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

Ufuk Saim Gunay, Muge Cetin, Ozgun Daglar, Gurkan Hizal, Umit Tunca, Hakan Durmaz*

Department of Chemistry, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey
E-mail: durmazh@itu.edu.tr

AZA-MICHAEL ADDITION REACTIONS WITH SECONDARY AMINES

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

\[
\begin{align*}
\text{P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of CHCl}_3 \text{ and transferred to a 10 mL round bottomed flask. Next diethylamine (73.9 µL, 0.720 mmol, 1.2 equiv per alkyne) was added to the solution and the resulting solution was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the solvent was removed by decantation. The dissolution–precipitation (CHCl}_3\text{-diethyl ether) procedure was repeated two times. The recovered viscous brown polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.12 g, 83 %, } M_{w,GPC} = 10100 \text{ g/mol, } D = 1.97, \\
\text{relative to PS standards). } ^1\text{H NMR (CDCl}_3, \delta) \text{ 4.58 (bs, 1H, NC=C=O), 4.35-4.03 (m, 4H, C=OOC}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OC=O), 3.17 (br, 4H, NC}_2\text{CH}_3, 1.86-1.66 (m, 4H, C=OOC}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OC=O), 1.29 (br, 6H, CH}_2\text{CH}_3); } ^{13}\text{C NMR (CDCl}_3, \delta) \text{ 167.79, 165.70, 153.87, 82.94, 65.57, 62.67, 44.77, 42.02, 24.95, 12.77.}
\end{align*}
\]
Figure S1. Overlaid GPC traces of P1 and P2 (at 30 °C in THF).

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

\[
\text{P1} \quad (0.1 \text{ g}, 0.6 \text{ mmol of alkyne, 1 equiv}) \text{ was dissolved in 3 mL of CHCl}_3 \text{ and transferred to a 10 mL round bottomed flask. Next diisopropylamine (100 µL, 0.720 mmol, 1.2 equiv per alkyne) was added to the solution and the resulting solution was stirred at room temperature for 2 min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the solvent was removed by decantation. The dissolution–precipitation (CHCl}_3\text{-diethyl ether) procedure was repeated two times. The recovered sticky orange color polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.11 g, 68 \%, } M_{w,GPC} = 13600 \text{ g/mol, } D = 2.08, \text{ relative to PS standards). } \]

\[ ^1H \text{ NMR (CDCl}_3, \delta) 4.74 \text{ (bs, 1H, } NC=CH_C=O), 4.34-4.02 \text{ (m, 4H, } C=OOCCH}_2\text{CH}_2\text{CH}_2\text{OC}=O), 3.66 \text{ (br, 2H, } NCH(CH}_3)_2), 1.86-1.66 \text{ (m, 4H,}\]


C=OOC\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OC\textsubscript{2}=O), 1.29 (br, 12H, NCH(CH\textsubscript{3})\textsubscript{2}); $^{13}$C NMR (CDCl\textsubscript{3}, $\delta$) 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).](image)
Figure S3. Overlaid GPC traces of P1 and P3 (at 30 °C in THF).

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

\[
\begin{align*}
\text{P1} & \quad (0.1 \text{ g, 0.6 mmol of alkyne, 1 equiv}) \quad \text{was dissolved in 3 mL of CHCl}_3 \quad \text{and transferred to a} \\
& \quad 10 \text{ mL round bottomed flask. Next piperidine} \quad (70.6 \mu\text{L, 0.720 mmol, 1.2 equiv per alkyne}) \quad \text{was added to the solution and the resulting solution was stirred at room temperature for 2} \\
& \quad \text{min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the} \\
& \quad \text{solvent was removed by decantation. The dissolution–precipitation (CHCl}_3\text{-diethyl ether}) \\
& \quad \text{procedure was repeated two times. The recovered viscous brown-orange polymer was dried} \\
& \quad \text{in a vacuum oven at 40 °C for 24 h (Yield = 0.12 g, 79 %, } M_{w,GPC} = 8950 \text{ g/mol, } D = 1.58, \\
& \quad \text{relative to PS standards).} \quad ^1\text{H NMR (CDCl}_3, \delta) \quad 4.71 \ (\text{bs, 1H, NC}=\text{CH}=\text{O}), \ 4.33\text{-}4.03 \ (\text{m, 4H,} \\
& \quad \text{C}=\text{OOC}\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}=\text{O}), \ 3.16 \ (\text{br, 4H, NCH}_2\text{CH}_2\text{CH}_2), \ 1.86\text{-}1.63 \ (\text{m,}}
\end{align*}
\]
C=OOC\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OC=O, NCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2} and NCH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, \delta) 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\textsubscript{3} (500 and 125 MHz, respectively).
Figure S5. Overlaid GPC traces of P1 and P4 (at 30 °C in THF).

Azah-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 CHCl₃ 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 (CHCl₃-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, $D = 1.67$, relative to PS standards). $^1$H NMR (CDCl₃, δ) 4.78 (bs, 1H, NC=C=O), 4.33-4.05 (m, 4H, C=OOC₂H₂CH₂CH₂CH₂OC=O), 3.74 (br, 4H, NCH₂CH₂O), 3.15 (br, 4H,
NCH₂CH₂O), 1.86-1.67 (m, 4H, C=OOC₂H₂CH₂OOC=O); ¹³C NMR (CDCl₃, δ)
167.23, 165.36, 154.69, 87.38, 67.97, 65.88, 63.03, 47.12, 25.61.

**Figure S6.** ¹H (up) and ¹³C NMR (down) spectra of P5 in CDCl₃ (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 CHCl₃. 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 CHCl₃ 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 (CHCl₃-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 ºC (Yield = 0.09 g, 59.4 %, $M_w$GPC = 12050 g/mol, $D = 2.15$, relative to PS standards). ¹H NMR (CDCl₃, δ) 4.79 (bs, 1H, O(CH₂CH₂)₂NC=CHC=O), 4.72 (bs, 1H,
CH$_2$(CH$_2$CH$_2$)$_2$NC=CHC=O, 4.59 (bs, 1H, (CH$_3$CH$_2$)$_2$NC=CHC=O), 4.35-4.05 (m, 4H, C=OOC$_2$CH$_2$CH$_2$CH$_2$OC=O), 3.74 (br, 4H, NCH$_2$CH$_2$O), 3.16 (m, NCH$_2$CH$_2$H, NCH$_2$CH$_3$ and NCH$_2$CH$_2$O), 1.87-1.63 (m, C=OOC$_2$CH$_2$CH$_2$CH$_2$OC=O, NCH$_2$CH$_2$H and NCH$_2$CH$_2$CH$_2$), 1.18 (br, 6H, CH$_2$CH$_3$); $^{13}$C NMR (CDCl$_3$, $\delta$) 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. $^1$H (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)

\[ \text{P1} \quad (0.1 \ g, \ 0.6 \ \text{mmol of alkyne}, \ 1 \ \text{equiv}) \ \text{was dissolved in} \ 3 \ \text{mL of CHCl}_3 \ \text{and transferred to a} \ 10 \ \text{mL round bottomed flask. Next propylamine (58.7 \ \mu L, \ 0.720 \ \text{mmol, 1.2 equiv per alkyne}) was added to the solution and the resulting solution was stirred at room temperature for 2} \ \text{min. After that time, the polymer solution was precipitated in 20 mL of diethyl ether and the solvent was removed by decantation. The dissolution–precipitation (CHCl}_3\text{-diethyl ether) procedure was repeated two times. The recovered viscous dark yellow color polymer was dried in a vacuum oven at 40 °C for 24 h (Yield = 0.11 g, 81 %,} \ M_{w,GPC} = 39400 \ \text{g/mol,} \ D = 6.07, \ \text{relative to PS standards).} \quad ^1\text{H NMR (CDCl}_3, \ \delta) \ 8.12 \ \text{(bs, 1H, NH)}, \ 5.00 \ \text{(bs, 1H, NC=CHC=O,} \ \text{trans)}, \ 4.68 \ \text{(bs, 1H, NC=CHC=O,} \ \text{cis)}, \ 4.26-4.10 \ \text{(m, 4H, C=OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}=O), \ 3.28 \ \text{(br, 2H, HNCH}_2\text{CH}_2), \ 2.99 \ \text{(br, 2H, HNCH}_2\text{CH}_2, \ \text{cis)}, \ 1.83-1.72 \ \text{(m, 4H, C=OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}=O), \ 1.57 \ \text{(br, 2H, HNCH}_2\text{CH}_2), \ 0.94 \ \text{(br, 3H, CH}_2\text{CH}_3); \quad ^{13}\text{C NMR (CDCl}_3, \ \delta) \ 170.20, \ 163.74, \ 151.98, \ 86.19, \ 76.80, \ 65.02, \ 62.47, \ 46.62, \ 25.52, \ 25.09, \ 24.16, \ 11.19. \]
**Figure S10.** Overlaid GPC traces of P1 and P8 (at 30 °C in THF).

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

![Reaction Scheme](image)

P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of CHCl₃ 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 (CHCl₃-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, \( D = 8.61 \), relative to PS standards). \(^1\)H NMR (CDCl₃, \( \delta \)) 8.12 (bs, 1H, \( \text{N-H} \)), 4.96 (bs, 1H, NC=C=O, trans), 4.71 (bs, 1H, NC=CHC=O, cis), 4.26-4.10 (m, 4H, C=OOCH₂CH₂CH₂CH₂OC=O), 3.53 (br, 1H, HNC=CH), 1.90-1.23 (m, 4H, C=OOCH₂CH₂CH₂CH₂OC=O).
C=O\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OC}=\text{O}, \text{HNCHCH}_2, \text{HNCHCH}_2\text{CH}_2\text{CH}_2, \text{HNCHCH}_2\text{CH}_2\text{CH}_2); \text{ }^{13}\text{C} \text{ NMR (CDCl}_3, \delta) 170.19, 164.06, 151.57, 86.29, 65.00, 62.44, 53.13, 34.55, 25.33, 24.52.

\text{Figure S11. }^{1}\text{H (up) and }^{13}\text{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 CHCl₃ 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 (CHCl₃-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, $D = 6.22$, relative to PS standards). $^1$H NMR (CDCl₃, $\delta$) 8.18 (bs, 1H, NH), 5.87 (m, 1H, CH=CH₂), 5.22 (m, 2H, CH=CH₂), 5.10 (bs, 1H, NC=CHC=O, trans), 4.72 (bs, 1H, NC=CHC=O, cis), 4.25-4.13 (m, 4H, C=OOC₂CH₂CH₂CH₂OC=O), 3.98 (bs, 2H, HNCH₂,
trans), 3.68 (bs, 2H, HNCH₂, cis), 1.81-1.73 (m, 4H, C=OCH₂CH₂CH₂CH₂OC=O); ¹³C NMR (CDCl₃, δ) 170.04, 163.58, 151.66, 135.14, 116.41, 87.41, 65.07, 62.62, 46.88, 25.05.

Figure S13. ¹H (up) and ¹³C NMR (down) spectra of P10 in CDCl₃ (500 and 125 MHz, respectively).
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 CHCl₃ 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 (CHCl₃-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, $D = 2.56$, relative to PS standards). $^{1}$H NMR (CDCl₃, δ) 8.32 (bs, 1H, NH), 4.87 (bs, 1H, NC=C=O, cis), 4.74 (bs, 1H, NC=CH=O, trans), 4.27-4.09 (m, 4H, C=OOCH₂CH₂CH₂CH₂OC=O), 1.84-1.70 (m, 4H, C=OOCH₂CH₂CH₂CH₂OC=O), 1.37-1.33
(m, 9H, HNC(\text{CH}_3)_3); $^{13}$C NMR ($\text{CDCl}_3$, $\delta$) 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).
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 CHCl₃ 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 (CHCl₃-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, $D = 3.64$, relative to PS standards). $^1$H NMR (CDCl₃, $\delta$) 8.43 (bs, 1H, NH), 7.32 (m, 5H, ArH), 5.14 (bs, 1H, NC=CHC=O, trans), 4.77 (bs, 1H, NC=CHC=O, cis), 4.55 (br, 2H, HNCH₂, trans),
4.24 (br, 2H, HNCH$_2$, cis) 4.17-4.06 (m, 4H, C=OOC$\text{H}_2$CH$_2$CH$_2$OC=O), 1.72-1.57 (m, 4H, C=OOC$\text{H}_2$CH$_2$CH$_2$OC=O); $^{13}$C NMR (CDCl$_3$, $\delta$) 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 CHCl₃ 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 (CHCl₃-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, $D = 2.86$, relative to PS standards). $^1$H NMR (CDCl₃, $\delta$) 8.31 (bs, 1H, NH), 7.33 (bs, 1H, =C=H), 6.28 (bs, 1H, CHCH=CHO), 6.17 (bs, 1H, CHCH=CHO), 5.19 (bs, 1H, NC=CH=O, $\text{trans}$), 4.82 (bs, 1H, NC=CH=O, $\text{cis}$), 4.55 (br, 2H, HNC=CH₂, $\text{trans}$), 4.24 (br,
2H, HNCH2, cis), 4.10 (br, 4H, C=OOC\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OC=O), 1.77-1.71 (m, 4H, C=OOC\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}OC=O); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, \textit{\delta}) 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.

\textbf{Figure S19.} \textsuperscript{1}H (up) and \textsuperscript{13}C NMR (down) spectra of P13 in CDCl\textsubscript{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 CHCl₃ 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 CHCl₃ 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, 82 %, \( M_{w,GPC} = 25000 \) g/mol, \( D = 3.34 \), relative to PS standards). \(^1\)H NMR (CDCl₃, δ) 6.30 (bs, 1H, SC=CHC=O, trans), 5.69 (bs, 1H, SC=CHC=O, cis), 4.30-4.13 (m, 4H, C=OOC₂H₂CH₂CH₂CH₂OC=O), 2.82 (br, 2H, SCH₂CH₂CH₃), 1.85-1.61 (m, C=OOC₂H₂CH₂CH₂CH₂OC=O and SCH₂CH₂CH₃), 1.26-0.99 (m, 3H, SCH₂CH₂CH₃); \(^{13}\)C NMR (CDCl₃, 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.
Thiol-Michael addition reaction between P1 and cyclopentanethiol (P15)

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

**P1** (1 g, 6 mmol of alkyne, 1 equiv) was dissolved in 30 mL of CHCl₃ 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 CHCl₃ 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, $D = 3.05$, relative to PS standards). $^1$H NMR (CDCl₃, $\delta$) 6.30 (bs, 1H, SC=C=O, trans), 5.71 (bs, 1H, SC=CH=C=O, cis), 4.30-4.13 (m, 4H, C=OOC₃H₂CH₂CH₂CH₂OC=O), 3.71 (bs, 1H, SCHCH₂CH₂, trans), 3.50 (bs, 1H,
$\text{SCHCH}_2\text{CH}_2$, cis), 2.13-1.58 (m, $\text{C}=\text{OOCH}_2\text{CH}_2\text{CH}_2\text{OC}=\text{O}$, $\text{SCHCH}_2\text{CH}_2$ and $\text{SCHCH}_2\text{CH}_2$); $^{13}\text{C}$ NMR (CDCl$_3$, $\delta$) 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.** $^{13}\text{C}$ 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 °C in a vacuum oven for 24 h (Yield = 0.11 g, 58 %, $M_{w,\text{GPC}} = 31900$ g/mol, $D = 2.91$, relative to PS standards). $^1$H NMR (CDCl$_3$, $\delta$) 6.29 (bs, 1H, SC=CH$_2$=O, trans), 5.68 (bs, 1H, SC=CH$_2$=O, cis), 4.28-4.13 (m, 4H, C=OOC$_2$H$_5$CH$_2$CH$_2$CH$_2$OC=O), 2.83 (bs, 2H, SCH$_2$(CH$_2$)$_6$CH$_3$), 1.85-1.26 (m, C=OOC$_2$H$_5$CH$_2$CH$_2$OC=O and SCH$_2$(CH$_2$)$_6$CH$_3$), 2.83 (b, 3H, SCH$_2$(CH$_2$)$_6$CH$_3$), $^{13}$C NMR (CDCl$_3$, $\delta$); 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 CHCl₃ 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 CHCl₃ and consequently precipitated in MeOH. The purified sticky pale yellow polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.13 g, 74 %, $M_w,\text{GPC} = 22350 \text{ g/mol}$, $D = 3.13$, relative to PS standards). $^1$H NMR (CDCl₃, δ) 7.34-7.23 (m, 5H, ArH), 6.31 (bs, 1H, SC=CHC=O, trans), 5.76 (bs, 1H, SC=CHC=O, cis), 4.26-4.04 (m, C=OOC₃H₂CH₂CH₂OC=O and SC₂H₂); $^{13}$C NMR (CDCl₃, 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 CHCl₃ 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 CHCl₃ and consequently precipitated in MeOH. The purified viscous brown polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.14 g, 85 %, $M_w,\text{GPC} = 28900$ g/mol, $D = 3.22$, relative to PS standards). $^1$H NMR (CDCl₃, δ) 6.53 (bs, 1H, SC=CHC=O, trans), 5.91 (bs, 1H, SC=CHC=O, cis), 4.27-4.14 (m, 4H, C=OOC₂H₂CH₂CH₂OC=O), 3.76 (br, 2H, SC₂H₂), 3.70-3.63 (m, 3H, C=OOC₂H₃), 1.86-1.75 (br, 4H, C=OOC₂H₂CH₂CH₂OC=O); $^{13}$C NMR (CDCl₃, 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 CHCl₃ 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 (CHCl₃-MeOH/diethyl ether (1:4)) procedure was repeated two times. The purified viscous pale yellow polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.10 g, 48 %, $M_w$,$\text{GPC} = 14850$ g/mol, $D = 2.82$, relative to PS standards). $^1$H NMR (CDCl₃, $\delta$) 6.80 (br, 1H, $NH$), 6.59 (bs, 1H, SC=C=O, trans), 5.91 (bs, 1H, SC=C=O, cis), 4.85-4.79 (m, 1H, SCH₂CH), 4.31-4.14 (m, 4H, C=OOCH₂CH₂CH₂CH₂OC=O), 3.77-3.73 (m, 3H, C=OOCH₃), 3.33-3.22 (m, 2H, SCH₂CH), 2.02 (br, 3H, C=OCH₃), 1.80-1.25 (m, 4H, C=OOCH₂CH₂CH₂CH₂OC=O); $^{13}$C NMR (CDCl₃, $\delta$) 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 CHCl₃ 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 CHCl₃ and consequently precipitated in MeOH. The purified viscous brown polymer was finally dried at 40 °C in a vacuum oven for 24 h (Yield = 0.09 g, 47 %, \( M_w,GPC = 26600 \text{ g/mol, } D = 1.76, \) relative to PS standards). 

\(^1\)H NMR (CDCl₃, \( \delta \)) 4.23 (m, 4H, C=OOC\( \text{H}_2\text{C}_2\text{H}_3\text{O}\)), 3.56-3.52 (m, 2H, SC\( \text{H}_2\text{C}=\text{O}\)), 2.68-2.64 (m, 4H, SC\( \text{H}_2\text{C}_2\text{H}_3\)), 1.82 (br, 4H, C=OOCH\( \text{H}_2\text{C}_2\text{H}_3\text{O}\)), 1.60 (m, 4H, SCH\( \text{H}_2\text{C}_2\text{H}_3\)), 1.02-0.97 (m, 6H, SCH\( \text{H}_2\text{C}_2\text{H}_3\)).

\(^1^3\)C NMR (CDCl₃, \( \delta \)) 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 CHCl₃ 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 CHCl₃ 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 %, $M_w$,$\text{GPC} = 24600$ g/mol, $D = 2.66$, relative to PS standards). $^1$H NMR (CDCl₃, $\delta$) 4.21 (m, 4H, C=OOC$_2$H$_2$CH$_2$CH$_2$CH$_2$C=O), 3.61-3.54 (m, 2H, SCHC=O), 3.30 (br, 2H,
SCHCH₂CH₂), 2.04-1.26 (m, C=OCH₂CH₂CH₂OC=O, SCHCH₂CH₂ and SCHCH₂CH₂); ¹³C NMR (CDCl₃, δ) 171.87, 170.72, 77.02, 64.65, 48.50, 45.59, 34.34, 33.38, 24.72.

Figure S32. ¹H (up) and ¹³C APT (down) spectra of P21 in CDCl₃ (500 and 125 MHz, respectively).
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 CHCl₃ 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 CHCl₃ 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 %, $M_w,\text{GPC} = 27000$ g/mol, $D = 2.20$, relative to PS standards). $^1$H NMR (CDCl₃,
δ) 4.21 (br, 4H, C=OOCH₂CH₂CH₂CH₂OC=O), 3.56 (m, 2H, SCH₂=O), 2.65 (m, 4H, SCH₂CH₂(CH₂)₂CH₃), 1.81 (br, 4H, C=OOCH₂CH₂CH₂CH₂OC=O), 1.56 (m, 4H, SCH₂CH₂(CH₂)₂CH₃), 1.27 (m, 20H, SCH₂CH₂(CH₂)₂CH₃), 0.89 (m, 6H, SCH₂CH₂(CH₂)₂CH₃); ¹³C NMR (CDCl₃, 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. ¹H (up) and ¹³C APT (down) spectra of P22 in CDCl₃ (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)**

![Diagram of the reaction](image)

P1 (0.1 g, 0.6 mmol of alkyne, 1 equiv) was dissolved in 3 mL of CHCl₃ 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 CHCl₃ 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 %, $M_w,\text{GPC} = 23000$ g/mol, $D = 2.59$, relative to PS standards). $^1$H NMR (CDCl₃, δ)
7.29 (m, 10H, ArH), 4.07 (m, 4H, C=OOCH₂CH₂CH₂CH₂OC=O), 3.86-2.52 (m, SCH=O and SCH₂), 1.63 (br, 4H, C=OOCH₂CH₂CH₂CH₂OC=O); ¹³C NMR (CDCl₃, 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.** ¹H (up) and ¹³C APT (down) spectra of P23 in CDCl₃ (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 CHCl₃ 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 CHCl₃ 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 %, Mₜₐₐₙ,GPC = 31600 g/mol, D = 3.85, relative to PS standards). ¹H NMR
(CDCl$_3$, $\delta$) 4.24-4.18 (m, 4H, C=OOC$_2$H$_2$CH$_2$CH$_2$OC=O), 3.82-3.42 (m, 4H, SCH$_2$), 3.75 (m, 6H, C=OOCH$_3$), 3.54 (bs, 2H, SCH=O), 1.81 (br, 4H, C=OOC$_2$H$_2$CH$_2$CH$_2$OC=O);

$^{13}$C NMR (CDCl$_3$, $\delta$) 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)**

![Image of chemical structure]

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 CHCl₃ 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 CHCl₃ 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 %, $M_{w,\text{GPC}} = 9970$ g/mol, $D = 1.32$, relative to PS standards). $^1$H NMR (CDCl$_3$, $\delta$) 4.85 (br, 2H, SCH$_2$CH), 4.25 (br, 4H, C=OOC$_2$CH$_2$CH$_2$CH$_2$OC=O), 3.79-3.76 (br, 6H, C=OOC$_3$H$_3$), 3.63-3.55 (m, 2H, SCH=O), 3.21-3.15 (m, 4H, SCH$_2$CH), 2.08 (br, 6H, C=OCH$_3$), 1.81-1.77 (br, 4H, C=OOC$_2$CH$_2$CH$_2$CH$_2$OC=O); $^{13}$C NMR (CDCl$_3$, $\delta$) 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 CHCl₃ 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 CHCl₃ 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, 78 %, $M_w,\text{GPC} = 26100$ g/mol, $D = 2.06$, relative to PS standards). $^1$H NMR (CDCl₃, δ) 4.25-4.20 (m, 4H, C=OOCH₂CH₂CH₂CH₂OC=O), 3.64-3.50 (m, CHSC=O and CH₂SCHC=O), 3.30 (br, 1H, SCHCH₂CH₂), 2.68-2.64 (br, 2H, SCH₂CH₂CH₃), 2.03-1.45 (m, C=OOCH₂CH₂CH₂CH₂OC=O, SCHCH₂CH₂, SCHCH₂CH₂ and SCH₂CH₂CH₃), 1.01-0.97 (m, 3H, SCH₂CH₂CH₃); $^{13}$C NMR (CDCl₃, 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 °C in a vacuum oven for 24 h (Yield = 0.11 g, 71 %, $M_w,GPC = 26500$ g/mol, $D = 1.88$, relative to PS standards). $^1$H NMR (CDCl$_3$, $\delta$) 4.23-4.18 (br, 4H, C=OOC$_2$H$_2$CH$_2$CH$_2$CH$_2$OC=O), 3.61-3.56 (m, CHSC$_2$H$_2$C=O and CH$_2$SC$\text{H}C=O), 3.30 (br, 1H, SCH$\text{H}C$H$_2$CH$_2$), 2.69-2.65 (br, 2H, SCH$_2$(CH$_2$)$_6$CH$_3$), 2.04-1.56 (m, C=OOC$_2$H$_2$CH$_2$CH$_2$OC=O, SCH$\text{H}C$H$_2$CH$_2$ and SCH$\text{H}C$H$_2$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$_3$, $\delta$) 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 CHCl₃ 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 CHCl₃ 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, $D = 2.45$, relative to PS standards). $^1$H NMR (CDCl₃, $\delta$) 7.32-7.30 (m, 5H, ArH), 4.19-4.12 (br, 4H, C=OOC(CH₂)₂CH₂OC=O), 3.89-3.86 (m,
2H, SCH₂Ph), 3.64-3.50 (m, CHSCH=O and CH₂SCH=O), 3.27-3.08 (m, 1H, SCHCH₂CH₂), 1.98-1.26 (m, C=OOCH₂CH₂CH₂CH₂OC=O, SCHCH₂CH₂ and SCHCH₂CH₂); ¹³C NMR (CDCl₃, 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 CHCl₃ 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 CHCl₃ 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 %, $M_w,\text{GPC} = 30850$ g/mol, $D = 2.54$, relative to PS standards). $^1$H NMR (CDCl₃, δ) 4.21-4.15 (br, 4H, C=OOC₂H₅CH₂CH₂CH₂OC=O), 3.73-3.60 (m, CHSC=O,
CH₂SC=O and C=OOCH₃), 3.45-3.43 (br, 2H, SCH₂C=O), 3.28 (br, 1H, SCHCH₂CH₂), 2.03-1.43 (m, C=OOCH₂CH₂CH₂CH₂OC=O, SCHCH₂CH₂ and SCHCH₂CH₂); ¹³C NMR (CDCl₃, 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 ¹³C APT (down) spectra of P29 in CDCl₃ (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 CHCl₃ 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 (CHCl₃-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, \(D = 1.94\), \(\bar{M}_n = 6500\) g/mol, 66 %).
relative to PS standards. $^1$H NMR (CDCl$_3$, $\delta$) 4.93 (br, 1H, SCH$_2$CH), 4.22 (br, 4H, C=OOCH$_2$CH$_2$CH$_2$CH$_2$OC=O), 3.79-3.76 (m, 3H, C=OOCH$_3$), 3.58 (m, CHSCH=O and CH$_2$SCH=O), 3.30-3.21 (m, SCHCH$_2$CH$_2$ and SCH$_2$CH), 2.09-1.26 (m, C=OOCH$_2$CH$_2$CH$_2$OC=O, SCHCH$_2$CH$_2$, SCHCH$_2$CH$_2$ and C=OCH$_3$); $^{13}$C NMR (CDCl$_3$, $\delta$) 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).