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Supporting Information

Synthesis of End-functionalized Poly(methyl methacrylate) by Organocatalyzed Group Transfer Polymerization Using Functional Silyl Ketene Acetals and α-Phenylacrylates

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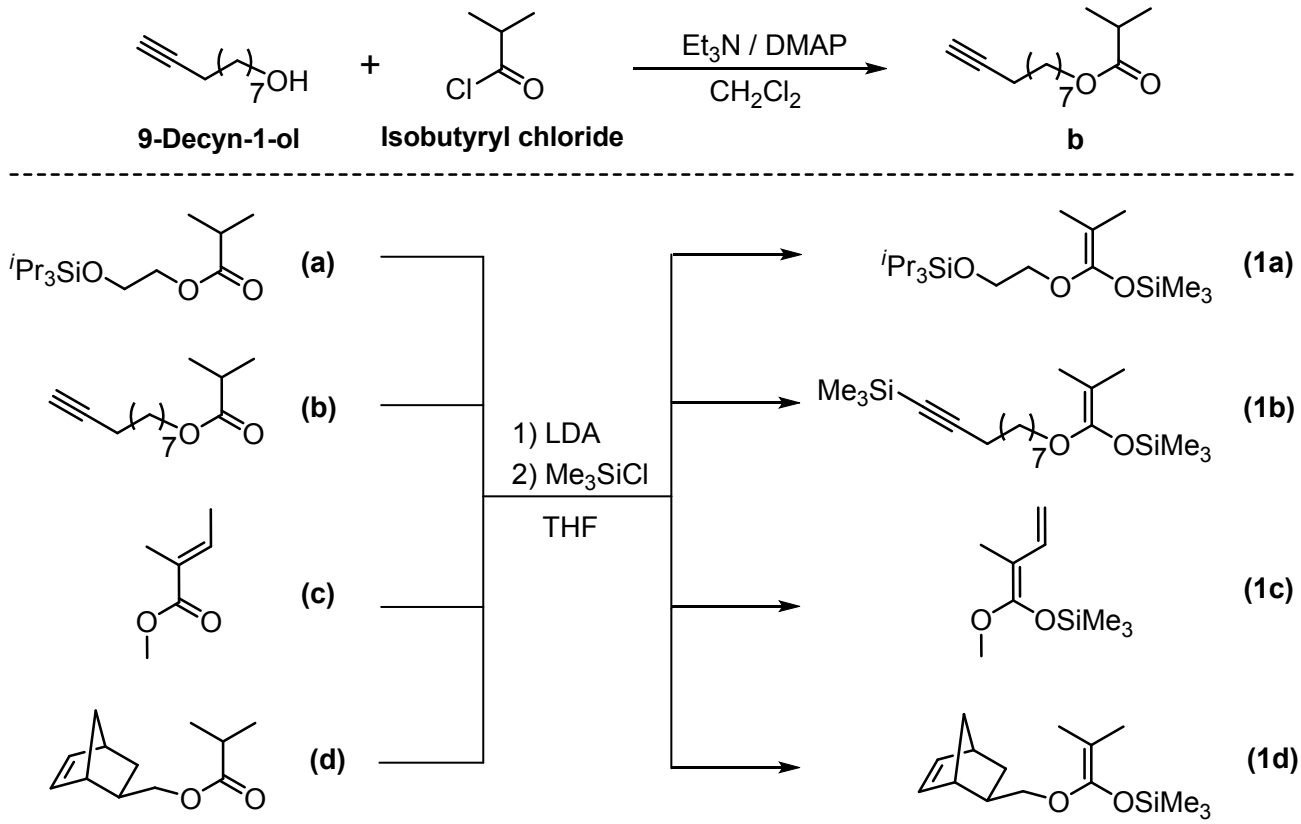
Scheme S1. Synthesis of functional trimethyl SKA initiators (**1a-1d**)



DMAP, 4-dimethylaminopyridine; LDA, lithium diisopropylamide; ^{i}Pr, *iso*-propyl group.

Experimental Section

2-Triisopropylsiloxyethyl isobutyrate (**a**) and (1*S*, 4*S*)-norborn-5-en-2-ylmethyl isobutyrate (**d**) were used as described in *Ref. 1*. Methyl tiglate (**c**) was commercially available from Tokyo Kasei Kogyo Co., Ltd.

Synthesis of dec-9-yn-1-yl isobutyrate (b). Isobutyryl chloride (4.75 mL, 45.0 mmol) was dropwise added to a solution of 9-decyn-1-ol (5.00 g, 32.4 mmol), triethylamine (5.40 mL, 36.0 mmol), and DMAP (190 mg, 1.56 mmol) in CH_2Cl_2 (100 mL) under a nitrogen atmosphere at 0 ºC. After 22 h of stirring at room temperature, the reaction mixture was filtered and washed with conc. aq. $NaHCO_3$ (50 mL × 3) and distilled water (50 mL × 3). The organic layer was then dried over Na_2SO_4. The

obtained crude product was purified by column chromatography using CH_2Cl_2/*n*-hexane = 2/3 (v/v) to give dec-9-yn-1-yl isobutyrate as a colorless liquid. Yield, 7.01 g (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 4.05 (t, 2H, *J* = 6.8 Hz, -COOC*H*$_2$-), 2.54 (sep, *J* = 7.0 Hz, 1H, $(CH_3)_2$C*H*-), 2.18 (dt, ^4J = 2.4 Hz and ^3J = 7.0 Hz, 2H, CH≡CC*H*$_2$-), 1.94 (t, *J* = 2.4 Hz, 1H, C*H*≡C-), 1.62 (m, 2H, -$COOCH_2$C*H*$_2$-), 1.53 (m, 2H, ≡CCH_2C*H*$_2$-), 1.46-1.24 (m, 8H, -$COOCH_2CH_2$(C*H*$_2$)$_4$-), 1.16 (d, *J* = 7.0 Hz, 6H, (C*H*$_3$)$_2$CH-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 177.1 (-*C*OO-), 84.6 (HC≡*C*-), 68.1 (H*C*≡C-), 64.2 (-COO*C*H$_2$-), 34.0 ((CH$_3$)$_2$*C*H-), 29.0-28.3 (-$COOCH_2$*C*H_2CH_2(*C*H$_2$)$_4$-), 25.8 (-$COOCH_2CH_2$*C*H$_2$-), 18.9 ((*C*H$_3$)$_2$CH-), 18.3 (CH≡C*C*H$_2$-). Anal. Calcd for $C_{14}H_{24}O_2$ (224.33): C, 74.95; H, 10.78. Found: C, 74.97; H, 10.94.

Synthesis of 1-(2-triisopropylsiloxyethoxy)-1-trimethylsiloxy-2-methyl-1-propene (1a). Method A: *n*-BuLi (18.1 mL, 1.62 mol L^{-1} in *n*-hexane, 29.1 mmol) was dropwise added to a solution of DIPA (5.31 mL, 29.1 mmol) in THF (40 mL) at 0 °C under an argon atmosphere, then the mixture was stirred for 30 min to produce lithium diisopropylamide (LDA). 2-Triisopropylsiloxyethyl isobutyrate (8.00 g, 27.7 mmol) was added to the LDA solution and the mixture was stirred for 30 min at 0 °C. Me_3SiCl (5.05 mL, 30.5 mmol) was then added to the reaction mixture at 0 °C. After stirring for 5 h at room temperature, the reaction mixture was directly distilled from the reaction container under reduced pressure to give **1a** as a colorless liquid. Yield, 7.10 g (71 %). b.p., 117 °C / 0.08 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.85 (t, *J* = 5.2 Hz, 2H, =C-OC*H*$_2$-), 3.78 (t, *J* = 5.2 Hz, 2H, -C*H*$_2$-OSi-), 1.59 (s, 3H, =C(^{Z}CH$_3$)(^{E}C*H*$_3$)), 1.52 (s, 3H, =C(^{Z}C*H*$_3$)(^{E}CH$_3$)), 1.02−1.18 (m, 21H, -OSi[C*H*(C*H*$_3$)$_2$]$_3$), 0.20 (s, 9H, -OSi(C*H*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 148.3, 91.9, 70.3, 62.3, 18.1, 17.1, 16.4, 12.1, 0.2.

Synthesis of 1-(10-trimethylsilyldec-9-yn-1-yloxy)-1-trimethylsiloxy-2-methyl-1-propene (1b). Method A was applied to *n*-BuLi (20.9 mL, 1.62 mol L^{-1} in *n*-hexane, 33.8 mmol), DIPA (4.74 mL, 33.8 mmol), THF (50 mL), 9-yn-1-yl isobutyrate (3.58 g, 16.0 mmol), and Me_3SiCl (7.60 mL, 60.0 mmol) to give **1b** as a pale yellow liquid. Yield, 2.87 g (49 %). b.p., 115 °C / 0.06 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.68 (t, *J* = 4.0 Hz, 2H, -OCH_2-), 2.21 (t, *J* = 7.0 Hz, 2H, -C≡CCH_2), 1.54 (s, 3H, =C(^{E}CH_3)(^{Z}CH_3)), 1.52 (s, 3H, =C(^{E}CH_3)(^{Z}CH_3)), 1.68-1.24 (m, 12H, -OCH_2(CH_2)$_6$-), 0.20 (s, 9H, -OSi(CH_3)$_3$), 0.15 (s, 9H, -C≡C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 148.44 (-*C*=C$(CH_3)_2$), 107.85 (≡*C*-Si$(CH_3)_3$), 91.56 (=*C*$(CH_3)_2$), 84.40 (-*C*≡CSi$(CH_3)_3$), 69.13 (-O*C*H_2-), 29.62, 29.45, 29.17, 28.89, 28.75, 26.23, 19.99 (≡C*C*H_2-), 17.10 (^{Z}CH_3C(^{E}*C*H_3)=), 16.50 (^{Z}*C*H_3C(^{E}CH_3)=), 0.34 (-OSi (*C*H_3)$_3$), 0.22 (≡CSi(*C*H_3)$_3$).

Synthesis of 1-methoxy-1-trimethylsiloxy-2-methyl-1,3-butadiene (1c). Method A was applied to *n*-BuLi (42.2 mL, 1.62 mol L^{-1} in *n*-hexane, 67.5 mmol), DIPA (9.48 mL, 67.5 mmol), THF (70 mL), methyl tiglate (7.00 g, 61.3 mmol), and Me_3SiCl (8.60 mL, 67.5 mmol) to give **1b** as a colorless liquid. Yield, 4.23 g (37 %). b.p., 55 °C / 7.50 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.71 (ddd, ^{3}*J-cis* = 10 Hz, ^{3}*J-trans* = 17.0 Hz, ^{3}*J-cis* = 10 Hz), 4.85 (dd, ^{3}*J-trans* = 17.0 Hz, ^{2}*J* =1.8 Hz), 4.78 (dd, ^{3}*J-cis* = 10 Hz, ^{2}*J* = 1.8 Hz, 4-H), 3.57 (s, 3H, -OCH_3), 1.63 (s, 3H, =CCH_3), 0.25 (s, 9H, -C≡C(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.32 (-*C*=CCH_3CH=CH_2), 134.83 (-*C*H=CH_2), 107.45 (-CH=*C*H_2), 97.43 (-C=*C*CH_3CH=CH_2), 57.62 (-O*C*H_3), 18.12 (-C=C*C*H_3CH=CH_2), 0.20 (-OSi (*C*H_3)$_3$).

Synthesis of 1-((1*S*, 4*S*)-norborn-5-en-2-ylmethoxy)-1-trimethylsiloxy-2-metylprop-1-ene (1d). Method A was applied to *n*-BuLi (11.5 mL, 1.64 mol L^{-1} in *n*-hexane, 18.9 mmol), DIPA (2.66 mL,

18.9 mmol), THF (20.0 mL), (1*S*,4*S*)-norborn-5-en-2-ylmethyl isobutyrate (3.50 g, 18.0 mmol), and Me_3SiCl (2.53 mL, 19.8 mmol) to give **1d** as a yellow liquid. Yield, 3.52 g (73 %). b.p.,77 °C / 0.08 mmHg. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.00-6.17 (m, 2H, -C*H*=C*H*-), 3.75 (dd, *J* = 6.0 Hz, *J* = 9.6 Hz, 1H, -OCH_2-), 3.65 (dd, *J* = 8.8 Hz, *J* = 9.6 Hz, 1H, -OCH_2-), 2.80 (br s, 2H, -C*H*-CH=CH-C*H*-), 1.70 (m, 1H, -CH-C*H*-CH_2-), 1.14-1.66 (m, 4H, bridgehead and -CH-CH-CH_2-), 1.60 (s, 3H, =C(^{E}CH_3)(^{Z}CH_3)), 1.52 (s, 3H, =C(^{E}CH_3)(^{Z}CH_3)), 0.20 (s, 9H, -OSi(CH_3)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 148.29 (-*C*=C$(CH_3)_2$), 136.65, 136.48, 91.47 (=*C*$(CH_3)_2$), 73.36 (-O*C*H_2-), 44.99, 43.81, 41.55, 33.60, 29.78, 16.98 (^{Z}CH_3C(^{E}*C*H_3)=), 16.38 (^{Z}*C*H_3C(^{E}CH_3)=), 0.09 (-OSi(*C*H_3)$_3$).

Reference

(1) Takada, K.; Fuchise, K.; Kubota, N.; Ito, T.; Chen, Y.G.; Satoh, T.; Kakuchi, T.; *Macromolecules* **2014**, *47*, 5514−5525.

(2) Rozkiewicz, D. I.; Jańczewski, D.; Verboom, W.; Ravoo, B. J.; Reinhoudt, D. N. *Angew. Chem. Int. Ed.* **2006**, *45*, 5292−5296.

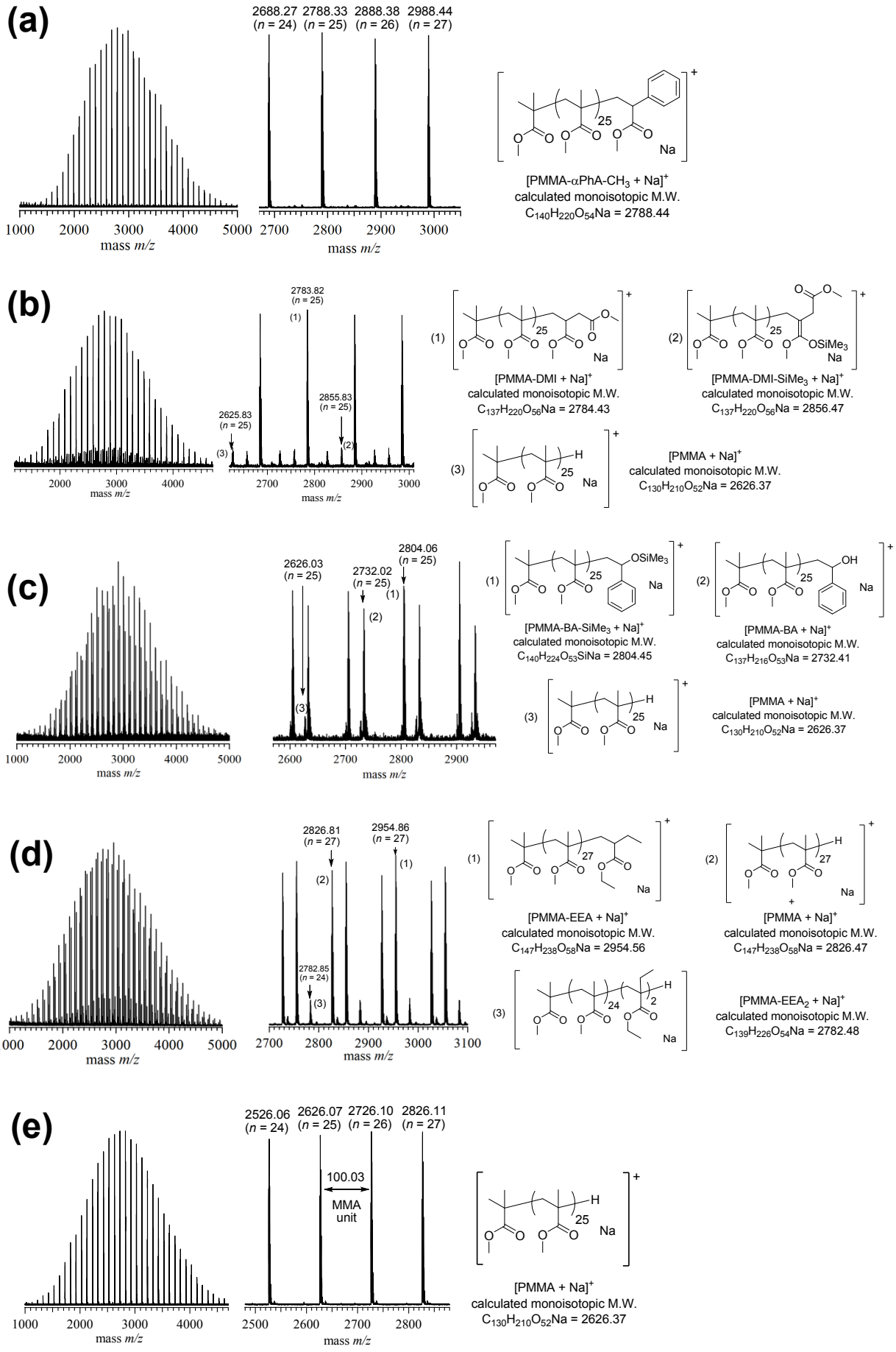


Figure S1. MALDI-TOF MS spectra of PMMAs terminated by (a) αPhA-Me, (b) DMI, (c) BA, (d) EEA, and (e) DMMAm.

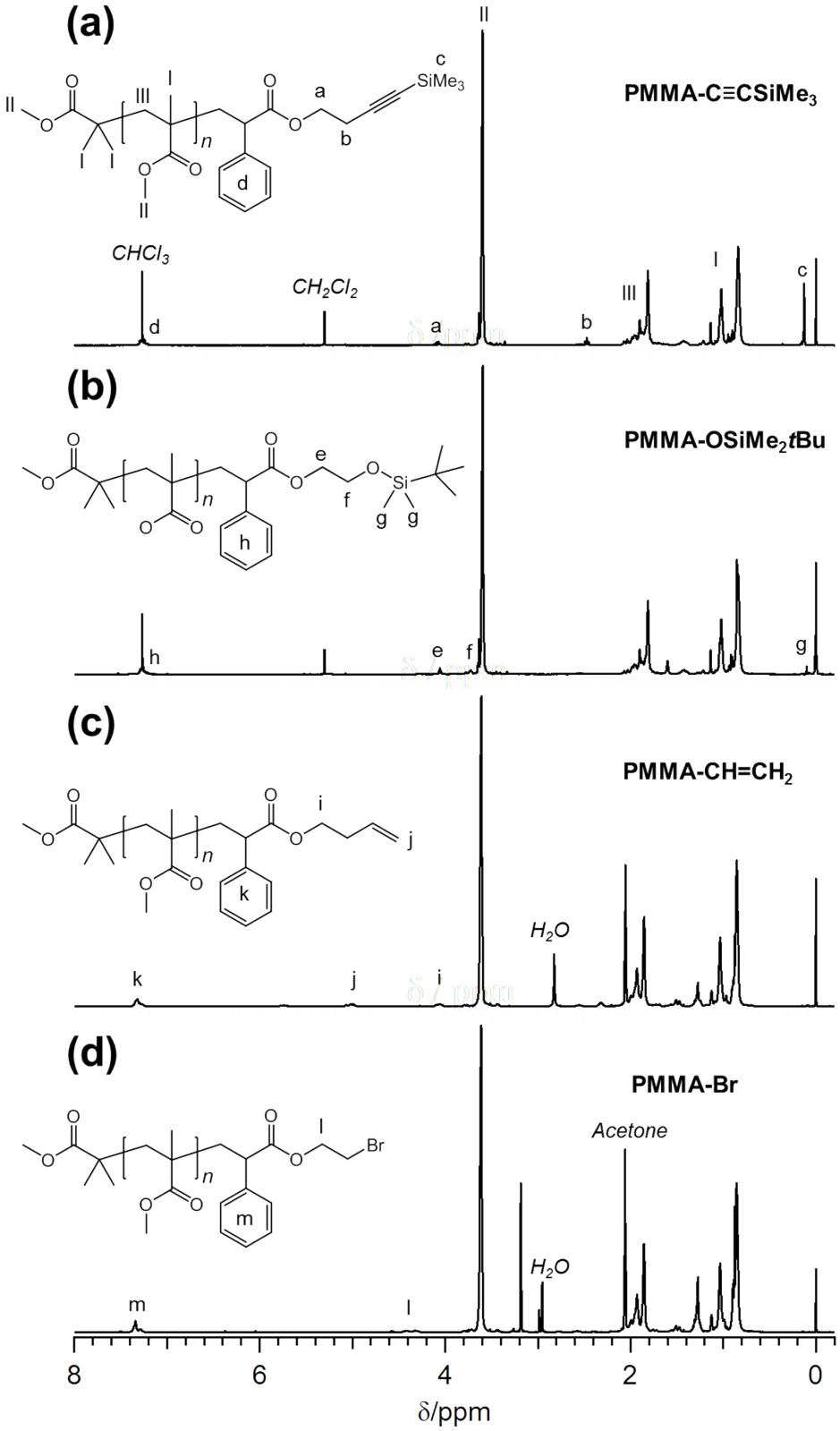


Figure S2. ^{1}H NMR spectra of (a) PMMA-C≡CSiMe$_3$ (Run 26, $M_{n,SEC}$ = 3,460; M_w/M_n = 1.07) in $CDCl_3$, (b) PMMA-OSiMe$_2$*t*Bu (Run 27, $M_{n,SEC}$ = 3,250; M_w/M_n = 1.06) in $CDCl_3$, (c) PMMA-CH=CH$_2$ (Run 28, $M_{n,SEC}$ = 3,730; M_w/M_n = 1.07) in acetone-d_6, and (d) PMMA-Br (Run 29, $M_{n,SEC}$ = 3,690; M_w/M_n = 1.07) in acetone-d_6.