_y and yield of MMA.

Typical UV-VIS Spectroscopic Analysis of CuBr and $CuBr_2$.[2] In a 10 mL Schlenk tube equipped with a stir bar, CuBr (17.2 mg, 0.12 mmol) or $CuBr_2$ (3.4 mg, 0.015 mmol) was added, using DMSO or NMP as solvent (6 mL), with or without PMDETA (n_{PMDETA} equal to n_{CuBrx}) as a ligand. The tube was sealed in an argon-filled glovebox and set in a heating device at 25 or 120 °C. After stirring for the specified duration, the sample was filtered and transferred to a quartz UV-VIS cell (1 mm path length). Prior to use, the cell was rinsed three times with the sample solution, followed by addition of 3 mL aliquot. The cell was then sealed under argon using a septum-sealed screw cap and immediately subjected to UV-Vis spectroscopic analysis.

General Procedures for synthesizing graft Copolymer $PMMA_x$-RCA_y-*graft*-PMA. The experiments were performed inside an argon-filled glovebox. In a 10 mL Schlenk tube equipped with a stir bar, a mixture of $CuBr_2$ (24.6 mg, 0.11 mmol), Cu(0) powder (28 mg, 0.44 mmol) and SaBOX ligand (115 mg, 0.22 mmol) in 3 mL DMSO was stirred at 25 °C for about 2 h. After that, $PMMA_{535}$-MCA_{43} (300 mg, [MMA unit] = 2.73 mmol, [MCA unit] = 0.22 mmol) and MA (0.25 mL, 2.73 mmol) were added into the Schlenk tube. The system was set in a heating device at 25 °C and stirred for 17 h. A small aliquot was taken and directly analyzed using ^{1}H NMR to give the conversion of MA. After completion of the reaction, the reaction mixture left was diluted in THF and the solution was filtered through a glass funnel with neutral alumina to remove the metal. The filtrate was concentrated under reduced pressure and redissolved with 5 mL THF. The solution was added into 500 mL cold methanol with rapid stirring to form the white precipitate. The formed precipitate was cold-filtered and dried overnight in a vacuum oven.

Supplementary Tables

Table S1. The Synthesis of C–Cl bonds-containing PMMA via FRP [a]



Entry	R	n_0(MMA)/n_0(RCA) /n_0(AIBN) (mmol)	M_n (kg/mol)	$Đ$	copolymer
1	2-Adamantyl	100/5/0.4	40.8	1.8	$PMMA_{358}$-2-$ADCA_{20.5}$
2	methyl	100/5/0.4	41.2	2.0	$PMMA_{378}$-$MCA_{28.2}$
3	methyl	100/2.6/0.4	57.0	1.8	$PMMA_{534}$-$MCA_{29.3}$
4	methyl	100/10/0.4	41.5	1.9	$PMMA_{347}$-$MCA_{55.5}$
5[b]	methyl	100/5/0.2	382	2.2	$PMMA_{3423}$-MCA_{326}
6[b]	methyl	200/5/0.04	771	1.7	$PMMA_{6708}$-MCA_{816}
7[b]	methyl	200/5/0.04	1010	1.6	$PMMA_{8851}$-MCA_{1028}

[a] Reaction condition: n(MMA) = 100 mmol, V_{EA} = 50 ml, 65 °C, 24 h. [b] n(MMA) = 100 mmol, bulk polymerization, 2 h.

Table S2. The Synthesis of C–Cl bonds-containing PMMA via ATRP[a]

Entry	n_0(MMA)/n_0(ECPA)	t (h)	$Conv._{MMA}$[b] (%)	M_n (kg/mol)	$Đ$	polymer
1	500	23	95	46.0	1.1	$PMMA_{457}$-Cl
2	100	10	72	7.70	1.2	$PMMA_{75}$-Cl

[a] Reaction condition: n_0(MMA)/n_0($CuCl_2$)/n_0(PMDETA)/n_0($Sn(EH)_2$) = 633/1.0/1.7/0.4, n_0(MMA) = 19 mmol, V_{DMF} = 2 mL, 70 °C, 10 h. [b] Determined by ^{1}H NMR.

Table S3. The Catalyst Components for the Depolymerization of $PMMA_{358}$-2-$ADCA_{20.5}$ [a]

Run	CuBr (mmol)	$CuBr_2$ (mmol)	Ligand (mmol)	Metal(0) (mmol)	$Conv._{depol.}$ [b] (%)
1	\	0.011	SaBOX (0.022)	Cu(0) (0.047)	19
2	\	\	SaBOX (0.022)	Cu(0) (0.047)	29
3	\	\	dNbpy (0.022)	Cu(0) (0.047)	20
4	\	\	PMDETA (0.022)	Cu(0) (0.047)	15
5	\	\	\	Cu(0) (0.047)	35
6	\	0.011	\	Cu(0) (0.047)	23
7	0.022	\	\	\	7
8	\	\	\	Cu(0) (0.280)	40
9	\	\	\	Fe(0) (0.280)	0

[a] Reaction condition: $m_{polymer}$ = 100 mg, [MMA units] = 439 mM, V_{DMSO} = 2 mL, 120 °C, 10 h. [b] The depolymerization conversion measured by ^{1}H NMR as the decrease in MMA units relative to mesitylene as internal standard.

Table S4. The Conditions for the Depolymerization of $PMMA_{358}$-2-$ADCA_{20.5}$ [a]

Run	T (°C)	Solvent	*n*(Cu(0)) (mmol)	[MMA unit] (mM)	$Conv._{depol.}$ [b] (%)
1	65	DMSO	0.280	439	0
2	100	DMSO	0.280	439	8
3	120	DMSO	0.280	439	40
4	160	DMSO	0.280	439	62
5	160	DMSO	0.110	439	55
6	160	DMSO	0.440	439	61
7	160	DMSO	0.880	439	60
8	160	NMP	0.280	439	7
9	160	GVL	0.280	439	7
10	160	TEGDME	0.280	439	19
11	160	TMSO	0.280	439	53
12	160	Tetramethylene sulfone	0.280	439	16
13	160	TCB	0.280	439	6
14	160	DMSO	0.280	96.5	55
15	160	DMSO	0.280	219	62
16	160	DMSO	0.280	877	56

[a] Reaction condition: $V_{Sol.}$ = 2 mL, 160 °C, 10 h. [b] The depolymerization conversion measured by ^{1}H NMR as the decrease in MMA units relative to mesitylene as internal standard.

Table S5. The Synthesis of C–Cl bonds-containing PMMA via the copolymerization of recovered MMA or virgin MMA with MCA [a]

Run	MMA	M_n (kg/mol)	$Đ$	transmittance	T_g (°C)	T_{d5} (°C)
1	recovered MMA	91.4	1.73	97%	124	249
2	virgin MMA	71.9	1.60	94%	122	230

[a] Reaction condition: n(MMA) = 10 mmol, n(MCA) = 0.5 mmol, n(AIBN) = 0.1 mmol, V_{EA} = 1 mL, 65 °C, 4 h.

Table S6. The recycling and reuse of copper gauze catalyst in a sealed depolymerization system of $PMMA_{1661}$-MCA_{246} [a]

Run	Cu(0)	cycle count	$Conv._{depol.}$[d](%)
1[b]	powder	/	73
2[c]	gauze	cycle 1	68
3[c]		cycle 2	63

[a] $m_{polymer}$ = 100 mg, 160 °C, using DMSO as solvent, 4 h, $[MMA\ unit]_0$ = 429 mM. [b] $m_{Cu(0)\ powder}$ = 17.8 mg. [c]The initial weight of the copper gauze is 660 mg, with a recovery rate of 99.7% in recovery cycle. [d]The depolymerization conversion measured by ^1H NMR as the decrease in MMA units relative to mesitylene as internal standard.

Table S7. The recycling and reuse of the entire depolymerization system (including catalyst and solvent) in a sealed depolymerization system of $PMMA_{378}$-$MCA_{28.2}$ [a]

Run	cycle count	$Conv._{depol.}$[b](%)
1	cycle 1	54
2	cycle 2	59
3	cycle 3	67

[a] $m_{polymer}$ = 100 mg, 180 °C, $m_{Cu(0)\ powder}$ = 17.8 mg, $[MMA\ unit]_0$ = 459 mM, using DMSO as solvent, 2 h. [b]The depolymerization conversion measured by ^1H NMR and calculated based on the yield of the MMA monomer.

Supplementary Figures

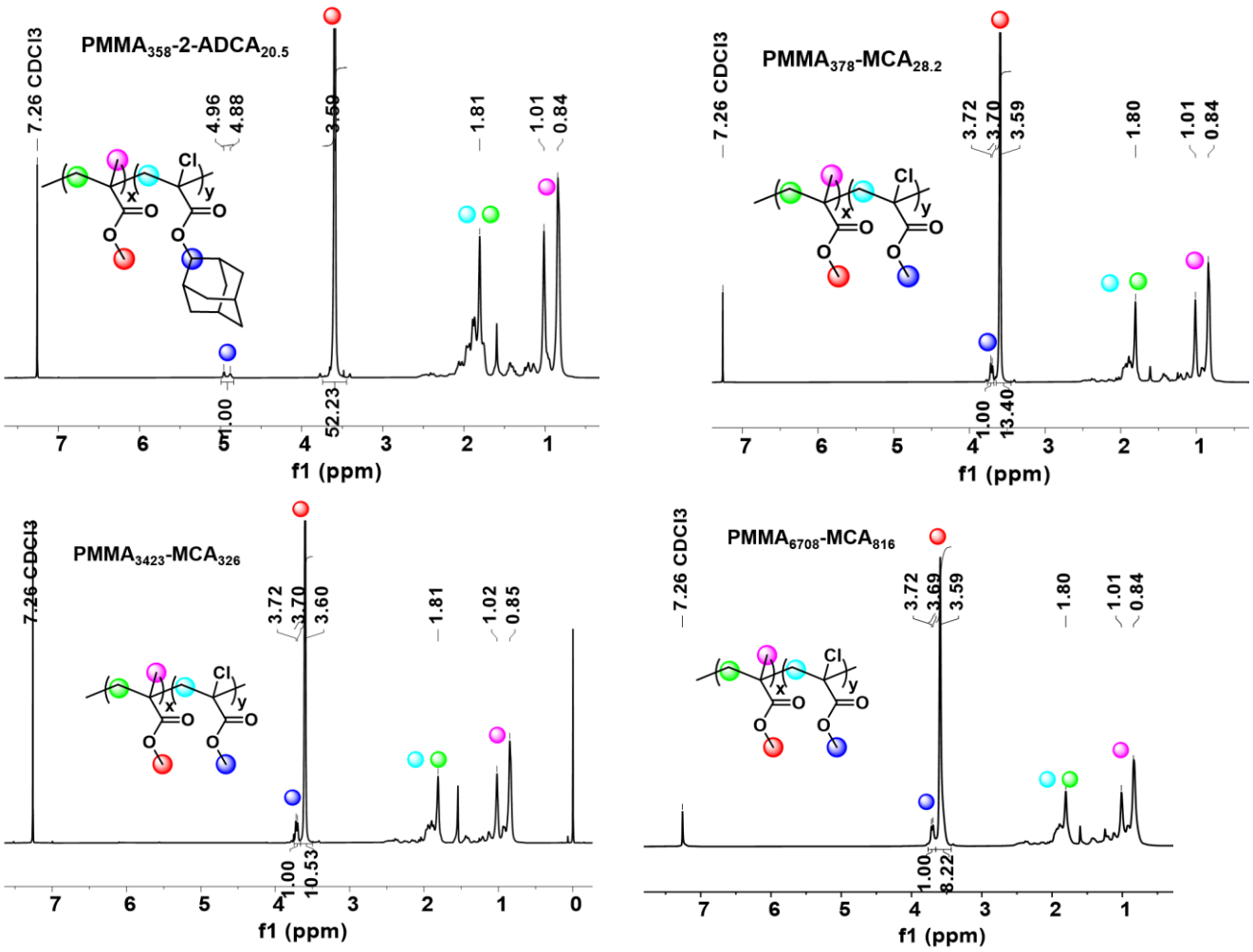


Figure S1. Quantitative ^{1}H NMR spectra of typical $PMMA_x$-RCA_y

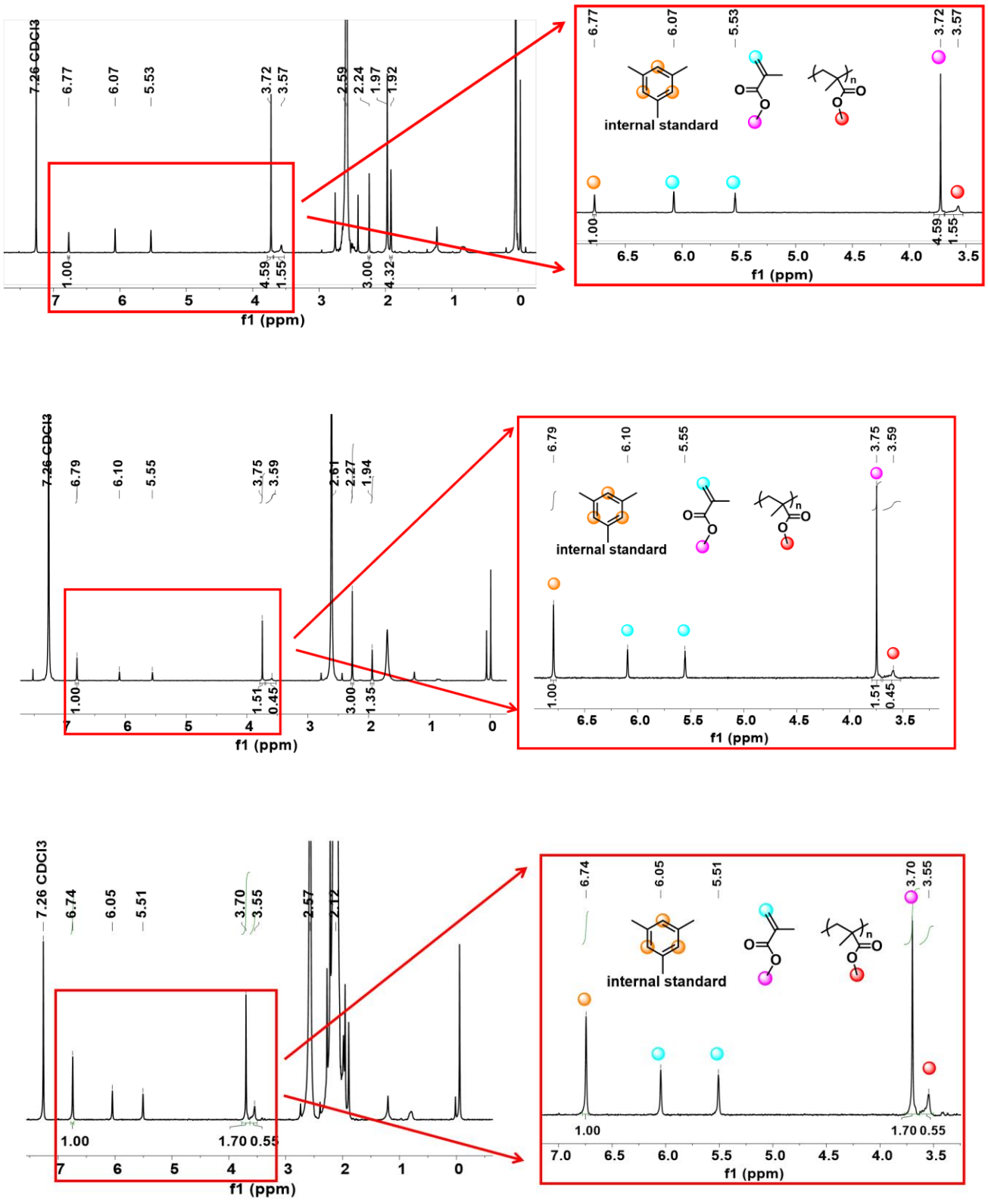


Figure S2. Quantitative ^{1}H NMR spectra of typical depolymerization system (Table 1, runs 8, 10 and 11; 25 μL mesitylene, 120 mg polymer for run 8, 40 mg polymer for run 10, 50 mg polymer for run 11)

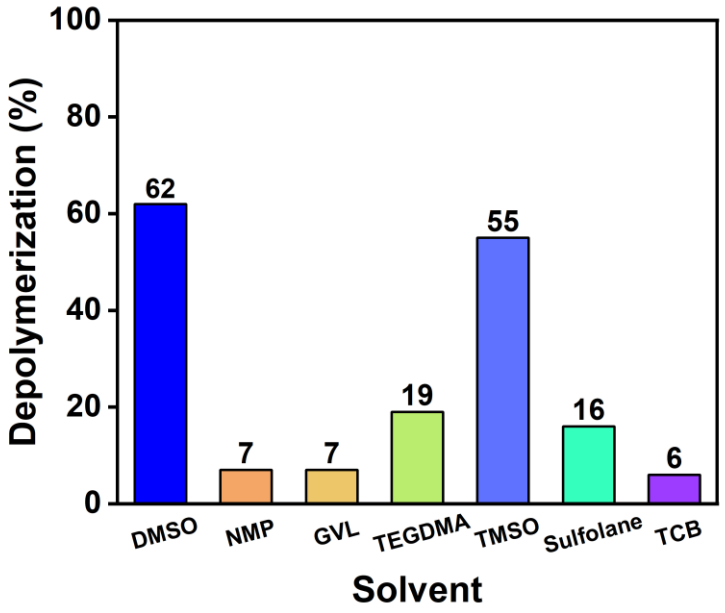


Figure S3. Effect of solvent on the depolymerization of $PMMA_{358}$-2-$ADCA_{20.5}$ (Table S4)

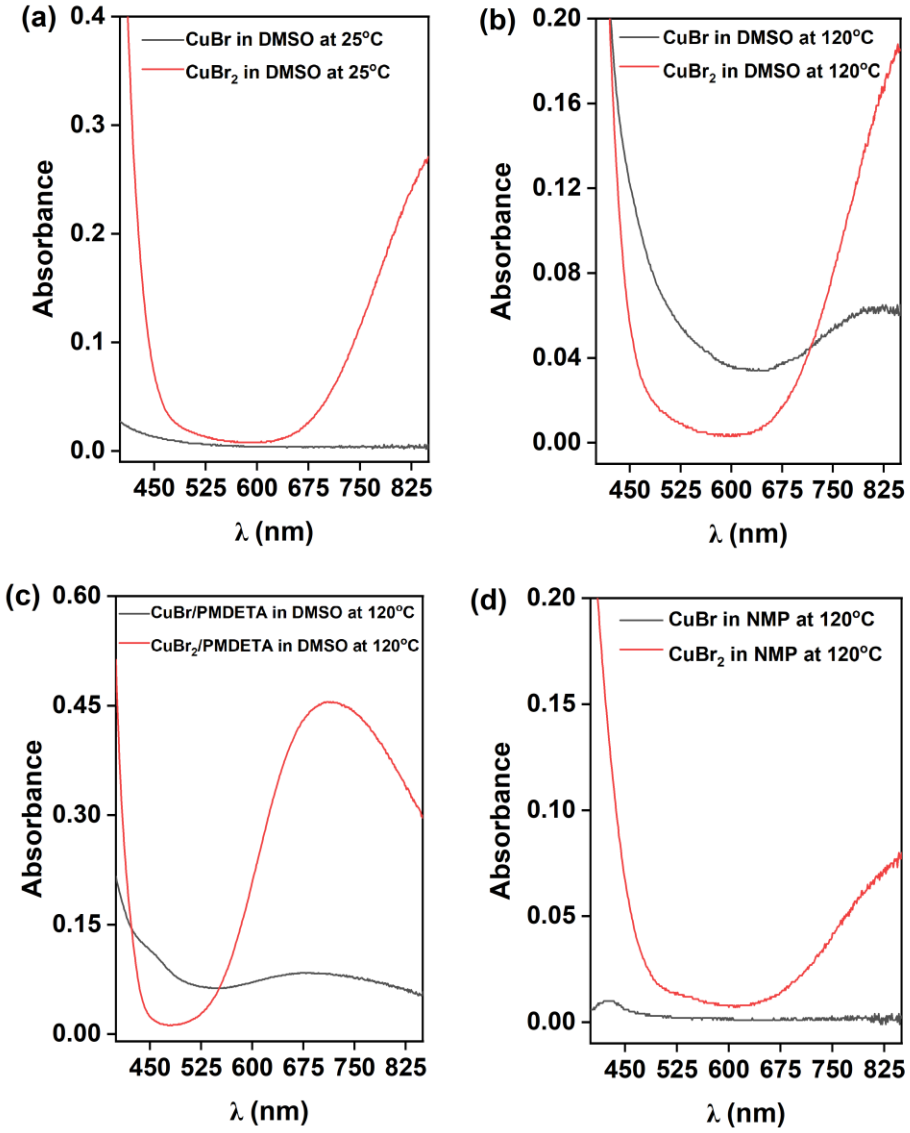


Figure S4. UV-VIS spectra of (a) $CuBr_2$ (0.0025 mmol/mL, red) and CuBr (0.02 mmol/mL, black), stirring in DMSO at 25°C for 4 h; (b) $CuBr_2$ (0.0025 mmol/mL, red) and CuBr (0.02 mmol/mL, black), stirring in DMSO at 120°C for 4 h; (c) $CuBr_2$/PMDETA (0.0025 mmol/mL, red) and CuBr/PMDETA (0.02 mmol/mL, black), stirring in DMSO at 120°C for 4 h; (d) $CuBr_2$ (0.0025 mmol/mL, red) and CuBr (0.02 mmol/mL, black), stirring in NMP at 120°C for 4 h. NOTE: By comparing the relative absorption intensity of the Cu(II) signal generated via disproportionation in the CuBr system to that in the $CuBr_2$ system, it is evident that elevated temperatures facilitate the disproportionation reaction and the solvent DMSO is essential for efficient disproportionation. Under these reaction conditions, the addition of ligand does not promote disproportionation. These results are in agreement with the findings from the depolymerization reactions and align with the activation mechanism catalyzed by Cu(0).

Figure S5. The reaction device for the depolymerization via intermittent evaporation

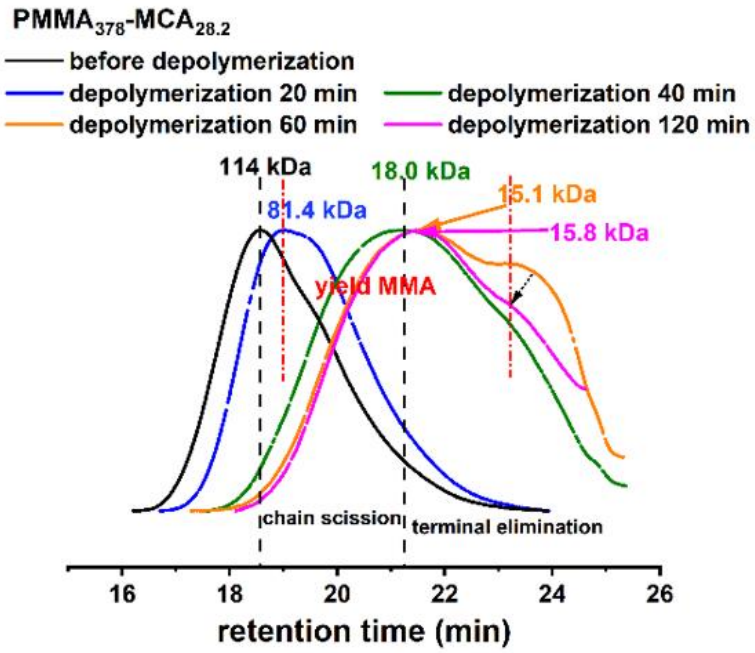


Figure S6. The variation of polymer molecular weight over time during depolymerization of $PMMA_{378}$-$MCA_{28.2}$

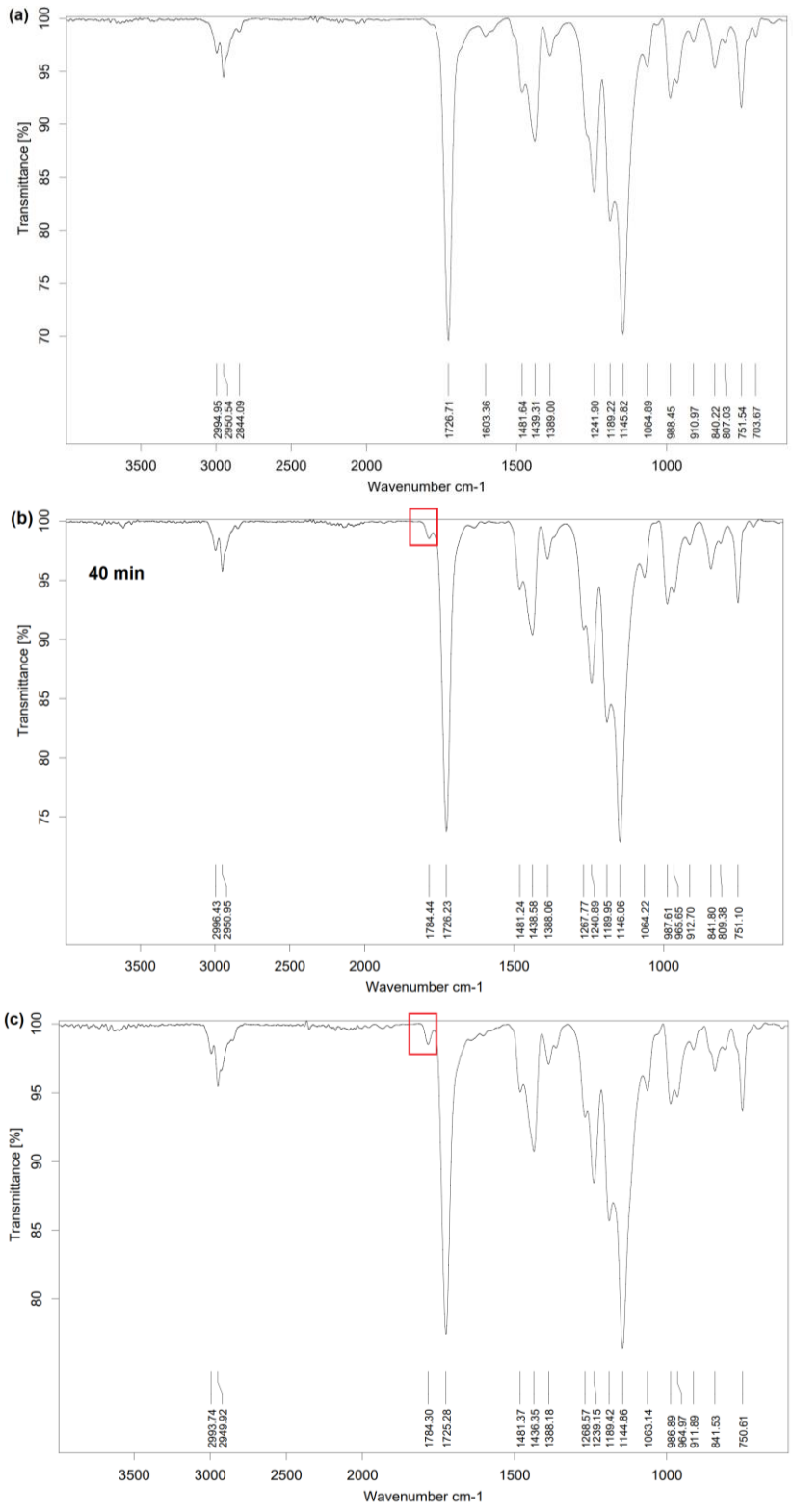


Figure S7. The variation of the infrared spectra of the remaining polymer during the depolymerization of $PMMA_{378}$-$MCA_{28.2}$: (a) 20 min, (b) 40 min, (c) 2 h. NOTE: According to the reference[3], the newly-generated carbonyl signal at ~1784 cm^{-1} is attributed to lactonization of the chain-end, leading to the loss of chain-end functionality.

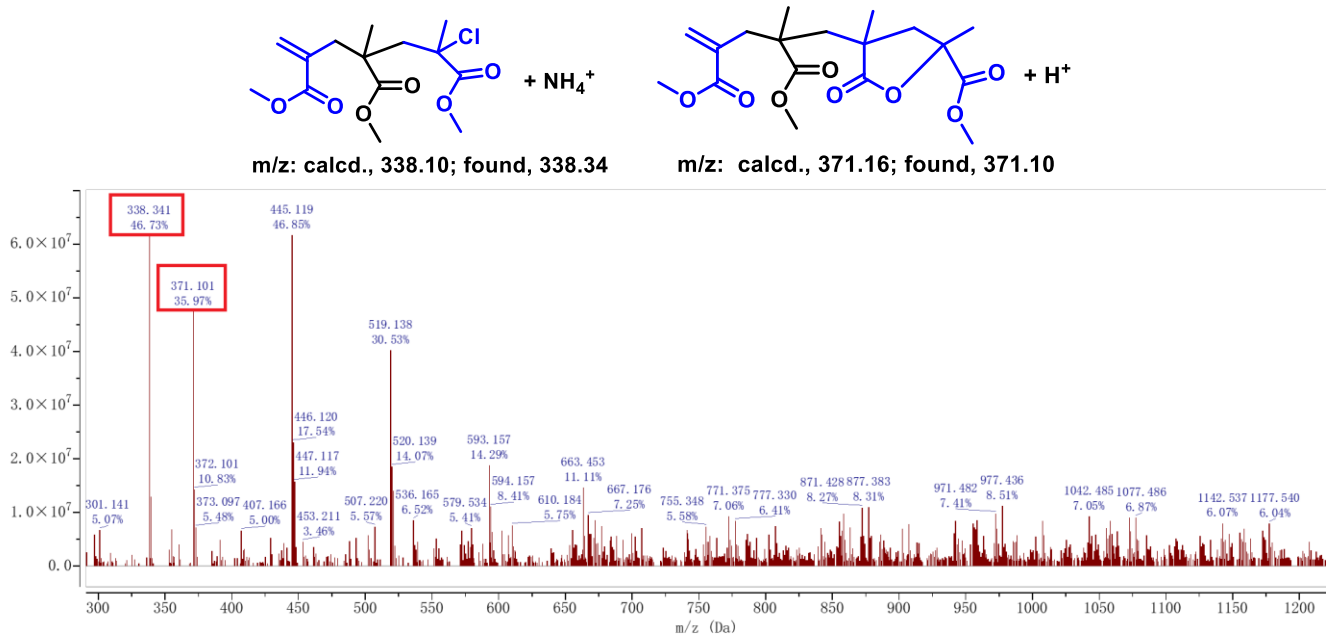


Figure S8. The mass spectrum of the remaining polymer during the depolymerization of $PMMA_{378}$-$MCA_{28.2}$ (2 h).

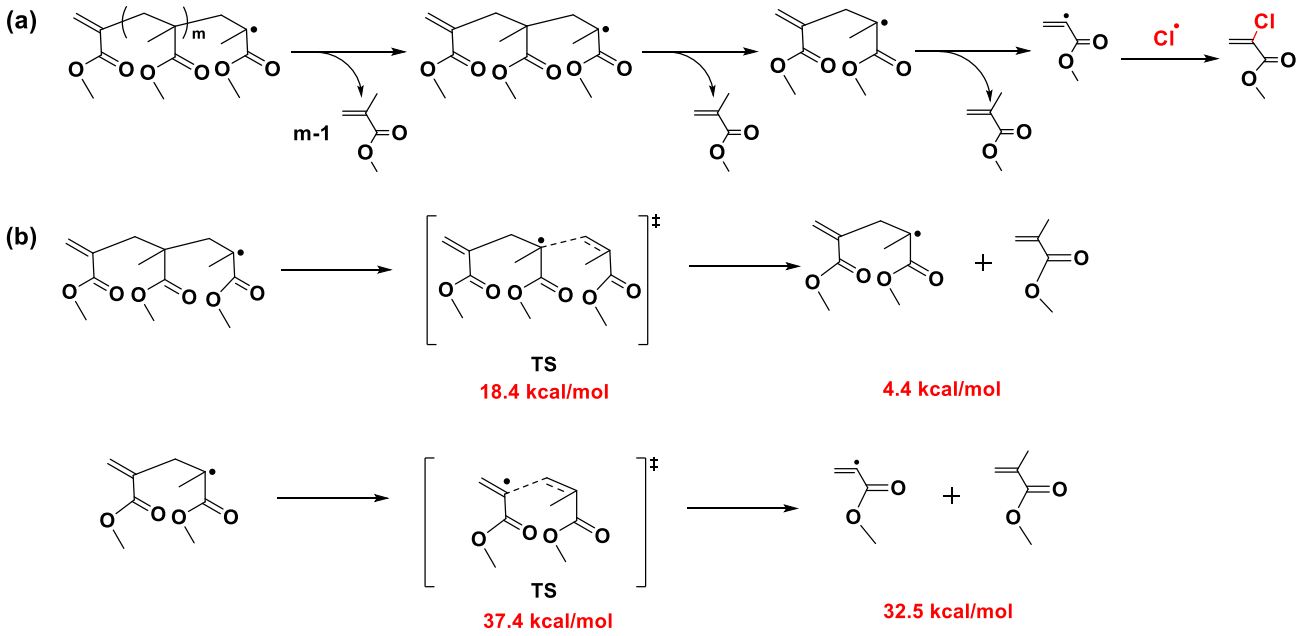


Figure S9. (a) The formation of MCA monomer during depolymerization. (b) DFT calculations for the formation of methacrylate alkyl radical versus acrylate vinyl radical during depolymerization.

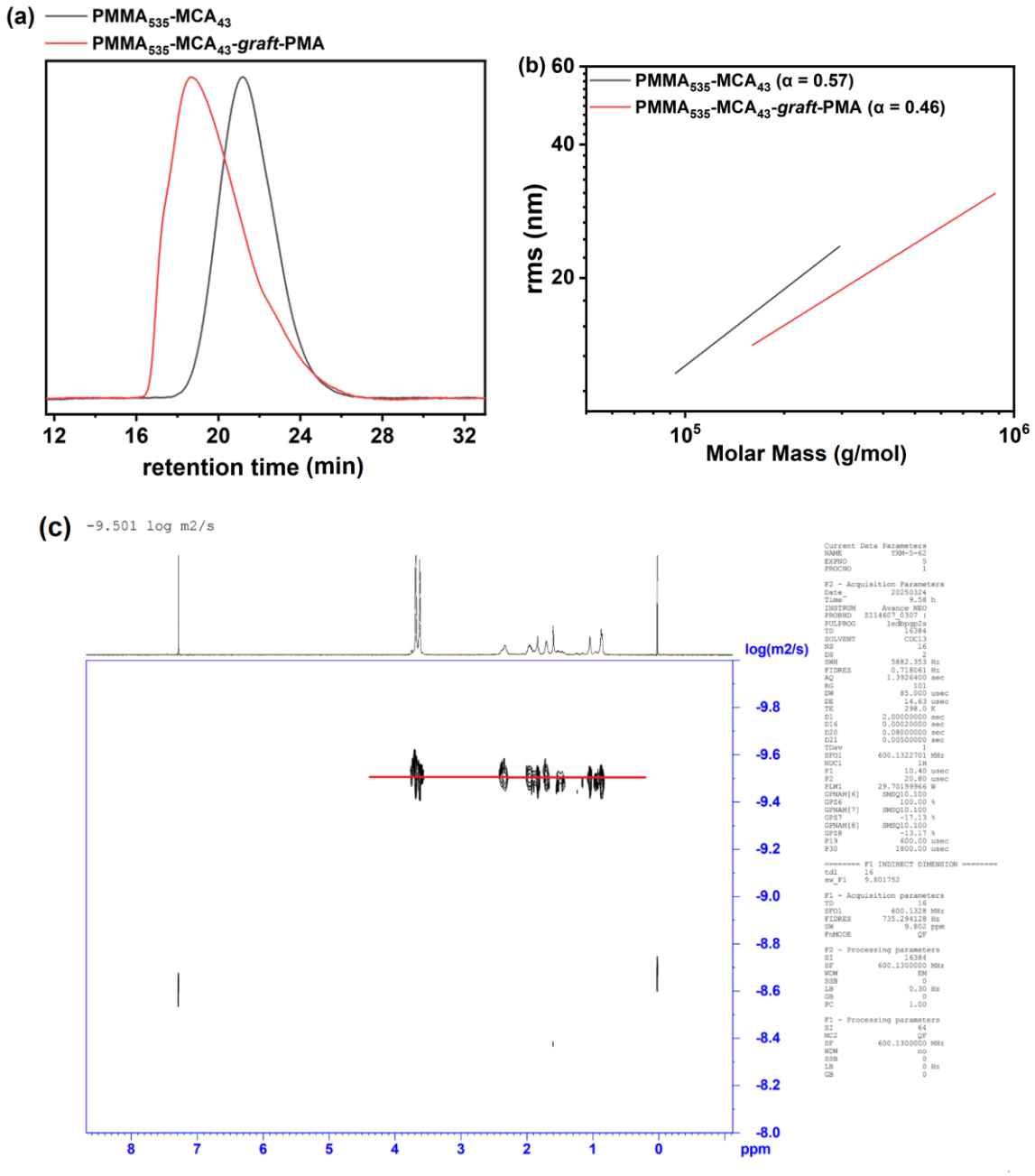
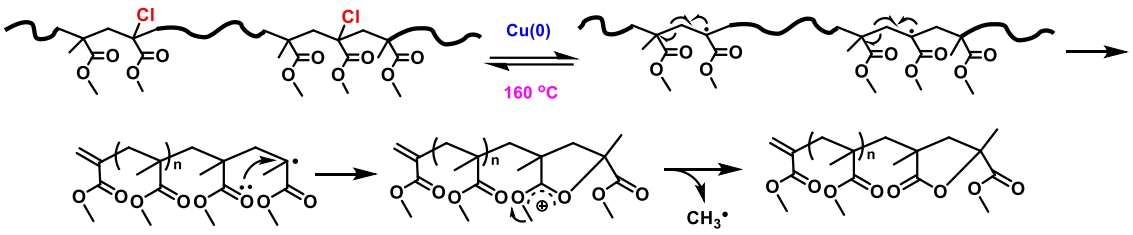


Figure S10. (a) GPC_{LS} curves and (b) rms conformation plots of $PMMA_{535}$-MCA_{43} and $PMMA_{535}$-MCA_{43}-*graft*-PMA. (c) The DOSY NMR ($CDCl_3$) spectrum of $PMMA_{535}$-MCA_{43}-*graft*-PMA.

Supplementary Scheme



Scheme S1. Proposed mechanism of lactonization

Supplementary References

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