

## Supporting Information for:

### **Poly( $\omega$ -methoxyalkyl acrylate)s: A nonthrombogenic polymer family with tunable protein adsorption**

Shingo Kobayashi<sup>1\*</sup>, Miyuki Wakui<sup>2</sup>, Yukihiwa Iwata<sup>2</sup>, and Masaru Tanaka<sup>1\*</sup>

<sup>1</sup>Institute for Materials Chemistry and Engineering, Kyushu University, CE41 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

<sup>2</sup>Department of Biochemical Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

<u>Table of Contents</u>	Page
1. Molecular Characterization Methods	S02
2. Materials	S02
3. Preparation of Monomers and Analytical Data	S03
Methoxymethyl acrylate ( <b>MC1A</b> , Figure S1-Figure S2)	S03
3-methoxypropyl acrylate ( <b>MC3A</b> , Figure S3-Figure S4)	S06
4-methoxybutyl acrylate ( <b>MC4A</b> , Figure S5-Figure S6)	S09
5-methoxypentyl acrylate ( <b>MC5A</b> , Figure S7-Figure S8)	S12
6-methoxyhexyl acrylate ( <b>MC6A</b> , Figure S9-Figure S10)	S15
12-methoxyhexyl acrylate ( <b>MC12A</b> , Figure S11-Figure S12)	S18
4. General Polymerization Procedure and Analytical Data	S21
Poly(methoxymethyl acrylate) ( <b>PMC1A</b> , Figure S13-Figure S14)	S24
Poly(2-methoxyethyl acrylate) ( <b>PMEA</b> , Figure S15-Figure S16)	S26
Poly(3-methoxypropyl acrylate) ( <b>PMC3A</b> , Figure S17-Figure S18)	S28
Poly(4-methoxybutyl acrylate) ( <b>PMC4A</b> , Figure S19-Figure S20)	S30
Poly(5-methoxypentyl acrylate) ( <b>PMC5A</b> , Figure S21-Figure S22)	S32
Poly(6-methoxyhexyl acrylate) ( <b>PMC6A</b> , Figure S23-Figure S24)	S34
Poly(12-methoxyhexyl acrylate) ( <b>PMC12A</b> , Figure S25-Figure S26)	S36
5. DSC thermograms of dried and hydrated PMC12A	
Cooling scan at 5 °C/min (Figure S27)	S38
Heating scan at 5 °C/min (Figure S28)	S39

## 1. Molecular Characterization Methods

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a JEOL ECX 500 MHz at room temperature.  $\text{CDCl}_3$  was used as solvents. Proton chemical shifts are referenced to TMS (0.00 ppm). Carbon chemical shifts are referenced to  $\text{CDCl}_3$  (77.1 ppm). Molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of polymers were determined by a size exclusion chromatography (SEC) instrument on a Tosoh HPLC HLC-8220 system equipped with a refractive index and ultraviolet detectors at 40 °C. The column set of SEC was as follows: four consecutive columns [Tosho TSK-GELs (bead size, exclusion-limited molecular weight): G4000H<sub>XL</sub> (5  $\mu\text{m}$ ,  $4 \times 10^5$ ), G3000H<sub>XL</sub> (5  $\mu\text{m}$ ,  $6 \times 10^4$ ), G2000H<sub>XL</sub> (5  $\mu\text{m}$ ,  $1 \times 10^4$ ), 30 cm each] and a guard column (TSK-guard column H<sub>XL</sub>-L, 4 cm). The system was operated at a flow rate of 1.0 mL/min using tetrahydrofuran (THF) as the eluent. Polystyrene standards were employed for calibration. Differential Scanning Calorimetry (DSC) measurement was performed on a Seiko Instruments Inc. X-DSC7000 with  $\text{N}_2$  as the purge gas at the rate of 5.0 °C/min from -100 °C to 50 °C. Water contact angle measurement was performed on Erma G-1-1000 with sessile drop method (2  $\mu\text{L}$  of water droplet). The polymer coated substrate for the measurement was prepared by spin-coating onto a 14 mm $\phi$  PET substrate, 0.2 wt/vol% polymer in THF solution was prepared and the solution was coated twice on the substrate using Mikasa spin coater MS-A100 at the rate of 500 rpm for 5 s, 2000 rpm for 10 s, slope for 5 s, 4000 rpm for 5 s, slope for 4 s, and dried.

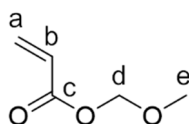
## 2. Materials

Butyl acrylate, 2-methoxyethyl acrylate, chloromethyl methyl ether, iodomethane, 3-methoxy-1-propanol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, triethylamine, acryloyl chloride, and 2,2'-azobis(isobutyronitrile) were purchased from Tokyo Chemical Industry Co. Ltd., Japan. Solvents for synthesizing monomers and polymers were purchased from Kanto Chemical Co. Inc., Japan. Other commercially available reagents were used as received unless otherwise specified.

### 3. Preparation of Monomers and Analytical Data

The synthesis of  $\omega$ -methoxyalkyl acrylates (MC<sub>x</sub>A, x=4, 5, and 6) was performed by two-step synthesis; 1) preparation of methoxy-terminated alkanediol and 2) acryloyl chloride-alcohol reaction. Commercially available 3-methoxy-1-propanol was used for MC3A synthesis. 2-methoxyethyl acrylate (MC2A = MEA) is commercially available. Methoxymethyl acrylate (MC1A) was synthesized as follows.

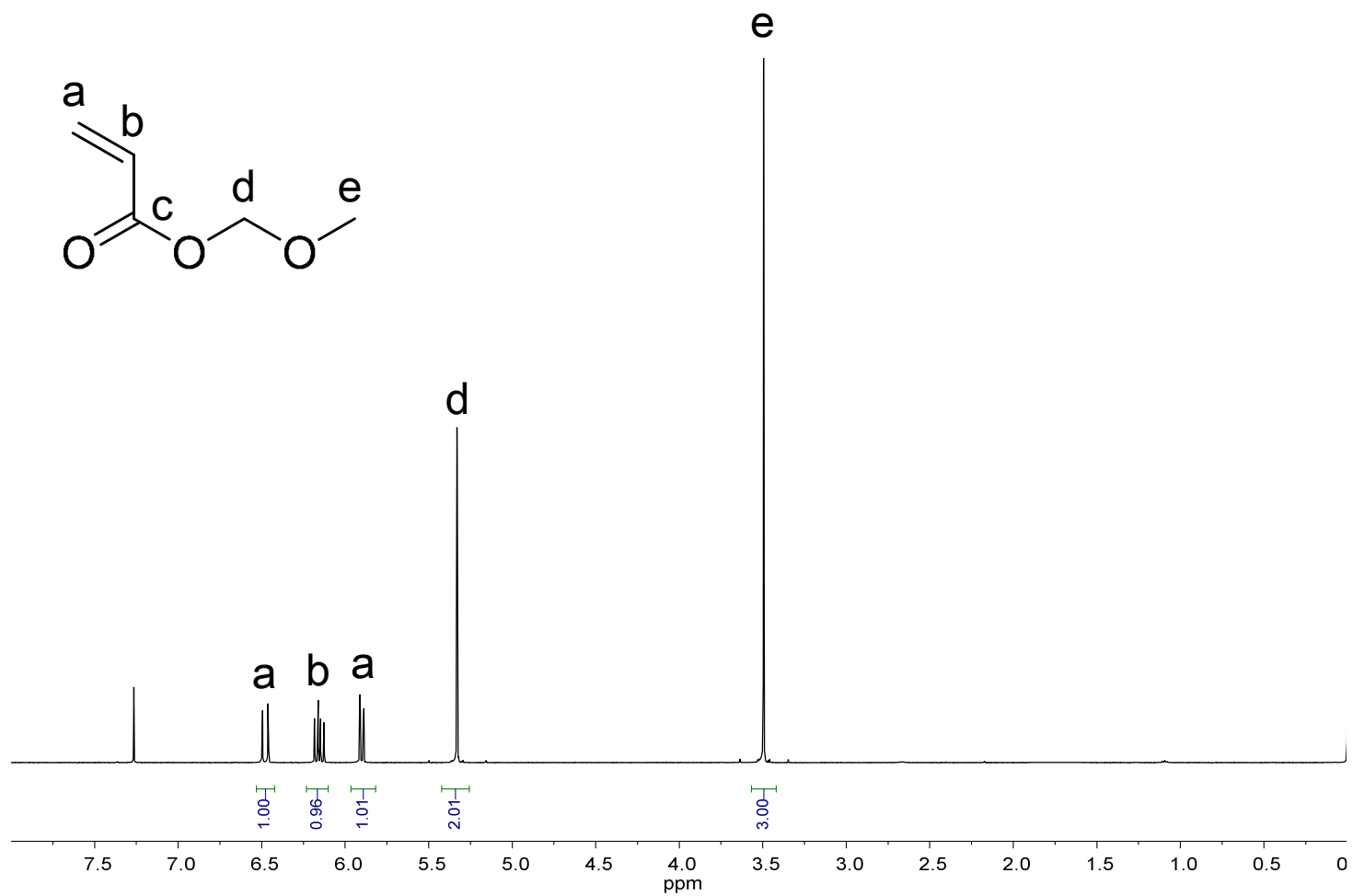
Preparation of methoxymethyl acrylate (**MC1A**) and analytical data (Figure S1-Figure S2):



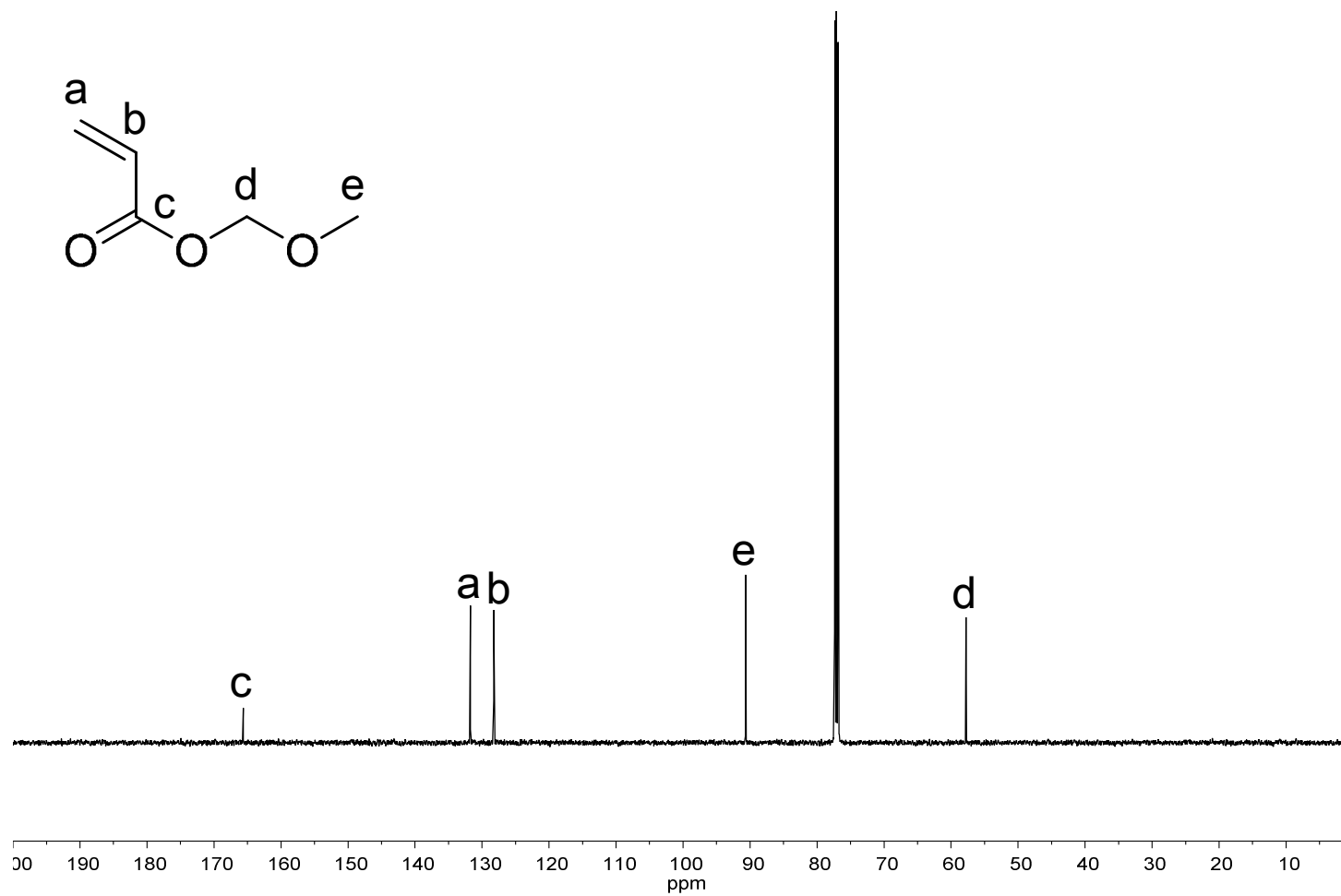
A mixture of acrylic acid (10.8 g, 150 mmol), triethylamine (19.2 g, 180 mmol), and 200 mL of dichloromethane was prepared in a 500 mL 2 neck flask and was stirred at room temperature. Chloromethyl methyl ether (12.9 g, 160 mmol) was added dropwise over 20 min at 0 °C and stirred for 2 h at room temperature. The white precipitate in the reaction mixture was filtered off by suction filtration and the filtrate was concentrated on rotary evaporator. The crude product was purified by fractional vacuum distillation afforded methoxymethyl acrylate (12.9 g, 70.8 mmol, 44% yield, bp = 68 °C at 35 Torr) as a colorless liquid.

<sup>1</sup>H NMR  $\delta$  (ppm): 3.49 (s, 3H, C(e)H), 5.33 (s, 2H, C(d)H), 5.88 (d, H, C(a')H), 6.15 (dd, H, C(b)H), 6.49 (d, H, C(a)H).

<sup>13</sup>C NMR  $\delta$  (ppm): 57.7 (Cd), 90.6 (Ce), 128.2 (Cb), 131.7 (Ca), 165.6 (Cc).

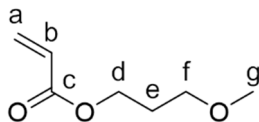


**Figure S1.**  $^1\text{H}$  NMR spectrum of methoxymethyl acrylate (MC1A, in  $\text{CDCl}_3$ , 500 MHz).



**Figure S2.**  $^{13}\text{C}$  NMR spectrum of methoxymethyl acrylate (MC1A, in  $\text{CDCl}_3$ , 125 MHz).

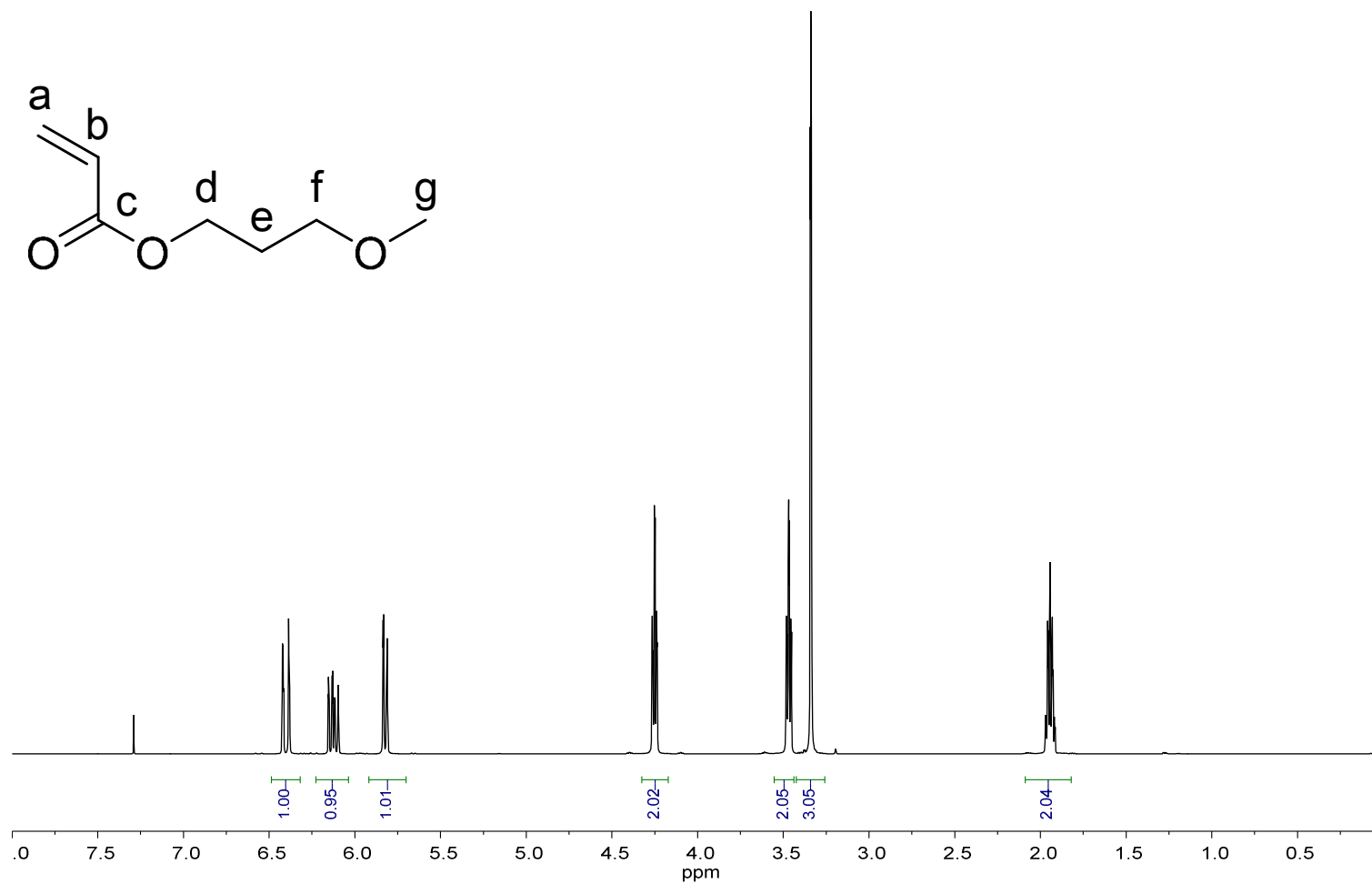
Preparation of 3-methoxypropyl acrylate (**MC3A**) and analytical data (Figure S3-Figure S4):



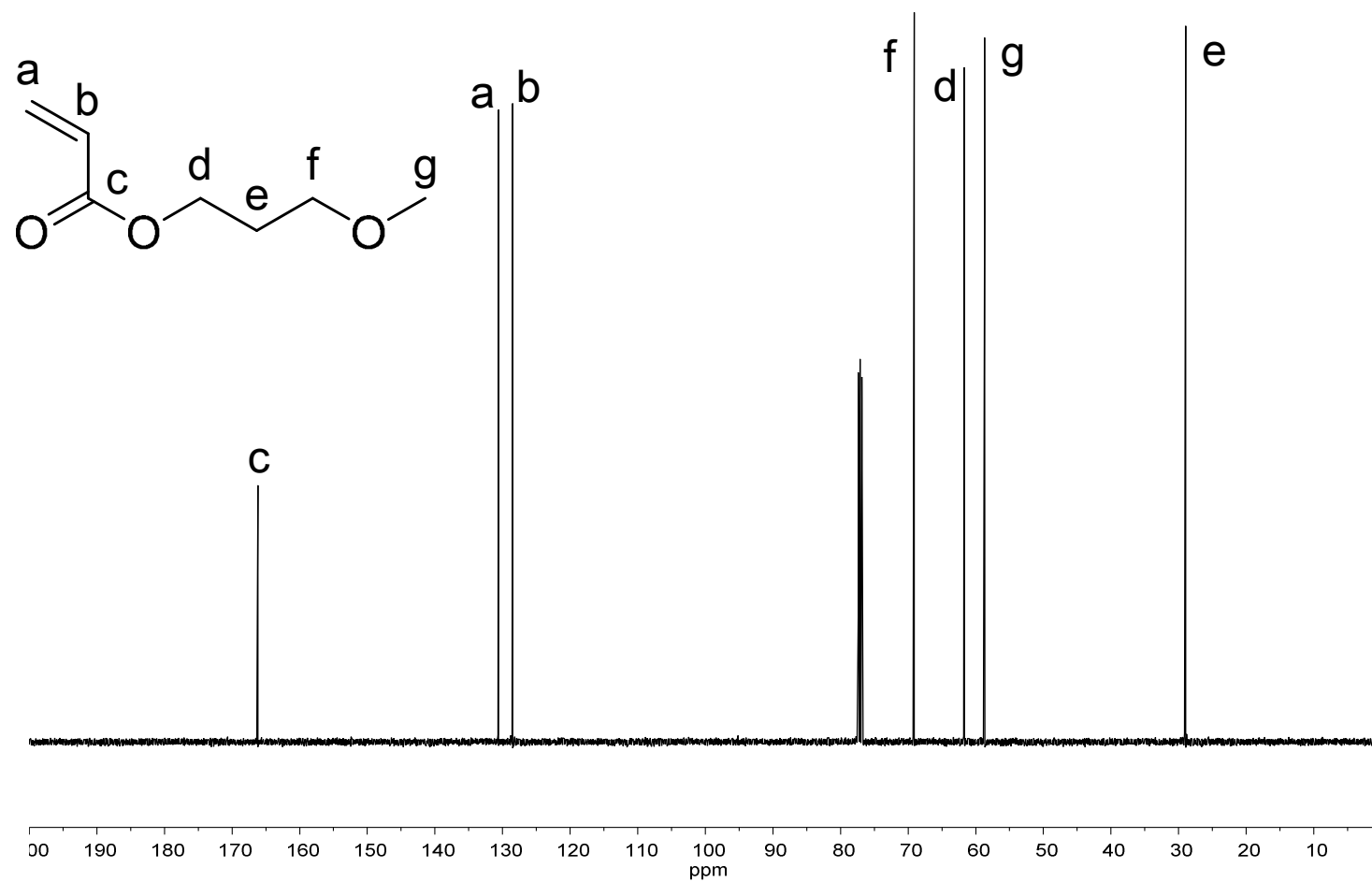
A mixture of 3-methoxy-1-propanol (27.1 g, 300 mmol), triethylamine (33.4 g, 330 mmol), and 400 mL of dichloromethane was prepared in a 1000 mL 2 neck flask and was stirred at room temperature. Acryloyl chloride (28.5 g, 315 mmol) was added dropwise over 15 min at 0 °C and stirred for overnight at room temperature. The white precipitate in the reaction mixture was filtered off by suction filtration and the filtrate was concentrated on rotary evaporator. The crude product was purified by fractional vacuum distillation afforded 3-methoxypropyl acrylate (27.6 g, 191 mmol, 64% yield, bp = 68 °C at 35 Torr) as a colorless liquid.

<sup>1</sup>H NMR δ (ppm): 1.94 (p, J = 6.4 Hz, 2H, C(e)H), 3.34 (t, J = 1.9 Hz, 3H, C(g)H<sub>3</sub>), 3.47 (t, J = 6.3 Hz, 2H, C(f)H), 4.25 (t, J = 6.0 Hz, 2H, C(d)H) 5.82 (d, J = 10.3 Hz, 1H, C(a')H), 6.12 (dd, J = 17.4, 10.5, Hz, 1H, C(b)H), 6.41 (d, J = 17.4 Hz, 1H, C(a)H).

<sup>13</sup>C NMR δ (ppm): 29.0 (Ce), 58.7 (Cg), 61.7 (Cd), 69.1 (Cf), 128.5 (Cb), 130.6 (Ca), 166.2 (Cc).



**Figure S3.** <sup>1</sup>H NMR spectrum of 3-methoxypropyl acrylate (**MC3A**, in CDCl<sub>3</sub>, 500 MHz).

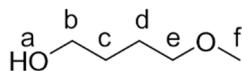


**Figure S4.**  $^{13}\text{C}$  NMR spectrum of 3-methoxypropyl acrylate (**MC3A**, in  $\text{CDCl}_3$ , 100 MHz).



Preparation of 4-methoxybutyl acrylate (**MC4A**) and analytical data (Figure S5-Figure S6):

1) 4-methoxy-1-butanol:

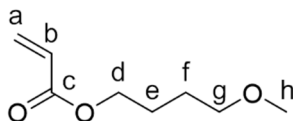


A 500 mL oven dried 2 neck flask was charged with 1,4-butanediol (27.0 g, 300 mmol) and 200 mL of THF. Sodium hydride (60% dispersion in mineral oil, 12.0 g, 300 mmol) was added portionwise with stirring. The reaction mixture was stirred for 1 h at room temperature and iodomethane (42.6 g, 300 mmol) was added dropwise over 15 min at 0 °C. The reaction mixture was stirred at room temperature for 14 h and the reaction was quenched by adding the solution into a small amount of 2N HCl aq. THF was removed on rotary evaporator and the obtained concentrate was diluted by adding diethyl ether. The precipitate was filtered off by suction filtration and the filtrate was dried over anhydrous MgSO<sub>4</sub>. After concentration of the solution, the resulting crude product was purified by flash column chromatography (silica gel, hexane, dichloromethane, and methanol was used in this order). Further purification by fractional vacuum distillation afforded 4-methoxy-1-butanol (18.5 g, 178 mmol, 30% yield, bp = 27 °C/0.08 Torr) as a colorless liquid.

<sup>1</sup>H NMR δ (ppm): 1.61 (m, 4H, C(c)H, C(d)H), 2.20 (s, 1H, O(a)H), 3.31 (s, 3H, C(f)H), 3.38 (t, 2H, C(e)H), 3.58 (t, 2H, C(b)H). (in CD<sub>2</sub>Cl<sub>2</sub>)

<sup>13</sup>C NMR δ (ppm): 26.7 (Cd), 30.1 (Cc), 58.6 (Cf), 62.6 (Ce), 72.8 (Cb).

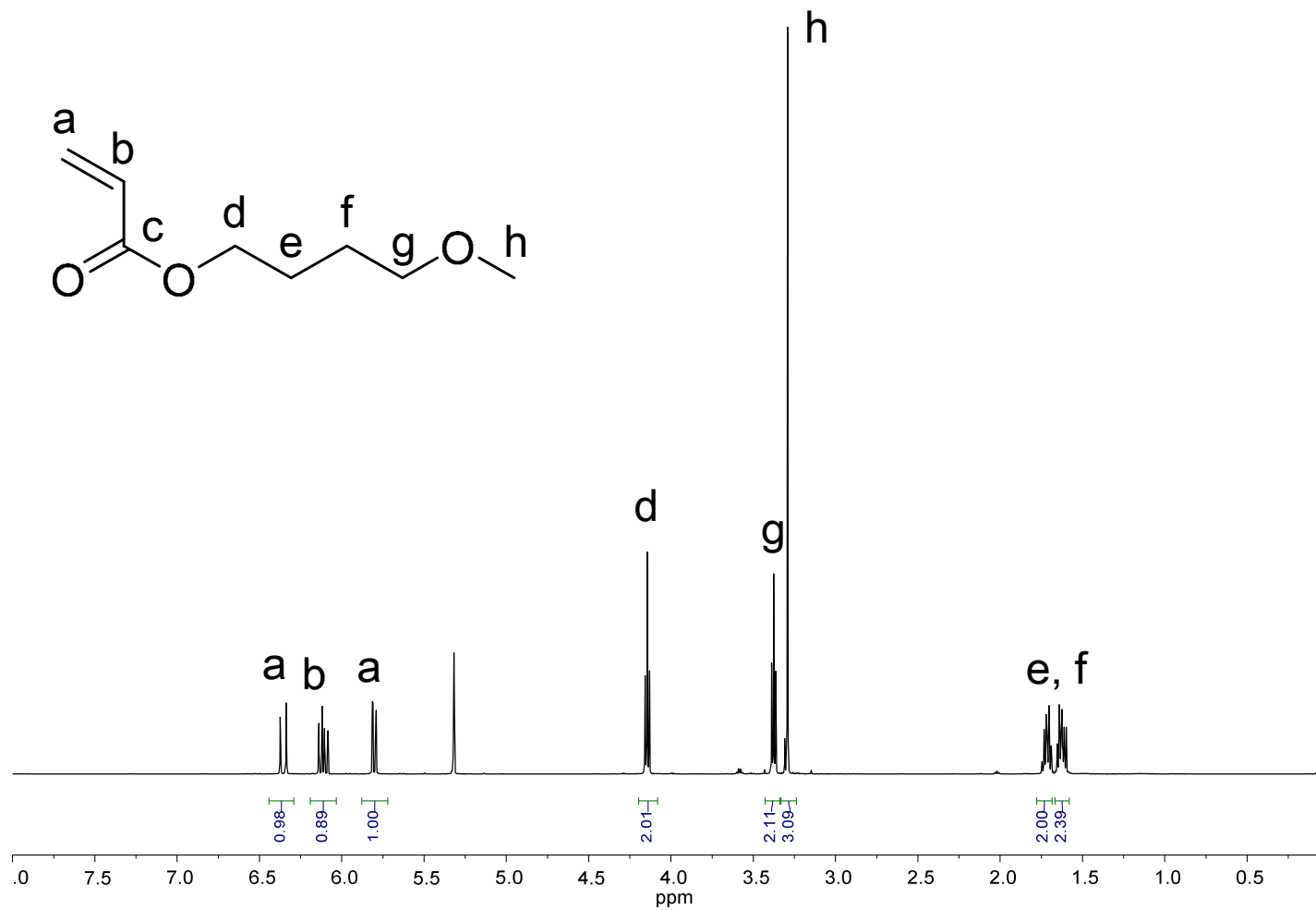
2) 4-methoxybutyl acrylate:



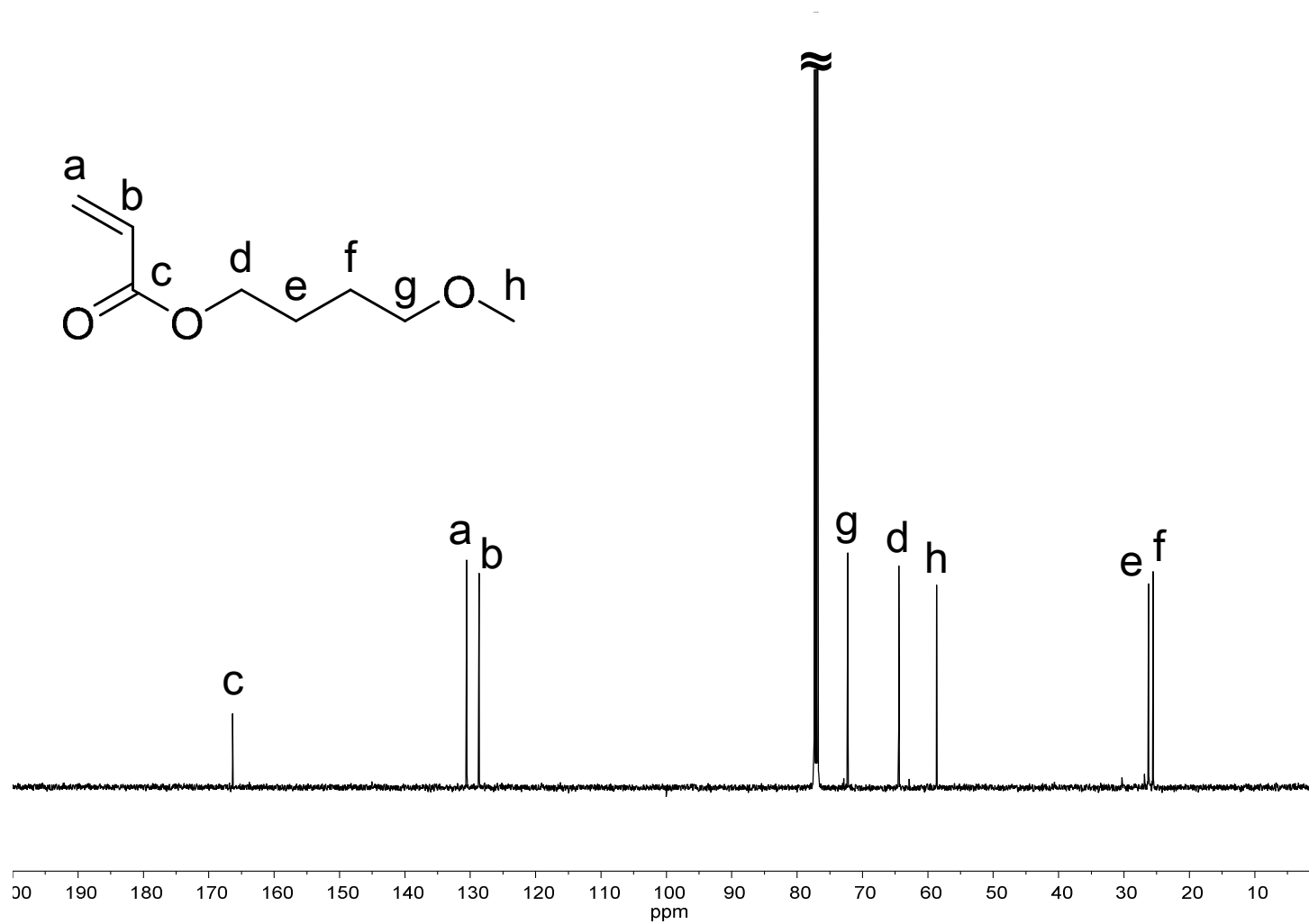
The same procedure was followed, as described above for MC3A, using 4-methoxy-1-butanol (15.8 g, 152 mmol), triethylamine (17.5 g, 173 mmol), acryloyl chloride (14.5 g, 160 mmol), and diethyl ether (250 mL). The reaction mixture was stirred for 3.5 h. After purification, 4-methoxybutyl acrylate (11.4 g, 72.1 mmol, 48% yield, bp = 50 °C at 0.08 Torr) was obtained as a colorless liquid.

<sup>1</sup>H NMR δ (ppm): 1.75~1.84 (m, 4H, C(e)H, C(f)H), 3.42 (s, 3H, C(h)H), 3.49 (t, 2H, C(d)H), 4.26 (t, 2H, C(g)H), 5.89 (d, 1H, C(a')H), 6.20 (dd, 1H, C(b)H), 6.47 (d, 1H, C(a)H).

<sup>13</sup>C NMR δ (ppm): 25.5 (Cf), 26.2 (Ce), 58.6 (Ch), 64.6 (Cd), 72.2 (Cg), 128.6 (Cb), 130.5 (Ca'/Ca), 166.3 (Cc).



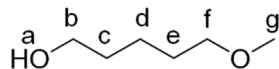
**Figure S5.**  $^1\text{H}$  NMR spectrum of 4-methoxybutyl acrylate (**MC4A**, in  $\text{CDCl}_3$ , 500 MHz).



**Figure S6.**  $^{13}\text{C}$  NMR spectrum of 4-methoxybutyl acrylate (MC4A, in  $\text{CDCl}_3$ , 125 MHz).

Preparation of 5-methoxypentyl acrylate (**MC5A**) and analytical data (Figure S7-Figure S8):

1) 5-methoxy-1-pentanol:

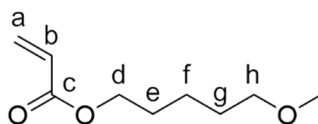


The same procedure was followed, as described above for **MC4A**, using 1,5- pentanediol (31.4 g, 302 mmol), sodium hydride (60% dispersion in mineral oil, 12.3 g, 308 mmol), iodomethane (43.8 g, 309 mmol), and THF (200 mL). The reaction mixture was stirred for 15 h. After purification, 4-methoxybutyl acrylate (14.4 g, 122 mmol, 41% yield, bp = 60-64 °C at 0.08 Torr) was obtained as a colorless liquid.

<sup>1</sup>H NMR δ (ppm): 1.35~1.85 (m, 7H, O(a)H, C(c)H, C(d)H, C(e)H), 3.31 (s, 3H, C(g)H), 3.36 (t, 2H, C(f)H), 3.61 (m, 2H, C(b)H).

<sup>13</sup>C NMR δ (ppm): 22.4 (Ce), 29.3 (Cc), 32.5 (Cd), 58.6 (Cg), 62.6 (Cf), 72.8 (Cb).

2) 5-methoxypentyl acrylate:



The same procedure was followed, as described above for **MC3A**, using 5-methoxy-1-pentanol (15.4 g, 130 mmol), triethylamine (14.5 g, 143 mmol), acryloyl chloride (12.4 g, 137 mmol), and diethyl ether (200 mL). The reaction mixture was stirred for 8 h. After purification, 4-methoxybutyl acrylate (5.95 g, 34.5 mmol, 27% yield, bp = 58 °C at 0.08 Torr) was obtained as a colorless liquid.

<sup>1</sup>H NMR δ (ppm): 1.43 (m, 2H, C(f)H), 1.58~1.67 (m, 4H, C(e)H, C(g)H), 3.31 (s, 3H, C(i)H), 3.38 (t, 2H, C(d)H), 4.17 (t, 2H, C(h)H), 5.79 (d, 1H, C(a')H), 6.11 (dd, 1H, C(b)H), 6.36 (d, 1H, C(a)H).

<sup>13</sup>C NMR δ (ppm): 22.7 (Cf), 28.5 (Cg), 29.3 (Ce), 58.6 (Ci), 64.6 (Ch), 72.6 (Cd), 128.6 (Cb), 130.6 (Ca/Ca'), 166.4 (Cc)..

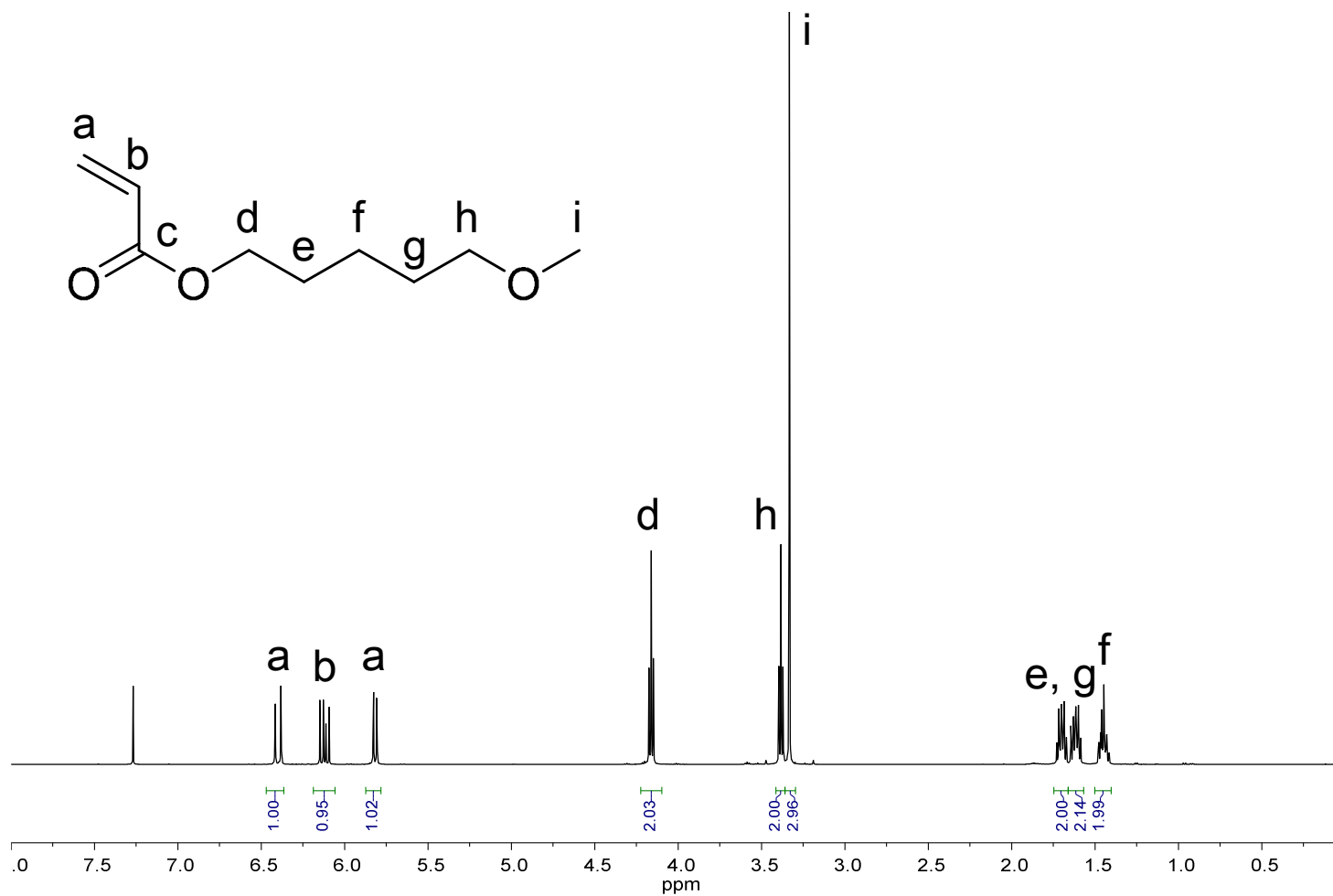


Figure S7.  $^1\text{H}$  NMR spectrum of 5-methoxypentyl acrylate (**MC5A**, in  $\text{CDCl}_3$ , 500 MHz).

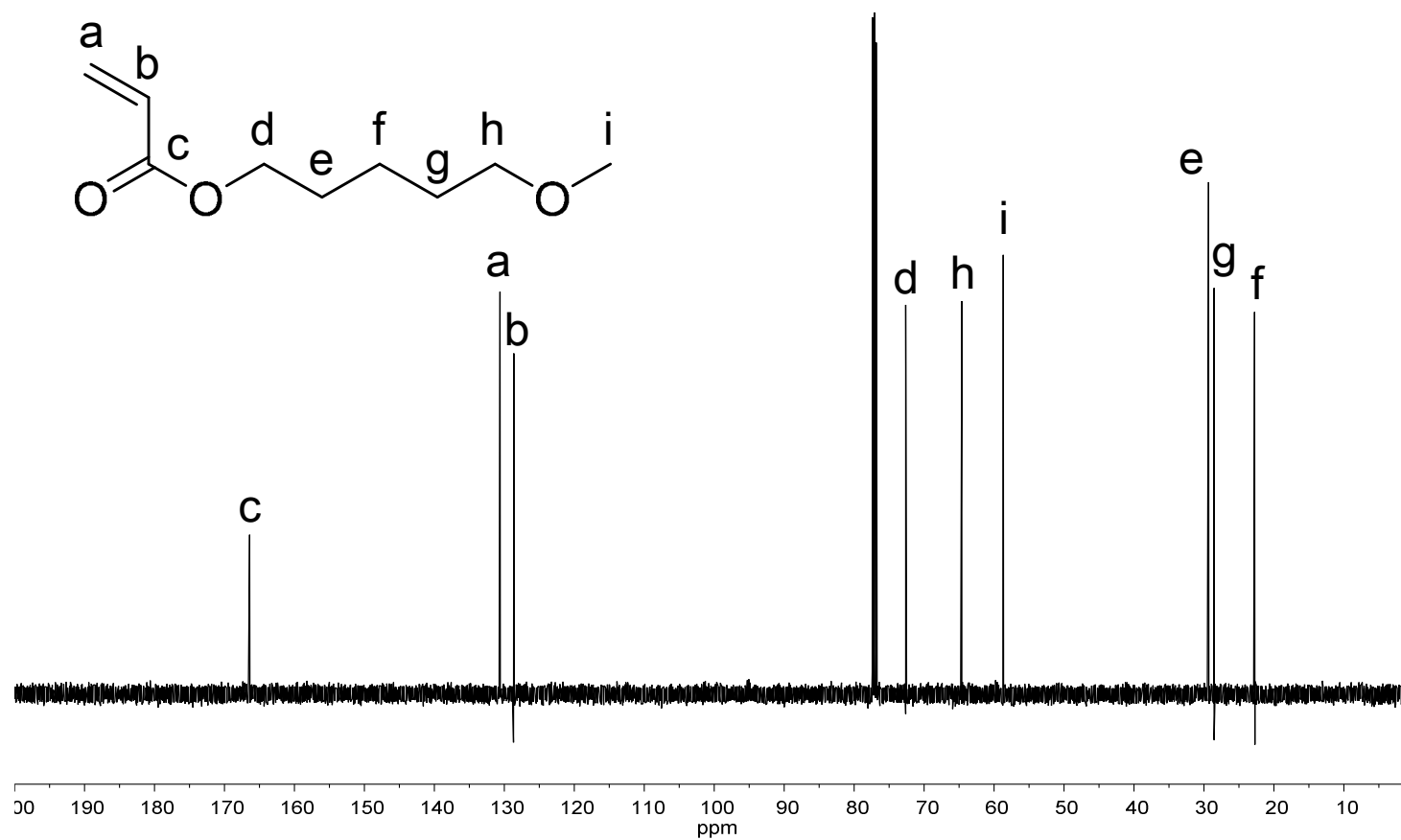
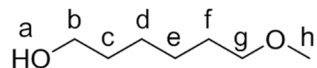


Figure S8. <sup>13</sup>C NMR spectrum of 5-methoxypentyl acrylate (MC5A, in CDCl<sub>3</sub>, 125 MHz).

Preparation of 6-methoxyhexyl acrylate (**MC6A**) and analytical data (Figure S9-Figure S10):

3) 6-methoxy-1-hexanol:

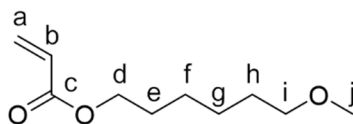


The same procedure was followed, as described above for **MC4A**, using 1,6-hexanediol (35.6 g, 301 mmol), sodium hydride (60% dispersion in mineral oil, 12.4 g, 310 mmol), iodomethane (42.6 g, 300 mmol), and THF (180 mL). The reaction mixture was stirred for 21 h. After purification, 6-methoxy-1-hexanol (10.2 g, 77.2 mmol, 26% yield, bp = 94-100 °C at 0.08 Torr) was obtained as a colorless liquid.

$^1\text{H}$  NMR  $\delta$  (ppm): 1.36~1.56 (m, 9H, O(a)H, C(d)H, C(f)H, C(e)H, C(f)H), 3.31 (s, 3H, C(h)H), 3.35 (t, 2H, C(g)H), 3.62 (t, 2H, C(b)H).

$^{13}\text{C}$  NMR  $\delta$  (ppm): 25.6 (Ce), 25.9 (Cd), 29.6 (Cf), 32.7 (Cc), 58.5 (Ch), 62.8 (Cg), 72.8 (Cb).

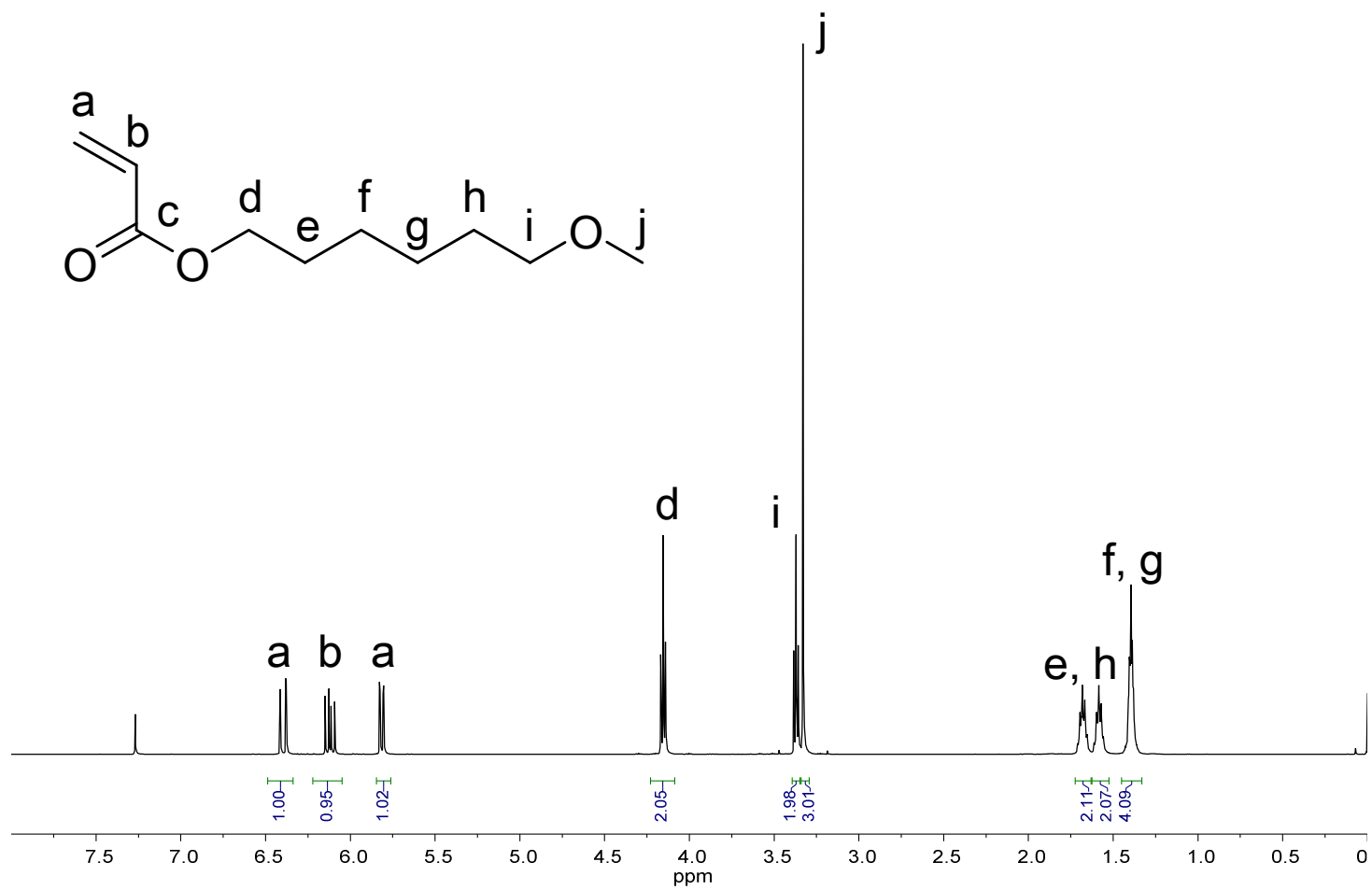
4) 6-methoxyhexyl acrylate:



The same procedure was followed, as described above for **MC3A**, using 6-methoxy-1-hexanol (9.25 g, 70.1 mmol), triethylamine (7.80 g, 77.0 mmol), acryloyl chloride (6.65 g, 73.5 mmol), and diethyl ether (200 mL). The reaction mixture was stirred for 8 h. After purification, 6-methoxyhexyl acrylate (5.77 g, 31.0 mmol, 44% yield, bp = 99 °C at 0.08 Torr) was obtained as a colorless liquid.

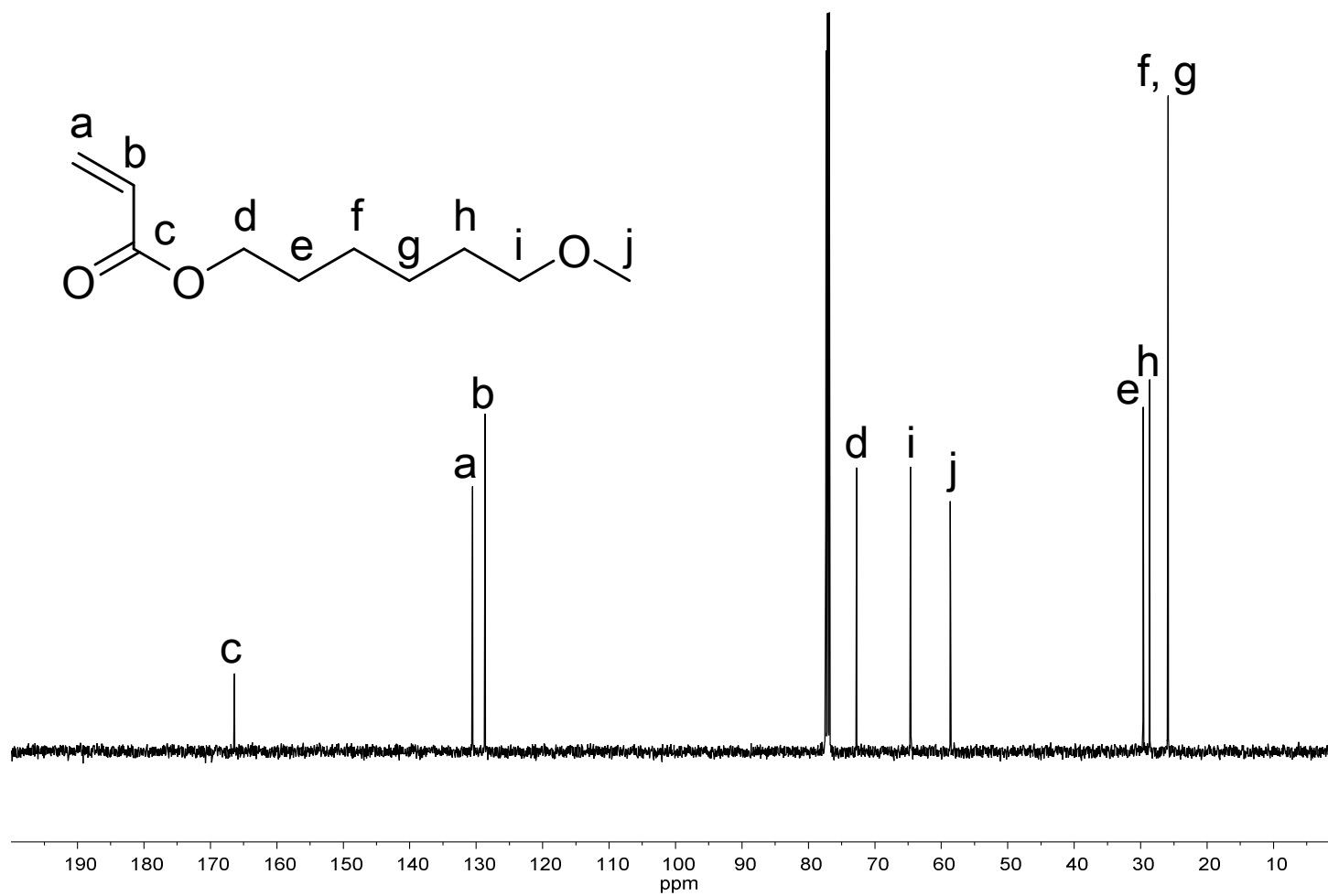
$^1\text{H}$  NMR  $\delta$  (ppm): 1.37 (m, 4H, C(f)H), 1.56~1.66 (m, 4H, C(e)H, C(h)H), 3.31 (s, 3H, C(d)H), 3.35 (t, 2H, C(d)H), 4.13 (t, 2H, C(i)H), 5.79 (d, 1H, C(a')H), 6.09 (dd, 1H, C(b)H), 6.36 (d, 1H, C(a)H).

$^{13}\text{C}$  NMR  $\delta$  (ppm): 25.8 (Cf, Cg), 26.8 (Ch), 29.6 (Ce), 58.6 (Cj), 64.6 (Ci), 72.7 (Cd), 128.6 (Cb), 130.5 (Ca/Ca'), 166.4 (Cc).



**Figure S9.** <sup>1</sup>H NMR spectrum of 6-methoxyhexyl acrylate (**MC6A**, in CDCl<sub>3</sub>, 500 MHz).





**Figure S10.**  $^{13}\text{C}$  NMR spectrum of 6-methoxyhexyl acrylate (MC6A, in  $\text{CDCl}_3$ , 125 MHz).

Preparation of 12-methoxydodecyl acrylate (**MC12A**) and analytical data (Figure S11-Figure S12):

5) 12-methoxy-1-dodecanol:

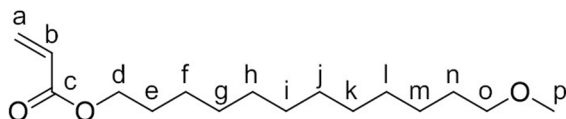


1,12-dodecanediol (30.5 g, 150 mmol) and dimethoxyethane (DME) was mixed in 500 mL two neck flask. The mixture was heated up to 90 °C to dissolve the diol and was cooled to 55 °C. Sodium hydride (60% dispersion in mineral oil, 6.57 g, 165 mmol) was added portionwise with stirring. The reaction mixture was stirred for 1 h at room temperature and dimethyl sulfate (18.9 g, 150 mmol) was added dropwise over 15 min. The reaction mixture was stirred at room temperature for 19 h and the reaction was quenched by adding the solution into a 100 mL saturated ammonium chloride solution. The mixture was extracted with ethyl acetate and the organic layer was washed with brine. The extract was dried over anhydrous  $\text{MgSO}_4$  and the desiccant was removed by suction filtration. After concentration of the solution, the resulting crude product was purified by flash column chromatography (silica gel, hexane : ethyl acetate = 100 : 0, 80: 20, and 70 : 30). 12-methoxy-1-dodecanol (13.7 g, 75.3 mmol, 42% yield) was obtained as a white solid.

$^1\text{H}$  NMR  $\delta$  (ppm): 1.26 (m, 20H, C(b)H), 3.32 (s, 3H, C(d)H), 3.35 (t,  $J$  = 6.7 Hz, 2H, C(c)H), 3.63 (t,  $J$  = 6.8 Hz, 2H, C(a)H).

$^{13}\text{C}$  NMR  $\delta$  (ppm): 29.6 (Cb), 58.6 (Cd), 63.1 (Cc), 73.1 (Ca)

6) 12-methoxydodecyl acrylate:

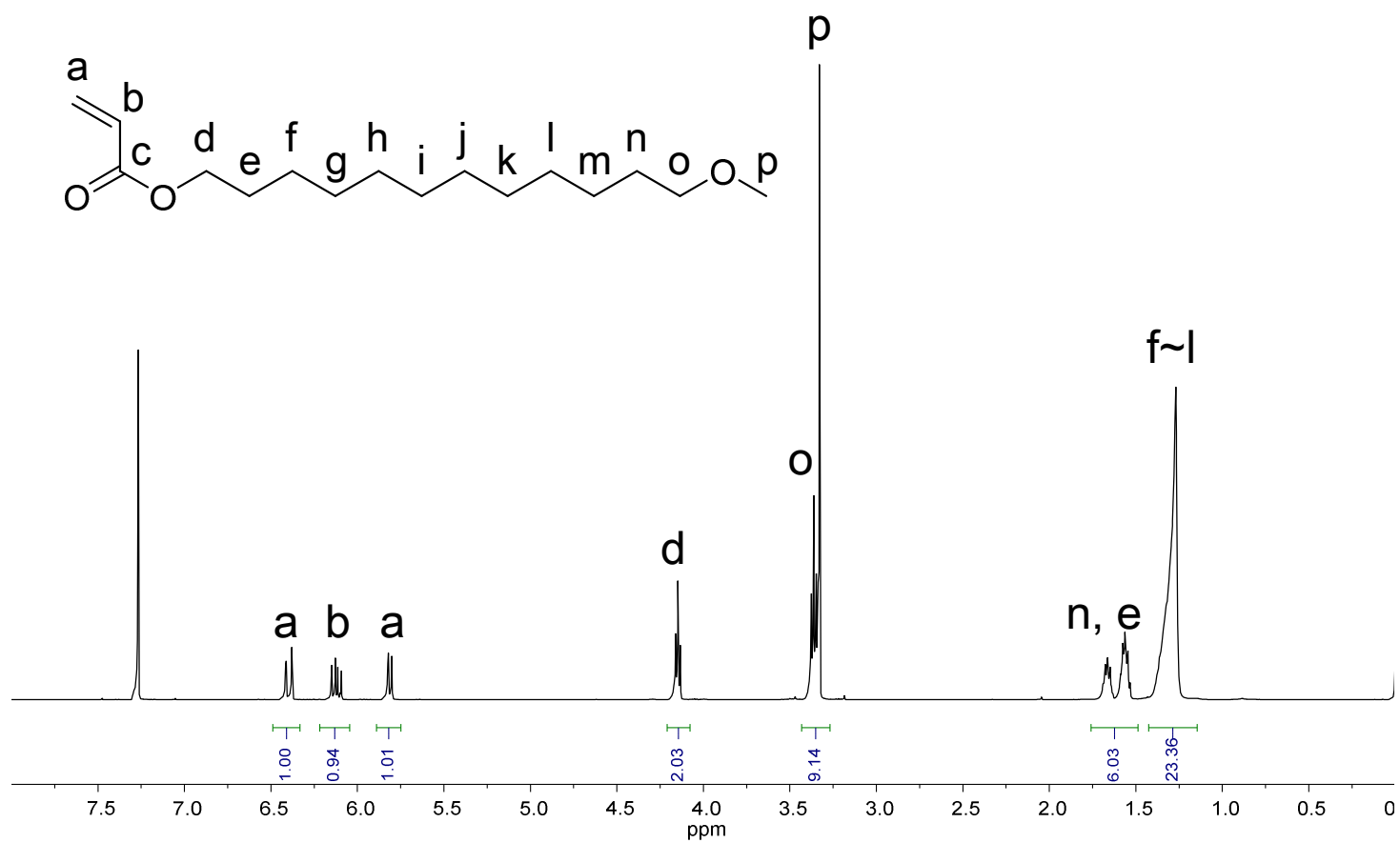


The same procedure was followed, as described above for **MC3A**, using 12-methoxy-1-dodecanol (13.0 g, 60.2 mmol), triethylamine (6.72 g, 66.4 mmol), acryloyl chloride (7.05 g, 77.9 mmol), and diethyl ether (150 mL). The reaction mixture was stirred for 8 h. After purification by column chromatography, 12-methoxydodecyl acrylate (7.96 g, 31.0 mmol, 49% yield) was obtained as a colorless liquid.

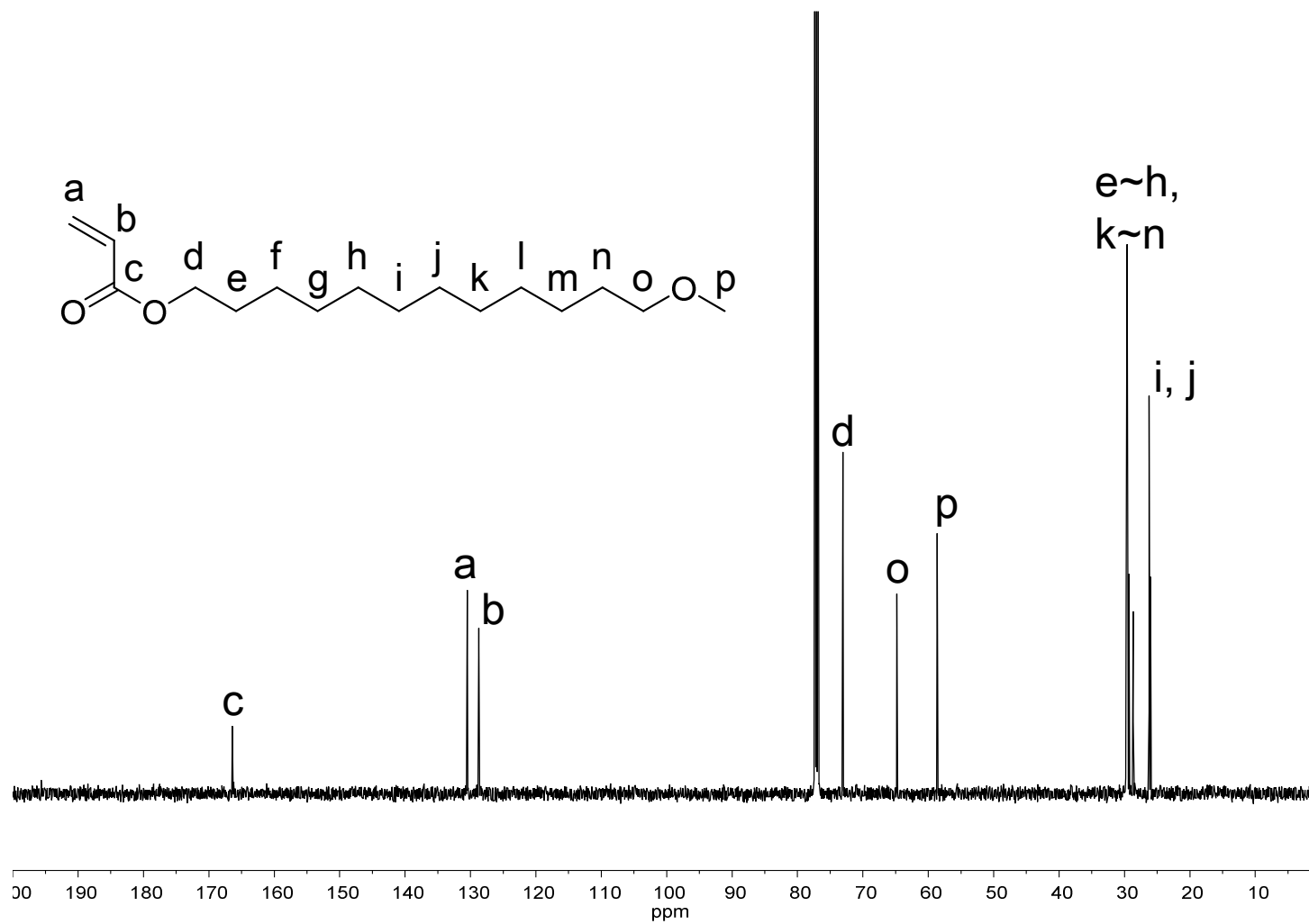
$^1\text{H}$  NMR  $\delta$  (ppm): 1.26 (m, 14H, C(f)H, C(g)H, C(h)H, C(i)H, C(j)H, C(k)H, C(l)H), 1.55 (m, 2H, C(e)H), 1.65 (m, 2H, C(n)H), 3.32 (m, 5H, C(o)H, C(p)H), 4.14 (t, 2H, C(d)H), 5.79 (d,  $J$  = 10.5 Hz, 1H, C(b)H), 6.12 (dd,  $J$  = 17.4, 10.5 Hz, 1H, C(c)H), 6.36 (d, 17.4 Hz, 1H, C(a)H).

$^{13}\text{C}$  NMR  $\delta$  (ppm): 26.0~26.2 (Ci, Cj), 28.7~29.4 (Ce, Cf, Cg, Ch, Ck, Cl, Cm, Cn), 58.6 (Cp), 64.8 (Co), 73.1 (Cd), 128.7 (Cb), 130.5 (Ca), 166.4 (Cc).





**Figure S11.**  $^1\text{H}$  NMR spectrum of 12-methoxydodecyl acrylate (**MC12A**, in  $\text{CDCl}_3$ , 500 MHz).

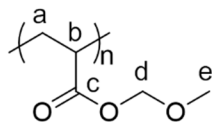


**Figure S12.**  $^{13}\text{C}$  NMR spectrum of 12-methoxydodecyl acrylate (**MC12A**, in  $\text{CDCl}_3$ , 125 MHz).

#### General Polymerization Procedure and Analytical Data

All polymerization reactions were carried out in the same weight ratio of monomer : solvent : initiator = 15 g : 60 g : 15 mg. An example of the polymerization procedure is described for the entry 3 in Table 1. A mixed solution of MC3A (15 g, 104 mmol), 1,4-dioxane (60 g, 681 mmol), and 2,2'-azobisisobutyronitrile (AIBN) (15 mg, 91  $\mu$ mol) was prepared in a 200 mL three neck round bottom flask equipped with reflux condenser. The mixed solution was thoroughly purged by N<sub>2</sub> gas with stirring for 30 min at room temperature. The reaction system was heated up to 75 °C and the polymerization was carried out for 6 h. The resulting polymer solution was poured into an excess amount of hexane to precipitate the product and the precipitate was further purified by precipitation twice using THF/hexanes as the good/bad solvent pair system. The precipitate was soaked in Milli-Q water for overnight with stirring and the purified polymer was collected by dissolving in THF. After concentration on rotary evaporator, the product was dried under reduced pressure at 60 °C for a couple of days afforded PMC3A (12.9 g, 86% yield) as a colorless highly viscous liquid. The following is the complete list.

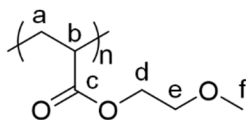
#### Poly(methoxymethyl acrylate) (**PMC1A**):



<sup>1</sup>H NMR  $\delta$  (ppm): 1.44~2.17 (m, 2H, C(a)H<sub>2</sub>), 2.26~2.57 (m, 1H, C(b)H), 3.46 (s, 3H, C(e)H), 5.07~5.39 (m, 2H, C(d)H).

<sup>13</sup>C NMR  $\delta$  (ppm): 30.2 (Ca), 41.6 (Cb), 57.8 (Ce), 90.8 (Cd), 173.9 (Cc).

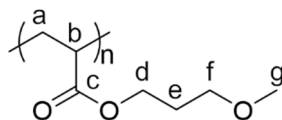
#### Poly(2-methoxyethyl acrylate) (**PMC2A**):



<sup>1</sup>H NMR  $\delta$  (ppm): 1.33~2.09 (m, 2H, C(a)H), 2.19~2.56 (m, 1H, C(b)H), 3.36 (s, 3H, C(f)H), 3.57 (br, 2H, C(e)H), 4.20 (br, 2H, C(d)H).

<sup>13</sup>C NMR  $\delta$  (ppm): 35.1 (Ca), 41.3 (Cb), 58.8 (Cf), 63.4 (Cd), 70.3 (Ce), 174.5 (Cc).

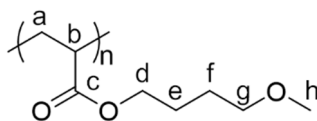
Poly(3-methoxypropyl acrylate) (**PMC3A**):



$^1\text{H}$  NMR  $\delta$  (ppm): 1.29~2.07 (m, 4H, C(a)H, C(e)H), 2.10~2.49 (m, 1H, C(b)H), 3.33 (s, 3H, C(g)H), 3.43 (br, 2H, C(g)H), 4.13 (br, 2H, C(d)H).

$^{13}\text{C}$  NMR  $\delta$  (ppm): 29.1 (Ce), 34.6 (Ca), 41.6 (Cb), 58.6 (Cg), 62.1 (Cd), 69.1 (Cf), 174.4 (Cc).

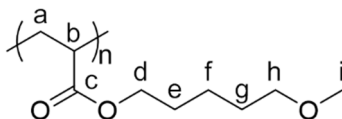
Poly(4-methoxybutyl acrylate) (**PMC4A**):



$^1\text{H}$  NMR  $\delta$  (ppm): 1.29~2.02 (m, 6H, C(a)H, C(e)H, C(f)H), 2.06~2.43 (m, 1H, C(b)H), 3.32 (s, 3H, C(h)H), 3.38 (t,  $J = 6.2$  Hz, 2H, C(g)H), 4.03 (br, 2H, C(d)H).

$^{13}\text{C}$  NMR  $\delta$  (ppm): 25.5 (C(e)), 26.1 (C(f)), 35.4 (Ca), 41.5 (Cb), 58.6 (Ch), 64.4 (Cd), 72.1 (Cg), 174.3 (Cc).

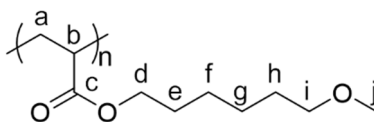
Poly(5-methoxyethyl acrylate) (**PMC5A**):



$^1\text{H}$  NMR  $\delta$  (ppm): 1.26~1.97 (m, 8H, C(a)H, C(e)H, C(f)H, C(g)H), 2.08~2.43 (m, 1H, C(b)H), 3.31 (s, 3H, C(i)H), 3.37 (t,  $J = 6.5$  Hz, 2H, C(h)H), 4.01 (br, 2H, C(d)H).

$^{13}\text{C}$  NMR  $\delta$  (ppm): 22.5 (Cf), 28.5 (Ce), 29.3 (Cg), 35.5 (Ca), 41.5 (Cb), 58.6 (Ci), 64.6 (Cd), 72.6 (Ch), 174.4 (Cc).

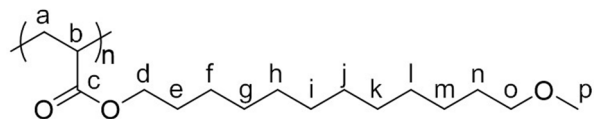
Poly(6-methoxyhexyl acrylate) (**PMC6A**):



$^1\text{H}$  NMR  $\delta$  (ppm): 1.19~1.97 (m, 10H, C(a)H, C(e)H, C(f)H, C(g)H, C(h)H), 2.06~2.40 (m, 1H, C(b)H), 3.31 (s, 3H, C(j)H), 3.35 (t, 6.5 Hz, 2H, C(d)H), 3.99 (br, 2H, C(i)H).

$^{13}\text{C}$  NMR  $\delta$  (ppm): 25.8~26.0 (Cf, Cg), 28.7 (Ce), 29.6 (Ch), 35.4 (Ca), 41.5 (Cb), 58.6 (Cj), 64.7 (Cd), 72.8 (Ci), 174.5 (Cc).

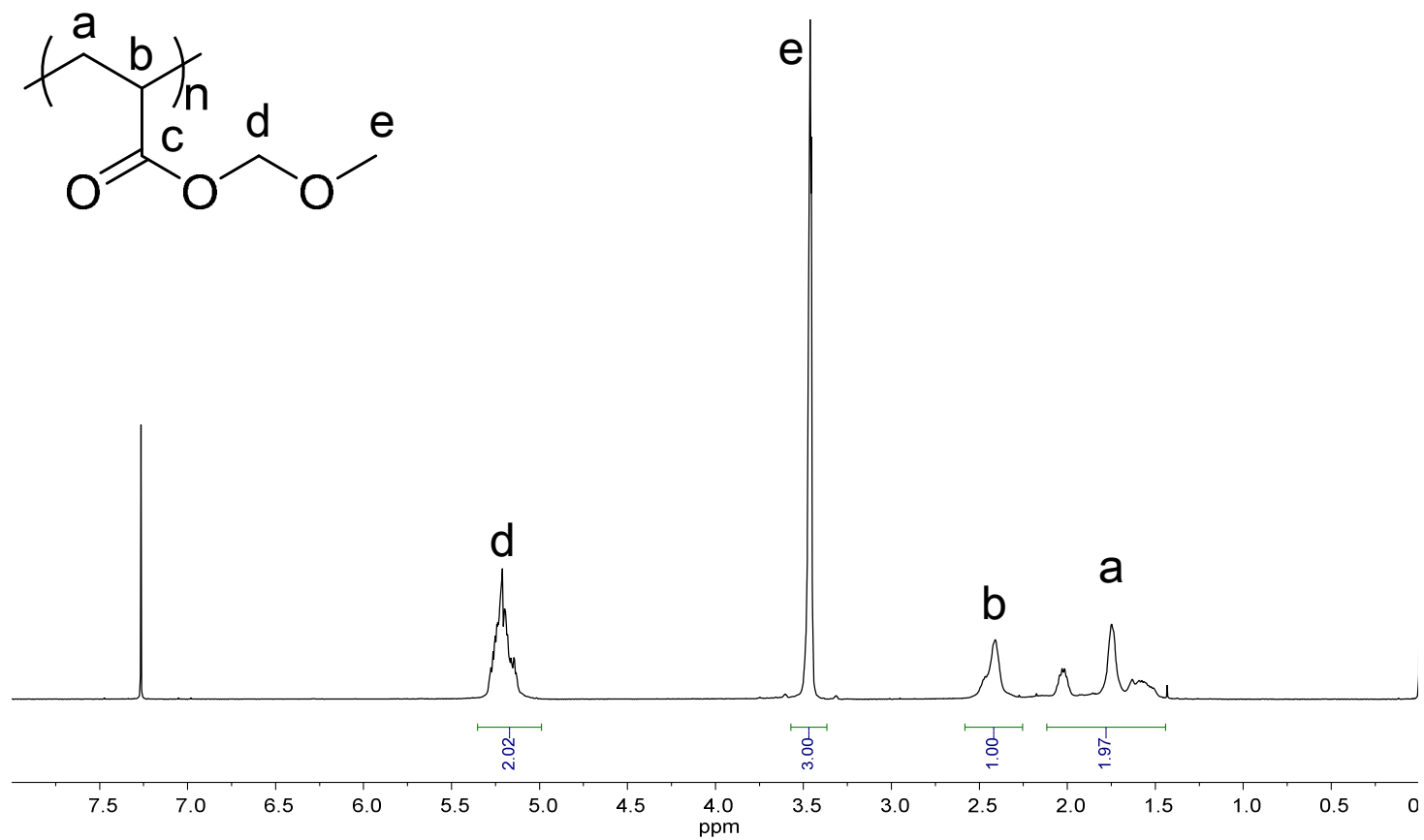
Poly(12-methoxydodecyl acrylate) (**PMC12A**):



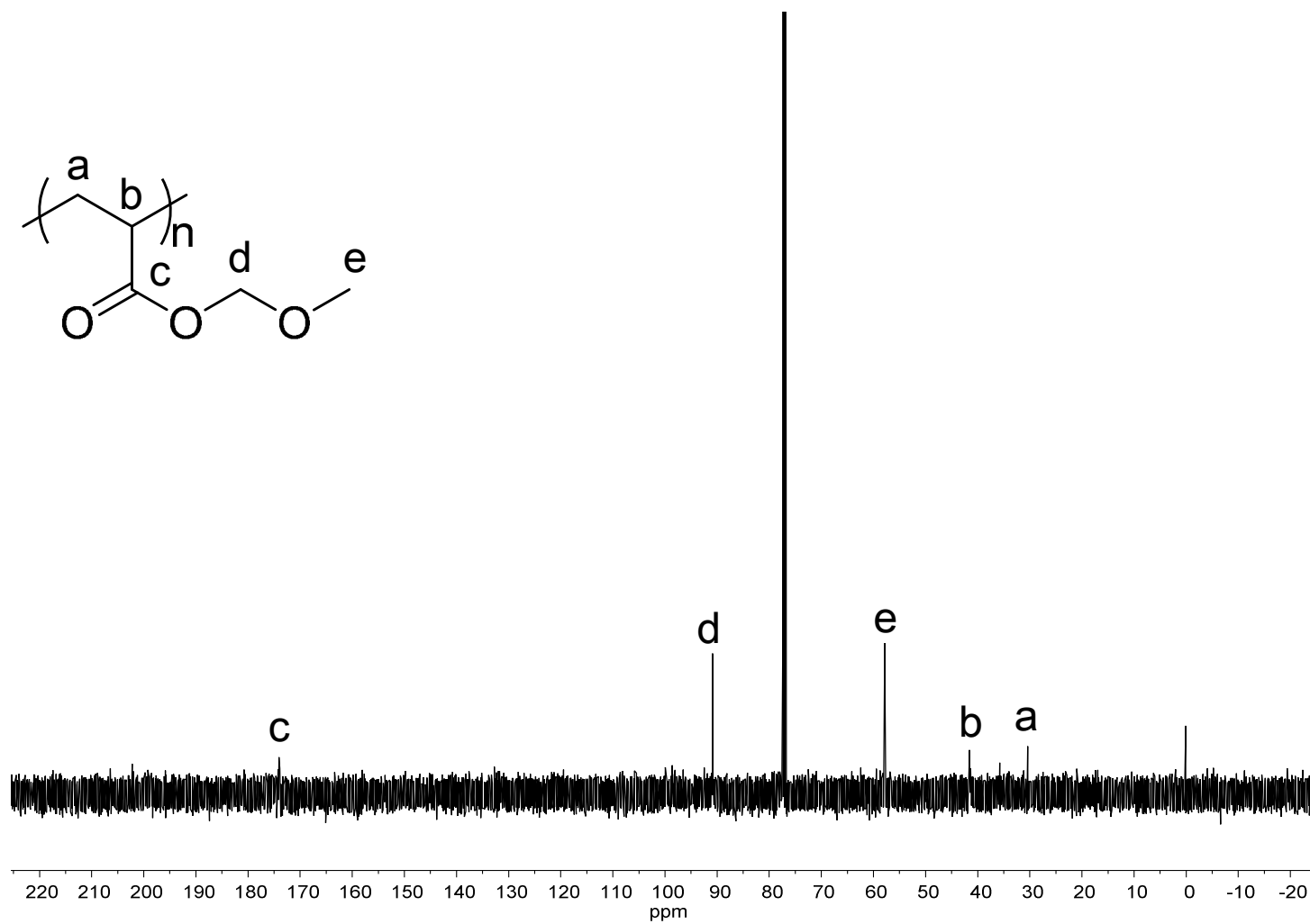
$^1\text{H}$  NMR  $\delta$  (ppm): 1.04~1.96 (m, 22H, C(a)H, C(d)H, C(e)H, C(f)H, C(g)H, C(h)H, C(i)H, C(j)H, C(k)H, C(l)H, C(m)H), 2.08~2.44 (m, 1H, C(b)H), 3.33 (s, 3H, C(o)H), 3.36 (t,  $J = 6.7$  Hz, 2H, C(n)H), 4.00 (br, 2H, C(c)H).

$^{13}\text{C}$  NMR  $\delta$  (ppm): 26.0~26.3 (Cm, Cn), 28.7 (Ce), 29.6~30.1 (Cf, Cg, Ch, Ci, Cj, Ck, Cl), 35.6 (Ca), 41.4 (Cb), 58.6 (Cp), 64.8 (Cd), 73.5 (Co), 174.3 (Cc).

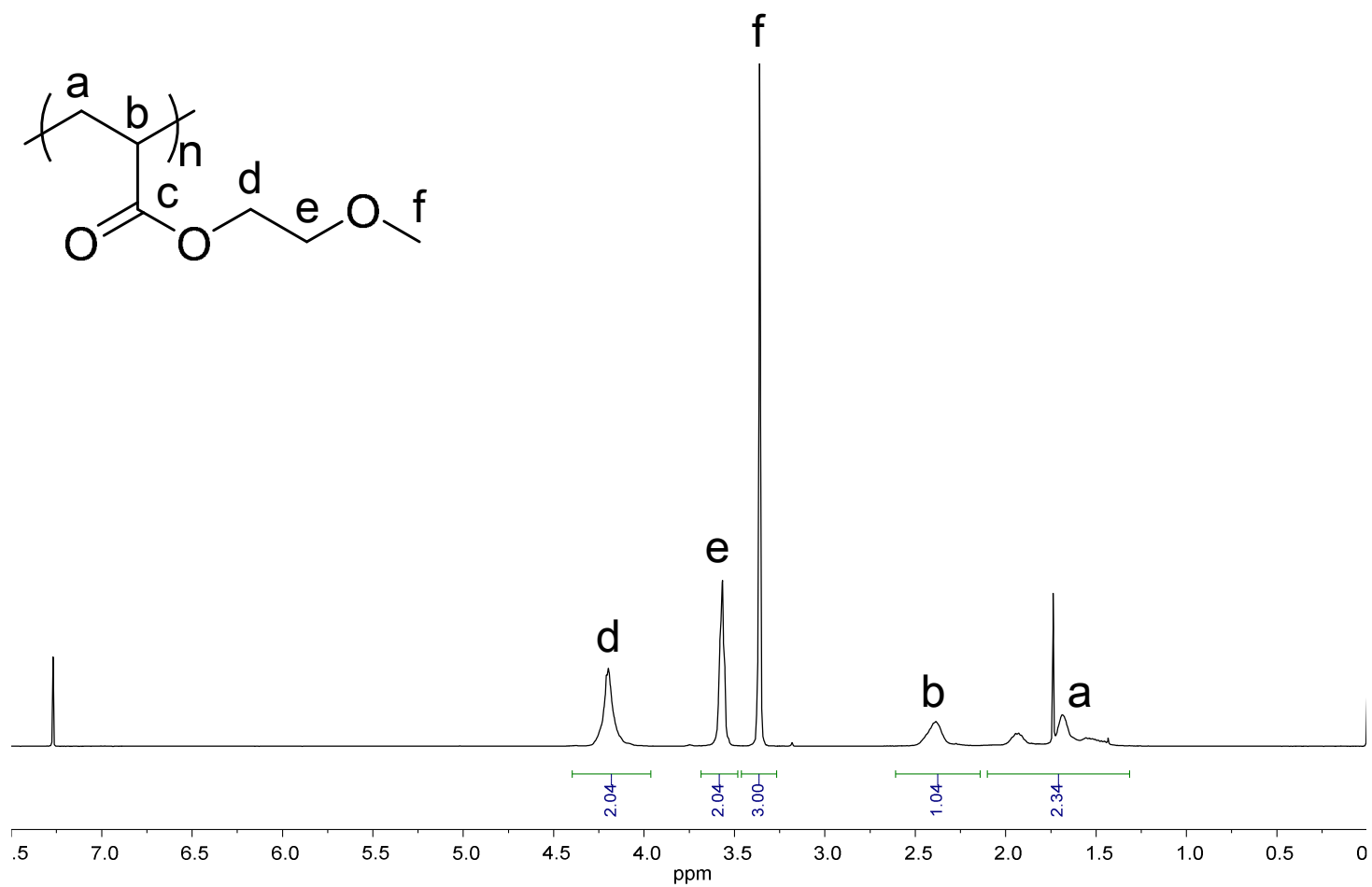




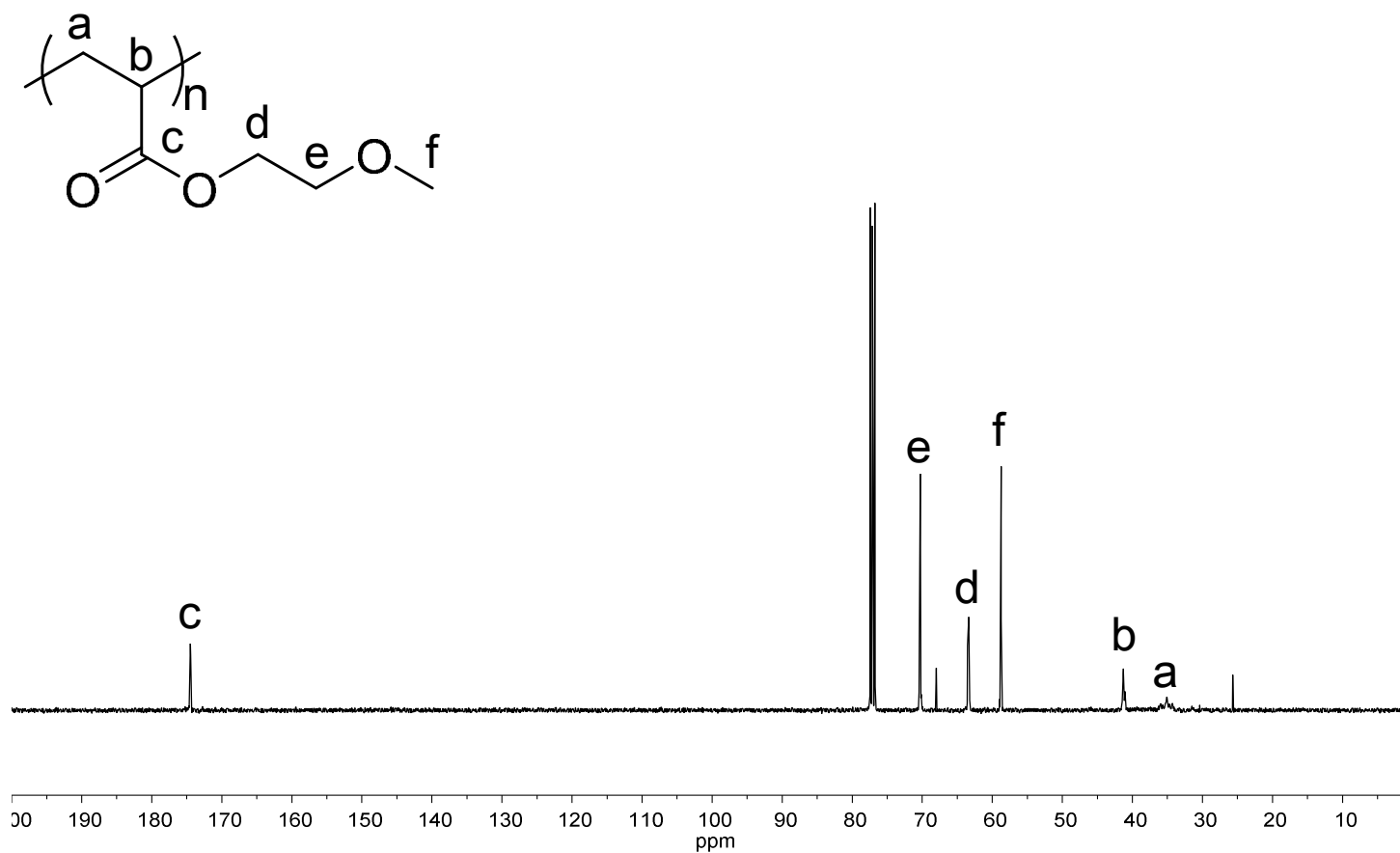
**Figure S13.**  $^1\text{H}$  NMR spectrum poly(methoxymethyl acrylate) (**PMc1A**, in  $\text{CDCl}_3$ , 500 MHz).



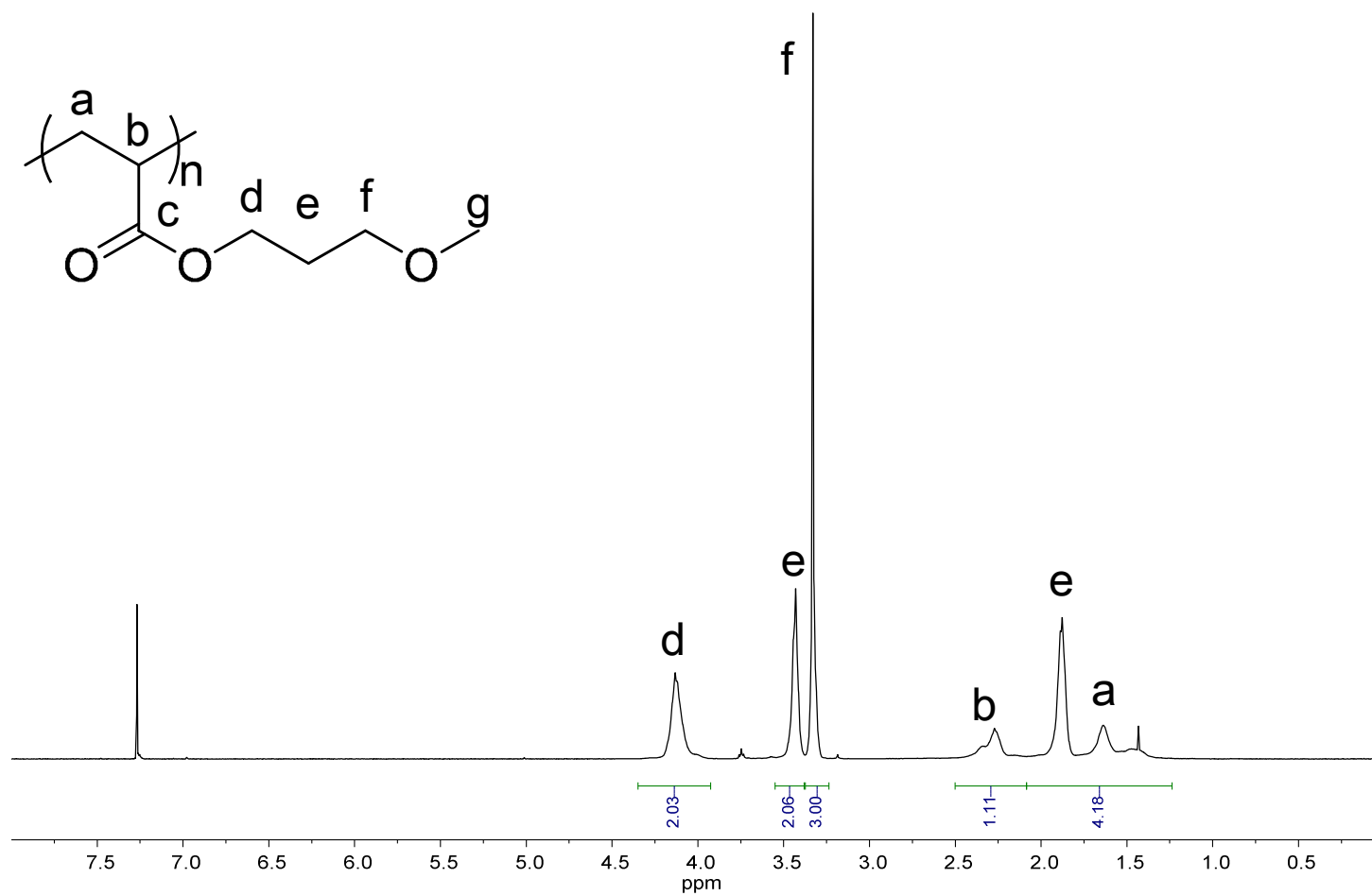
**Figure S14.**  $^{13}\text{C}$  NMR spectrum of poly(methoxymethyl acrylate) (PMc1A, in  $\text{CDCl}_3$ , 125 MHz).



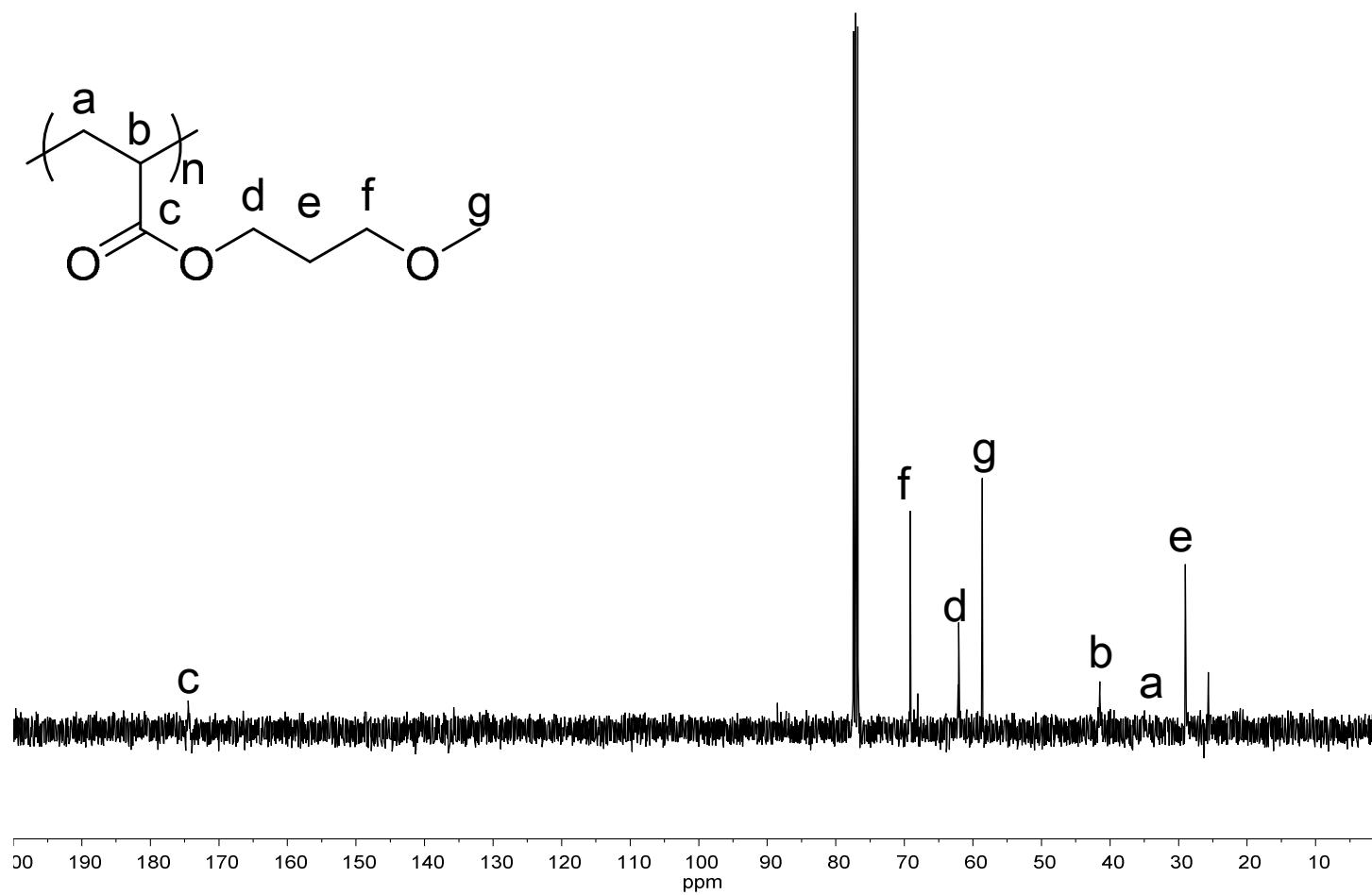
**Figure S15.**  $^1\text{H}$  NMR spectrum poly(2-methoxyethyl acrylate) (PMEA, in  $\text{CDCl}_3$ , 500 MHz).



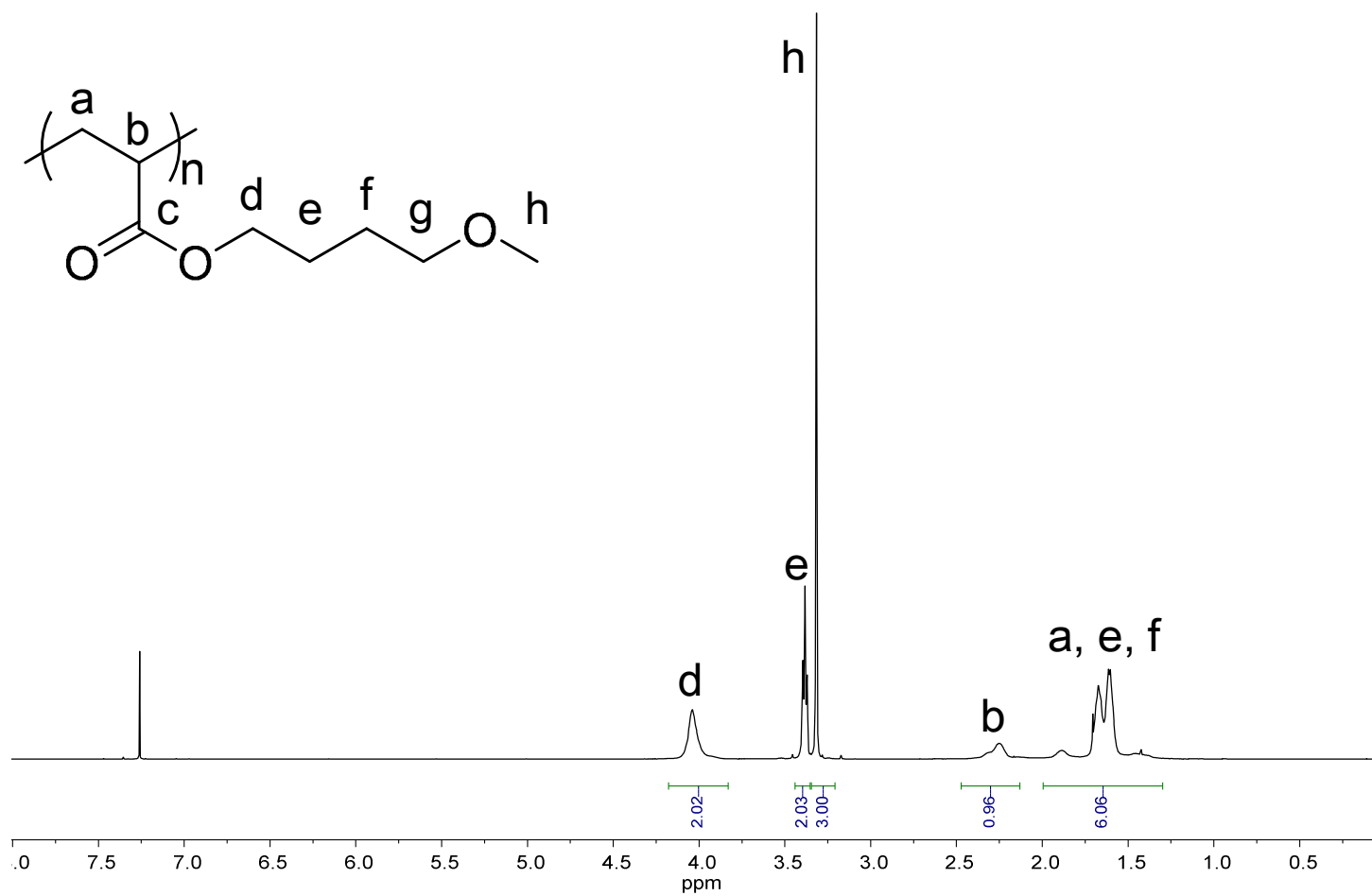
**Figure S16.**  $^{13}\text{C}$  NMR spectrum of poly(2-methoxyethyl acrylate) (PMEA, in  $\text{CDCl}_3$ , 125 MHz).



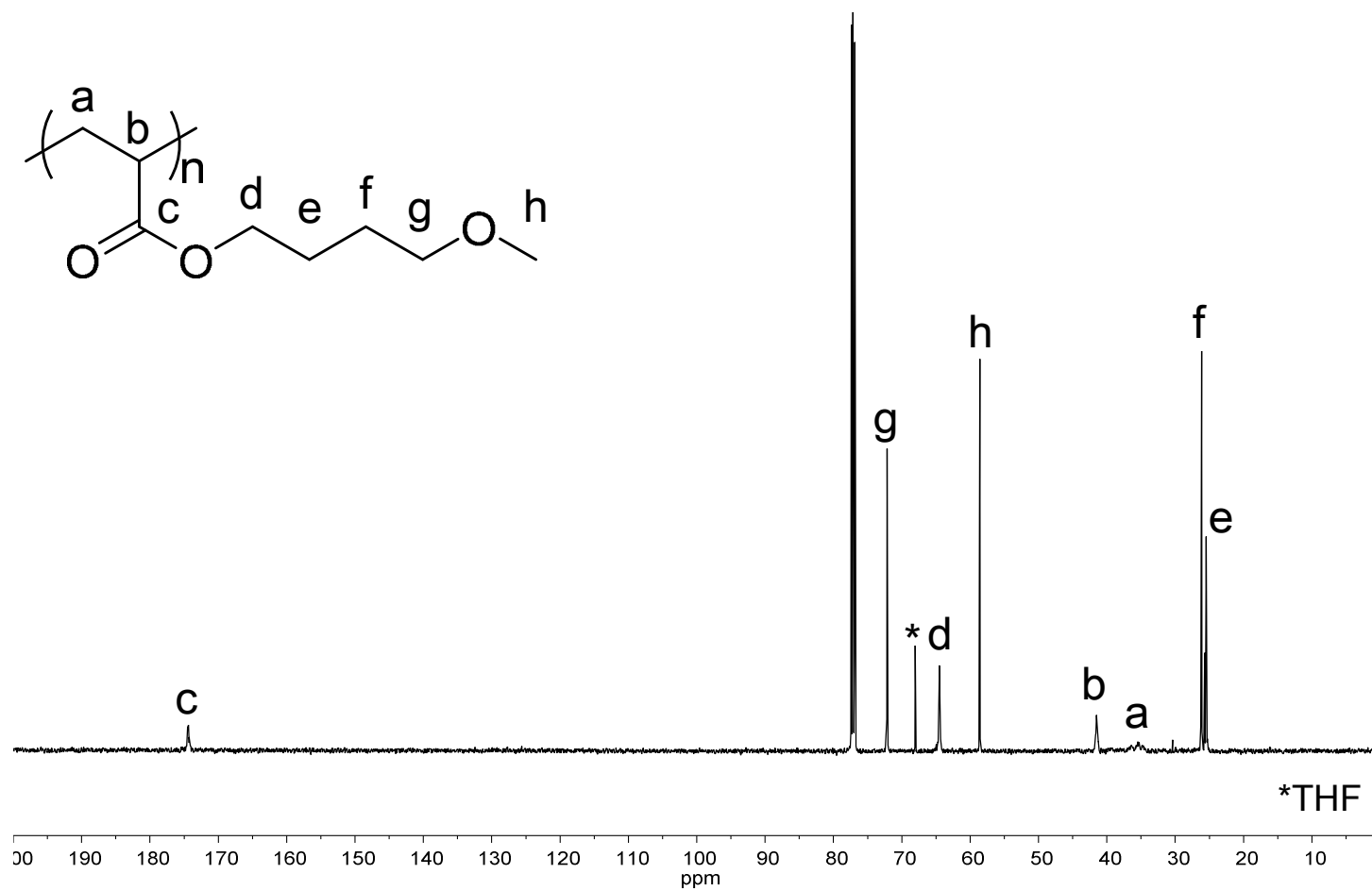
**Figure S17.**  $^1\text{H}$  NMR spectrum poly(3-methoxypropyl acrylate) (**PMC3A**, in  $\text{CDCl}_3$ , 500 MHz).



**Figure S18.**  $^{13}\text{C}$  NMR spectrum of poly(3-methoxypropyl acrylate) (PMC3A, in  $\text{CDCl}_3$ , 125 MHz).

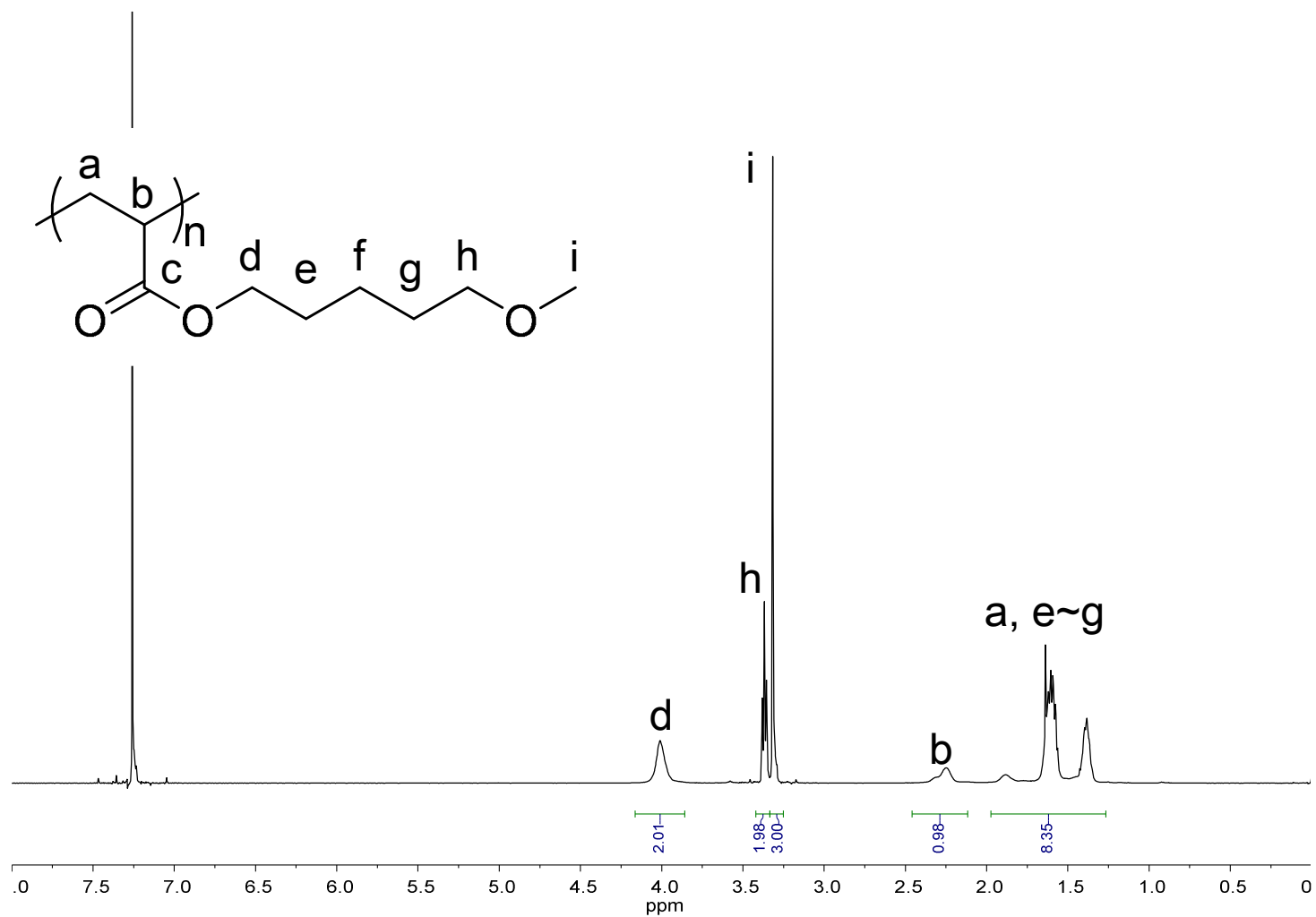


**Figure S19.**  $^1\text{H}$  NMR spectrum poly(4-methoxybutyl acrylate) (**PMC4A**, in  $\text{CDCl}_3$ , 500 MHz).



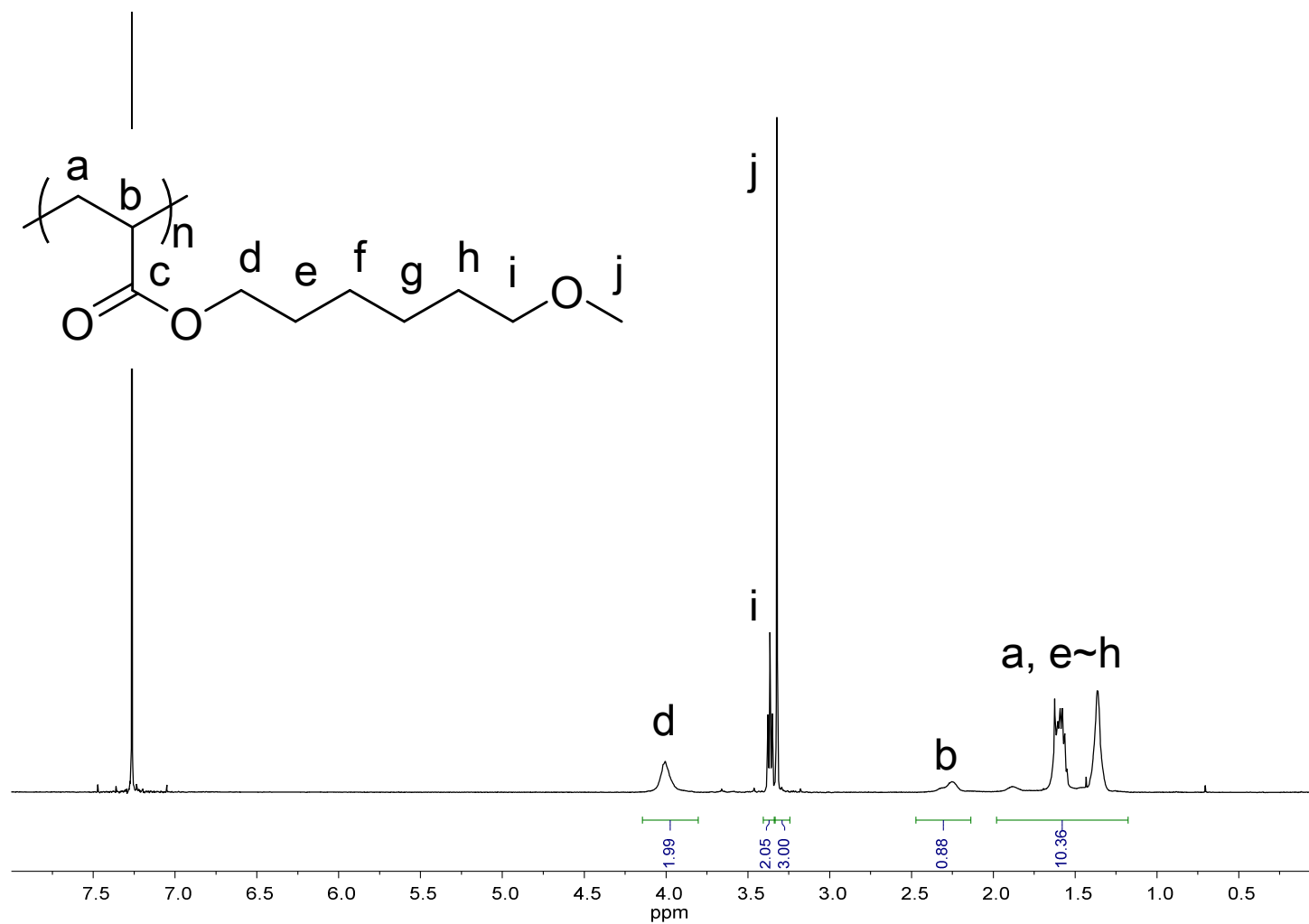
**Figure S20.**  $^{13}\text{C}$  NMR spectrum of poly(4-methoxybutyl acrylate) (PMC4A, in  $\text{CDCl}_3$ , 125 MHz).





**Figure S21.**  $^1\text{H}$  NMR spectrum poly(5-methoxypentyl acrylate) (PMC5A, in  $\text{CDCl}_3$ , 500 MHz).

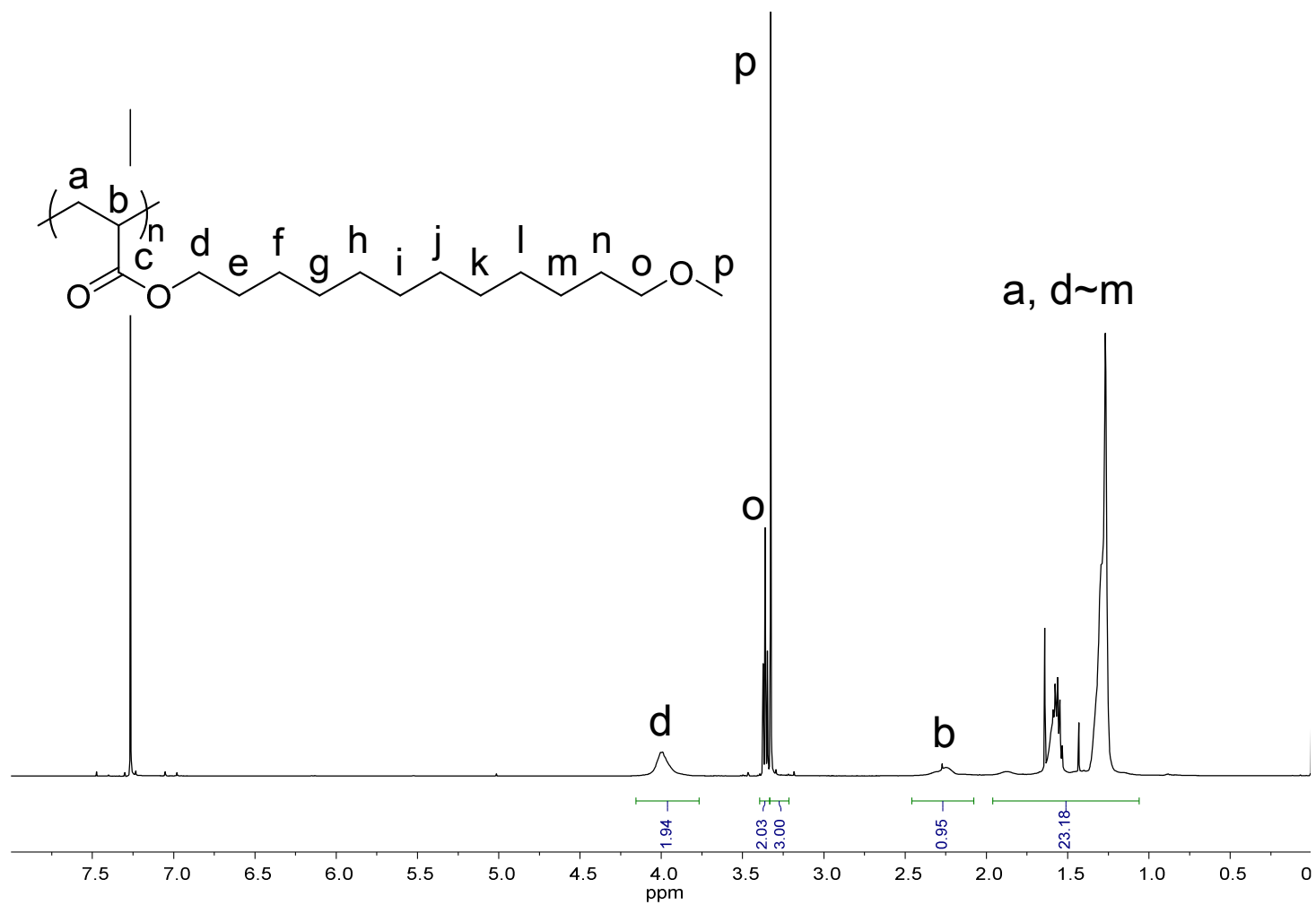




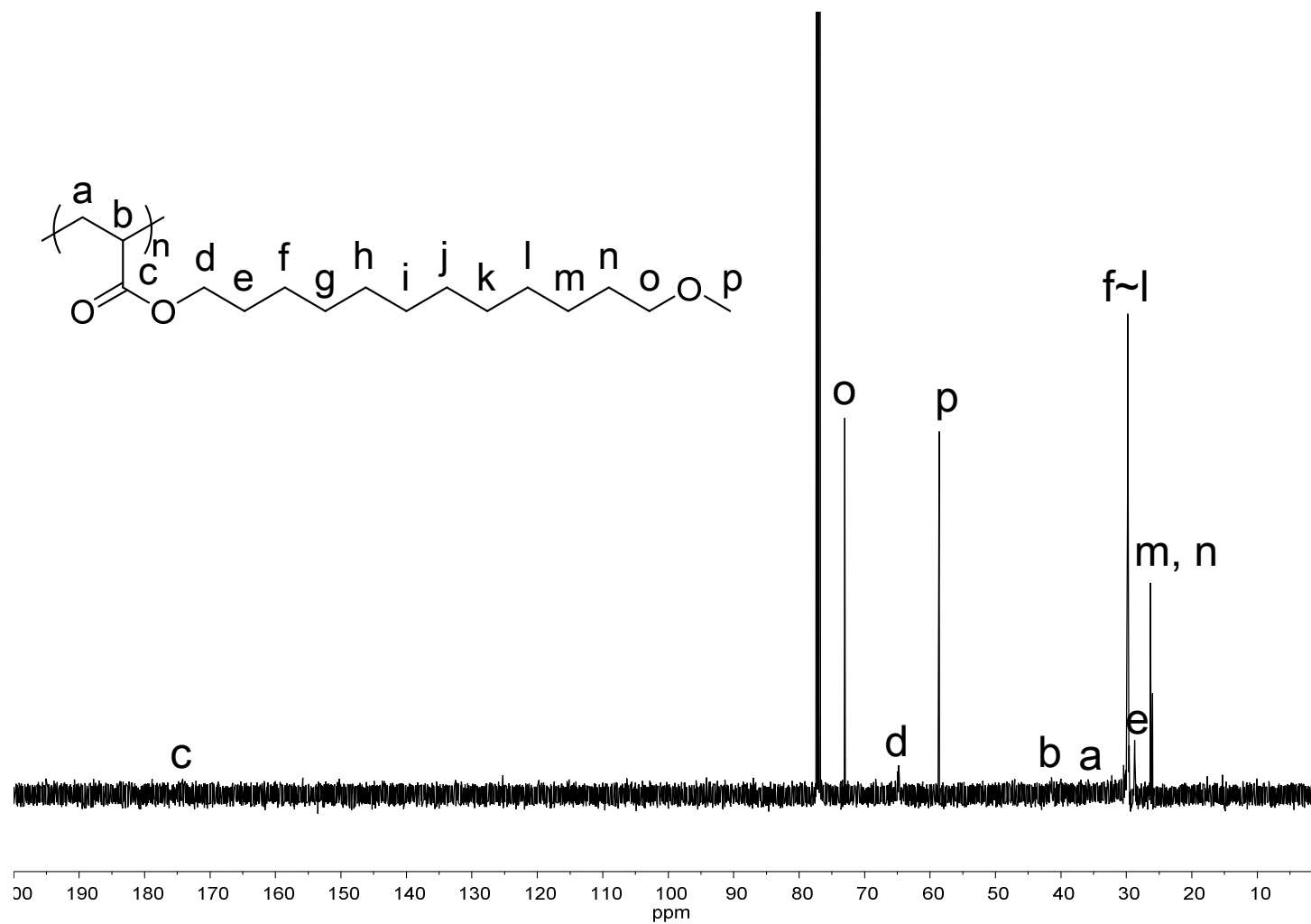
**Figure S23.**  $^1\text{H}$  NMR spectrum poly(6-methoxyhexyl acrylate) (**PMC6A**, in  $\text{CDCl}_3$ , 500 MHz).



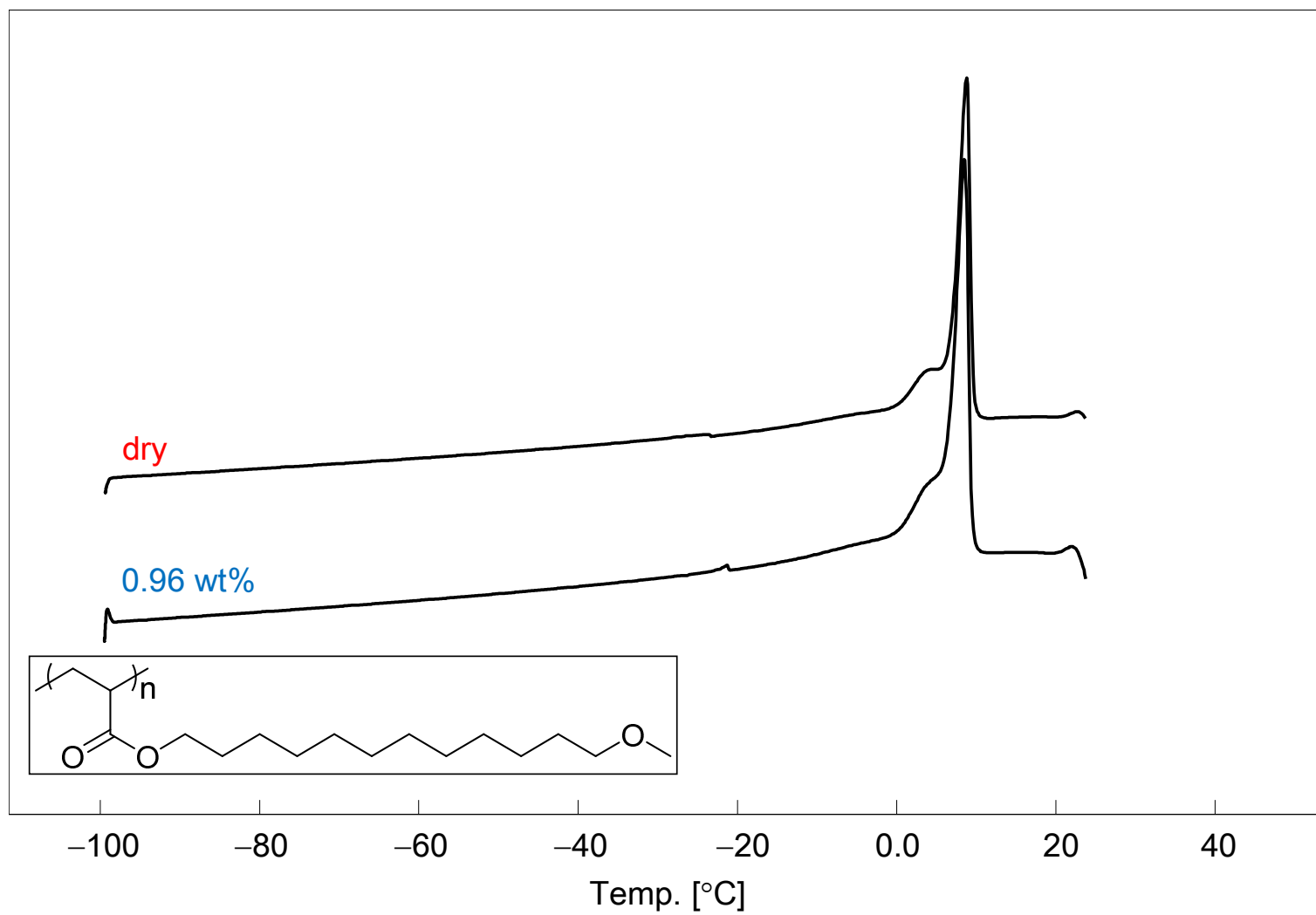
Figure S24.  $^{13}\text{C}$  NMR spectrum of poly(6-methoxyhexyl acrylate) (PMC6A, in  $\text{CDCl}_3$ , 125 MHz).



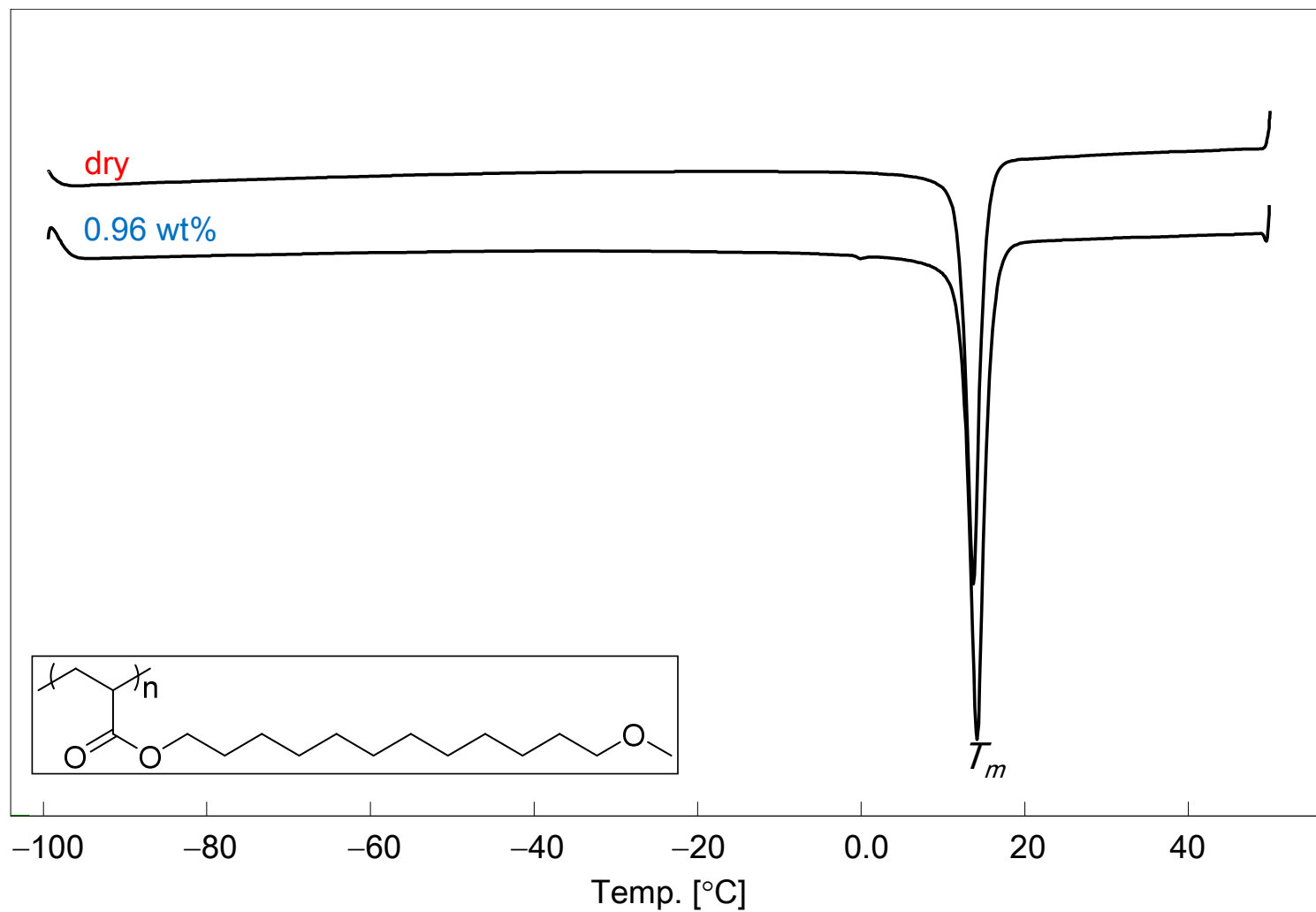
**Figure S25.**  $^1\text{H}$  NMR spectrum poly(12-methoxydodecyl acrylate) (PMC12A, in  $\text{CDCl}_3$ , 500 MHz).



**Figure S26.**  $^{13}\text{C}$  NMR spectrum of poly(12-methoxydodecyl acrylate) (**PMC12A**, in  $\text{CDCl}_3$ , 125 MHz).



**Figure S27.** DSC thermogram of dried and hydrated **PMC12A** at 5 °C/min. (cooling scan).



**Figure S28.** DSC thermogram of dried and hydrated **PMC12A** at 5 °C/min. (heating scan).