Supporting information for

Difluoromethylthio Moiety Lowers LCST of Oligo(ethylene glycol)-Based Homopolymers

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Experimental Section

Materials

N-(3-bromopropyl)phthalimide (Aladdin, >98%), tetrabutylammonium bromide (TBAB, Aladdin, >98%), sodium hydrosulfide (NaHS, Aladdin, >98%), boron tribromide (BBr_3, Adamas, 99.99%), (trifluoromethyl)trimethylsilane ($TMSCF_3$, Adamas, 98%), hydrazine hydrate (Aladdin, >98%), carbon disulfide (CS_2, J&K, >98%), acryloyl chloride (TCI, >98%), benzyl bromide (Aladdin, >98%), 3-mercaptopropionic acid (Adamas, 99.99%), potassium hydroxide (KOH, Adamas, 99.99%), 2-methoxyethanol (TCI, >98%), triethylene glycol monomethyl ether (TCI, >98%), methyl tetraglycol (Adamas, 99.99%) and pentaethylene glycol monomethyl ether (TCI, >98%) were used as received. 2,2'-Azobis(isobutyronitrile) (AIBN, Aldrich, 98%) was recrystallized from ethanol twice prior use. Dichloromethane (DCM, Aldrich, 99%) and *N*,*N*-dimethylformamide (DMF, Alfar Aesar, 99%) were dried over CaH_2 and distilled over CaH_2 prior to use. Triethylamine (Et_3N, Aldrich, 99.5%) was dried over KOH and distilled over CaH_2 prior to use. 3-(Benzylthio-carbonothioylthio)propanoic acid was synthesized according to a previous literature.[1]

Characterization

FT-IR spectra are recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a 4 cm^{-1} resolution. All ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a JEOL resonance ECZ 400S spectrometer (400 MHz) in $CDCl_3$. Tetramethylsilane (TMS) and $CDCl_3$ were used as internal standards for ^1H and ^{13}C NMR, respectively;

CF_3CO_2H was used as an external standard for ^{19}F NMR. Electrospray ionization mass spectrometry (ESI-MS) was measured by an Agilent FTMS-7.0 Fourier transformation mass spectrometer. Relative molar mass and dispersity were measured by a conventional gel permeation chromatography (GPC) system equipped with a Waters 515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR3, HR4 and HR5, 7.8×300 mm, particle size: 5 μm). GPC measurements were carried out at 35°C using THF as eluent with a flow rate of 1.0 mL/min. The system was calibrated with linear poly(methyl methacrylate) standards. The phase transition temperature of homopolymer was measured by UV/vis using a Hitachi U-2910 spectrophotometer over a temperature range between 0°C and 70°C, the temperature was controlled and measured by using a DC-1006 variable temperature cryostat with an ascending rate of 1°C/min. The data were obtained after the sample was equilibrated at each temperature for 15 min.

Synthesis of 3-difluoromethylthio-1-propylamine

The key intermediate, 3-difluoromethylthio-1-propylamine, was prepared from *N*-(3-bromopropyl)phthalimide via three steps (Scheme 1) as below.

N-(3-bromopropyl)phthalimide (100.0 g, 373.1 mmol), NaHS (41.8 g, 74.6 mmol) and TBAB (62.7 g, 298.6 mmol) were stirred in 500 mL of DMF at room temperature for 12 h followed by adding water (150 mL) to quench the reaction. The mixture was extracted with DCM (100 mL×3), and the organic phase was then collected and washed with water (200 mL×3). After rotary evaporation, the crude product was

purified by flash column chromatography on silica gel (eluent: EtOA/*n*-hexane, v:v = 1:5), affording 45.6 g (55.1%) of *N*-(3-mercaptopropyl)phthalimide **1** as a white crystal. ^{1}H NMR ($CDCl_3$): δ (ppm): 7.84, 7.71 (4H, phenyl), 3.80 (2H, $NCH_2CH_2CH_2SH$), 2.53 (2H, $NCH_2CH_2CH_2SH$), 1.98 (2H, $NCH_2CH_2CH_2SH$), 1.58 (1H, $NCH_2CH_2CH_2SH$). ^{13}C NMR ($CDCl_3$): δ (ppm): 168.3, 133.9, 132.0, 123.2, 36.3, 32.6, 21.8. FT-IR: ν (cm^{-1}): 3451, 2940, 2554, 2081, 1761, 1693, 1467, 1435. ESI-MS *m/z*: 222.06 $[M+H]^{+1}$. HR-MS (ESI) *m/z*: $[M+H]^{+1}$, calcd for $C_{11}H_{12}O_2NS^{+1}$ 222.0583, Found 222.0582.

N-(3-Mercaptopropyl)phthalimide **1** (16.0 g, 72.1 mmol) and KOH (24.2 g, 96.9 mL, 20% aq) were first added to 200 mL of DCM and the solution was cooled to 0°C. $TMSCF_2Br$ (22.4 mL, 144.2 mmol) in 50 mL of DCM was then added dropwise within 30 min under stirring. The reaction lasted 1 h and was quenched by water. The organic phase was collected and washed with water (200 mL×3). After rotary evaporation, the crude product was purified by column chromatography on silica gel (eluent: *n*-hexane), affording 10.2 g (54.3%) of *N*-(3-difluoromethylthiopropyl)-phthalimide **2** as a white solid. ^{1}H NMR ($CDCl_3$): δ (ppm): 7.84, 7.72 (4H, phenyl), 6.80 (1H, $NCH_2CH_2CH_2SCF_2H$), 3.80 (2H, $NCH_2CH_2CH_2SCF_2H$), 2.82 (2H, $NCH_2CH_2CH_2SCF_2H$), 2.06 (2H, $NCH_2CH_2CH_2SCF_2H$). ^{13}C NMR ($CDCl_3$): δ (ppm): 168.2, 134.1, 131.9, 123.3, 120.5 (SCF_2H), 36.6, 29.3, 24.5. ^{19}F NMR ($CDCl_3$): δ (ppm): -92.74 (2F, SCF_2H). FT-IR: ν (cm^{-1}): 3459, 2942, 1769, 1701, 1612, 1464, 1437. ESI-MS *m/z*: 294.04 $[M+Na]^{+1}$. HR-MS (ESI) *m/z*: $[M+Na]^{+1}$, calcd for $C_{12}H_{11}O_2NF_2NaS^{+1}$ 294.0371, Found 294.0372.

N-(3-difluoromethylthiopropyl)phthalimide **2** (8.60 g, 31.7 mmol) and hydrazine hydrate (50 mL, 20 eq) were refluxed in DCM (100 mL) at 75°C for 8 h. The mixture was washed by dichloromethane. The solution was cooled to room temperature and filtered. The obtained white solid was washed with DCM (50 mL×3) followed by drying over anhydrous Na_2SO_4. After rotary evaporation, the residue was distilled at 50°C under reduced pressure to give 3.00 g (67.1%) of 3-difluoromethylthio-1-propylamine **3** as a colorless liquid. ^{1}H NMR (CD_3OD): δ (ppm): 7.01 (1H, $NH_2CH_2CH_2CH_2SCF_2\mathit{H}$), 2.83 (2H, $NH_2\mathit{CH}_2CH_2CH_2SCF_2H$), 2.70 (2H, $NH_2CH_2CH_2\mathit{CH}_2SCF_2H$), 1.79 (2H, $NH_2CH_2\mathit{CH}_2CH_2SCF_2H$). ^{13}C NMR ($CD_3OD$): δ (ppm): 120.7 ($S\mathit{C}F_2H$), 40.6, 33.4, 24.5. ^{19}F NMR (CD_3OD): δ (ppm): -94.44 (2F, $SC\mathit{F}_2H$). FT-IR: ν (cm^{-1}): 2936, 2863, 1653, 1591, 1442, 1325. ESI-MS *m/z*: 142.05 $[M+H]^{+1}$. HR-MS (ESI) *m/z*: $[M+H]^{+1}$, calcd for $C_4H_{10}O_2NF_2S^{+1}$ 142.0497, Found 142.0496.

Synthesis of MEO_nA (n = 2~5)

The with different number of ethylene glycol unit, MEO_nA (n = 2~5), were prepared via esterification reaction between acryloyl chloride and the corresponding oligo(ethylene glycol) methyl ether. Taking MEO_2A as an example, the procedure is as below.

Diethylene glycol monomethyl ether (25.0 g, 208 mmol) and Et_3N (26.0 mL, 188 mmol) were dissolved in 150 mL of anhydrous dichloromethane. The solution was cooled to 0°C followed by adding acryloyl chloride (20.4 mL, 250 mmol) dropwise

within 10 min. The mixture was slowly warmed up to room temperature and stirred at room temperature for 12 h. The precipitated salt was removed by filtration and the filtrate was washed with brine three times. The organic layer was evaporated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane, v:v = 1:3), affording 29.5 g (81.5 %) of MEO_2A as a light yellow oil. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.43, 6.13, 5.80 (3H, C*H*=CH_2), 4.31 (2H, $CO_2CH_2CH_2$), 3.73 (2H, $CO_2CH_2CH_2$), 3.63 (2H, $OCH_2CH_2OCH_3$), 3.53 (2H, $OCH_2CH_2OCH_3$), 3.36 (3H, OCH_3).

MEO_3A: 75.5% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.36, 6.09, 5.77 (3H, C*H*=CH_2), 4.25 (2H, $CO_2CH_2CH_2$), 3.68 (2H, $CO_2CH_2CH_2$), 3.60 (6H, $OCH_2CH_2OCH_2CH_2OCH_3$), 3.49 (2H, $OCH_2CH_2OCH_2CH_2OCH_3$), 3.32 (3H, OCH_3).

MEO_4A: 68.0% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.37, 6.09, 5.77 (3H, C*H*=CH_2), 4.25 (2H, $CO_2CH_2CH_2$), 3.43-3.74 (14H, $CO_2CH_2CH_2(OCH_2CH_2)_3OCH_3$), 3.31 (3H, OCH_3). ^{13}C NMR ($CDCl_3$): δ (ppm): 166.2, 130.8, 128.2, 71.9, 70.6, 70.4, 69.1, 63.6, 59.0. FT-IR: ν (cm^{-1}): 2872, 1722, 1635, 1453, 1407,1352, 1295. ESI-MS *m/z*: 263.15 $[M+H]^{+1}$. HR-MS (ESI) *m/z*: $[M+H]^{+1}$, calcd for $C_{12}H_{23}O_6^{+1}$ 263.1489, Found 263.1489.

MEO_5A: 52.4% yield as a colorless oil. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.41, 6.13, 5.81 (3H, C*H*=CH_2), 4.27 (2H, $CO_2CH_2CH_2$), 3.49-3.67 (18H, $CO_2CH_2CH_2(OCH_2CH_2)_4OCH_3$), 3.40 (s, OCH_3). FT-IR: ν (cm^{-1}): 2878, 2822, 1722, 1636, 1453, 1407, 1355, 1271. ESI-MS *m/z*: 307.18 $[M+H]^{+1}$. HR-MS (ESI) *m/z*: $[M+H]^{+1}$, calcd for $C_{14}H_{27}O_7^{+1}$ 307.1751, Found 307.1751.

Synthesis of DFTP-MEO$_n$-AM (n = 2~5)

The acrylamide monomers with difluoromethylthio moiety and different number of ethylene glycol unit, DFTP-MEO$_n$-AM (n = 2~5), were prepared through aza-Michael addition reaction between 3-difluoromethylthio-1-propylamine and the corresponding MEO$_n$A (n = 2~5), followed by amidation reaction with acryloyl chloride (Scheme 1). Taking DFTP-MEO$_2$-AM as an example, the procedure is as below.

3-Difluoromethylthio-1-propylamine **3** (3.50 g, 24.8 mmol) and MEO$_2$A (4.23 g, 24.3 mmol) were added to a 25 mL flask at ambient temperature. The mixture was stirred at room temperature for 12 h, then the residue (7.50 g) and Et_3N (5.0 mL, 36.1 mmol) were dissolved in DCM (30 mL). The solution was cooled to 0°C followed by adding acryloyl chloride (2.5 mL, 30.9 mmol) dropwise within 10 min. The mixture was slowly warmed up to room temperature and stirred at room temperature for 12 h. The precipitated salt was removed by filtration and the filtrate was washed with brine three times. After rotary evaporation, the residue was purified by flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane, v:v = 1:2), affording 3.62 g (39.5 %) of DFTP-MEO$_2$-AM **5a** as a yellow oil. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.79 (1H, $CH_2CH_2NCH_2CH_2CH_2SCF_2\mathit{H}$), 6.54 (1H, CH_2=CH), 6.34, 5.69 (2H, CH_2=CH), 4.23 (2H, $CO_2C\mathit{H}_2CH_2$), 3.64, 3.51 (6H, $CO_2CH_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2OCH_3$; 4H, $CH_2C\mathit{H}_2NC\mathit{H}_2CH_2CH_2SCF_2H$), 3.36 (3H, $OC\mathit{H}_3$), 2.79 (2H, $CH_2CH_2NCH_2CH_2C\mathit{H}_2SCF_2H$), 2.63 (2H, $C\mathit{H}_2CH_2NCH_2CH_2CH_2SCF_2H$), 1.86 (2H, $CH_2CH_2NCH_2C\mathit{H}_2CH_2SCF_2H$). ^{13}C NMR ($CDCl_3$): δ (ppm): 172.1, 166.3, 128.6, 127.1, 121.7 (S$\mathit{C}F_2H$), 71.8, 70.4, 68.9, 63.7, 59.0, 47.4, 43.7, 34.2, 29.9, 24.7. ^{19}F

NMR ($CDCl_3$): δ (ppm): -92.6 (2F, SCF_2H). FT-IR: ν (cm^{-1}): 3475, 2929, 2883, 1730, 1645, 1609, 1450, 1430, 1378, 1313. ESI-MS *m/z*: 370.15 $[M+H]^{+1}$. HR-MS (ESI) *m/z*: $[M+H]^{+1}$, calcd for $C_{15}H_{26}O_5NF_2S^{+1}$ 370.1494, Found 370.1494.

DFTP-MEO$_3$-AM 5b: 41.0% yield as a yellow oil. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.79 (1H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$), 6.40 (1H, CH_2=C*H*), 6.15, 5.82 (2H, CH_2=CH), 4.29 (2H, $CO_2CH_2CH_2$), 3.68, 3.53, 3.43 (10H, $CO_2CH_2CH_2(OCH_2CH_2)_2OCH_3$; 4H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$), 3.35 (3H, OCH_3), 2.83 (2H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$), 2.61 (2H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$), 1.91 (2H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$). ^{13}C NMR ($CDCl_3$): δ (ppm): 172.0, 166.3, 128.8, 127.2, 120.3 (S*C*F$_2$H), 71.9, 70.6, 68.9, 64.0, 63.8, 59.0, 47.4, 43.7, 34.2, 29.8, 24.7. ^{19}F NMR ($CDCl_3$): δ (ppm): -92.6 (SCF_2H). FT-IR: ν (cm^{-1}): 3503, 2877, 1729, 1646, 1610, 1451, 1378, 1253. ESI-MS *m/z*: 414.18 $[M+H]^{+1}$. HR-MS (ESI) *m/z*: $[M+H]^{+1}$, calcd for $C_{17}H_{30}O_6NF_2S^{+1}$ 414.1756, Found 414.1756.

DFTP-MEO$_4$-AM 5c: 47.5% yield as a yellow oil. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.80 (1H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$), 6.56 (1H, CH_2=C*H*), 6.34, 5.70 (2H, CH_2=CH), 4.22 (2H, $CO_2CH_2CH_2$), 3.70-3.44 (14H, $CO_2CH_2CH_2(OCH_2CH_2)_3OCH_3$; 4H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$), 3.35 (3H, OCH_3), 2.79 (2H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$), 2.68 (2H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$), 1.93 (2H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$). ^{13}C NMR ($CDCl_3$): δ (ppm): 172.1, 166.4, 128.6, 127.3, 120.5 (S*C*F$_2$H), 71.9, 70.6, 68.9, 64.1, 63.9, 59.0, 47.5, 43.7, 34.3, 30.0, 24.8. ^{19}F NMR ($CDCl_3$): δ (ppm): -92.6 (2F, CF_2H). FT-IR: ν (cm^{-1}): 3482, 2876, 1730, 1644, 1608, 1451, 1377, 1351, 1308. ESI-MS *m/z*: 458.20 $[M+H]^{+1}$. HR-MS (ESI)

m/z: $[M+H]^{+1}$, calcd for $C_{19}H_{34}O_6NF_2S^{+1}$ 458.2019, Found 458.2018.

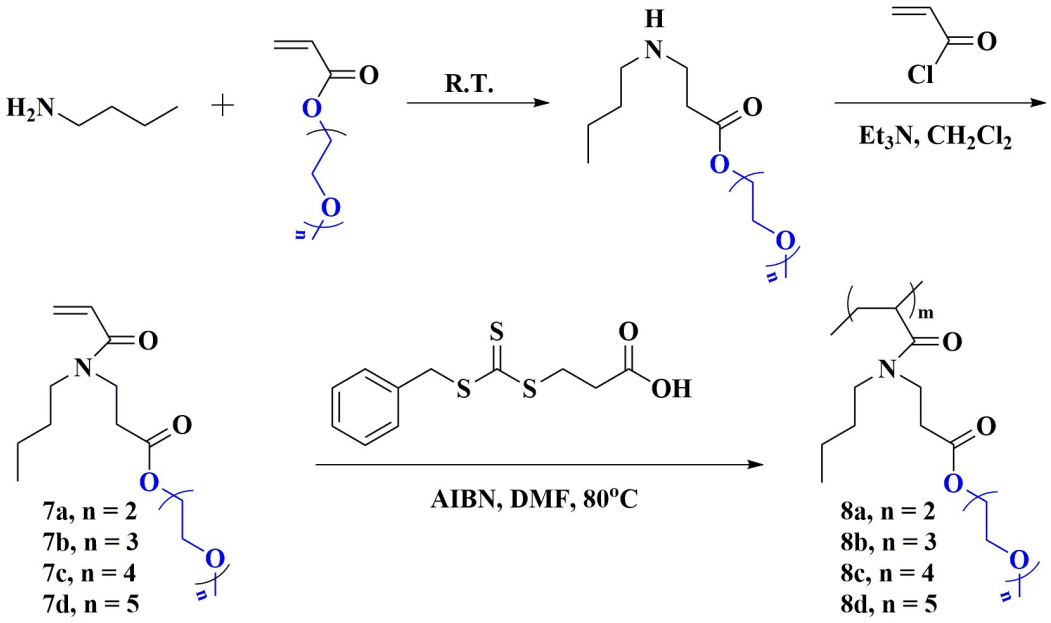
DFTP-MEO$_5$-AM 5d: 40.6% yield as a yellow oil. ^{1}H NMR ($CDCl_3$):δ (ppm): 6.80 (1H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$), 6.56 (1H, CH_2=C*H*), 6.35, 5.70 (CH_2=CH), 4.22 (2H, $CO_2CH_2CH_2$), 3.72-3.44 (18H, $CO_2CH_2CH_2(OCH_2CH_2)_4OCH_3$; 4H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$), 3.35 (3H, OCH_3), 2.80 (2H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$), 2.65 (2H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$), 1.94 (2H, $CH_2CH_2NCH_2CH_2CH_2SCF_2H$). ^{13}C NMR ($CDCl_3$): δ (ppm): 172.1, 166.4, 128.8, 127.3, 120.4 (S*C*F$_2$H), 71.9, 70.6, 69.0, 64.1, 63.8, 59.0, 47.4, 43.7, 34.3, 29.8, 24.7. ^{19}F NMR ($CDCl_3$): δ (ppm): -92.6 (2F, SC*F*$_2$H). FT-IR: ν (cm^{-1}): 2923, 2853, 1716, 1663, 1462, 1375, 1242, 1169. ESI-MS *m/z*: 502.23 $[M+H]^{+1}$. HR-MS (ESI) *m/z*: $[M+H]^{+1}$, calcd for $C_{21}H_{38}O_8NF_2S^{+1}$ 502.2281, Found 502.2281.

Synthesis of Bu-MEO$_n$-AM (n = 2~5)

The acrylamide monomers with different number of ethylene glycol unit, Bu-MEO$_n$-AM (n = 2~5), were prepared through similar steps as DFTP-MEO$_n$-AM, starting from *n*-butylamine (Scheme S1). Taking Bu-MEO$_2$-AM as an example, the procedure is as below.

n-Butylamine (2.75 g, 37.6 mmol) and MEO$_2$A (3.98 g, 22.9 mmol) were added to a 25 mL flask at ambient temperature. The mixture was stirred at room temperature for 12 h, then the residue (6.31 g) and Et_3N (5.3 mL, 38.3 mmol) were dissolved in DCM (30 mL). The solution was cooled to 0°C followed by adding acryloyl chloride (2.7 mL, 33.1 mmol) dropwise within 10 min. The mixture was slowly warmed up to

room temperature and stirred at room temperature for 12 h. The precipitated salt was removed by filtration and the filtrate was washed with brine three times. After rotary evaporation, the residue was purified by flash column chromatography on silica gel (eluent: EtOAc/*n*-hexane, v:v = 1:2), affording 3.75 g (49.3%) of Bu-MEO$_2$-AM **7a** as a yellow oil. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.51 (1H, CH_2=C*H*), 6.32, 5.65 (2H, C*H*$_2$=CH), 4.22 (2H, $CO_2CH_2CH_2$), 3.67 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_3$), 3.62 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_3$), 3.52 (6H, $CO_2CH_2CH_2OCH_2CH_2OCH_3$), 3.35 (3H, OCH_3), 2.64 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_2$), 1.52 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_3$), 1.28 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_3$), 0.90 (3H, $CH_2CH_2NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ (ppm): 172.1, 166.3, 127.9, 127.6, 71.9, 70.6, 69.0, 63.7, 59.1, 48.8, 43.1, 32.8, 31.8, 19.9, 13.8. FT-IR: ν (cm^{-1}): 3471, 2930, 2873, 1731, 1645, 1608, 1400, 1377, 1281, 1252. ESI-MS *m/z*: 302.20 $[M+H]^{+1}$. HR-MS (ESI) *m/z*: $[M+H]^{+1}$, calcd for $C_{15}H_{28}O_5N^{+1}$ 302.1962, Found 302.1962.



Scheme S1. Synthesis and RAFT homopolymerization of Bu-MEO$_n$-AM monomers (n = 2~5).

Bu-MEO$_3$-AM 7b: 38.7% yield as a yellow oil. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.51 (1H, CH_2=C*H*), 6.30, 5.66 (2H, C*H*$_2$=CH), 4.20 (2H, $CO_2CH_2CH_2$), 3.64, 3.52 (4H, $CH_2CH_2NCH_2CH_2CH_2CH_3$; 10H, $CO_2CH_2CH_2(OCH_2CH_2)_2OCH_3$), 3.35 (3H, OCH_3), 2.65 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_2$), 1.51 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_3$), 1.27 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_3$), 0.90 (3H, $CH_2CH_2NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ (ppm): 172.1, 166.3, 127.9, 127.6, 71.9, 70.6, 69.0, 63.7, 59.1, 48.8, 43.1, 32.8, 31.8, 19.9, 13.8. FT-IR: ν (cm^{-1}): 3500, 3315, 2930, 2871, 1732, 1645, 1608, 1450, 1375, 1251. ESI-MS *m/z*: 346.22 $[M+H]^{+1}$. HR-MS (ESI) *m/z*: $[M+H]^{+1}$, calcd for $C_{17}H_{32}O_6N^{+1}$ 346.2224, Found 346.2224.

Bu-MEO$_4$-AM 7c: 52.5% yield as a yellow oil. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.50 (1H, CH_2=C*H*), 6.32, 5.66 (2H, C*H*$_2$=CH), 4.21 (2H, $CO_2CH_2CH_2$), 3.65, 3.53 (4H, $CH_2CH_2NCH_2CH_2CH_2CH_3$; 14H, $CO_2CH_2CH_2(OCH_2CH_2)_3OCH_3$), 3.35 (3H, OCH_3), 2.65 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_2$), 1.53 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_3$), 1.30 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_3$), 0.92 (3H, $CH_2CH_2NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ (ppm): 172.1, 166.3, 128.0, 127.6, 71.9, 70.6, 69.0, 63.8, 59.0, 48.8, 43.1, 32.8, 31.8, 20.0, 13.8. FT-IR: ν (cm^{-1}): 2928, 2870, 1732, 1646, 1611, 1450, 1376, 1250, 1189. ESI-MS *m/z*: 390.25 $[M+H]^{+1}$. HR-MS (ESI) *m/z*: $[M+H]^{+1}$, calcd for $C_{19}H_{36}O_7N^{+1}$ 390.2486, Found 390.2486.

Bu-MEO$_5$-AM 7d: 45.0% yield as a yellow oil. ^{1}H NMR ($CDCl_3$): δ (ppm): 6.50 (1H, CH_2=C*H*), 6.32, 5.65 (2H, C*H*$_2$=CH), 4.21 (2H, $CO_2CH_2CH_2$), 3.66, 3.52 (4H, $CH_2CH_2NCH_2CH_2CH_2CH_3$; 18H, $CO_2CH_2CH_2(OCH_2CH_2)_4OCH_3$), 3.35 (3H, OCH_3), 2.65 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_2$), 1.53 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_3$), 1.30

(2H, $CH_2CH_2NCH_2CH_2C\mathit{H}_2CH_3$), 0.90 (3H, $CH_2CH_2NCH_2CH_2CH_2C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$): δ (ppm): 172.0, 166.2, 128.0, 127.5, 71.9, 70.5, 69.0, 63.8, 59.0, 48.8, 43.1, 32.7 31.8, 19.9, 13.7. FT-IR: ν (cm^{-1}): 3523, 2870, 1731, 1645, 1609, 1451, 1376, 1283, 1251, 1100. ESI-MS *m/z*: 434.27 $[M+H]^{+1}$. HR-MS (ESI) *m/z*: $[M+H]^{+1}$, calcd for $C_{21}H_{40}O_8N^{+1}$ 434.2748, Found 434.2749.

RAFT homopolymerization of DFTP-MEO$_n$-AM (n = 2~5)

In a typical procedure ([monomer]:[CTA]:[AIBN] = 100:2:1), AIBN (3.4 mg, 0.021 mmol), 3-(benzylthiocarbonothioylthio)propanoic acid (11.2 mg, 0.041 mmol) and DFTP-MEO_2-AM **5a** (761.0 mg, 2.06 mmol) were first added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. Next, dry DMF (0.6 mL) was charged via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 80°C. The polymerization lasted 24 h and was terminated by putting the flask into liquid N_2. The reaction mixture was precipitated into *n*-hexane/Et_2O (v:v = 1:1). The crude product was purified by repeated dissolution in DCM and precipitation in *n*-hexane/Et_2O (v:v = 1:1) followed by drying *in vacuo* overnight to give 290.4 mg of poly(DFTP-MEO_2-AM) **6a** as a yellow oil. GPC: M_n = 8,000 g/mol, M_w/M_n = 1.27. ^1H NMR ($CDCl_3$): δ (ppm): 6.90 (1H, $CH_2CH_2NCH_2CH_2CH_2SCF_2\mathit{H}$), 4.19 (2H, $CO_2C\mathit{H}_2CH_2$), 3.63, 3.53 (6H, $CO_2CH_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2OCH_3$; 4H, $CH_2C\mathit{H}_2NC\mathit{H}_2CH_2CH_2SCF_2H$), 3.34 (1H, $OC\mathit{H}_3$), 2.75, 2.55 (4H, $C\mathit{H}_2CH_2NCH_2CH_2C\mathit{H}_2SCF_2H$; 1H, $CH_2C\mathit{H}$), 1.85 (2H,

$CH_2CH_2NCH_2CH_2CH_2SCF_2H$; 2H, CH_2CH). ^{19}F NMR ($CDCl_3$): δ (ppm): -92.5 (2F, SCF_2H). FT-IR: ν (cm^{-1}): 3293, 3080, 2933, 1641, 1531, 1440.

RAFT Homopolymerization of Bu-MEO$_n$-AM (n = 2~5)

In a typical procedure ([monomer]:[CTA]:[AIBN] = 100:2:1), AIBN (4.4 mg, 0.027 mmol), 3-(benzylthiocarbonothioylthio)propanoic acid (14.5 mg, 0.054 mmol), and Bu-MEO$_2$-AM **7a** (798.5 mg, 2.66 mmol) were first added to a 25 mL Schlenk flask (flame-dried under vacuum prior to use) sealed with a rubber septum for degassing and kept under N_2. Next, dry DMF (0.6 mL) was charged via a gastight syringe. The flask was degassed by three cycles of freezing-pumping-thawing followed by immersing the flask into an oil bath set at 80°C. The polymerization lasted 24 h and was terminated by putting the flask into liquid N_2. The reaction mixture was precipitated into *n*-hexane/Et_2O (v:v = 1:1). The crude product was purified by repeated dissolution in DCM and precipitation in *n*-hexane/Et_2O (v:v = 1:1) followed by drying *in vacuo* overnight to give 361.4 mg of poly(Bu-MEO$_n$-AM) **8a** as a yellow oil of. GPC: M_n = 6,000 g/mol, M_w/M_n = 1.04. ^1H NMR ($CDCl_3$): δ (ppm): 4.20 (2H, $CO_2CH_2CH_2$), 3.64, 3.53 (4H, $CH_2CH_2NCH_2CH_2CH_2CH_3$; 6H, $CO_2CH_2CH_2OCH_2CH_2OCH_3$), 3.36 (3H, OCH_3), 2.67 (2H, $CH_2CH_2NCH_2CH_2CH_2CH_2$), 2.17 (2H, CH_2CH), 1.39 (2H, CH_2CH; 4H, $CH_2CH_2NCH_2CH_2CH_2CH_3$), 0.92 (3H, $CH_2CH_2NCH_2CH_2CH_2CH_3$). FT-IR: ν (cm^{-1}): 2929, 2872, 1730, 1634, 1450, 1379, 1307.

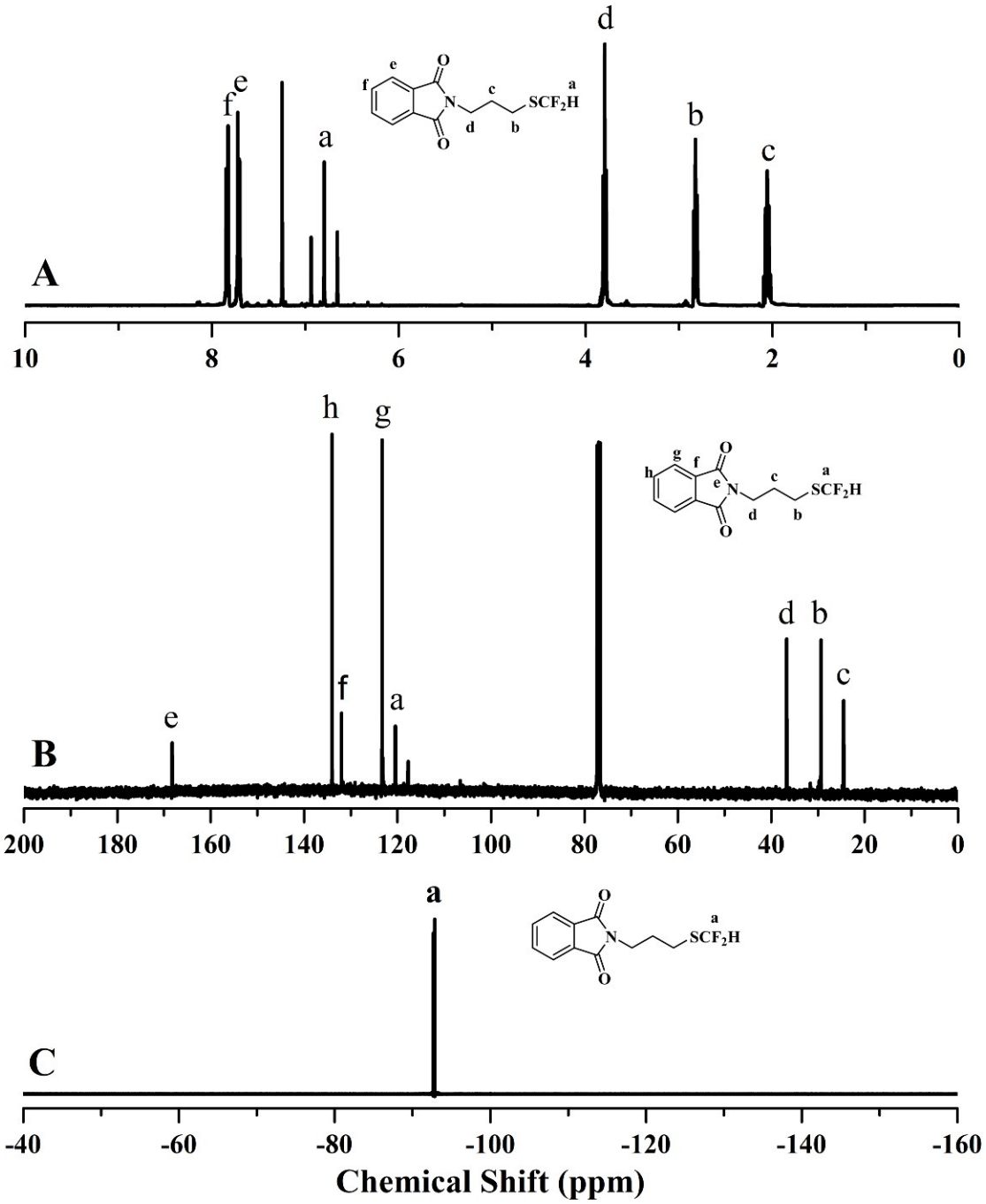


Figure S1. ^{1}H (A), ^{13}C (B), and ^{19}F (C) NMR spectra of *N*-(3-difluorothiomethyl)-phthalimide **2** in $CDCl_3$.

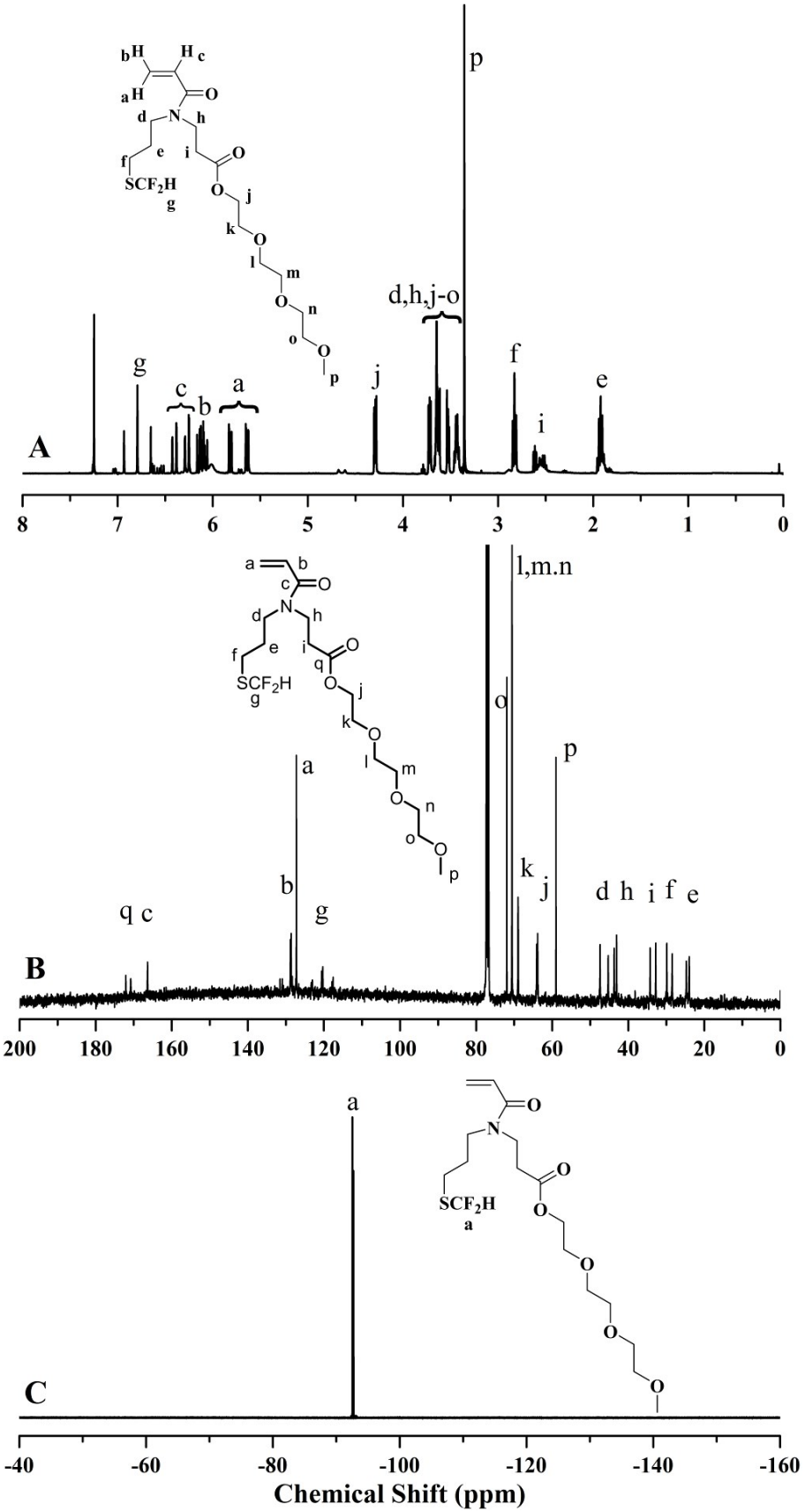


Figure S2. ^{1}H (A), (B) ^{13}C and (C) ^{19}F NMR spectra of DFTP-MEO_3-AM **5b** in $CDCl_3$.

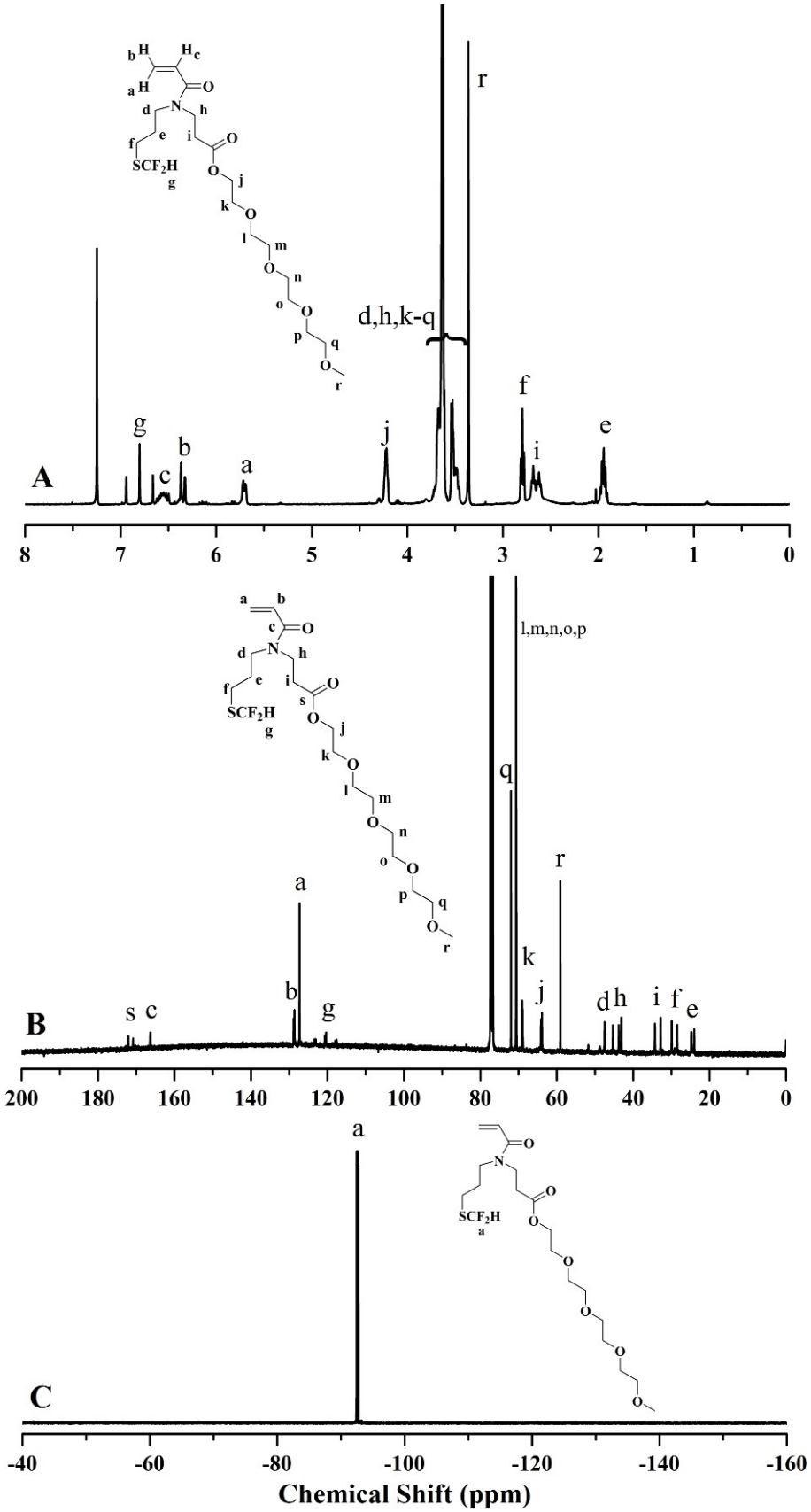


Figure S3. ^{1}H (A), ^{13}C (B) and (C) ^{19}F NMR spectra of DFTP-MEO_4-AM **5c** in $CDCl_3$.

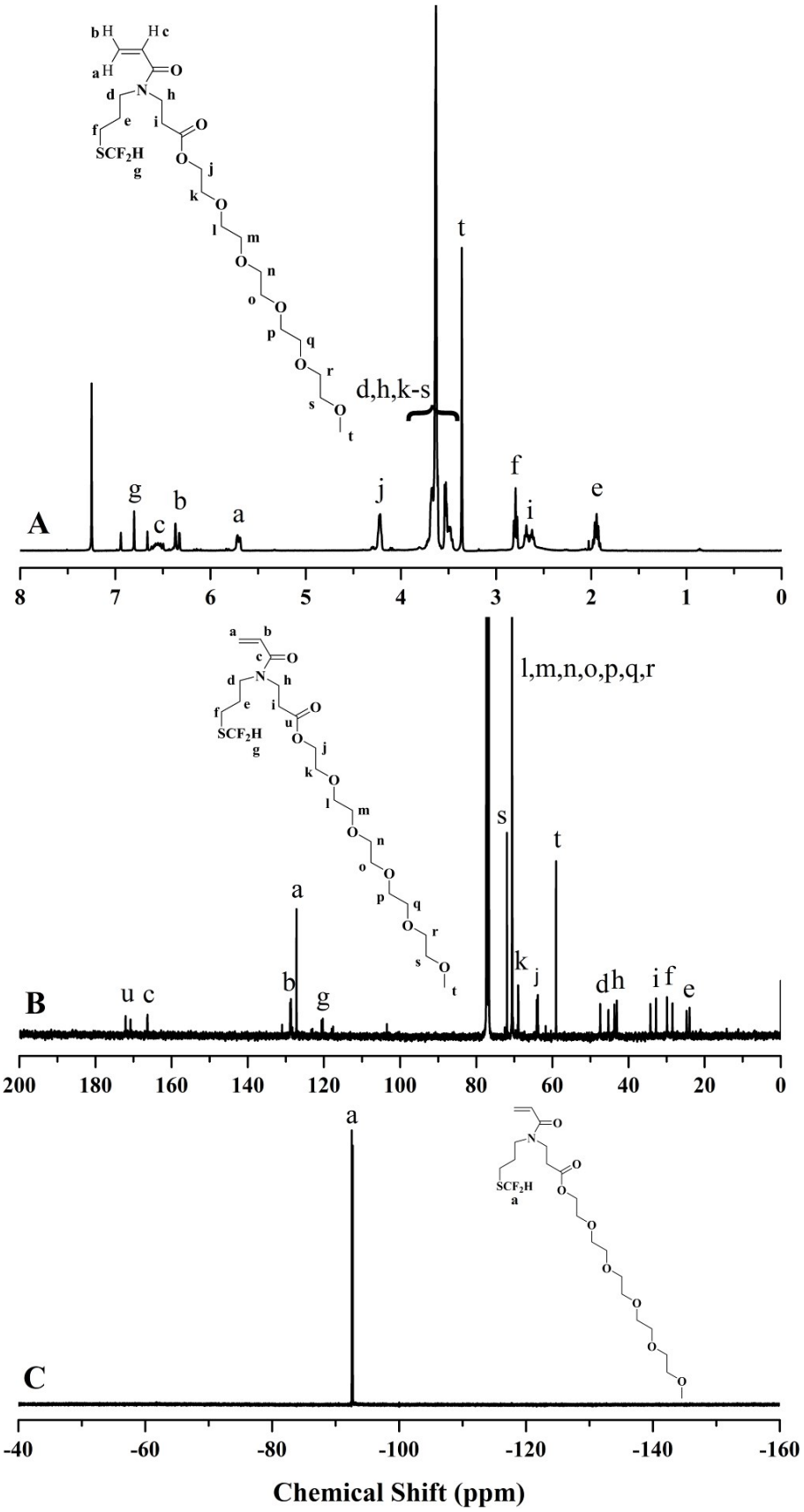


Figure S4. ^{1}H (A), ^{13}C (B) and ^{19}F(C) NMR spectra of DFTP-MEO_5-AM **5d** in $CDCl_3$.

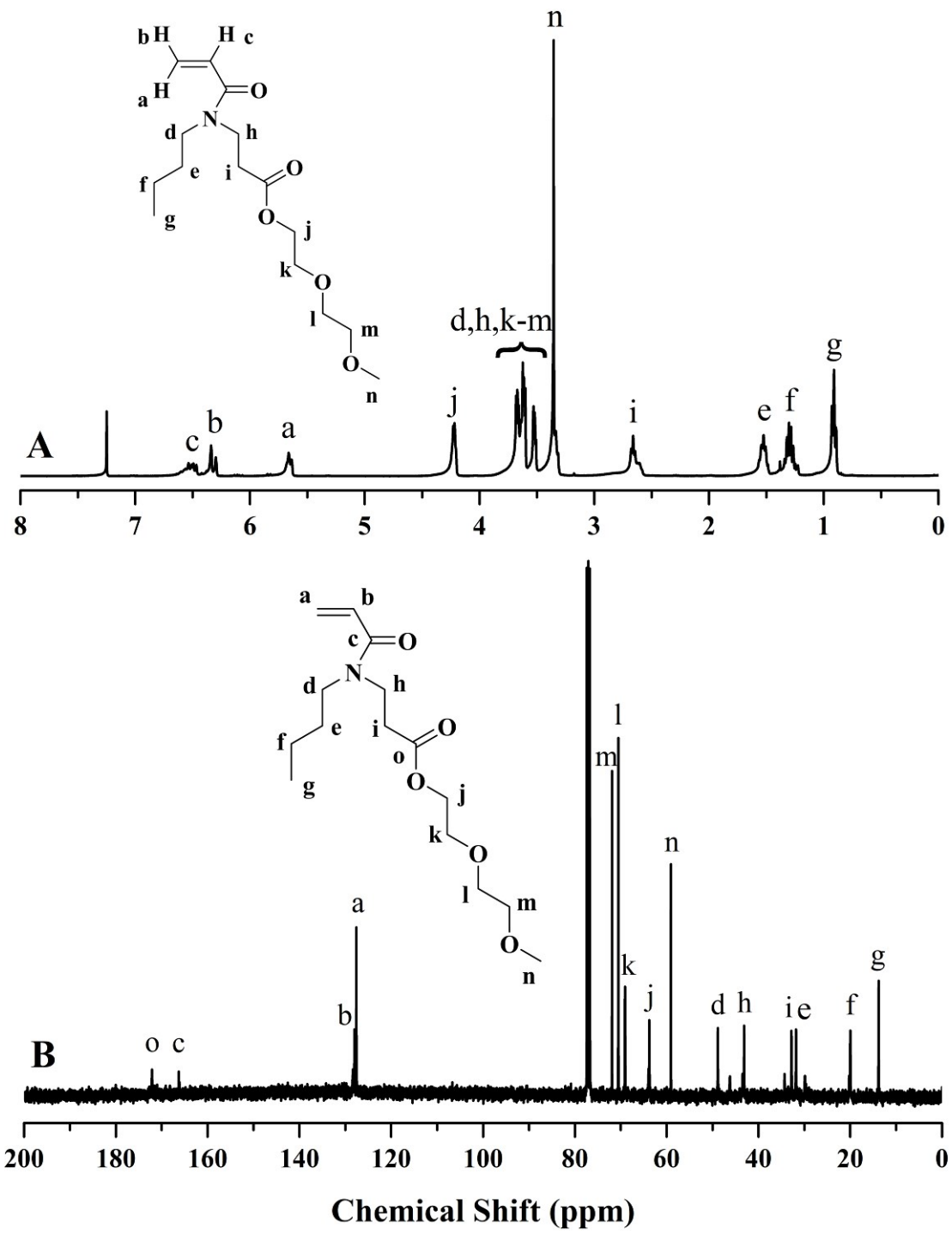


Figure S5. ^{1}H (A) and ^{13}C (B) NMR spectra of Bu-MEO_2-AM **7a** in $CDCl_3$.

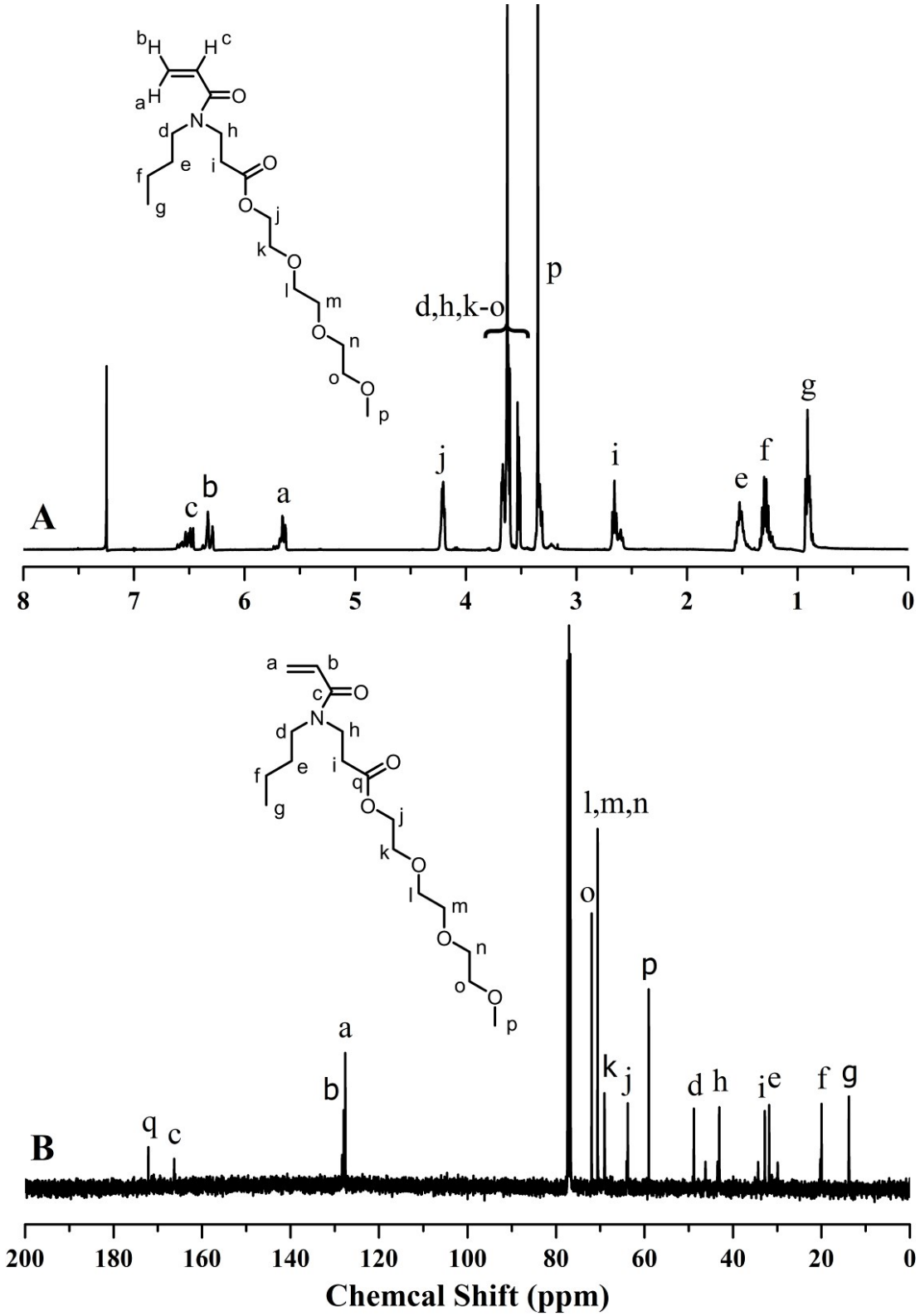


Figure S6. ^{1}H (A) and ^{13}C (B) NMR spectra of Bu-MEO_3-AM **7b** in $CDCl_3$.

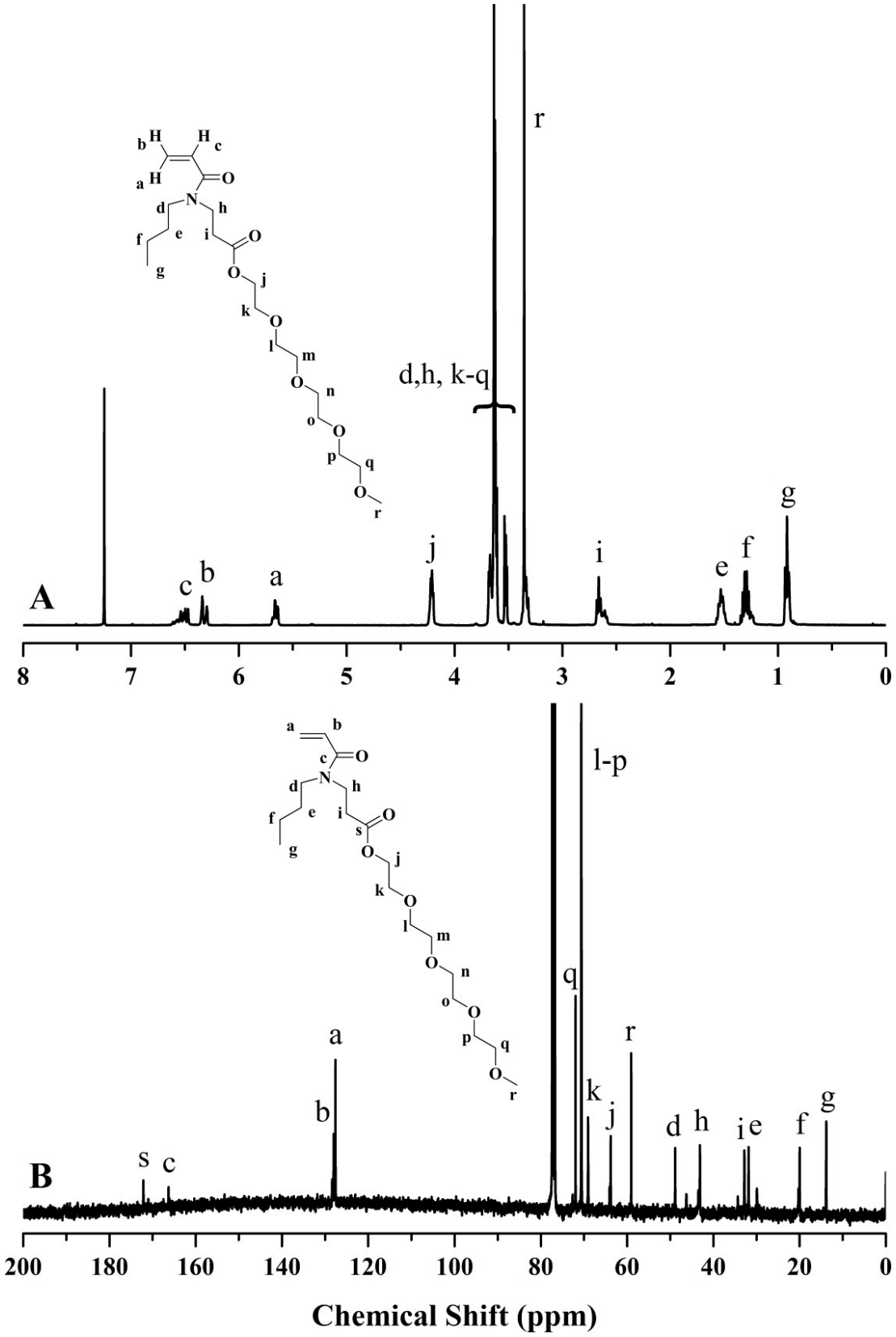


Figure S7. ^{1}H (A) and ^{13}C (B) NMR spectra of Bu-MEO_4-AM **7c** in $CDCl_3$.

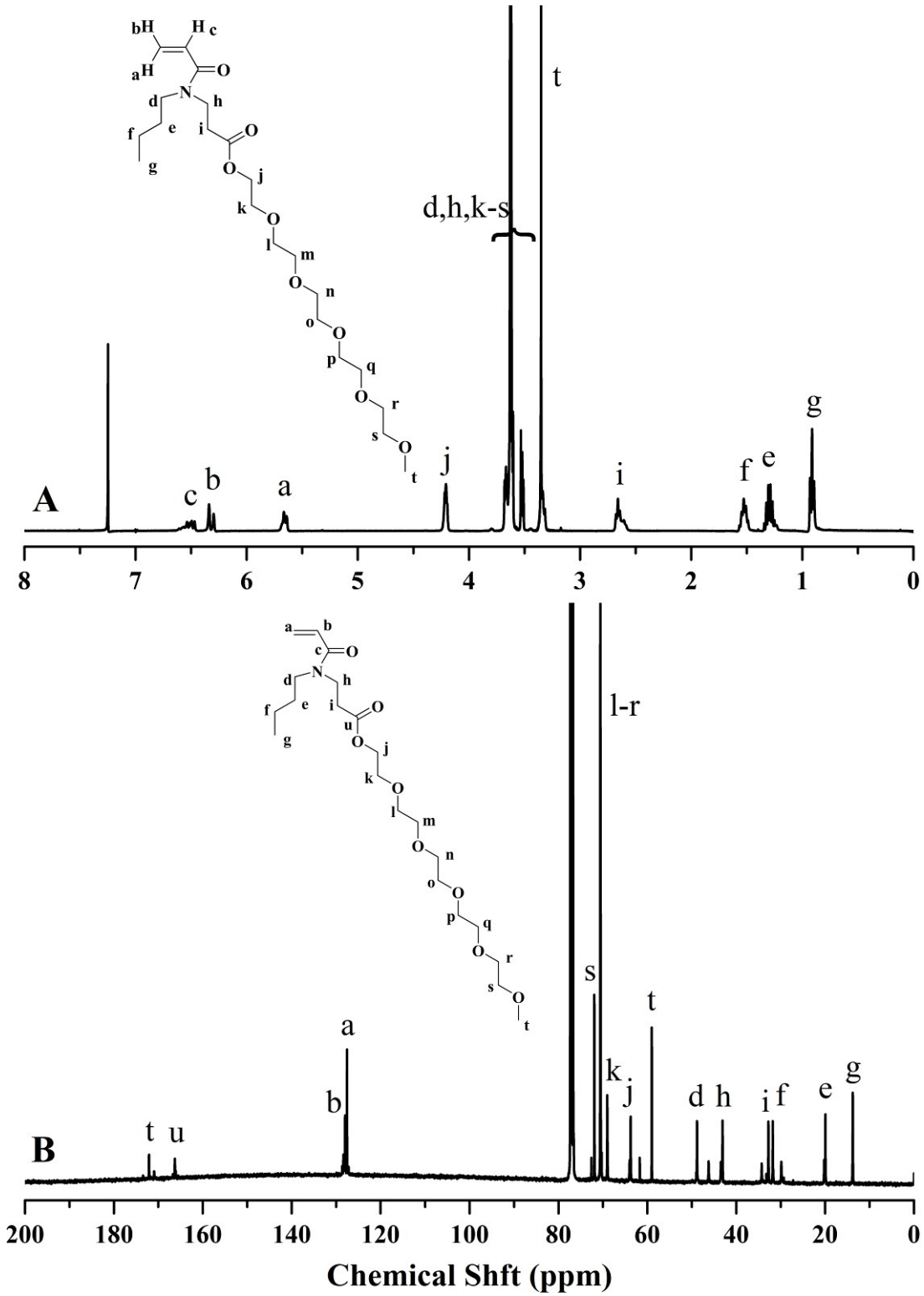


Figure S8. ^{1}H (A) and ^{13}C (B) NMR spectra of Bu-MEO_5-AM **7d** in $CDCl_3$.

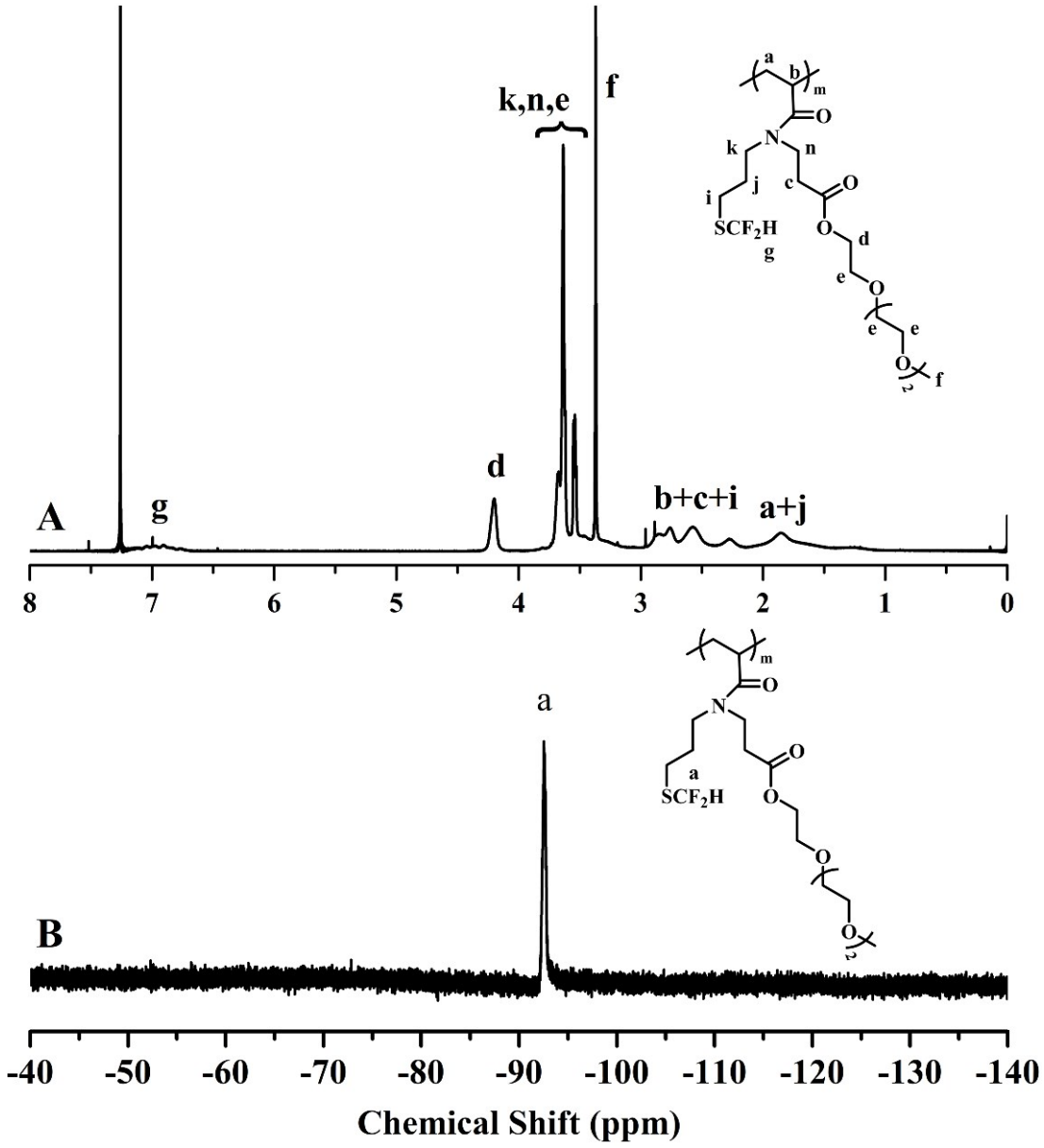


Figure S9. ^{1}H (A) and ^{19}F (B) NMR spectra of poly(DFTP-MEO_3-AM) **6b** in $CDCl_3$.

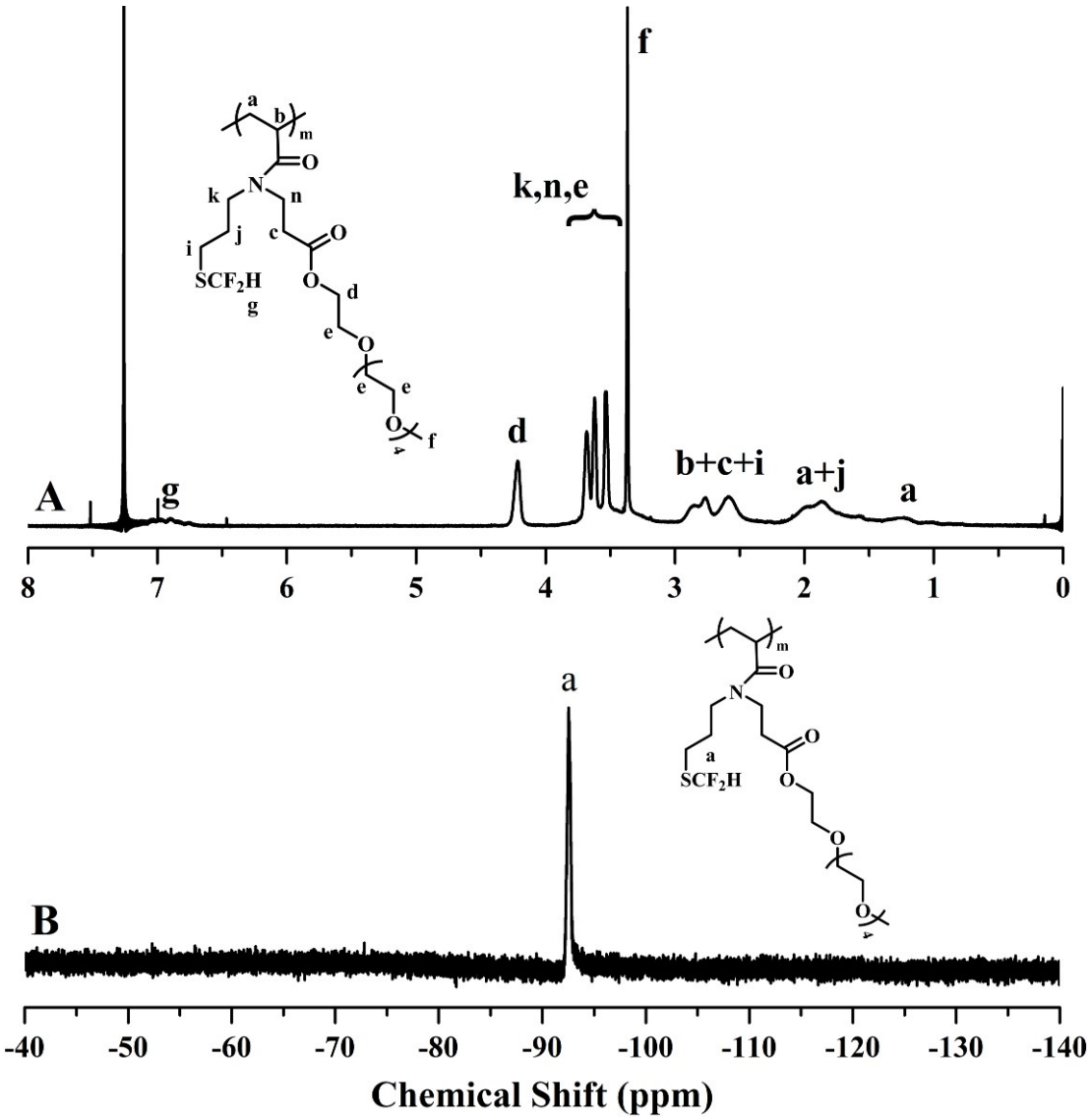


Figure S10. ^{1}H (A) and ^{19}F (B) NMR spectra of poly(DFTP-MEO_5-AM) **6d** in $CDCl_3$.

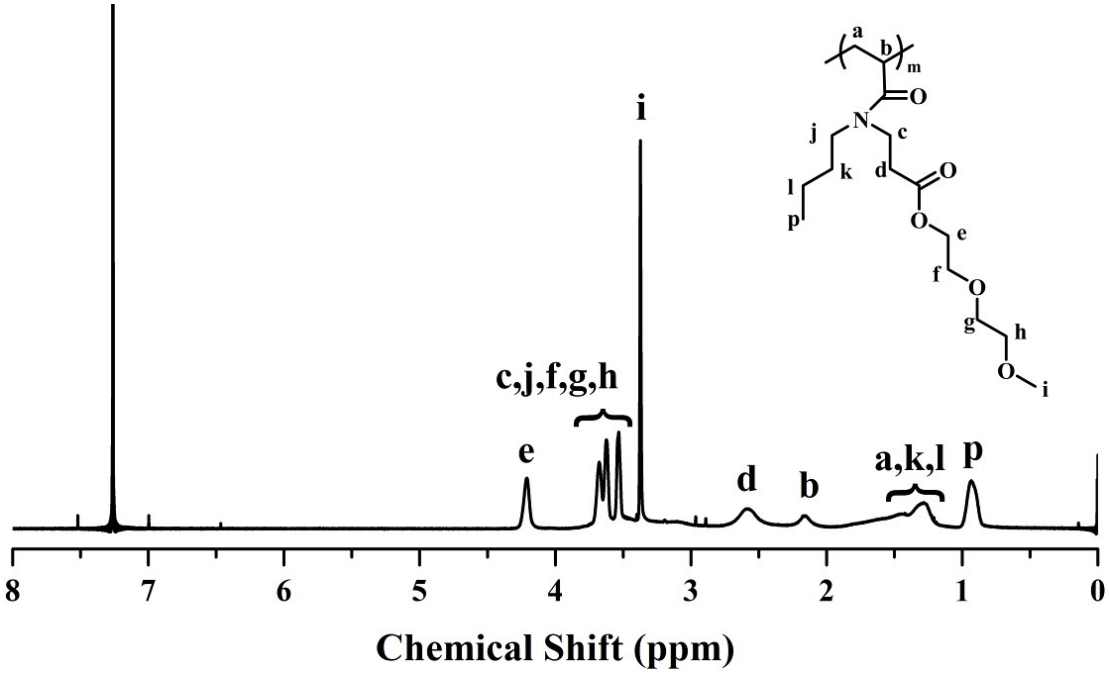


Figure S11. ^{1}H NMR spectrum of poly(Bu-MEO$_2$-AM) **8a** in $CDCl_3$.

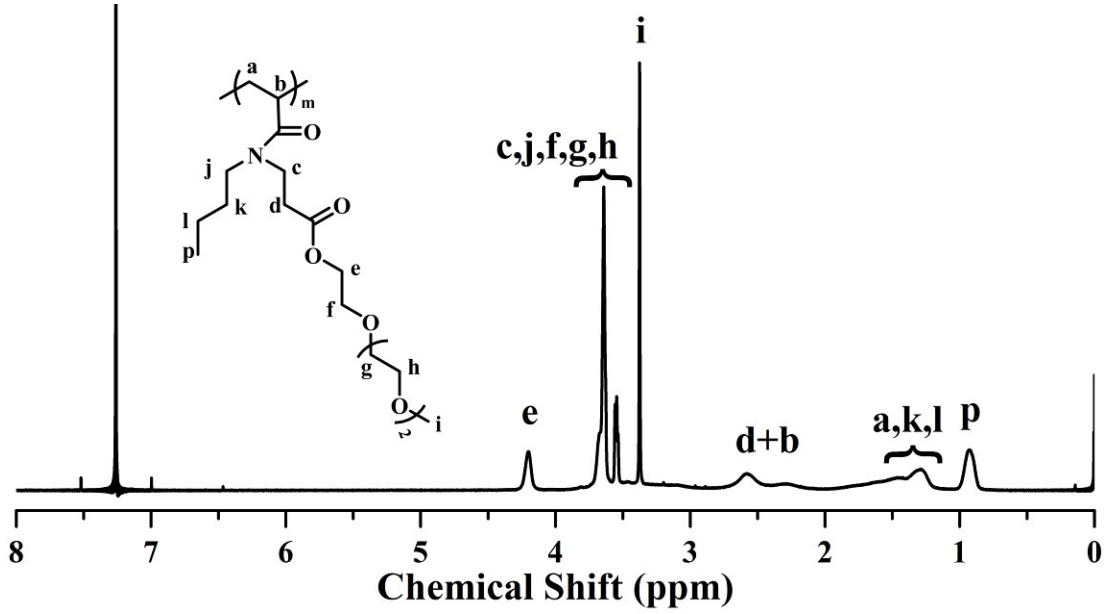


Figure S12. ^{1}H NMR spectrum of poly(Bu-MEO$_3$-AM) **8b** in $CDCl_3$.

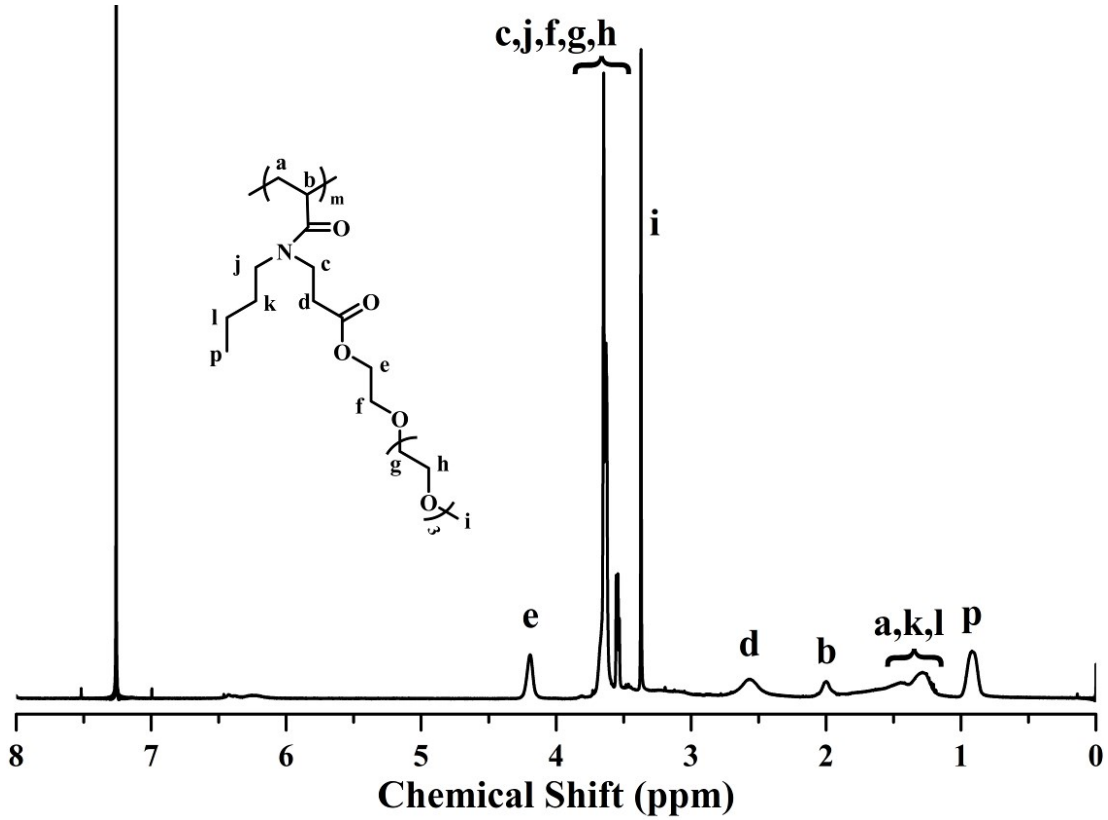


Figure S13. ^{1}H NMR spectrum of poly(Bu-MEO$_4$-AM) **8c** in $CDCl_3$.

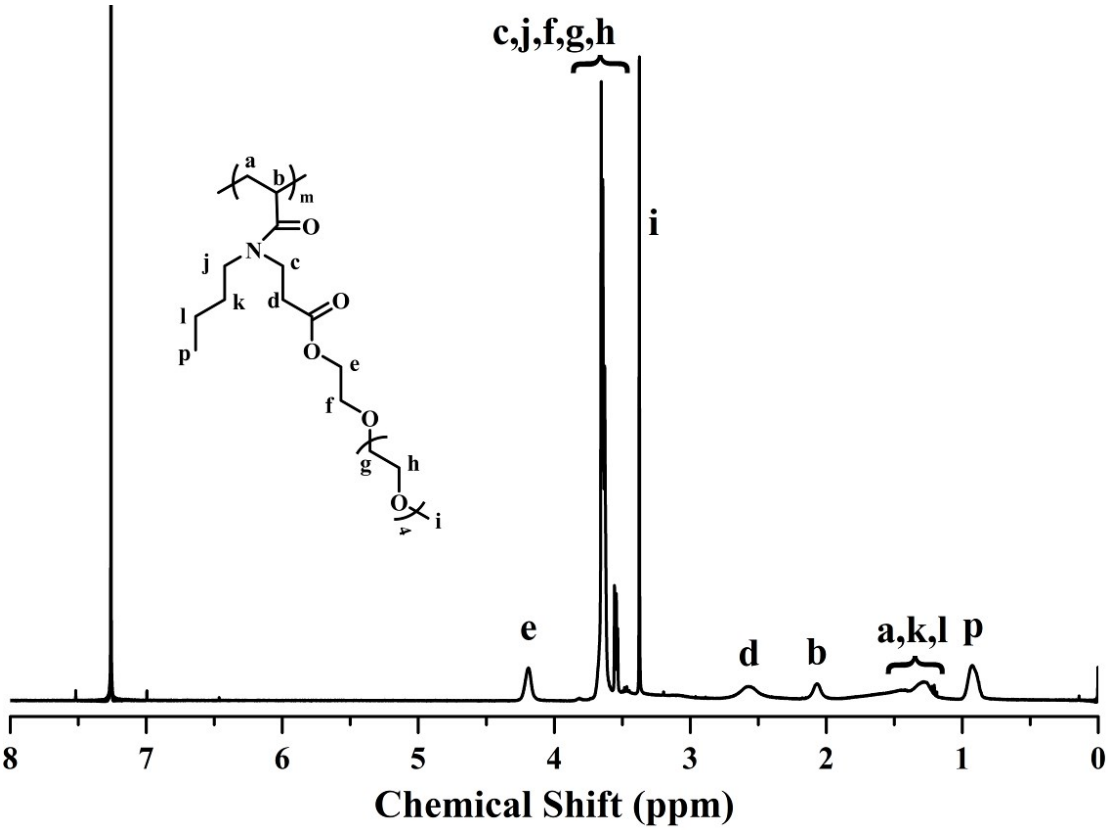


Figure S14. ^{1}H NMR spectrum of poly(Bu-MEO$_2$-AM) **8d** in $CDCl_3$.

References

1. Benaglia, M.; Alberti, A.; Spisni, E.; Papi, A.; Treossia, E.; Palermo, V. Polymeric Micelles Using Pseudo-amphiphilic Block Copolymers and Their Cellular Uptake. *J. Mater. Chem.* **201**1, *21*, 2555-2562.