Supporting Information

$B(C_6F_5)_3$-catalyzed Group Transfer Polymerization of *N,N*-Disubstituted Acrylamide Using Hydrosilane: Effect of Hydrosilane and Monomer Structures, Polymerization Mechanism, and Synthesis of α-End-functionalized Polyacrylamides

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1. Experimental section

Materials. Dichloromethane (CH_2Cl_2, >99.5%; water content, <0.001%), toluene (>99.5%; water content, <0.001%), methanol (MeOH), calcium hydride (CaH_2), deuterated chloroform ($CDCl_3$, > 99.8%), and potassium carbonate (K_2CO_3) were purchased from Kanto Chemicals Co., Inc. *N*,*N*-Diethylacrylamide (DEtAAm), *N*,*N*-dimethylacrylamide (DMeAAm), *N*-acryloylmorpholine (MorAAm), *N*-(trimethylsilyl)bis(trifluoromethanesulfonyl)imide (**Me_3SiNTf_2**), dimethylphenylsilane (Me_2PhSiH), methyldiphenylsilane ($MePh_2SiH$), triisopropylsilane ($i Pr_3SiH$), triphenylsilane (Ph_3SiH), *tert*-butyldimethylsilane ($t BuMe_2SiH$), tri-*n*-butylsilane ($n Bu_3SiH$), triethylsilane (Et_3SiH), dimethylethylsilane (Me_2EtSiH), dimethylethylchlorosilane ($Me_2EtSiCl$), *tert*-butyldimethylchlorosilane (*tert*-$BuMe_2SiCl$), *N,N*-dimethylmethacrylamide (DMeMAm), imidazole, *N,N,N,N*-tetramethylethylenediamine (TMEDA), and *trans*-3-indoleacrylic acid were purchased from Tokyo Kasei Kogyo Co., Ltd. 1-Methylimidazole, sodium trifluoroacetate, silver trifluoroacetate, and 1,8-dihydroxy-9-(10*H*)-anthracenone were purchased from the Sigma-Aldrich Chemicals Co. Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) was purchased from Wako Pure Chemical Industries, Ltd., and used after recrystallization from *n*-hexane at −30 °C. DEtAAm, DMeAAm, MorAAm, DMeMAm, CH_2Cl_2, and H*Si*s, except for Ph_3SiH, were distilled from CaH_2, degassed by three freeze-pump-thaw cycles, and stored under an Ar atmosphere prior to use. Ph_3SiH was used after recrystallization from *n*-hexane. *N,N*-Diallyacrylamide (DAlAAm),[1] *N,N*-bis(2-methoxyethyl)acrylamide (BMEAAm),[1]

2,2,5-trimethyl-1,3-dioxan-5-ylmethanol-tosylate,[2] and *N*-(2-*tert*-butyldimethylsilyloxyethyl)-*N*-(prop-2-ynyl)amine,[3] were synthesized according to a previous report. The Spectra/Por® 6 Membrane (MWCO: 1000) was used for the dialysis. All other chemicals were purchased from available suppliers and used without purification.

Measurements. The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a JEOL ECS400. The preparation of the polymerization solution was carried out in an MBRAUN stainless steel glove box equipped with a gas purification system (molecular sieves and copper catalyst) and a dry argon atmosphere (H_2O, O_2 <1 ppm). The moisture and oxygen contents in the glove box were monitored by an MB-MO-SE 1 and MB-OX-SE 1, respectively. Size exclusion chromatography (SEC) in DMF containing lithium chloride (LiCl; 0.01 mol L^{-1}) was performed at 40 °C using a Jasco high performance liquid chromatography (HPLC) system (PU-980 Intelligent HPLC pump, CO-965 column oven, RI-930 Intelligent RI detector, and Shodex DEGAS KT-16) equipped with a Shodex Asahipak GF-310 HQ column (linear, 7.6 mm × 300 mm; pore size, 20 nm; bead size, 5 μm; exclusion limit, 4×10^4) and a Shodex Asahipak GF-7M HQ column (linear, 7.6 mm × 300 mm; pore size, 20 nm; bead size, 9 μm; exclusion limit, 4×10^7) at the flow rate of 0.6 mL min^{-1}. The $M_{n,SEC}$ and M_w/M_n of the acrylamide polymers were determined by the RI based on poly(methyl methacrylate) (PMMA) with the M_w (M_w/M_n)s of 1.25×10^6 g mol^{-1} (1.07), 6.59×10^5 g mol^{-1} (1.02), 3.003×10^5 g mol^{-1} (1.02), 1.385×10^5 g mol^{-1} (1.05), 6.015×10^4 g mol^{-1} (1.03), 3.053×10^4 g mol^{-1} (1.02), and 1.155×10^4 g mol^{-1} (1.04), 4.90×10^3 g mol^{-1} (1.10), 2.87×10^3 g mol^{-1} (1.06), and 1.43×10^3 g mol^{-1}

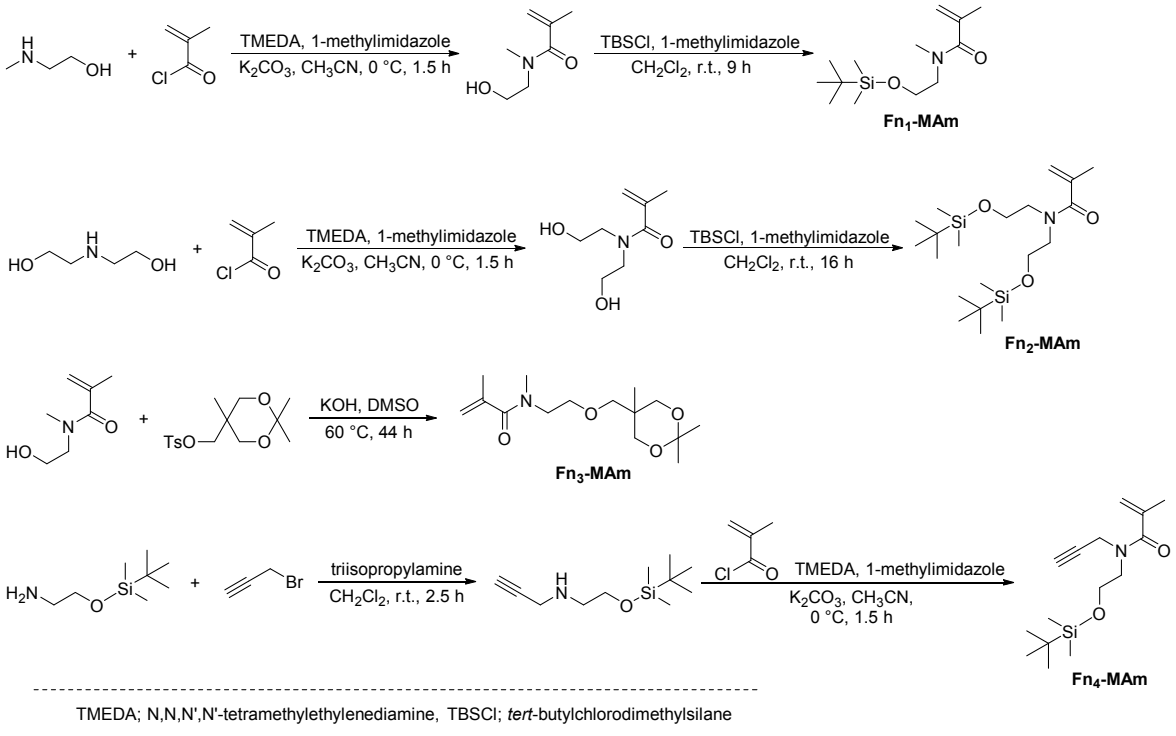
(1.15), respectively. The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed using an Applied Biosystems Voyager-DE STR-H mass spectrometer with a 25 kV acceleration voltage. The positive ions were detected in the reflector mode (25 kV). A nitrogen laser (337 nm, 3 ns pulse width, 106–107 W cm^{-2}) operating at 3 Hz was used to produce the laser desorption, and the 100-300 shots were summed. The spectra were externally calibrated using a sample prepared from narrow-dispersed polystyrene (Chemco Scientific Co., Ltd., M_n, 3.6 kg mol^{-1}; M_w/M_n, 1.08; 30 μL, 10 mg mL^{-1} in THF), the matrix (1,8-dihydroxy-9-(10*H*)-anthracenone, 30 mg mL^{-1}, 100 μL), and the cationizing agent (silver trifluoroacetate, 10 mg mL^{-1}, 15 μL) with a linear calibration. Samples for the MALDI-TOF MS were prepared by mixing the polymer (1.5 mg mL^{-1}, 10 μL), the matrix (*trans*-3-indoleacrylic acid, 10 mg mL^{-1}, 90 μL), and the cationizing agent (sodium trifluoroacetate, 10 mg mL^{-1}, 10 μL) in THF.

2. Synthesis of 1-(4-morpholinyl)-1-dimethylethylsiloxy-1-propene (Mor-SKAm^{Me_2Et}). To a solution of diisopropylamine (3.37 mL, 24.0 mmol) in dry-THF (30 mL) in a 100-mL three-necked flask, *n*-butyllithium (13.6 mL, 22.0 mmol; 1.60 mol L^{-1} in *n*-hexane) was dropwise added at 0 °C under an argon atmosphere. After stirring for 30 min, 1-(4-morpholinyl)-1-propanone (2.68 mL, 20 mmol) was slowly added. The reaction mixture was stirred at 0 °C for 1 h. $Me_2EtSiCl$ (4.18 mL, 52.2 mmol) was then added. After stirring for 90 min at 0 °C, the solvent was removed under reduced pressure. The product was then directly

distilled under reduced pressure (98-101 °C/4.50 mmHg) to afford Mor-SKAm^{Me_2Et} as a transparent liquid. Yield, 2.11 g (46.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.13 (s, 6H, -Si(CH_3)$_2$), 0.63 (q, J = 8.3 Hz, 2H, -SiCH_2CH$_3$), 0.94 (t, J = 8.4 Hz, 3H, -SiCH$_2$CH_3), 1.49 (d, J = 6.8 Hz, 3H, CH_3CH=C-), 2.72 (t, J = 5.6 Hz, 4H, N(CH_2CH$_2$)$_2$O), 3.64 (t, J = 5.4 Hz, 4H, N(CH$_2$CH_2)$_2$O), 3.69 (q, J = 6.8 Hz, 1H, CH$_3$CH=C-). ^{13}C NMR (100 MHz): δ (ppm) –2.0, 6.8, 8.5, 10.5, 49.2, 66.9, 82.2, 154.0.

3. Synthesis of functional methacrylamides (Fn-MAms)

Scheme S1. Synthetic route of functional methacrylamides (Fn-MAms).



Synthesis of *N*-(2-hydroxyethyl)-*N*-methylmethacrylamide. Method SA: To a suspension of 2-(methylamino)ethanol (20.0 mL, 250 mmol), 1-methylimidazole (1.64 mL, 20.8 mmol), TMEDA (3.10 mL, 20.8 mmol), and K_2CO_3 (34.5 g, 250 mmol) in acetonitrile (200 mL), methacryloyl chloride (20.1 mL, 208 mmol) was added dropwise at 0 °C under a N_2 atmosphere. After stirring for 1 h, the reaction mixture was filtered and then condensed under reduced pressure. The crude product was purified by silica gel column chromatography (ethyl acetate → acetone), affording *N*-(2-hydroxyethyl)-*N*-methylmethacrylamide as transparent liquid. Yield, 22.1 g (74.2 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.94 (s, 3H, CH_2=C(C*H*$_3$)-), 2.96, 3.07 (s, 3H, NC*H*$_3$), 3.40-3.60 (m, 3H, -NC*H*$_2$CH$_2$O*H*), 3.66-3.82 (m, 2H, -NCH$_2$C*H*$_2$OH), 5.00-5.24 (m, 2H, C*H*$_2$=C(CH$_3$)-). ^{13}C NMR (100 MHz):δ (ppm) 20.0, 20.6, 32.5, 37.9, 50.0, 52.8, 59.3, 60.2, 115.3, 115.9, 140.3, 140.7, 173.7.

Synthesis of *N,N*-bis(2-hydroxyethyl)methacrylamide. Method SA was used to react diethanolamine (21.0 g, 200 mmol), 1-methylimidazole (1.30 mL, 16.5 mmol), TMEDA (2.45 mL, 16.5 mmol), K_2CO_3 (34.5 g, 200 mmol), acetonitrile (150 mL), and methacryloyl chloride (16.0 mL, 165 mmol). *N,N*-Bis(2-hydroxyethyl)methacrylamide was obtained as a transparent liquid purified by silica gel column chromatography (ethyl acetate → acetone). Yield, 11.0 g (38.6 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.91 (s, 3H, CH_2=C(C*H*$_3$)-), 2.96, 3.07 (s, 3H, NC*H*$_3$), 3.51 (m, 4H, -N(C*H*$_2$CH$_2$OH)$_2$), 3.62-3.85 (m, 4H, -N(CH$_2$C*H*$_2$OH)$_2$), 4.2-4.7 (br, 2H, -N(CH$_2$CH$_2$O*H*)$_2$), 5.05, 5.14 (m, 2H, C*H*$_2$=C(CH$_3$)-). ^{13}C NMR (100 MHz):δ (ppm) 20.7, 31.0, 49.3, 53.1, 60.6, 116.1, 140.6, 174.8.

Synthesis of *N*-(2-*tert*-butyldimethylsiloxyethyl)-*N*-methylmethacrylamide (Fn_1-MAm). Method SB: To a solution of *N*-(2-hydroxyethyl)-*N*-methylmethacrylamide (5.00 g, 34.9 mmol), imidazole (3.56 g, 52.4 mmol), and CH_2Cl_2 (100 mL), a solution of *tert*-butyldimethylchlorosilane (7.89 g, 52.4 mmol) in CH_2Cl_2 (10.0 mL) was added at room temperature under a N_2 atmosphere. After stirring for 9 h, the reaction mixture was filtered and washed with 0.5 N HCl aq. (100mL × 1), saturated $NaHCO_3$ aq. (100 mL × 2), and distilled water (100 mL × 1). The organic layer was concentrated under reduced pressure after drying with anhydrous $MgSO_4$. The residue was purified by distillation under reduced pressure (83 °C/0.03 mmHg) to afford Fn_1-MAm as a transparent liquid. Yield, 6.13 g (68.2 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) -0.02, (s, 6H, -Si(C*H*$_3$)$_2$C(CH$_3$)$_3$), 0.82 (s, 9H, -Si(CH$_3$)$_2$C(C*H*$_3$)$_3$) 1.88 (s, 3H, CH$_2$=C(C*H*$_3$)-), 2.90, 3.04 (s, 3H, NC*H*$_3$), 3.39-3.46 (m, 2H, -NC*H*$_2$CH$_2$O-), 3.61-3.77 (m, 2H, -NCH$_2$C*H*$_2$O-), 4.94, 5.30-5.11 (m, 2H, C*H*$_2$=C(CH$_3$)-). ^{13}C NMR (100 MHz): δ (ppm) -5.4, 18.2, 20.2, 21.0, 26.0, 32.6, 38.6, 49.7, 52.6, 60.9, 61.5, 115.0, 141.0, 172.0, 173.2. Anal. Calcd. for $C_{13}H_{27}NO_2Si$ (257.18): C, 60.65; H, 10.57; N, 5.44. Found: C, 60.31; H, 10.63; N, 5.42.

Synthesis of *N,N*-bis(2-*tert*-butyldimethylsiloxyethyl) methacrylamide (Fn_2-MAm). Method SB was used to react *N,N*-bis(2-hydroxyethyl)methacrylamide (6.00 g, 34.6 mmol), imidazole (5.89 g, 86.6 mmol), and CH_2Cl_2 (100 mL), and *tert*-butyldimethylchlorosilane (13.1 g, 86.6 mmol). Fn_2-MAm was obtained as a transparent liquid purified by distillation under reduced pressure (130-134 °C/0.03 mmHg). Yield, 6.99 g (50.3 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ

(ppm) -0.13, (s, 12H, (-Si(CH_3)$_2$C(CH_3)$_3$)$_2$), 0.71 (s, 18H, (-Si(CH_3)$_2$C(CH_3)$_3$)$_2$), 1.78 (s, 3H, CH_2=C(CH_3)-), 3.31-3.46 (m, 4H, -N($CH_2$$CH_2$O-)$_2$), 3.46-3.67 (m, 4H, -N($CH_2$$CH_2$O-)$_2$), 4.83, 4.95 (m, 2H, CH_2=C(CH_3)-). ^{13}C NMR (100 MHz): δ (ppm) -5.5, 20.8, , 25.8, 47.4, 51.8, 61.1, 114.6, 141.0, 172.8. Anal. Calcd. for $C_{20}H_{43}NO_3Si_2$ (401.73): C, 59.79; H, 10.79; N, 3.49. Found: C, 59.32; H, 10.90; N, 3.48.

Synthesis of *N*-(2,2,5-trimethyl-1,3-dioxan-5-ylmethoxyethyl)-*N*-methylmethacrylamide (Fn$_3$-MAm). To a suspension of *N*-(2-hydroxyethyl)-*N*-methylmethacrylamide (5.00 g, 34.9 mmol), KOH (3.91 g, 69.8 mmol), and DMSO (100 mL), 2,2,5-trimethyl-1,3-dioxan-5-ylmethanol-tosylate (13.2 g, 41.9 mmol) was added. After stirring for 45 h at 60 °C, distilled water (300 mL) was added after the reaction mixture was cooled to r.t., then the mixture was extracted with diethyl ether (200 mL × 4). The organic layer was concentrated under reduced pressure following by drying over anhydrous $MgSO_4$. The residue was purified by silica gel column chtomatography (ethyl acetate, R_f = 0.40) and distillation under reduced pressure (95 °C/0.03 mmHg) to afford Fn$_3$-MAm as a transparent liquid. Yield, 1.10 g (11.0 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.78-0.86 (m, 3H, CH_3C(CH_2-)$_3$), 1.35, 1.39 (s, 6H, C(CH_3)$_2$), 1.92 (s, 3H, CH_2=C(CH_3)-), 2.95, 3.06 (s, 3H, NCH_3), 3.38-3.69 (m, 10H, NCH_2CH_2OCH_2C(CH_3)(CH_2O-)$_2$), 5.00, 5.10-5.18 (m, 2H, CH_2=C(CH_3)-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 18.2, 20.3, 20.8, 21.1, 26.5, 27.3, 32.9, 34.4, 38.3, 47.0, 50.4, 66.5, 69.5, 69.8, 74.0, 74.4, 97.9, 115.3, 141.0, 172.4. Anal. Calcd. for $C_{15}H_{27}NO_4$ (285.38): C, 63.13; H, 9.54; N, 4.91. Found: C, 62.68; H, 9.56; N, 4.88.

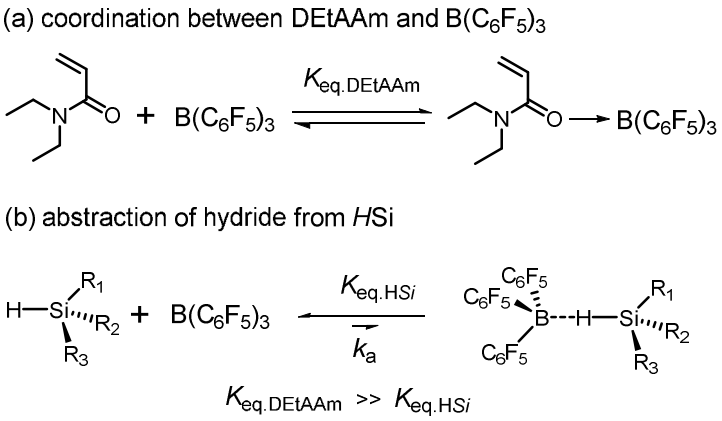
Synthesis of *N*-(2-*tert*-butyldimethylsilyloxyethyl)-*N*-(prop-2-ynyl)methacrylamide (Fn$_4$-MAm). Method SB was used to react *N*-(2-*tert*-butyldimethylsilyloxyethyl)-*N*-(prop-2-ynyl)amine (13.3 g, 62.5 mmol), 1-methylimidazole (0.49 mL, 6.25 mmol), TMEDA (0.93 mL, 6.25 mmol), K_2CO_3 (10.4 g, 75.0 mmol), acetonitrile (100 mL), and methacryloyl chloride (5.46 mL, 62.5 mmol). Fn$_4$-MAm was obtained as a transparent liquid purified by silica gel column chromatography (CH_2Cl_2, R_f = 0.10) and distillation under reduced pressure (83 °C/0.03 mmHg). Yield, 0.69 g (3.92 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) -0.02, (s, 6H, -Si(C*H*$_3$)$_2$C(CH$_3$)$_3$), 0.81 (s, 9H, -Si(CH$_3$)$_2$C(C*H*$_3$)$_3$), 1.90 (s, 3H, CH$_2$=C(C*H*$_3$)-), 2.21 (s, 1H, -C≡C*H*), 3.51-3.59 (m, 2H, -NC*H*$_2$CH$_2$O-), 3.62-3.80 (m, 2H, -NCH$_2$C*H*$_2$O-), 4.22 (s, 2H, -C*H*$_2$C≡CH), 4.98-5.18 (m, 2H, C*H*$_2$=C(CH$_3$)-). ^{13}C NMR (100 MHz): δ (ppm) -5.4, 18.2, 20.6, 26.0, 33.7, 40.5, 46.9, 49.5, 61.0, 61.7, 72.0, 72.4, 79.0, 79.4, 115.9, 140.3, 172.2. Anal. Calcd. for $C_{15}H_{27}NO_2Si$ (281.47): C, 64.01; H, 9.67; N, 4.98. Found: C, 63.89; H, 9.76; N, 4.96.

4. Polymerization procedure

Polymerization of acrylamide monomers using hydrosilane and B(C$_6$F$_5$)$_3$. The typical polymerization procedure was as follows: Me$_2$EtSiH (5.28 μL, 40 μmol) was added to a solution of MorAAm (126 μL, 1.00 mmol) and B(C$_6$F$_5$)$_3$ (10.2 mg, 20.0 μmol) in CH_2Cl_2 (869 μL) at room temperature (~25 °C). After 13 h, MeOH was added to the solution to quench the polymerization. The crude product was purified by dialysis against MeOH. Yield, 60.4 mg (43%); $M_{n,NMR}$, 3.11 kg mol^{-1}, M_w/M_n, 1.04.

Synthesis of α-end functionalized poly(*N*,*N*-diethylacrylamide)s (Fn-PDEAAs) using hydrosilane and functional mthacrylamides. The typical procedure for the polymerization was as follows: Me_2EtSiH (14.5 μL, 110 μmol) was added to a solution of Fn_1-MAm (100 μL, 100 μmol; 1.00 mol L^{-1} in toluene) and $B(C_6F_5)_3$ (5.10 mg, 10.0 μmol) in toluene (96 μL) at room temperature (25 °C). After stirring for 6 h, a small portion of the reaction mixture was sampled to determine the efficiency of the 1,4-hydrosilylation. A mixture of DEtAAm (343 μL, 2.5 mmol) and Me_3SiNTf_2 (20.0 μL, 2.00 μmol; 0.10 mol L^{-1} in CH_2Cl_2) in CH_2Cl_2 (1.93 mL) was then added to the residual mixture to start the polymerization. After stirring for 15 min, a small amount of MeOH was added to the solution to quench the polymerization. The α-end functionalized PDEtAAm with the dimethyl-*tert*-butylsiloxy group was deprotected using tetrabutylammoniumfluoride (TBAF; 500 μL, 500 μmol, 1.00 mol L^{-1} in THF) in MeOH. The crude product was purified by dialysis against MeOH. Yield, 260 mg (82%); $M_{n,NMR}$ = 3.89 kg mol^{-1}, M_w/M_n = 1.06.

5. Scheme S2. Schematic representation for (a) coordination between DEtAAm and $B(C_6F_5)_3$ and (b) abstraction of hydride from H*Si*



6. Figures

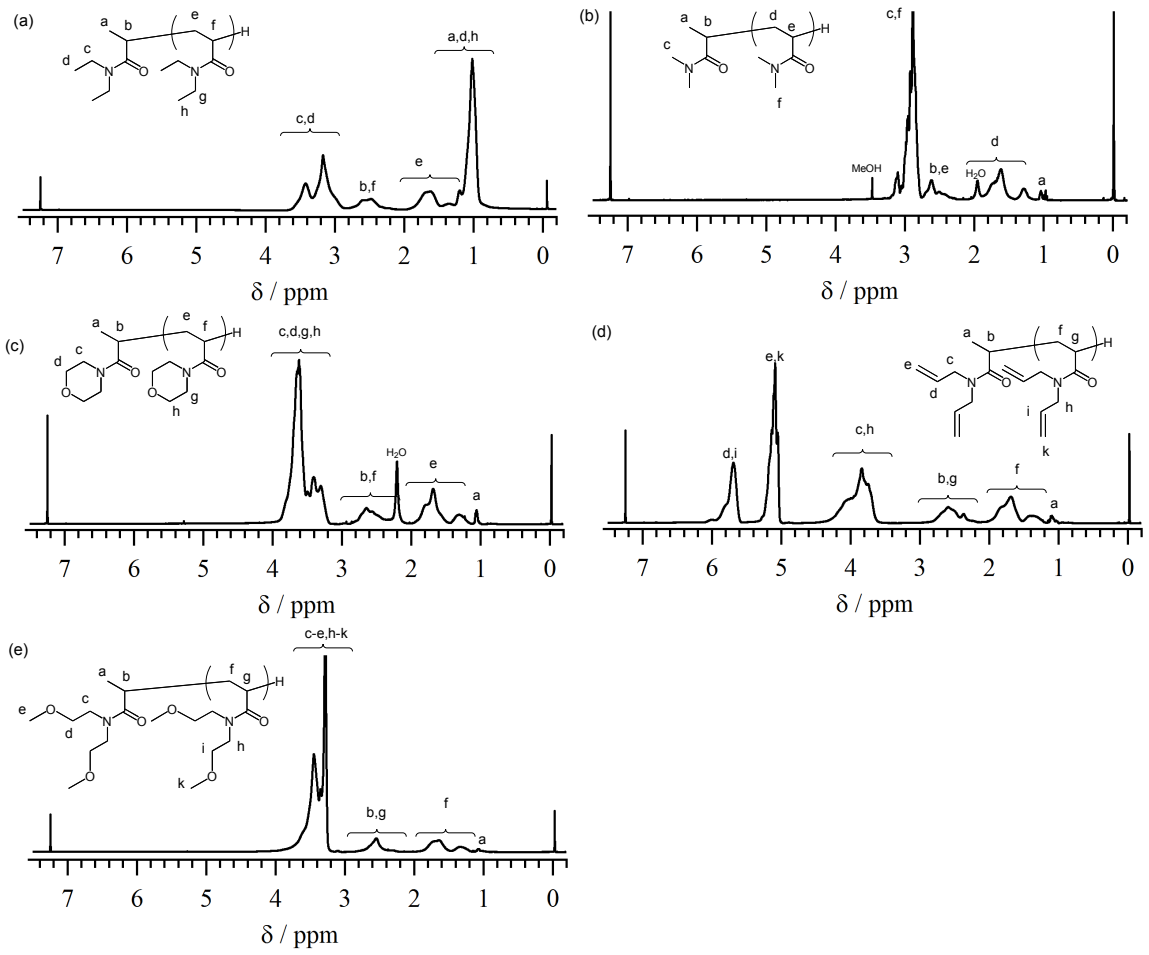


Figure S1. ^{1}H NMR spectra of the obtained polymer by $B(C_6F_5)_3$-catalyzed GTP of DAAm using Me_2EtSiH, (a) PDEtAAm (run 8), (b) PDMeAAm, (run 12) (c) PMorAAm (run 18), (d) PDAlAAm (run 14), and (e) PBMEAAm (run 16) in $CDCl_3$ (400 MHz).

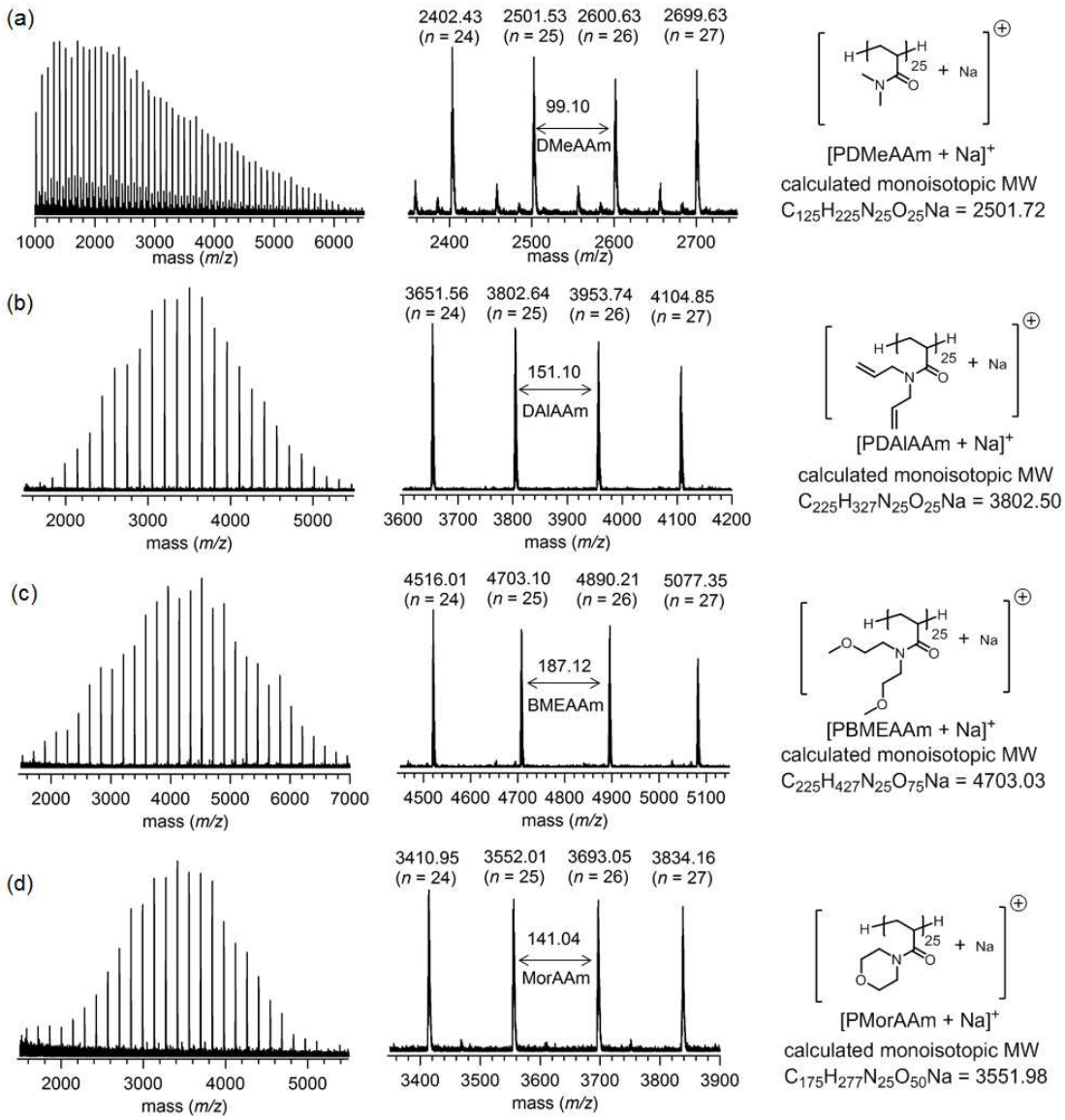


Figure S2. MALDI-TOF MS spectra of the obtained polymer by $B(C_6F_5)_3$-catalyzed GTP of DAAm using Me_2EtSiH, (a) PDMeAAm (run 12), (b) PDAlAAm (run 14), (c) PBMEAAm (run 16), and (d) the obtained polymer by $B(C_6F_5)_3/Me_3SiNTf_2$-catalyzed GTP of MorAAm using Me_2EtSiH.

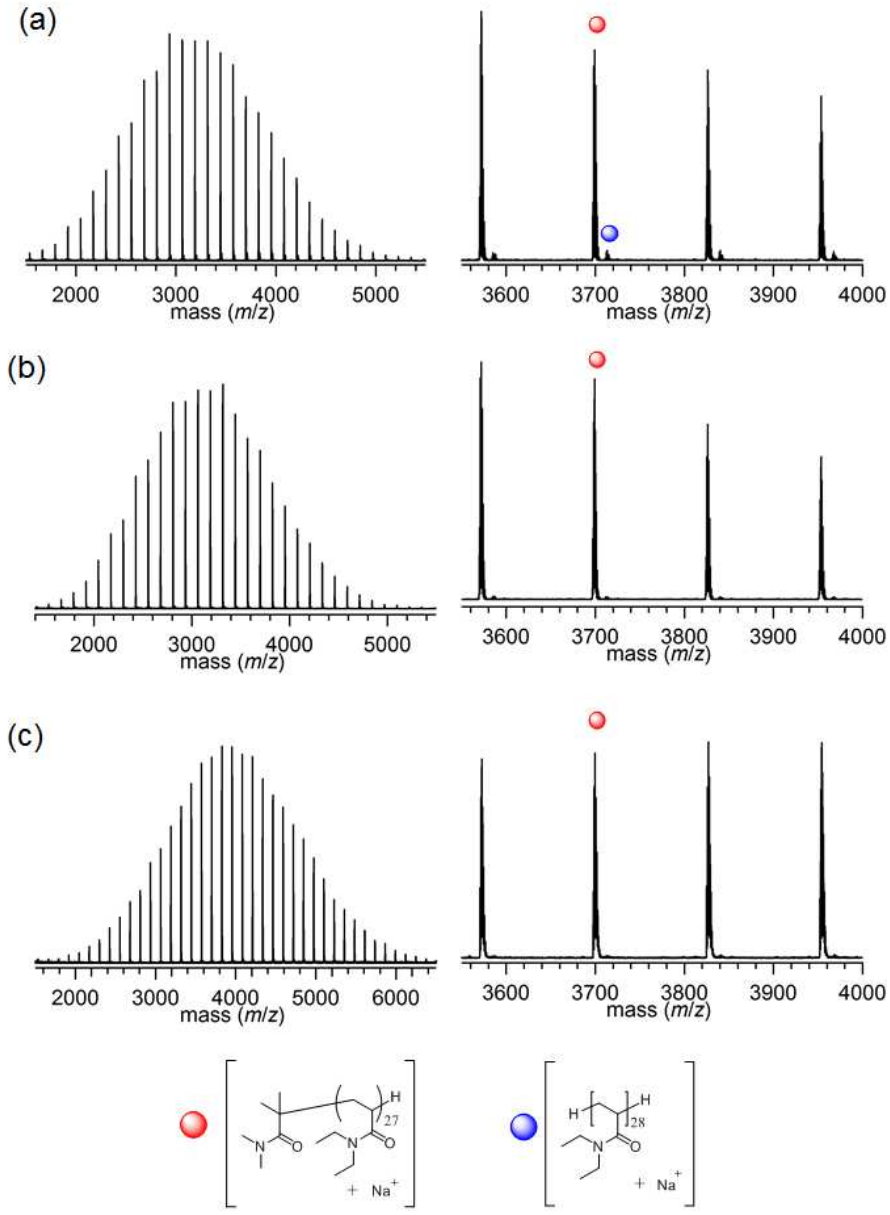


Figure S3. MALDI-TOF MS spectra of the products from (a) run 22, (b) run 23, and (c) run 24, obtained by the $B(C_6F_5)_3$-catalyzed GTPs of DEtAAm using Me_2EtSiH and DMeMAm under various $[DMeMAm]_0/[Me_2EtSiH]_0/[B(C_6F_5)_3]_0$ ratios.

7. References

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