Supporting Information

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

Yougen Chen,§* Kenji Takada,‡ Naoya Kubota,‡ Ofosu-Twum Eric,§ Takahiro Ito,‡ Takuya Isono,† Toshifumi Satoh,†,‡ and Toyoji Kakuchi§,†,‡,*

§ Frontier Chemistry Center, † Division of Biotechnology and Macromolecular Chemistry, and ‡ Graduate School of Chemical Sciences and Engineering, Faculty of Engineering, Hokkaido University, Sapporo, 060-8628, Japan

CORRESPONDING AUTHOR FOOTNOTE

Tel & Fax: +81-11-706-6602. E-mail: chen@poly-bm.eng.hokudai.ac.jp and kakuchi@poly-bm.eng.hokudai.ac.jp

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

Experimental Section

2-Triisopropylsiloxyethyl isobutyrate (a) and (1S, 4S)-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 CH₂Cl₂ (100 mL) under a nitrogen atmosphere at 0 °C. After 22 h of stirring at room temperature, the reaction mixture was filtered and washed with conc. aq. NaHCO₃ (50 mL × 3) and distilled water (50 mL × 3). The organic layer was then dried over Na₂SO₄. The
obtained crude product was purified by column chromatography using CH$_2$Cl$_2$/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$_3$): $\delta$ (ppm) 4.05 (t, 2H, $J = 6.8$ Hz, -COOCH$_2$-), 2.54 (sep, $J = 7.0$ Hz, 1H, (CH$_3$)$_2$CH-), 2.18 (dt, $^4J = 2.4$ Hz and $^3J = 7.0$ Hz, 2H, CH≡CH$_2$-), 1.94 (t, $J = 2.4$ Hz, 1H, CH=CH-), 1.62 (m, 2H, -COOCH$_2$CH$_2$-), 1.53 (m, 2H, CH=CCH$_2$-), 1.46-1.24 (m, 8H, -COOCH$_2$CH$_2$(CH$_3$)$_2$-), 1.16 (d, $J = 7.0$ Hz, 6H, (CH$_3$)$_2$CH-). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (ppm) 177.1 (-COO-), 84.6 (HC≡C-), 68.1 (HC≡C-), 64.2 (-COOCH$_2$-), 34.0 ((CH$_3$)$_2$CH-), 29.0-28.3 (-COOCH$_2$CH$_2$CH$_2$(CH$_3$)$_4$-), 25.8 (-COOCH$_2$CH$_2$CH$_2$-), 18.9 ((CH$_3$)$_2$CH-), 18.3 (CH≡CCH$_2$-). 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$_3$SiCl (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$_3$): $\delta$ (ppm) 3.85 (t, $J = 5.2$ Hz, 2H, =C-CH$_2$-), 3.78 (t, $J = 5.2$ Hz, 2H, -OCH$_2$-), 1.59 (s, 3H, =C($^2$CH($^2$CH$_3$)), 1.52 (s, 3H, =C($^2$CH($^2$CH$_3$))(CH$_3$)), 1.02–1.18 (m, 21H, -OSi[(CH($^2$CH$_3$)$_2$)$_3$], 0.20 (s, 9H, -OSi(CH$_3$)$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ (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\(_3\)SiCl (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, -OC\(_2\)H\(_2\)-), 2.21 (t, \(J = 7.0\) Hz, 2H, -C≡CH\(_2\)), 1.54 (s, 3H, =C(ECH\(_3\))(ZC\(_3\))), 1.52 (s, 3H, =C(ECH\(_3\))(ZCH\(_3\))), 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=CH(CH\(_3\))\(_2\)), 107.85 (-C≡C(CH\(_3\))\(_3\)), 91.56 (=C(CH\(_3\))\(_2\)), 84.40 (-C≡CSi(CH\(_3\))\(_3\)), 69.13 (-OCH\(_2\)-), 29.62, 29.45, 29.17, 28.89, 28.75, 26.23, 19.99 (=CCH\(_2\)-), 17.10 (\(\ell\)CH\(_3\)(\(\ell\)CH\(_3\))=), 16.50 (\(\ell\)CH\(_3\)(\(\ell\)CH\(_3\))=), 0.34 (-OSi (CH\(_3\))\(_3\)), 0.22 (=CSi(CH\(_3\))\(_3\)).

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\(_3\)SiCl (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, \(\tilde{J}\)-cis = 10 Hz, \(\tilde{J}\)-trans = 17.0 Hz, \(\tilde{J}\)-cis = 10 Hz), 4.85 (dd, \(\tilde{J}\)-trans = 17.0 Hz, \(\tilde{J}\)=1.8 Hz), 4.78 (dd, \(\tilde{J}\)-cis = 10 Hz, \(\tilde{J}\)=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\(_3\)CH=CH\(_2\)), 134.83 (-CH=CH\(_2\)), 107.45 (-CH=CH\(_2\)), 97.43 (-C=CCH\(_3\)CH=CH\(_2\)), 57.62 (-OCH\(_3\)), 18.12 (-C=CCH\(_3\)CH=CH\(_2\)), 0.20 (-OSi (CH\(_3\))\(_3\)).

Synthesis of 1-((1S, 4S)-norborn-5-en-2-ylmethoxy)-1-trimethylsiloxy-2-methylprop-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), (1S,4S)-norborn-5-en-2-ylmethyl isobutyrate (3.50 g, 18.0 mmol), and Me₃SiCl (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. ^1H NMR (400 MHz, CDCl₃); δ (ppm) 6.00-6.17 (m, 2H, -CH=CH-), 3.75 (dd, J = 6.0 Hz, J = 9.6 Hz, 1H, -OCH₂-), 3.65 (dd, J = 8.8 Hz, J = 9.6 Hz, 1H, -OCH₂-), 2.80 (br s, 2H, -CH=CH-CH₂-), 1.70 (m, 1H, -CH-CH-CH₂-), 1.14-1.66 (m, 4H, bridgehead and -CH-CH-CH₂-), 1.60 (s, 3H, =C(²CH₃)(²CH₃)), 1.52 (s, 3H, =C(³CH₃)(³CH₃)), 0.20 (s, 9H, -OSi(CH₃)₃). ^13C NMR (100 MHz, CDCl₃); δ (ppm) 148.29 (-C=C(CH₃)₂), 136.65, 136.48, 91.47 (=C(CH₃)₂), 73.36 (-OCH₂-), 44.99, 43.81, 41.55, 33.60, 29.78, 16.98 (²CH₃C(²CH₃)=), 16.38 (³CH₂C(³CH₃)=), 0.09 (-OSi(CH₃)₃).

Reference


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$_2$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-$d_6$. 
