

Supporting information

A platform for accelerated continuous-flow radical polymerization of acrylates and styrene with copper-wire threads

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Typical procedure for continuous-flow Cu(0)-mediated SET-LRP of MMA (Entry-MMA-1, Table 1): To a clean and dried 50 mL glass vial, equipped with a magnetic stirring bar, MMA (4 mL, 3.76 g, 37.55 mmol), methyl- α -bromophenylacetate (MBPA) (119 μ L, 75.6×10^{-2} mmol), CuBr₂ (8.4 mg, 37.55×10^{-3} mmol) and PMDETA (59 μ L, 28.26×10^{-2} mmol) was dissolved in IPA/DMF (9:1, v/v) (16 mL). The polymerization mixture was deoxygenated by purging with argon gas for 45 min at low temperature (in an ice bath). The reaction mixture was then taken in to a Hamilton gas-tight syringe under complete argon atmosphere. The reaction solution was infused with desired flow rate (e.g., 0.1 mL min⁻¹) to Cu-wire threaded tube reactor which was preheated at 40 °C in an oil bath. At the end of Cu wire reactor, THF (flow rate = 1 mL min⁻¹) was introduced to quench the polymerization and the outlet of reactor was connected to neutral alumina column to remove dissolved copper catalyst. A small portion of crude reaction mixture was used to examine the conversion by ¹H NMR in CDCl₃. The monomer conversion was determined by comparing the peak area of monomer proton at 5.55 ppm (1H, vinyl proton) and polymer proton at 3.62 ppm (3H, -OCH₃). Purified crude mixture was precipitated in hexane. The polymer was collected and dried under reduced pressure at 60 °C for 12h. Polymer was analysis by ¹H NMR and GPC. The $M_n(\text{theor})$ was calculated by following equation.

$$M_n(\text{theor}) = \frac{[\text{MMA}]_0}{[\text{MBPA}]_0} (X_{\text{MMA}} \cdot M_{\text{MMA}}) + M_{\text{MBPA}}$$

Where $[\text{MMA}]_0$ and $[\text{MBPA}]_0$ is initial concentration, M_{MMA} and M_{MBPA} is molecular mass of MMA and MBPA, respectively. X_{MMA} is monomer to polymer conversion obtained from NMR.

Typical procedure for continuous-flow Cu(0)-mediated SET-LRP of MA (Entry-MA-1, Table 2): To a clean and dried 50 mL glass vial, equipped with a magnetic stirring bar, MA (4 mL, 3.82 g, 44.37 mmol), methyl- α -bromophenylacetate (MBPA) (119 μ L, 75.6×10^{-2} mmol), CuBr₂ (4.2 mg, 18.80×10^{-3} mmol) and PMDETA (30 μ L, 14.13×10^{-2} mmol) was dissolved in IPA/DMF (9:1, v/v)

(16 mL). The polymerization mixture was deoxygenated by purging with argon gas for 45 min at low temperature (in an ice bath). The reaction mixture was then taken in to a Hamilton gas-tight syringe under complete argon atmosphere. The reaction solution was infused with desired flow rate (e.g., 0.1 mL min⁻¹) to Cu-wire threaded tube reactor which was preheated at 60 °C in an oil bath. At the end of Cu wire reactor, THF (flow rate = 1 mL min⁻¹) was introduced to quench the polymerization and the outlet of reactor was connected to neutral alumina column to remove dissolved copper catalyst. A small portion of crude reaction mixture was used to examine the conversion by ¹H NMR in CDCl₃. The monomer conversion was determined by comparing the peak area of monomer proton at 5.63 ppm (1H, vinyl proton) and polymer proton at 3.62 ppm (3H, -OCH₃). Purified crude mixture was precipitated in hexane. The polymer was collected and dried under reduced pressure at 60 °C for 12h. Polymer was analysis by ¹H NMR and GPC. The $M_n(\text{theor})$ was calculated by following equation.

$$M_n(\text{theor}) = \frac{[\text{MA}]_0}{[\text{MBPA}]_0} (X_{\text{MA}} \cdot M_{\text{MA}}) + M_{\text{MBPA}}$$

Where $[\text{MA}]_0$ and $[\text{MBPA}]_0$ is initial concentration, M_{MA} and M_{MBPA} is molecular mass of MA and MBPA, respectively. X_{MA} is monomer to polymer conversion obtained from NMR.

Typical procedure for continuous-flow Cu(0)-mediated SET-LRP of St (Entry-St-1, Table 3):

To a clean and dried 50 mL glass vial, equipped with a magnetic stirring bar, St (4 mL, 3.64 g, 34.95 mmol), methyl- α -bromophenylacetate (MBPA) (119 μ L, 75.6×10^{-2} mmol), CuBr₂ (4.2 mg, 18.80×10^{-3} mmol) and PMDETA (30 μ L, 14.13×10^{-2} mmol) was dissolved in IPA/DMF (9:1, v/v) (16 mL). The polymerization mixture was deoxygenated by purging with argon gas for 45 min at low temperature (in an ice bath). The reaction mixture was then taken in to a Hamilton gas-tight syringe under complete argon atmosphere. The reaction solution was infused with desired flow rate (e.g., 0.1 mL min⁻¹) to Cu-wire threaded tube reactor which was preheated at 60 °C in an oil bath. At the end of Cu wire reactor, THF (flow rate = 1 mL min⁻¹) was introduced to quench the polymerization and

the outlet of reactor was connected to neutral alumina column to remove dissolved copper catalyst. The monomer conversion was determined by comparing the peak area of monomer proton at 5.73 ppm or 6.67 ppm (1H, vinyl proton) and polymer proton at 6.88-7.25 ppm (3 aryl proton). Purified crude mixture was precipitated in hexane. A small portion of crude reaction mixture was used to examine the conversion by ^1H NMR in CDCl_3 . The polymer was collected and dried under reduced pressure at 60 °C for 12h. Polymer was analysis by ^1H NMR and GPC. The $M_n(\text{theor})$ was calculated by following equation.

$$M_n(\text{theor}) = \frac{[\text{St}]_0}{[\text{MBPA}]_0} (X_{\text{St}} \cdot M_{\text{St}}) + M_{\text{MBPA}}$$

Where $[\text{St}]_0$ and $[\text{MBPA}]_0$ is initial concentration, M_{St} and M_{MBPA} is molecular mass of St and MBPA, respectively. X_{St} is monomer to polymer conversion obtained from NMR.

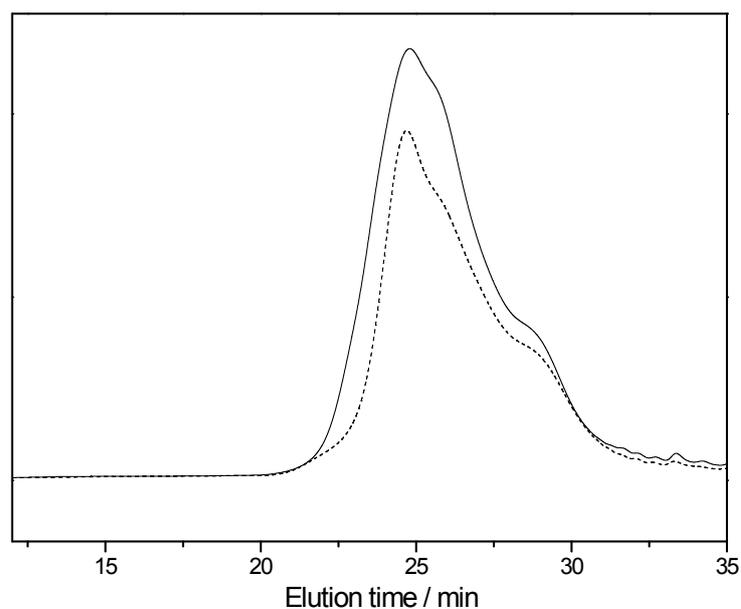


Figure S1: The GPC curves of PMMA obtained by polymerization in Cu-wire threaded PFA reactor using DMF (dotted line) and DMSO (solid line) solvent at flow rate 0.4 mL min^{-1} .

Table S1: Cu(0)-mediated polymerization of methyl methacrylate in a conventional batch system at 40°C .

Entry	[MMA]/[MBPA]/[CuBr ₂] /[PMDETA]	Solvent	Time (h)	$M_n(\text{GPC})^a$	MWDs ^a
PMMA-B-1h	100 : 1 : 0.05 : 0.36	IPA/DMF (9:1)	1	19,500	1.23
PMMA-B-2h	100 : 1 : 0.05 : 0.36	IPA/DMF (9:1)	2	74,100	1.59
PMMA-B-3h	100 : 1 : 0.05 : 0.36	IPA/DMF (9:1)	3	87,200	1.50
PMMA-B-3.5h	100 : 1 : 0.05 : 0.36	IPA/DMF (9:1)	3.5	51,300	1.76
PMMA-BD-1h	100 : 1 : 0.05 : 0.36	IPA/DMSO (9:1)	1	44,500 ^b	2.76
PMMA-BD-2h	100 : 1 : 0.05 : 0.36	IPA/DMSO (9:1)	2	38,600 ^b	2.94

^aMolecular weight (g mol^{-1}) and MWDs were determined by gel permeation chromatography (THF, 1 mL min^{-1} / 0.5 mL min^{-1} 40°C). ^bmolecular weight of peaks at high elution time (14.5 to 18.5 min).

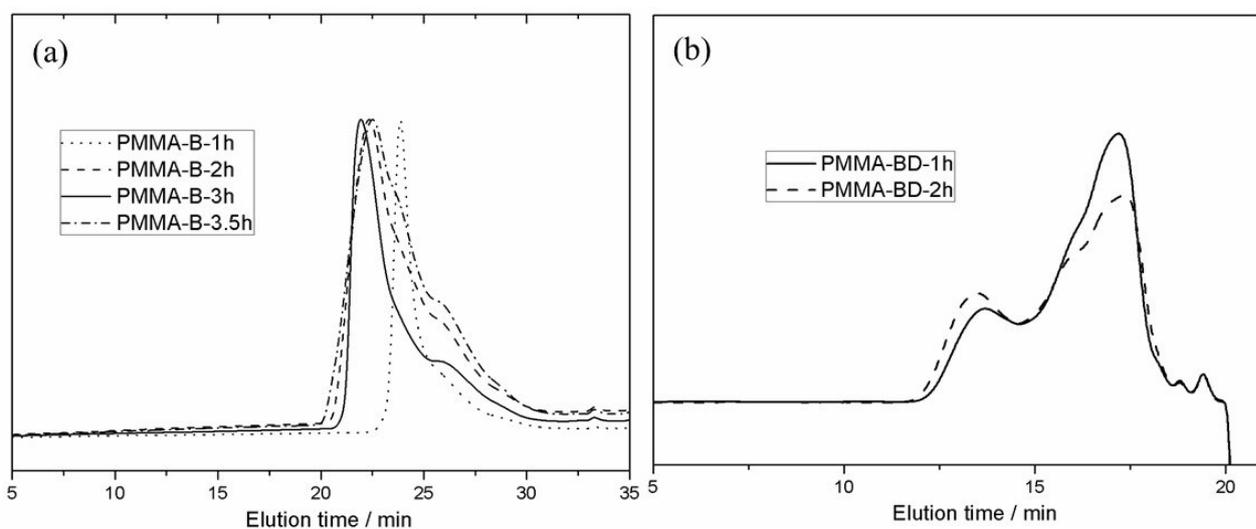


Figure S2: The GPC curves of PMMA obtained by polymerization in conventional batch system using (a) IPA/DMF (9:1, v/v), GPC (THF, 0.5 mL min⁻¹, 40 °C) and (b) IPA/DMSO (9:1, v/v) GPC (THF, 1.0 mL min⁻¹, 40 °C), Table S1.

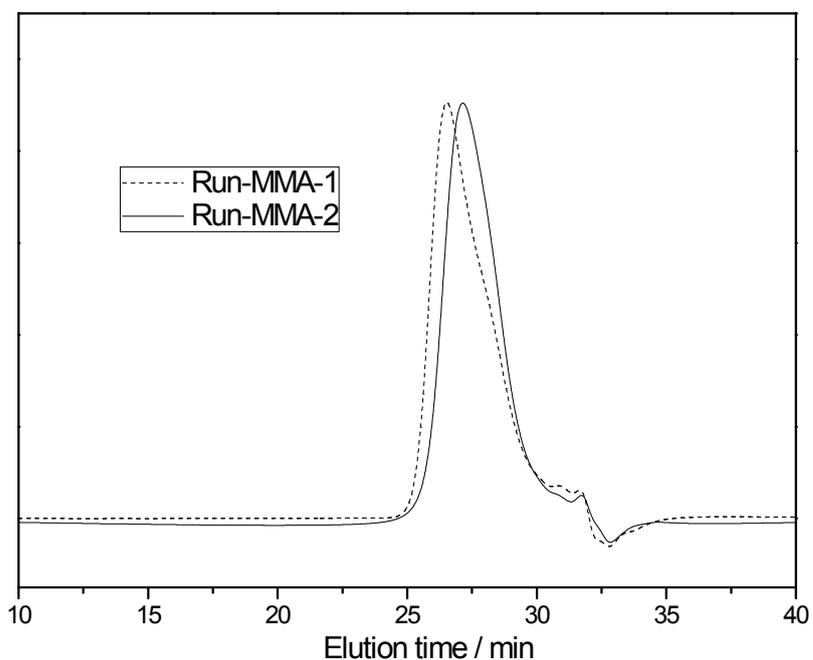


Figure S3: The GPC curves of PMMA of Run-MMA-1 and Run-MMA-2, Table 1, solvent: MMA = 1:4.

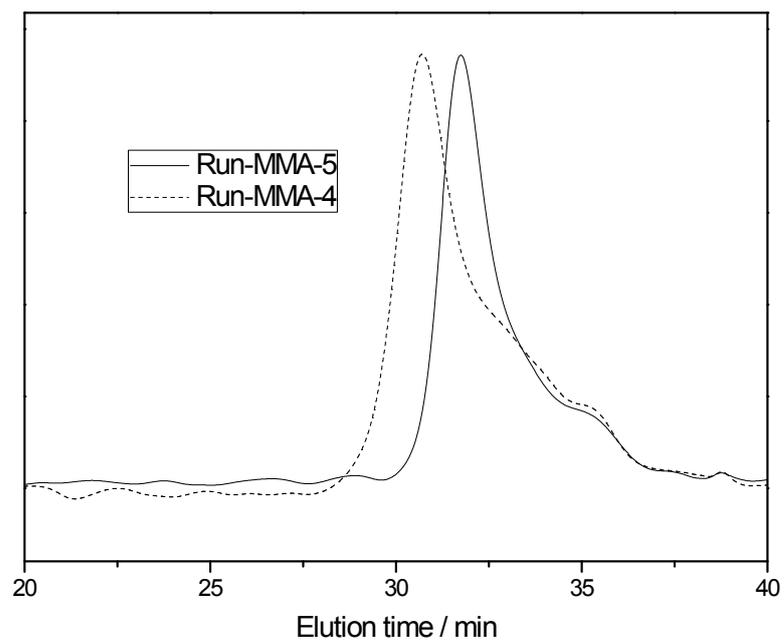


Figure S4: The GPC curves of PMMA of Run-MMA-4 and Run-MMA-5, Table 1, solvent: MMA = 1:2.

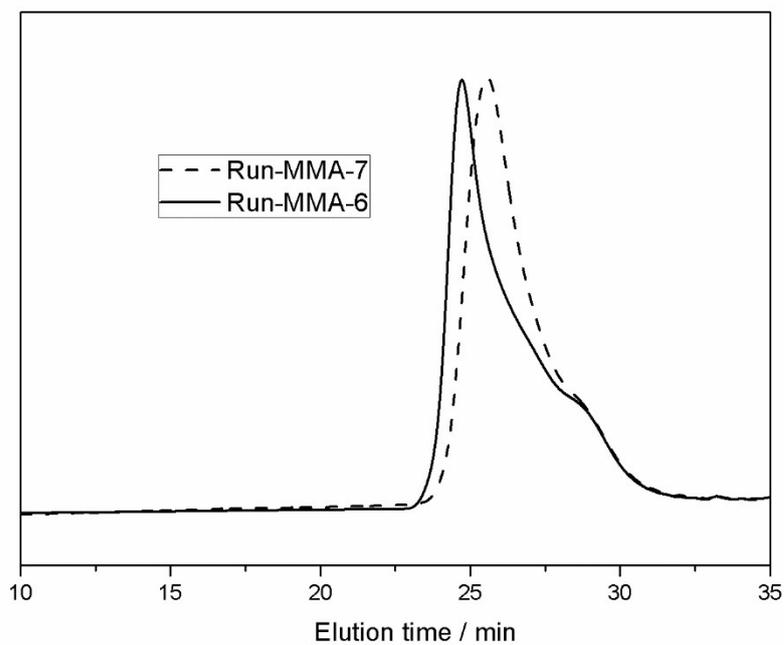


Figure S5: The GPC curves of PMMA of Run-MMA-6 and Run-MMA-7, Table 1, solvent: MMA = 1:1.

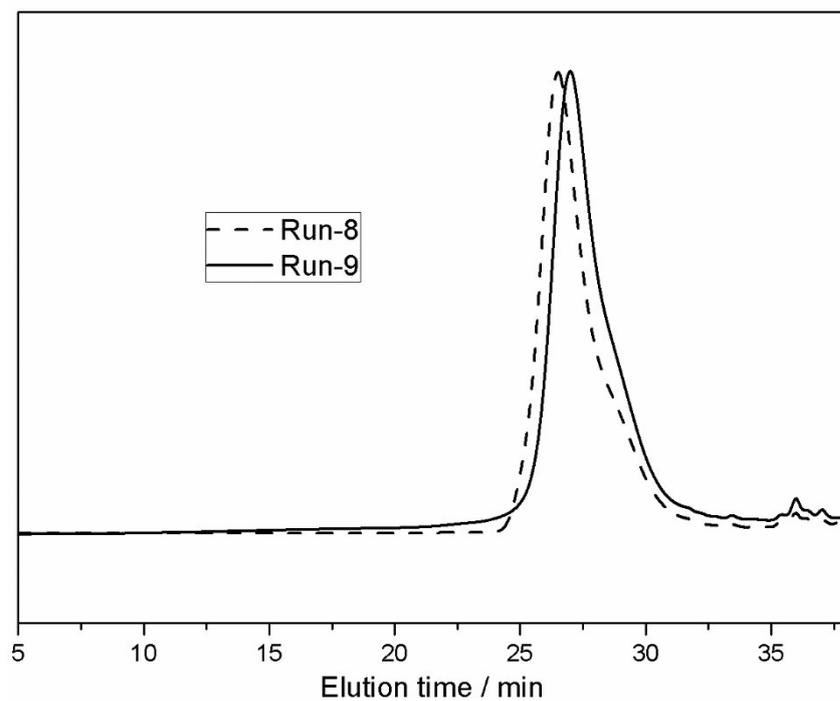


Figure S6: The GPC curves of PMMA of Run-MMA-8 and Run-MMA-9, Table 1, solvent: MMA = 1:1.

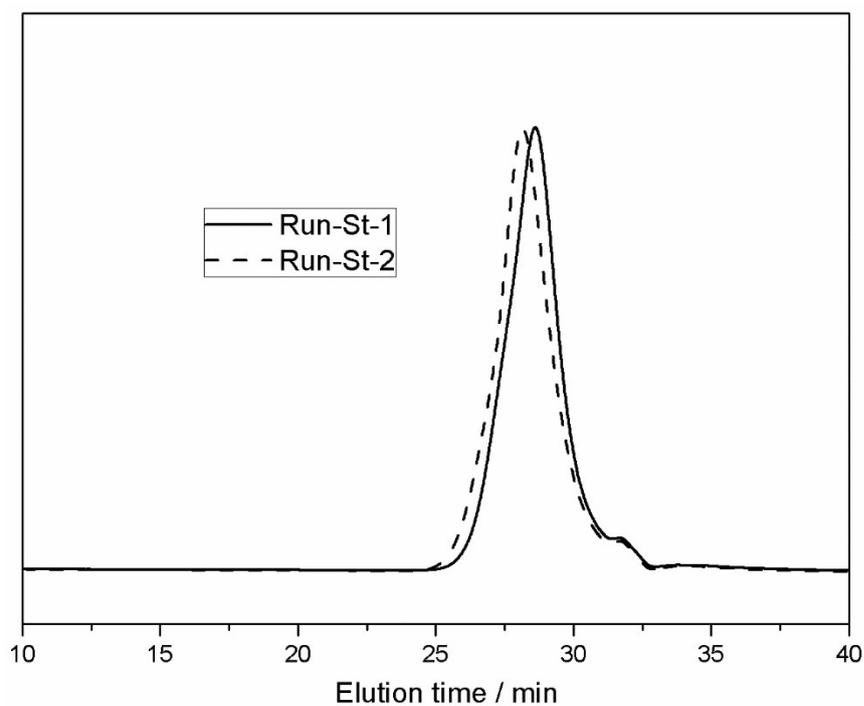


Figure S7: The GPC curves of PSt of Run-St-1 and Run-St-2, Table 3, solvent:St = 1:1.

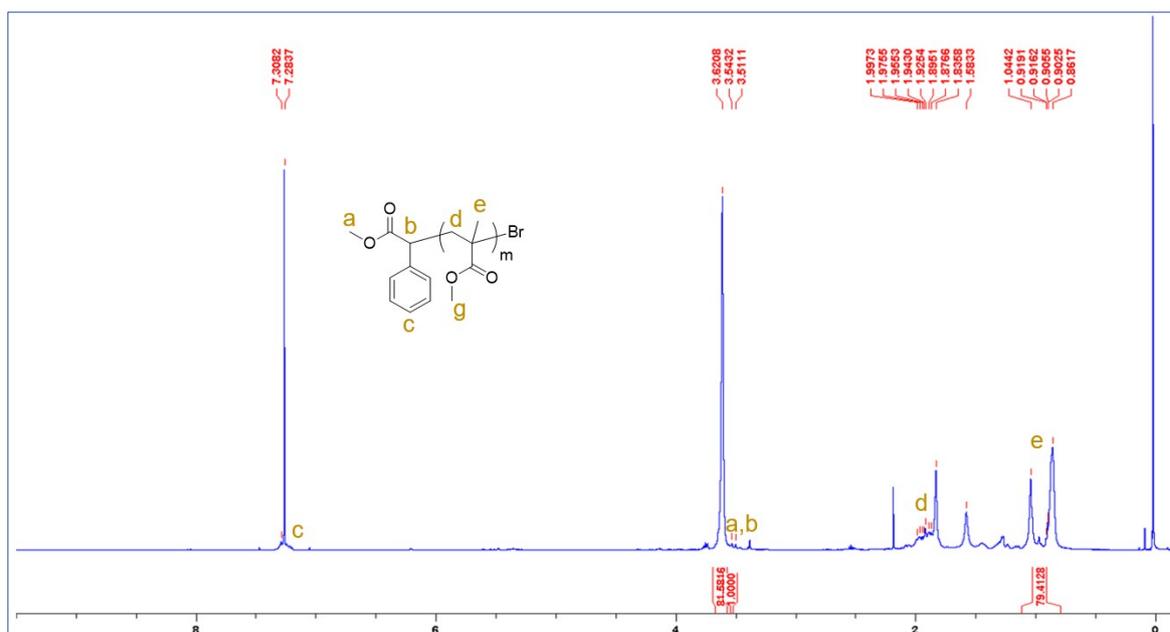


Figure S8: ¹H NMR spectra of PMMA confirming the presence of end group/livingness of polymerization.

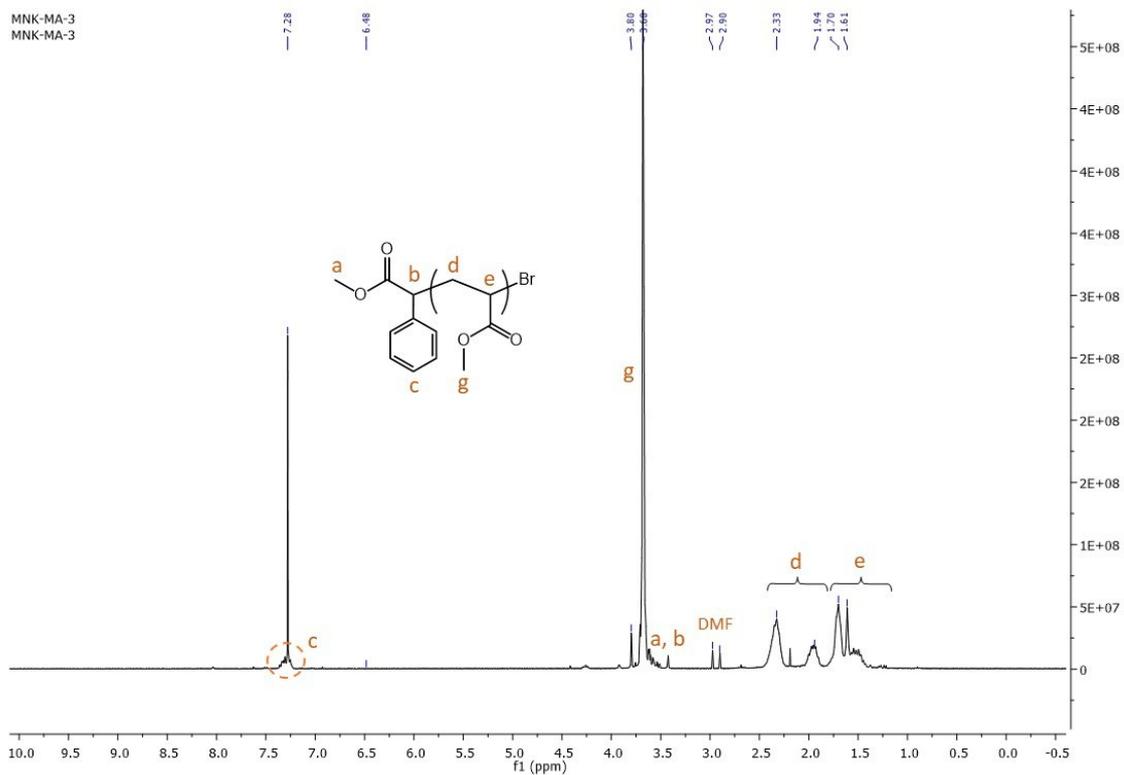


Figure S9: ^1H NMR spectra of PMA confirming the presence of end group/livingness of polymerization.

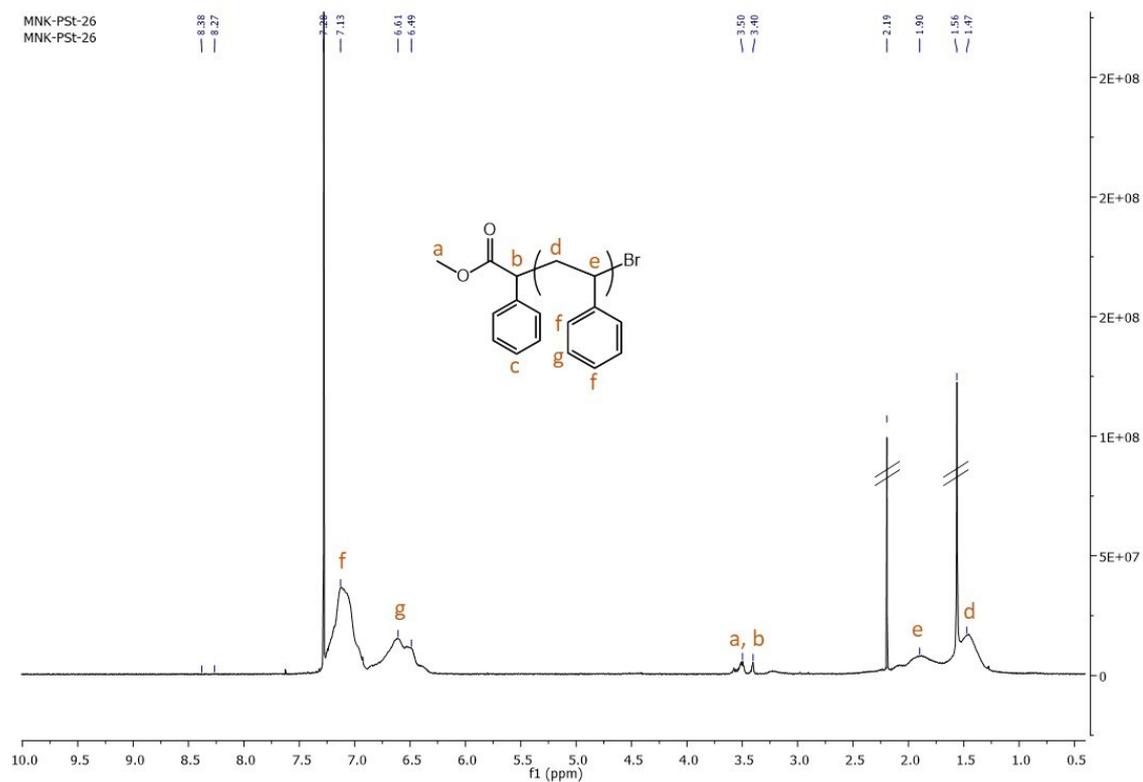


Figure S10: ^1H NMR spectra of PSt confirming the presence of end group/livingness of polymerization.

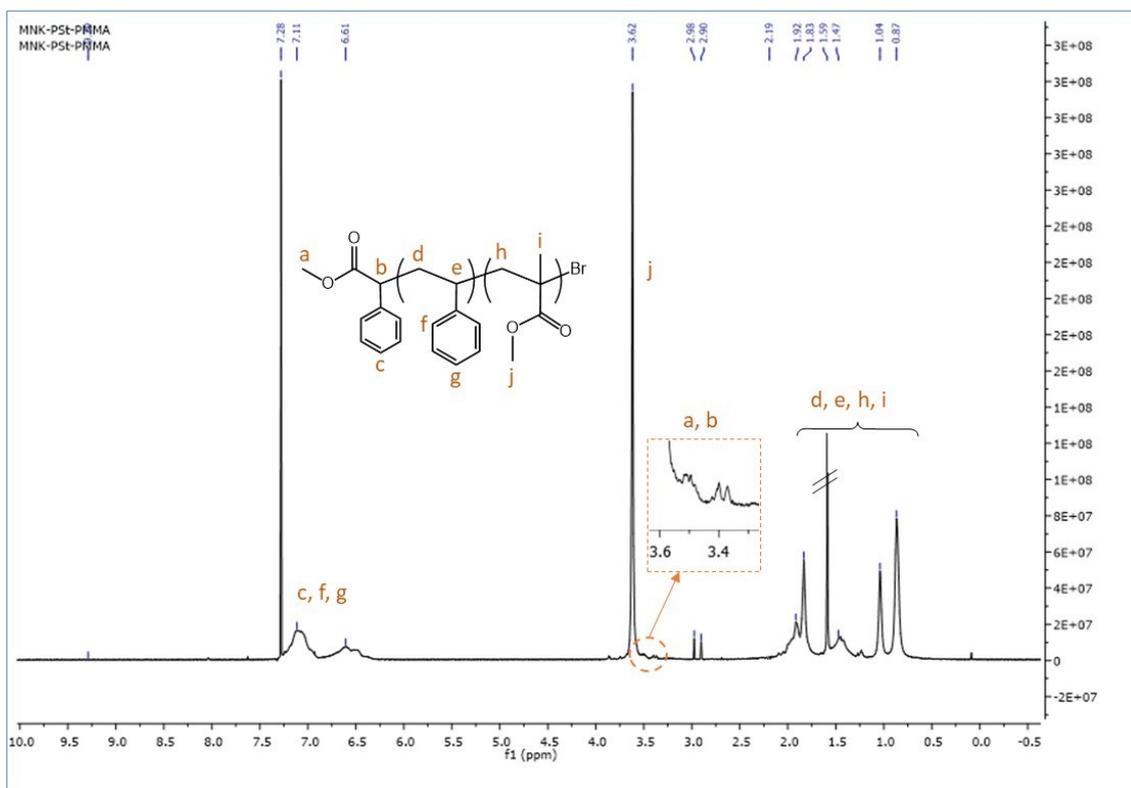


Figure S11: ^1H NMR spectra of PSt-*b*-PMMA obtained by heterochain extension of PSt (Run-St-3, Table 3) with MMA monomer.

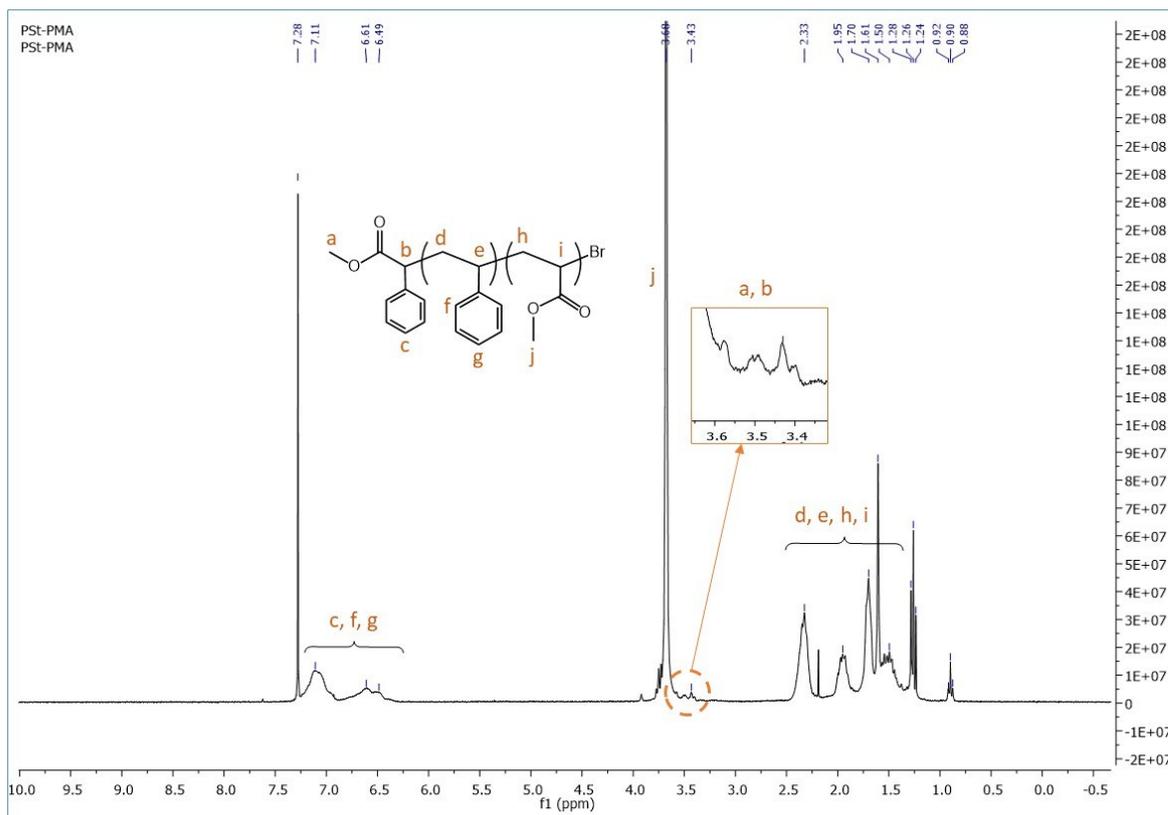


Figure S12: ^1H NMR spectra of PST-*b*-PMA obtained by heterochain extension of PSt (Run-St-3, Table 3) with MA monomer.