Supporting Information

Enhanced Recyclability of Methacrylic Resins by Copolymerization or Pendant Modification Using Trityl Esters

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Experimental procedure

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^{1}H NMR spectra were recorded in DSMO-d_6 (99.9 atom % D, Kanto Chemical) and $CDCl_3$ (99.8 atom % D with 0.03vol% TMS, Kanto Chemicals) on AVANCE NEO (Bruker) spectrometers. Chemical shifts in ^{1}H spectra were referred to the signal of tetramethylsilane (TMS) or solvent (DMSO or $CHCl_3$), respectively. Molar mass and its distributions were determined at 40 °C by size-exclusion chromatography (SEC) on an EXTREMA chromatograph (JASCO) equipped with two SEC columns [Shodex HK-404L × 2], using chloroform ($CHCl_3$; Wako Pure Chemical Industries, GPC grade) as an eluent (flow rate = 0.6 mL min^{-1}), and calibrated against standard poly(methyl methacrylate) (PMMA) samples (TSK-gel oligomer kit, Tosoh, M_p: 6.03×10^5, 2.52×10^5, 1.42×10^5, 2.91×10^4, 8.59×10^3, 4.25×10^3, 1.46×10^3, 8.30×10^2 g/mol) and detected with UV (UV-4070, JASCO) and RI (RI-4035, JASCO) detectors. Thermogravimetric/differential thermal analysis (TG/DTA) was carried out from room temperature to 500 °C at a heating rate of 10 °C min^{-1} with a Rigaku Thermo plus II TG8120 under an N_2 atmosphere. Differential scanning calorimetry (DSC) was performed at a heating rate of 20 °C min^{-1} with a Rigaku Thermo plus II TG8230 under an N_2 atmosphere. Tensile tests were performed using a Shimadzu Autograph AGS-500NX STD.

Materials

Trityl chloride (>98.0%), methacrylic acid (>99.0%), MMA (>99.8%), BA (>99%), trimethylsilyldiazomethane (ca. 10% in hexane, ca. 0.6 M), poly(vinyl alcohol) (*n* = ca. 2000, degree of saponification ca. 80mol%) were purchased from Tokyo Chemical Industry Co., Ltd. TEA (GR), 2,2′-azobis(isobutyronitrile) (AIBN), acetic acid, and sodium chloride for brine were purchased from Fujifilm Wako Pure Chemical Co. Methanol, *n*-hexane, ethyl acetate, dichloromethane (CH_2Cl_2), $CHCl_3$, tetrahydrofuran (THF), sodium sulfate ($MgSO_4$), and conc. HCl aq. were purchased from Yoneyama Yakuhin Kogyo Co., Ltd. PMMA sheets was purchased from AS ONE Corporation. MMA was used in polymerization after distillation.

Synthesis of triphenylmethyl methacrylate (TMA)

Methacrylic acid (28.2 g, 324 mmol) was added dropwise to a THF (200 mL) solution of trityl chloride (51.0 g, 179 mmol) and triethylamine (27.4 g, 268 mmol) cooled in an ice bath. After stirring at 25 °C for 24 h, the solution was heated to 30 °C for 24 h. After the complete conversion of trityl chloride to TMA confirmed by ^{1}H NMR spectroscopy, the solution was concentrated under reduced pressure. The obtained white solid was dissolved in CH_2Cl_2 and washed by saturated $NaHCO_3$ aq. (300 mL, three times) and brine (300 mL). The organic layer was dried over $MgSO_4$ and concentrated. The obtained solid was recrystallized from hexane/ethyl acetate (200 mL / 15 mL) to yield TMA as colorless crystals (56.1 g, yield: 95.5%). ^{1}H NMR spectrum (DMSO-d_6, 25 °C, 400 MHz): δ/ppm, 7.42–7.23 (15H, m, ArH), 6.17 (1H, s, =C*H*H), 5.75 (1H, s,=CH*H*), 3.36 (3H, s,-OCH3), 1.95 (3H, s, –CH_3).

Bulk (co)polymerization

A typical procedure (**Table 1**, **CP-5**): A mixture of MMA (2.85 g, 28.5 mmol), TMA (0.493 g, 1.50 mmol), and AIBN (16.4 mg, 0.100 mmol) was heated at 65 °C for 18 h in a test tube after degassing three times by freeze-pump-thaw cycles. The obtained solid was dissolved in $CHCl_3$ (30 mL), and the solution was poured into methanol (800 mL). The precipitation was collected by filtration and dried *in vacuo* to yield **CP-5** (3.21 g, yield: 96%, M_n = 127600 g/mol, $Đ$ = 4.59).

Suspension (co)polymerization

A typical procedure (**Table 1**, **CP-S5**): A three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a three-way cock was degassed followed by argon replacement three times. 7.1 wt% aqueous solution of poly(vinyl alcohol) (250 mL) was added to the flask, and the mixture was refluxed for 1 h and cooled to 65 °C. In another flask, a mixture of MMA (47.6 g, 47.5 mmol), TMA (8.21 g, 2.50 mmol), and AIBN (274 mg, 0.167 mmol) was degassed three times by freeze-pump-thaw cycles, and the mixture was transferred into the aqueous solution. The suspension was vigorously stirred at 65 °C for 18 h. The formed particles were collected by centrifugation, washed using water and methanol, and dried *in vacuo* to yield **CP-S5** (55.8 g, yield: 84%).

Conversion of poly(MMA-co-TMA) to PMMA

A typical procedure: conc HCl aq. (0.75 mL) was added to a suspension of **CP-5** (0.250 g) in methanol (15 mL). The suspension was refluxed for 23 h. The acidic solvent was removed by concentration, and the residue was dissolved in toluene/methanol (v/v = 4/1, 10 mL). A solution of trimethylsilyldiazomethane in hexane (ca. 0.6 M, 1 mL) was added carefully, and the reaction solution was allowed to be stirred at 25 °C for 21 h. Acetic acid was added carefully to the solution to quench excess trimethylsilyldiazomethane. The solution was washed by water (15 mL, twice). The organic layer was dried over $MgSO_4$ and concentrated. The residue was dried *in vacuo* to afford PMMA (0.223 g, yield: 89.3%).

Monomer recovery from poly(MMA-co-TMA)

A typical procedure (**Table 2**, Entry 1): **CP-5** (1.00 g) was placed in a reaction flask equipped with a receiving flask and a vacuum pump (**Figure 2C**). The system was vacuumed to 27 hPa, and the receiving flask was cooled with liquid N_2. The reaction flask was heated to 270 °C from room temperature by a mantle heater. The temperature reached 270 °C after 15 min; **CP-5** in the reaction flask disappeared, whereas white solids appeared in the receiving flask. The system was filled with N_2 gas and returned to atmospheric pressure, and liquid N_2 for cooling the received flask was removed. The collected solid in the receiving flask, which melted to a transparent liquid at room temperature, was identified as MMA by ^{1}H NMR spectrometry (**Figure 2D**). The recovery yield was evaluated to be 94.5% according to the following equations;

$$(\text{MMA recovery}) = w_{\text{MMA}}/W_{\text{MMA}} \times 100\%$$

$$W_{\text{MMA}} = W_0 \times (F_{\text{MMA}} \times M_{\text{MMA}})/(F_{\text{MMA}} \times M_{\text{MMA}} + F_{\text{TMA}} \times M_{\text{TMA}})$$

Here, w_{MMA} and W_{MMA} are the weights of recovered MMA and MMA in the initial copolymer, respectively. F_{MMA} and F_{TMA} are the mole fractions of MMA and TMA in the initial copolymer, respectively. M_{MMA} and M_{TMA} are the molar masses MMA and TMA, respectively.

Pendant Modification (Hydrolysis and Tritylation)

A Typical procedure: PMMA (**HP**, 10.0 g) was added in small portions into conc. H_2SO_4 (240 mL) at 50 °C. The viscous solution with slight dissolution residue was stirred for 10 min and poured into water (3.0 L) in small portions, and the precipitate was collected by decantation. The obtained solids were washed with water and dried *in vacuo,* yielding poly(MMA-*co*-MAA) (8.90 g). The hydrolysis ratio was evaluated to be 10% from ^{1}H NMR spectrometry (**Figure S11**). The obtained poly(MMA-*co*-MAA) (8.90 g) and TEA (2.72 g, 26.9 mmol) were dissolved in DMF (100 mL) at 90 °C. Trityl chloride (7.50 g, 26.9 mol) was added to the solution. The solution was stirred for 60 min, cooled to room temperature, and poured into methanol (2.0 L) in small portions. The precipitates were collected from the solution by filtration, washed using methanol, and dried *in vacuo* to yield poly(MMA-*co*-TMA) (9.7 g). The content of TMA unit was evaluated to be 7% from the integral intensity of aromatic signals to those of methylene and α-methyl signals in ^{1}H NMR spectra (**Figure S12**).

Conversion of PMMA sheets to CP-Mb

Crushed PMMA sheets were ground in a milling jar (10 mL) with two stainless steel balls (diameter: 0.5 mm) at 30 Hz for 20 min using a MM200 (Retsch) mixer mill. The obtained powder pf PMMA (10.0 g) was modified according to the above mentioned procedure of hydrolysis and tritylation to afford poly(MMA-*co*-TMA) (13.0 g, yield: 93.5%). The content of TMA unit was evaluated to be 17% from the integral intensity of aromatic signals to those of methylene and α-methyl signals in ^{1}H NMR spectra (**Figure S13**).

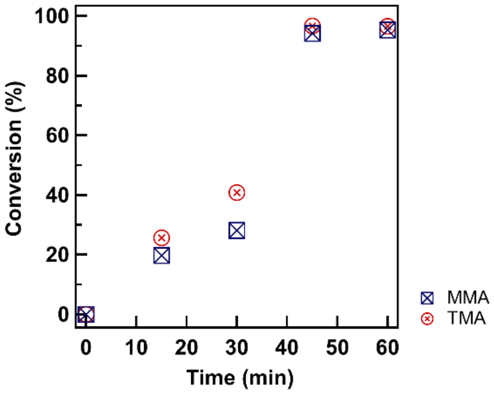


Figure S1. Time conversion of MMA (95 mol%) and TMA (5mol%) in bulk copolymerization at 65 °C (**Table 1**, **CP-5**), calculated by signals derived from vinyl groups of each monomer in ^{1}H NMR spectra (400 MHz, 25 °C, $CDCl_3$)

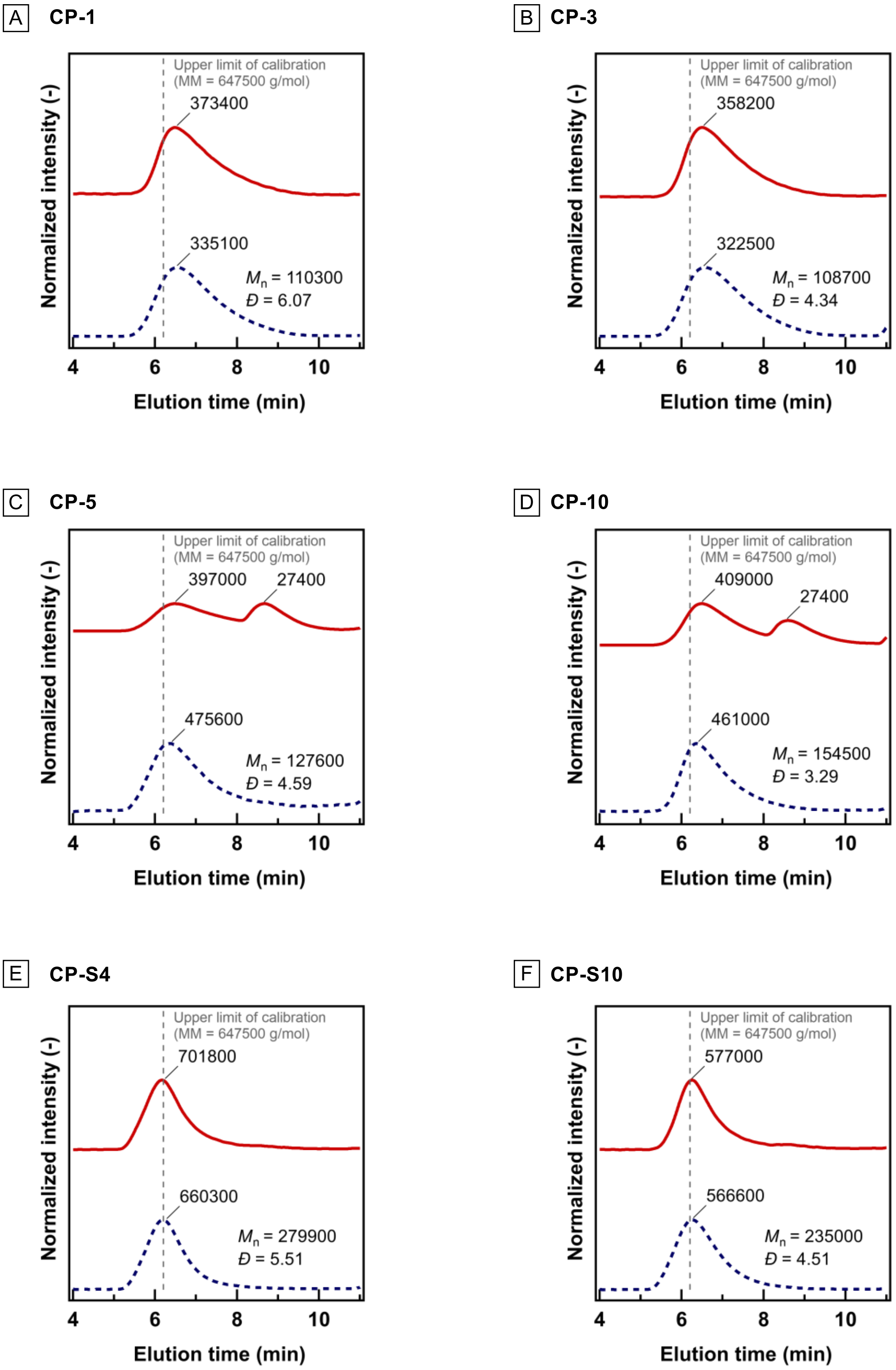


Figure S2. SEC profiles ($CHCl_3$, 40 °C, PMMA-standard) of poly(MMA-*co*-TMA) (red curves) and the converted PMMAs (blue dotted curves).

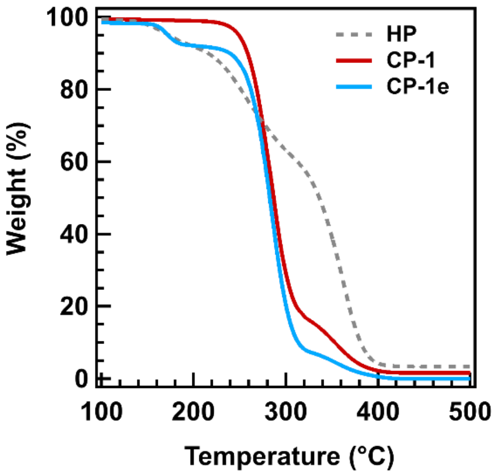


Figure S3. TG curves (Heating rate: 10 °C/min, under N_2) for **HP**, **CP-1**, and **CP-1e**. **CP-1e** was prepared by quenching the bulk polymerization in the early stage, in which the conversions of MMA and TMA were 27.9% and 48.9%, respectively).

Differences in the thermal degradation behavior of **CP** and **HP**

In the TG curves, **HP** demonstrated thermal degradation in three distinct steps corresponding to the chain-end structure (**Figure S3**). As outlined in the main manuscript, this degradation pattern is well established. Conversely, **CP-1** exhibited a single-step thermal degradation. Because no degradation was observed below 200 °C, it was anticipated that **CP-1** did not contain polymer chains formed by combination termination. To investigate this, bulk copolymerization was halted before the reaction mixture lost fluidity. At this point, the conversions of MMA and TMA were 27.9% and 48.9%, respectively. The resulting copolymer, **CP-1e**, exhibited thermal degradation below 200 °C, indicating the presence of a head-to-head linkage formed by combination termination. Notably, combination termination is a reversible reaction, particularly at elevated temperatures, whereas disproportionation is irreversible. Additionally, bulk polymerization often leads to a temperature increase owing to the Norrish-Trommsdorf effect (gel effect). Therefore, we anticipated that the conversion of head-to-head linkage to disproportionate chain ends would occur under thermodynamic control, leading to an absence of thermal degradation below 200 °C.

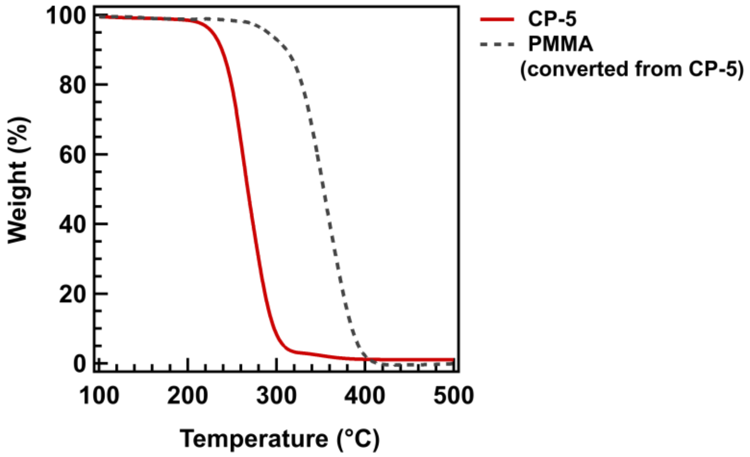
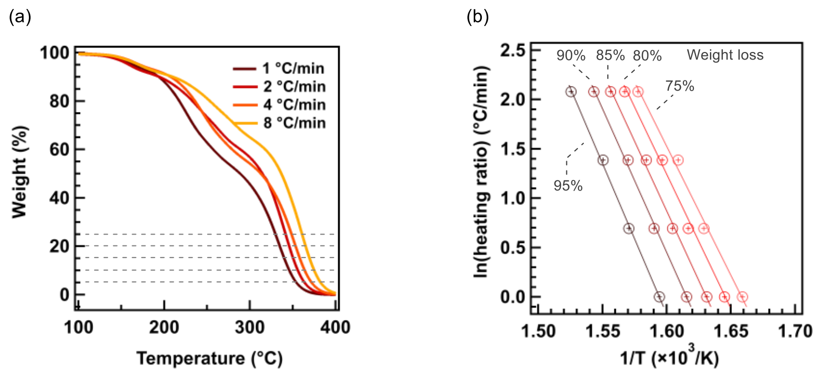
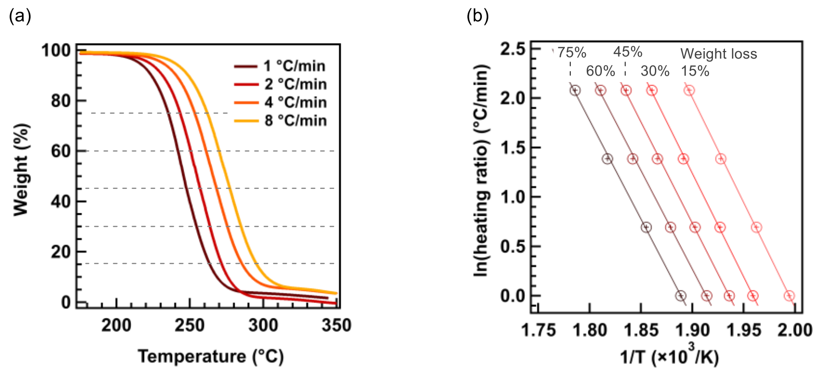


Figure S4. TG curves of **CP-5** and PMMA converted from **CP-5**. (Heating rate: 10 °C/min, under N_2)

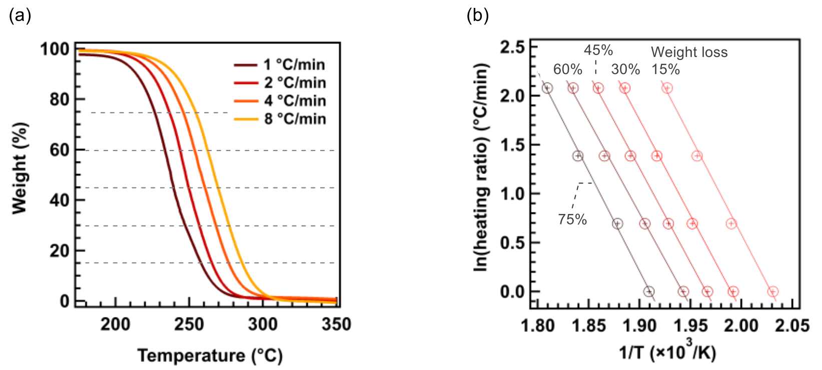
A **HP**



B **CP-3**



C **CP-5**



D **CP-10**

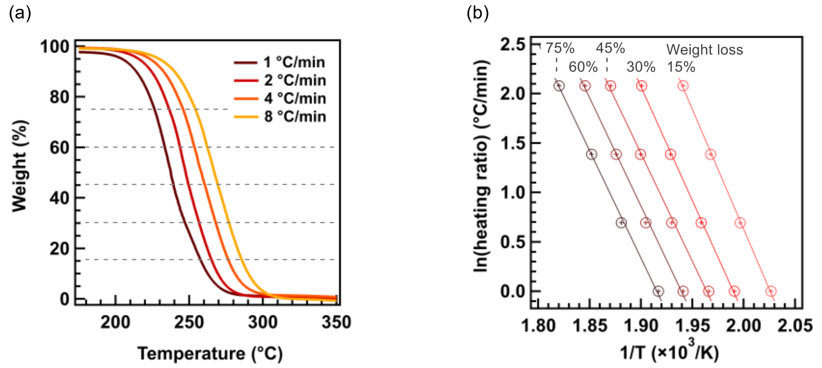


Figure S5. (a) TG curves of **HP** and **CPs** with different heating rate and (b) Flynn–Wall–Ozawa plot for **HP** and **CPs**.

Table S1. E_a for the decomposition of **HP** and **CP**s, calculated by Flynn–Wall–Ozawa plot.

Weight loss [%]	E_a [kJ/mol] **HP**	 **CP-3**	 **CP-5**	 **CP-10**
15.0	-	168.0	158.1	192.1
20.0	-	167.7	157.4	187.9
25.0	-	166.9	155.4	185.2
30.0	-	165.6	154.3	182.0
35.0	-	165.0	154.1	178.3
40.0	-	162.8	154.6	175.0
45.0	-	161.9	152.5	172.6
50.0	-	159.9	152.2	172.9
55.0	-	157.6	150.2	173.3
60.0	-	157.9	149.9	173.4
65.0	-	158.1	151.1	173.6
70.0	-	157.8	155.7	172.8
75.0	206.5	158.0	160.1	171.6
80.0	215.1	156.8	166.1	169.9
85.0	223.5	155.2	169.9	166.6
90.0	230.5	150.6	174.2	162.8
95.0	241.8	133.3	180.5	156.1
average	223.4	159.0	158.6	176.5

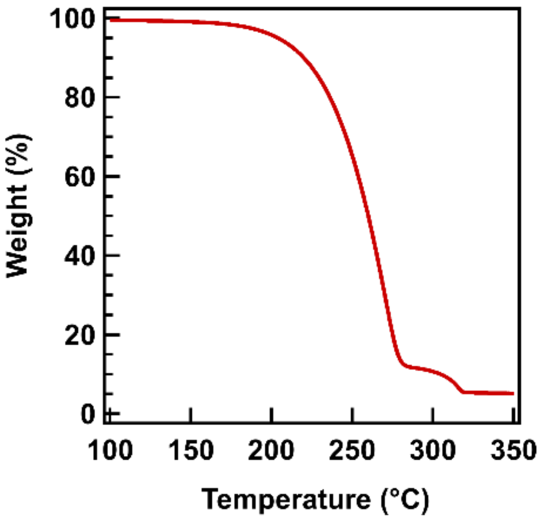


Figure S6. The TG curve for TMA (heating ratio: 10 °C/min).

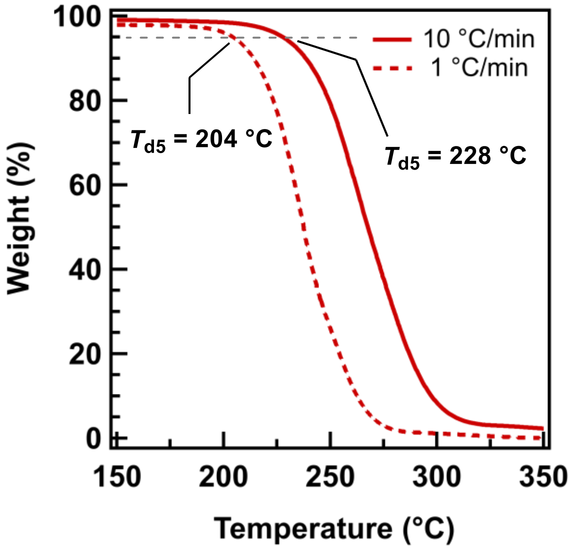


Figure S7. The TG curves for **CP-5** with heating rate of 1 °C/min and 10 °C/min

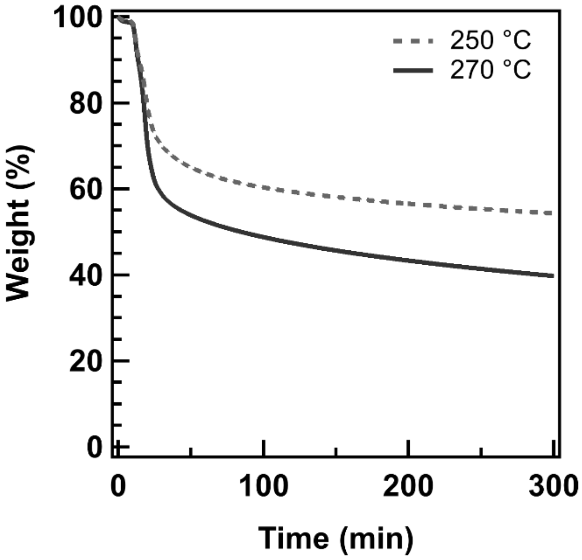


Figure S8. The TG curves for **HP** under constant temperature conditions at 250 and 270 °C.

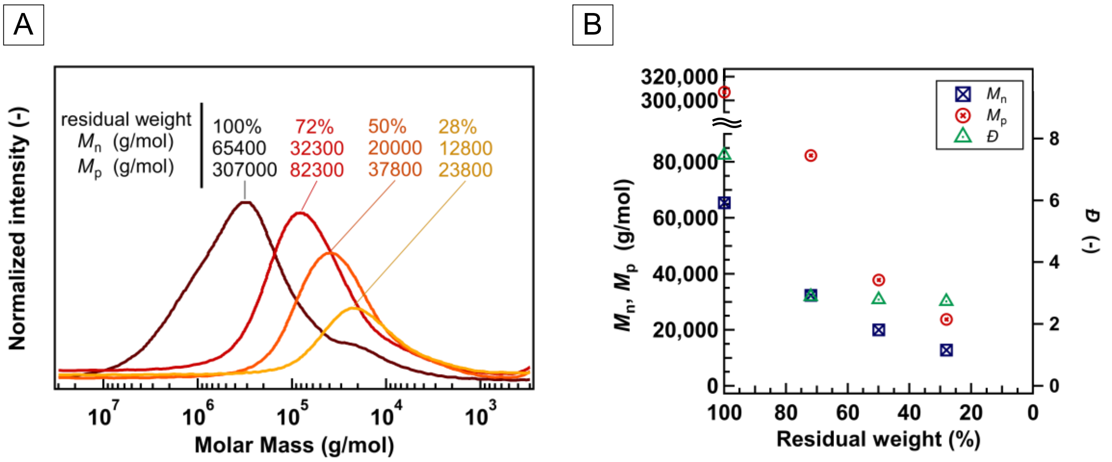


Figure S9. (A) SEC curve changes during thermal degradation of **CP-5** at the constant temperature of 250 °C in TG analysis ($\mathrm{CHCl_3}$, 40 °C, PMMA standard). The RI Intensities were normalized using sample weight before TG analysis. (B) Plots of M_n, M_p, and *Đ* against residual sample weights observed in TG analysis.

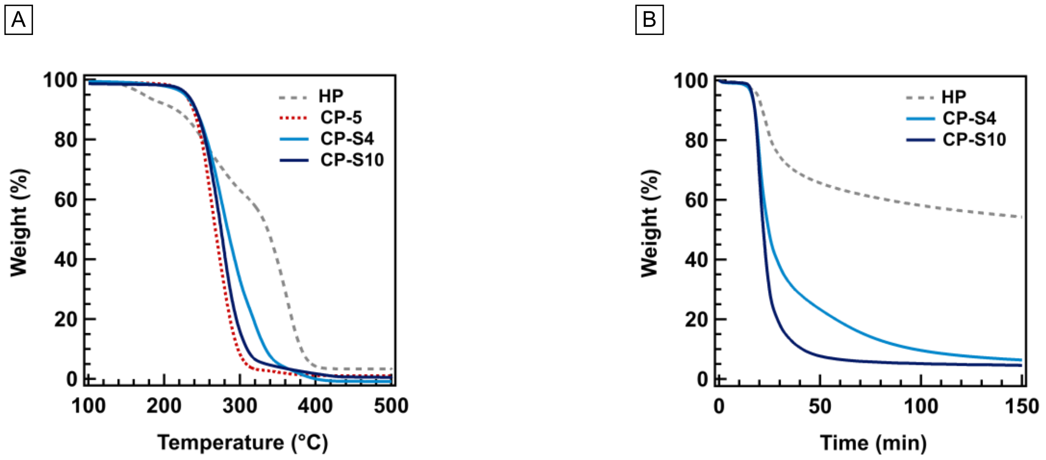


Figure S10. The TG curves for **CP-S4** and **CP-S10** (A) at heating rate of 10 °C/min (B) under constant temperature conditions of 270 °C.

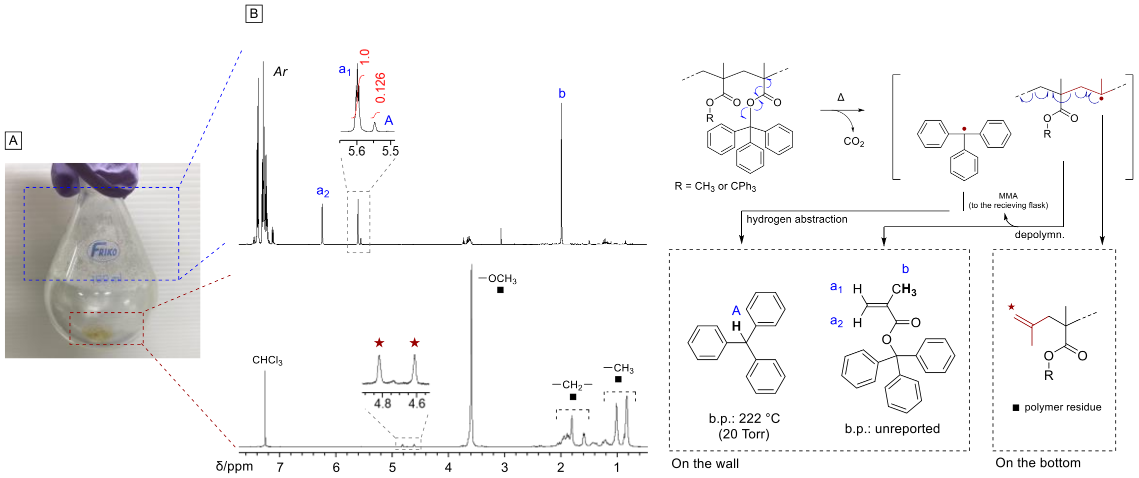


Figure S11. (A) The photo of the reactor after monomer recovery from **CP-5** at 270 °C for 60 min. The transparent liquid on the wall and the slight yellow residue on the bottom were observed. (B) ^{1}H NMR spectra of (upper) the transparent liquid on the wall and (below) the yellow residue on the bottom (400 MHz, 25 °C, $CDCl_3$).

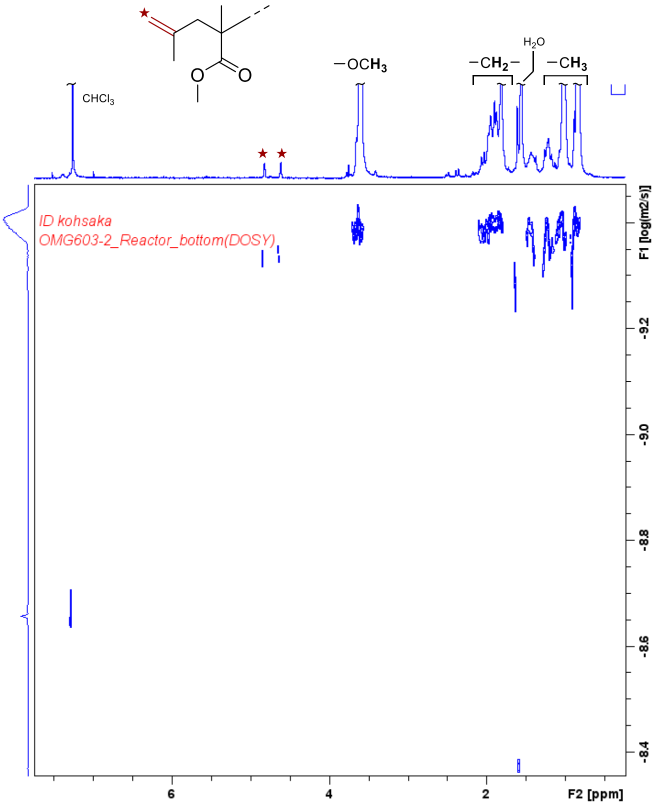


Figure S12. DOSY NMR spectra (400 MHz, 25 °C, $CDCl_3$) of the yellow residue on the bottom of reactor after the monomer recovery from **CP-5** at 270 °C for 60 min.

Figure S13. A photo of **CP-5** film prepared by thermo-pressing at 200 °C.

Figure S14. (A) Transmittance of films prepared from **CP-S10**. The photos of **CP-S10** films prepared by thermo-pressing at (B) 180 °C and (C) 200 °C.

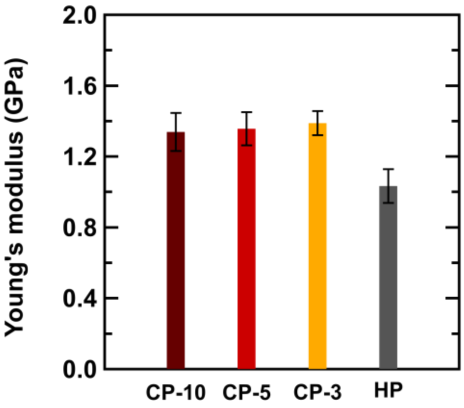


Figure S15. Young's modulus of poly(MMA-*co*-TMA)s and **HP**.

Table S2. Mechanical properties of poly(MMA-co-TMA) and PMMA.

Entry	Stress (MPa)	Strain (%)	Toughness (kJ)	Young’s modulus (GPa)
HP	26.3±4.0	2.81±0.42	4.35±1.35	1.03±0.95
CP-3	40.0±13.1	3.21±1.25	5.74±3.71	1.39±0.68
CP-5	44.5±6.3	3.45±0.71	4.16±1.39	1.36±0.09
CP-10	14.3±2.5	1.12±0.24	0.53±0.22	1.39±0.11

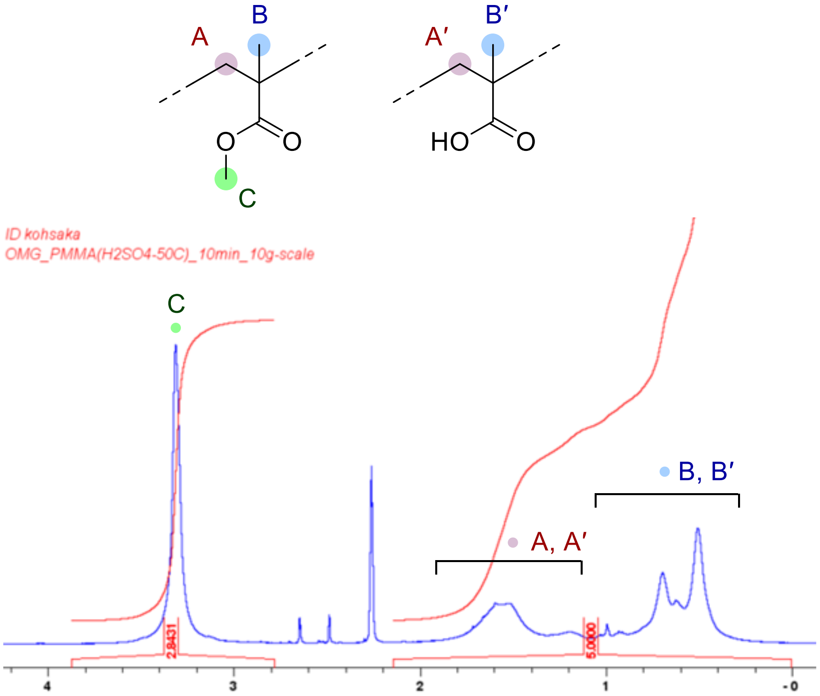
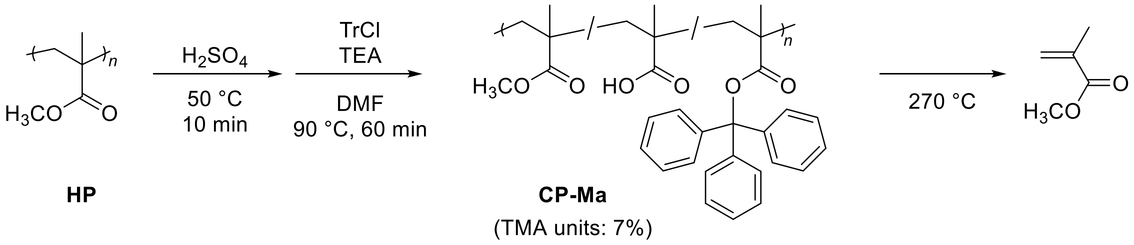


Figure S16. ^{1}H NMR spectrum of partial hydrolyzed **HP** (400 MHz, DMSO-d_6, 25 °C).



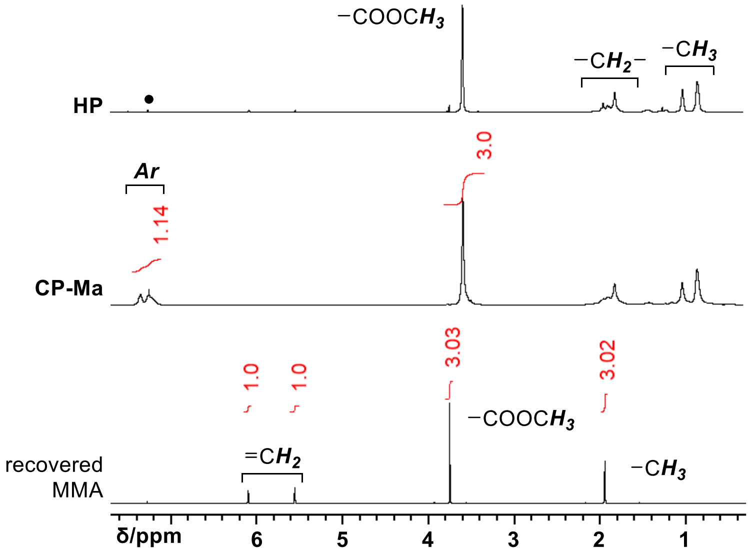


Figure S17. ^{1}H NMR spectra of **HP**, **CP-Ma**, and recovered MMA (400 MHz, CDCl$_3$, 25 °C)

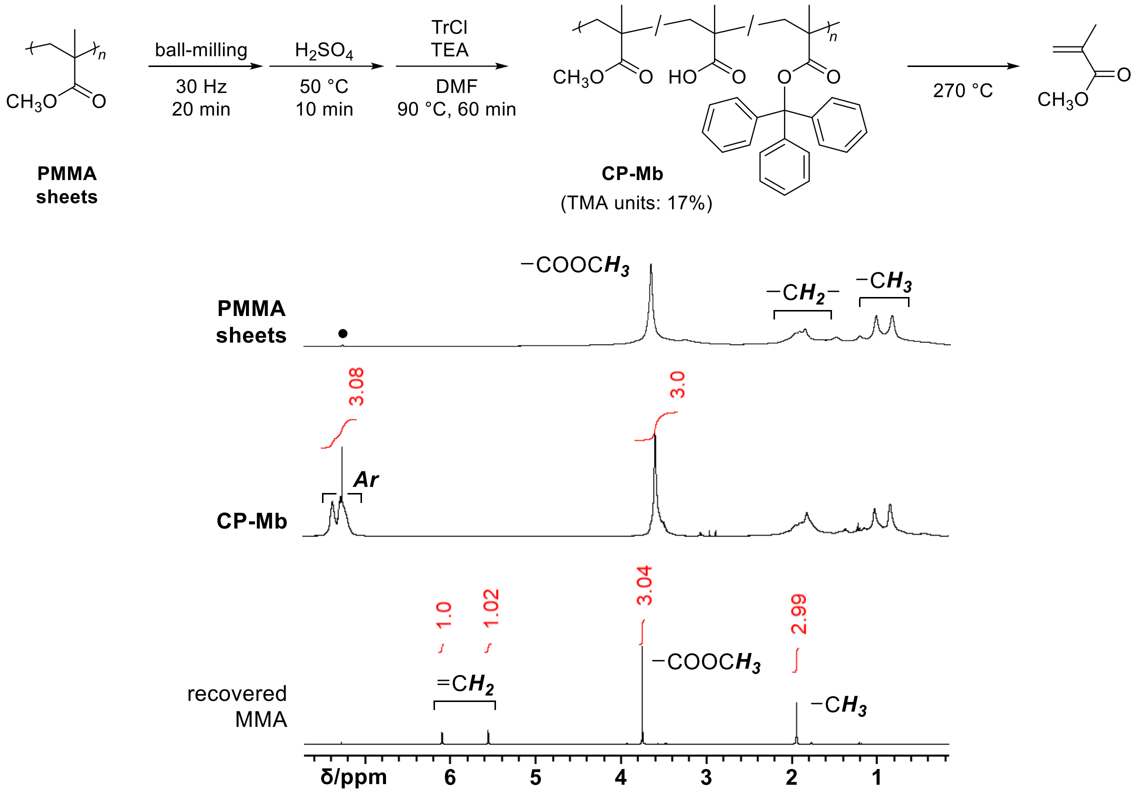


Figure S18. ^1H NMR spectra of **PMMA sheets**, **CP-Mb**, and recovered MMA (400 MHz, $CDCl_3$, 25 °C)

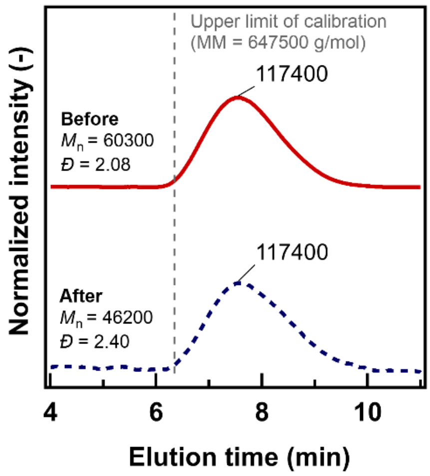


Figure S19. SEC profiles of PMMA sheets before and after ball-milling at 30 Hz for 20 min ($CHCl_3$, 40 °C, PMMA-standard)

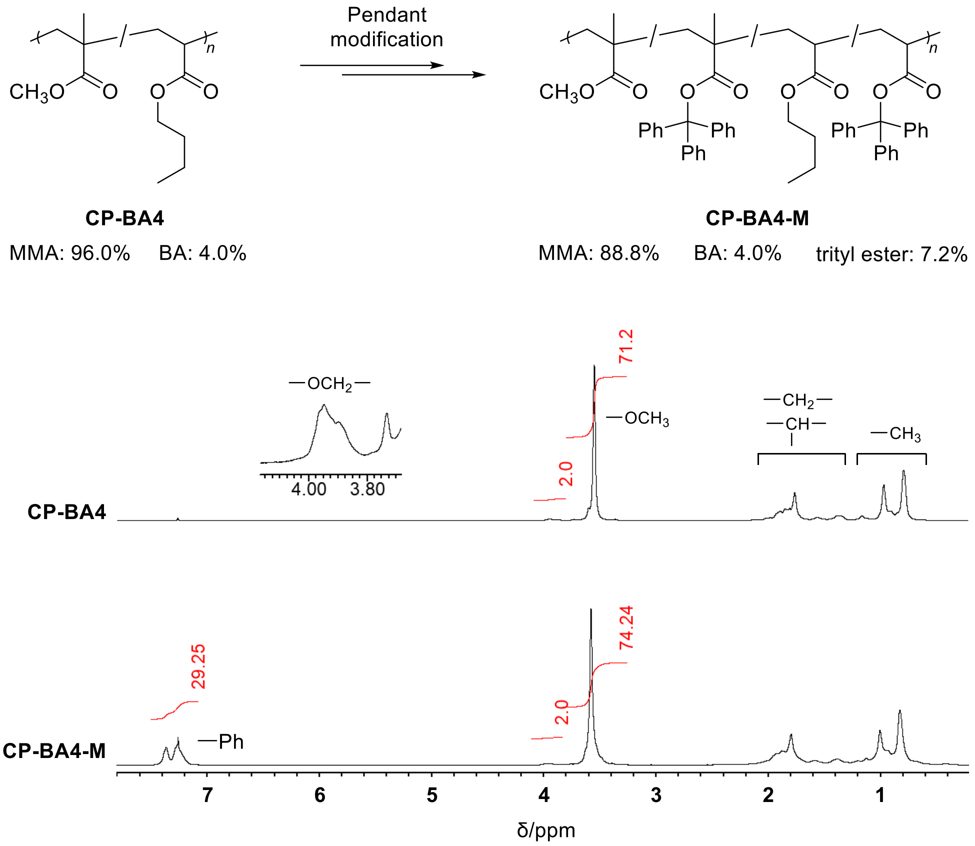


Figure S20. ^{1}H NMR spectra of **CP-BA4** and **CP-BA4-M** (400 MHz, 25 °C, $CDCl_3$). The modified polymer can contain trityl acrylate units, which are induced from BA units by reaction with trityl chloride following hydrolysis. The trityl ester incorporation ratio includes both TA and TMA units because TA units cannot be distinguished from TMA units in the ^{1}H NMR spectra. The possibility of TA units as the depolymerization initiation points is currently under investigation.

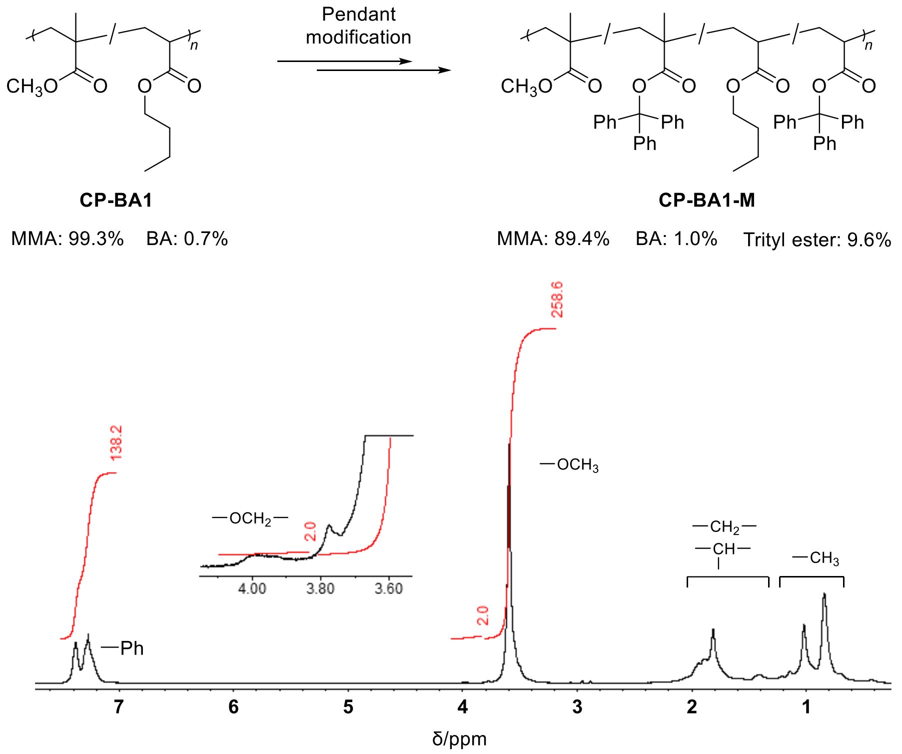


Figure S21. ^{1}H NMR spectrum of **CP-BA1-M** (400 MHz, 25 °C, CDCl$_3$).

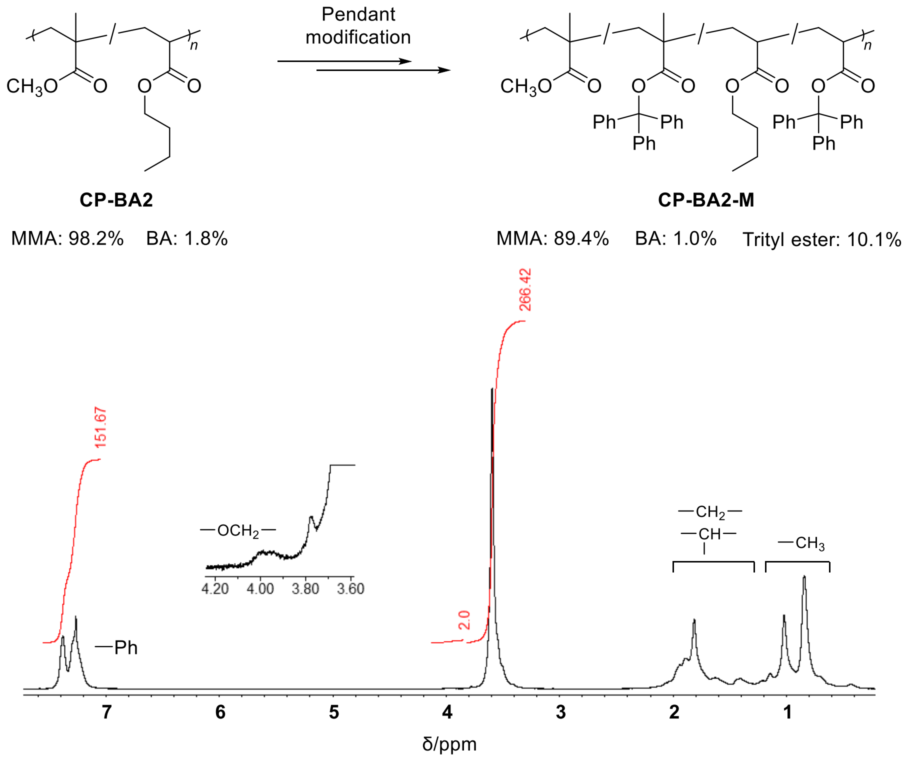


Figure S22. ^{1}H NMR spectrum of **CP-BA2-M** (400 MHz, 25 °C, CDCl$_3$).

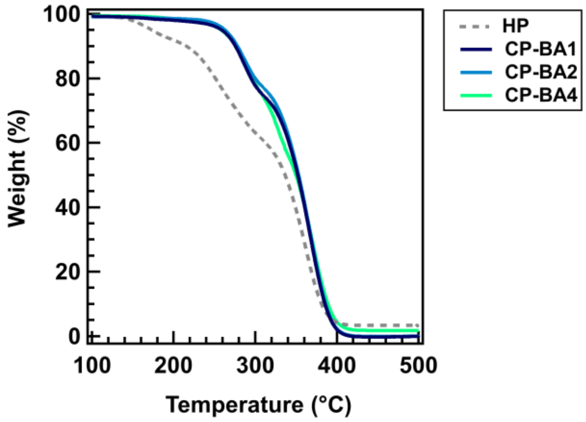


Figure S23. The TG curves for **CP-BA1**– **CP-BA4** at heating rate of 10 °C/min.

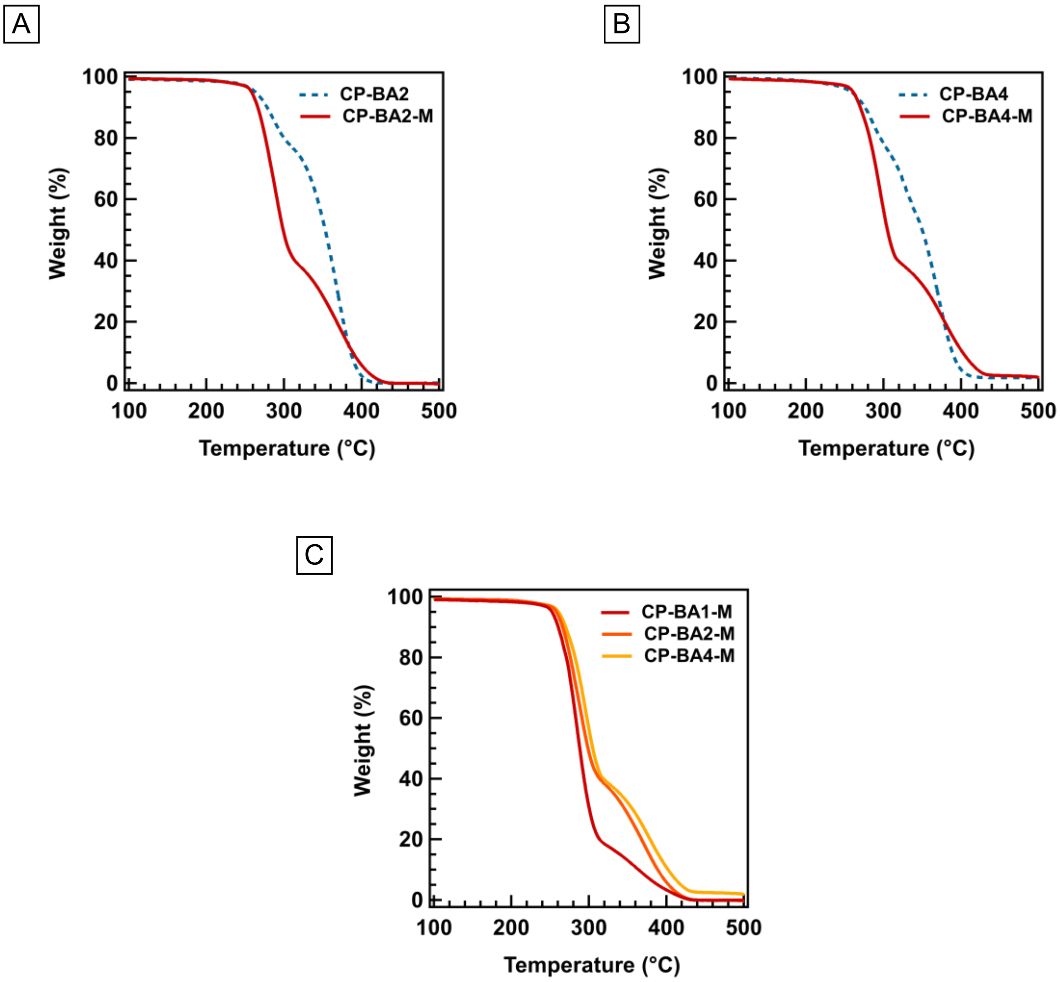


Figure S24. TG curves (heating ratio: 10 °C/min) for (A) **CP-BA2** and **CP-BA2-M**, (B) **CP-BA1** and **CP-BA1-M**, and (C) **CP-BA1-M**– **CP-BA4-M.**

Table S3. Used and calculated values in eq. (1) to (8).

	F_{MMA} [%]	F_{BA} [%]	M_1 [g/mol]	M_n [g/mol]	X_n [-]	Y_n [-]	F_T [%]	Z_n [-]	MEV [%]
HP	**100**	**0**	**100**	**340400**	**3404**	**3404**	**7.0**	**14.2**	**99.6**
CP-BA1	**99.3**	**0.7**	**100**	**80000**	**798**	**121**	**9.5**	**9.7**	**92.0**
CP-BA2	**98.2**	**1.8**	**101**	**86100**	**857**	**52**	**10.1**	**8.3**	**84.0**
CP-BA4	**95.9**	**4.1**	**101**	**46400**	**459**	**23**	**7.2**	**8.7**	**62.5**

The following values were used for the constants: M_{MMA} = 100 g/mol, M_{BA} = 128 g/mol.

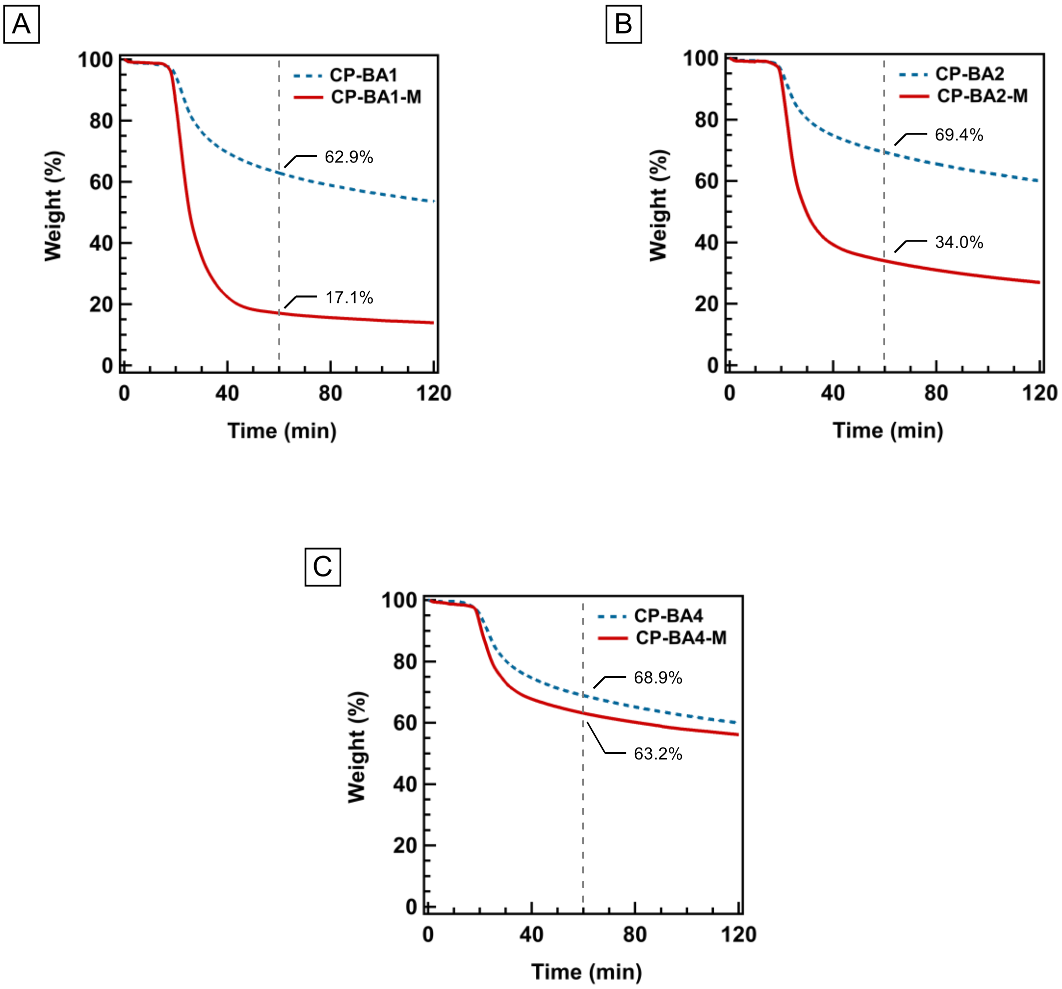


Figure S25. TG curves (constant temperature: 270 °C) for (A) **CP-BA1** and **CP-BA1-M**, (B) **CP-BA2** and **CP-BA2-M**, and (C) **CP-BA4** and **CP-BA4-M.**

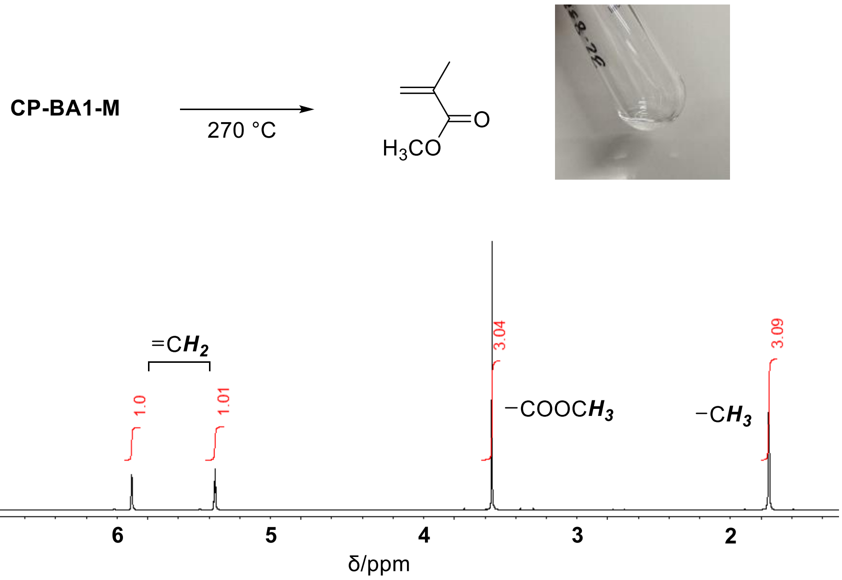


Figure S26. ^{1}H NMR spectra (400 MHz, 25 °C, $CDCl_3$) and photo of MMA recovered from **CP-BA1-M**.