Electronic Supplementary Material (ESI) for Polymer Chemistry.

SUPPORTING INFORMATION

Ultrafast and Efficient Aza- and Thiol-Michael Reactions on Polyester Scaffold with Internal Electron Deficient Triple Bonds

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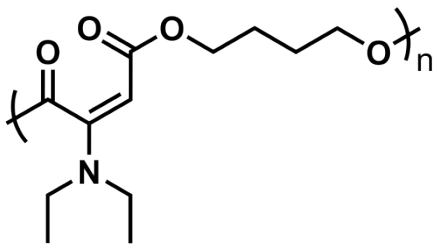
AZA-MICHAEL ADDITION REACTIONS WITH SECONDARY AMINES

Aza-Michael addition reaction between P1 and diethylamine (P2)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next diethylamine (73.9 µL, 0.720 mmol, 1.2 equiv per alkyne) was added to the solution and the resulting solution was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-diethyl ether) procedure was repeated two times. The recovered viscous brown polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.12 g, 83 %, $M_{w,GPC}$ = 10100 g/mol, $Đ$ = 1.97, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.58 (bs, 1H, NC=C*H*C=O), 4.35-4.03 (m, 4H, C=OOC*H*$_2$CH$_2$CH$_2$C*H*$_2$OC=O), 3.17 (br, 4H, NC*H*$_2$CH$_3$), 1.86-1.66 (m, 4H, C=OOCH$_2$C*H*$_2$C*H*$_2$CH$_2$OC=O), 1.29 (br, 6H, CH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, δ) 167.79, 165.70, 153.87, 82.94, 65.57, 62.67, 44.77, 42.02, 24.95, 12.77.

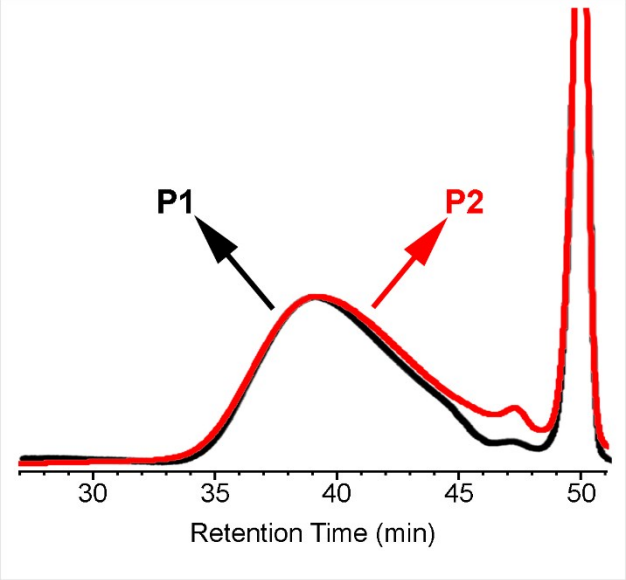
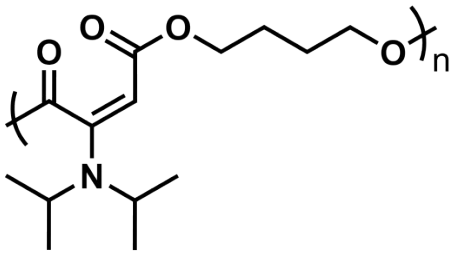


Figure S1. Overlaid GPC traces of **P1** and **P2** (at 30 °C in THF).

Aza-Michael Addition reaction between P1 and diisopropylamine (P3)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next diisopropylamine (100 µL, 0.720 mmol, 1.2 equiv per alkyne) was added to the solution and the resulting solution was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-diethyl ether) procedure was repeated two times. The recovered sticky orange color polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.11 g, 68 %, $M_{w,GPC}$ = 13600 g/mol, $Đ$ = 2.08, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.74 (bs, 1H, NC=C*H*C=O), 4.34-4.02 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.66 (br, 2H, NC*H*(CH$_3$)$_2$), 1.86-1.66 (m, 4H,

C=OOCH$_2$C*H$_2$*C*H$_2$*CH$_2$OC=O), 1.29 (br, 12H, NCH(C*H*$_3$)$_2$); ^{13}C NMR ($CDCl_3$, δ) 167.61, 166.21, 152.39, 84.30, 65.69, 62.62, 49.87, 46.77, 25.57, 24.95, 20.00.

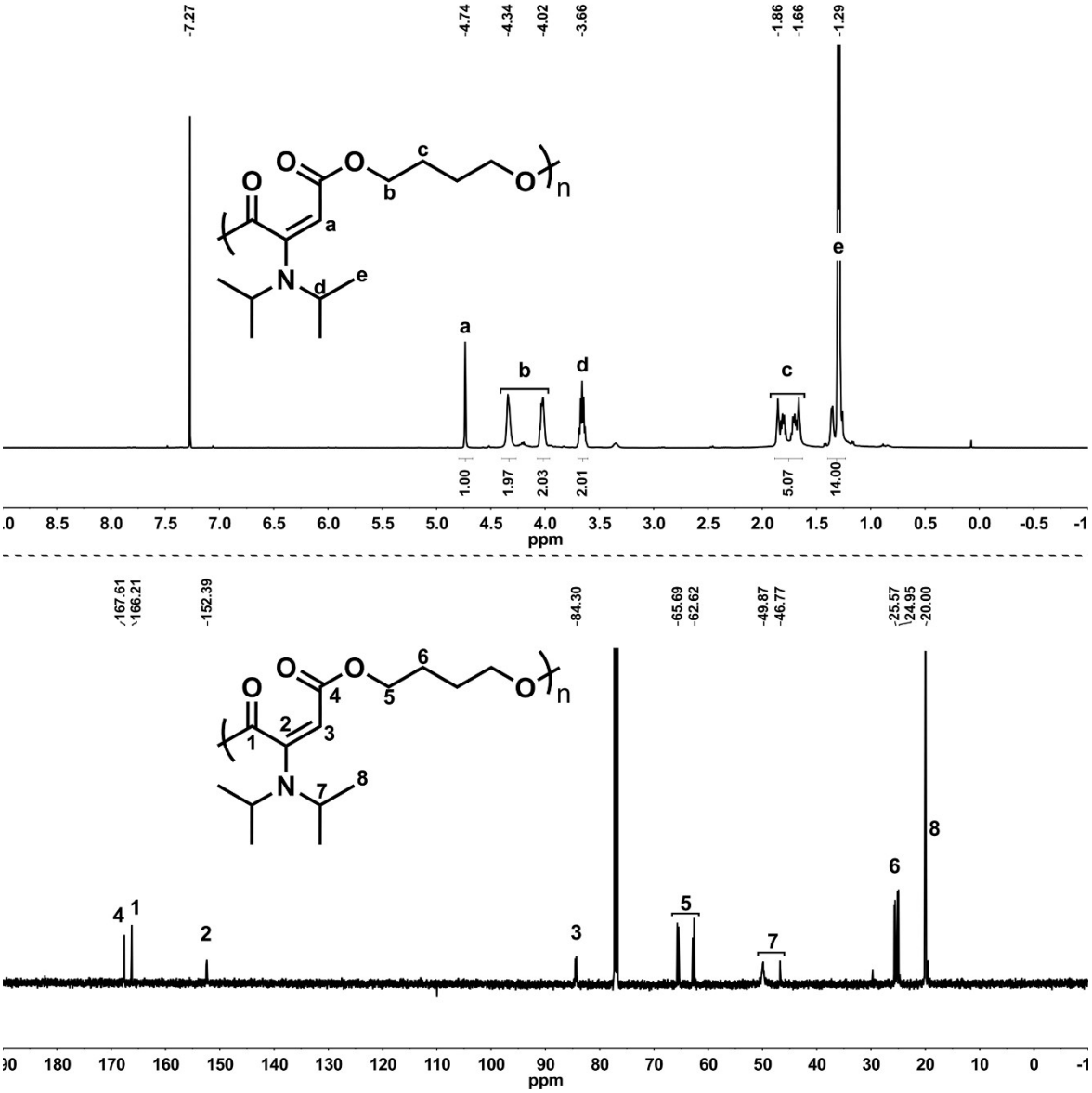


Figure S2. ^{1}H (up) and ^{13}C NMR (down) spectra of **P3** in $CDCl_3$ (500 and 125 MHz, respectively).

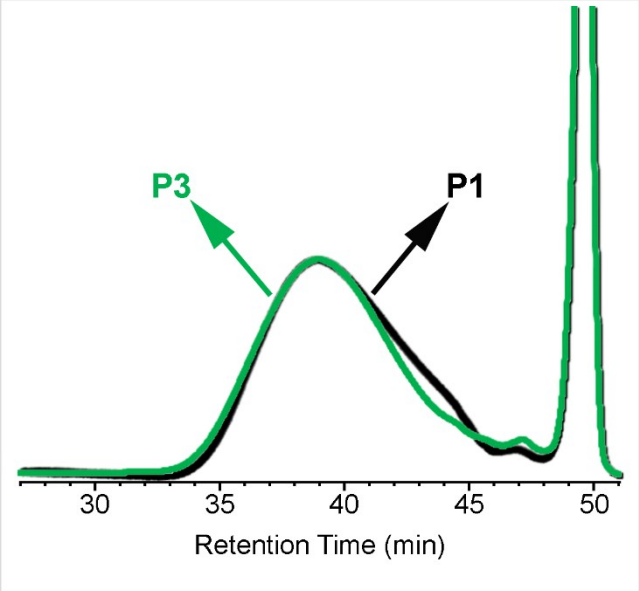
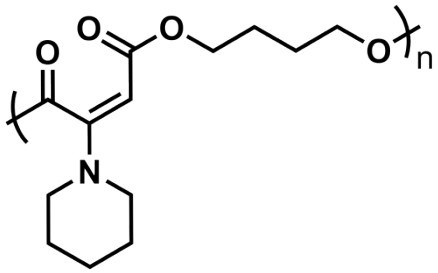


Figure S3. Overlaid GPC traces of **P1** and **P3** (at 30 °C in THF).

Aza-Michael addition reaction between P1 and piperidine (P4)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next piperidine (70.6 µL, 0.720 mmol, 1.2 equiv per alkyne) was added to the solution and the resulting solution was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-diethyl ether) procedure was repeated two times. The recovered viscous brown-orange polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.12 g, 79 %, $M_{w,GPC}$ = 8950 g/mol, $Đ$ = 1.58, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.71 (bs, 1H, NC=C*H*C=O), 4.33-4.03 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.16 (br, 4H, NCH_2CH$_2$CH$_2$), 1.86-1.63 (m,

C=OOCH$_2$C*H$_2$*C*H$_2$*CH$_2$OC=O, NCH$_2$C*H$_2$*CH$_2$ and NCH$_2$CH$_2$C*H$_2$*); ^{13}C NMR ($CDCl_3$, δ) 167.80, 165.85, 154.59, 84.75, 65.52, 62.78, 48.55, 25.13, 23.97, 23.20.

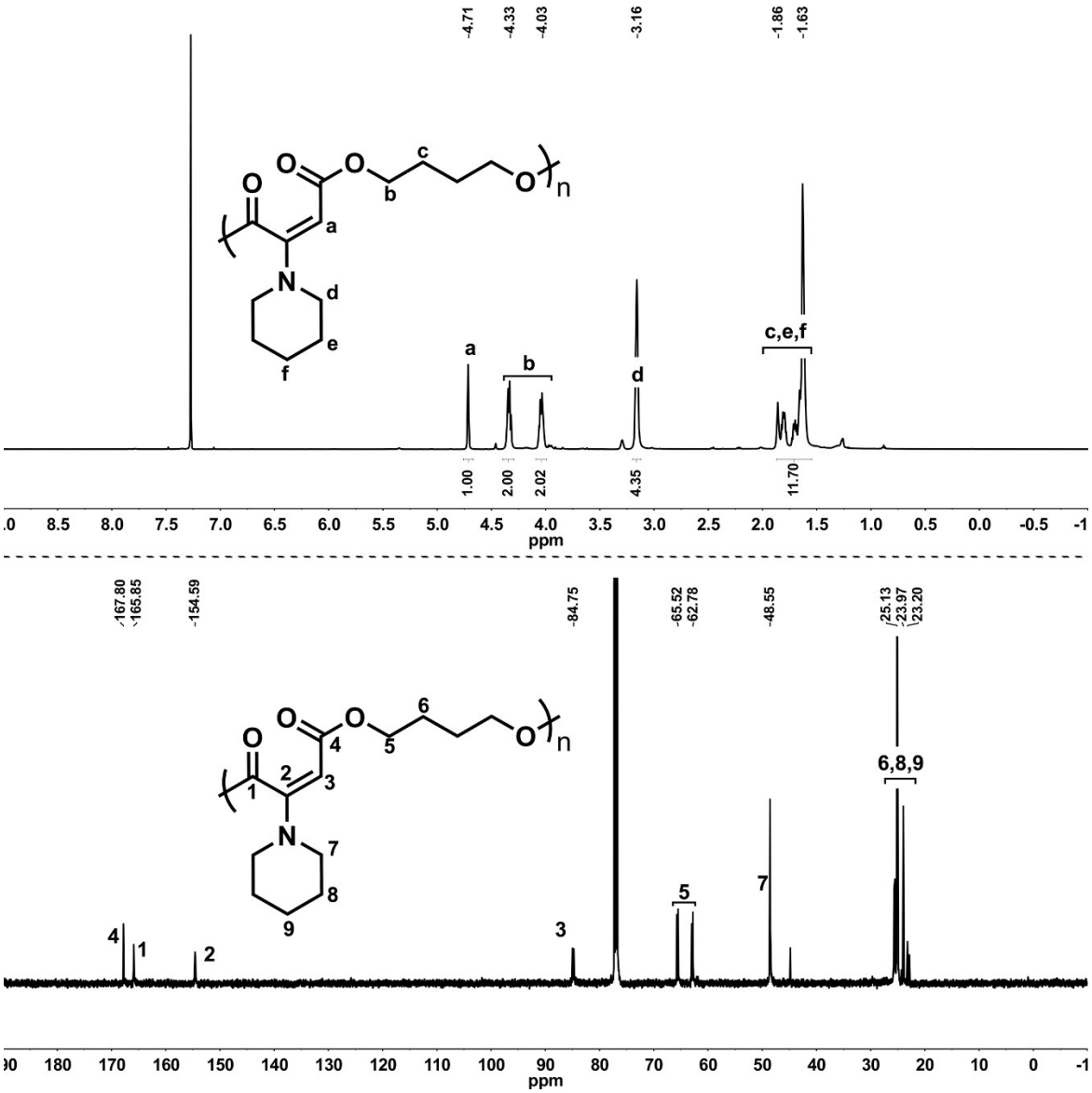


Figure S4. ^{1}H (up) and ^{13}C NMR (down) spectra of **P4** in $CDCl_3$ (500 and 125 MHz, respectively).

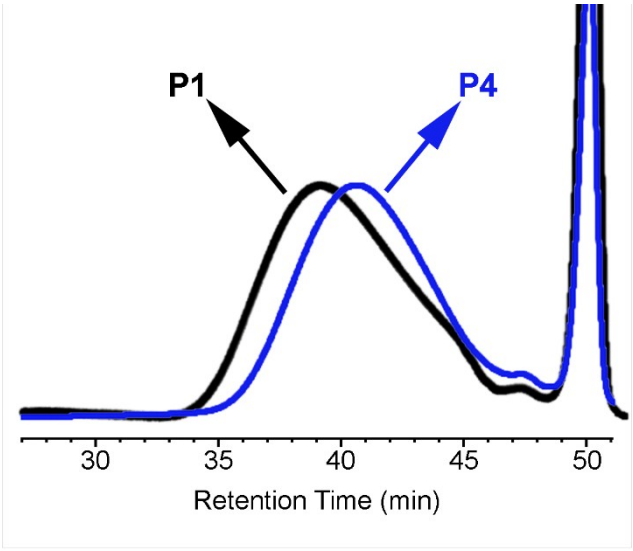
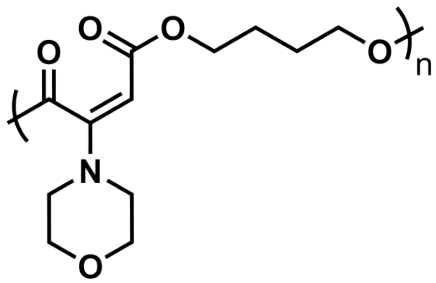


Figure S5. Overlaid GPC traces of **P1** and **P4** (at 30 °C in THF).

Aza-Michael addition reaction between P1 and morpholine (P5)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next morpholine (62.5 µL, 0.720 mmol, 1.2 equiv per alkyne) was added to the solution and the resulting solution was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH/diethyl ether (1:4) and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-MeOH/diethyl ether (1:4)) procedure was repeated two times. The recovered pale yellow polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.10 g, 65 %, $M_{w,GPC}$ = 9000 g/mol, $Đ$ = 1.67, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.78 (bs, 1H, NC=C*H*C=O), 4.33-4.05 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.74 (br, 4H, NCH$_2$CH_2O), 3.15 (br, 4H,

NCH_2CH_2O), 1.86-1.67 (m, 4H, C=OOCH_2CH_2CH_2CH_2OC=O); ^{13}C NMR ($CDCl_3$, δ) 167.23, 165.36, 154.69, 87.38, 67.97, 65.88, 63.03, 47.12, 25.61.

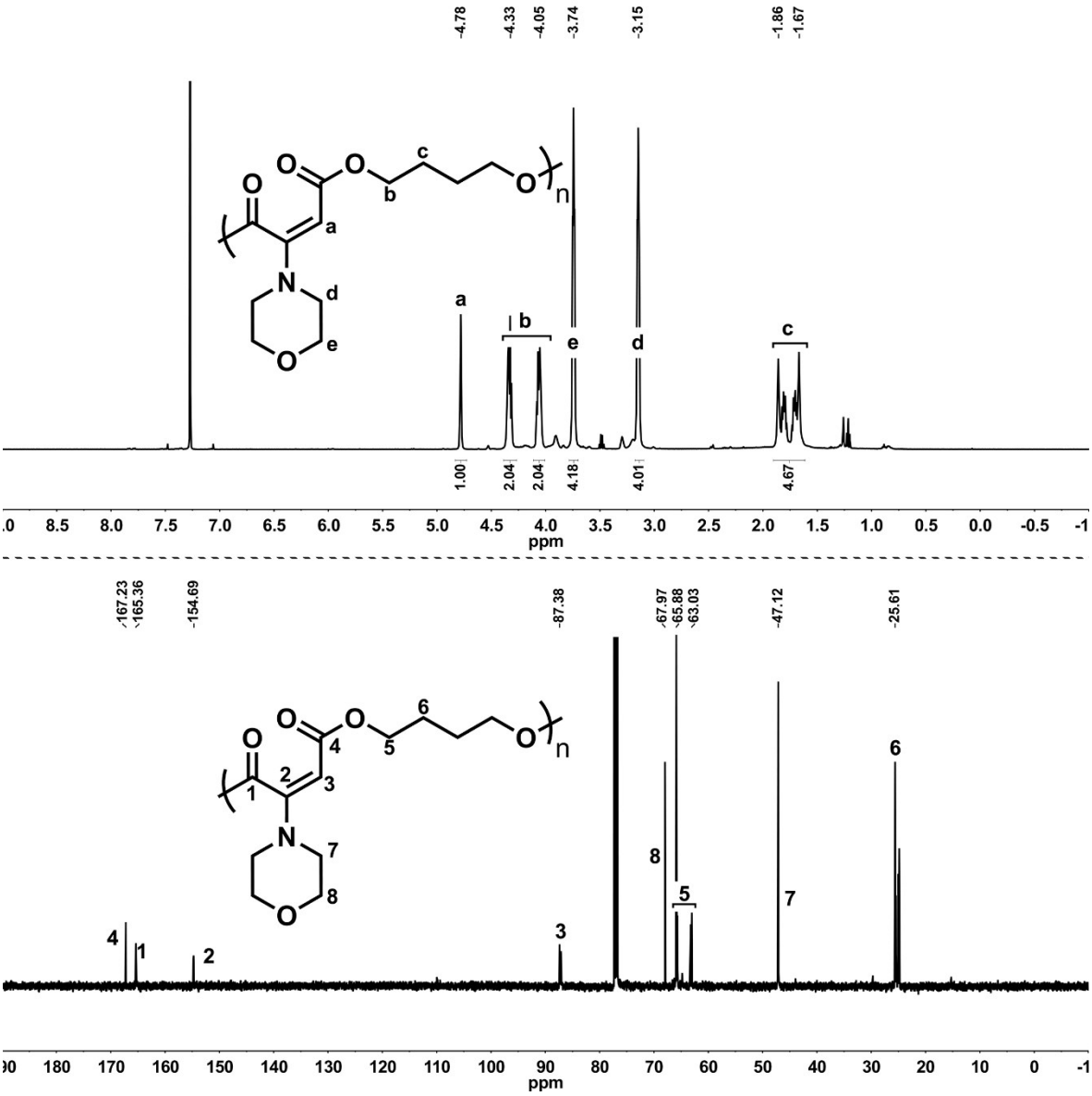


Figure S6. ^{1}H (up) and ^{13}C NMR (down) spectra of **P5** in $CDCl_3$ (500 and 125 MHz, respectively).

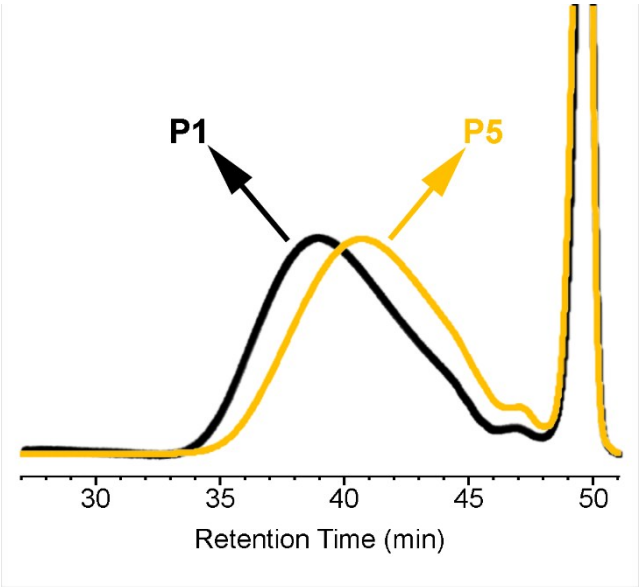


Figure S7. Overlaid GPC traces of **P1** and **P5** (at 30 °C in THF).

Heterofunctionalization of P1 with a mixture of secondary amines (diethylamine, piperidine and morpholine) via one-pot Aza-Michael addition reaction (P6)

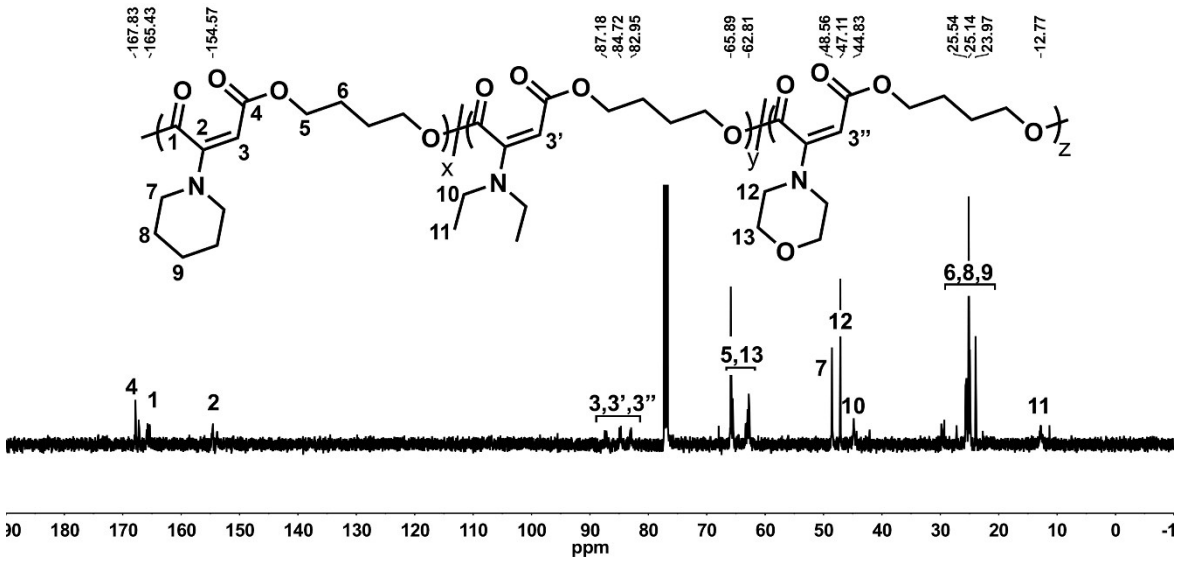
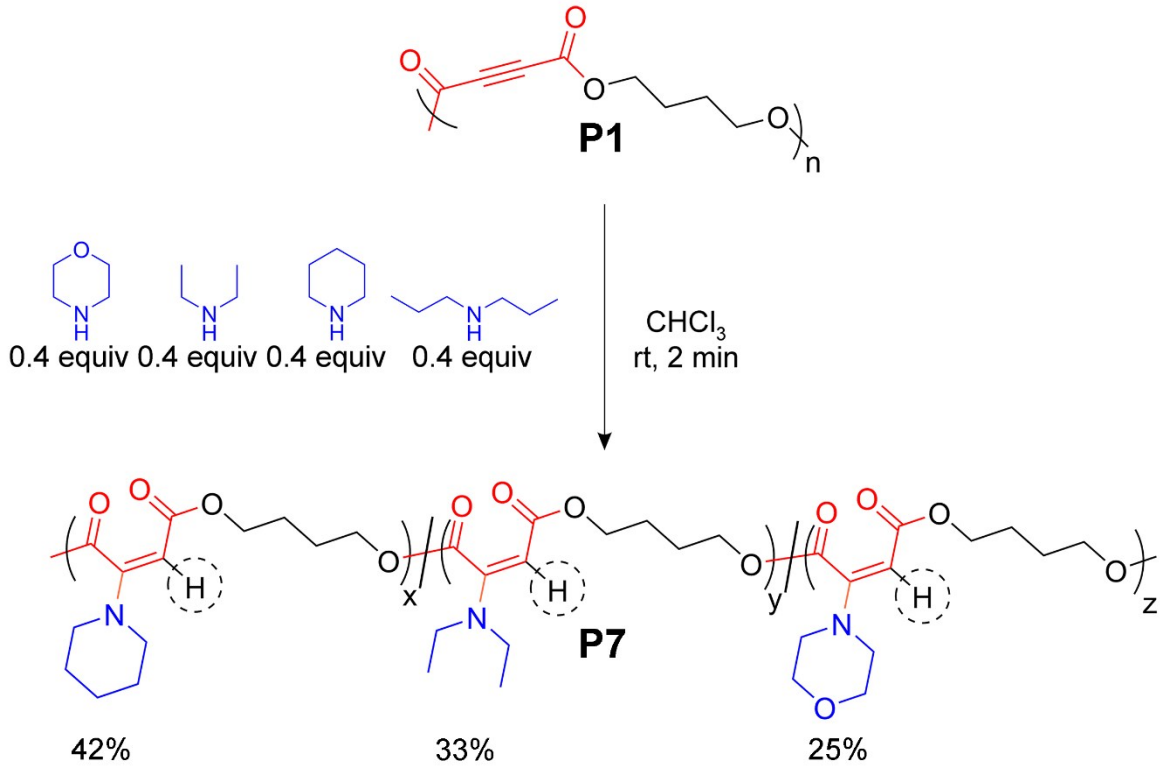


Figure S8. ^{13}C NMR spectrum of **P6** in $CDCl_3$ (125 MHz).

Heterofunctionalization of P1 with a mixture of secondary amines (diethylamine, piperidine, morpholine and diisopropylamine) via one-pot Aza-Michael addition reaction (P7)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was placed in a round bottomed flask dissolved in 2 mL of $CHCl_3$. Diethylamine (24.6 µL, 0.240 mmol, 0.4 equiv per alkyne), piperidine (23.5 µL, 0.240 mmol, 0.4 equiv per alkyne), morpholine (20.8 µL, 0.240 mmol, 0.4 equiv per alkyne) and dipropylamine (32.6 µL, 0.240 mmol, 0.4 equiv per alkyne) were dissolved in 1 mL of $CHCl_3$ in another flask and added to the polymer solution via syringe. The solution was stirred for 2 min at room temperature. After the specified time, the polymer solution was precipitated in 20 mL of MeOH/diethyl ether (1:4) and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-MeOH/diethyl ether (1:4)) procedure was repeated two times. The obtained viscous brown polymer was dried for 24 h in a vacuum oven at 40 °C (Yield = 0.09 g, 59.4 %, $M_{w,GPC}$ = 12050 g/mol, $Đ$ = 2.15, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.79 (bs, 1H, $O(CH_2CH_2)_2NC{=}CHC{=}O$), 4.72 (bs, 1H,

$CH_2(CH_2CH_2)_2NC{=}CHC{=}O$), 4.59 (bs, 1H, $(CH_3CH_2)_2NC{=}CHC{=}O$), 4.35-4.05 (m, 4H, $C{=}OOCH_2CH_2CH_2CH_2OC{=}O$), 3.74 (br, 4H, NCH_2CH_2O), 3.16 (m, $NCH_2CH_2CH_2$, NCH_2CH_3 and NCH_2CH_2O), 1.87-1.63 (m, $C{=}OOCH_2CH_2CH_2CH_2OC{=}O$, $NCH_2CH_2CH_2$ and $NCH_2CH_2CH_2$), 1.18 (br, 6H, CH_2CH_3); ^{13}C NMR ($CDCl_3$, δ) 167.83, 165.90, 154.65, 87.47, 84.97, 82.93, 65.89, 62.79, 48.56, 47.12, 44.77, 25.54, 25.14, 23.98, 12.71.

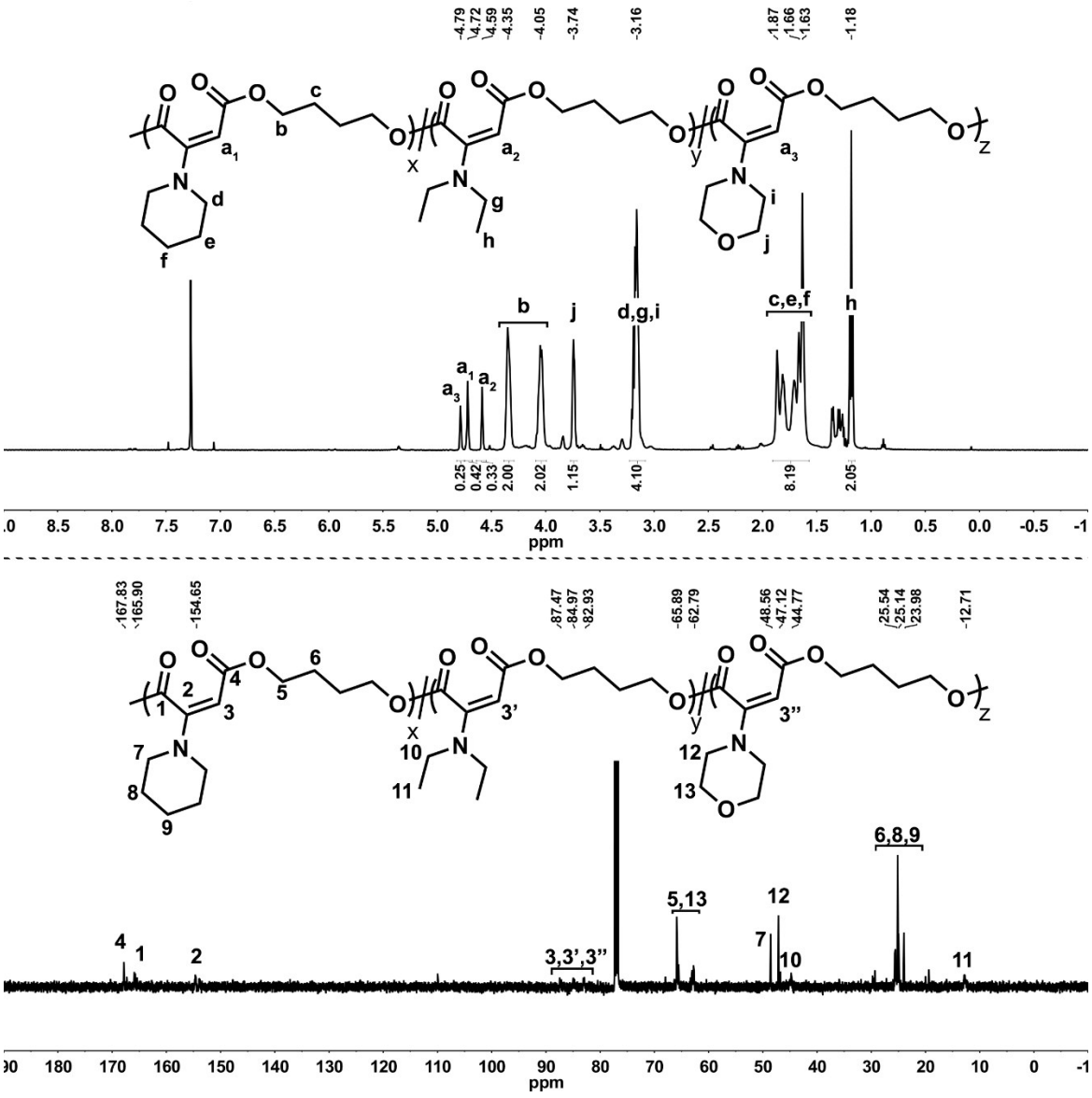
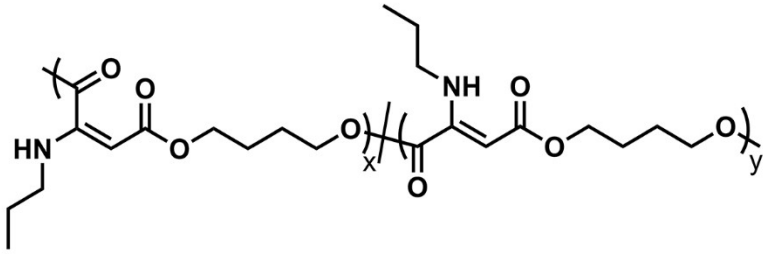


Figure S9. ^1H (up) and ^{13}C NMR (down) spectra of **P7** in $CDCl_3$ (500 and 125 MHz, respectively).

AZA-MICHAEL ADDITION REACTIONS WITH PRIMARY AMINES

Aza-Michael reaction between P1 and propylamine (P8)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next propylamine (58.7 µL, 0.720 mmol, 1.2 equiv per alkyne) was added to the solution and the resulting solution was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-diethyl ether) procedure was repeated two times. The recovered viscous dark yellow color polymer was dried in a vacuum oven at 40 ^oC for 24 h (Yield = 0.11 g, 81 %, $M_{w,GPC}$ = 39400 g/mol, $Đ$ = 6.07, relative to PS standards). ^1H NMR ($CDCl_3$, δ) 8.12 (bs, 1H, N*H*), 5.00 (bs, 1H, NC=C*H*C=O, *trans*), 4.68 (bs, 1H, NC=C*H*C=O, *cis*), 4.26-4.10 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.28 (br, 2H, HNCH_2CH$_2$, *trans*), 2.99 (br, 2H, HNCH_2CH$_2$, *cis*), 1.83-1.72 (m, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O), 1.57 (br, 2H, HNCH$_2$CH_2), 0.94 (br, 3H, CH$_2$CH_3); ^{13}C NMR ($CDCl_3$, δ) 170.20, 163.74, 151.98, 86.19, 76.80, 65.02, 62.47, 46.62, 25.52, 25.09, 24.16, 11.19.

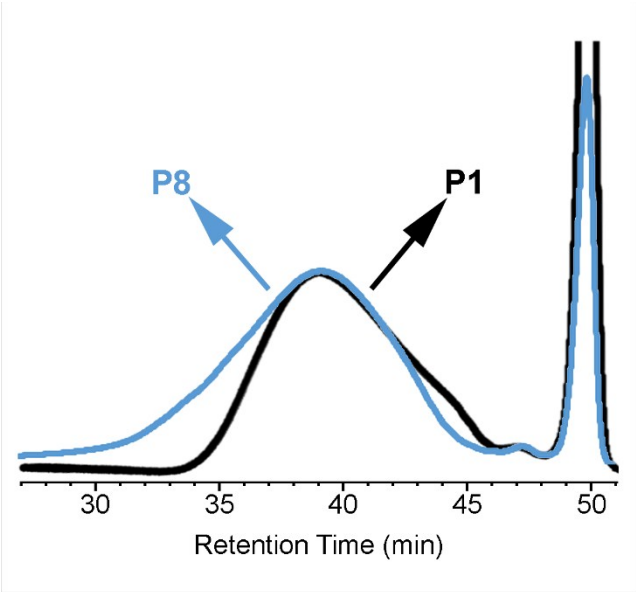
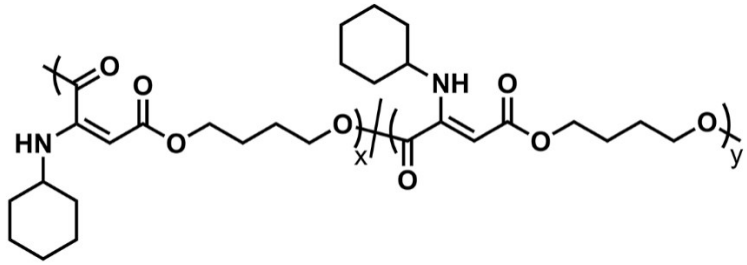


Figure S10. Overlaid GPC traces of **P1** and **P8** (at 30 °C in THF).

Aza-Michael addition reaction between P1 and cyclohexylamine (P9)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next cyclohexylamine (81.7 µL, 0.720 mmol, 1.2 equiv per alkyne) was added to the solution and the resulting solution was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-diethyl ether) procedure was repeated two times. The recovered viscous dark yellow color polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.11 g, 67 %, $M_{w,GPC}$ = 60100 g/mol, $Đ$ = 8.61, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.12 (bs, 1H, N*H*), 4.96 (bs, 1H, NC=C*H*C=O, *trans*), 4.71 (bs, 1H, NC=C*H*C=O, *cis*), 4.26-4.10 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.53 (br, 1H, HNC*H*CH$_2$), 1.90-1.23 (m,

C=OOCH$_2$C*H*$_2$C*H*$_2$CH$_2$OC=O, HNCHC*H*$_2$, HNCHCH$_2$C*H*$_2$CH$_2$, HNCHCH$_2$CH$_2$C*H*$_2$); ^{13}C NMR ($CDCl_3$, δ) 170.19, 164.06, 151.57, 86.29, 65.00, 62.44, 53.13, 34.55, 25.33, 24.52.

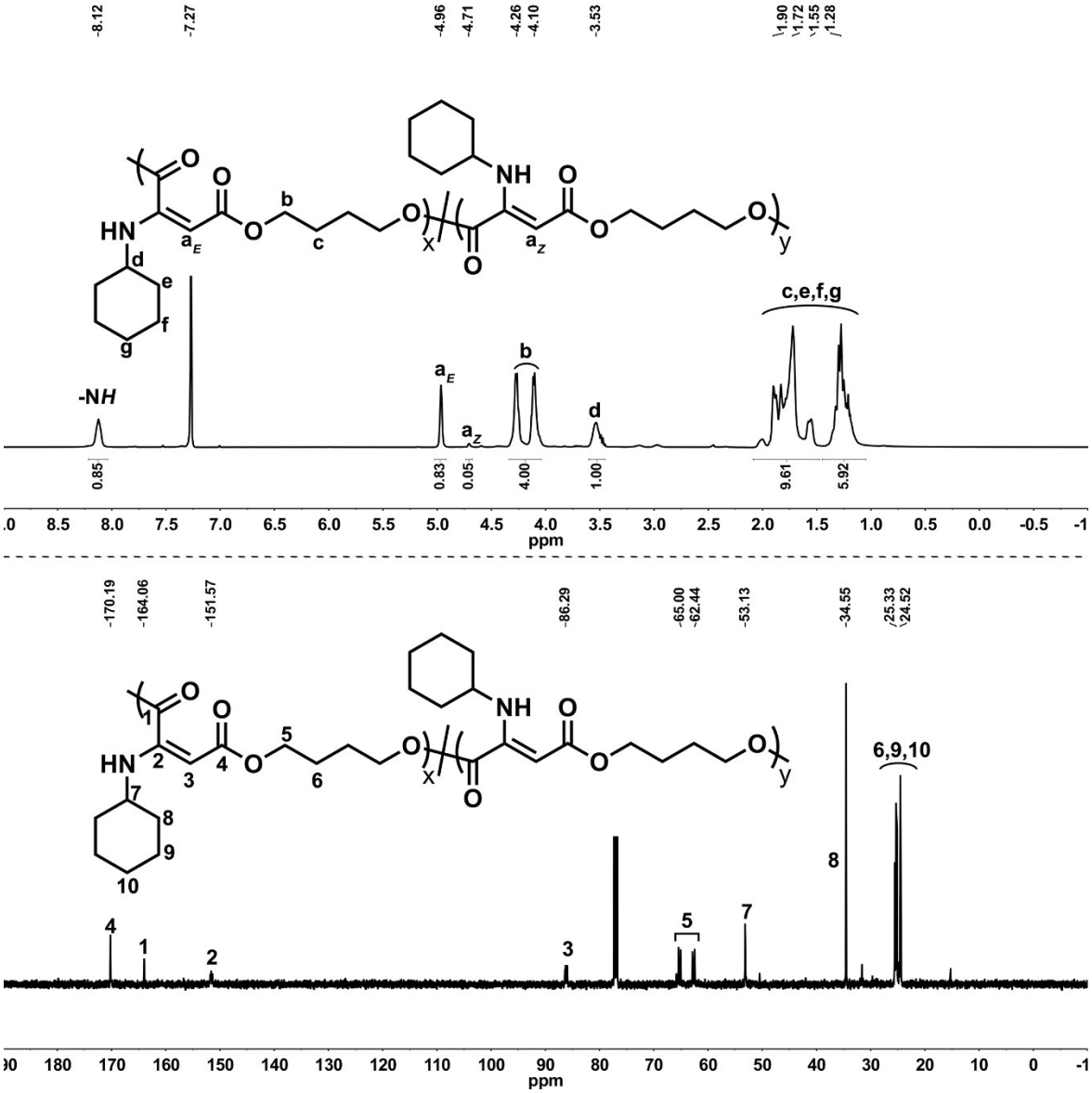


Figure S11. ^{1}H (up) and ^{13}C NMR (down) spectra of **P9** in $CDCl_3$ (500 and 125 MHz, respectively).

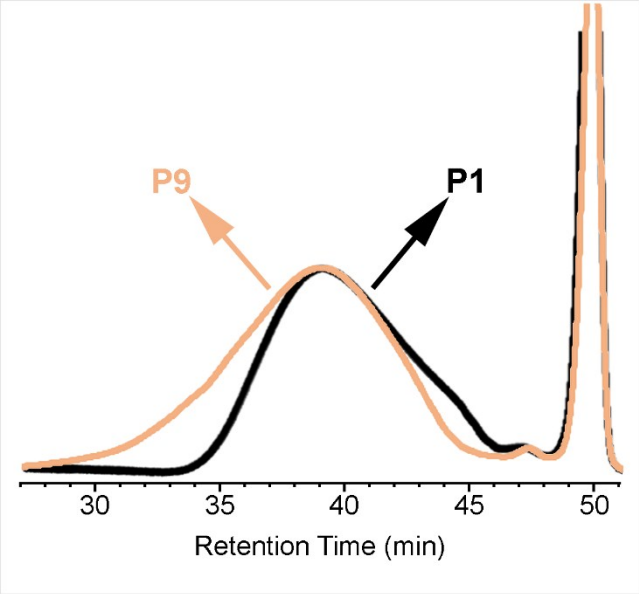
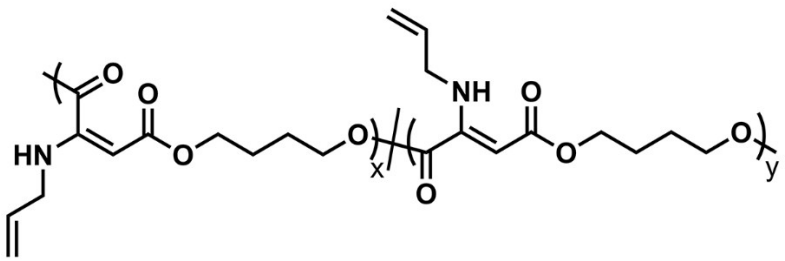


Figure S12. Overlaid GPC traces of **P1** and **P9** (at 30 °C in THF).

Aza-Michael addition reaction between P1 and allylamine (P10)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next allylamine (53.6 µL, 0.720 mmol, 1.2 equiv per alkyne) was added to the solution and the resulting solution was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-diethyl ether) procedure was repeated two times. The recovered viscous dark yellow color polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.10 g, 74 %, $M_{w,GPC}$ = 38500 g/mol, $Đ$ = 6.22, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.18 (bs, 1H, N*H*), 5.87 (m, 1H, C*H*=CH_2), 5.22 (m, 2H, CH=CH_2), 5.10 (bs, 1H, NC=C*H*C=O, *trans*), 4.72 (bs, 1H, NC=C*H*C=O, cis), 4.25-4.13 (m, 4H, C=OOC$H_2$$CH_2$$CH_2CH_2$OC=O), 3.98 (bs, 2H, HNC$H_2$,

trans), 3.68 (bs, 2H, HNCH_2, *cis*), 1.81-1.73 (m, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O); ^{13}C NMR ($CDCl_3$, δ) 170.04, 163.58, 151.66, 135.14, 116.41, 87.41, 65.07, 62.62, 46.88, 25.05.

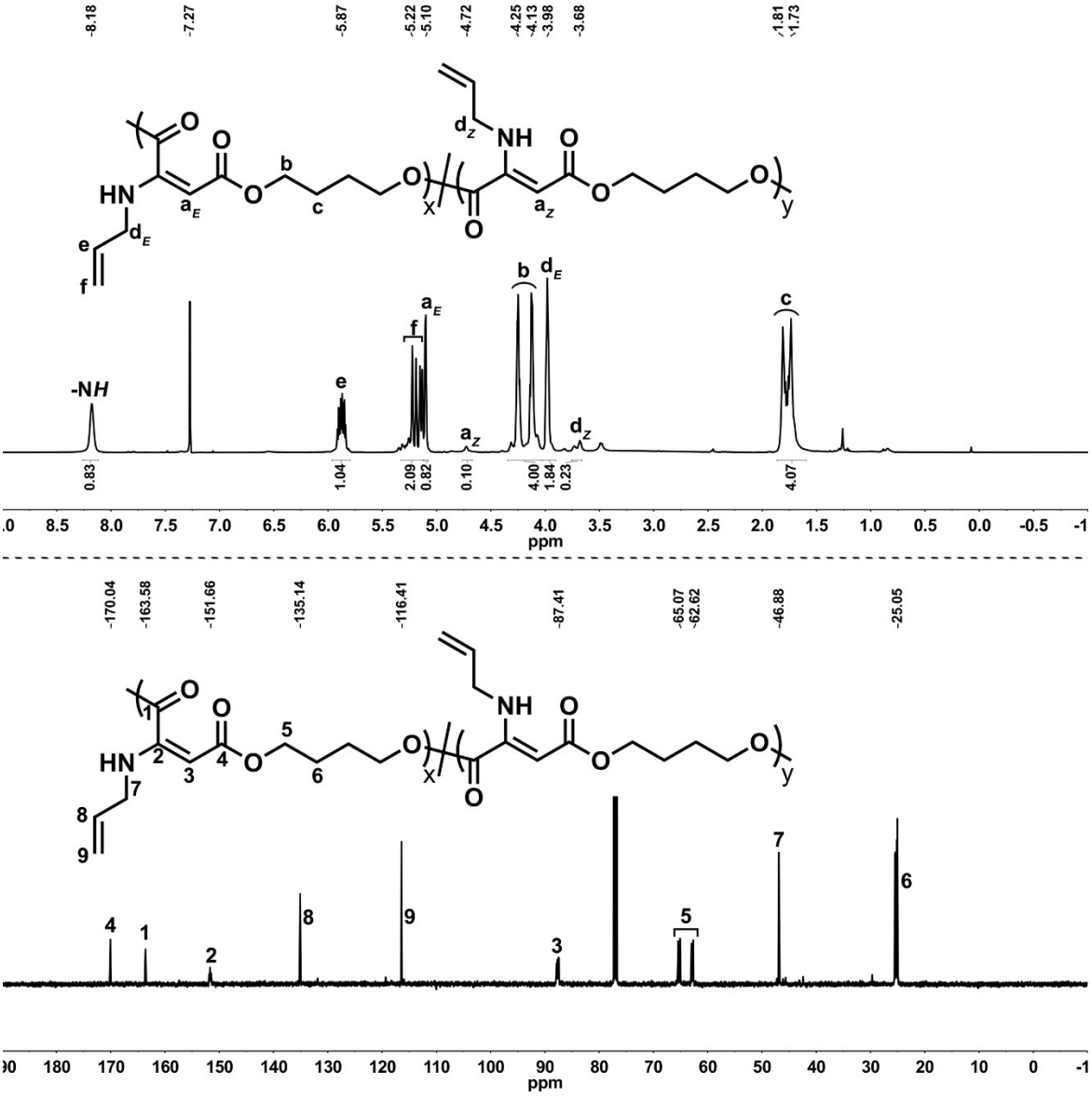


Figure S13. ^{1}H (up) and ^{13}C NMR (down) spectra of **P10** in $CDCl_3$ (500 and 125 MHz, respectively).

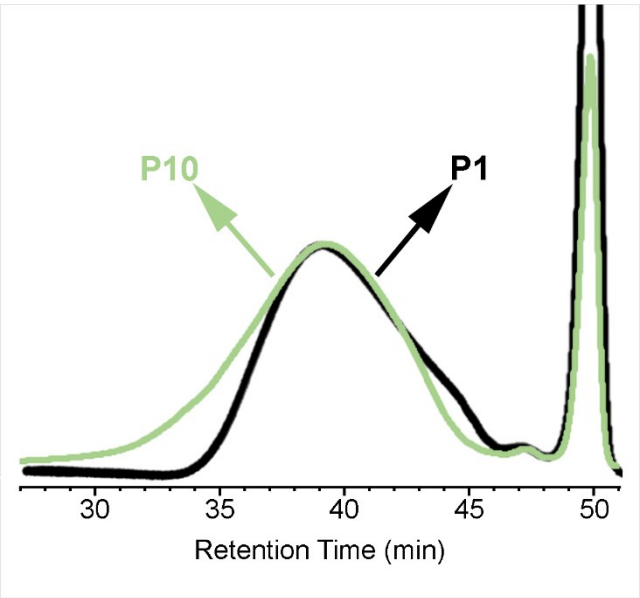
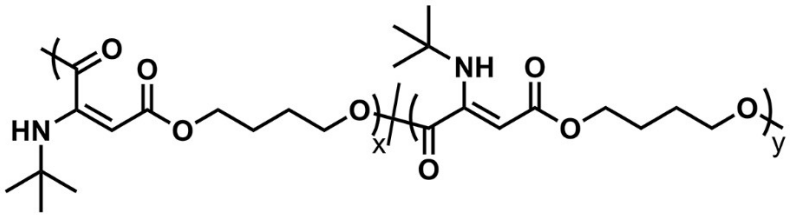


Figure S14. Overlaid GPC traces of **P1** and **P10** (at 30 °C in THF).

Aza-Michael addition reaction between P1 and *tert*-butylamine (P11)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next *tert*-butylamine (75.1 µL, 0.720 mmol, 1.2 equiv per alkyne) was added to the solution and the resulting solution was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-diethyl ether) procedure was repeated two times. The recovered viscous dark brown polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.14 g, 97 %, $M_{w,GPC}$ = 24000 g/mol, $Đ$ = 2.56, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.32 (bs, 1H, N*H*), 4.87 (bs, 1H, NC=C*H*C=O, *cis*), 4.74 (bs, 1H, NC=C*H*C=O, *trans*), 4.27-4.09 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 1.84-1.70 (m, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O), 1.37-1.33

(m, 9H, HNC(CH_3)$_3$); ^{13}C NMR ($CDCl_3$, δ) 170.02, 165.50, 153.17, 85.92, 76.75, 65.24, 64.46, 53.43, 30.63, 28.12, 24.98.

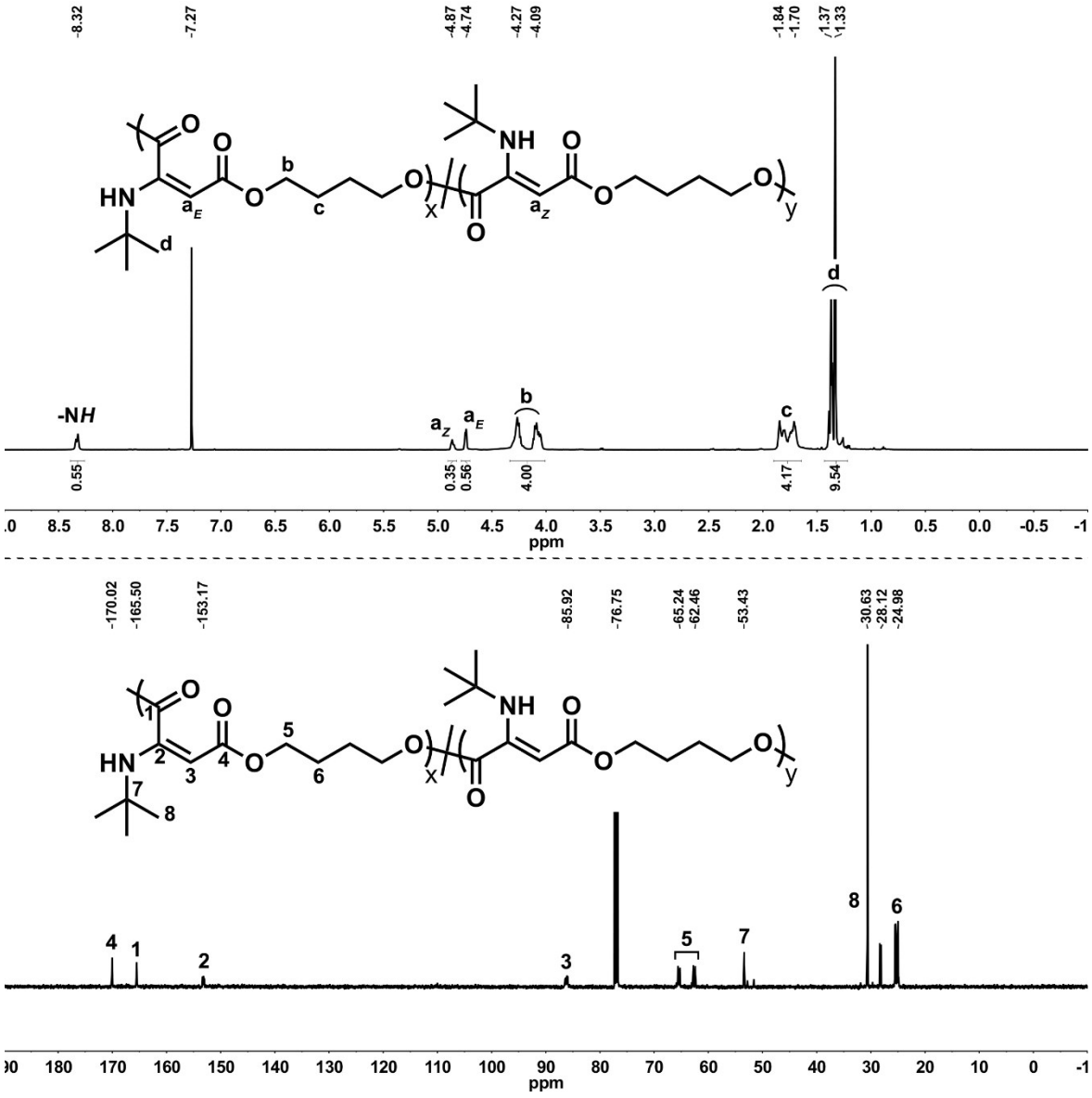


Figure S15. ^{1}H (up) and ^{13}C NMR (down) spectra of **P11** in $CDCl_3$ (500 and 125 MHz, respectively).

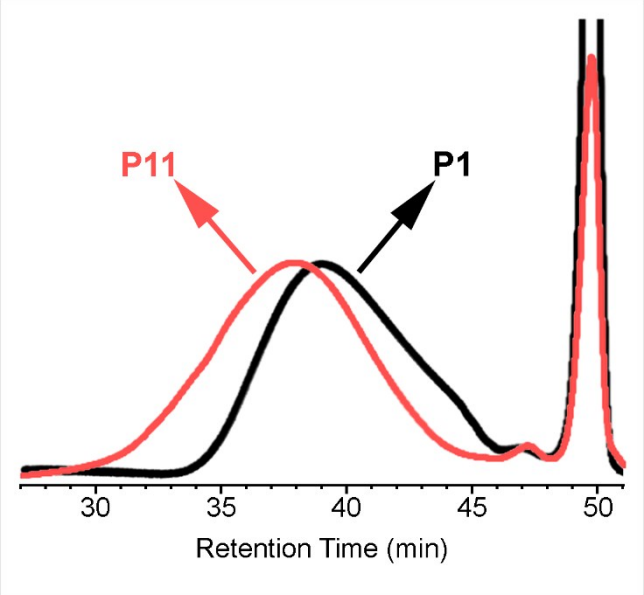
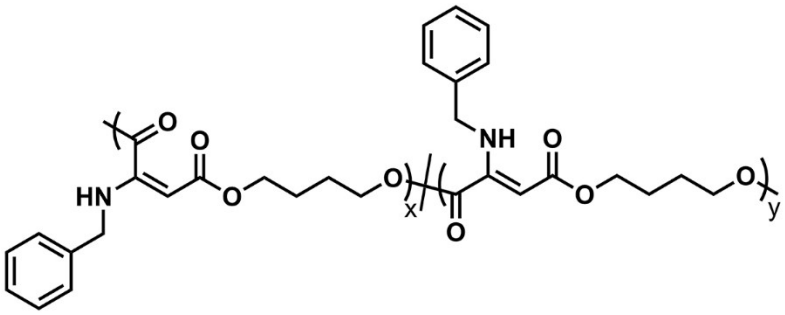


Figure S16. Overlaid GPC traces of **P1** and **P11** (at 30 °C in THF).

Aza-Michael addition reaction between P1 and benzylamine (P12)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next benzylamine (78 µL, 0.72 mmol, 1.2 equiv per alkyne) was added to the solution and the resulting solution was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-diethyl ether) procedure was repeated two times. The recovered sticky pale yellow color polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.14 g, 85 %, $M_{w,GPC}$ = 34700 g/mol, $Đ$ = 3.64, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.43 (bs, 1H, N*H*), 7.32 (m, 5H, Ar*H*), 5.14 (bs, 1H, NC=C*H*C=O, trans), 4.77 (bs, 1H, NC=C*H*C=O, *cis*), 4.55 (br, 2H, HNCH_2, *trans*),

4.24 (br, 2H, HNCH_2, *cis*) 4.17-4.06 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 1.72-1.57 (m, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O); ^{13}C NMR ($CDCl_3$, δ) 170.06, 163.53, 151.43, 138.76, 128.67, 127.24, 87.78, 65.45, 63.02, 48.48, 25.27.

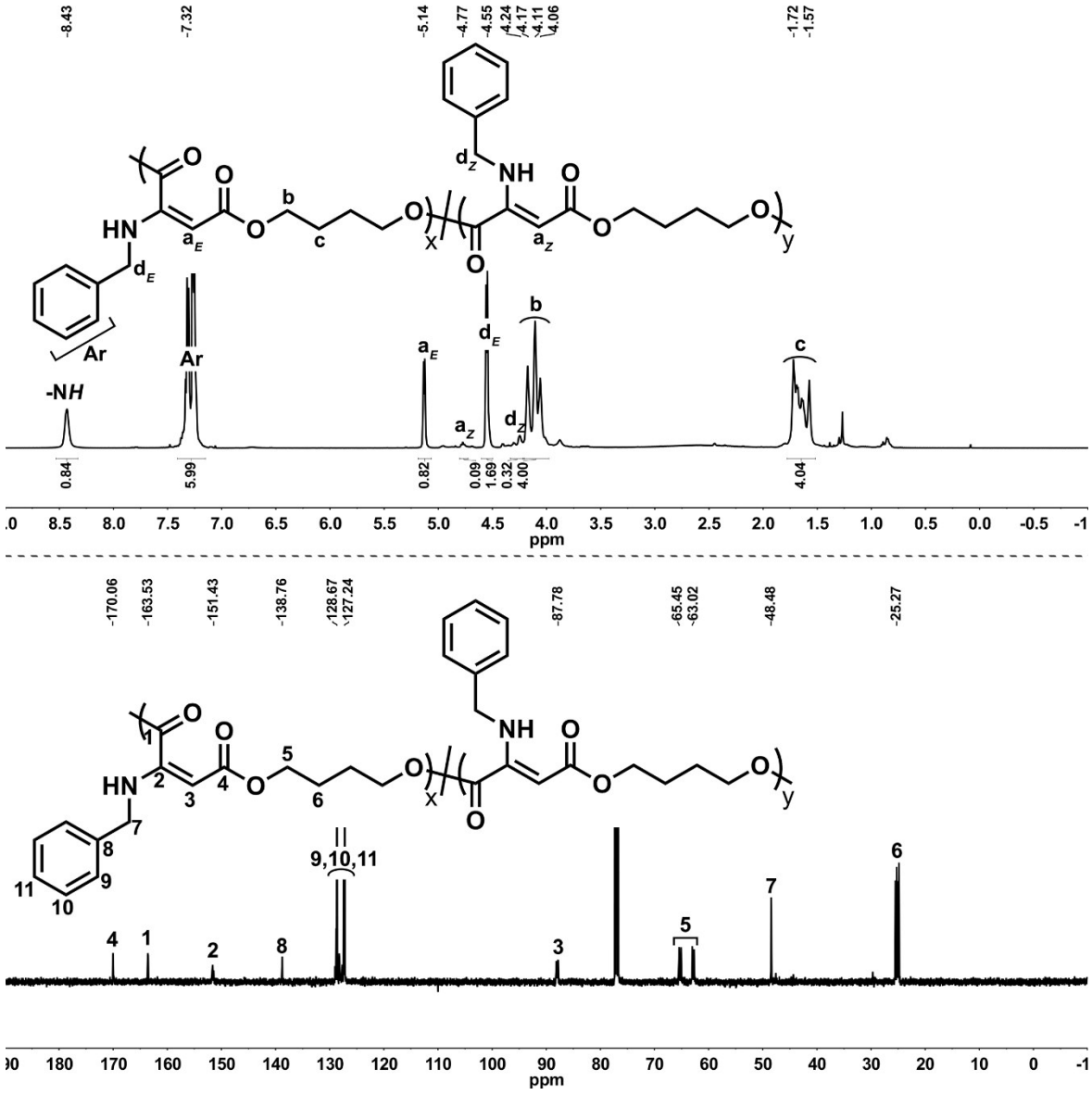


Figure S17. ^{1}H (up) and ^{13}C NMR (down) spectra of **P12** in $CDCl_3$ (500 and 125 MHz, respectively).

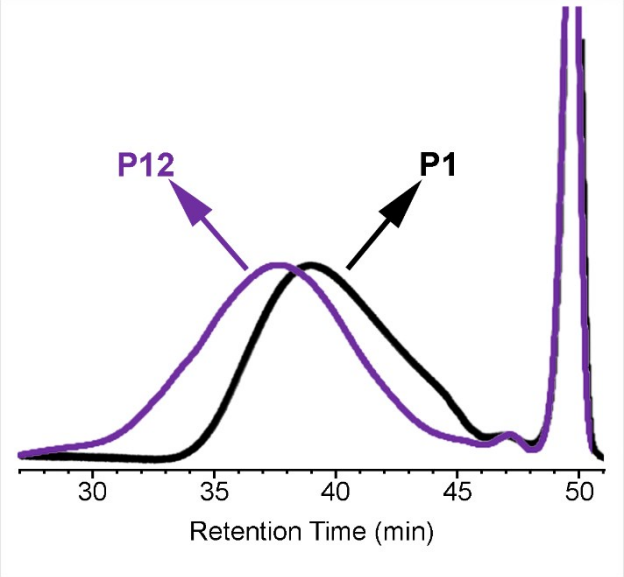
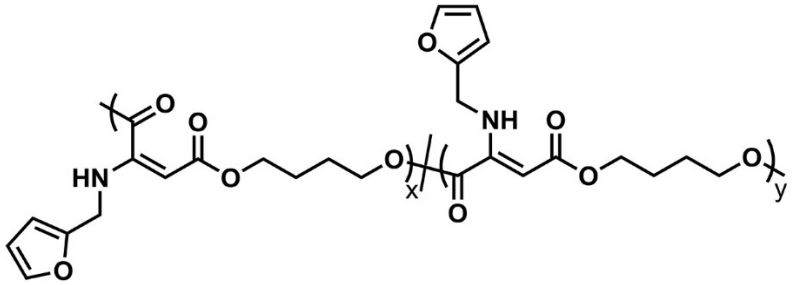


Figure S18. Overlaid GPC traces of **P1** and **P12** (at 30 °C in THF).

Aza-Michael addition reaction between P1 and furfurylamine (P13)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next furfurylamine (63.1 µL, 0.720 mmol, 1.2 equiv per alkyne) was added to the solution and the resulting solution was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-diethyl ether) procedure was repeated two times. The recovered sticky pale yellow color polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.14 g, 88 %, $M_{w,GPC}$ = 20500 g/mol, $Đ$ = 2.86, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 8.31 (bs, 1H, N*H*), 7.33 (bs, 1H, =C*H*O), 6.28 (bs, 1H, C*H*CH=CHO), 6.17 (bs, 1H, CHC*H*=CHO), 5.19 (bs, 1H, NC=C*H*C=O, *trans*), 4.82 (bs, 1H, NC=C*H*C=O, *cis*), 4.55 (br, 2H, HNCH_2, *trans*), 4.24 (br,

2H, HNCH_2, *cis*), 4.10 (br, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 1.77-1.71 (m, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O); ^{13}C NMR ($CDCl_3$, δ) 169.81, 163.44, 152.08, 150.76, 142.33, 110.30, 107.26, 89.07, 76.81, 65.48, 62.79, 41.32, 25.00.

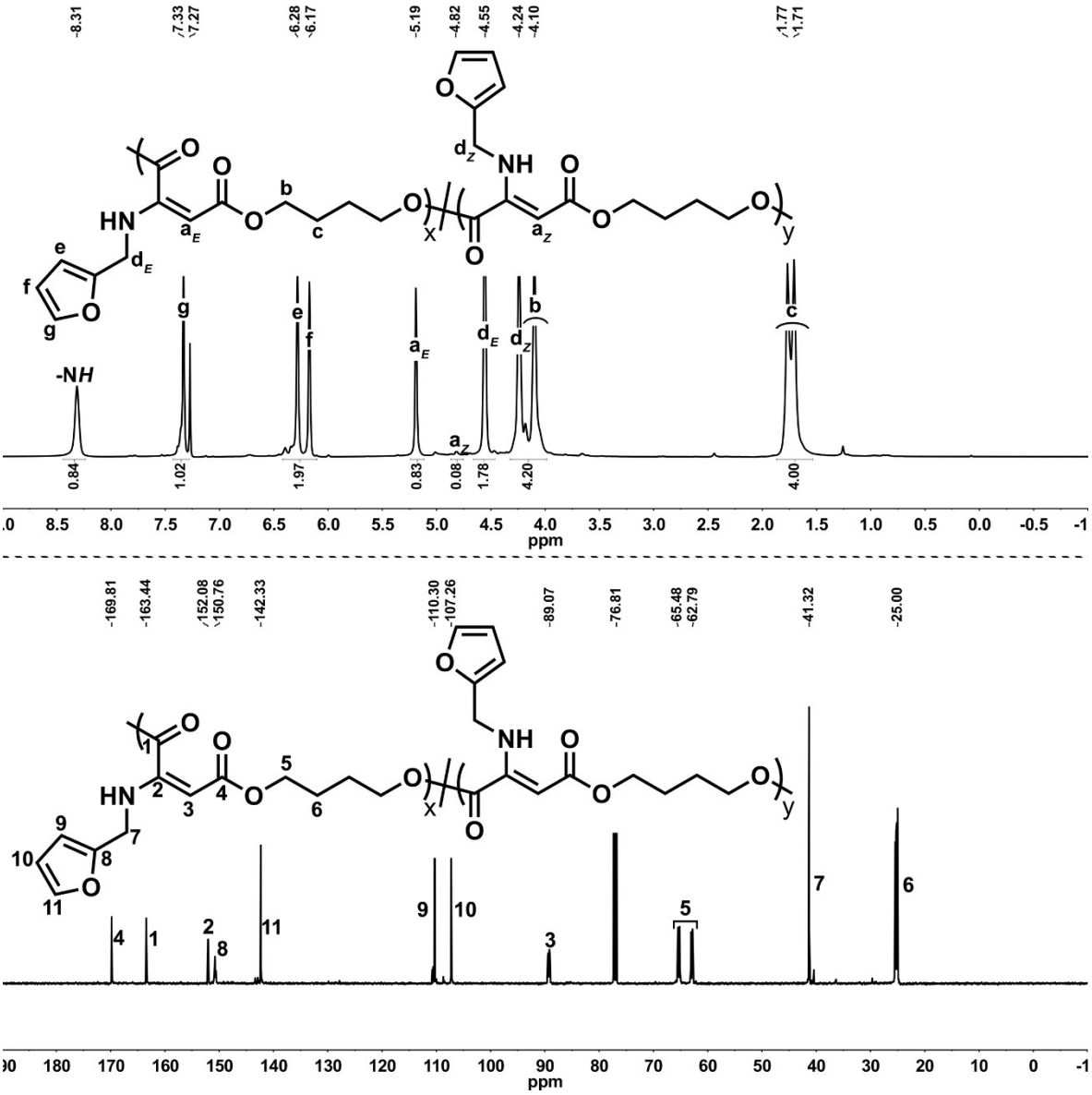


Figure S19. ^{1}H (up) and ^{13}C NMR (down) spectra of **P13** in $CDCl_3$ (500 and 125 MHz, respectively).

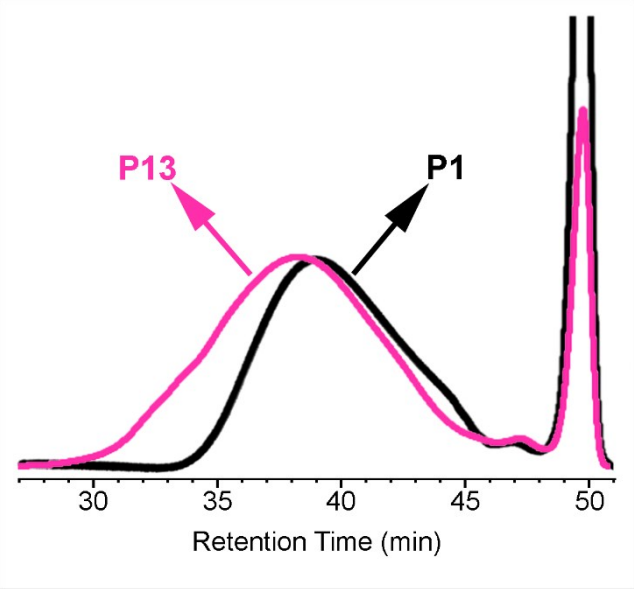
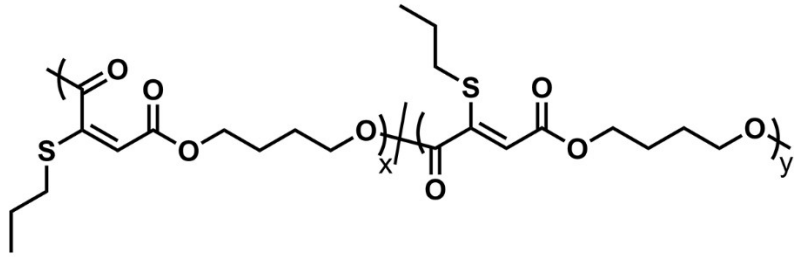


Figure S20. Overlaid GPC traces of **P1** and **P13** (at 30 °C in THF).

MONO THIOL-MICHAEL ADDITION REACTIONS

Thiol-Michael addition reaction between P1 and 1-propanethiol (P14)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, 1-propanethiol (66.3 µL, 0.720 mmol, 1.2 equiv per alkyne) and DABCO (6.7 mg, 0.060 mmol, 0.1 equiv) were added to the solution and the reaction mixture was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified sticky brown polymer was finally dried at 40 ^{o}C in a vacuum oven for 24 h (Yield = 0.12 g, 82 %, $M_{w,GPC}$ = 25000 g/mol, $Đ$ = 3.34, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 6.30 (bs, 1H, SC=C*H*C=O, *trans*), 5.69 (bs, 1H, SC=C*H*C=O, *cis*), 4.30-4.13 (m, 4H, C=OOC*H*$_2$CH$_2$CH$_2$C*H*$_2$OC=O), 2.82 (br, 2H, SC*H*$_2$CH$_2$CH$_3$), 1.85-1.61 (m, C=OOCH$_2$C*H*$_2$C*H*$_2$CH$_2$OC=O and SCH$_2$C*H*$_2$CH$_3$), 1.26-0.99 (m, 3H, SCH$_2$CH$_2$C*H*$_3$); ^{13}C NMR ($CDCl_3$, δ) 165.64, 165.17, 164.47, 163.59, 150.94, 149.61, 118.53, 112.22, 65.80, 64.17, 34.55, 25.23, 23.14, 21.49, 13.55.

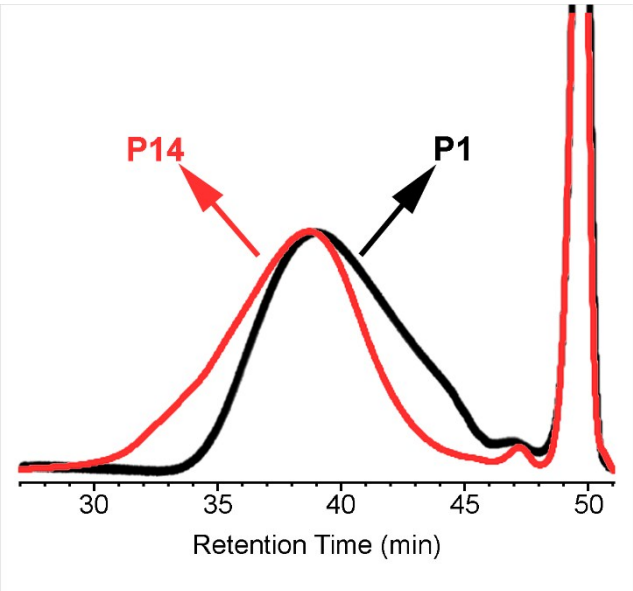
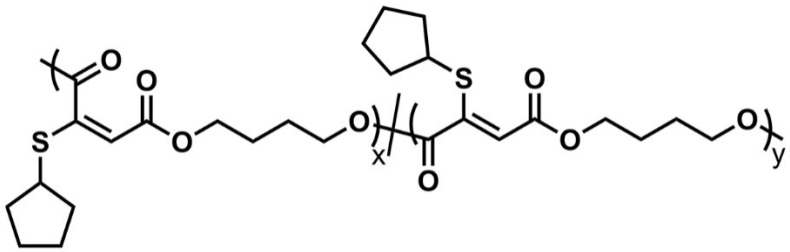


Figure S21. Overlaid GPC traces of **P1** and **P14** (at 30 °C in THF).

Thiol-Michael addition reaction between P1 and cyclopentanethiol (P15)



P1 (1 g, 6 mmol of alkyne, 1 equiv) was dissolved in 30 mL of $CHCl_3$ and transferred to a 50 mL round bottomed flask. Next, cyclopentanethiol (764 µL, 7.20 mmol, 1.2 equiv per alkyne) and DABCO (66.8 mg, 0.600 mmol, 0.1 equiv) were added to the solution and the reaction mixture was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 200 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified sticky brown polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 1.15 g, 71 %, $M_{w,GPC}$ = 23300 g/mol, $Đ$ = 3.05, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 6.30 (bs, 1H, SC=C*H*C=O, trans), 5.71 (bs, 1H, SC=C*H*C=O, *cis*), 4.30-4.13 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.71 (bs, 1H, SC*H*CH$_2$CH$_2$, *trans*), 3.50 (bs, 1H,

SC*H*CH_2CH_2, *cis*), 2.13-1.58 (m, C=OOCH_2C*H_2*C*H_2*CH_2OC=O, SCHC*H_2*CH_2 and SCHCH_2C*H_2*); ^{13}C NMR ($CDCl_3$, δ) 165.78, 165.22, 164.80, 163.64, 151.50, 149.88, 119.04, 112.47, 65.89, 64.15, 44.40, 34.08, 33.14, 29.32, 25.01.

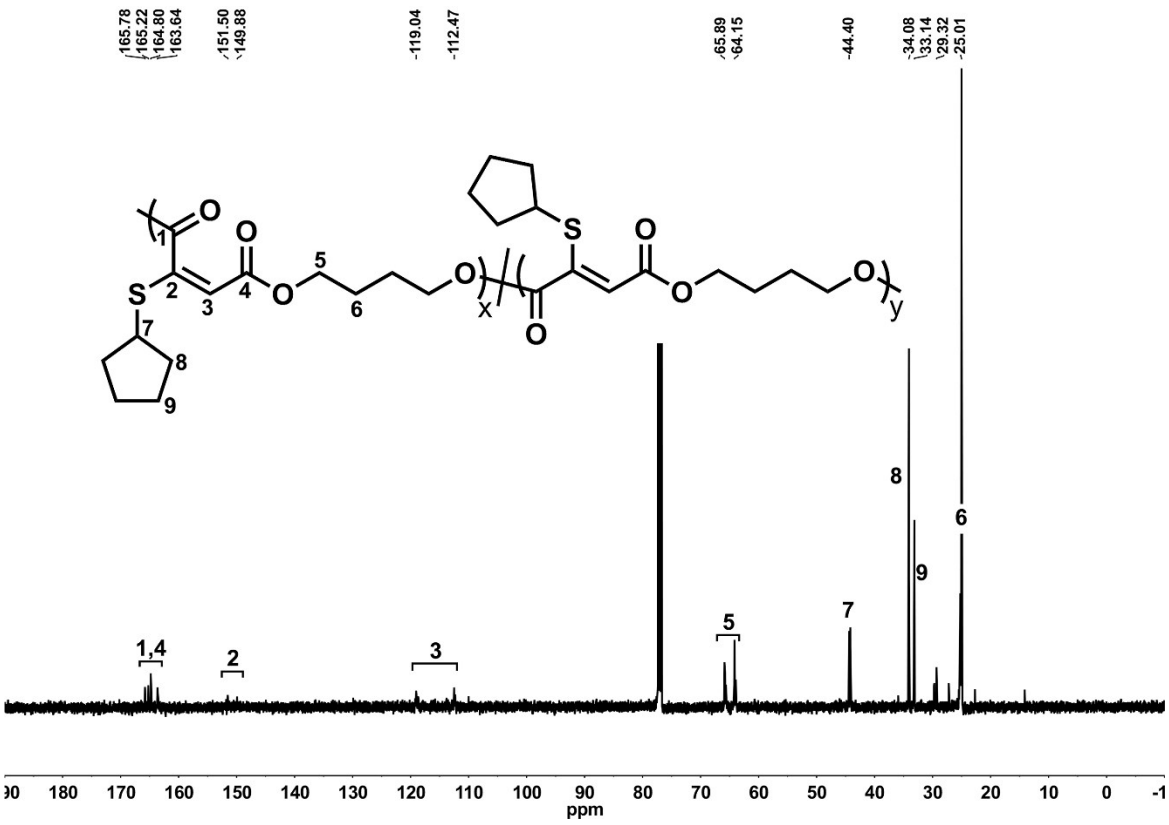
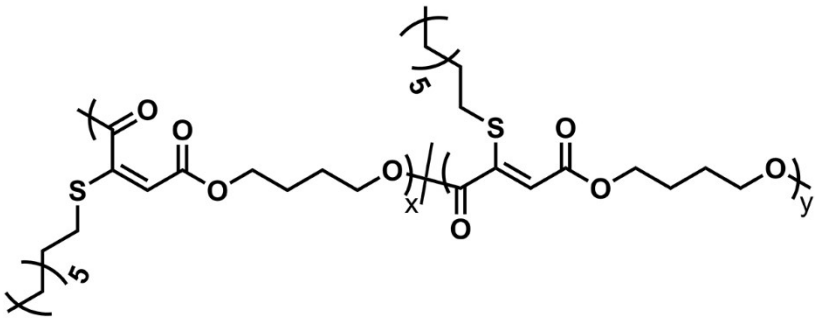


Figure S22. ^{13}C NMR spectrum of **P15** in $CDCl_3$ (125 MHz).

Thiol-Michael addition reaction between P1 and 1-octanethiol (P16)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, 1-octanethiol (124 µL, 0.720 mmol, 1.2 equiv per alkyne) and DABCO (6.7 mg, 0.060 mmol, 0.1 equiv) were added to the solution and the reaction mixture was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified viscous brown polymer was finally dried at 40 ^{o}C in a vacuum oven for 24 h (Yield = 0.11 g, 58 %, $M_{w,GPC}$ = 31900 g/mol, $Đ$ = 2.91, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 6.29 (bs, 1H, SC=C*H*C=O, *trans*), 5.68 (bs, 1H, SC=C*H*C=O, *cis*), 4.28-4.13 (m, 4H, C=OOC*H*$_2$CH$_2$CH$_2$C*H*$_2$OC=O), 2.83 (bs, 2H, SC*H*$_2$(CH$_2$)$_6$CH$_3$), 1.85-1.26 (m, C=OOCH$_2$C*H*$_2$C*H*$_2$CH$_2$OC=O and SCH$_2$(C*H*$_2$)$_6$CH$_3$), 2.83 (b, 3H, SCH$_2$(CH$_2$)$_6$C*H*$_3$), ^{13}C NMR ($CDCl_3$, δ); 165.66, 165.21, 164.47, 163.60, 151.08, 149.77, 118.58, 112.00, 65.78, 64.15, 32.65, 31.76, 29.68, 29.09, 28.72, 25.23, 22.63, 14.10.

Figure S23. ^{13}C NMR spectrum of **P16** in $CDCl_3$ (125 MHz).

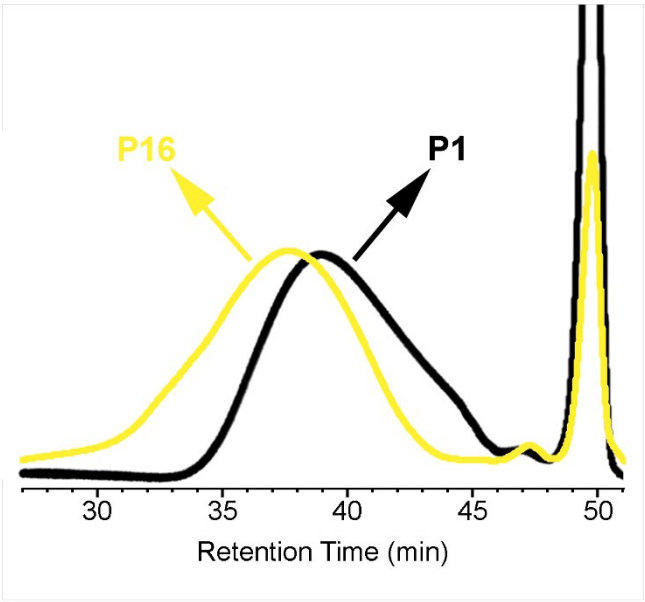
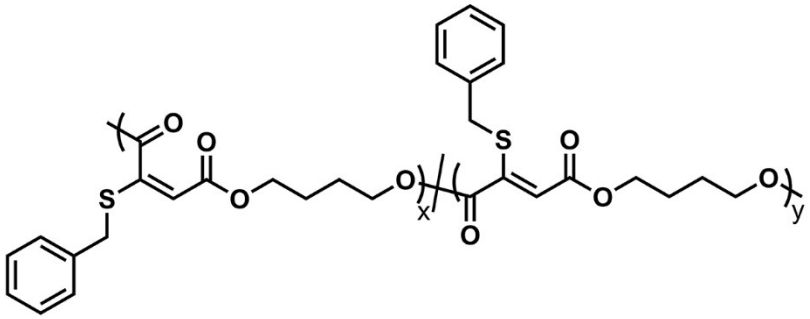


Figure S24. Overlaid GPC traces of **P1** and **P16** (at 30 °C in THF).

Thiol-Michael addition reaction between P1 and benzyl mercaptan (P17)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, benzyl mercaptan (83.9 µL, 0.720 mmol, 1.2 equiv per alkyne) and DABCO (6.7 mg, 0.060 mmol, 0.1 equiv) were added to the solution and the reaction mixture was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified sticky pale yellow polymer was finally dried at 40 ^{o}C in a vacuum oven for 24 h (Yield = 0.13 g, 74 %, $M_{w,GPC}$ = 22350 g/mol, $Đ$ = 3.13, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.34-7.23 (m, 5H, Ar*H*), 6.31 (bs, 1H, SC=C*H*C=O, *trans*), 5.76 (bs, 1H, SC=C*H*C=O, *cis*), 4.26-4.04 (m, C=OOCH_2CH$_2$CH$_2$CH_2OC=O and SCH_2), 1.68-1.62 (m, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O); ^{13}C NMR ($CDCl_3$, δ) 165.10, 164.03, 150.14, 148.41, 136.28, 129.14, 128.62, 128.07, 127.56, 119.81, 112.96, 65.82, 64.25, 36.84, 24.91.

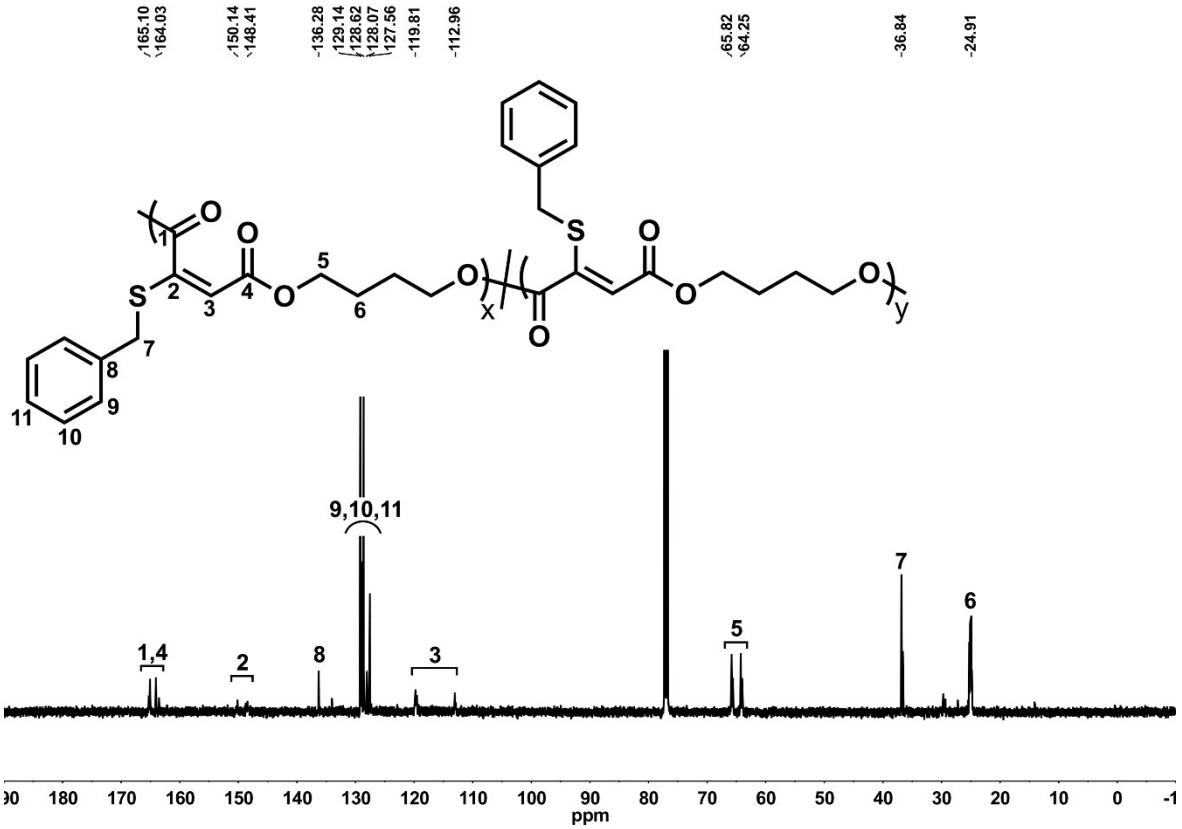


Figure S25. ^{13}C NMR spectrum of **P17** in $CDCl_3$ (125 MHz).

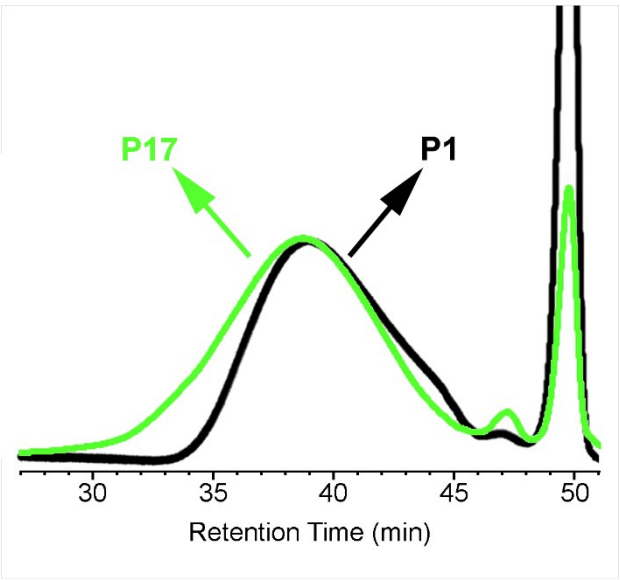
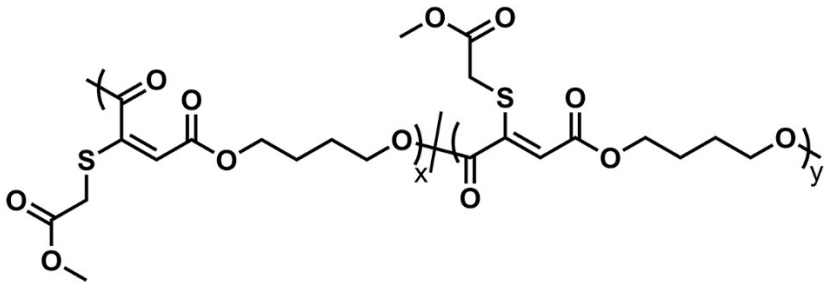


Figure S26. Overlaid GPC traces of **P1** and **P17** (at 30 °C in THF).

Thiol-Michael addition reaction between P1 and methyl thioglycolate (P18)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, methyl thioglycolate (63.9 µL, 0.720 mmol, 1.2 equiv per alkyne) and DABCO (6.7 mg, 0.060 mmol, 0.1 equiv) were added to the solution and the reaction mixture was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified viscous brown polymer was finally dried at 40 ^{o}C in a vacuum oven for 24 h (Yield = 0.14 g, 85 %, $M_{w,GPC}$ = 28900 g/mol, $Đ$ = 3.22, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 6.53 (bs, 1H, SC=C*H*C=O, *trans*), 5.91 (bs, 1H, SC=C*H*C=O, *cis*), 4.27-4.14 (m, 4H, C=OOC*H*$_2$CH$_2$CH$_2$C*H*$_2$OC=O), 3.76 (br, 2H, SC*H*$_2$), 3.70-3.63 (m, 3H, C=OOC*H*$_3$), 1.86-1.75 (br, 4H, C=OOCH$_2$C*H*$_2$C*H*$_2$CH$_2$OC=O); ^{13}C NMR ($CDCl_3$, δ) 169.60, 168.02, 165.06, 163.60, 146.35, 121.67, 115.22, 65.97, 64.41, 52.68, 33.40, 24.97.

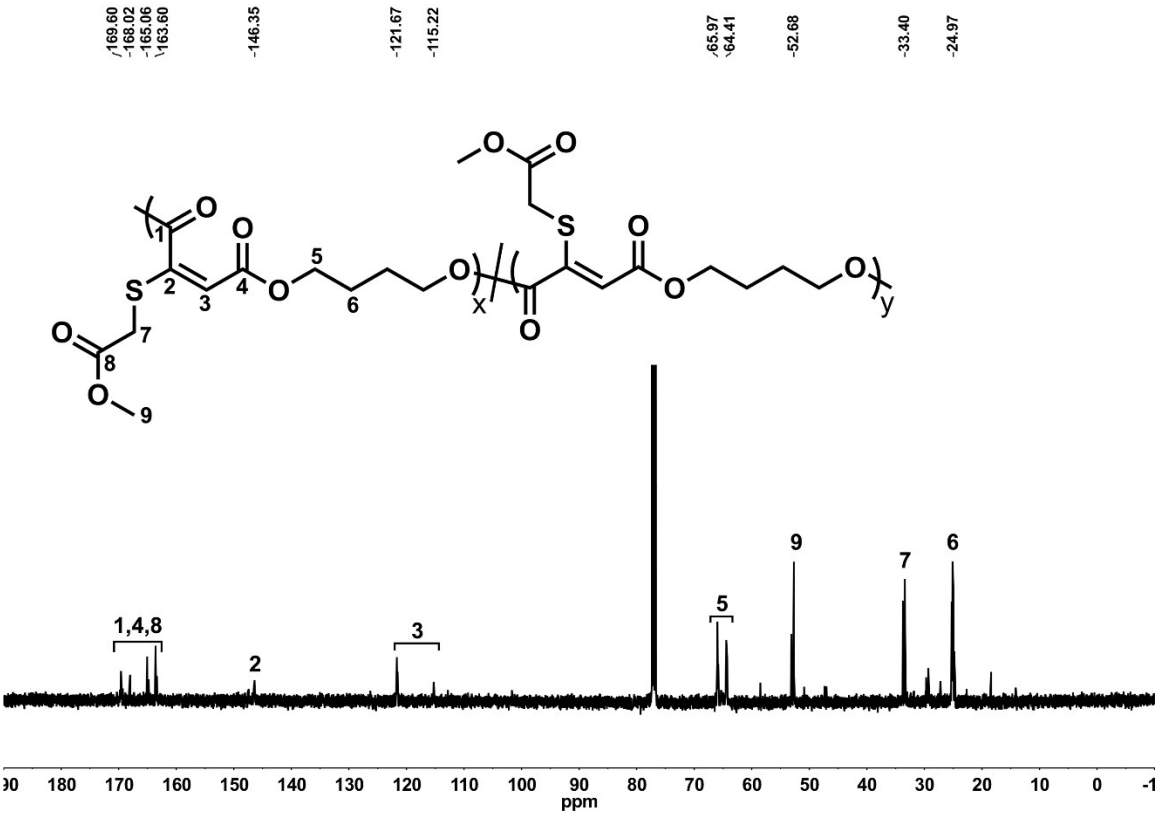


Figure S27. ^{13}C NMR spectrum of **P18** in $CDCl_3$ (125 MHz).

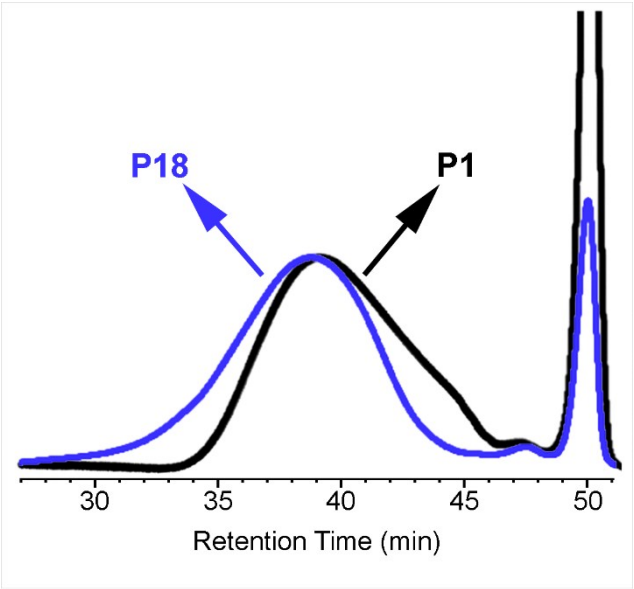
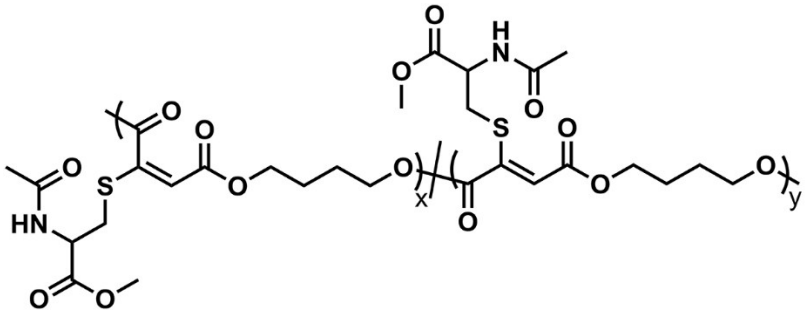


Figure S28. Overlaid GPC traces of **P1** and **P18** (at 30 °C in THF).

Thiol-Michael addition reaction between P1 and *N*-acetyl-L-cysteine methyl ester (P19)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) and *N*-acetyl-L-cysteine methyl ester (126.6 mg, 0.7200 mmol, 1.2 equiv per alkyne) were dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, DABCO (6.7 mg, 0.060 mmol, 0.1 equiv) was added to the solution and the reaction mixture was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH/diethyl ether (1:4) and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-MeOH/diethyl ether (1:4)) procedure was repeated two times. The purified viscous pale yellow polymer was finally dried at 40 ^oC in a vacuum oven for 24 h (Yield = 0.10 g, 48 %, $M_{w,GPC}$ = 14850 g/mol, $Đ$ = 2.82, relative to PS standards). ^1H NMR ($CDCl_3$, δ) 6.80 (br, 1H, N*H*), 6.59 (bs, 1H, SC=C*H*C=O, *trans*), 5.91 (bs, 1H, SC=C*H*C=O, *cis*), 4.85-4.79 (m, 1H, SCH_2CH), 4.31-4.14 (m, 4H, $C=OOCH_2CH_2CH_2CH_2OC=O$), 3.77-3.73 (m, 3H, $C=OOCH_3$), 3.33-3.22 (m, 2H, SCH_2CH), 2.02 (br, 3H, $C=OCH_3$), 1.80-1.25 (m, 4H, $C=OOCH_2CH_2CH_2CH_2OC=O$); ^{13}C NMR ($CDCl_3$, δ) 170.38, 164.85, 163.88, 148.02, 145.22, 124.51, 115.44, 76.79, 66.24, 64.38, 53.02, 52.85, 52.48, 51.70, 34.60, 33.58, 29.68, 25.16, 22.99.

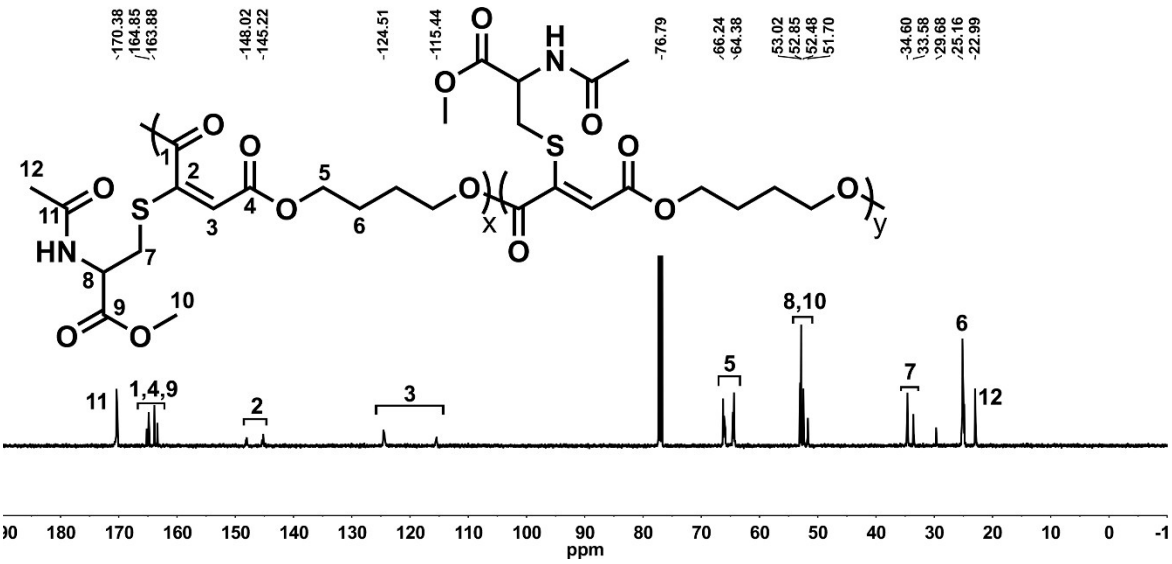


Figure S29. ^{13}C NMR spectrum of **P19** in $CDCl_3$ (125 MHz).

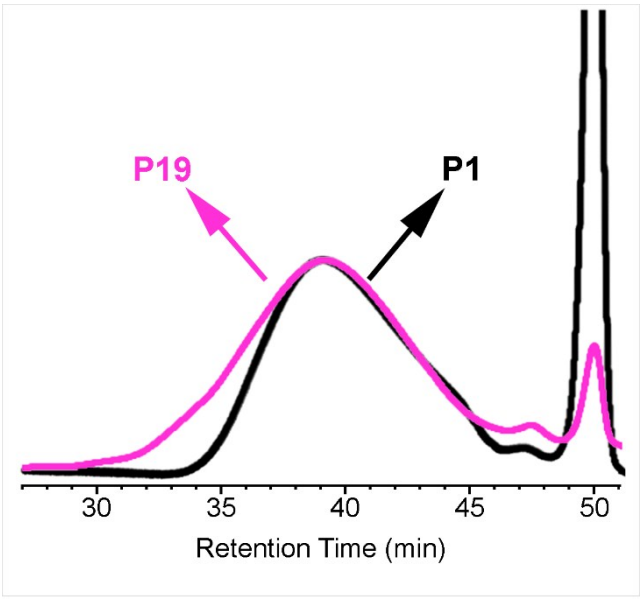
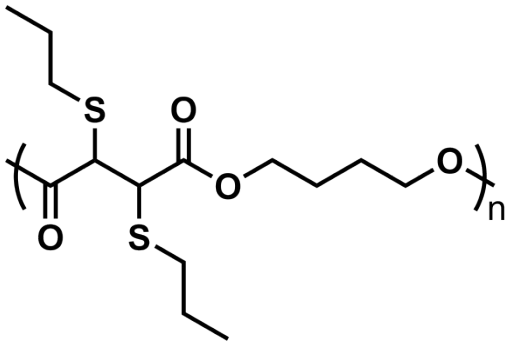


Figure S30. Overlaid GPC traces of **P1** and **P19** (at 30 °C in THF).

HOMO DOUBLE THIOL-MICHAEL ADDITION REACTIONS

Homo Double Thiol-Michael addition reaction between P1 and 1-propanethiol (P20)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, 1-propanethiol (138.2 µL, 1.500 mmol, 2.5 equiv per alkyne) and TBD (20.7 mg, 0.150 mmol, 0.25 equiv) were added to the solution and the reaction mixture was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified viscous brown polymer was finally dried at 40 ^{o}C in a vacuum oven for 24 h (Yield = 0.09 g, 47 %, $M_{w,GPC}$ = 26600 g/mol, $Đ$ = 1.76, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.23 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.56-3.52 (m, 2H, SCHC=O), 2.68-2.64 (m, 4H, SCH_2CH$_2$CH$_3$), 1.82 (br, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O), 1.60 (m, 4H, SCH$_2$CH_2CH$_3$), 1.02-0.97 (m, 6H, SCH$_2$CH$_2$CH_3); ^{13}C NMR ($CDCl_3$, δ) 170.19, 64.69, 47.73, 34.43, 25.14, 22.67, 13.34.

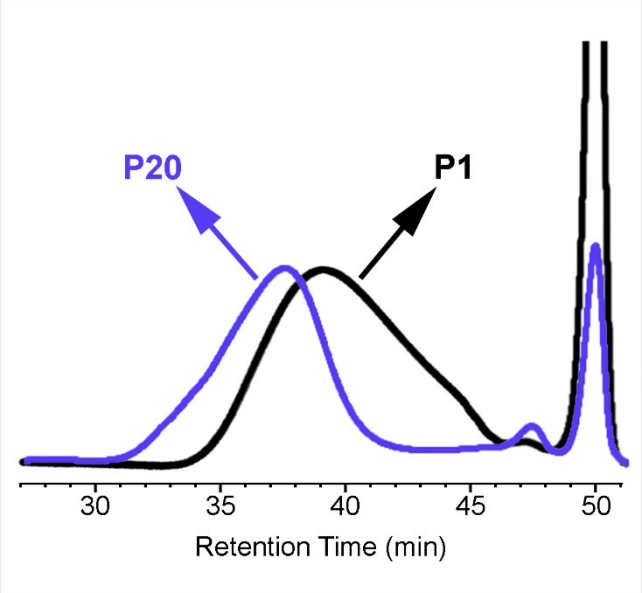
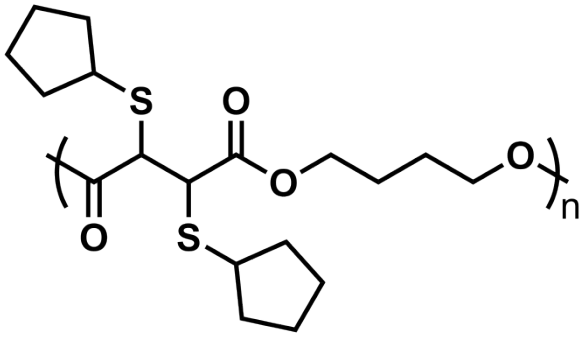


Figure S31. Overlaid GPC traces of **P1** and **P20** (at 30 °C in THF).

Homo double Thiol-Michael addition reaction between P1 and cyclopentanethiol (P21)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, cyclopentanethiol (159.2 µL, 1.500 mmol, 2.5 equiv per alkyne) and TBD (20.7 mg, 0.150 mmol, 0.25 equiv) were added to the solution and the reaction mixture was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified viscous brown polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.15 g, 67 %, $M_{w,GPC}$ = 24600 g/mol, $Đ$ = 2.66, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.21 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.61-3.54 (m, 2H, SC*H*C=O), 3.30 (br, 2H,

SC*H*CH_2CH_2), 2.04-1.26 (m, C=O$OCH_2CH_2CH_2CH_2$OC=O, SCHCH_2CH_2 and SCHCH_2CH_2); ^{13}C NMR ($CDCl_3$, δ) 171.87, 170.72, 77.02, 64.65, 48.50, 45.59, 34.34, 33.38, 24.72.

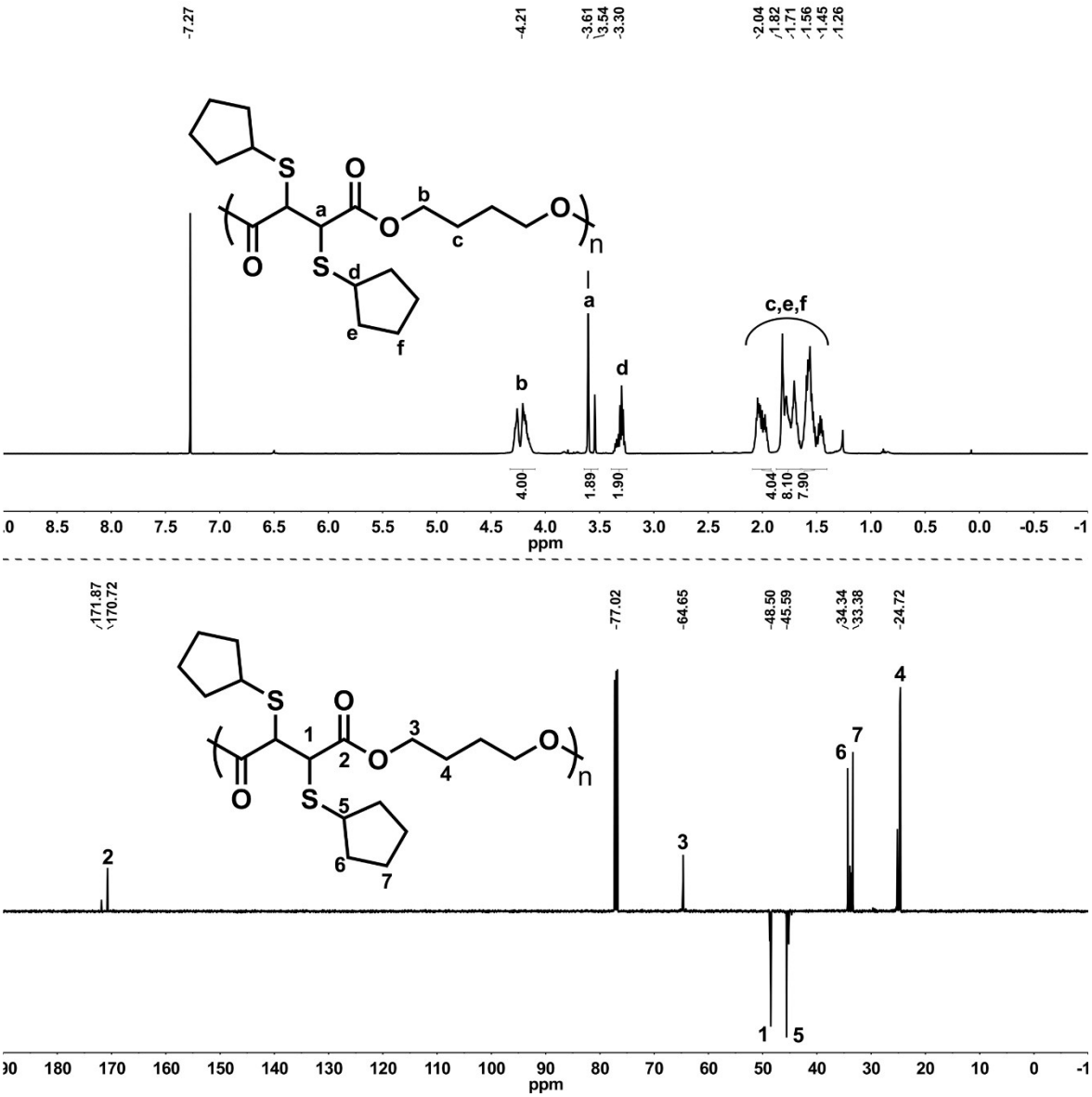


Figure S32. ^{1}H (up) and ^{13}C APT (down) spectra of **P21** in $CDCl_3$ (500 and 125 MHz, respectively).

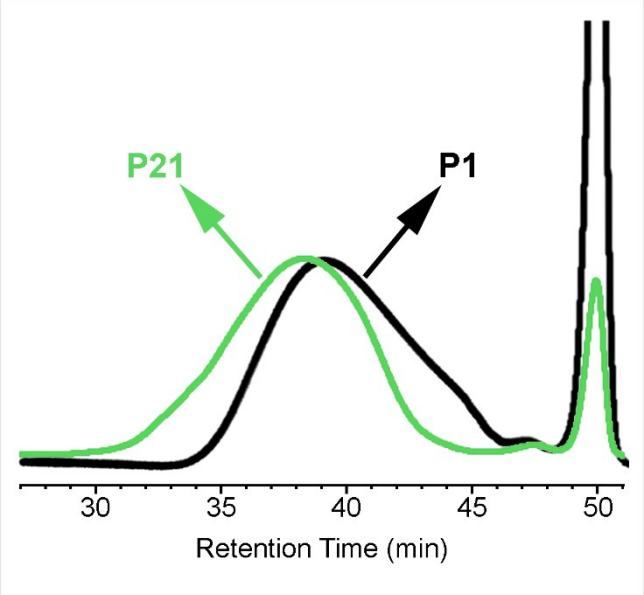
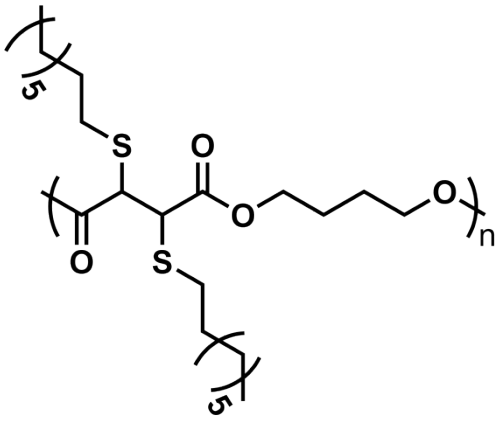


Figure S33. Overlaid GPC traces of **P1** and **P21** (at 30 °C in THF).

Homo double Thiol-Michael addition reaction between P1 and 1-octanethiol (P22)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, 1-octanethiol (258.2 µL, 1.500 mmol, 2.5 equiv per alkyne) and TBD (20.7 mg, 0.150 mmol, 0.25 equiv) were added to the solution and the reaction mixture was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified viscous brown polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.18 g, 65 %, $M_{w,GPC}$ = 27000 g/mol, $Đ$ = 2.20, relative to PS standards). ^{1}H NMR ($CDCl_3$,

δ) 4.21(br, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.56 (m, 2H, SC*H*C=O), 2.65 (m, 4H, SCH_2CH$_2$(CH$_2$)$_5$CH$_3$), 1.81(br, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O), 1.56 (m, 4H, SCH$_2$CH_2(CH$_2$)$_5$CH$_3$), 1.27 (m, 20H, SCH$_2$CH$_2$(CH_2)$_5$CH$_3$), 0.89 (m, 6H, SCH$_2$CH$_2$(CH$_2$)$_5$CH_3); ^{13}C NMR (CDCl$_3$, *δ*) 171.40, 170.13, 77.27, 76.76, 64.62, 47.74, 32.37, 31.80, 29.18, 25.13, 22.65, 14.11

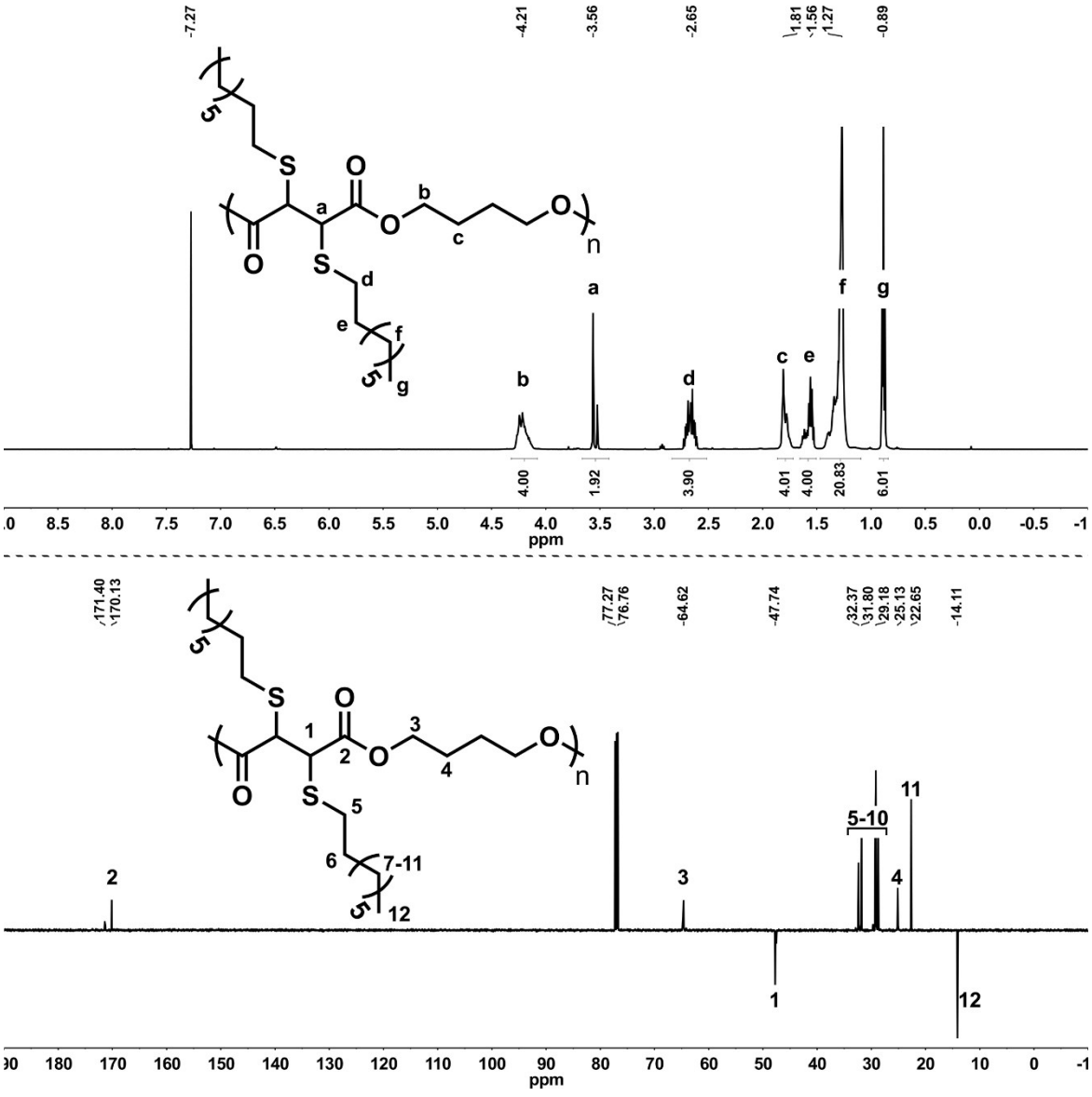


Figure S34. ^{1}H (up) and ^{13}C APT (down) spectra of **P22** in CDCl$_3$ (500 and 125 MHz, respectively).

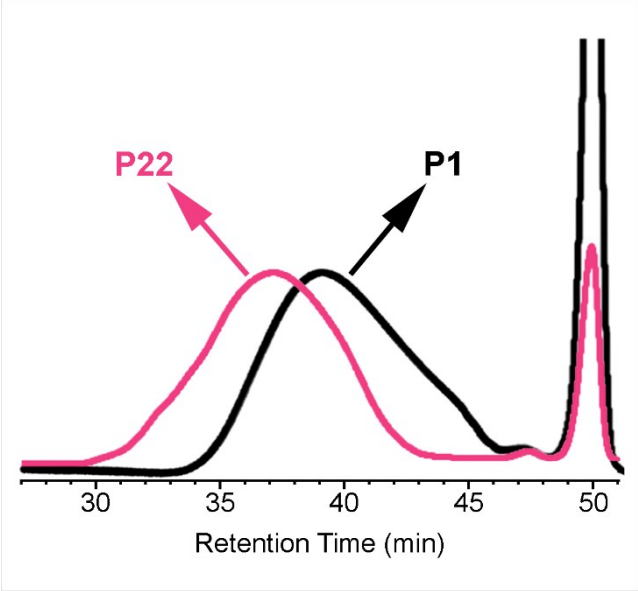
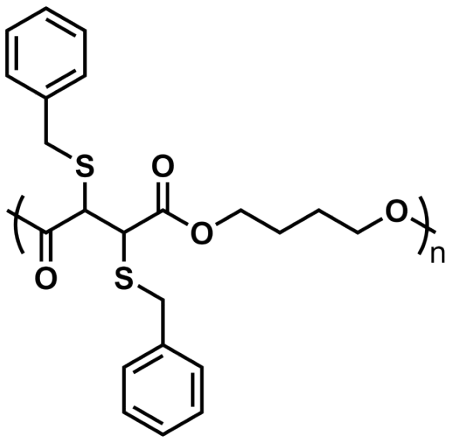


Figure S35. Overlaid GPC traces of **P1** and **P22** (at 30 °C in THF).

Homo double Thiol-Michael addition reaction between P1 and benzyl mercaptan (P23)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, benzyl mercaptan (174.7 µL, 1.500 mmol, 2.5 equiv per alkyne) and TBD (20.7 mg, 0.150 mmol, 0.25 equiv) were added to the solution and the reaction mixture was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified sticky brown polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.18 g, 72 %, $M_{w,GPC}$ = 23000 g/mol, $Đ$ = 2.59, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ)

7.29 (m, 10H, Ar*H*), 4.07 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.86-2.52 (m, SC*H*C=O and SCH_2), 1.63 (br, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O); ^{13}C NMR ($CDCl_3$, δ) 170.98, 169.81, 136.80, 128.56, 127.43, 76.77, 67.98, 64.71, 47.34, 46.41, 36.75, 35.64, 25.04.

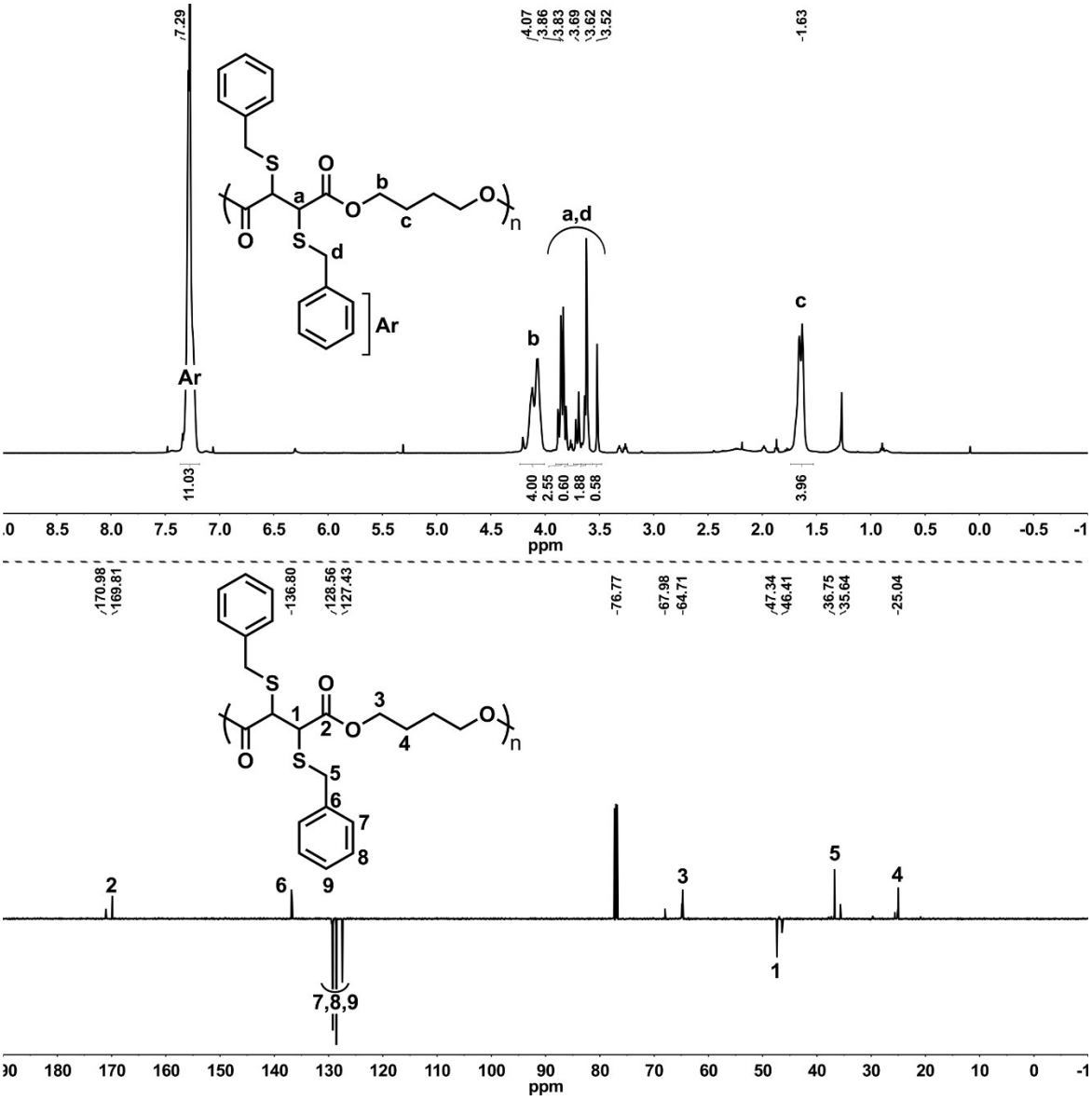


Figure S36. ^{1}H (up) and ^{13}C APT (down) spectra of **P23** in $CDCl_3$ (500 and 125 MHz, respectively).

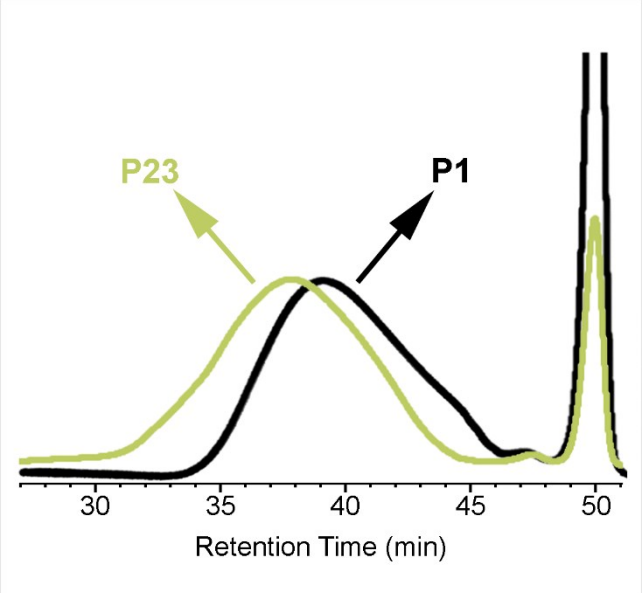
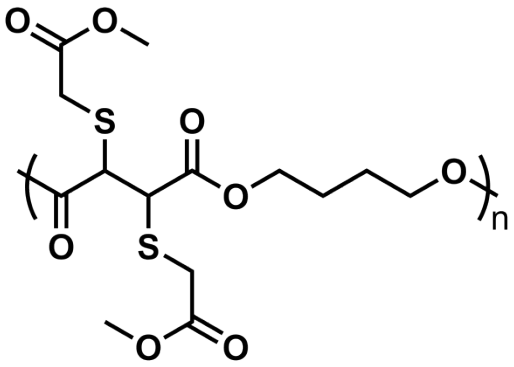


Figure S37. Overlaid GPC traces of **P1** and **P23** (at 30 °C in THF).

Homo double Thiol-Michael addition reaction between P1 and methyl thioglycolate (P24)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, methyl thioglycolate (133.1 µL, 1.500 mmol, 2.5 equiv per alkyne) and TBD (20.7 mg, 0.150 mmol, 0.25 equiv) were added to the solution and the reaction mixture was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified viscous pale yellow polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.16 g, 70 %, $M_{w,GPC}$ = 31600 g/mol, $Đ$ = 3.85, relative to PS standards). ^{1}H NMR

($CDCl_3$, δ) 4.24-4.18 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.82-3.42 (m, 4H, SCH_2), 3.75 (m, 6H, C=OOCH_3), 3.54 (bs, 2H, SCHC=O), 1.81 (br, 4H, C=OOCH$_2$CH_2CH_2CH$_2$OC=O); ^{13}C NMR ($CDCl_3$, δ) 169.29, 77.27, 65.15, 52.65, 47.32, 33.54, 24.99.

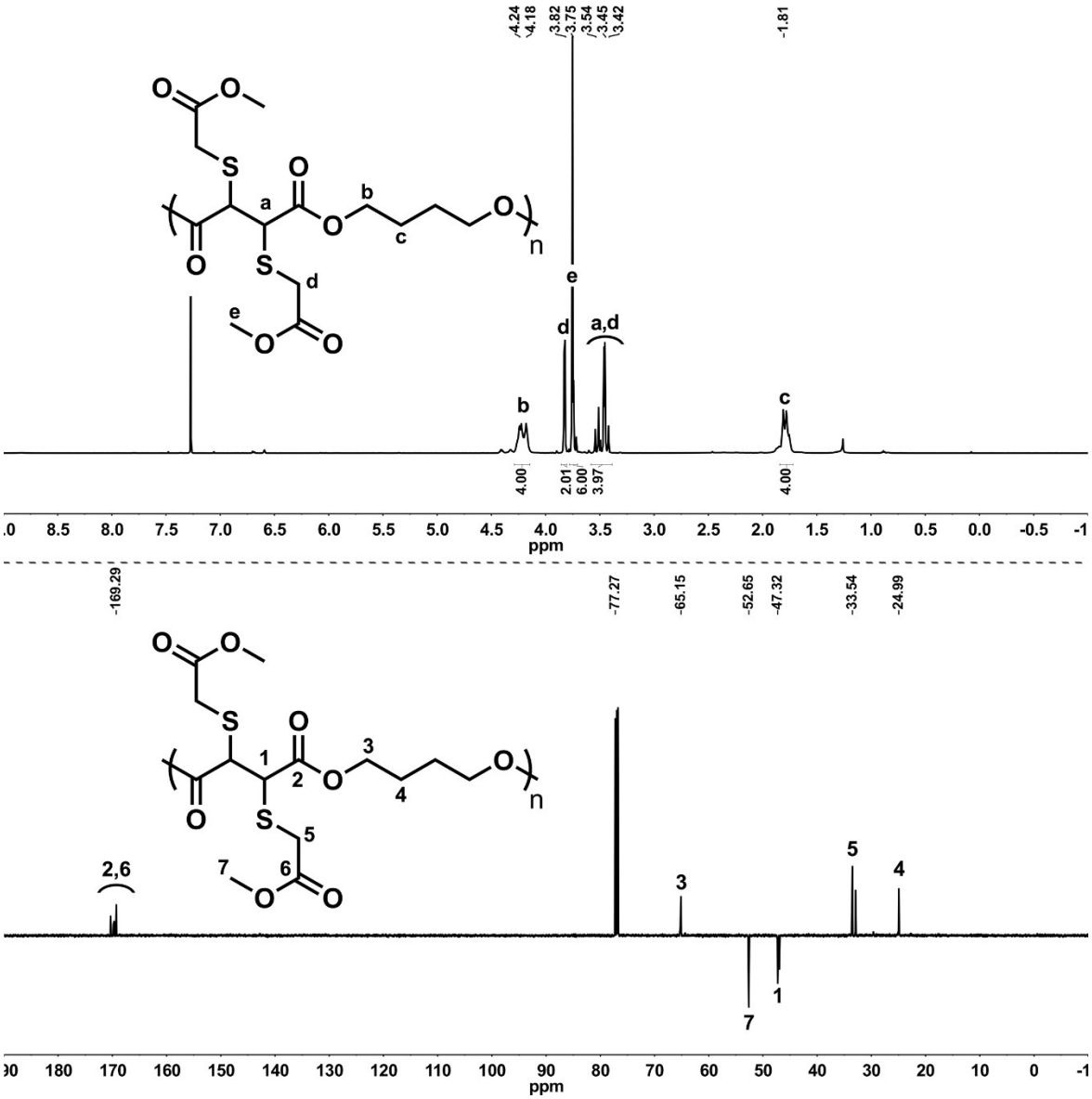


Figure S38. ^{1}H (up) and ^{13}C APT (down) spectra of **P24** in $CDCl_3$ (500 and 125 MHz, respectively).

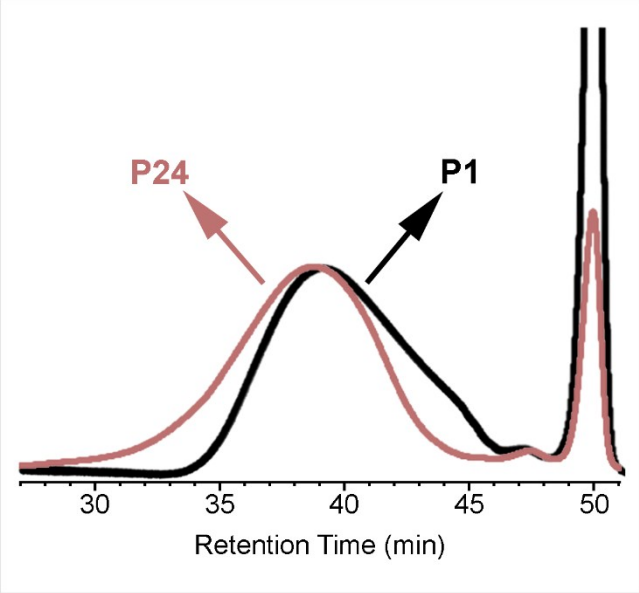
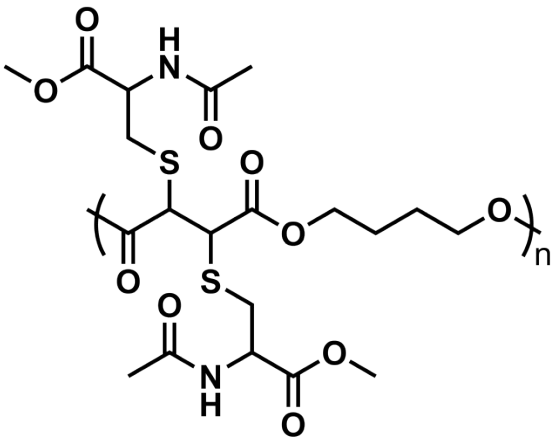


Figure S39. Overlaid GPC traces of **P1** and **P24** (at 30 °C in THF).

Homo double Thiol-Michael addition reaction between P1 and *N*-acetyl-L-cysteine methyl ester (P25)



P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) and *N*-acetyl-L-cysteine methyl ester (263.7 mg, 0.7200 mmol, 2.5 equiv per alkyne) were dissolved in 4 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, TBD (20.7 mg, 0.150 mmol, 0.25 equiv) was added to the solution and the reaction mixture was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified viscous brown polymer was finally dried at 40 °C in a vacuum oven for

24 h (Yield = 0.13 g, 42 %, $M_{w,GPC}$ = 9970 g/mol, $Đ$ = 1.32, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.85 (br, 2H, SCH_2CH), 4.25 (br, 4H, $C{=}OOCH_2CH_2CH_2CH_2OC{=}O$), 3.79-3.76 (br, 6H, $C{=}OOCH_3$), 3.63-3.55 (m, 2H, $SCHC{=}O$), 3.21-3.15 (m, 4H, SCH_2CH), 2.08 (br, 6H, $C{=}OCH_3$), 1.81-1.77 (br, 4H, $C{=}OOCH_2CH_2CH_2CH_2OC{=}O$); ^{13}C NMR ($CDCl_3$, δ) 170.73, 77.28, 65.24, 52.80, 48.17, 34.60, 25.00, 22.93.

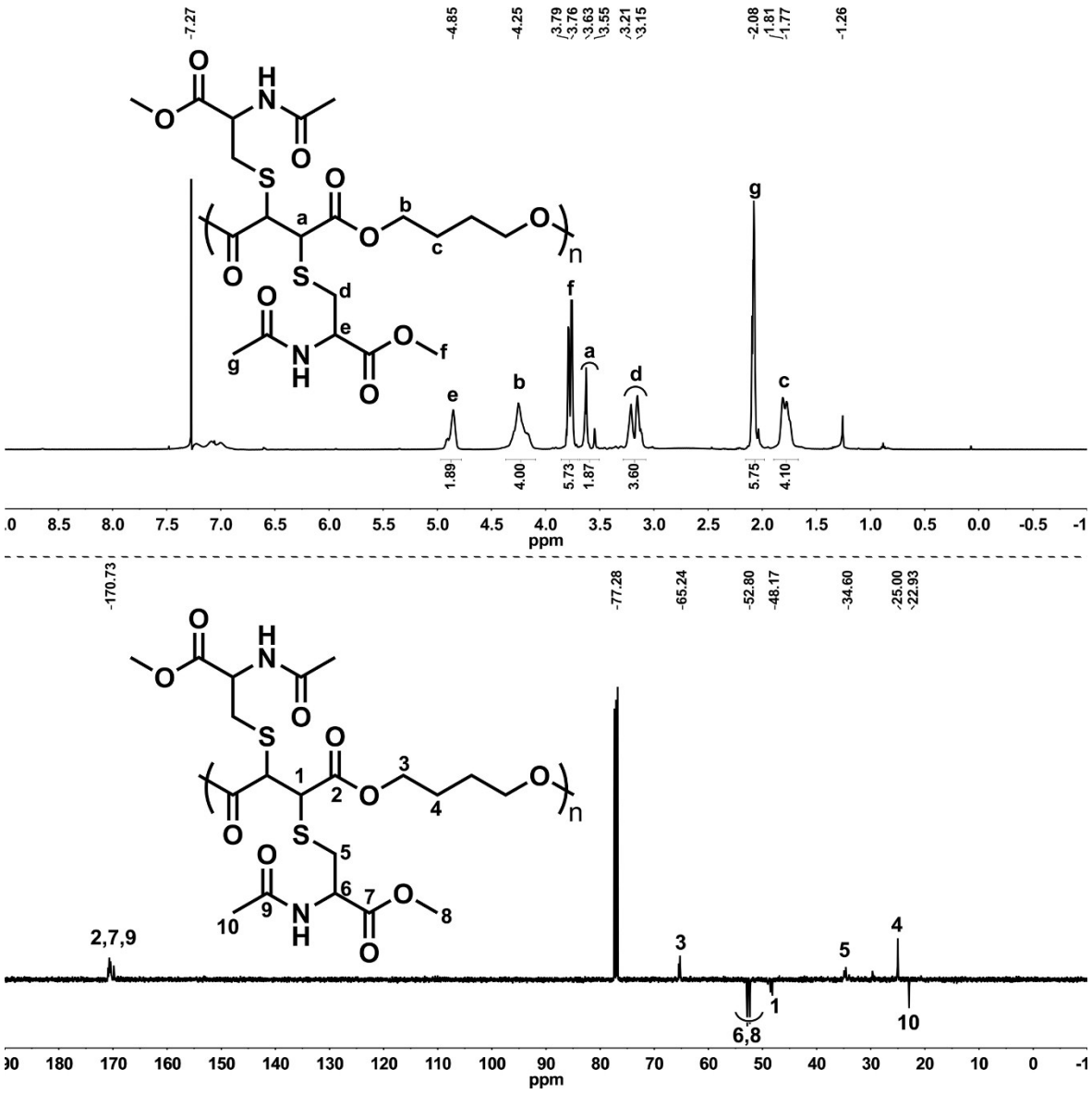


Figure S40. ^{1}H (up) and ^{13}C APT (down) spectra of **P25** in $CDCl_3$ (500 and 125 MHz, respectively).

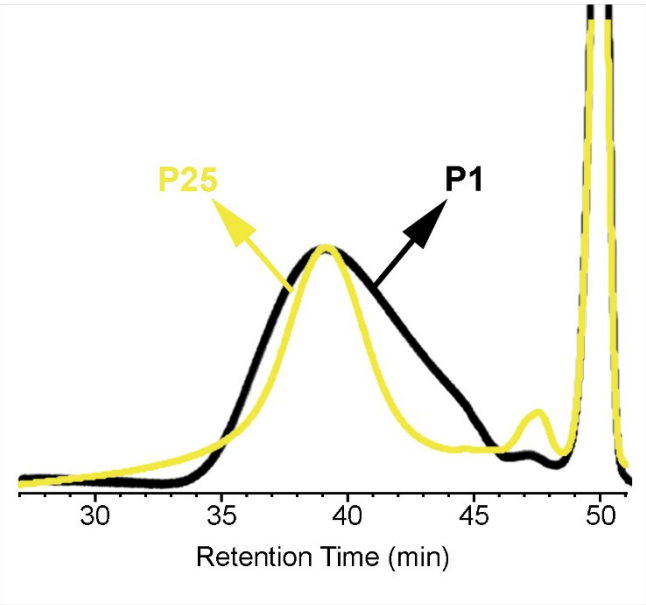
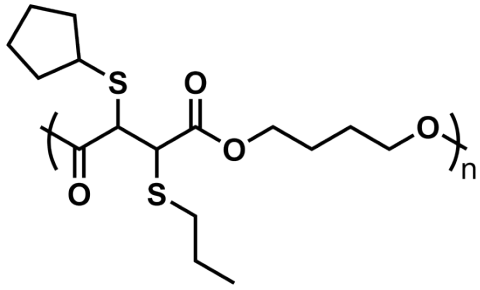


Figure S41. Overlaid GPC traces of **P1** and **P25** (at 30 °C in THF).

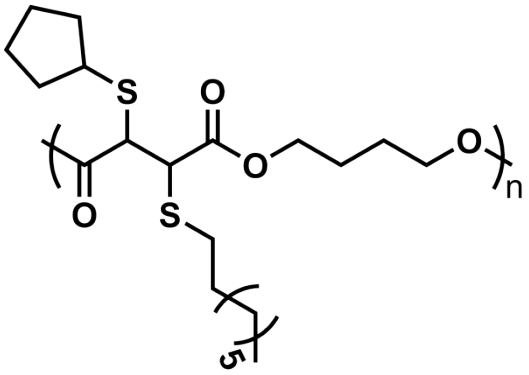
MIXED DOUBLE THIOL-MICHAEL ADDITION REACTIONS

Thiol-Michael addition reaction between P15 and 1-propanethiol (P26)



P15 (0.1 g, 0.4 mmol of alkene, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, 1-Propanethiol (41.3 μL, 0.480 mmol, 1.2 equiv per alkene) and TBD (12.9 mg, 0.100 mmol, 0.25 equiv) were added to the solution and the reaction mixture was at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified sticky brown polymer was finally dried at 40 ^{o}C in a vacuum oven for 24 h (Yield = 0.10 g, 78 %, $M_{w,GPC}$ = 26100 g/mol, $Đ$ = 2.06, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.25-4.20 (m, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.64-3.50 (m, CHSCHC=O and CH$_2$SCHC=O), 3.30 (br, 1H, SCHCH$_2$CH$_2$), 2.68-2.64 (br, 2H, SCH_2CH$_2$CH$_3$), 2.03-1.45 (m, C=OOCH$_2$CH_2CH_2CH$_2$OC=O, SCHCH_2CH$_2$, SCHCH$_2$CH_2 and SCH$_2$CH_2CH$_3$), 1.01-0.97 (m, 3H, SCH$_2$CH$_2$CH_3); ^{13}C NMR ($CDCl_3$, δ) 170.63, 76.76, 64.68, 48.28, 45.64, 34.36, 33.35, 24.60, 22.66, 13.36.

Thiol-Michael addition reaction between P15 and 1-octanethiol (P27)



P15 (0.1 g, 0.4 mmol of alkene, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, 1-Octanethiol (77.1 μL, 0.480 mmol, 1.2 equiv per alkene) and TBD (12.9 mg, 0.100 mmol, 0.25 equiv) were added to the solution and the reaction mixture was at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified sticky brown polymer was finally dried at 40 ^oC in a vacuum oven for 24 h (Yield = 0.11 g, 71 %, $M_{w,GPC}$ = 26500 g/mol, $Đ$ = 1.88, relative to PS standards). ^1H NMR ($CDCl_3$, δ) 4.23-4.18 (br, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.61-3.56 (m, CHSC*H*C=O and CH$_2$SC*H*C=O), 3.30 (br, 1H, SC*H*CH$_2$CH$_2$), 2.69-2.65 (br, 2H, SCH_2(CH$_2$)$_6$CH$_3$), 2.04-1.56 (m, C=OOCH$_2$CH_2CH_2CH$_2$OC=O, SCHCH_2CH$_2$ and SCHCH$_2$CH_2), 1.27 (br, 12H, SCH$_2$(CH_2)$_6$CH$_3$), 0.88 (br, 3H, SCH$_2$(CH$_2$)$_6$CH_3); ^{13}C NMR ($CDCl_3$, δ) 171.77, 170.59, 64.62, 47.97, 45.63, 34.36, 33.34, 31.78, 29.10, 24.59, 22.63, 14.10.

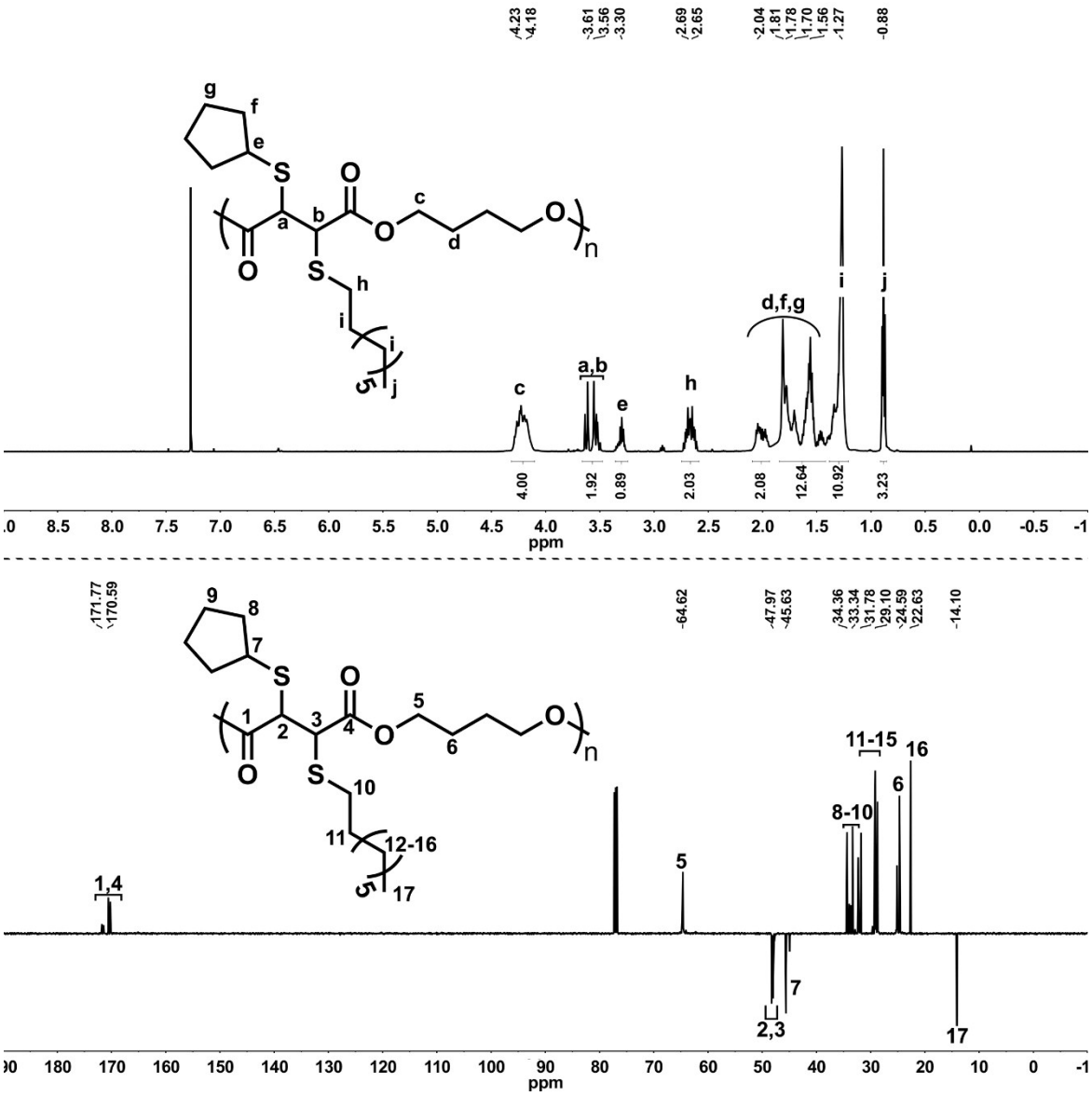


Figure S42. ^{1}H (up) and ^{13}C APT (down) spectra of **P27** in $CDCl_3$ (500 and 125 MHz, respectively).

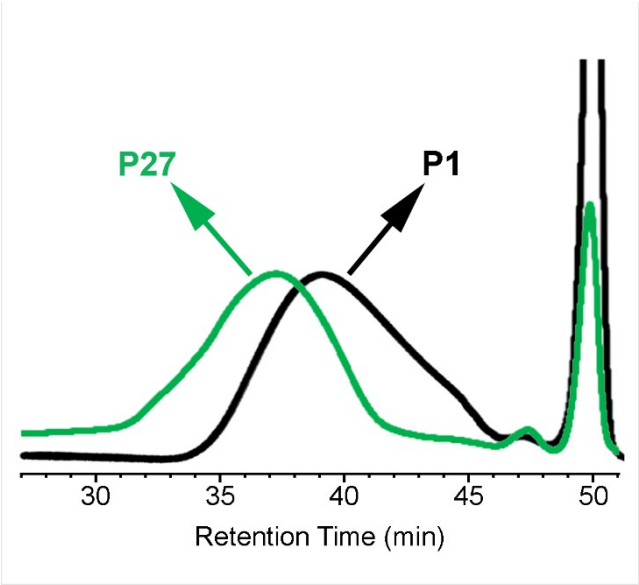
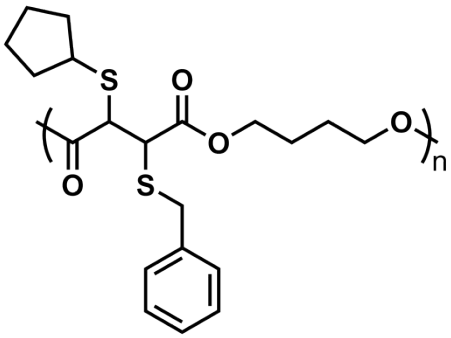


Figure S43. Overlaid GPC traces of **P1** and **P27** (at 30 °C in THF).

Thiol-Michael addition reaction between P15 and benzyl mercaptan (P28)



P15 (0.1 g, 0.4 mmol of alkene, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, benzyl mercaptan (52.2 µL, 0.480 mmol, 1.2 equiv per alkene) and TBD (12.9 mg, 0.100 mmol, 0.25 equiv) were added to the solution and the reaction mixture was at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified sticky brown polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.10 g, 68 %, $M_{w,GPC}$ = 23500 g/mol, $Đ$ = 2.45, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 7.32-7.30 (m, 5H, Ar*H*), 4.19-4.12 (br, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.89-3.86 (m,

2H, SC*H*$_2$Ph), 3.64-3.50 (m, CHSC*H*C=O and CH$_2$SC*H*C=O), 3.27-3.08 (m, 1H, SC*H*CH$_2$CH$_2$), 1.98-1.26 (m, C=OOCH$_2$C*H*$_2$C*H*$_2$CH$_2$OC=O, SCHC*H*$_2$CH$_2$ and SCHCH$_2$C*H*$_2$); ^{13}C NMR ($CDCl_3$, δ) 171.63, 169.95, 136.90, 129.19, 128.54, 127.40, 77.30, 64.68, 48.21, 45.69, 36.62, 34.32, 33.31, 24.59.

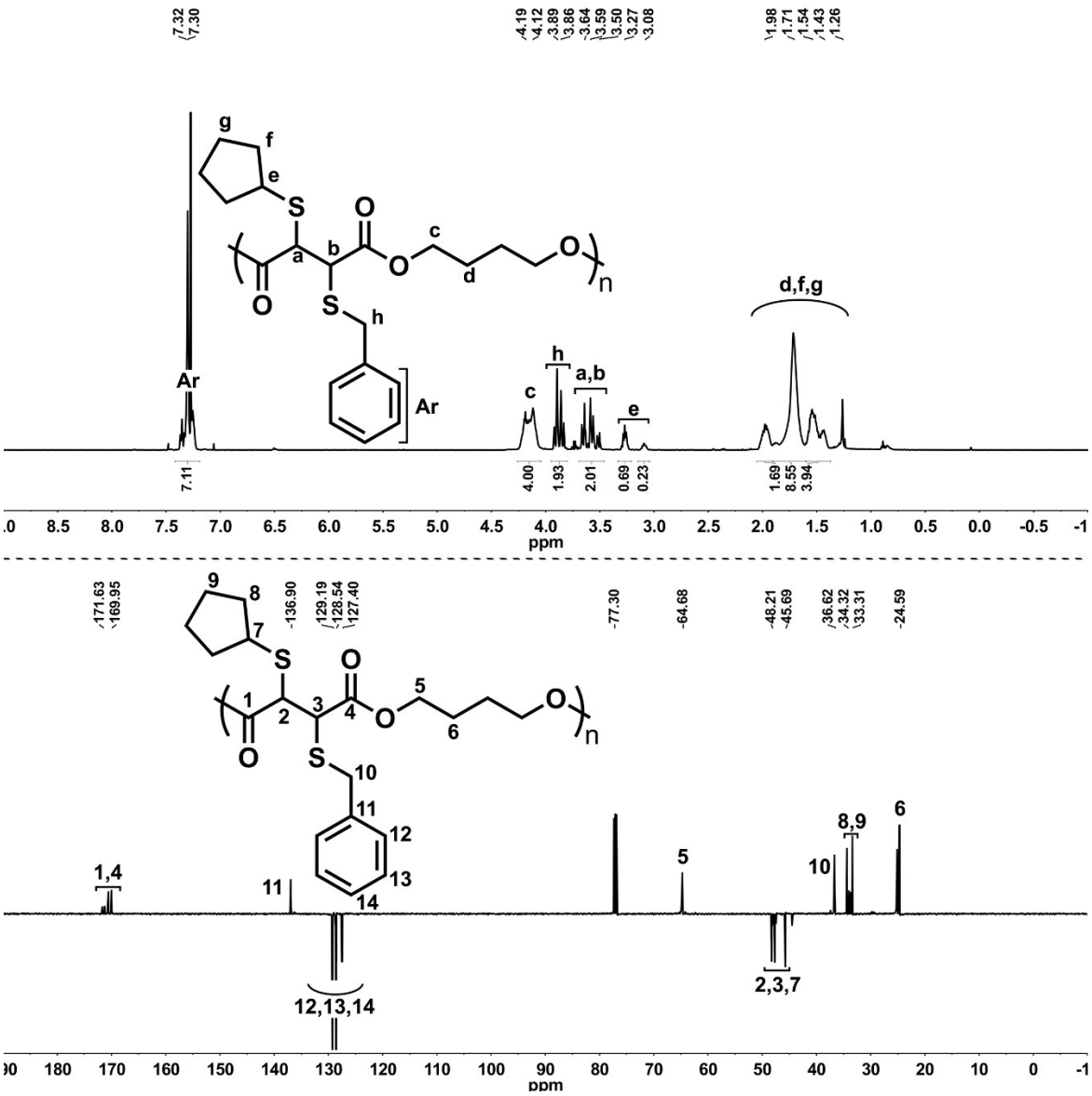


Figure S44. ^{1}H (up) and ^{13}C APT (down) spectra of **P28** in $CDCl_3$ (500 and 125 MHz, respectively).

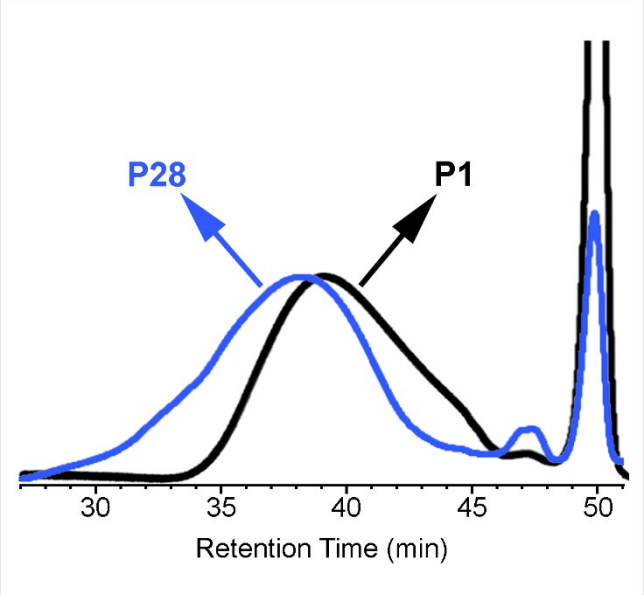
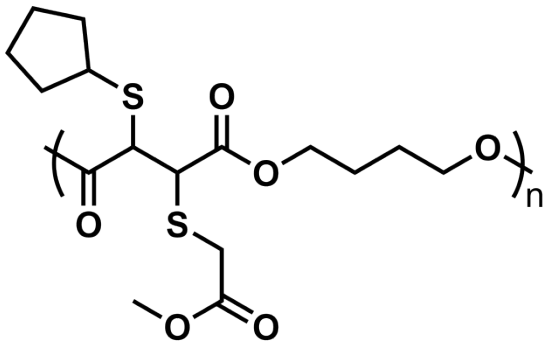


Figure S45. Overlaid GPC traces of **P1** and **P28** (at 30 °C in THF).

Thiol-Michael addition reaction between P15 and methyl thioglycolate (P29)



P15 (0.1 g, 0.4 mmol of alkene, 1 equiv) was dissolved in 3 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, methyl thioglycolate (39.8 µL, 0.480 mmol, 1.2 equiv per alkene) and TBD (12.9 mg, 0.100 mmol, 0.25 equiv) were added to the solution and the reaction mixture was at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH and the solvent was removed by decantation. The residual polymer was dissolved in $CHCl_3$ and consequently precipitated in MeOH. The purified sticky brown polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.12 g, 86 %, $M_{w,GPC}$ = 30850 g/mol, $Đ$ = 2.54, relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.21-4.15 (br, 4H, C=OOCH_2CH$_2$CH$_2$CH_2OC=O), 3.73-3.60 (m, CHSC*H*C=O,

$CH_2SCHC{=}O$ and $C{=}OOCH_3$), 3.45-3.43 (br, 2H, $SCH_2C{=}O$), 3.28 (br, 1H, $SCHCH_2CH_2$), 2.03-1.43 (m, $C{=}OOCH_2CH_2CH_2CH_2OC{=}O$, $SCHCH_2CH_2$ and $SCHCH_2CH_2$); ^{13}C NMR ($CDCl_3$, δ) 171.35, 170.69, 169.50, 76.81, 64.92, 52.58, 48.04, 45.65, 44.75, 44.17, 34.26, 33.95, 33.63, 33.31, 25.03, 24.57.

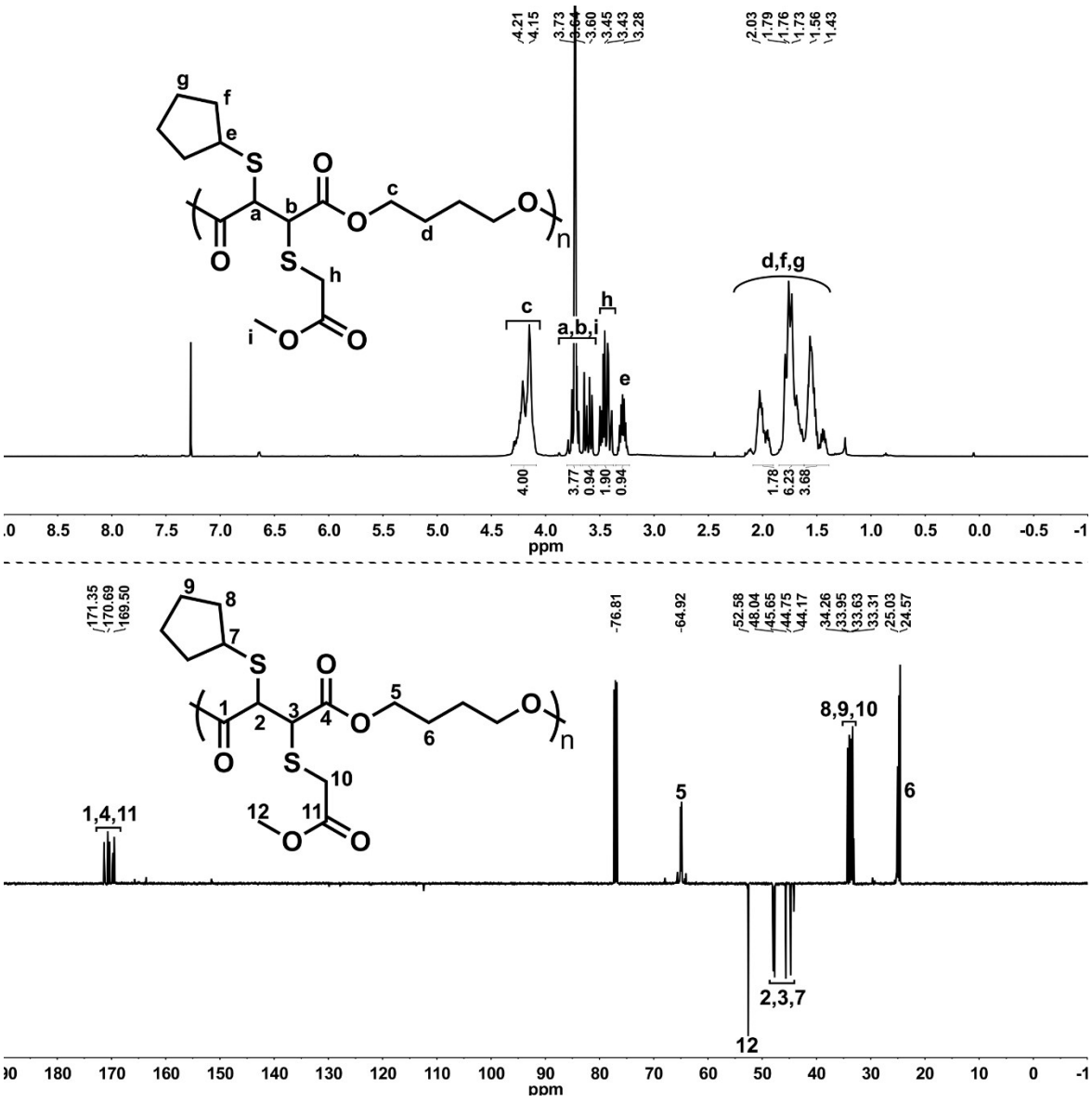


Figure S46. ^1H (up) and ^{13}C APT (down) spectra of **P29** in $CDCl_3$ (500 and 125 MHz, respectively).

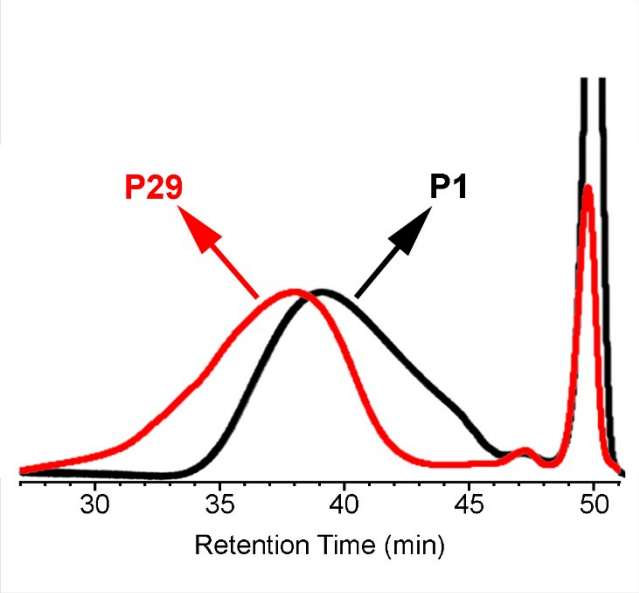
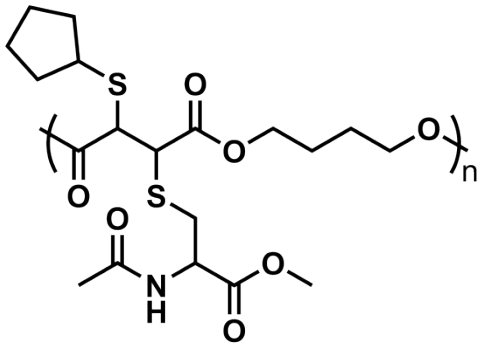


Figure S47. Overlaid GPC traces of **P1** and **P29** (at 30 °C in THF).

Thiol-Michael addition reaction between P15 and *N*-acetyl-L-cysteine methyl ester (P30)



P15 (0.1 g, 0.4 mmol of alkene, 1 equiv) and *N*-acetyl-L-cysteine methyl ester (78.8 mg, 0.480 mmol, 1.2 equiv per alkene) were dissolved in 4 mL of $CHCl_3$ and transferred to a 10 mL round bottomed flask. Next, TBD (12.9 mg, 0.100 mmol, 0.25 equiv) was added to the solution and the reaction mixture was at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of MeOH/diethyl ether (1:4) and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-MeOH/diethyl ether (1:4)) procedure was repeated two times. The purified sticky brown polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.11 g, 66 %, $M_{w,GPC}$ = 12900 g/mol, $Đ$ = 1.94,

relative to PS standards). ^{1}H NMR ($CDCl_3$, δ) 4.93 (br, 1H, SCH_2CH), 4.22 (br, 4H, $C{=}OOCH_2CH_2CH_2CH_2OC{=}O$), 3.79-3.76 (m, 3H, $C{=}OOCH_3$), 3.58 (m, $CHSCHC{=}O$ and $CH_2SCHC{=}O$), 3.30-3.21 (m, $SCHCH_2CH_2$ and SCH_2CH), 2.09-1.26 (m, $C{=}OOCH_2CH_2CH_2CH_2OC{=}O$, $SCHCH_2CH_2$, $SCHCH_2CH_2$ and $C{=}OCH_3$); ^{13}C NMR ($CDCl_3$, δ) 171.41, 170.05, 65.07, 52.72, 48.43, 46.88, 45.53, 37.67, 34.42, 33.27, 24.56, 22.90, 20.81.

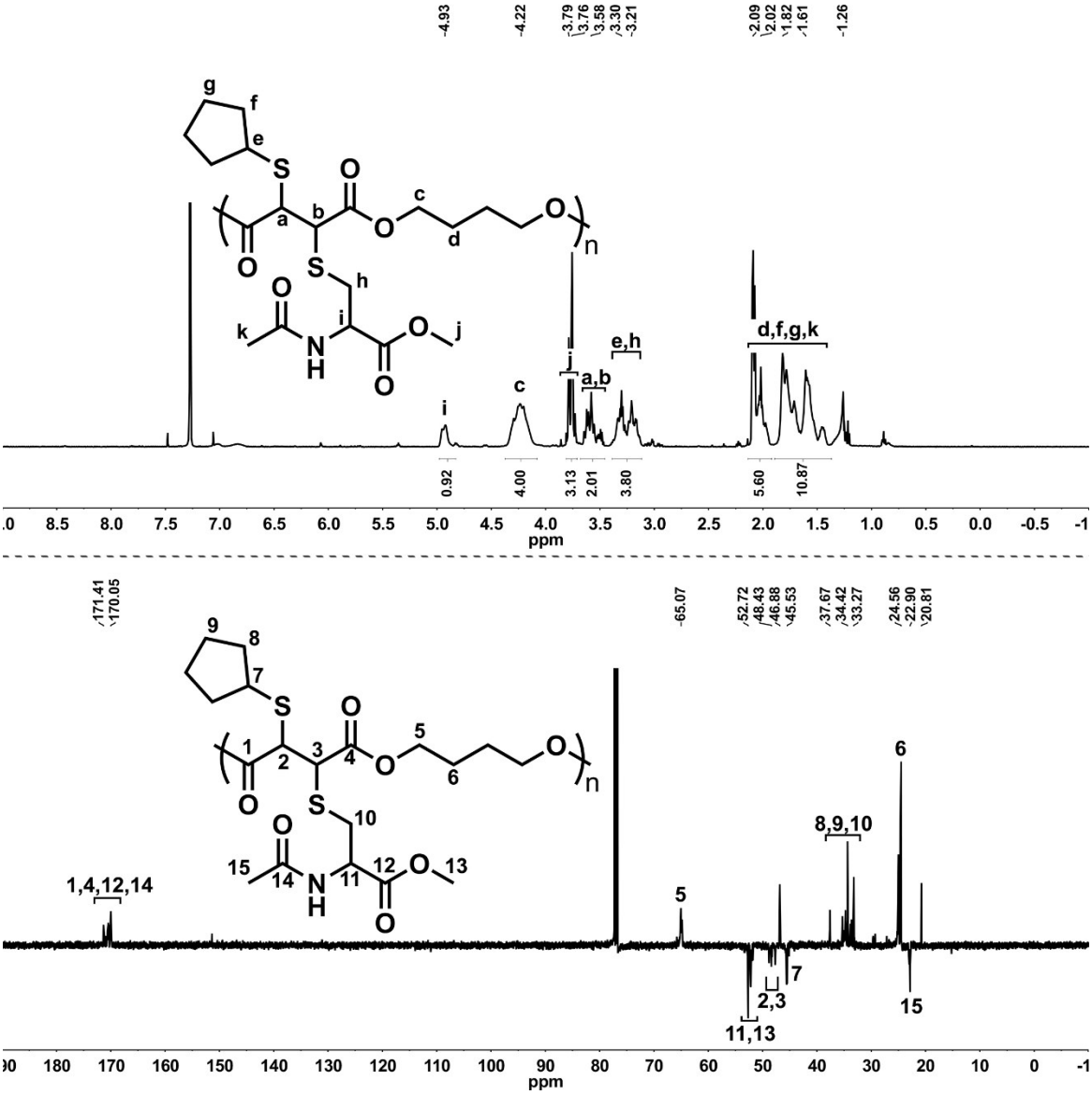


Figure S48. ^{1}H (up) and ^{13}C APT (down) spectra of **P30** in $CDCl_3$ (500 and 125 MHz, respectively).

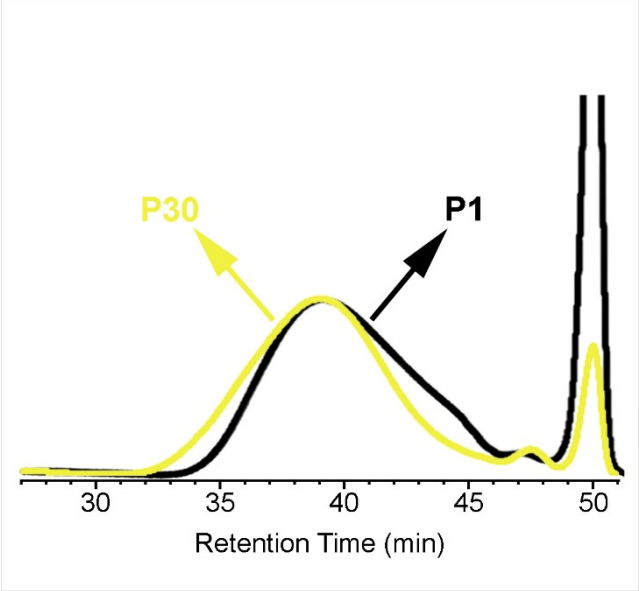


Figure S49. Overlaid GPC traces of **P1** and **P30** (at 30 °C in THF).

ONE-POT AZA- AND THIOL-MICHAEL REACTIONS

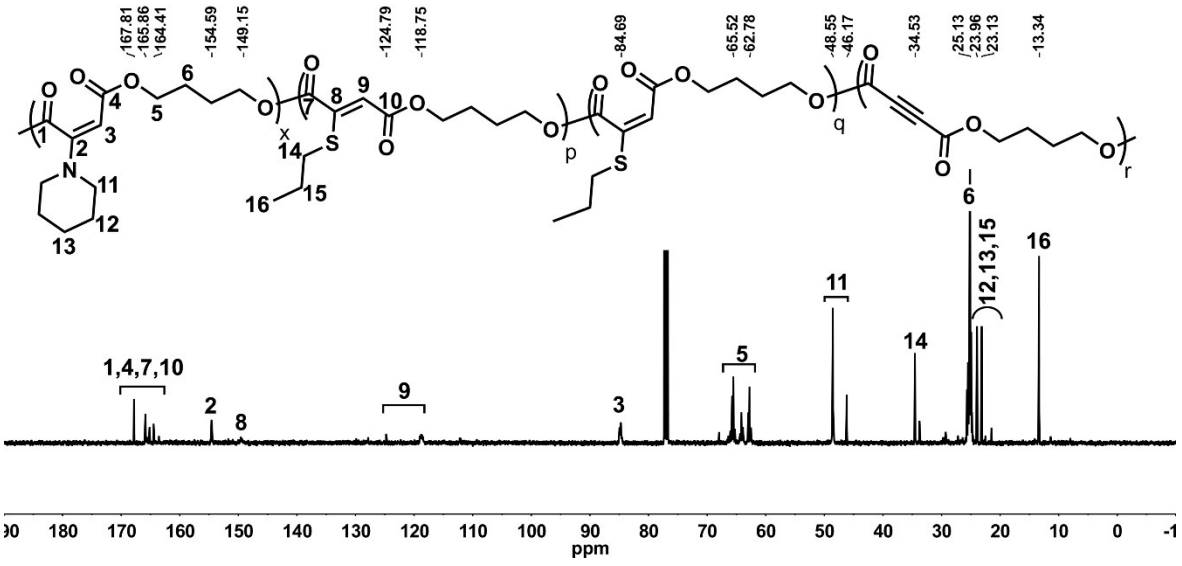


Figure S50. ^{13}C NMR spectrum of **P31** in $CDCl_3$ (125 MHz).