

Synthesis of star- and block-copolymers using ADMET: head-to-tail selectivity during step-growth polymerization

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SUPPORTING INFORMATION

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1. Materials

10-undecen-1-ol, acryloyl chloride, triethylamine, methyl acrylate, glycerol, 1-octanol, tin(II) 2-ethylhexanoate, ethyl vinyl ether, mercaptoethanol, benzylidene[1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(tricyclohexylphosphine)ruthenium (Grubbs catalyst 2nd generation) and [1,3-*bis*-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(*o*-isopropoxyphenylmethylene)ruthenium (Hoveyda-Grubbs catalyst 2nd generation) were purchased from Aldrich and used as received. ϵ -caprolactone was purchased from Acros Organics. Dichloromethane was distilled from calcium hydride and THF was distilled previously to use.

2. Characterization

Thin layer chromatography (TLC) was performed on silica gel TLC-cards (layer thickness 0.20 mm, Fluka). Compounds were visualized by permanganate reagent. For column chromatography silica gel 60 (0.035-0.070 mm, Fluka) was used.

¹H-NMR and ¹³C-NMR spectra were recorded in CDCl₃ on a Bruker AVANCE DPX spectrometer operating at 300 MHz and 75 MHz respectively. Chemical shifts (δ) are reported in parts per million (ppm) relative to the internal standard tetramethylsilane (TMS, δ = 0.00 ppm). The relaxation time (d1) was set to 5 seconds for ¹H-NMR measurements.

Polymer molecular weights were determined using an SEC System LC-20A from Shimadzu equipped with a SIL-20A auto sampler, three PSS SDV columns (5 μ m, 300mm x 7.5mm, 100Å, 1000 Å, 10000Å), and a RID-10A refractive index detector. THF was used as eluent at a flow rate of 1 mL/min at 50 °C. The determination of molar masses was performed relative to PMMA standards (Polymer Standards Service, Mp 1100–981.000 Da).

MALDI-TOF MS was performed on an AXIMA Assurance from Shimadzu using dithranol as matrix and NaI as doping salt.

3. Synthetic procedures

Synthesis of 10-undecenoyl acrylate (1)

10-undecen-1-ol (5g, 29.4 mmol) and 15 mL of dichloromethane were placed in a 50 mL two-necked round bottomed flask under nitrogen and cooled with an ice bath. Acryloyl chloride (3.57 mL, 44.0 mmol) was added followed by dropwise addition of triethylamine (8.2 mL, 58.7 mmol). The reaction mixture was stirred at room temperature for 1h and the crude product was filtered through a short pad of silica eluting with hexane/ethyl acetate 1/1. The product was purified by column chromatography using hexane/ethyl acetate 40/1. Yield 78%.

^1H NMR (300 MHz, CDCl_3 , δ in ppm): 6.39 (dd, $J = 17.32, 1.54$ Hz, 1H, $\text{CH}=\text{CH}_2$), 6.11 (dd, $J = 17.32, 10.38$ Hz, 1H, $\text{CH}=\text{CH}_2$), 5.87-5.73 (m, 1H, $\text{CH}=\text{CH}_2$ terminal olefin), 5.80 (dd, $J = 10.38, 1.54$ Hz, 1H, $\text{CH}=\text{CH}_2$), 5.02-4.90 (m, 2H, $\text{CH}=\text{CH}_2$ terminal olefin), 4.98 (ddd, $J = 17.38, 3.61, 1.76$ Hz, 1H), 4.14 (t, $J = 6.73$ Hz, 2H), 2.03 (q, $J = 6.82$ Hz, 1H, $\text{CH}_2\text{CH}=\text{CH}_2$), 1.71-1.60 (m, 2H, $\text{CH}_2\text{CH}_2\text{O}$), 1.42-1.22 (m, 12H, CH_2).

^{13}C NMR (75 MHz, CDCl_3 , δ in ppm): 166.50 (COOR), 139.35 ($\text{CH}_2=\text{CH}$), 130.50 (COCH= CH_2), 128.88 (COCH= CH_2), 114.31 ($\text{CH}_2=\text{CH}$), 64.89 (CH_2O), 33.98 ($\text{CH}_2\text{CH}=\text{CH}_2$), 29.63 (CH_2), 29.58 (CH_2), 29.42 (CH_2), 29.28 (CH_2), 29.12 (CH_2), 28.82 (CH_2), 26.12 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$).

Synthesis of glycerol triacrylate (GTA)

Glycerol (2 g, 21.7 mmol) and 10 mL of dichloromethane were placed in a 25 mL two-necked round bottomed flask under nitrogen and cooled with an ice bath. Acryloyl chloride (7.94 mL, 97.7 mmol) was added followed by careful dropwise addition of triethylamine (18.2 mL, 130.3 mmol). The reaction mixture was stirred at room temperature for 1h and the crude product was filtered through a short pad of silica eluting with hexane/ethyl acetate 1/1. The product was purified by column chromatography using hexane/ethyl acetate 10/1. Yield: 92 %.

^1H NMR (300 MHz, CDCl_3 , δ in ppm): 6.43 (dd, $J = 17.28, 1.41$ Hz, 1H, $\text{CH}=\text{CH}_2$), 6.41 (dd, $J = 17.29, 1.41$ Hz, 2H, $\text{CH}=\text{CH}_2$), 6.11 (dd, $J = 17.28, 10.41$ Hz, 1H, $\text{CH}=\text{CH}_2$), 6.11 (dd, $J = 17.29, 10.42$ Hz, 2H, $\text{CH}=\text{CH}_2$), 5.87 (dd, $J = 10.41, 1.41$ Hz, 1H, $\text{CH}=\text{CH}_2$), 5.85 (dd, $J =$

10.42, 1.41 Hz, 2H, CH=CH₂), 5.42 (tt, *J* = 5.84, 4.40 Hz, 1H, CH), 4.41 (dd, *J* = 11.99, 4.40 Hz, 2H, CH₂), 4.32 (dd, *J* = 11.99, 5.84 Hz, 2H, CH₂).

¹³C NMR (75 MHz, CDCl₃, δ in ppm): 165.63 (COOR), 165.21 (COOR), 131.97 (CH=CH₂), 131.77 (CH=CH₂), 127.91 (CH=CH₂), 127.84 (CH=CH₂), 62.46 (2C, CH₂), 60.47 (CH).

Synthesis of poly(epsilon-caprolactone) initiated by 1-octanol

1-octanol (0.114 g, 0.87 mmol) and ε-caprolactone (1.000 g, 8.76 mmol) were placed in a round bottomed flask and purged with nitrogen. The mixture was heated at 130 °C with vigorous stirring during 15 minutes followed by addition of tin(II) 2-ethylhexanoate (0.01g, 0.02 mmol). Stirring at 130 °C was maintained 50 minutes more and then the reaction mixture was cooled down rapidly in an ice bath. The product was precipitated as a white powdery solid from hexane with 94% yield.

¹H NMR (300 MHz, CDCl₃, δ in ppm): 4.00 (t, *J* = 6.65 Hz, CH₂O), 3.57 (t, *J* = 6.48 Hz, CH₂OH), 2.25 (t, *J* = 7.47 Hz, CH₂CO), 1.66-1.50 (m, CH₂), 1.38-1.18 (m, CH₂), 0.82 (t, *J* = 6.71 Hz).

¹³C NMR (75 MHz, CDCl₃, δ in ppm): 173.60 (COOR), 64.61 (CH₂O initiator), 64.25 (CH₂O), 62.66 (CH₂OH), 34.36 (CH₂CO end group), 34.24 (CH₂CO backbone), 32.46 (CH₂CH₂OH), 31.88 (CH₂CH₂CH₃), 29.31 (CH₂ initiator), 29.27 (CH₂ initiator), 28.77 (CH₂CH₂O, initiator), 28.48 (CH₂CH₂O backbone), 26.04 (CH₂ initiator), 25.66 (CH₂ backbone), 25.45 (CH₂ end group), 24.83 (CH₂ end group), 24.70 (CH₂CH₂CO), 22.73 (CH₂CH₃), 14.18 (CH₃).

Synthesis of acrylated poly(ε-caprolactone) (3)

3 (0.5 g, 0.39 mmol) and 4 mL of dichloromethane were placed in a 10 mL two-necked round bottomed flask under nitrogen at room temperature. Acryloyl chloride (0.07 mL, 0.78 mmol) was added followed by dropwise addition of triethylamine (0.14 mL, 0.98 mmol). The reaction mixture was stirred at room temperature for 1h and the solvent was removed at reduced pressure. The crude product was filtered through a short pad of silica eluting with ethyl acetate to remove salts and the product was precipitated from hexane as a white solid using a concentrated dichloromethane solution. Yield: 65%.

^1H NMR (300 MHz, CDCl_3 , δ in ppm): 6.39 (dd, $J = 17.32, 1.54$ Hz, $\text{CH}=\text{CH}_2$ acrylate end group), 6.11 (dd, $J = 17.31, 10.38$ Hz, $\text{CH}=\text{CH}_2$ acrylate end group), 5.81 (dd, $J = 10.38, 1.54$ Hz, $\text{CH}=\text{CH}_2$ acrylate end group), 4.15 (t, $J = 6.61$ Hz, CH_2OCO acrylate), 4.05 (t, $J = 6.68$ Hz, CH_2O), 2.30 (t, $J = 7.49$ Hz, CH_2CO), 1.71-1.57 (m, $\text{CH}_2\text{CH}_2\text{OCO}$ acrylate, $\text{CH}_2\text{CH}_2\text{O}$ and $\text{CH}_2\text{CH}_2\text{CO}$), 1.44-1.24 (m, CH_2), 0.87 (t, $J = 6.73$ Hz, CH_3 end group).

^{13}C NMR (75 MHz, CDCl_3 , δ in ppm): 173.62 (COOR), 130.60 ($\text{CH}=\text{CH}_2$ acrylate end group), 128.72 ($\text{CH}=\text{CH}_2$ acrylate end group), 64.63 (CH_2O initiator), 64.46 (CH_2O acrylate), 62.26 (CH_2O), 34.32 (CH_2CO end group), 34.26 (CH_2CO), 31.91 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 29.33 (CH_2 initiator), 29.30 (CH_2 initiator), 28.79 ($\text{CH}_2\text{CH}_2\text{O}$, initiator), 28.50 ($\text{CH}_2\text{CH}_2\text{O}$ backbone and chain end), 26.06 (CH_2 initiator), 25.68 (CH_2 backbone and chain end), 24.73 ($\text{CH}_2\text{CH}_2\text{CO}$), 22.76 (CH_2CH_3), 14.20 (CH_3 end group).

ADMET polymerization of **1** (**2**)

1 (0.15 g, 0.67 mmol) and dichloromethane (0.15 mL) were placed in a 3 mL conical vial (Supelco) equipped with screw cap and septa. The mixture was heated to 40 °C while stirring and then a solution of **C1** (2.1 mg, 0.0033 mmol, 0.5 mol% to **1**) in dichloromethane (0.15 mL) was added in one shot. A needle was placed to allow ethylene to be removed and the reaction was stirred for 5h at 40 °C (no previous N_2 purging). The catalyst was quenched by addition of THF (0.2 mL) and ethyl vinyl ether (20 μL) and stirring 30 minutes at room temperature. Polymer **2** was purified by precipitation from methanol in quantitative yield.

^1H NMR (300 MHz, CDCl_3 , δ in ppm): 6.96 (dt, $J = 15.59, 6.94, 6.94$ Hz), 6.40 (dd, $J = 17.32, 1.56$ Hz, $\text{CH}=\text{CH}_2$ acrylate end group), 6.12 (dd, $J = 17.32, 10.37$ Hz, $\text{CH}=\text{CH}_2$ acrylate end group), 5.81 (d, $J = 15.60$ Hz, $\text{COCH}=\text{CH}$ and acrylate end group $\text{CH}=\text{CH}_2$ overlapped), 5.41-5.35 (m, $\text{CH}=\text{CH}$ self metathesis terminal double bonds), 5.03-4.90 (m, $\text{CH}_2=\text{CH}$ terminal double bond end group), 4.15 (t, $J = 6.90$ Hz, CH_2O end group), 4.11 (t, $J = 6.75$ Hz, CH_2O), 2.19 (q, $J = 6.75$ Hz, $=\text{CHCH}_2$), 1.71-1.59 (m, $\text{CH}_2\text{CH}_2\text{O}$), 1.51-1.23 (CH_2).

^{13}C NMR (75 MHz, CDCl_3 , δ in ppm): 166.82 (CO acrylate), 149.32 ($\text{COCH}=\text{CH}$), 130.34 ($\text{CH}=\text{CH}_2$ acrylate end group), 128.62 ($\text{CH}=\text{CH}_2$ acrylate end group), 121.21 ($\text{COCH}=\text{CH}$), 64.63 (CH_2O end group), 64.29 (CH_2O), 32.15 ($=\text{CHCH}_2$), 29.35 (CH_2), 29.27 (CH_2), 29.19 (CH_2), 29.10 (CH_2), 28.66 ($\text{CH}_2\text{CH}_2\text{O}$), 27.99 ($=\text{CHCH}_2\text{CH}_2$), 25.90 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$).

ADMET polymerization of **1** in presence of selective chain stoppers

1 (0.15g, 0.67 mmol), the desired amount of selective chain stopper (**3** or glycerol triacrylate) and dichloromethane (0.15 mL) were placed in a 3 mL conical vial (Supelco) equipped with screw cap and septa. The mixture was heated to 40 °C while stirring and then a solution of **C1** (2.1 mg, 0.0033 mmol, 0.5 mol% to **1**) in dichloromethane (0.15 mL) was added in one shot. A needle was placed to allow ethylene to be removed and the reaction was stirred for 5h at 40 °C (no previous N₂ purging). For the step-wise synthesis, a new batch of **1** dissolved in 0.15 mL of DCM was injected to the reaction mixture and after 1 minute stirring **C1** (dissolved in 0.15 mL of DCM) was also injected. The catalyst was quenched by addition of THF (0.2 mL) and ethyl vinyl ether (2 μL) and stirring 30 minutes at room temperature. The end-capped polymers were purified by precipitation from methanol to remove oligomers, except in the case of **4a**, **4b** and **4c**, which were precipitated from hexane.

Characterization of diblock copolymers **4a-c**

¹H NMR (300 MHz, CDCl₃, δ in ppm): 6.95 (td, *J* = 15.54, 6.94, 6.94 Hz, COCH=CH), 6.40 (dd, *J* = 17.32, 1.53 Hz, CH=CH₂ acrylate end group), 6.12 (dd, *J* = 17.32, 10.38 Hz, CH=CH₂ acrylate end group), 5.81 (d, *J* = 15.56 Hz, COCH=CH and end group CH=CH₂ overlapped), 4.15 (t, *J* = 6.71 Hz, CH₂OCO acrylate), 4.11 (t, *J* = 6.75 Hz, CH₂O), 4.06 (t, *J* = 6.73, 6.73 Hz, CH₂O), 2.31 (t, *J* = 7.49 Hz, CH₂CO), 2.19 (q, *J* = 6.82 Hz, =CHCH₂), 1.72-1.58 (m, CH₂CH₂OCO acrylate, CH₂CH₂O and CH₂CH₂CO), 1.50-1.24 (m, CH₂), 0.88 (t, *J* = 6.66 Hz, CH₃ end group).

¹³C NMR (75 MHz, CDCl₃, δ in ppm): 173.46 (CO), 166.81 (CO acrylate), 149.45 (COCH=CH end group), 149.31 (COCH=CH), 130.32 (CH=CH₂ acrylate end group), 128.64 (CH=CH₂ acrylate end group), 121.23 (COCH=CH), 121.13 (COCH=CH end group), 64.63 (CH₂O ROP initiator), 64.47 (CH₂O end group), 64.29 (CH₂O), 64.10 (CH₂O), 63.94 (CH₂O transition repeating unit), 34.15 (CH₂CO end group), 34.10 (CH₂CO), 32.15 (=CHCH₂), 31.74 (CH₂CH₂CH₃), 29.35 (CH₂, CH₂ of ROP initiator overlapped in this area of the spectrum), 29.27 (CH₂), 29.19 (CH₂), 29.10 (CH₂), 28.62 (CH₂CH₂O), 28.57 (transition repeating unit), 28.39 (CH₂CH₂O chain end), 28.33 (CH₂CH₂O), 27.99 (=CHCH₂CH₂), 25.90 (CH₂CH₂CH₂O), 25.87 (CH₂ initiator), 25.51 (CH₂ backbone and chain end), 24.59 (CH₂CH₂CO), 24.55 (CH₂CH₂CO), 22.59 (CH₂CH₃), 14.03 (CH₃).

Characterization of star-shaped polymers from **1** and glycerol triacrylate as core (**5-7**)

^1H NMR (300 MHz, CDCl_3 , δ in ppm): 6.93 (dt, $J = 15.29, 6.94, 6.94$ Hz, $\text{COCH}=\text{CH}$), 6.37 (dd, $J = 17.30, 1.24$ Hz, $\text{CH}=\text{CH}_2$ end group), 6.09 (dd, $J = 17.30, 10.36$ Hz, $\text{CH}=\text{CH}_2$ end group), 5.78 (d, $J = 15.29$ Hz, $\text{COCH}=\text{CH}$ and end group $\text{CH}=\text{CH}_2$ overlapped), 5.40-5.30 (m, CH glycerol), 4.38-4.22 (m, CH_2 glycerol), 4.12 (t, $J = 6.85$ Hz, CH_2O end group), 4.08 (t, $J = 6.70$ Hz, CH_2O), 2.16 (q, $J = 6.94$ Hz, $=\text{CHCH}_2$), 1.68-1.56 (m, $\text{CH}_2\text{CH}_2\text{O}$), 1.48-1.20 (CH_2).

^{13}C NMR (75 MHz, CDCl_3 , δ in ppm): 166.95 (CO acrylate), 149.46 ($\text{COCH}=\text{CH}$), 130.49 ($\text{CH}=\text{CH}_2$ end group), 128.81 ($\text{CH}=\text{CH}_2$ end group), 121.41 ($\text{COCH}=\text{CH}$), 64.78 (CH_2O end group), 64.45 (CH_2O), 32.32 ($=\text{CHCH}_2$), 29.52 (CH_2), 29.44 (CH_2), 29.36 (CH_2), 29.26 (CH_2), 28.84 ($\text{CH}_2\text{CH}_2\text{O}$), 28.16 ($=\text{CHCH}_2\text{CH}_2$), 26.07 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$).

End group functionalization of **5** with mercaptoethanol (**8**)

5 (0.1 g, 0.02 mmol), mercaptoethanol (0.019 g, 0.24 mmol) and triethylamine (8.4 μL , 0.06 mmol) were dissolved in 0.5 mL of THF in a 10 mL round-bottomed flask and stirred overnight at room temperature. The product (**8**) was then precipitated quantitatively from methanol.

^1H NMR (300 MHz, CDCl_3 , δ in ppm): 6.96 (dt, $J = 15.30, 6.96, 6.96$ Hz, $\text{COCH}=\text{CH}$), 5.81 (d, $J = 15.64$ Hz, $\text{COCH}=\text{CH}$), 5.40-5.30 (m, CH glycerol), 4.41-4.25 (m, CH_2 glycerol), 4.11 (t, $J = 6.72$ Hz, CH_2O and CH_2O end group), 3.81-3.69 (m, CH_2OH), 2.82 (t, $J = 7.16$ Hz, CH_2S), 2.75 (t, $J = 5.89$ Hz, $\text{SCH}_2\text{CH}_2\text{OH}$), 2.62 (t, $J = 7.14$ Hz, $\text{COCH}_2\text{CH}_2\text{S}$), 2.19 (q, $J = 6.84$ Hz, $=\text{CHCH}_2$), 1.72-1.58 (m, $\text{CH}_2\text{CH}_2\text{O}$), 1.52-1.20 (CH_2).

^{13}C NMR (75 MHz, CDCl_3 , δ in ppm): 172.00 (CO end group), 166.81 (CO acrylate), 149.30 ($\text{COCH}=\text{CH}$), 121.25 ($\text{COCH}=\text{CH}$), 64.93 (CH_2O end group), 64.30 (CH_2O), 60.61 (CH_2OH), 35.43 ($\text{SCH}_2\text{CH}_2\text{OH}$), 34.94 ($\text{CH}_2\text{CH}_2\text{S}$), 32.16 ($=\text{CHCH}_2$), 29.36 (CH_2), 29.28 (CH_2), 29.20 (CH_2), 29.11 (CH_2), 28.68 ($\text{CH}_2\text{CH}_2\text{O}$), 28.57 (CH_2S), 28.02 ($=\text{CHCH}_2\text{CH}_2$), 25.91 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$), 25.85 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{O}$, end group).

4. GPC figures

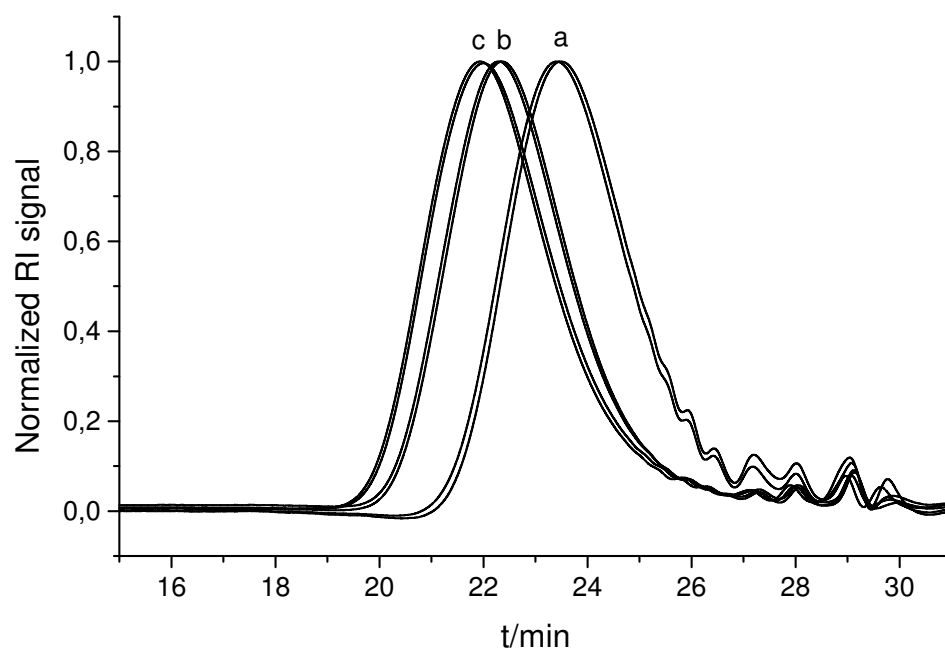


Figure S1. GPC traces of the synthesis of star shaped polymer **6** at different GTA/**1** ratios and times: a) Initial reaction mixture (ratio 1/15) after 5h and 6h; b) Traces after 5h and 6h following to addition of 15 equivalents more of **1** and a new batch of **C1**; c) Traces after 5h and 6h following to addition of 15 equivalents more of **1** and a new batch of **C1**.

5. Relevant ^1H -NMR spectra

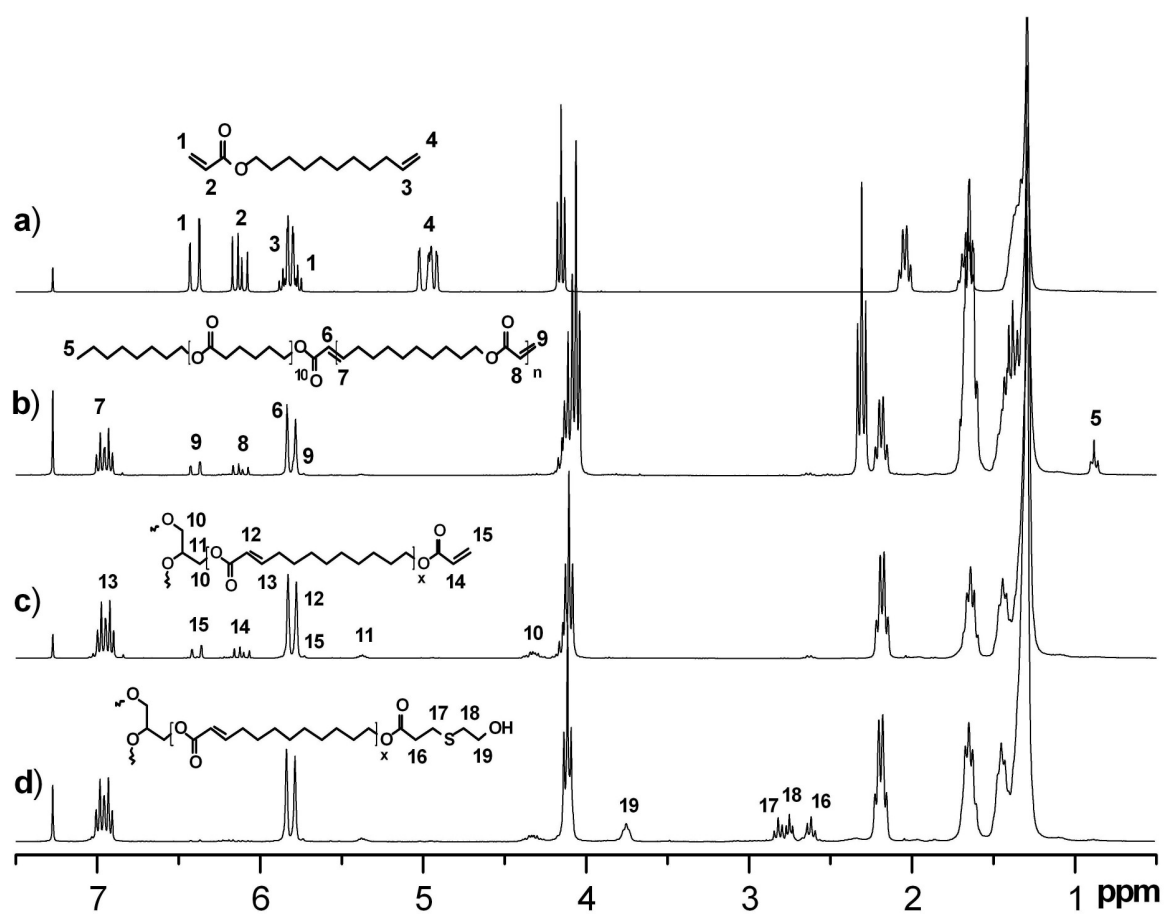


Figure S2. ^1H NMR spectra of a) monomer **1**, b) diblock copolymer **4a**, c) star-shaped polymer **5** and d) end group functionalized star-shaped polymer **8**.

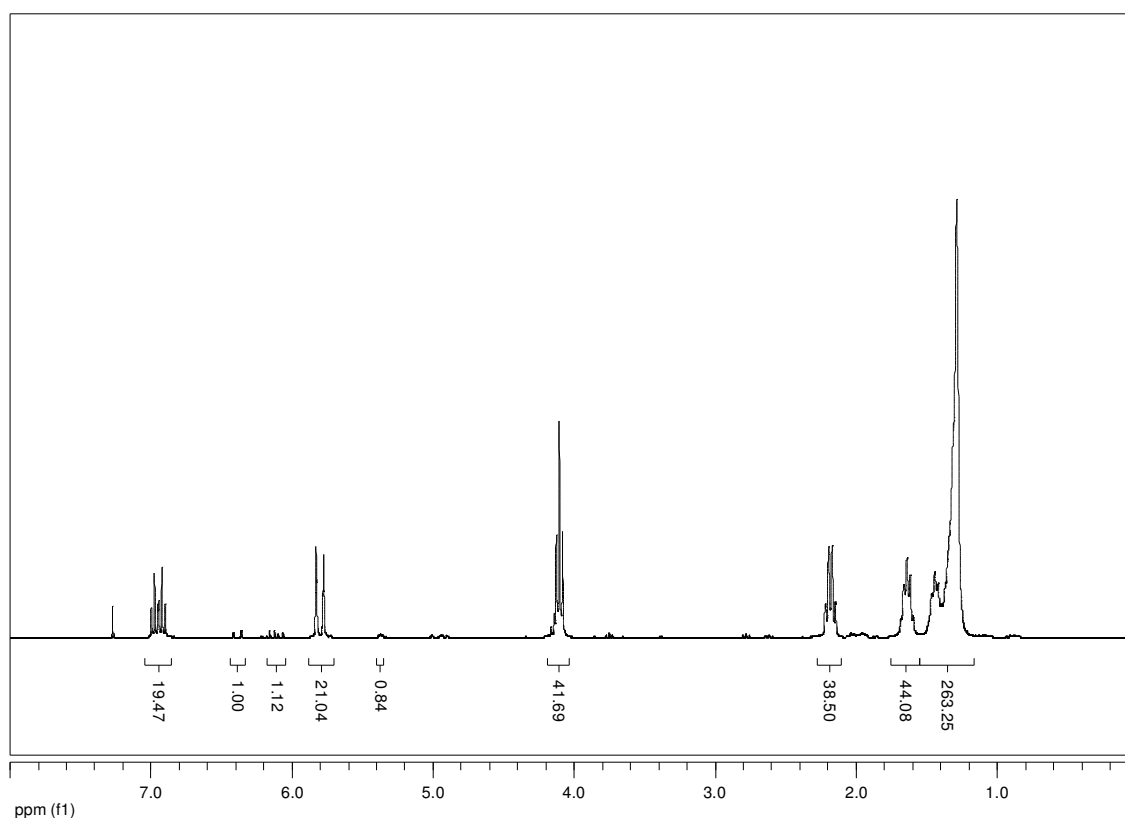


Figure S3. Integrated ^1H NMR spectrum of polymer 2.

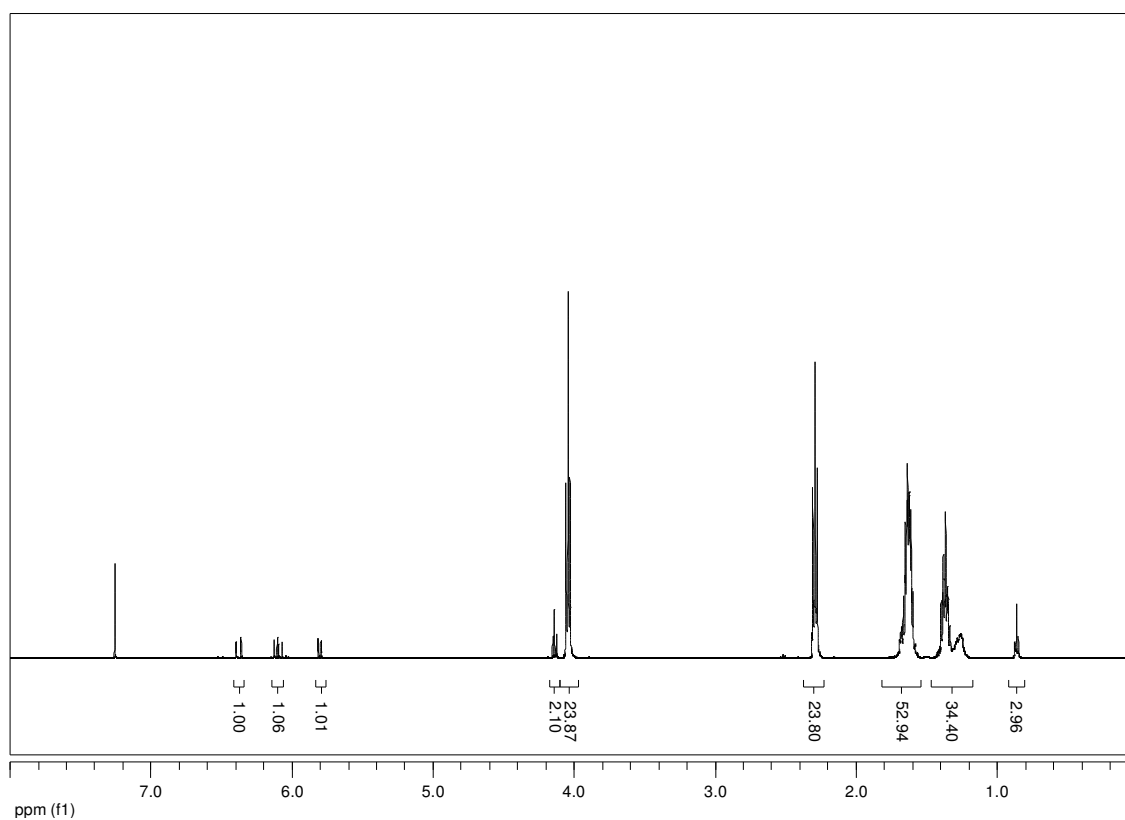


Figure S4. Integrated ^1H NMR spectrum of polymer 3.

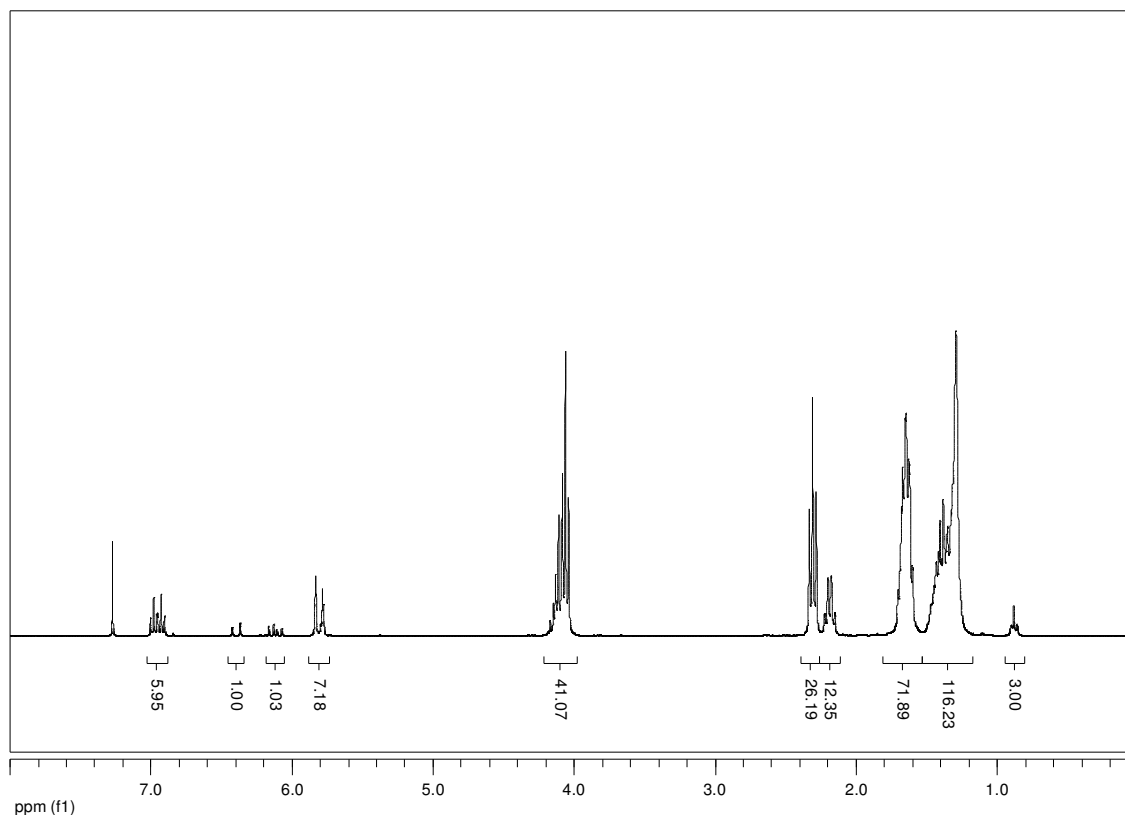


Figure S5. Integrated ^1H NMR spectrum of polymer **4a**.

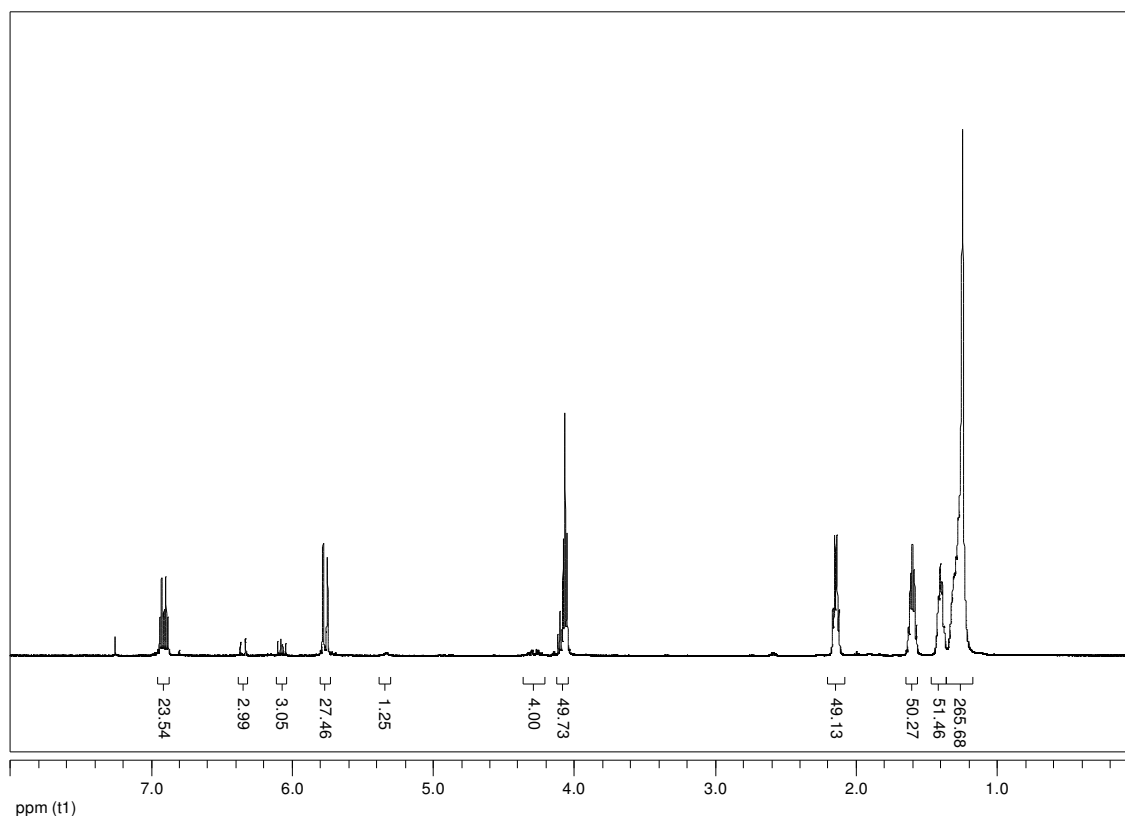


Figure S6. Integrated ^1H NMR spectrum of polymer **5**.

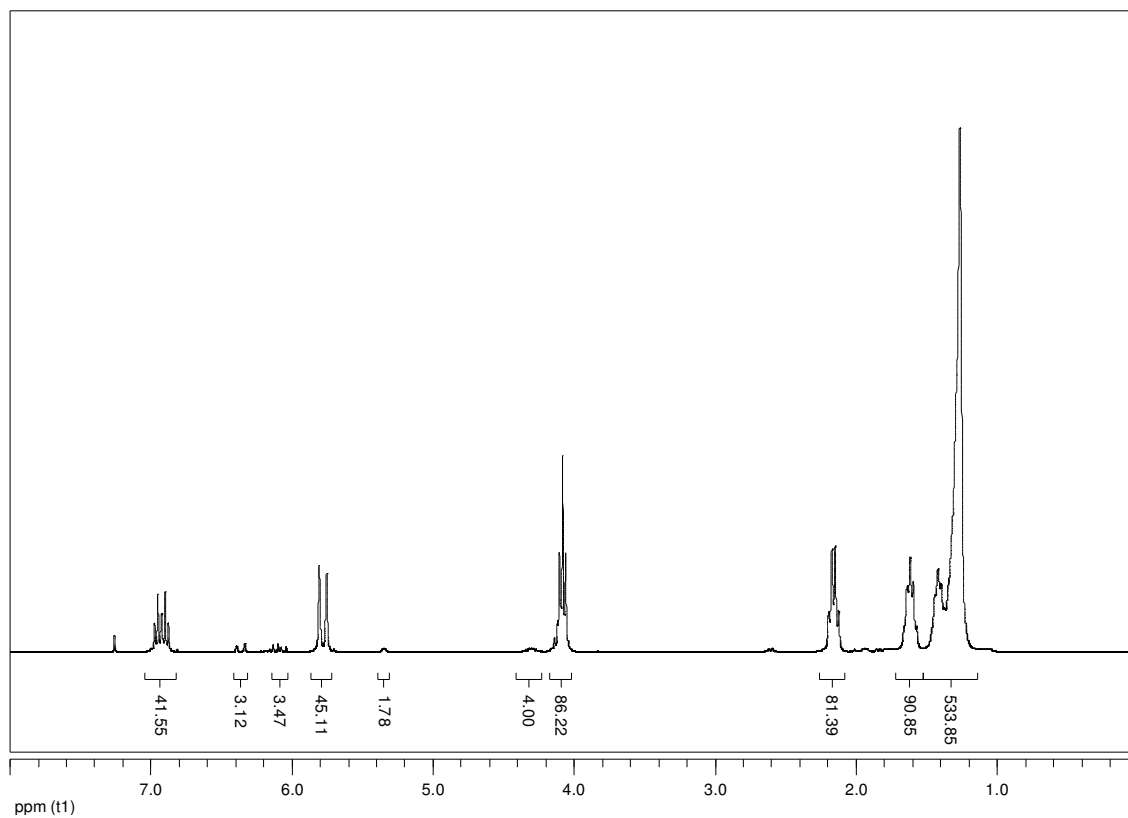


Figure S7. Integrated ¹H NMR spectrum of polymer **6**.