Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Organic Acids as Efficient Catalyst for Group Transfer Polymerization of *N*,*N*-Disubstituted Acrylamide with Silyl Ketene Acetal; Polymerization Mechanism and Synthesis of Diblock Copolymers

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Experimental Section

Synthesis of *N,N*-di-*n*-propylacrylamide (D*n*PAA). To a suspension of di-*n*-propylamine (25.0 mL, 182 mmol), 1-methylimidazole (1.37 mL, 17.3 mmol), *N,N,N',N'*-tetramethyl-ethylenediamine (TMEDA, 2.58 mL, 17.3 mmol), and K_2CO_3 (25.2 g, 182 mmol) in acetonitrile (300 mL), acryloyl chloride (14.0 mL, 173 mmol) was added dropwise at 0 °C. After stirring for 6 h, the reaction mixture was filtered, and then condensed under reduced pressure. The crude product was purified by column chromatography (hexane:ethyl acetate = 2:1, R_f = 0.35) followed by distillation over CaH_2 under reduced pressure (50 °C/ 0.17 mmHg), affording *N,N*-di-*n*-propylacrylamide as a transparent liquid. Yield, 11.1 g (41.2 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.78-0.88 (m, 6H, -C*H*$_3$), 1.45-1.58 (m, 4H, -C*H*$_2$CH$_3$), 3.15-3.29 (m, 4H, -NC*H*$_2$-), 5.52-5.59 (m, 1H, CH$_2$=C*H*-), 6.20-6.28 (m, 1H, *trans* C*H*$_2$=CH-), 6.42-6.52 (m, 1H, *cis* C*H*$_2$=CH-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 11.2, 11.5, 21.0, 22.9, 48.3, 49.8, 127.4, 127.9.

Synthesis of *N*-acryloylpiperidine (API). To a solution of piperidine (25.0 mL, 253 mmol), trimethylamine (42.0 mL, 303 mmol), and CH_2Cl_2 (300 mL), acryloyl chloride was added dropwise at 0 °C. After stirring for 16 h at r.t., the reaction mixture was extracted by 0.5N HCl, NaCl aq., and distilled water. Organic layer was dried over $MgSO_4$, and then condensed under reduced pressure. The crude product was purified by distillation using CaH_2 under reduced pressure (97 °C/ 6.0 mmHg), affording *N*-acryloylpiperidine as a transparent liquid. Yield, 9.79 g (29.3 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.49-1.59 (m, 4H, -C*H*$_2$CH$_2$C*H*$_2$-), 1.59-1.67 (m, 2H, -CH$_2$C*H*$_2$CH$_2$-), 3.40-3.64 (m, 4H, -NC*H*$_2$-), 5.58-5.65 (m, 1H, CH$_2$=C*H*-), 6.17-6.25 (m, 1H,

trans CH_2=CH-), 6.50-6.59 (m, 1H, *cis* CH_2=CH-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 24.6, 25.5, 26.6, 43.0, 47.0, 127.0, 128.1, 165.2.

Synthesis of *N*-methoxyethyl-*N*-methyl-acrylamide (MMEAA). To a suspension of KOH (22.4 g, 400 mmol) in DMSO (200 mL), *N*-2-hydroxy-*N*-methylacrylamide (11.5 g, 100 mmol) was added, and then iodomethane (24.9 mL, 400 mmol) was added at room temperature. After stirring for 30 min with exothermic reaction, reaction mixture was quenched by excess amount of water followed by the extraction with ethyl acetate. The organic phase dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography (ethyl acetate, R_f = 0.31) and distillation from CaH_2 under reduced pressure (55-56 °C/ 0.10 mmHg), affording *N*-methoxyethyl-*N*-methyl-acrylamide as pale yellow solid. Yield, 3.46 g (24.2 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.92, 3.04 (s, 3H, NCH_3), 3.23 (s, 3H, OCH_3), 3.37-3.53 (m, 4H, -CH_2CH_2-), 5.51-5.60 (m, 1H, CH_2=C*H*-), 6.15-6.24 (m, 1H, *trans* CH_2=CH-), 6.46-6.57 (m, 1H, *cis* CH_2=CH-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 34.5, 37.1, 48.0, 49.7, 58.8, 59.2, 70.6, 71.0, 127.4, 127.7, 127.8, 128.0, 166.3, 166.9. Anal. Calcd for $C_7H_{13}NO_2$ (143.18): C, 58.72; H, 9.15; N, 9.78. Found: C, 58.72; H, 9.23; N, 9.81.

Synthesis of *N,N*-bis(methoxyethyl)acrylamide (BMEAA). The procedure of synthesis of D*n*PAA was applied to bis(methoxyethyl)amine (15.0 mL, 102 mmol), 1-methylimidazole (0.87 mL, 11.0 mmol), TMEDA (1.64 mL, 11.0 mmol), K_2CO_3 (34.5 g, 250 mmol), acetonitrile (200 mL), and acryloyl chloride (8.89 mL, 110 mmol). *N,N*-bis(methoxyethyl)acrylamide was obtained as transparent liquid purified by distillation using CaH_2 under reduced pressure (77 °C/

0.03 mmHg). Yield, 6.08 g (32.5 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.20 (s, 6H, OC*H*$_3$), 3.35-3.54 (m, 8H, -C*H*$_2$C*H*$_2$-), 5.50-5.57 (m, 1H, CH_2=C*H*-), 6.15-6.23 (m, 1H, *trans* C*H*$_2$=CH-), 6.50-6.59 (m, 1H, *cis* C*H*$_2$=CH-). ^{13}C NMR (100 MHz, CDCl3): δ (ppm) 47.0, 48.9, 58.7, 59.0, 71.0, 71.1, 127.6, 128.1, 166.6. Anal. Calcd for $C_9H_{17}NO_3$ (187.23): C, 57.73; H, 9.15; N, 7.48. Found: C, 57.42; H, 9.18; N, 7.48.

Synthesis of *N,N*-diallylacrylamide (DAlAA). The procedure for the synthesis of API was applied to diallylamine (25.0 mL, 203 mmol), trimethylamine (36.6 mL, 264 mmol), CH_2Cl_2 (300 mL), and acryloyl chloride (14.8 mL, 183 mmol). *N,N*-diallylacrylamide was obtained as a transparent liquid purified after distillation over CaH_2 under reduced pressure (61 °C/ 0.07 mmHg). Yield, 14.7 g (53.2 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.85-4.10 (m, 4H, -NC*H*$_2$-), 5.05-5.25 (m, 4H, -CH_2CH=C*H*$_2$), 5.60-5.70 (m, 1H, CH_2=C*H*-), 5.70-5.85 (m, 2H, -CH_2C*H*=CH_2), 6.30-6.40 (m, 1H, *trans* C*H*$_2$=CH-), 6.40-6.50 (m, 1H, *cis* C*H*$_2$=CH-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 48.5, 49.2, 116.9, 117.6, 127.7, 128.4, 132.9, 133.1, 166.5. Anal. Calcd for $C_9H_{13}NO$ (151.21): C, 71.49; H, 8.67; N, 9.25. Found: C, 71.08; H, 8.77; N, 9.18.

Synthesis of *N*-propargylacrylamide. To a solution of propargylamide (13.0 mL, 204 mmol), *N,N*-dimethylaminopyridine (2.44 g, 20.0 mmol), and CH_2Cl_2 (150 mL), acryloyl chloride was added dropwise at 0 °C. After stirring for 8 h at r.t., the reaction mixture was filtered, and then condensed under reduced pressure. The crude product was purified by column chromatography (hexane:ethyl acetate = 1:1, R_f = 0.29), affording *N*-propargylacrylamide as transparent liquid. Yield, 6.20 g (29.9 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.22-2.26 (t, 1H, -C≡C*H*), 4.10-

414 (m, 2H, -NCH_2-), 5.64-5.70 (m, 1H, CH_2=CH-), 5.90-6.10 (br, 1H, NH), 6.06-6.15 (m, 1H, *trans* CH_2=CH-), 6.27-6.34 (m, 1H, *cis* CH_2=CH-).

***N*-methyl-*N*-propargyl acrylamide (MPAA).** To a suspension of NaH (3.72 g, 60 wt%, 85.2 mmol) in dry-THF (200 mL), *N*-propargylacrylamide (6.20 g, 56.8 mmol) was added at 0 °C under nitrogen atmosphere. After stirring for 1 h, iodomethane (10.6 mL, 170 mmol) was added at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at r.t. for 24 h, and then, quenched with a portion of water followed by extraction with ethyl acetate. The organic phase was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by distillation over CaH_2 under reduced pressure (85 °C/ 6.0 mmHg), affording *N*-propargyl-*N*-methylacrylamide as a pale yellow solid. Yield, 2.34 g (33.5 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.19-2.23, 2.29-2.33 (t, 1H, -C≡CH), 3.03-3.07, 3.12-3.16 (s, 3H, NCH_3), 4.08-412, 4.26-4.29 (m, 2H, -NCH_2-), 5.68-5.75 (m, 1H, CH_2=CH-), 6.26-6.39 (m, 1H, *trans* CH_2=CH-), 6.50-6.62 (m, 1H, *cis* CH_2=CH-). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 33.6, 34.5, 36.5, 39.7, 72.2, 73.1, 78.0, 78.5, 127.3, 127.6, 128.2, 128.8, 166.1, 166.6.

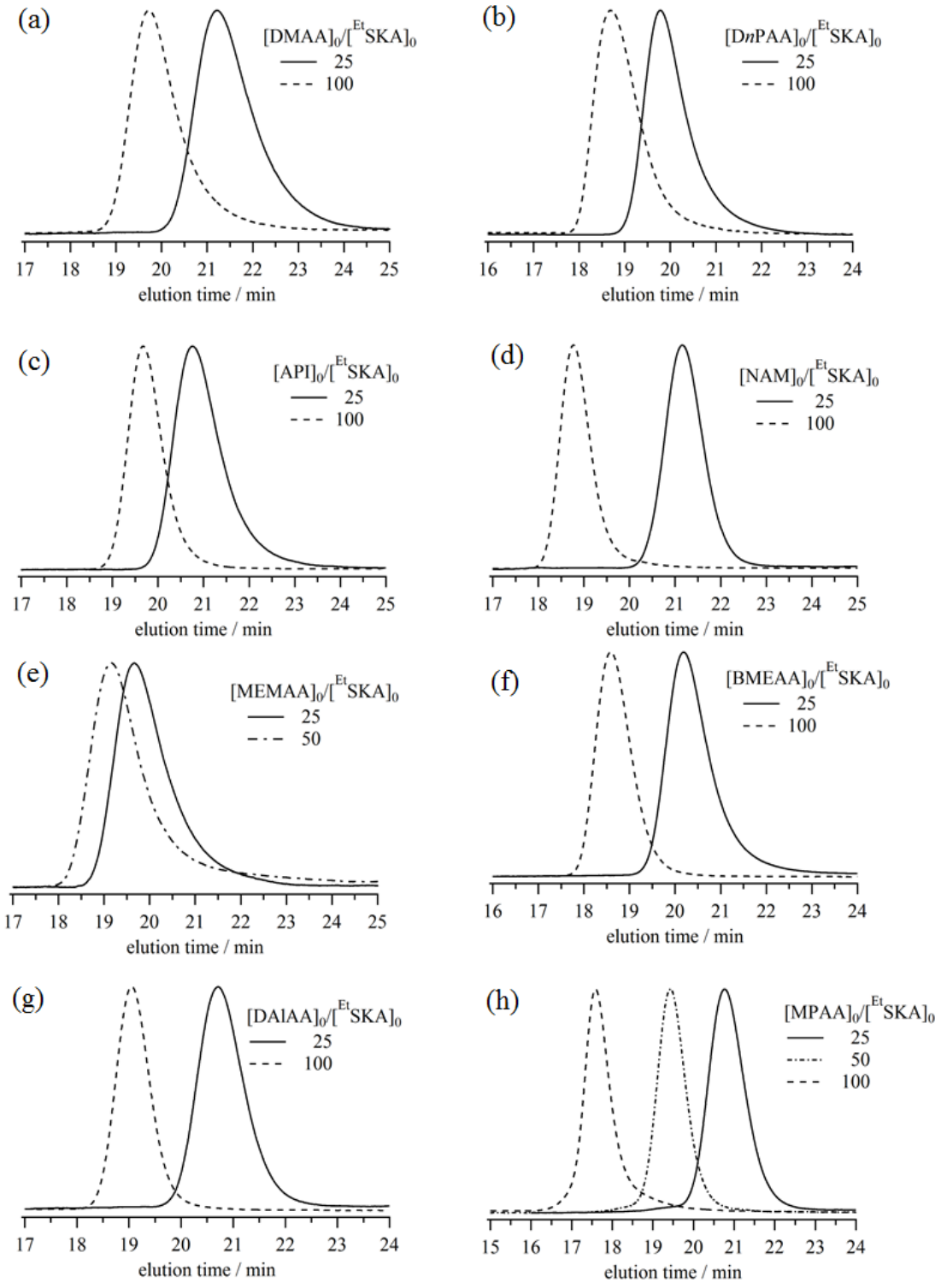


Figure S1. SEC traces of the PDAAs obtained from the $B(C_6F_5)_3$-catalyzed GTPs of (a) DMAA, (b) D*n*PAA, (c) API, (d) NAM, (e) MMEAA, (f) BMEAA, (g) DAlAA, and (h) MPAA at various $[monomer]_0$ to $[^{Et}SKA]_0$ ratios (eluent, DMF containing 0.01 mol L^{-1} LiCl; flow rate, 0.6 mL min^{-1}).

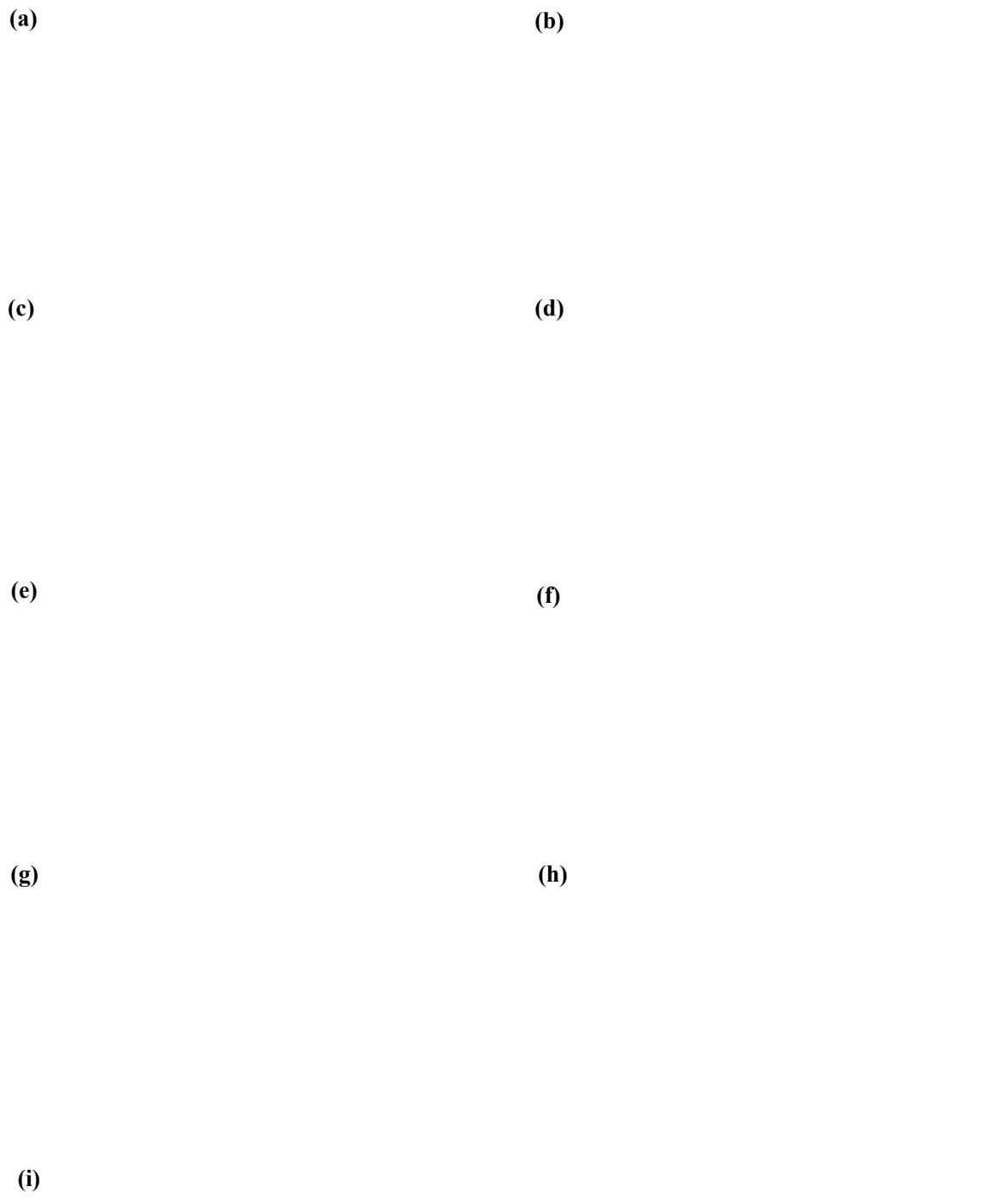
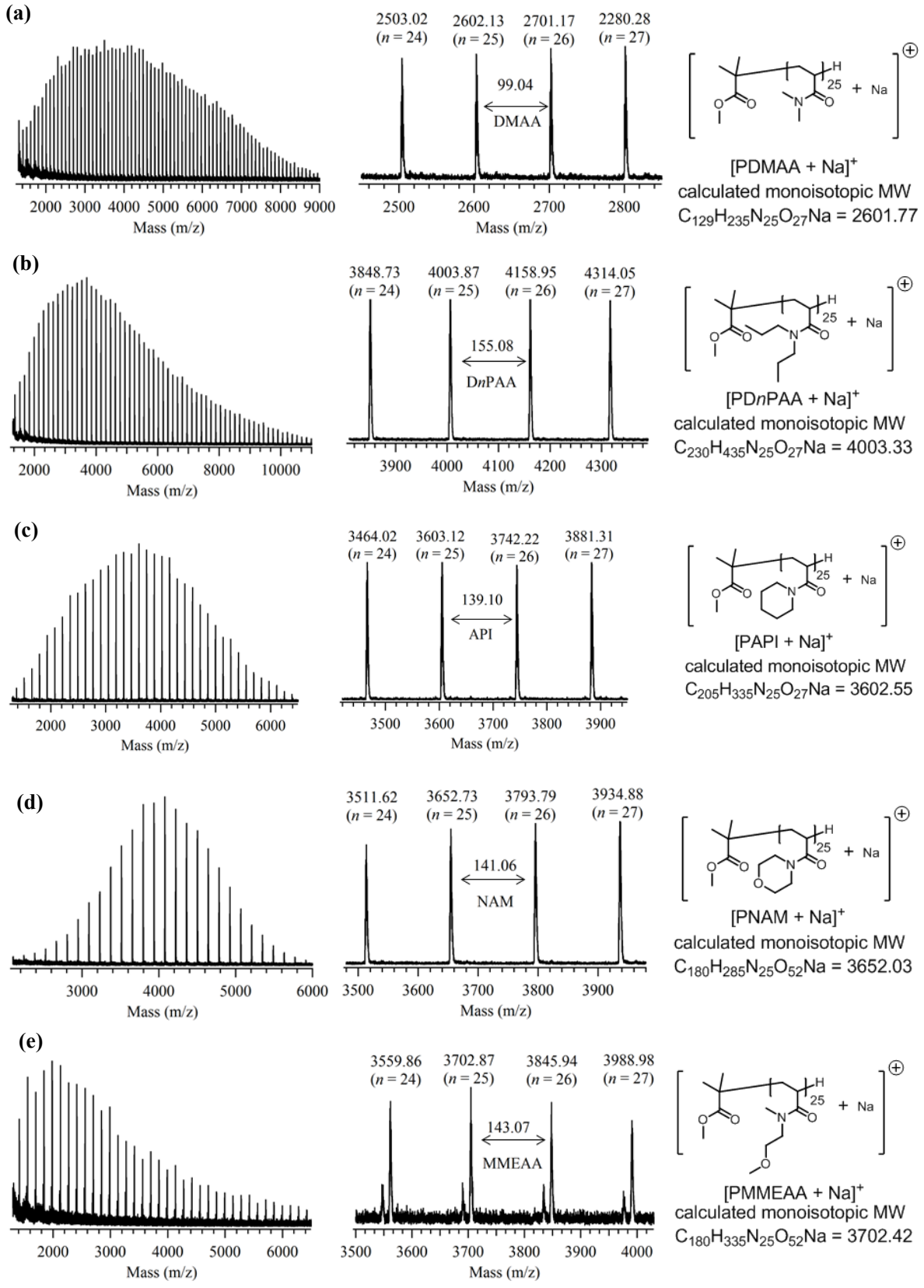


Figure S2. ^{1}H NMR spectra of (a) PDEAA, (b) PDMAA, (c) PD*n*PAA, (d) PAPI, (e) PNAM, (f) PMMEAA, (g) PBMEAA, (h) PDAlAA, and (i) PMPAA in $CDCl_3$. (Theoretical DP, 25)


(a)
2503.02 (n = 24)
2602.13 (n = 25)
2701.17 (n = 26)
2280.28 (n = 27)
99.04
DMAA
Mass (m/z)
[PDMAA + Na]+
calculated monoisotopic MW
C129H235N25O27Na = 2601.77
(b)
3848.73 (n = 24)
4003.87 (n = 25)
4158.95 (n = 26)
4314.05 (n = 27)
155.08
DnPAA
Mass (m/z)
[PDnPAA + Na]+
calculated monoisotopic MW
C230H435N25O27Na = 4003.33
(c)
3464.02 (n = 24)
3603.12 (n = 25)
3742.22 (n = 26)
3881.31 (n = 27)
139.10
API
Mass (m/z)
[PAPI + Na]+
calculated monoisotopic MW
C205H335N25O27Na = 3602.55
(d)
3511.62 (n = 24)
3652.73 (n = 25)
3793.79 (n = 26)
3934.88 (n = 27)
141.06
NAM
Mass (m/z)
[PNAM + Na]+
calculated monoisotopic MW
C180H285N25O52Na = 3652.03
(e)
3559.86 (n = 24)
3702.87 (n = 25)
3845.94 (n = 26)
3988.98 (n = 27)
143.07
MMEAA
Mass (m/z)
[PMMEAA + Na]+
calculated monoisotopic MW
C180H335N25O52Na = 3702.42

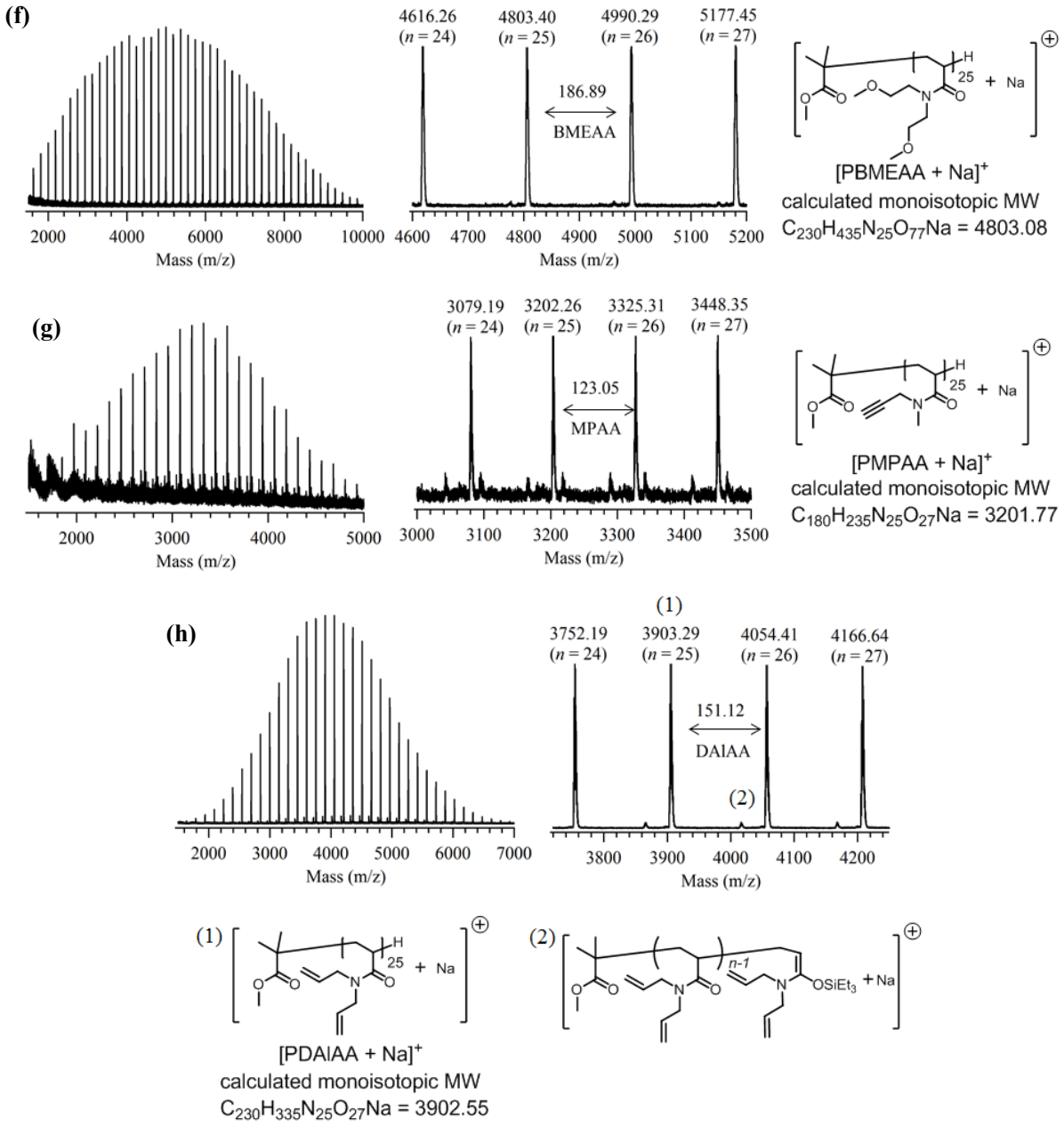


Figure S3. MALDI-TOF MS spectra of (a) PDMAA, (b) PD*n*PAA, (c) PAPI, (d) PNAM, (e) PMMEAA, (f) PBMEAA, (g) PMPAA, and (h) PDAlAA. (Theoretical DP for each polymer, 25)

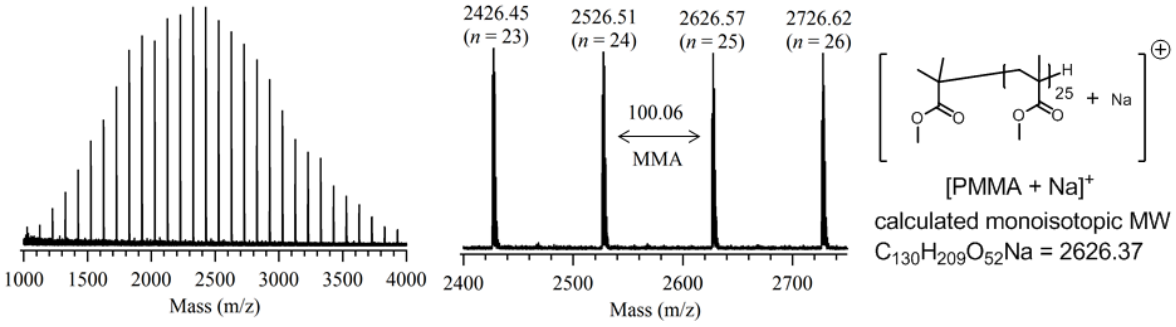


Figure S4. MALDI-TOF MS spectrum of the PMMA residue obtained from the low molecular weight part of run 31 shown in Figure 6(b) (dashed line) after purification by preparative SEC.

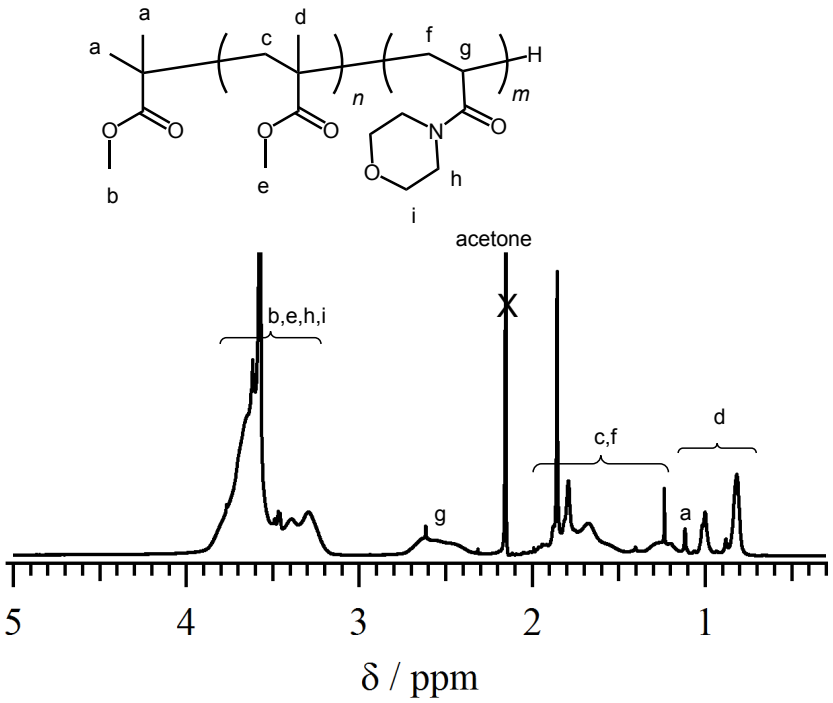


Figure S5. ^{1}H NMR spectrum of the obtained block copolymer from run 35 in $CDCl_3$ (400 MHz).