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Electronic Supplementary Information:

Installing a functional group into inactive ω-chain end of PMMA and PS-*b*-PMMA by terminal-selective transesterification

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1. Experimental section

1.1. Synthesis of PMMA Homopolymer.

sec-BuLi (0.98 mol L^{-1}, 2.57 mL, 2.52 mmol), DPE (664 μL, 3.78 mmol), and a solution of LiCl in THF (500 mmol L^{-1}, 7.55 mL, 3.78 mmol) were sequentially added to THF (132 mL) at −78 °C, and the mixture was stirred for 30 min. Methyl methacrylate (MMA; 8.00 mL, 75.5 mmol) was added to the mixture and polymerization was terminated after 1 h by the addition of a small amount of methanol. The mixture was diluted with THF and passed through a short column of alumina. After removal of the solvent, the crude product was dialyzed with a cellophane tube (Spectra/Por® 6 Membrane; MWCO: 1,000) in acetone and finally precipitated three times from THF solution into hexane to give PMMA (**M3**) as white powder (Yield: 38.6%; $M_{n,NMR}$ = 3,300 g mol^{-1}; $M_{n,SEC}$ = 3,760 g mol^{-1}, $Đ$ = 1.08 (THF)). ^{1}H NMR ($CDCl_3$): δ 7.32−7.08 (br, 10H, aromatic), 3.82−3.38 (br, −OCH_3), 2.49 (br, ω-terminal, −CH(CH_3)COO−), 2.24−1.36 (br, main chain −CH_2C−), 0.59−0.52 (m, 6H, α-terminal −CH_3, −CH_2CH_3).

1.2. Transesterification of PMMA Homopolymer

Transesterification of M3 with 1-Pentanol. The following is a typical terminal-selective transesterification procedure (Procedure B): Ti(O*i*Pr)$_4$ (81.1 μL, 277 μmol), 1-pentanol (200 μL, 1.85 mmol), and toluene (1.00 mL) were added to a Schlenk flask an under argon atmosphere. The mixture was stirred at 80 °C for 1 h and then cooled with liquid nitrogen. The solvent and the 2-propanol generated from Ti(O*i*Pr)$_4$ were removed by evaporation under high vacuum, to yield the titanium alkoxide of 1-propanol. A solution of **M3** (300 mg, 92.3 μmol) and 1-pentanol (200 μL, 1.85 mmol) in toluene (5.43 mL) was added to the Schlenk flask containing the titanium alkoxide. then the mixture was stirred at 100 °C for 24 h. After cooling to room

temperature, a small amount of water was added. The mixture was stirred for 30 min, then diluted with THF, and filtrated using a membrane filter (0.45 μm pore size) to remove the catalyst as titanium oxide. After evaporating the solvent, the residue was dialyzed using a cellophane tube (Spectra/Por® 6 Membrane; MWCO: 1,000) against acetone and finally reprecipitated from THF solution into hexane to give **M3-B** as a white powder. Yield: 51.3%. $M_{n,NMR}$ = 3,290 g mol^{-1}, $M_{n,SEC}$ = 4,040 g mol^{-1}, $Đ$ = 1.06 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.08 (br, 10H, −C(*Ph*)$_2$−), 4.02 (m, ω-terminal, 2H, −OC*H*$_2$(CH$_2$)$_3$CH$_3$), 3.60 (−OC*H*$_3$, PMMA), 2.47 (br, ω-terminal, −C*H*(CH$_3$)COO−), 0.60−2.12 (br, main chain −C*H*$_2$C−, −CC*H*$_3$), 0.59−0.52 (m, 6H, α-terminal −C*H*$_3$, −CH$_2$C*H*$_3$).

Transesterification of M3 with Benzyl Alcohol. By following the Procedure B, the transesterification of M3 (300 mg, 92.3 μmol) with benzyl alcohol (123 μL, 1.85 mmol) was performed using the titanium alkoxide, which had been prepared from Ti(O*i*Pr)$_4$ (81.1 μL, 277 μmol) and benzyl alcohol (123 μL, 1.85 mmol) in toluene (1.00 mL), in toluene (3.00 mL) to give **M3-C** as a white powder. Yield: 48.3%. $M_{n,NMR}$ = 3,340 g mol^{-1}, $M_{n,SEC}$ = 4,090 g mol^{-1}, $Đ$ = 1.06 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (br, ω-terminal, 5H, −OCH$_2$*Ph*), 7.25−7.08 (br, 10H, −C(*Ph*)$_2$−), 5.07 (m, ω-terminal, 2H, −OC*H*$_2$Ph), 3.60 (−OC*H*$_3$, PMMA), 2.53 (br, ω-terminal, −C*H*(CH$_3$)COO−), 0.60−2.12 (br, main chain −C*H*$_2$C−, −CC*H*$_3$), 0.59−0.52 (m, 6H, α-terminal −C*H*$_3$, −CH$_2$C*H*$_3$).

Transesterification of M3 with 1-Naphthalenemethanol. The following is a typical terminal-selective transesterification procedure (Procedure C): Ti(O*i*Pr)$_4$ (81.1 μL, 277 μmol), 1-naphthalenemethanol (583 mL, 3.69 mmol), and toluene (1.00 mL) were added to a Schlenk flask under an argon atmosphere. The mixture was stirred at 80 °C for 1 h and then cooled with liquid nitrogen. The solvent and the 2-propanol generated from the Ti(O*i*Pr)$_4$ were removed by

evaporation under high vacuum, to yield the corresponding titanium alkoxide. A solution of **M3** (300 mg, 92.3 μmol) in toluene (5.43 mL) was added to the Schlenk flask containing the titanium alkoxide, then the mixture was stirred at 100 °C for 24 h. After cooling to room temperature, a small amount of water was added. The mixture was stirred for 30 min, then diluted with THF and filtrated using a membrane filter (0.45 μm pore size) to remove the catalyst as titanium oxide. After evaporating the solvent, the residue was dialyzed using a cellophane tube (Spectra/Por® 6 Membrane; MWCO: 1,000) against acetone and finally reprecipitated from THF solution into hexane to give **M3-D** as a white powder. Yield: 40.0%. $M_{n,NMR}$ = 3,060 g mol^{-1}, $M_{n,SEC}$ = 3,890 g mol^{-1}, $Đ$ = 1.07 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91−7.70 (br, 3H, naphthalene), 7.55−7.40 (br, 3H, naphthalene), 7.25−7.08 (br, 10H, −C(*Ph*)$_2$−), 5.23 (m, ω-terminal, 2H, −OC*H*$_2$−naphthalene), 3.60 (−OC*H*$_3$, PMMA), 2.56 (br, ω-terminal, −C*H*(CH$_3$)COO−), 0.60−2.12 (br, main chain −C*H*$_2$C−, −CC*H*$_3$), 0.59−0.52 (m, α-terminal −C*H*$_3$, −CH$_2$C*H*$_3$).

Transesterification of M3 with 1-Pyrenemethanol. By following the Procedure C, the transesterification of **M3** (300 mg, 92.3 μmol) with 1-pyrenemethanol (81.1 μL, 277 μmol) was performed using Ti(O*i*Pr)$_4$ (10.5 μL, 35.7 μmol) in toluene (5.43mL) to give **M3-E** as a white powder. Yield: 67.0%. $M_{n,NMR}$ = 3,410 g mol^{-1}, $M_{n,SEC}$ = 3,770 g mol^{-1}, $Đ$ = 1.07 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43−8.00 (br, 9H, pyrene), 7.25−7.08 (br, 10H, −C(*Ph*)$_2$−), 5.80 (m, ω-terminal, 2H, −OC*H*$_2$−pyrene), 3.60 (−OC*H*$_3$, PMMA), 2.55 (br, ω-terminal, −C*H*(CH$_3$)COO−), 0.60−2.12 (br, main chain −C*H*$_2$C−, −CC*H*$_3$), 0.59−0.52 (m, 6H, α-terminal −C*H*$_3$, −CH$_2$C*H*$_3$).

Transesterification of M3 with Ethylene glycol. By following the Procedure B, the transesterification of **M3** (300 mg, 92.3 μmol) with ethylene glycol (35.4 μL, 1.85 mmol) was performed using the titanium alkoxide, which had been prepared from Ti(O*i*Pr)$_4$ (81.1 μL, 277

μmol) and ethylene glycol (35.4 μL, 1.85 mmol) in toluene (5.43 mL), in toluene (5.43 mL) to give **M3-F**. The reaction progress was monitored by MALDI-TOF mass analysis.

Transesterification of M3 with Triethylene Glycol Monomethyl Ether. By following the Procedure B, the transesterification of **M3** (300 mg, 92.3 μmol) with triethylene glycol monomethyl ether (289 μL, 1.85 mmol) was performed using the titanium alkoxide, which had been prepared from Ti(O*i*Pr)$_4$ (81.1 μL, 277 μmol) and triethylene glycol monomethyl ether (289 μL, 1.85 mmol) in toluene (1.00 mL), in toluene (5.43 mL) to give **M3-G** as a white powder. Yield: 56.0%. $M_{n,NMR}$ = 3,150 g mol^{-1}, $M_{n,SEC}$ = 4,030 g mol^{-1}, $Đ$ = 1.06 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.08 (br, 10H, −C(*Ph*)$_2$−), 4.20 (m, ω-terminal, 2H, −C*H*$_2$CH$_2$(O(CH$_2$)$_2$)$_2$OCH$_3$), 3.60 (−OC*H*$_3$, PMMA), 3.34 (s, ω-terminal, 3H, −(O(CH$_2$)$_2$)$_3$OC*H*$_3$), 2.50 (br, ω-terminal, −C*H*(CH$_3$)COO−), 0.60−2.12 (br, main chain −C*H*$_2$C−, −CC*H*$_3$), 0.59−0.52 (m, 6H, α-terminal −C*H*$_3$, −CH$_2$C*H*$_3$).

Transesterification of M3 with HFIP. By following the Procedure B, the transesterification of **M3** (300 mg, 92.3 μmol) with HFIP (192 μL, 1.85 mmol) was performed using the titanium alkoxide, which had been prepared from Ti(O*i*Pr)$_4$ (81.1 μL, 277 μmol) and HFIP (192 μL, 1.85 mmol) in toluene (1.00 mL), in toluene (5.43 mL) to give **M3-H**. The reaction progress was monitored by MALDI-TOF mass analysis.

Transesterification of M3 with 4,4,5,5,5-Pentafluoro-1-pentanol. By following the Procedure B, the transesterification of **M3** (300 mg, 92.3 μmol) with 4,4,5,5,5-pentafluoro-1-pentanol (244 μL, 1.85 mmol) was performed using the titanium alkoxide, which had been prepared from Ti(O*i*Pr)$_4$ (81.1 μL, 277 μmol) and 4,4,5,5,5-pentafluoro-1-pentanol (244 μL, 1.85 mmol) in toluene (1.00 mL), in toluene (5.43 mL) to give **M3-I** as a white powder. Yield: 19.7%. $M_{n,NMR}$ = 3,430 g mol^{-1}, $M_{n,SEC}$ = 4,280 g mol^{-1}, $Đ$ = 1.05 (THF). ^{1}H NMR (400 MHz,

$CDCl_3$): δ 7.25−7.08 (br, 10H, −C(*Ph*)$_2$−), 4.10 (m, ω-terminal, 2H, −OC*H*$_2$(CH$_2$)$_2$CF$_2$CF$_3$), 3.60 (−OC*H*$_3$, PMMA), 2.50 (br, ω-terminal, −C*H*(CH$_3$)COO−), 2.16 (m, ω-terminal, 2H, −O(CH$_2$)$_2$C*H*$_2$CF$_2$CF$_3$), 0.60−2.12 (br, main chain −C*H*$_2$C−, −CC*H*$_3$), 0.59−0.52 (m, 6H, α-terminal −C*H*$_3$, −CH$_2$C*H*$_3$).

Transesterification of M3 with Pentafluorobenzyl Alcohol. By following the Procedure C, the transesterification of **M3** (300 mg, 92.3 μmol) with pentafluorobenzyl alcohol (731 mg, 3.69 mmol) was performed using Ti(O*i*Pr)$_4$ (81.1 μL, 277 μmol) in toluene (5.43 mL) to give **M3-J** as a white powder. Yield: 47.7%. $M_{n,NMR}$ = 3,370 g mol^{-1}, $M_{n,SEC}$ = 4,040 g mol^{-1}, $Đ$ = 1.06 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.08 (br, 10H, −C(*Ph*)$_2$−), 5.15 (m, ω-terminal, 2H, −OC*H*$_2$C$_5$F$_5$), 3.60 (−OC*H*$_3$, PMMA), 2.50 (br, ω-terminal, −C*H*(CH$_3$)COO−), 0.60−2.12 (br, main chain −C*H*$_2$C−, −CC*H*$_3$), 0.59−0.52 (m, 6H, α-terminal −C*H*$_3$, −CH$_2$C*H*$_3$).

Transesterification of M3 with 6-Azido-1-hexanol. By following the Procedure C, the transesterification of **M3** (300 mg, 92.3 μmol) with 6-azido-1-hexanol (513 μg, 3.69 mmol) was performed using Ti(O*i*Pr)$_4$ (81.1 μL, 277 μmol) in toluene (5.43 mL) to give **M3-K** as a white powder. Yield: 47.7%. $M_{n,NMR}$ = 3,310 g mol^{-1}, $M_{n,SEC}$ = 3,890 g mol^{-1}, $Đ$ = 1.07 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.08 (br, 10H, −C(*Ph*)$_2$−), 4.02 (m, ω-terminal, 2H, −C*H*$_2$(CH$_2$)$_5$N$_3$), 3.60 (−OC*H*$_3$, PMMA), 3.29 (t, ω-terminal, 2H, −C*H*$_2$N$_3$), 2.47 (br, ω-terminal, −C*H*(CH$_3$)COO−), 0.60−2.12 (br, main chain −C*H*$_2$C−, −CC*H*$_3$), 0.59−0.52 (m, 6H, α-terminal −C*H*$_3$, −CH$_2$C*H*$_3$).

1.3. Transesterification of PS-*b*-PMMA

Transesterification of S21M21 with 2-Propanol. By following the Procedure A, the transesterification of **S21M21** (500 mg, 11.9 μmol) with 2-propanol (17.7 μL, 476 mmol) was

performed using Ti(O*i*Pr)$_4$ (10.5 μL, 35.7 μmol) in toluene (3.00 mL) to give **S21M21-A** as a white powder. Yield: 23.2%. $M_{n,SEC}$ = 35,200 g mol^{-1}, $Đ$ = 1.03 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−6.26 (br, aromatic), 4.94 (m, J = 6.4 Hz, ω-terminal, 1H, −OC*H*(CH$_3$)$_2$), 3.82−3.38 (br, −OC*H*$_3$, PMMA), 2.42 (br, ω-terminal, 1H, −C*H*(CH$_3$)COO−), 2.24−0.77 (br, main chain −C*H*$_2$C−, −CC*H*$_3$, −C*H*$_2$C*H*−, −C*H*$_2$C*H*−, PMMA, PS).

Transesterification of S21M21 with 1-Pentanol. By following the Procedure B, the transesterification of **S21M21** (500 mg, 11.9 μmol) with 1-pentanol (25.8 μL, 238 mmol) was performed using the titanium alkoxide, which had been prepared from Ti(O*i*Pr)$_4$ (10.5 μL, 35.7 μmol) and 1-pentanol (25.8 μL, 238 mmol) in toluene (1.00 mL), in toluene (3.00 mL) to give **S21M21-B** as a white powder. Yield: 79.0%. $M_{n,SEC}$ = 36,700 g mol^{-1}, $Đ$ = 1.03 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−6.26 (br, aromatic), 4.02 (m, ω-terminal, 2H, −OC*H*$_2$(CH$_2$)$_3$CH$_3$), 3.82−3.38 (br, −OC*H*$_3$, PMMA), 2.47 (br, ω-terminal, −C*H*(CH$_3$)COO−), 2.24−0.77 (br, main chain −C*H*$_2$C−, −CC*H*$_3$, −C*H*$_2$C*H*−, −C*H*$_2$C*H*−, PMMA, PS).

Transesterification of S21M21 with Benzyl Alcohol. By following the Procedure B, the transesterification of **S21M21** (500 mg, 11.9 μmol) with benzyl alcohol (15.9 μL, 238 mmol) was performed using the titanium alkoxide, which had been prepared from Ti(O*i*Pr)$_4$ (10.5 μL, 35.7 μmol) and benzyl alcohol (15.9 μL, 238 mmol) in toluene (1.00 mL), in toluene (3.00 mL) to give **S21M21-C** as a white powder. Yield: 62.2%. $M_{n,SEC}$ = 35,400 g mol^{-1}, $Đ$ = 1.03 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (br, ω-terminal, 5H, −OCH$_2$*Ph*), 7.32−6.26 (br, aromatic), 5.07 (m, ω-terminal, 2H, −OC*H*$_2$Ph), 3.82−3.38 (br, −OC*H*$_3$, PMMA), 2.54 (br, ω-terminal, −C*H*(CH$_3$)COO−), 2.24−0.77 (br, main chain −C*H*$_2$C−, −CC*H*$_3$, −C*H*$_2$C*H*−, −C*H*$_2$C*H*−, PMMA, PS).

Transesterification of S21M21 with Triethylene Glycol Monomethyl Ether. By following the Procedure B, the transesterification of **S21M21** (500 mg, 11.9 μmol) with triethylene glycol monomethyl ether (37.2 μL, 238 mmol) was performed using the titanium alkoxide, which had been prepared from Ti(O*i*Pr)$_4$ (10.5 μL, 35.7 μmol) and triethylene glycol monomethyl ether (37.2 μL, 238 mmol) in toluene (1.00 mL), in toluene (3.00 mL) to give **S21M21-G** as a white powder. Yield: 78.2%. $M_{n,SEC}$ = 36,800 g mol^{-1}, $Đ$ = 1.03 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−6.26 (br, aromatic), 4.20 (m, ω-terminal, 2H, −C*H*$_2$CH$_2$(O(CH$_2$)$_2$)$_2$OCH$_3$), 3.82−3.38 (br, −OC*H*$_3$, PMMA), 3.39 (s, ω-terminal, 3H, −(O(CH$_2$)$_2$)$_3$OC*H*$_3$), 2.50 (br, ω-terminal, −C*H*(CH$_3$)COO−), 2.24−0.77 (br, main chain −C*H*$_2$C−, −CC*H*$_3$, −C*H*$_2$C*H*−, −C*H*$_2$C*H*−, PMMA, PS).

Transesterification of S21M21 with 4,4,5,5,5-Pentafluoro-1-pentanol. By following the Procedure B, the transesterification of **S21M21** (500 mg, 11.9 μmol) with 4,4,5,5,5-pentafluoro-1-pentanol (31.4 μL, 238 mmol) was performed using the titanium alkoxide, which had been prepared from Ti(O*i*Pr)$_4$ (10.5 μL, 35.7 μmol) and 4,4,5,5,5-pentafluoro-1-pentanol (31.4 μL, 238 mmol) in toluene (1.00 mL), in toluene (5.43 mL) to give **S21M21-I** as a white powder. Yield: 47.4%. $M_{n,SEC}$ = 36,000 g mol^{-1}, $Đ$ = 1.03 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−6.26 (br, aromatic), 4.10 (m, ω-terminal, 2H, −OC*H*$_2$(CH$_2$)$_2$CF$_2$CF$_3$), 3.82−3.38 (br, −OC*H*$_3$, PMMA), 2.50 (br, ω-terminal, −C*H*(CH$_3$)COO−), 2.24−0.77 (br, main chain −C*H*$_2$C−, −CC*H*$_3$, −C*H*$_2$C*H*−, −C*H*$_2$C*H*−, PMMA, PS).

Transesterification of S21M21 with Pentafluorobenzyl Alcohol. By following the Procedure C, the transesterification of **S21M21** (500 mg, 11.9 μmol) with pentafluorobenzyl alcohol (94.3 mg, 476 mmol) was performed using Ti(O*i*Pr)$_4$ (10.5 μL, 35.7 μmol) in toluene (3.00 mL) to give **S21M21-J** as a white powder. Yield: 39.8%. $M_{n,SEC}$ = 37,500 g mol^{-1}, $Đ$ = 1.03

(THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−6.26 (br, aromatic), 5.07 (m, ω-terminal, 2H, −OCH_2C$_5$F$_5$), 3.82−3.38 (br, −OCH_3, PMMA), 2.54 (br, ω-terminal, −CH(CH_3)COO−), 2.24−0.77 (br, main chain −CH_2C−, −CCH_3, −CH_2CH−,−CH_2CH−, PMMA, PS).

Transesterification of S21M21 with 6-Azido-1-hexanol. By following the Procedure C, the transesterification of **S21M21** (300 mg, 7.14 μmol) with 6-azido-1-hexanol (12.6 mg, 143 mmol) was performed using Ti(O*i*Pr)$_4$ (6.28 μL, 12.4 μmol) in toluene (2.00 mL) to give **S21M21-K** as a white powder. Yield: 86.3%. $M_{n,SEC}$ = 35,200 g mol^{-1}, $Đ$ = 1.03 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−6.26 (br, aromatic), 4.02 (m, ω-terminal, 2H, −CH_2(CH_2)$_5$N$_3$), 3.82−3.38 (br, −OCH_3, PMMA), 3.29 (t, J = 6.6 Hz, ω-terminal, 2H, −CH_2N$_3$), 2.47 (br, ω-terminal, −CH(CH_3)COO−), 2.24−0.77 (br, main chain −CH_2C−, −CCH_3, −CH_2CH−, −CH_2CH−, PMMA, PS).

Transesterification of S21M21 with Poly(ethylene Glycol) Monomethyl Ether. By following the Procedure C, the transesterification of **S21M21** (300 mg, 7.14 μmol) with poly(ethylene glycol) monomethyl ether (780 mg, 143 mmol) was performed using Ti(O*i*Pr)$_4$ (6.28 μL, 12.4 μmol) in toluene (2.00 mL). The obtained crude product was precipitated three times from THF solution into hot water to give **S21M21-L** as a white powder. Yield: 32.9%. $M_{n,SEC}$ = 42,000 g mol^{-1}, $Đ$ = 1.04 (THF). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−6.26 (br, aromatic), 4.20 (m, ω-terminal, 2H, −CH_2CH$_2$(O(CH_2)$_2$)$_n$OCH$_3$), 3.82−3.38 (br, −OCH_3, PMMA), 3.38 (s, ω-terminal, 3H, −(O(CH_2)$_2$)$_n$OCH_3), 2.50 (br, ω-terminal, −CH(CH_3)COO−), 2.24−0.77 (br, main chain −CH_2C−, −CCH_3, −CH_2CH−, −CH_2CH−, PMMA, PS).

1.4. Small-Angle X-ray Scattering Experiments. Small-angle X-ray scattering (SAXS) experiments for the bulk samples were performed on BL-6A beamline of the Photon Factory at

High Energy Accelerator Research Organization (KEK, Tsukuba, Japan). The X-ray wavelength and exposure time were 1.50 Å (8.27 keV) and 60 s, respectively. A PILATUS 1M (Dectris Ltd., Switzerland) detector, with 981 × 1043 pixels at a pixel size of 172 × 172 μm, and a counter depth of 20 bits (1,048,576 counts), was used for data acquisition. The sample-to-detector distance was calibrated using the scattering patterns of silver behenate (Nagara Science Co., Ltd., Japan). Bulk samples for the SAXS experiments were placed in 1.5-mm-diameter soda glass capillaries (Hilgenderg, Germany) and annealed under vacuum at 200 °C for 24 h. The SAXS data were acquired under ambient conditions, and 1D profiles were obtained as plots of scattering intensity as functions of scattering vector (q), where $q = (4\pi/\lambda)\sin(\theta/2)$ (λ, wave length; θ, scattering angle).

2. Additional Results

2.1. SEC, IR, and ^{1}H NMR Data of Modified PMMA Homopolymers

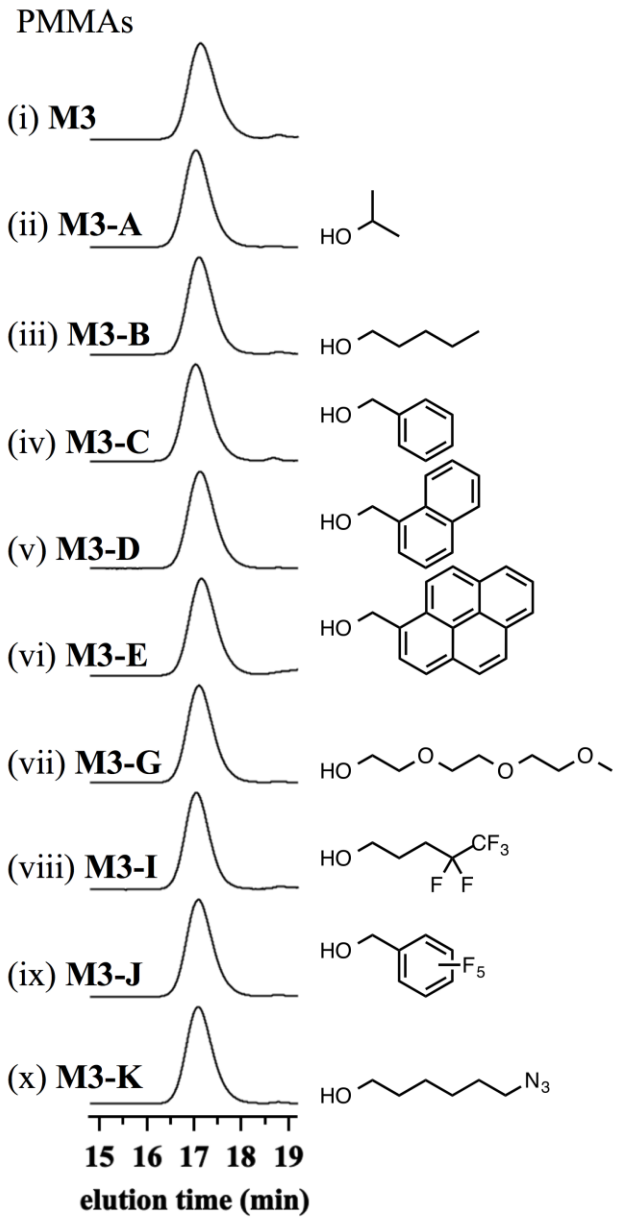

Figure S1. SEC traces of modified **M3**s and the corresponding parent polymer (eluent, THF; flow rate, 1.0 mL min^{-1}).

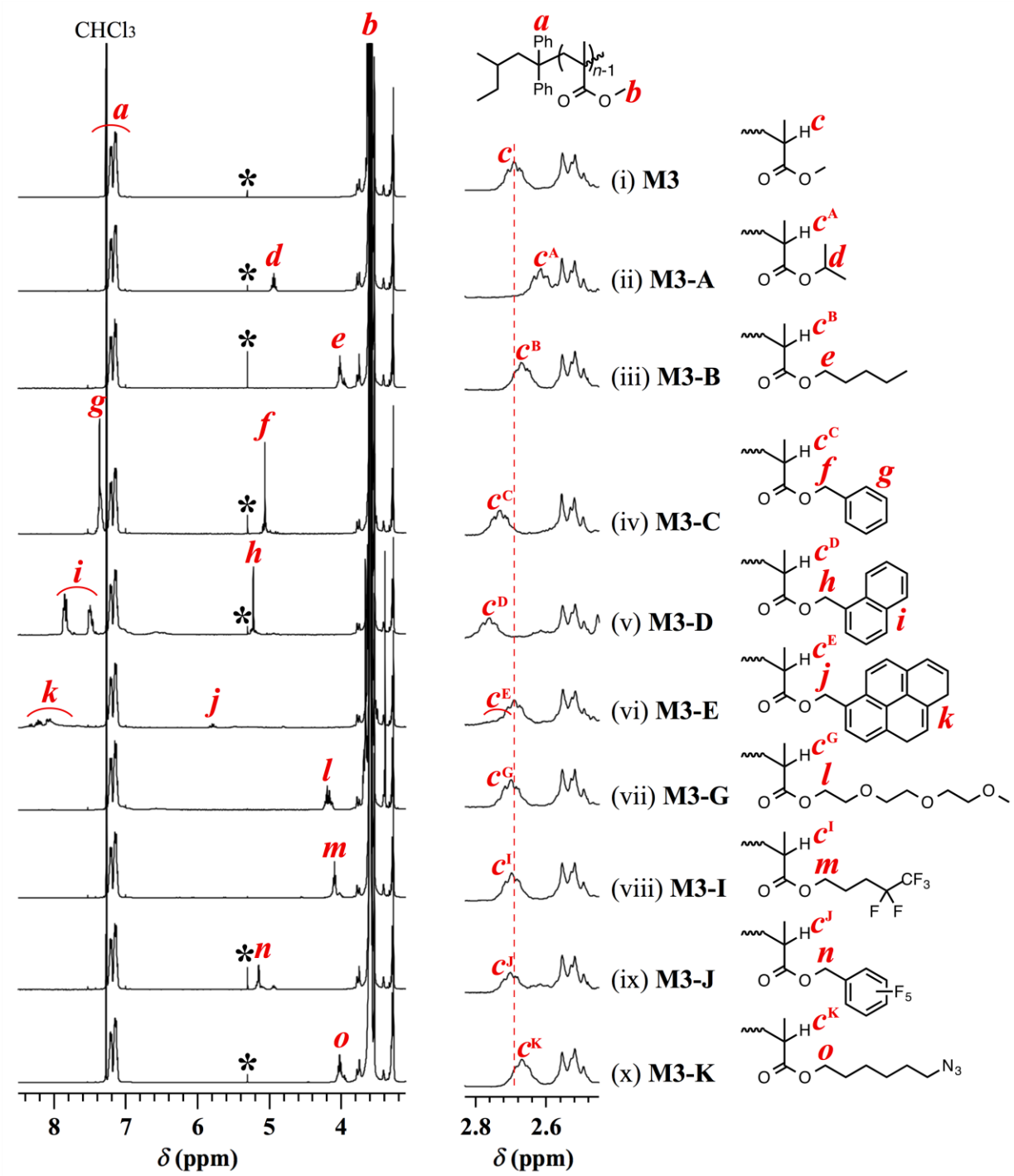

Figure S2. ^{1}H NMR spectra of the modified PMMAs and the corresponding parent polymer in $CDCl_3$ (400 MHz). The asterisks indicate the residual solvent signals.

Table S1. MALDI-TOF MS peak intensity ratio for the unreacted and singly- and doubly-transesterified materials in **M3-X**s[a]

	unreacted/single/double
M3-A	0/100/0
M3-B	0/79/21
M3-C	0/85/15
M3-D	0/93/7
M3-G	0/88/12
M3-I	12/74/14
M3-J	9/64/27
M3-K	12/82/6

[a] Calculated based on the peaks corresponding to the 27-mer.

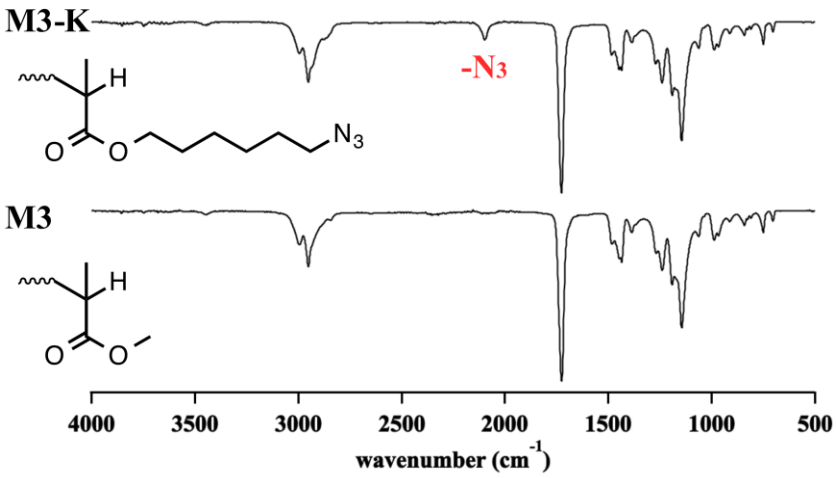

Figure S3. FT-IR spectra of the **M3-K** (upper) and **M3** (lower).

2.2. SEC, ^{1}H NMR, and SAXS Data of Modified PS-*b*-PMMAs

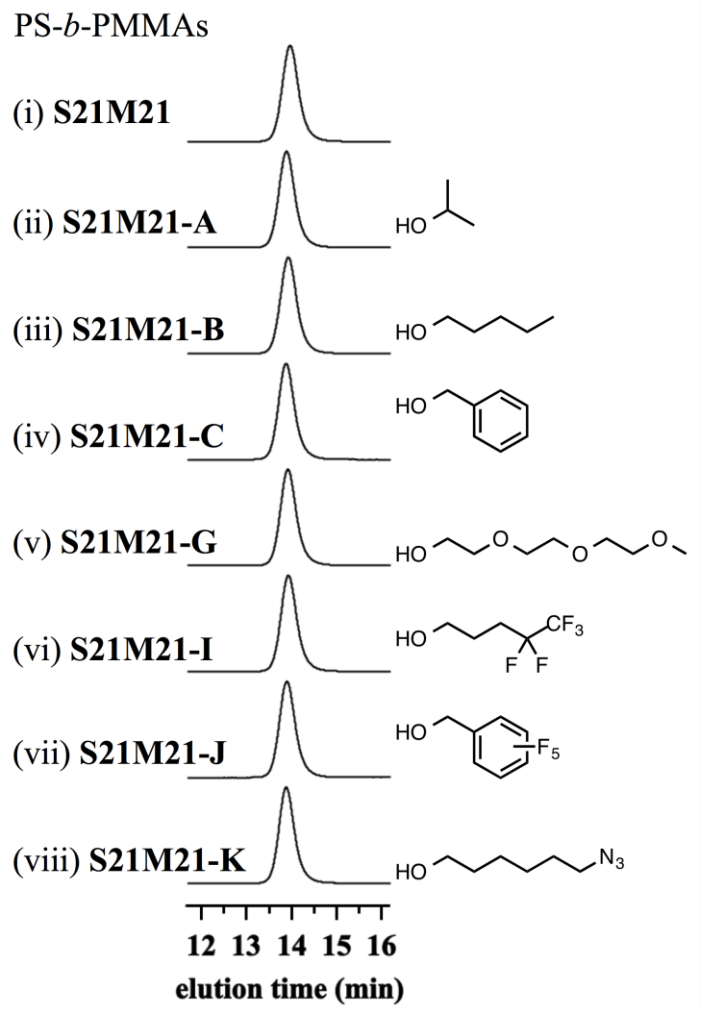

Figure S4. SEC traces of modified **S21M21**s and the corresponding parent polymer (eluent, THF; flow rate, 1.0 mL min^{-1}).

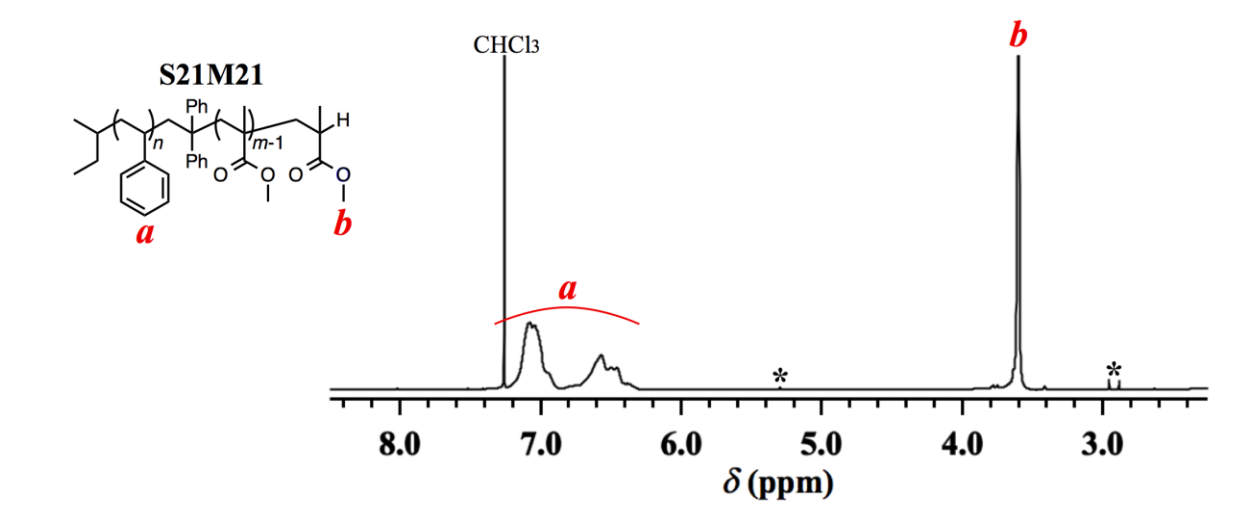

Figure S5. ^{1}H NMR spectrum of **S21M21** in $CDCl_3$ (400 MHz).

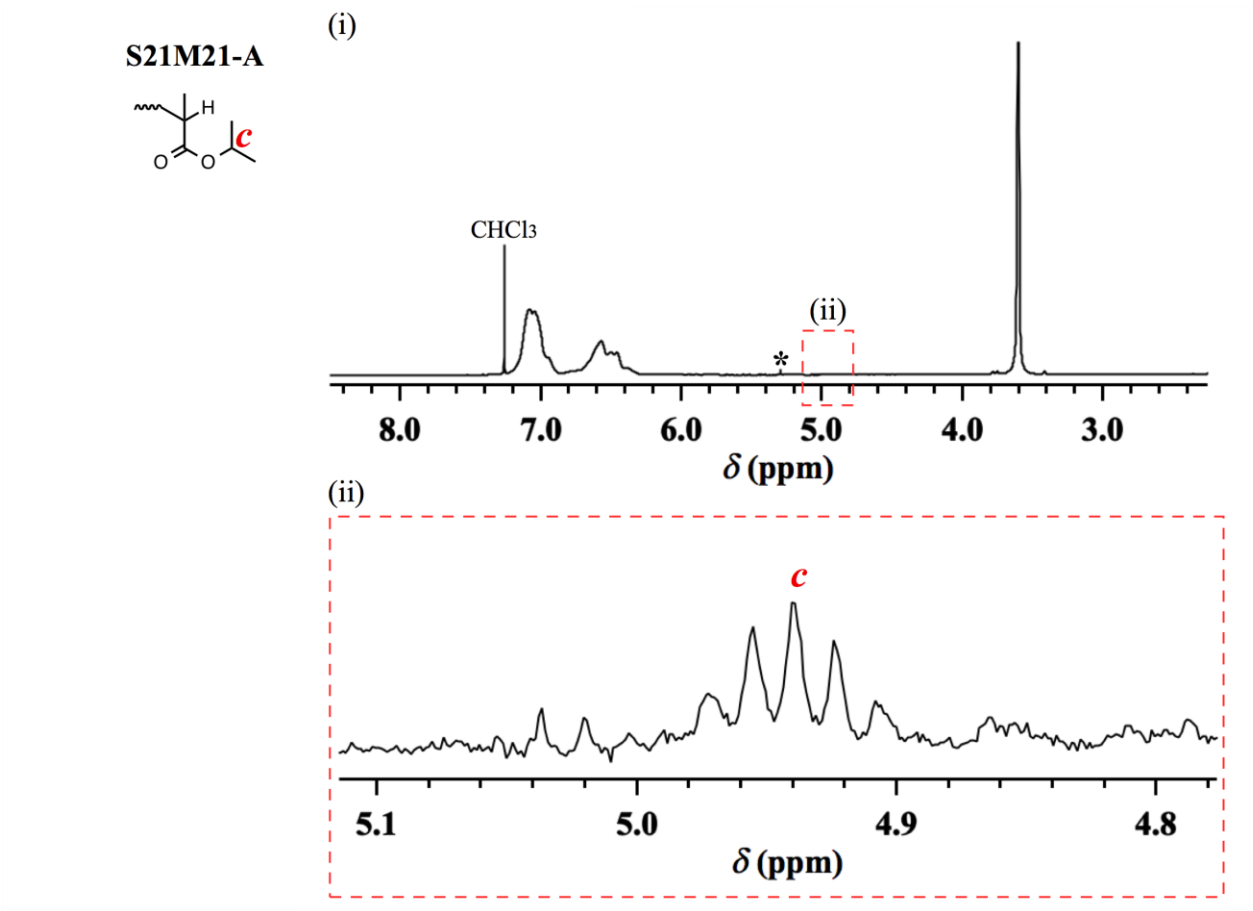

Figure S6. ^{1}H NMR spectrum of **S21M21-A** in $CDCl_3$ (400 MHz).

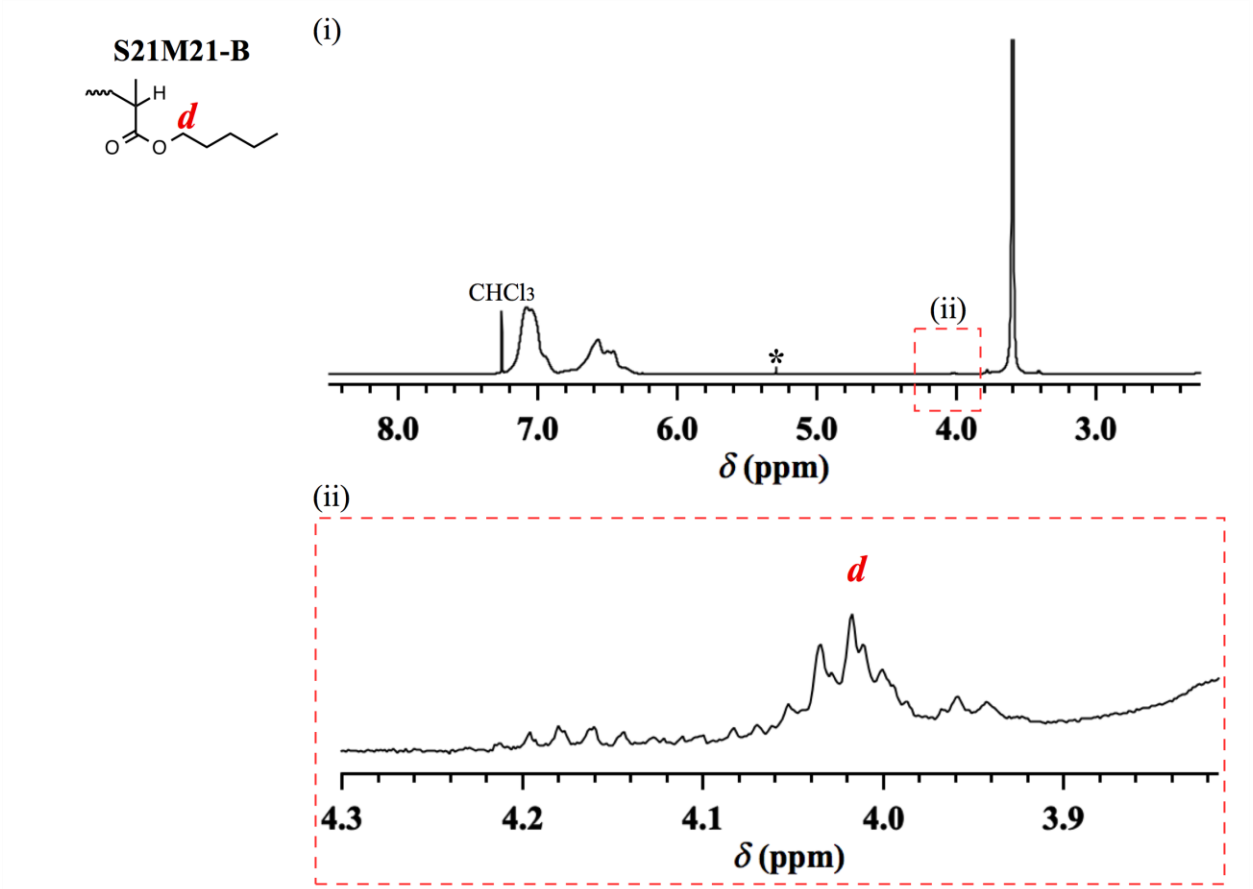

Figure S7. ^{1}H NMR spectrum of **S21M21-B** in $CDCl_3$ (400 MHz).

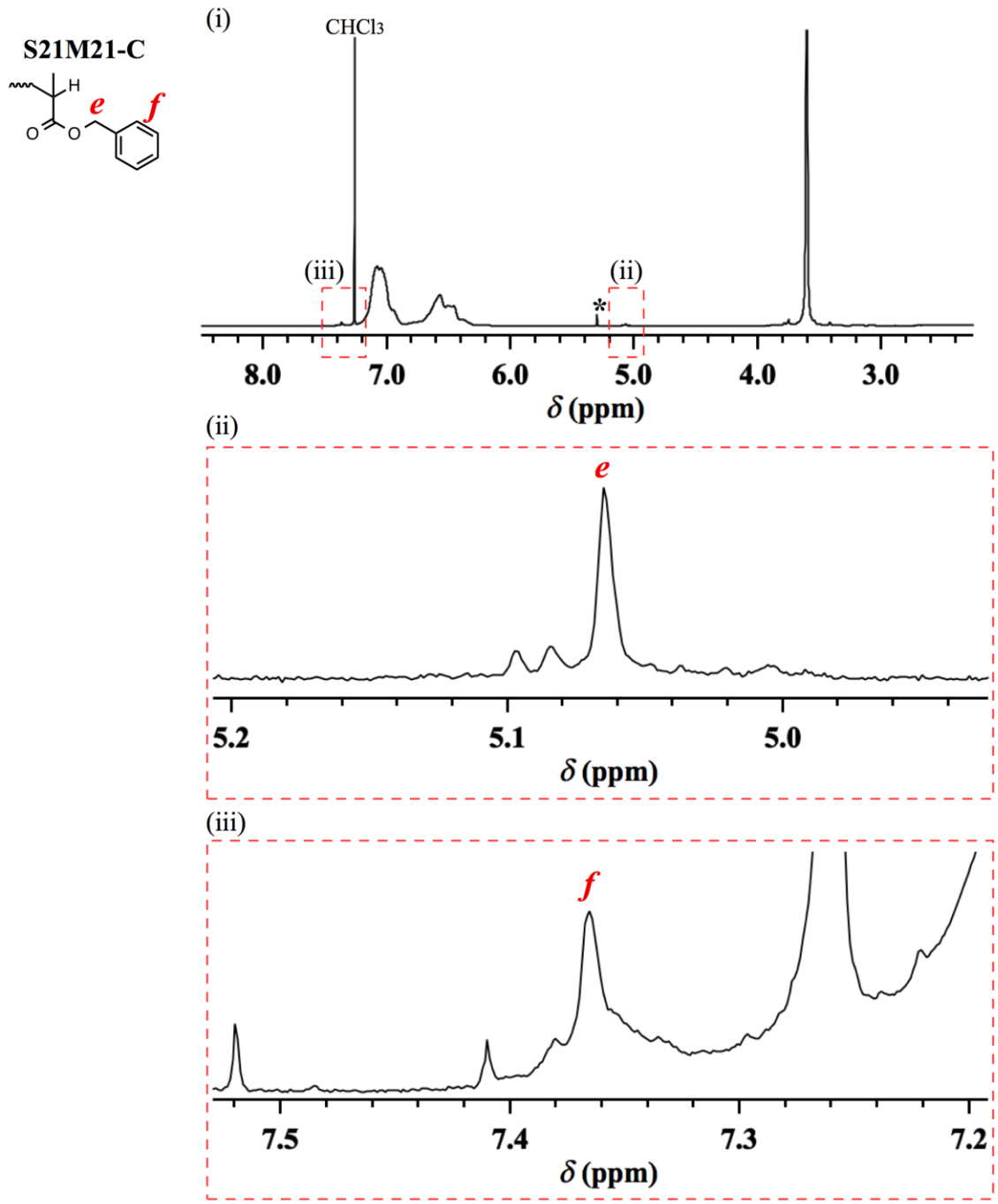

Figure S8. ^{1}H NMR spectrum of **S21M21-C** in $CDCl_3$ (400 MHz).

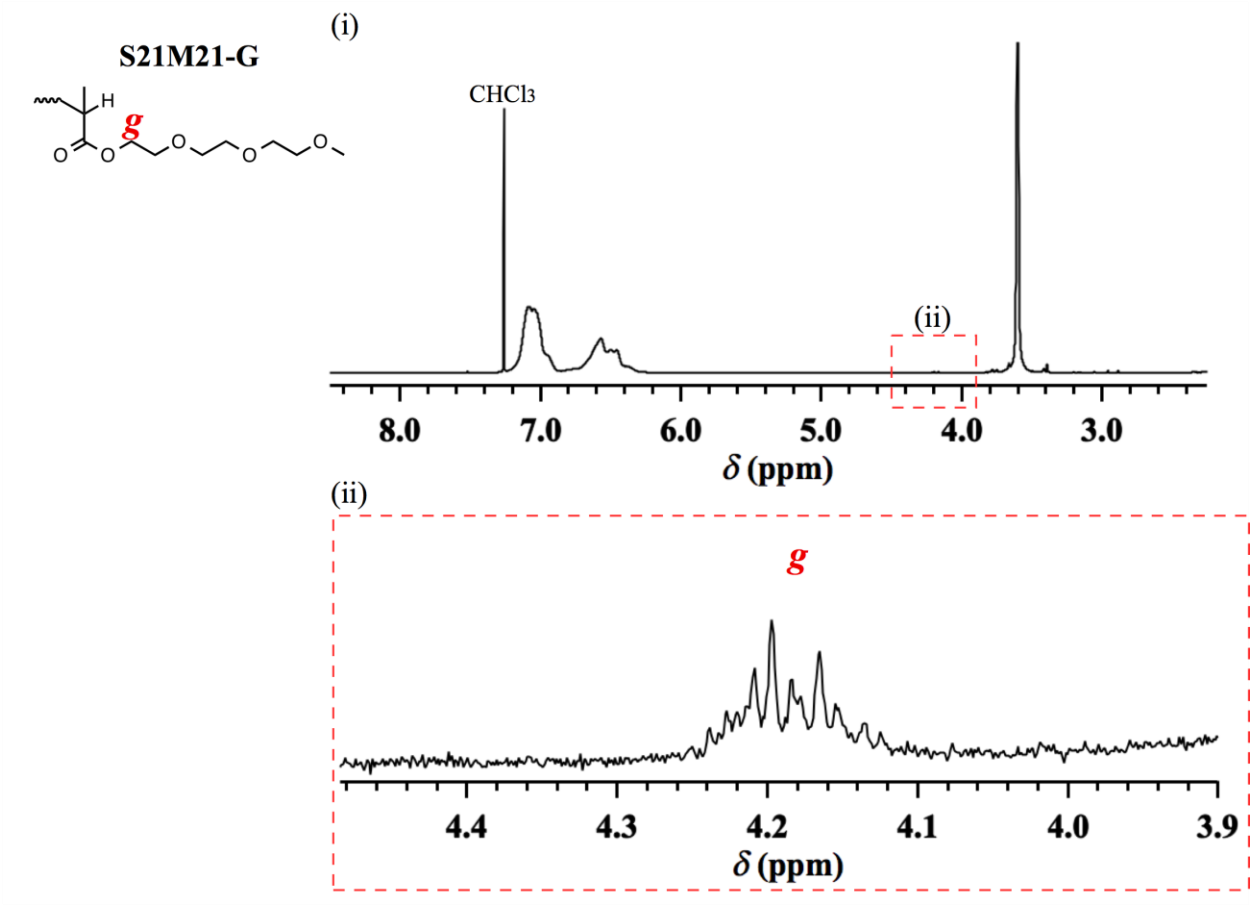

Figure S9. ^{1}H NMR spectrum of **S21M21-G** in $CDCl_3$ (400 MHz).

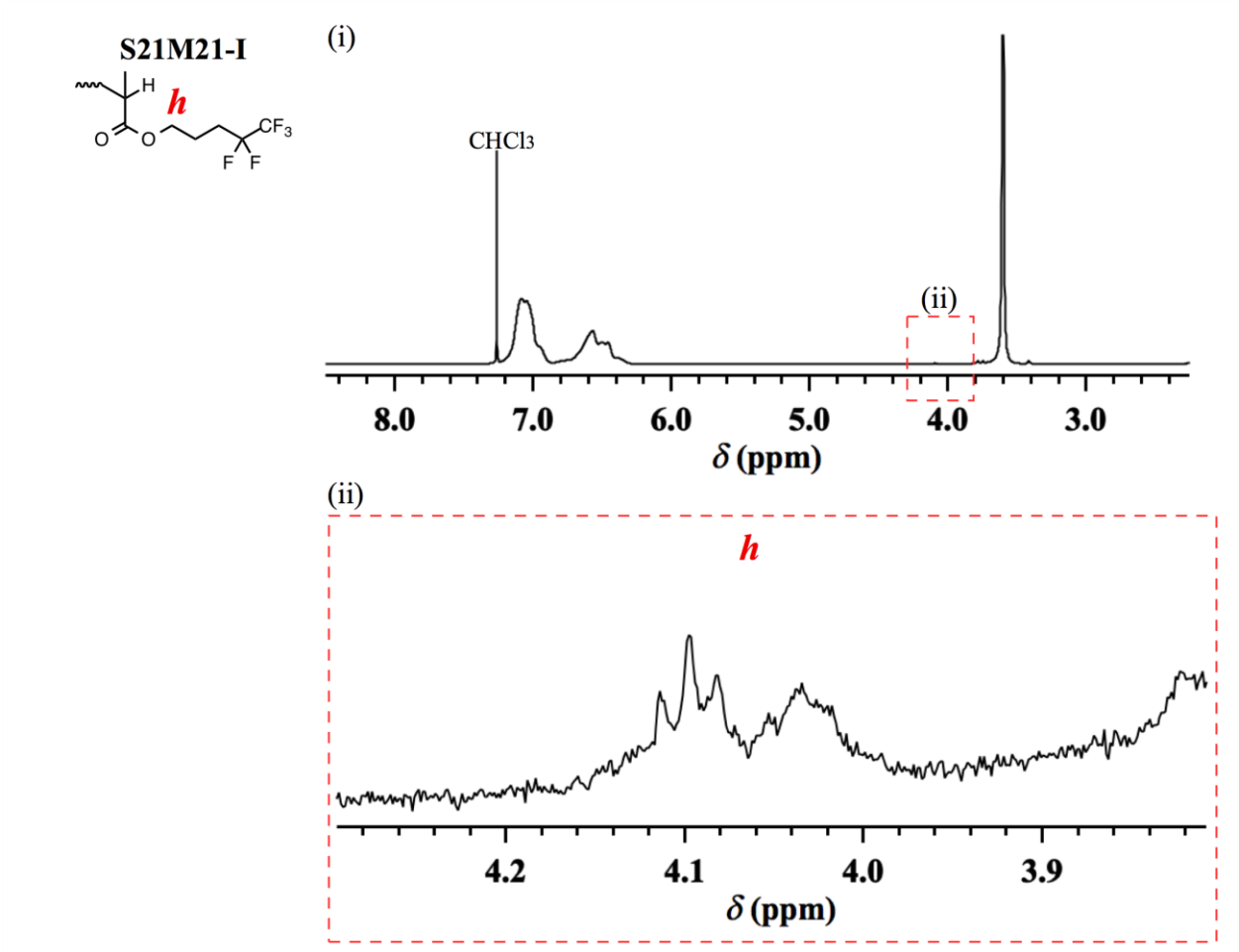

Figure S10. ^{1}H NMR spectrum of **S21M21-I** in $CDCl_3$ (400 MHz).

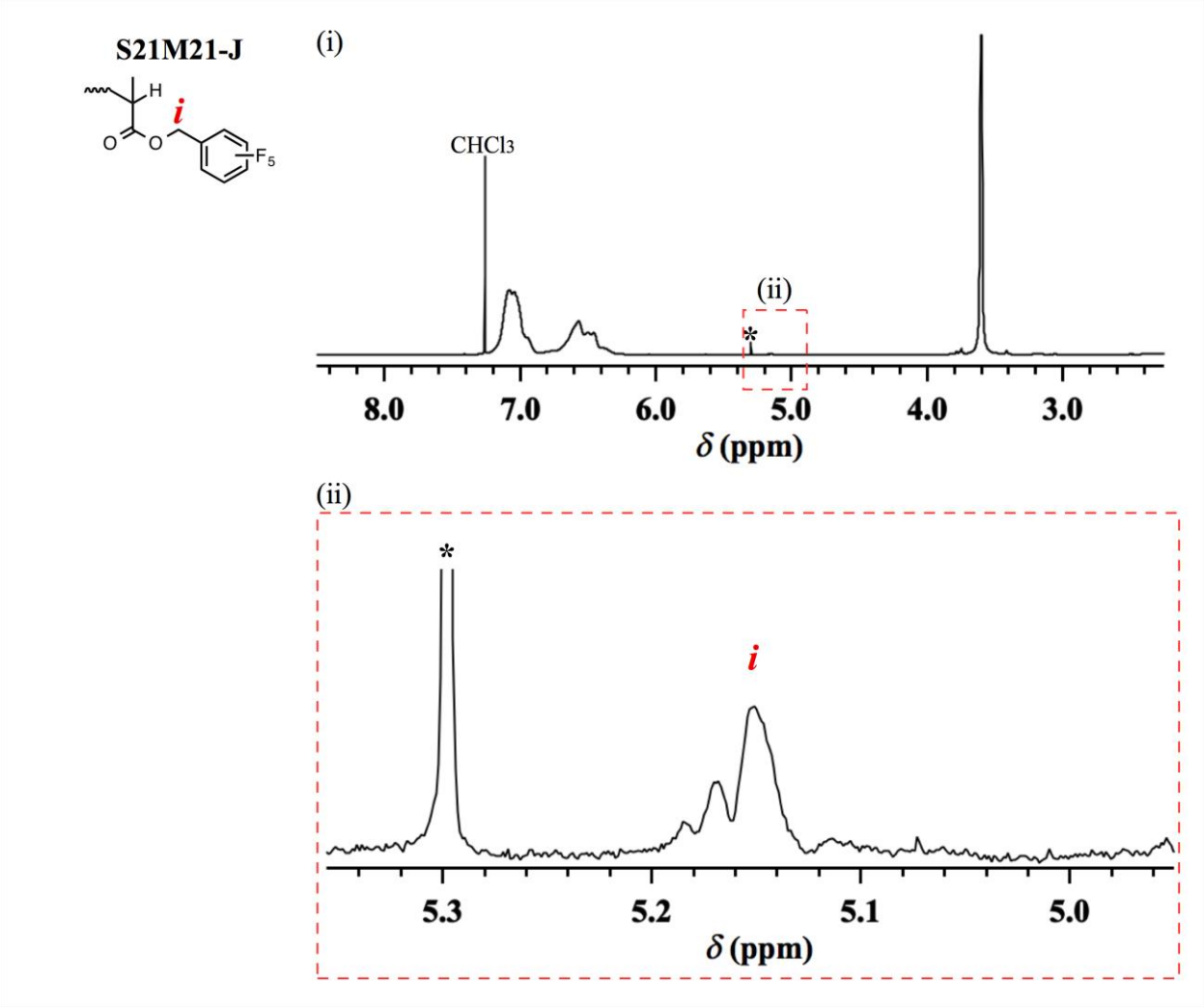

Figure S11. ^{1}H NMR spectrum of **S21M21-J** in $CDCl_3$ (400 MHz).

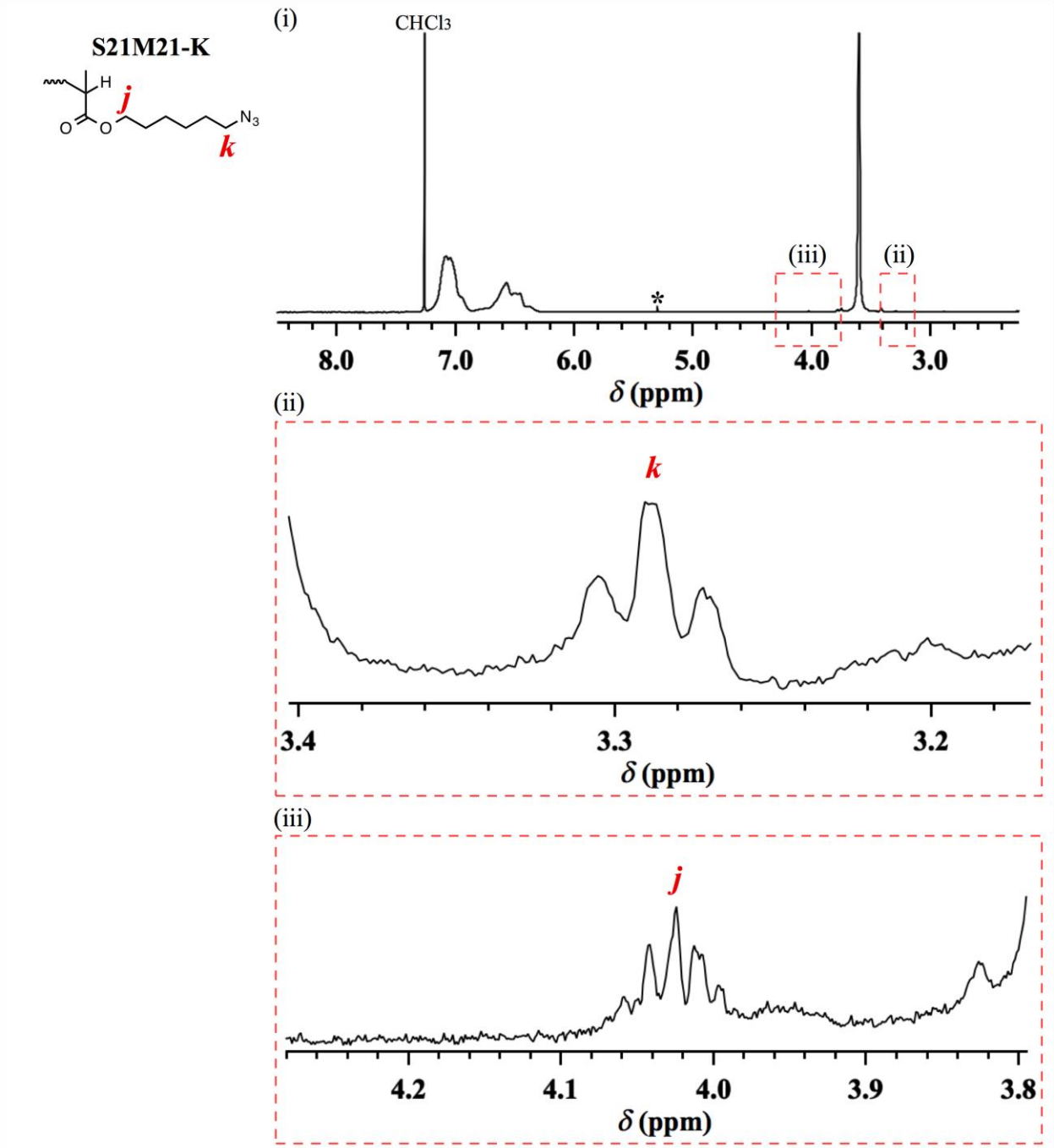

Figure S12. ^{1}H NMR spectrum of **S21M21-K** in $CDCl_3$ (400 MHz).

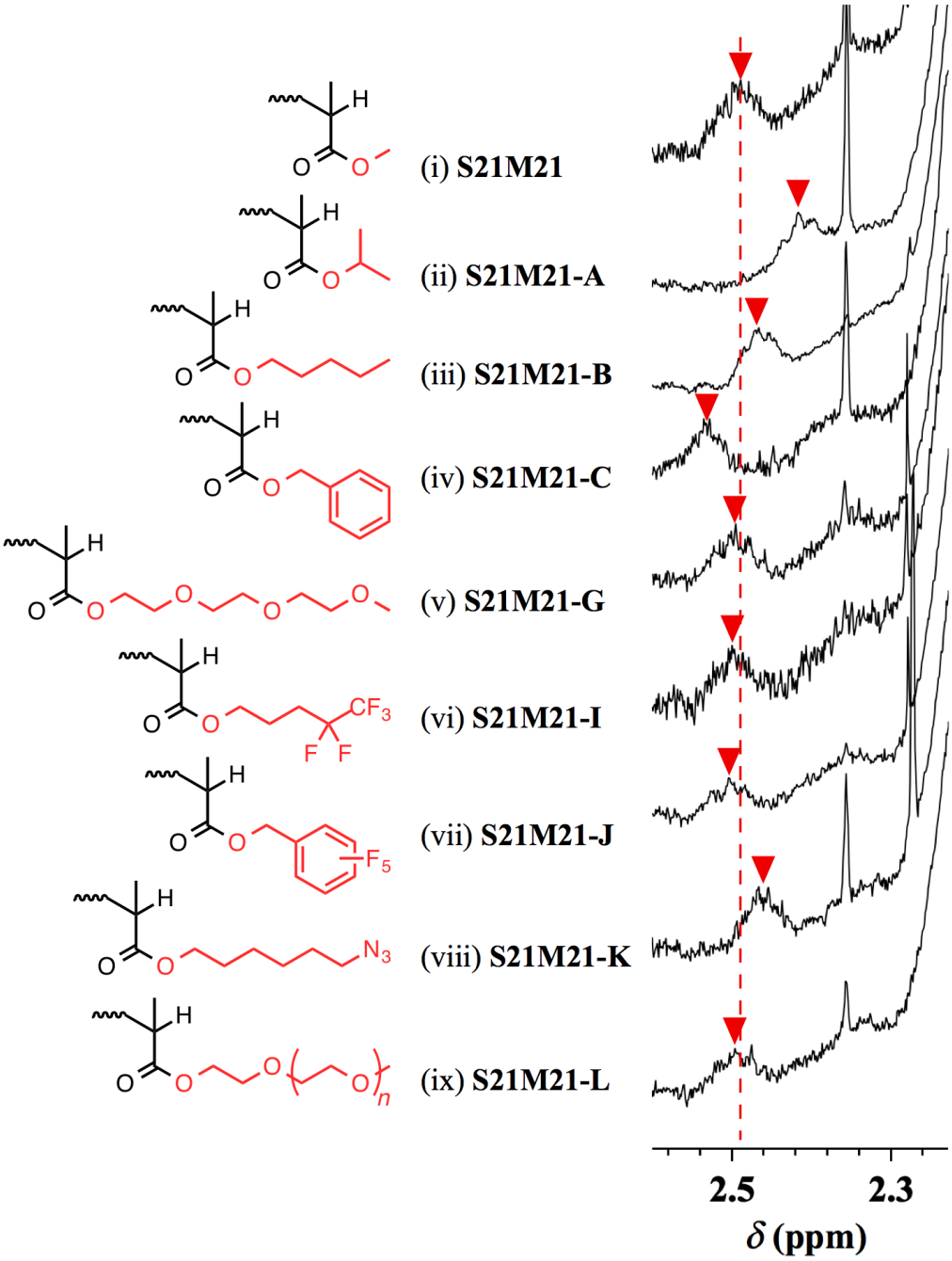

Figure S13. ^{1}H NMR spectra of the modified **S21M21**s and the corresponding parent polymer in $CDCl_3$ (400 MHz).

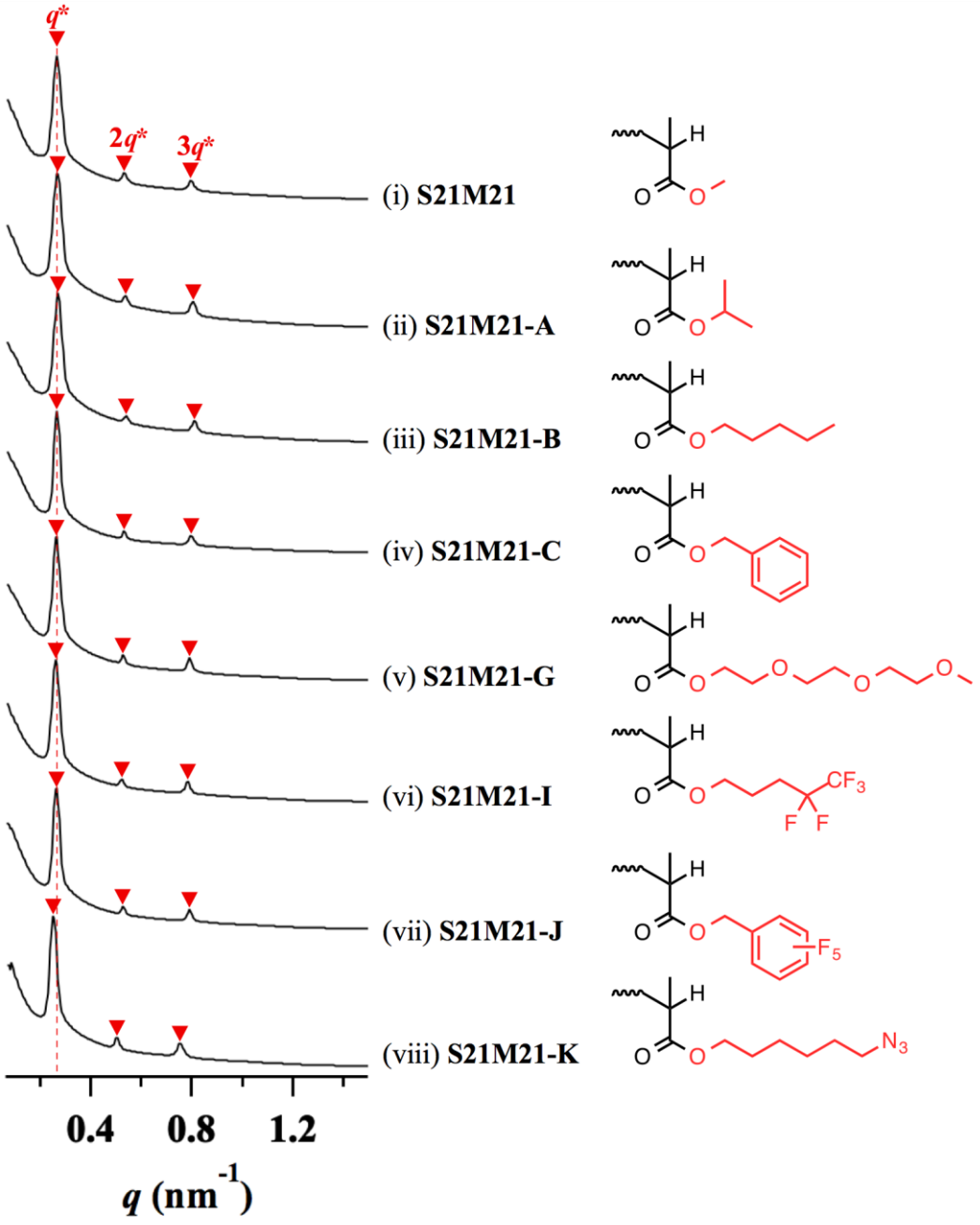

Figure S14. SAXS profiles of the modified **S21M21**s in the bulk states after the thermal annealing at 200 °C for 24 h.

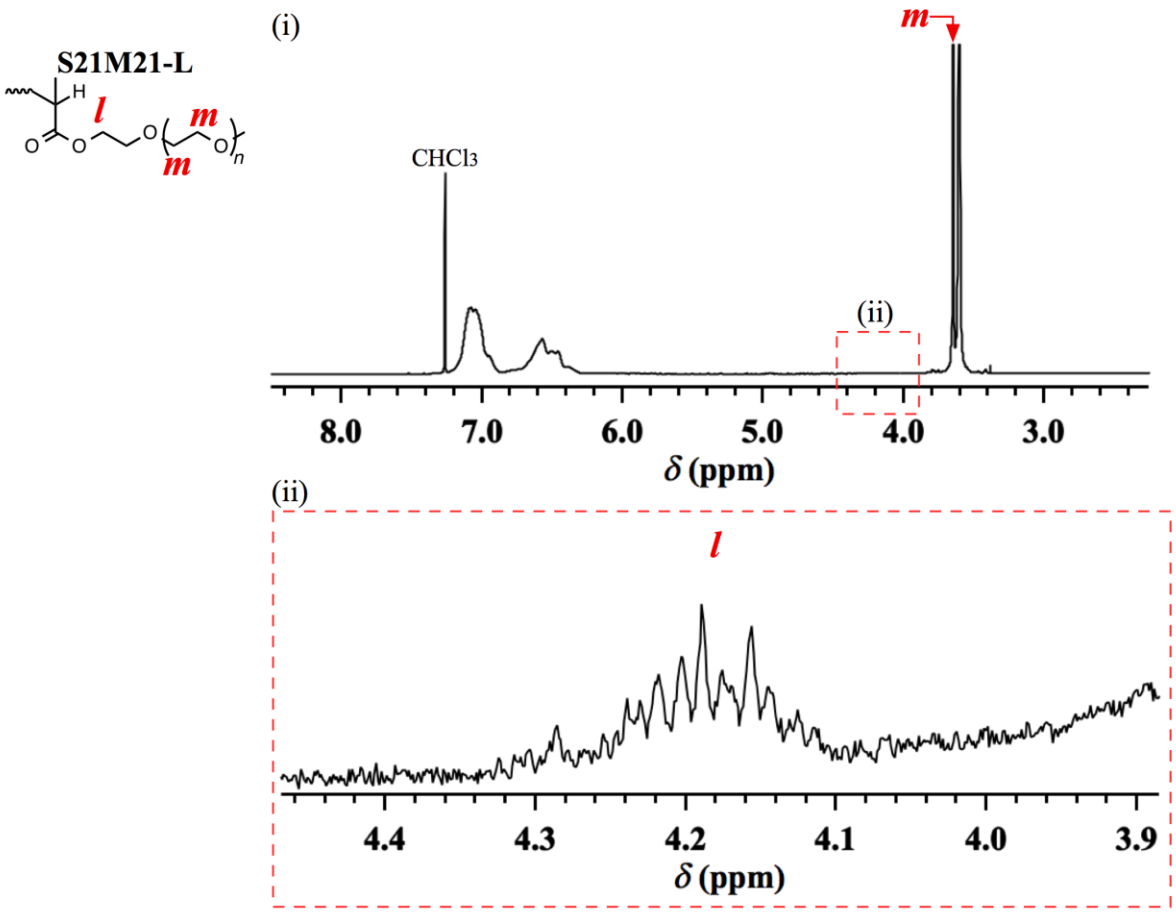

Figure S15. ^{1}H NMR spectrum of **S21M21-L** in $CDCl_3$ (400 MHz).