Supporting Information for

Facile Synthesis of Polymethionine Oxides through Polycondensation of Activated Urethane Derivative of α-Amino Acid and their Application to Antifouling Polymer against Proteins and Cells

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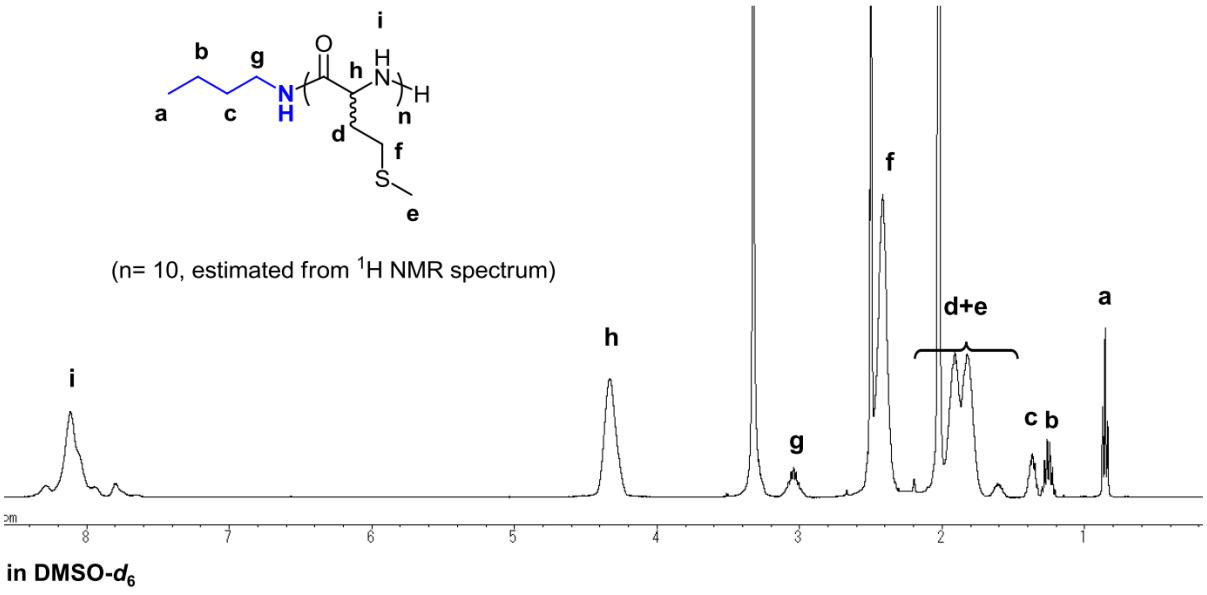

Figure S1. ^{1}H NMR spectrum of poly(DL-methionine) by polycondensation of **DL-Met** in the presence of *n*-$BuNH_2$ (entry 2 in Table 1)

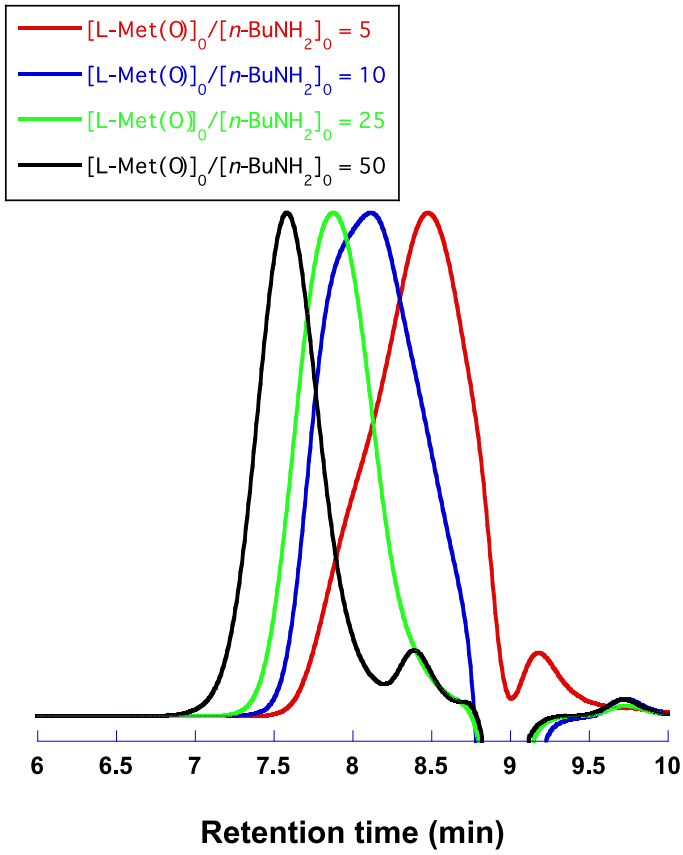

Figure S2. SEC traces of poly(L-methionine) by polycondensation of **L-Met(O)** in the presence of *n*-$BuNH_2$ (entries 5-8, in Table 2)

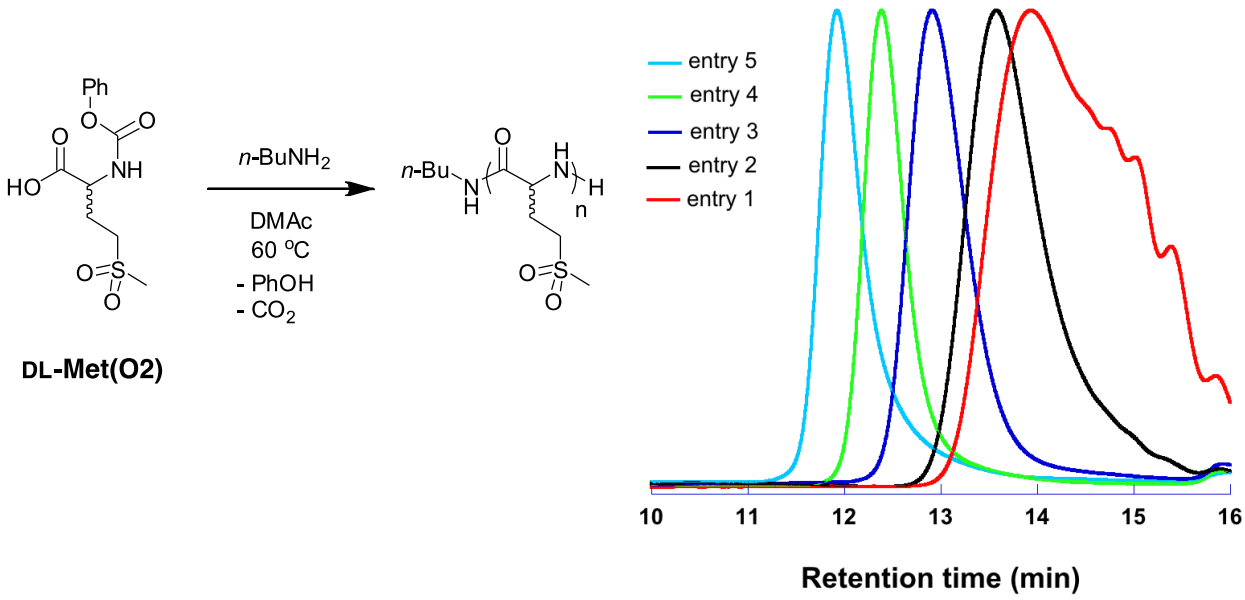

Figure S3. SEC traces of poly(DL-methionine sulfone) by polycondensation of **DL-Met(O2)** in the presence of *n*-$BuNH_2$ (entries 1-5, in Table S1)

Table S1. Synthesis of poly(DL-methionine sulfone) by polycondensation of **DL-Met(O2)** in the presence of *n*-$BuNH_2$

entry	feed ratio [**DL-Met(O2)**]$_0$ /[*n*-$BuNH_2$]$_0$	reaction time (h)	conv. (%) [a]	yield (%) [b]	M_n [c]	M_w/M_n [c]
1	5	5	>99	95	1,400	1.41
2	10	12	>99	93	2,500	1.36
3	25	20	>99	98	7,300	1.31
4	50	24	>99	92	15,000	1.14
5	100	48	>99	95	28,000	1.21

[a] Calculated by ^{1}H NMR spectra

[b] Ether-insoluble parts

[c] Estimated by SEC (eluent: DMF solution of LiBr (10 mM), calibrated by Polystyrene standards)

Table S2. Synthesis of poly(L-methionine sulfone) by polycondensation of **L-Met(O2)** in the presence of *n*-$BuNH_2$

entry	feed ratio [**L-Met(O2)**]$_0$ /[*n*-$BuNH_2$]$_0$	reaction time (h)	conv. (%) [a]	yield (%) [b]	M_n [c]	M_w/M_n [c]
1	5	5	>99	94	-	-
2	10	12	>99	96	-	-
3	25	48	>99	98	-	-

[a] Calculated by ^{1}H NMR spectra

[b] Ether-insoluble parts

[c] Estimated by SEC (eluent: DMF solution of LiBr (10 mM), calibrated by Polystyrene standards)

M_n and M_w/M_n were not determined due to a low solubility of polypeptide for an eluent.

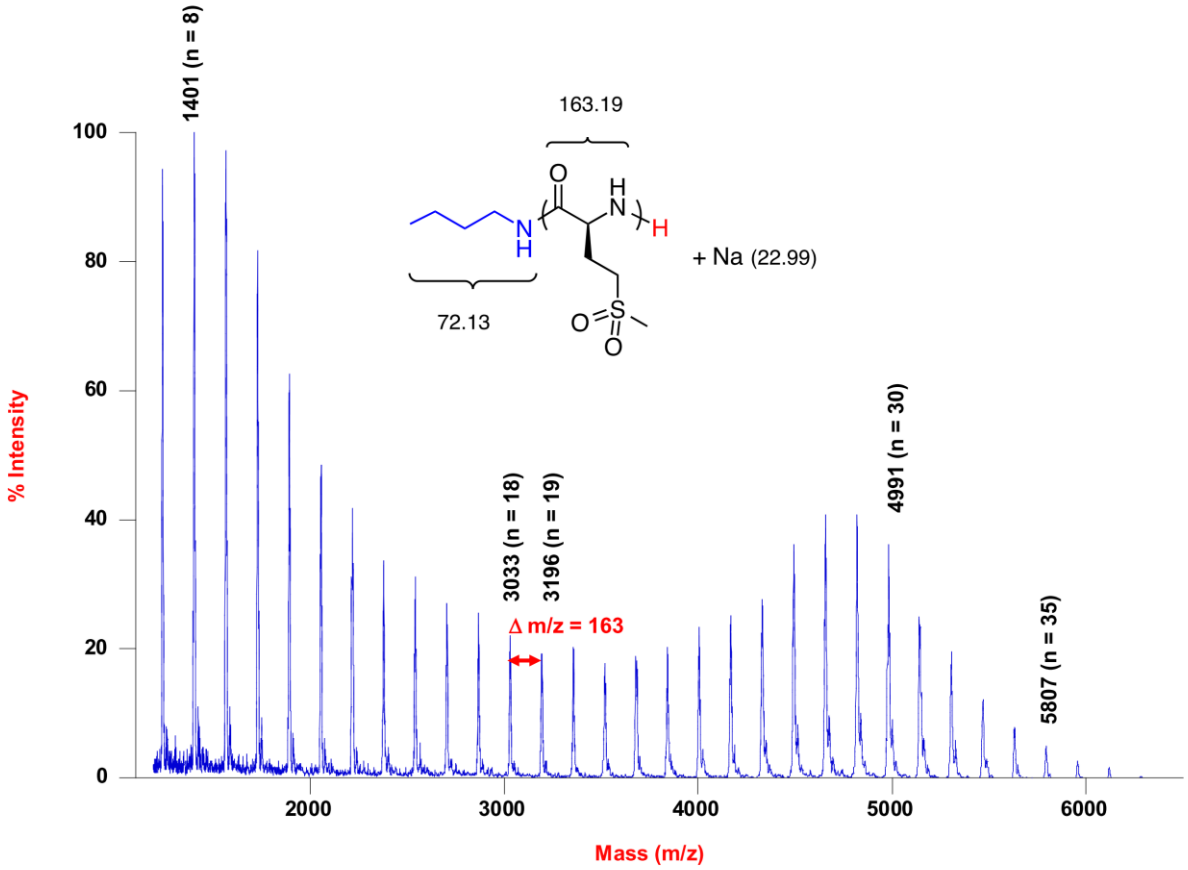

Figure S4. MALDI-TOF mass result of poly(L-methionine sulfone) obtained from polycondensation of **L-Met(O2)** in the presence of *n*-$BuNH_2$ (entry 3, in Table S2)

Table S3. Synthesis of diblock copolymer through polycondensation of urethane derivative in the presence of an amine-terminated poly(ethylene glycol) (PEG-NH_2)

entry	urethane derivative	feed ratio $[\mathbf{M}]_0/[\text{amine}]_0$	reaction time (h)	conv. (%) [a]	yield (%) [b]	M_n	M_w/M_n
1	**DL-Met**	10	10	>99	82	13700 [c]	1.19 [c]
2	**DL-Met**	25	20	>99	92	16,900 [c]	1.20 [c]
3	**DL-Met**	50	24	>99	87	23,000 [c]	1.18 [c]
4	**DL-Met(O))**	10	10	>99	90	5,600 [d]	1.17 [d]
5	**DL-Met(O)**	25	20	>99	91	6,460 [d]	1.21 [d]
6	**DL-Met(O)**	50	24	>99	93	8,200 [d]	1.32 [d]
7	**DL-Met(O2)**	10	10	>99	89	12,800 [c]	1.12 [c]
8	**DL-Met(O2)**	25	15	>99	93	22,000 [c]	1.12 [c]
9	**DL-Met(O2)**	50	24	>99	95	29,000 [c]	1.14 [c]

[a] Calculated by ^{1}H NMR spectra

[b] Ether-insoluble parts

[c] Estimated by SEC (eluent: DMF solution of LiBr (10 mM), calibrated by Polystyrene standards)

[d] Estimated by SEC (eluent: PBS, calibrated by Poly(ethylene glycol) standards)

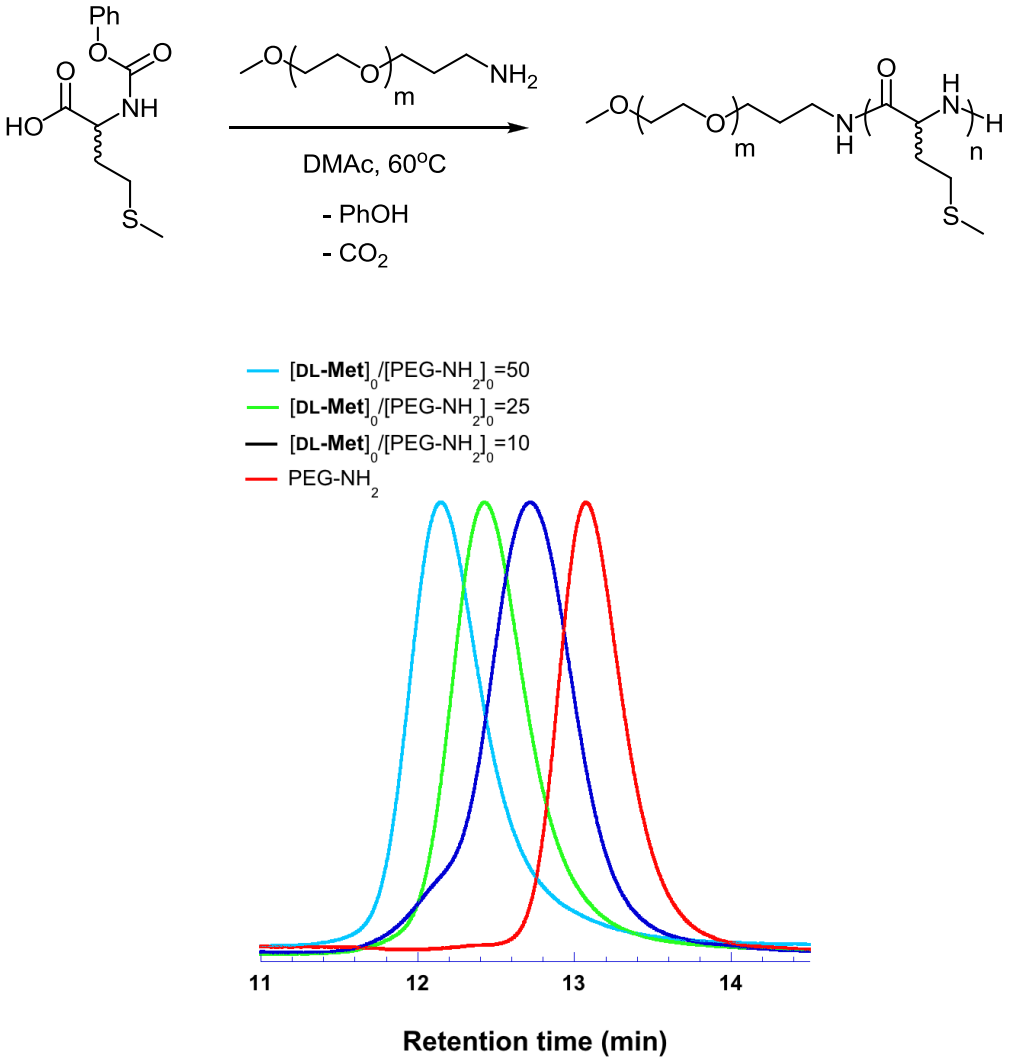

Figure S5. SEC traces of poly(DL-methionine) by polycondensation of **DL-Met** in the presence of PEG-NH_2 (M_n = 5,300 and PDI =1.04).

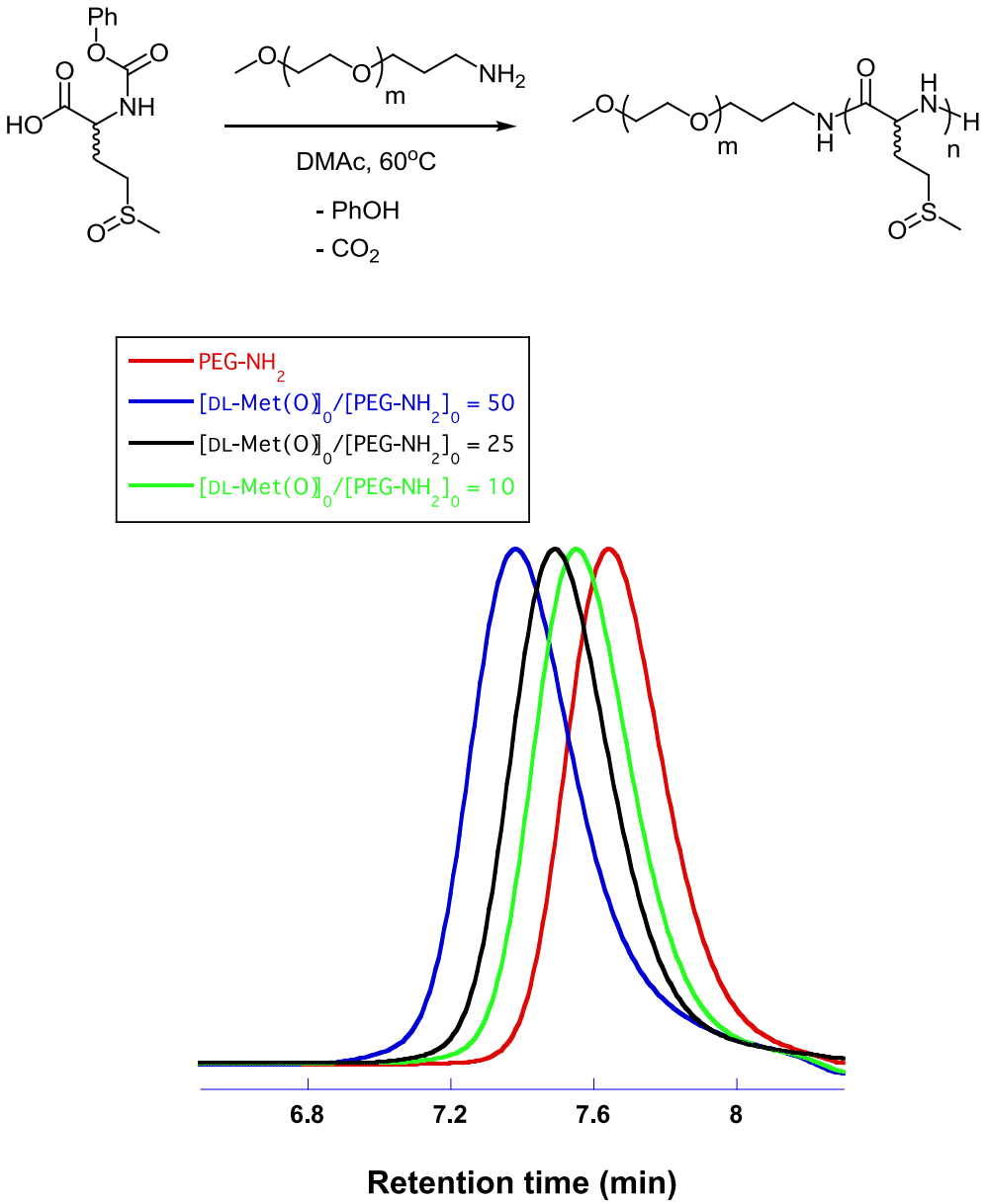

Figure S6. SEC traces of poly(DL-methionine) by polycondensation of **DL-Met(O)** in the presence of PEG-NH_2 (M_n = 5,000 and PDI =1.06).

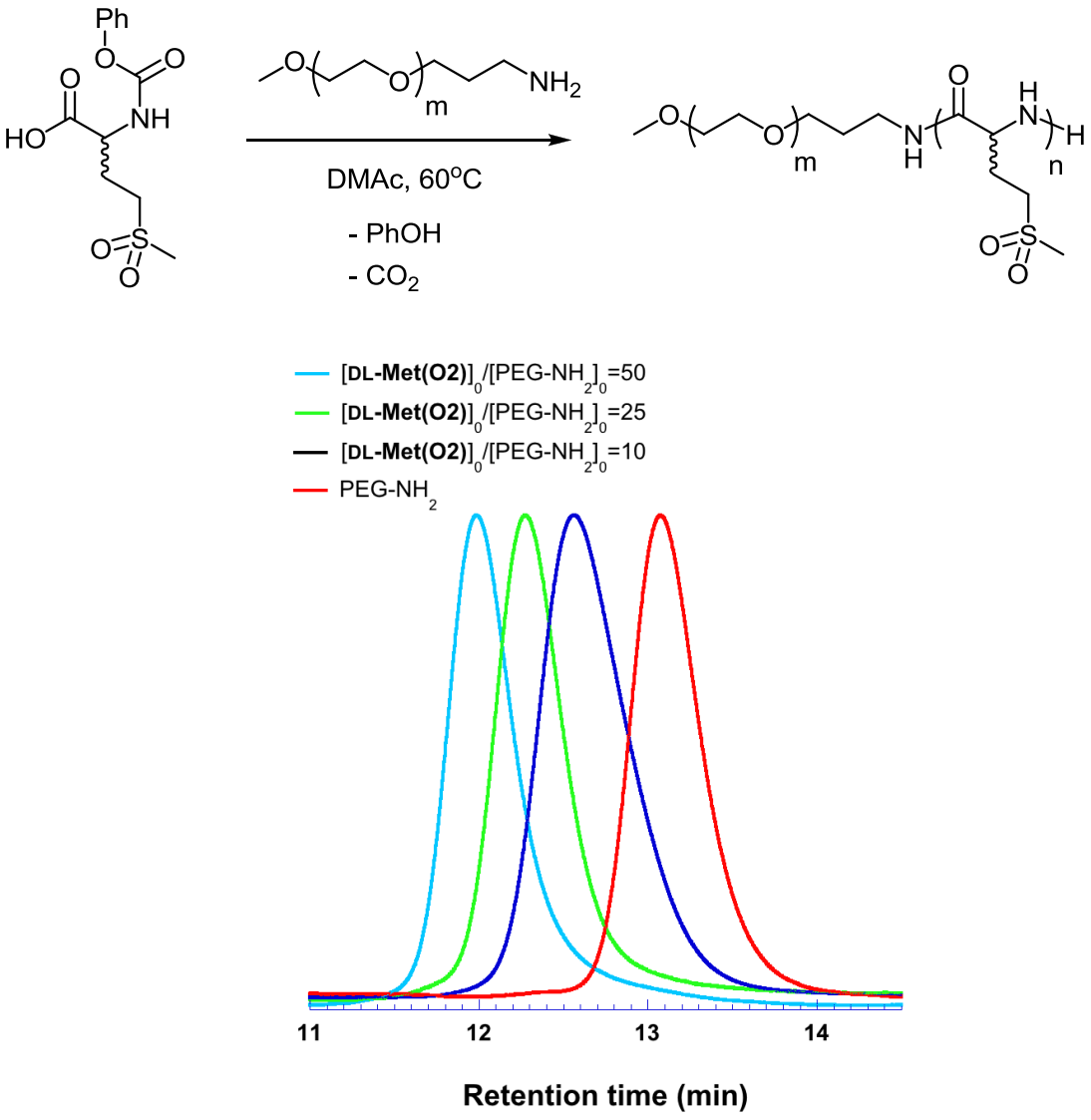

Figure S7. SEC traces of poly(DL-methionine) by polycondensation of **DL-Met(O2)** in the presence of PEG-NH_2 (M_n = 5,300 and PDI =1.04).

After polycondensation, the desired oligopeptide with a polymerizable group at the terminal was isolated as ether-insoluble parts in good yield (85%).

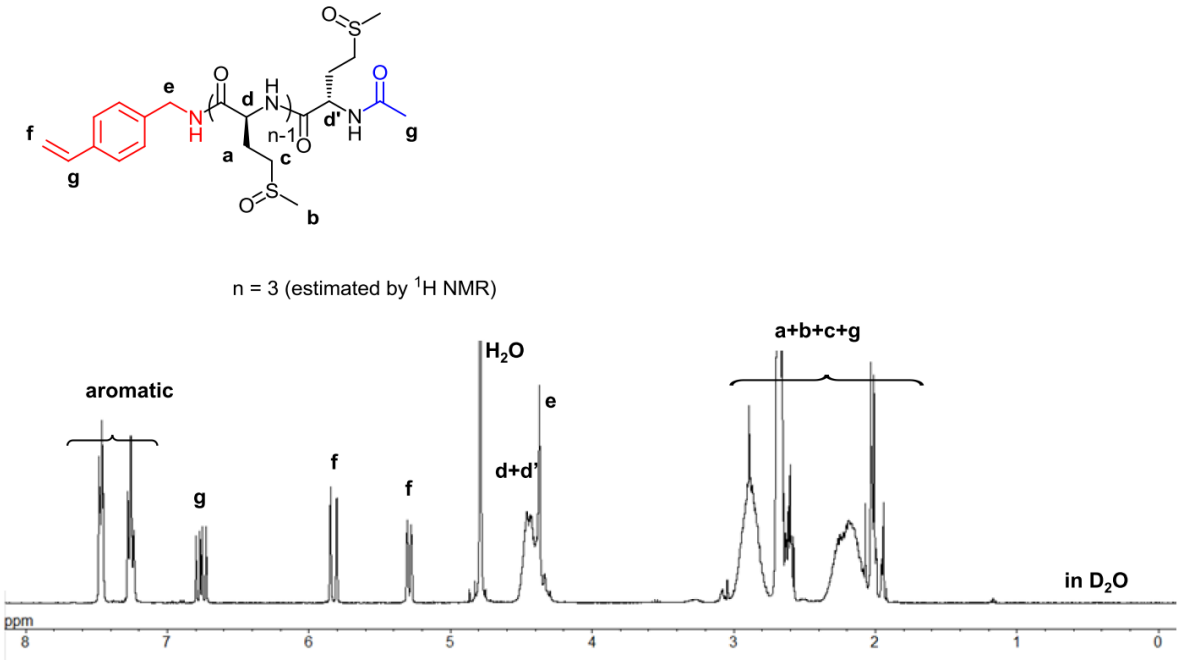

Figure S8. ^{1}H NMR spectrum of oligo(L-methionine sulfoxide) with styrene group at the terminal prepared by polycondensation of **L-Met(O)** in the presence of 4-vinylbenzylamine.

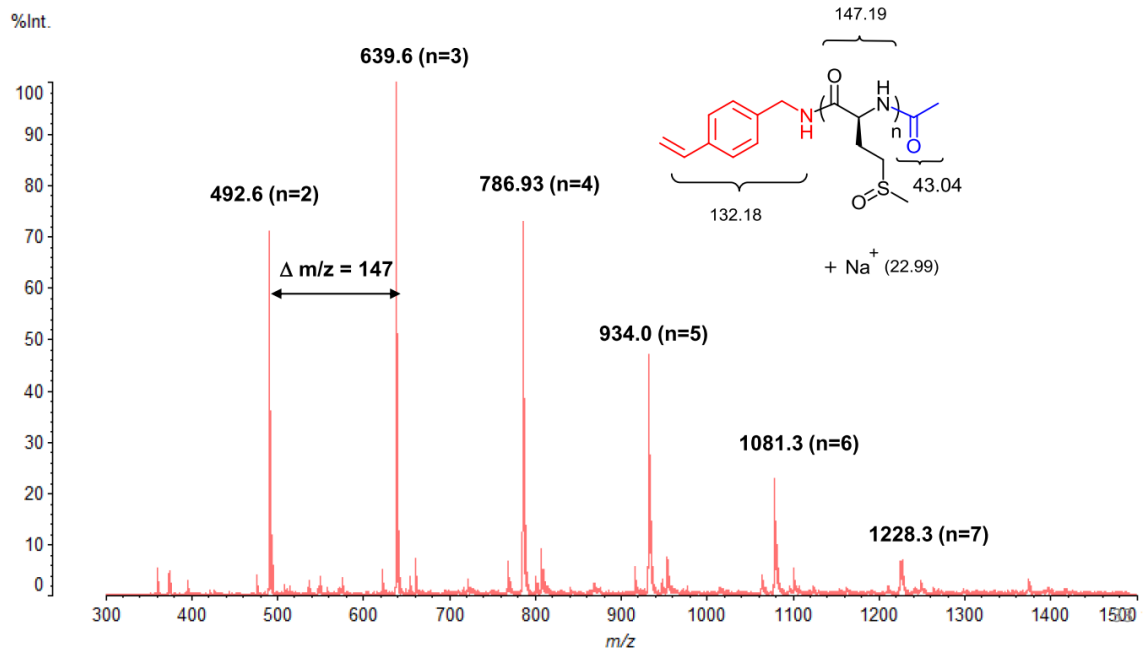

Figure S9. MALDI-TOF mass result of oligo(L-methionine sulfoxide) with styrene group at the terminal.

Radical polymerization of oligopeptide with styrene group was performed in aqueous solution (10 wt%) with V-501 (5 mol%) as an initiator at 70 ^{o}C for 15 hours. The resultant reaction mixture was purified by a dialysis in cellulose tube (M_w cutoff = 3,500). Freeze drying of the aqueous solution gave a desired polymer as a white powder in high yield (94%)

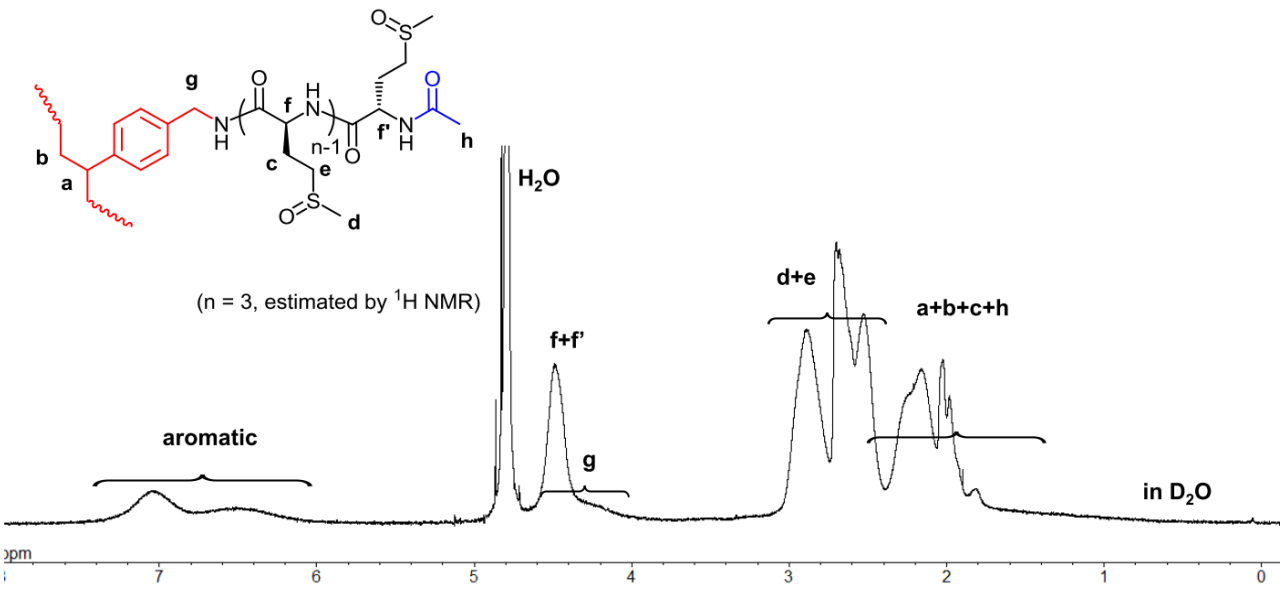

Figure S10. ^{1}H NMR spectrum of polystyrene bearing oligo(L-methionine sulfoxide), **PSt-PLMet(O)**.

The effect of terminal amine on the side chain on cytotoxicity against F9 cells was also evaluated using CCK-8 assay. Each polystyrene bearing oligo(L-methionine sulfoxide) showed high biocompatibility even in the concentration of 1mg/mL.

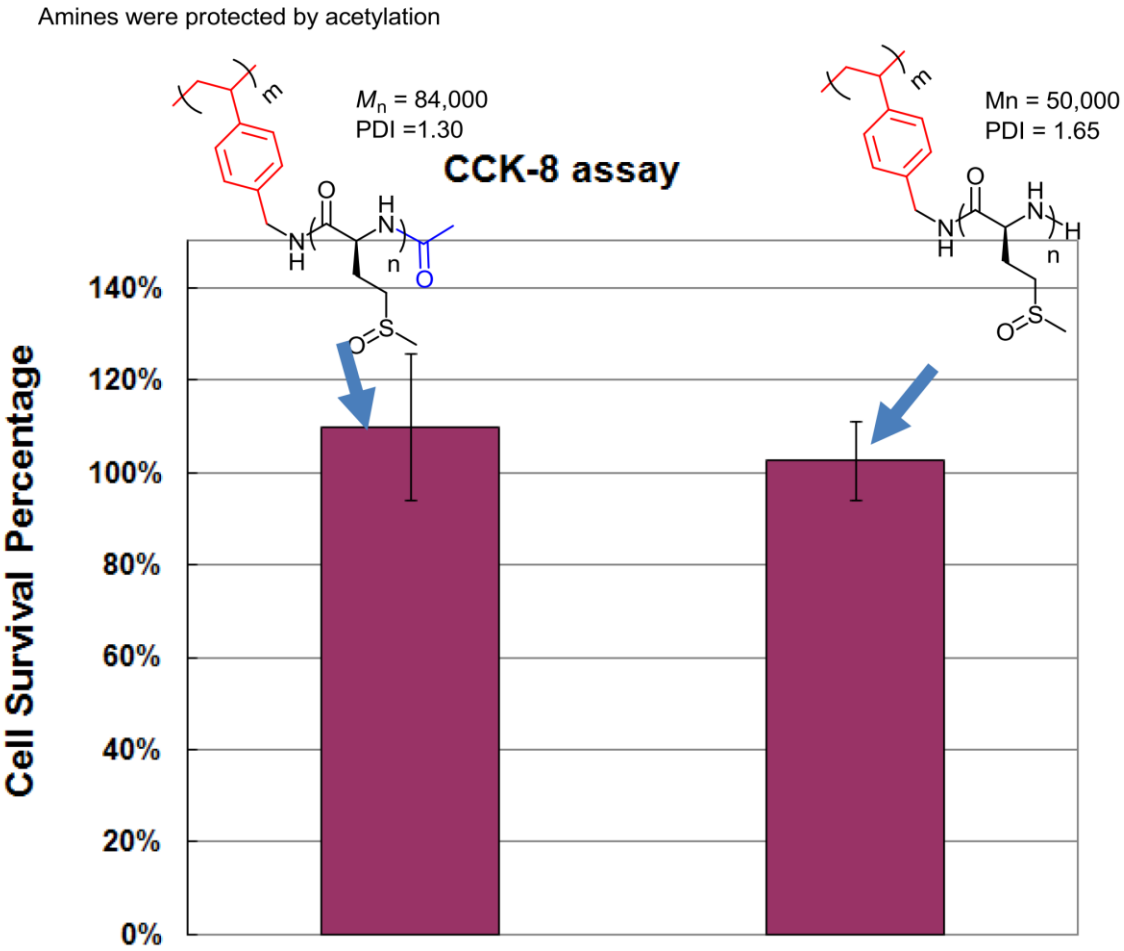

Figure S11. Calculation of F9 cells survival percentage in the presence of polystyrene bearing oligo(L-methionine sulfoxide) (1mg/mL) by CCK-8 assay.