

Supporting Information for Manuscript Entitled with

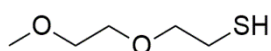
**Biodegradable Thermal- and Redox-Responsive  
Poly(L-glutamate) with Y-shaped Oligo(ethylene glycol)  
Side-chain and Tunable Phase Transition Temperature**

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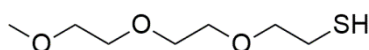
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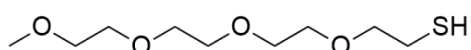
**2-(2-methoxyethoxy)ethane thiol (OEG<sub>2</sub>-SH)**

<sup>1</sup>H NMR of EG<sub>2</sub>-SH (400 MHz, CDCl<sub>3</sub>, δ, ppm): 1.51-1.62 (t, 1H), 2.65-2.80 (m, 2H),  
3.35-3.42 (s, 3H), 3.50-3.68 (br, 6H).



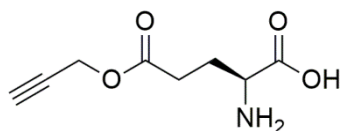
**2-(2-(2-methoxyethoxy)ethoxy)ethane thiol (OEG<sub>3</sub>-SH)**

<sup>1</sup>H NMR of EG<sub>3</sub>-SH (400 MHz, CDCl<sub>3</sub>, δ, ppm): 1.50-1.60 (t, 1H), 2.60-2.74 (m, 2H),  
3.29-3.36 (s, 3H), 3.46-3.70 (br, 10H).



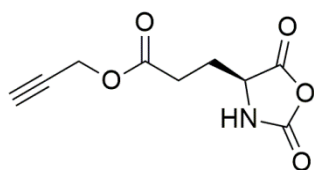
**2-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethane thiol (OEG<sub>4</sub>-SH)**

<sup>1</sup>H NMR of EG<sub>4</sub>-SH (400 MHz, CDCl<sub>3</sub>, δ, ppm): 1.45-1.55 (t, 1H), 2.53-2.67 (m, 2H),  
3.24-3.32 (s, 3H), 3.41-3.61 (br, 14H).



**$\gamma$ -Propargyl-L-glutamate (PLG)**

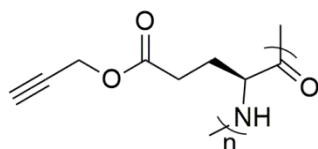
$^1\text{H}$  NMR of PLG (400 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ , ppm): 2.18 (dm, 2H), 2.62 (t, 2H), 2.93 (t, 1H), 3.82 (t, 1H), 4.76 (d, 2H).



**$\gamma$ -Propargyl-L-glutamate *N*-carboxyanhydride (PLG-NCA)**

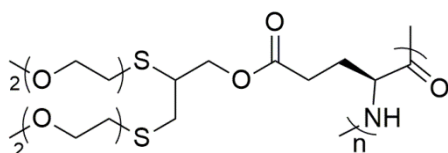
$^1\text{H}$  NMR of PLG-NCA (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 2.23 (m, 2H), 2.51 (t, 1H), 2.61 (t, 2H), 4.44 (t, 1H), 4.71 (d, 2H), 6.79 (s, br, 1H).

$^{13}\text{C}$  NMR of PLG-NCA (101 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 172.20, 169.48, 152.12, 131.58, 118.97, 65.86, 56.87, 29.59 and 26.85.



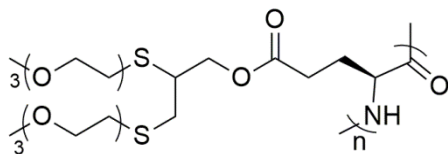
**Poly( $\gamma$ -propargyl-L-glutamate) (PPLG)**

$^1\text{H}$  NMR of PPLG (400 MHz,  $\text{CDCl}_3/\text{TFA-d}$ , v : v = 85 : 15,  $\delta$ , ppm): 1.98-2.28 (br, 2H), 2.46-2.53 (br, 1H), 2.54-2.62 (br, 2H), 4.55-4.65 (br, 1H), 4.66-4.76 (br, 2H).



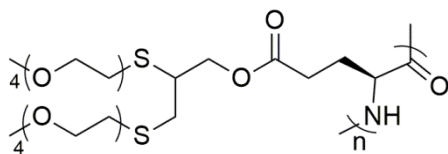
**Poly( $\gamma$ -propargyl-L-glutamate)-graft-methoxydiethyleneglycolthioether (PPLG-*g*-EG<sub>2</sub>)**

$^1\text{H}$  NMR of PPLG-*g*-EG<sub>2</sub> (400 MHz, CDCl<sub>3</sub>/TFA-d, v : v = 85 : 15,  $\delta$ , ppm): 1.88-2.20 (br, 2H), 2.39-2.58 (br, 2H), 2.68-3.12 (br, 6H), 3.40-3.57 (br, 6H), 3.62-3.81 (br, 13H), 4.15-4.39 (br, 2H), 4.48-4.64 (br, 1H).



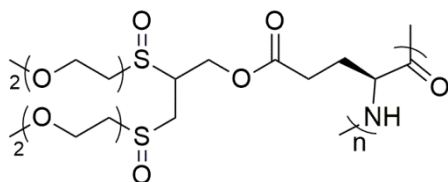
**Poly( $\gamma$ -propargyl-L-glutamate)-graft-methoxytriethyleneglycolthioether (PPLG-*g*-EG<sub>3</sub>)**

$^1\text{H}$  NMR of PPLG-*g*-EG<sub>3</sub> (400 MHz, CDCl<sub>3</sub>/TFA-d, v : v = 85 : 15,  $\delta$ , ppm): 1.88-2.26 (br, 2H), 2.45-2.69 (br, 2H), 2.73-3.16 (br, 6H), 3.43-3.59 (br, 6H), 3.69-3.92 (br, 21H), 4.15-4.49 (br, 2H), 4.54-4.76 (br, 1H).



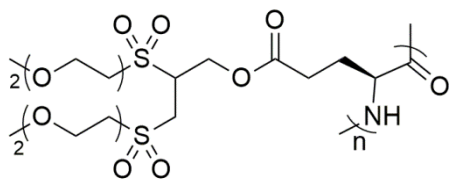
**Poly( $\gamma$ -propargyl-L-glutamate)-graft-methoxytetraethyleneglycolthioether(PPLG-*g*-EG<sub>4</sub>)**

$^1\text{H}$  NMR of PPLG-*g*-EG<sub>4</sub> (400 MHz, CDCl<sub>3</sub>/TFA-d, v : v = 85 : 15,  $\delta$ , ppm): 1.88-2.22 (br, 2H), 2.41-2.62 (br, 2H), 2.72-3.11 (br, 6H), 3.44-3.65 (br, 6H), 3.70-3.98 (br, 29H), 4.13-4.46 (br, 2H), 4.50-4.72 (br, 1H).



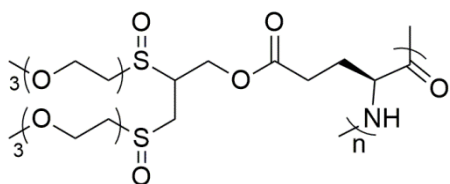
**Poly( $\gamma$ -propargyl-L-glutamate)-graft-methoxydiethyleneglycolsulfoxide (PPLG-*g*-<sup>0</sup>EG<sub>2</sub>)**

$^1\text{H}$  NMR of PPLG-*g*-<sup>0</sup>EG<sub>2</sub> (400 MHz, CDCl<sub>3</sub>/TFA-d, v : v = 85 : 15,  $\delta$ , ppm): 1.75-2.32 (br, 2H), 2.40-2.76 (br, 2H), 3.12-4.23 (br, 25H), 4.38-4.91 (br, 3H).



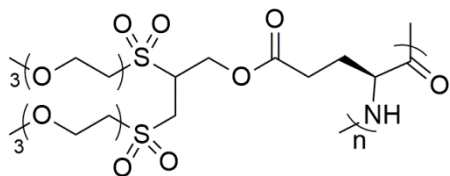
**Poly( $\gamma$ -propargyl-L-glutamate)-graft-methoxydiethyleneglycol sulfone (PPLG- $g$ - $^{02}EG_2$ )**

$^1H$  NMR of PPLG- $g$ - $^{02}EG_2$  (400 MHz,  $CDCl_3/TFA-d$ ,  $v : v = 85 : 15$ ,  $\delta$ , ppm): 1.83-2.42 (br, 2H), 2.43-2.90 (br, 2H), 3.17-4.32 (br, 25H), 4.42-5.03 (br, 3H).



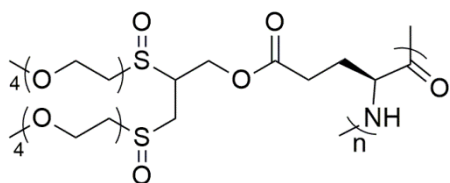
**Poly( $\gamma$ -propargyl-L-glutamate)-graft-methoxytriethyleneglycol sulfone (PPLG- $g$ - $^{0EG_3}$ )**

$^1H$  NMR of PPLG- $g$ - $^{0EG_3}$  (400 MHz,  $CDCl_3/TFA-d$ ,  $v : v = 85 : 15$ ,  $\delta$ , ppm): 1.86-2.22 (br, 2H), 2.41-2.70 (br, 2H), 3.11-3.60 (br, 12H), 3.61-4.09 (br, 21H), 4.33-4.80 (br, 3H).



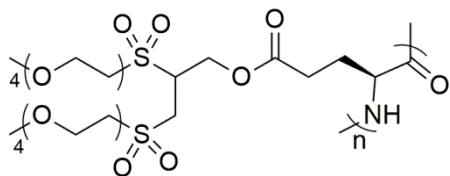
**Poly( $\gamma$ -propargyl-L-glutamate)-graft-methoxytriethyleneglycol sulfone (PPLG- $g$ - $^{02}EG_3$ )**

$^1H$  NMR of PPLG- $g$ - $^{02}EG_3$  (400 MHz,  $CDCl_3/TFA-d$ ,  $v : v = 85 : 15$ ,  $\delta$ , ppm): 1.85-2.41 (br, 2H), 2.43-2.90 (br, 2H), 3.17-4.32 (br, 33H), 4.42-5.03 (br, 3H).



**Poly( $\gamma$ -propargyl-L-glutamate)-graft-methoxytetraethyleneglycol sulfone (PPLG- $g$ - $^{0E G_4}$ )**

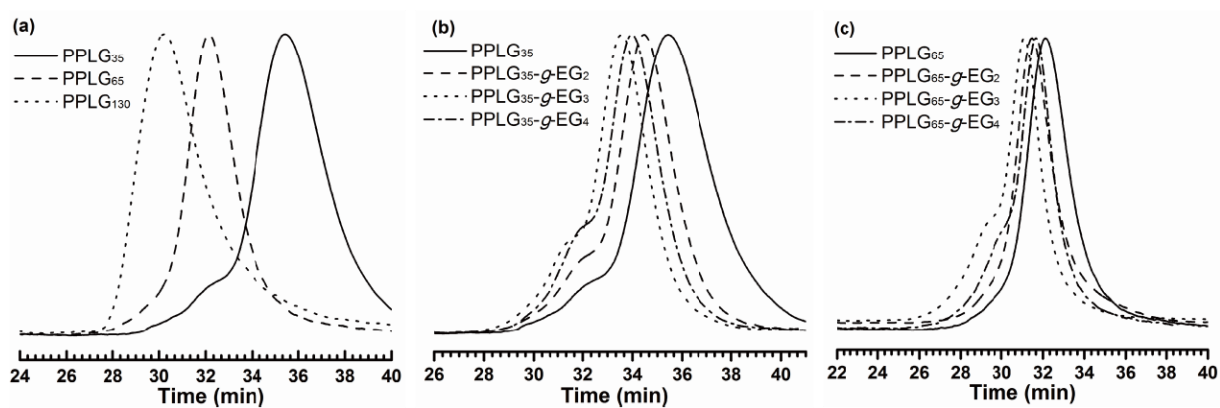
$^1\text{H}$  NMR of PPLG-*g*- $^0\text{EG}_3$  (400 MHz,  $\text{CDCl}_3/\text{TFA-d}_4$ ,  $v : v = 85 : 15$ ,  $\delta$ , ppm): 1.86-2.22 (br, 2H), 2.41-2.70 (br, 2H), 3.18-3.65 (br, 12H), 3.68-4.19 (br, 29H), 4.46-4.87 (br, 3H).



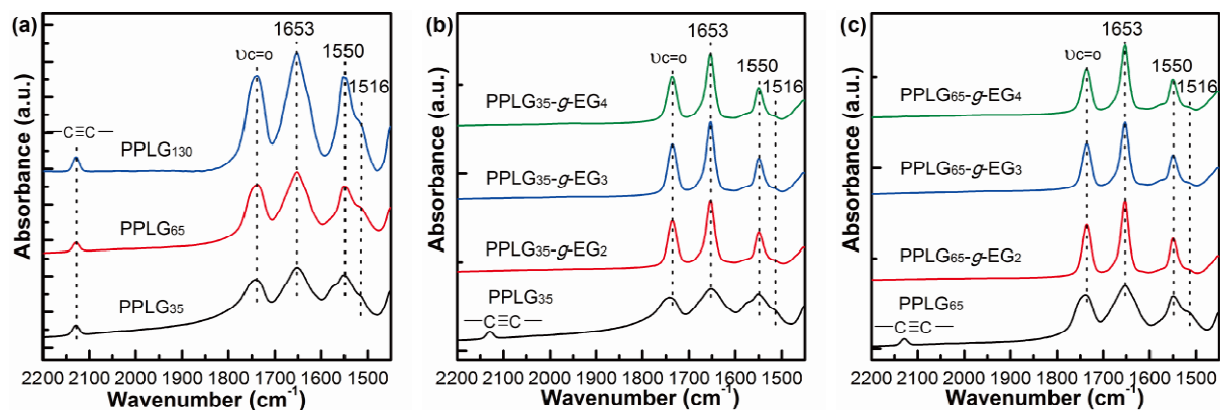
**Poly( $\gamma$ -propargyl-L-glutamate)-graft-methoxytetraethyleneglycol sulfone(PPLG-*g*- $^0\text{EG}_4$ )**

4)

$^1\text{H}$  NMR of PPLG-*g*- $^0\text{EG}_4$  (400 MHz,  $\text{CDCl}_3/\text{TFA-d}_4$ ,  $v : v = 85 : 15$ ,  $\delta$ , ppm): 1.81-2.39 (br, 2H), 2.40-2.83 (br, 2H), 3.10-4.37 (br, 41H), 4.39-5.02 (br, 3H).



**Figure S1.** GPC chromatographs of (a) PPLG<sub>35</sub>, PPLG<sub>65</sub>, and PPLG<sub>130</sub>; (b) PPLG<sub>35</sub>, PPLG<sub>35</sub>-*g*-EG<sub>2</sub>, PPLG<sub>35</sub>-*g*-EG<sub>3</sub>, and PPLG<sub>35</sub>-*g*-EG<sub>4</sub>; (c) PPLG<sub>65</sub>, PPLG<sub>65</sub>-*g*-EG<sub>2</sub>, PPLG<sub>65</sub>-*g*-EG<sub>3</sub>, and PPLG<sub>65</sub>-*g*-EG<sub>4</sub>.



**Figure S2.** FTIR spectra of (a) PPLG<sub>35</sub>, PPLG<sub>65</sub>, and PPLG<sub>130</sub>; (b) PPLG<sub>35</sub>, PPLG<sub>35-g-EG2</sub>, PPLG<sub>35-g-EG3</sub>, and PPLG<sub>35-g-EG4</sub>; (c) PPLG<sub>65</sub>, PPLG<sub>65-g-EG2</sub>, PPLG<sub>65-g-EG3</sub>, and PPLG<sub>65-g-EG4</sub> in the solid state.

**Table S1.** Solubility of PPLG-*g*-EG<sub>x</sub>

Entry	PPLG- <i>g</i> -EG <sub>2</sub>	PPLG- <i>g</i> -EG <sub>3</sub>	PPLG- <i>g</i> -EG <sub>4</sub>
H <sub>2</sub> O	I	L	L
DMSO	S	S	S
DMF	S	S	S
DCM	S	S	S
CHCl <sub>3</sub>	S	S	S
MeOH	S	S	S
THF	S	S	S
Acetone	S	S	S
EtOAc	S	S	S

I) Insoluble (<0.2 mg/mL); S) soluble (>2 mg/mL); L) LCST-type phase transition.