

## Supplementary Information

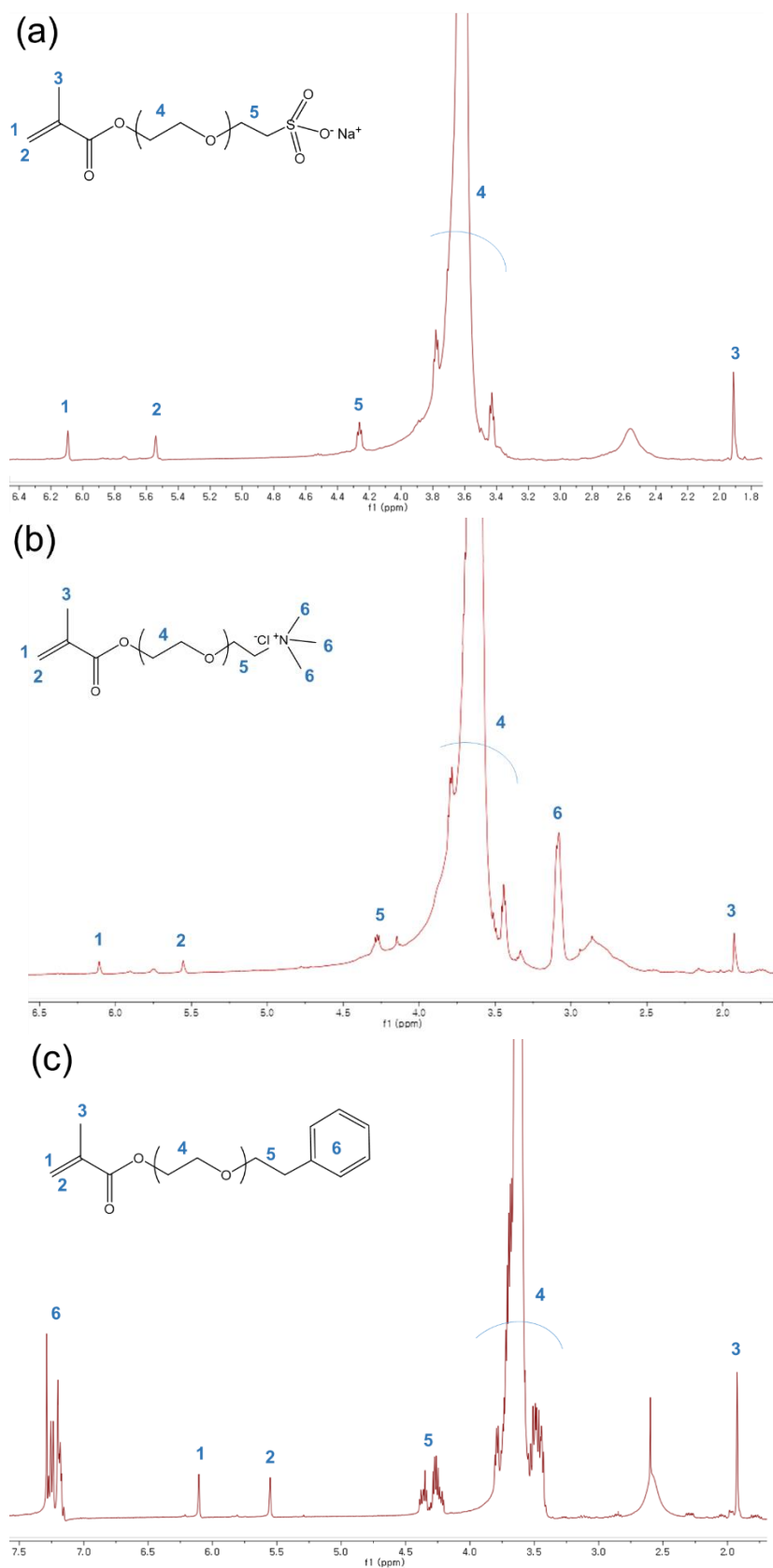
Modulation of functional pendant chains within poly(ethylene glycol) hydrogels for refined control of protein release

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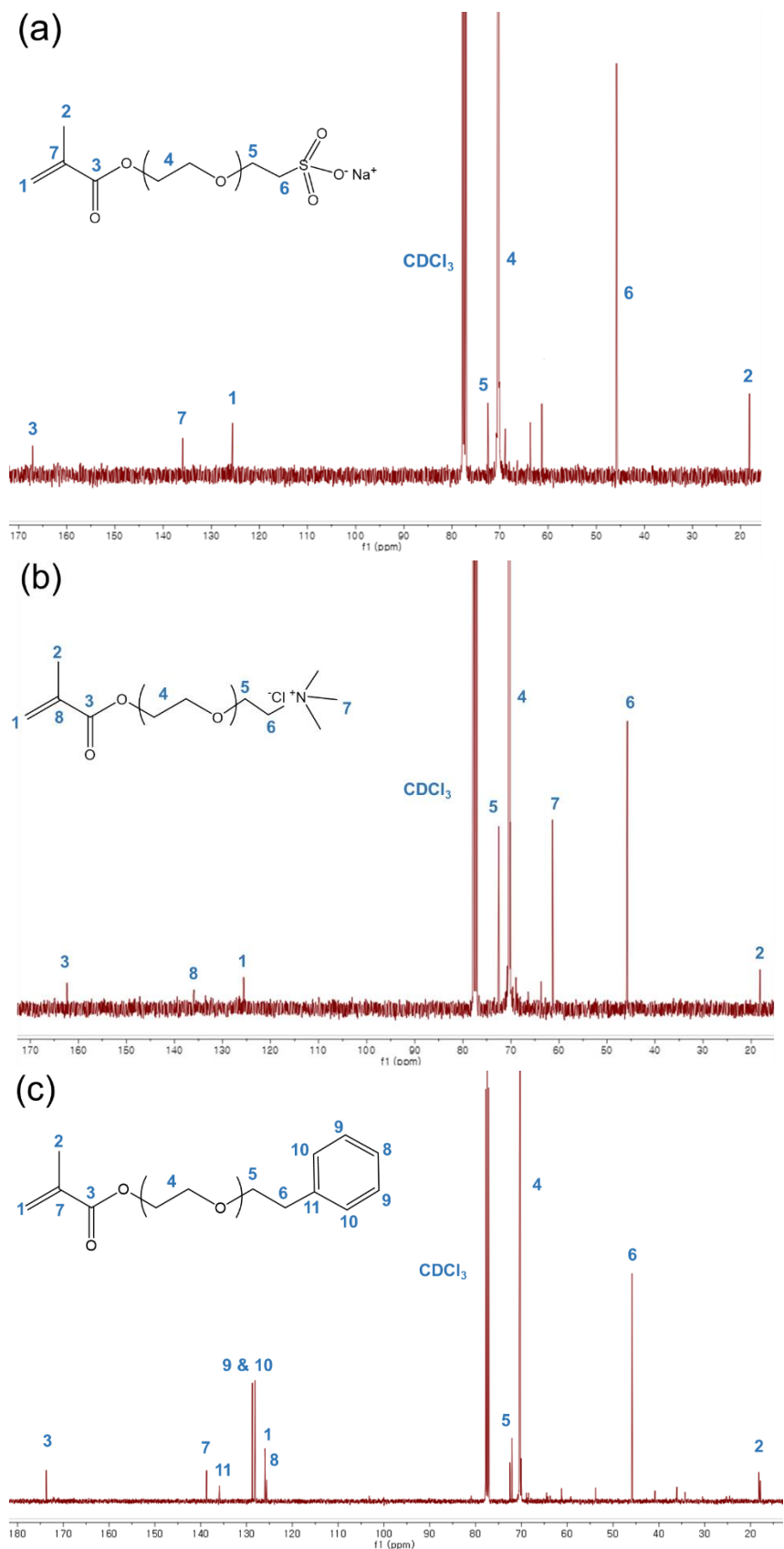
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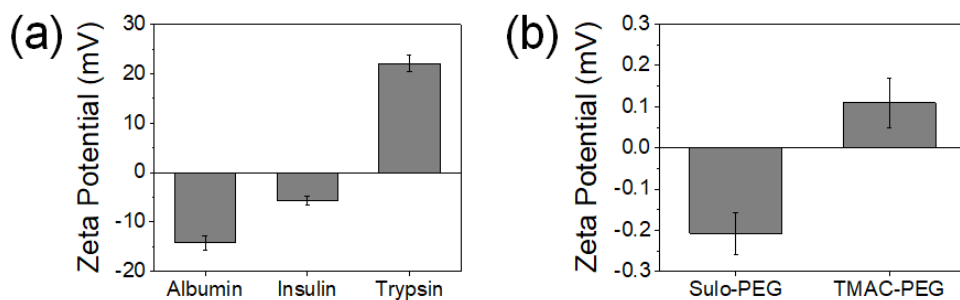
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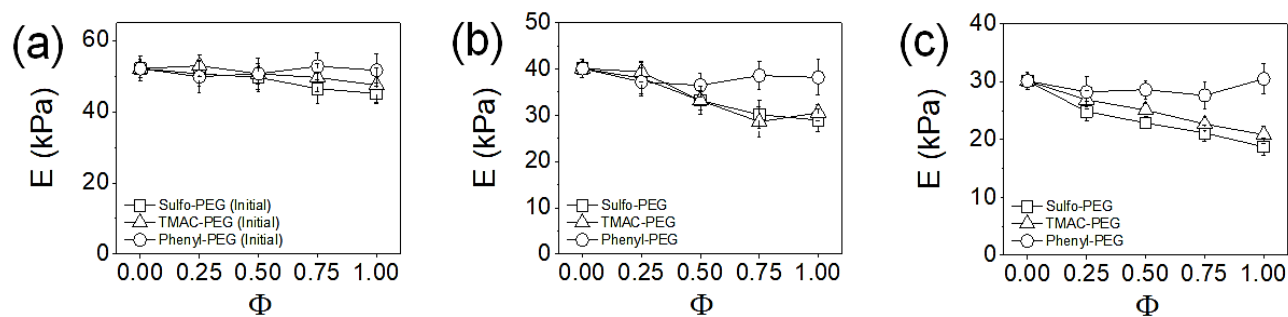
**FIGURE S1.**  $^1\text{H-NMR}$  spectra of (a) Sulfo-PEG, (b) TMAC-PEG, and (c) Ph-PEG.



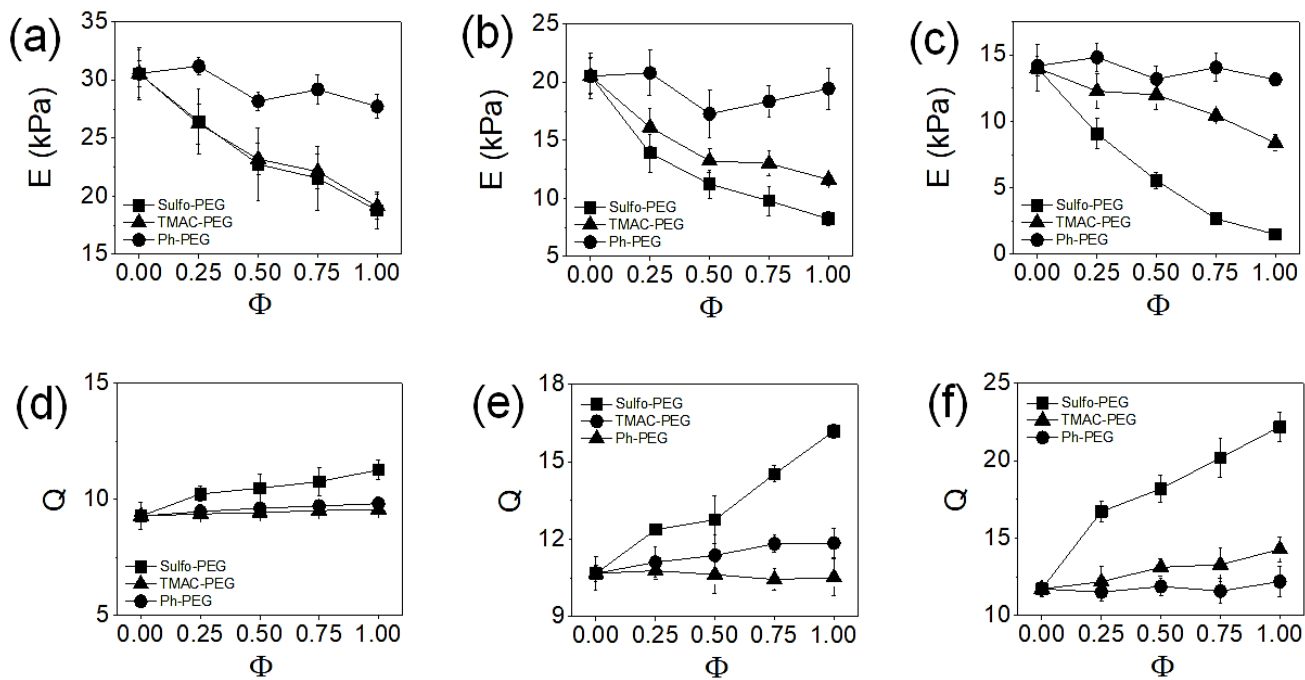
**FIGURE S2.**  $^{13}\text{C}$ -NMR spectra of (a) Sulfo-PEG, (b) TMAC-PEG, and (c) Ph-PEG.



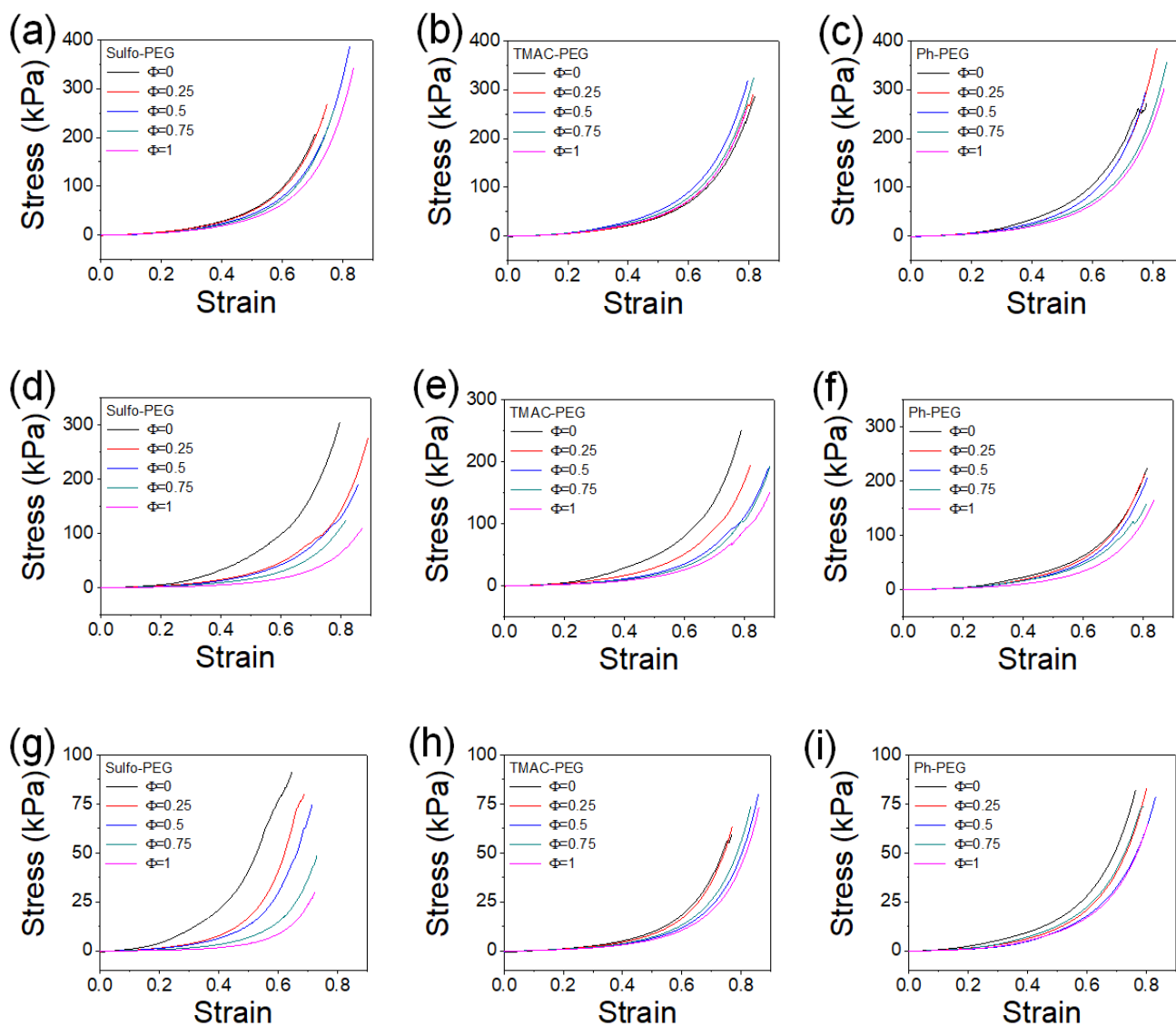
**FIGURE S3.** Zeta potential values of (a) proteins (albumin, insulin, and trypsin) and (b) Sulfo-PEGMA and TMAC-PEGMA, measured at 0.1 % (w/v) in 10 mM NaCl.



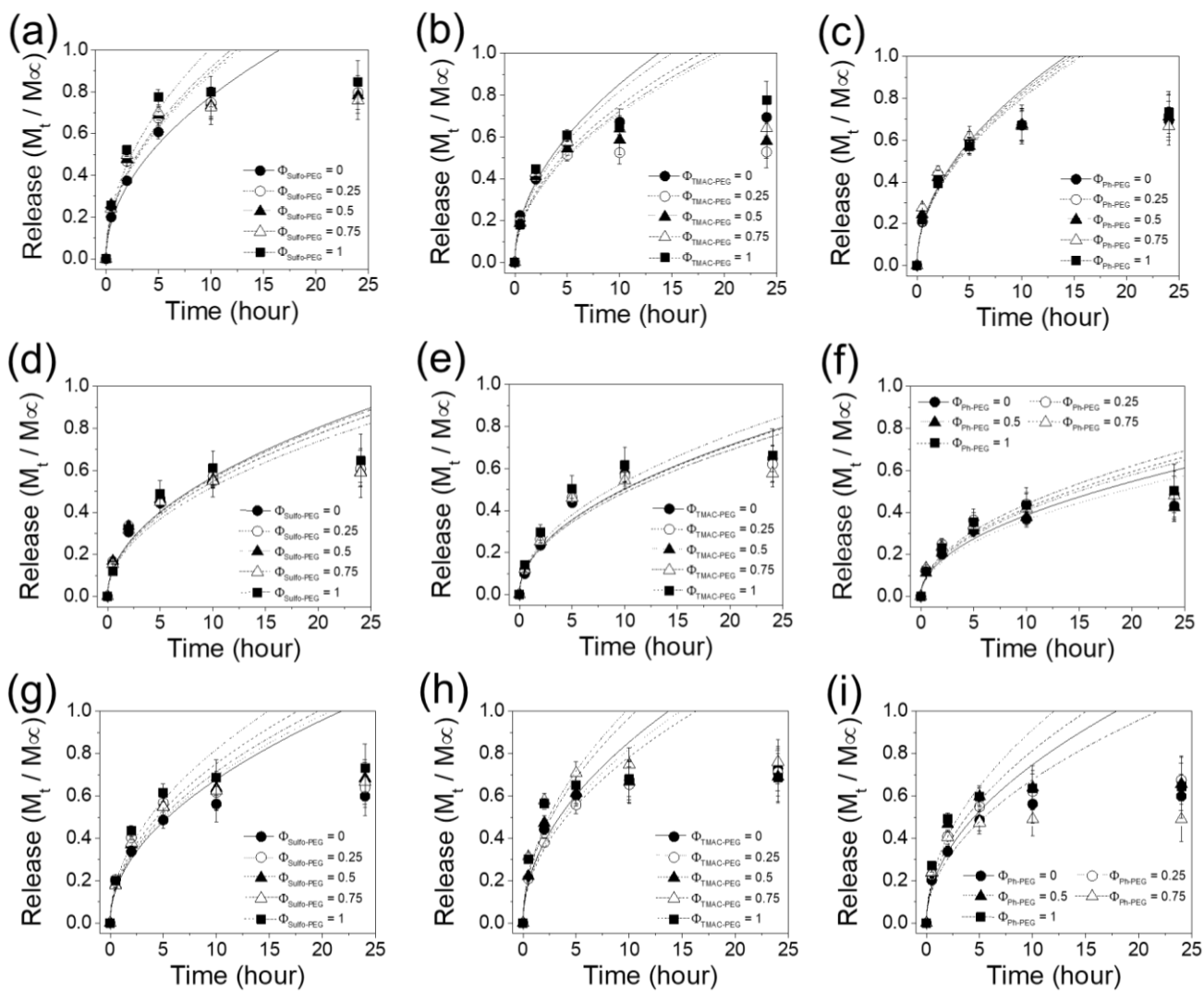
**FIGURE S4.** Elastic moduli ( $E$ ) of Sulfo-PEG, TMAC-PEG, and Ph-PEG hydrogels measured right after fabrication ('initial moduli'). The PEGDA and PEGMA concentrations of the hydrogels were (a) 10 % and 2 %, (b) 8 % and 4 %, and (c) 6 % and 6 %.



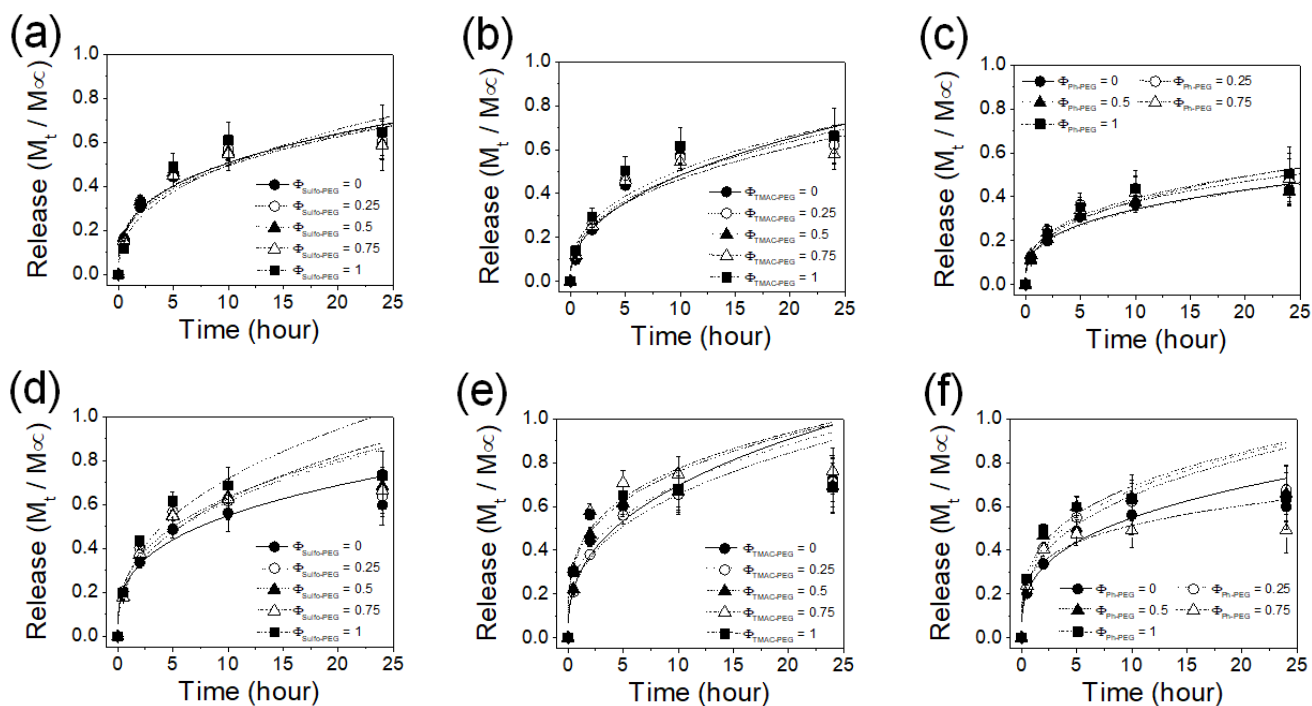
**FIGURE S5.** (a-c) Elastic moduli ( $E$ ) and (d-e) swelling ratios ( $Q$ ) of Sulfo-PEG, TMAC-PEG, and Ph-PEG hydrogels. The PEGDA and PEGMA concentrations of the hydrogels were (a,d) 10 % and 2 %, (b,e) 8 % and 4 %, and (c,f) 6 % and 6 %.  $E$  and  $Q$  were measured after 1 day of incubation in PBS.



**FIGURE S6.** Strain-stress curves of (a, d, g) Sulfo-PEG, (b, e, h) TMAC-PEG, and (c, f, i) Ph-PEG hydrogels obtained by uniaxial compression. The PEGDA and PEGMA concentrations of the hydrogels were (a-c) 10 % and 2 %, (d-f) 8 % and 4 %, and (g-i) 6 % and 6 %.

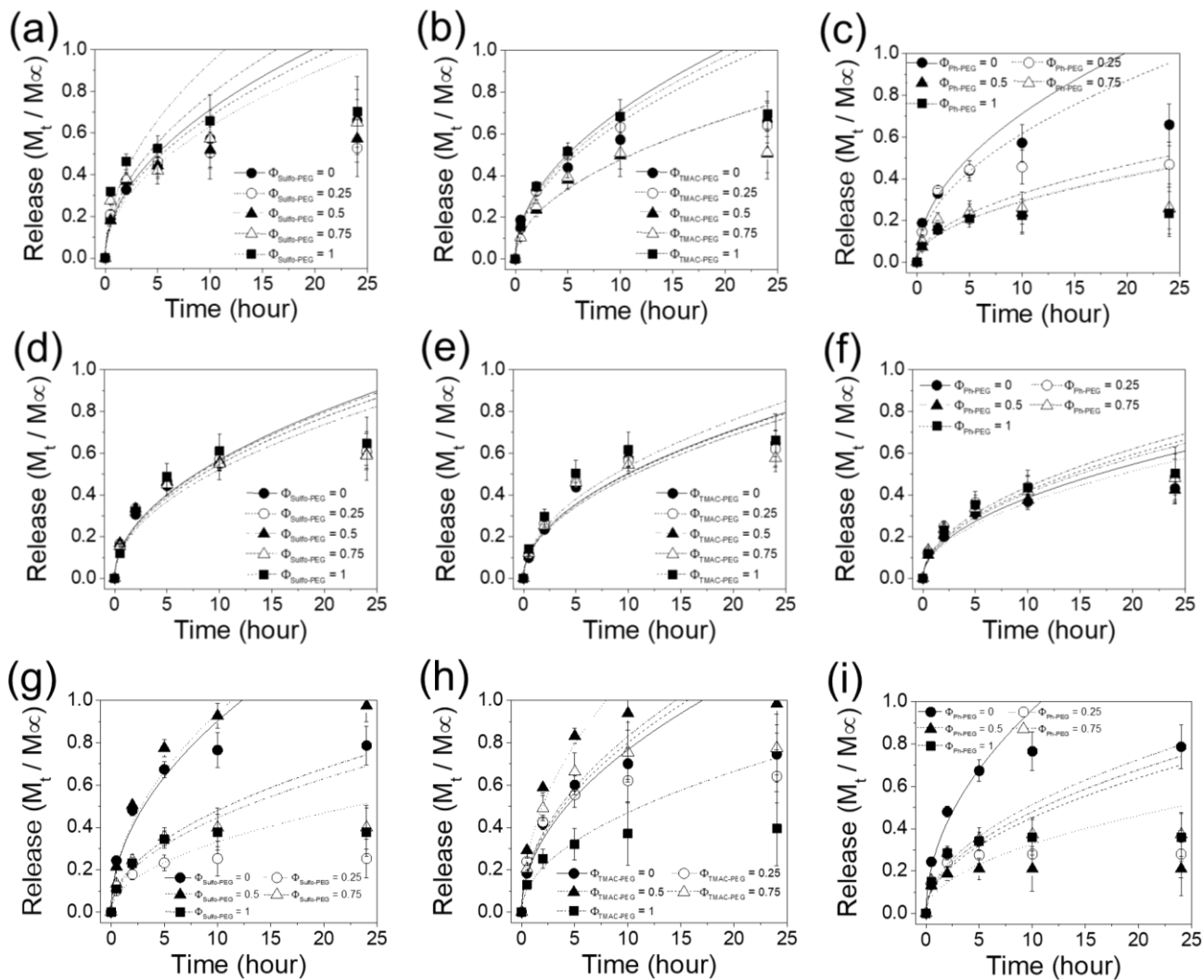


**FIGURE S7.** Release profiles of albumin from (a, d, g) Sulfo-PEG hydrogels, (b, e, h) TMAC-PEG hydrogels, and (c, f, i) Ph-PEG hydrogels. The profiles were fitted with Eq. (2). The PEGDA and PEGMA concentrations of the hydrogels were (a-c) 8 % and 4 %, (d-f) 10 % and 2 %, and (g-i) 6 % and 6 %.

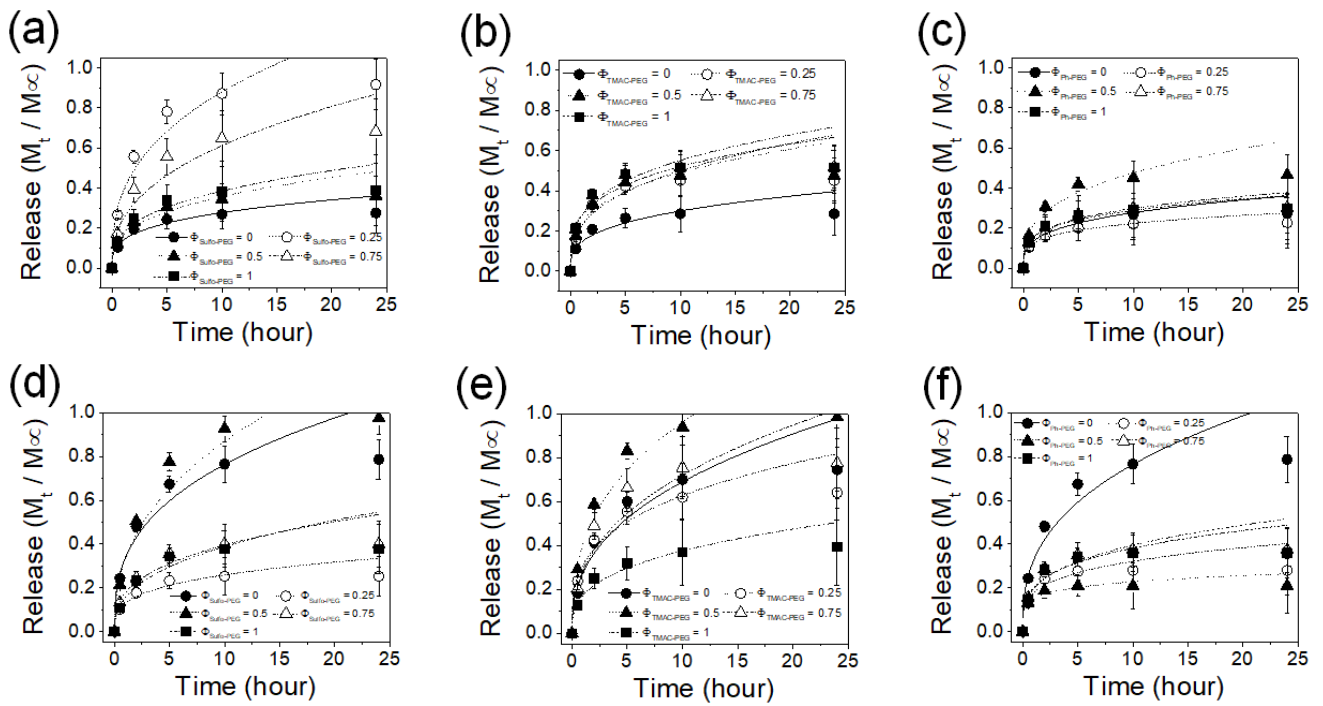


**FIGURE S8.** Release profiles of albumin from (a, d) Sulfo-PEG hydrogels, (b, e) TMAC-PEG hydrogels, and (c, f) Ph-PEG hydrogels. The profiles were fitted with Eq. (1). (a-c) 10% PEGDA and 2% PEGMA, (d-f) 6% PEGDA and 6% PEGMA.

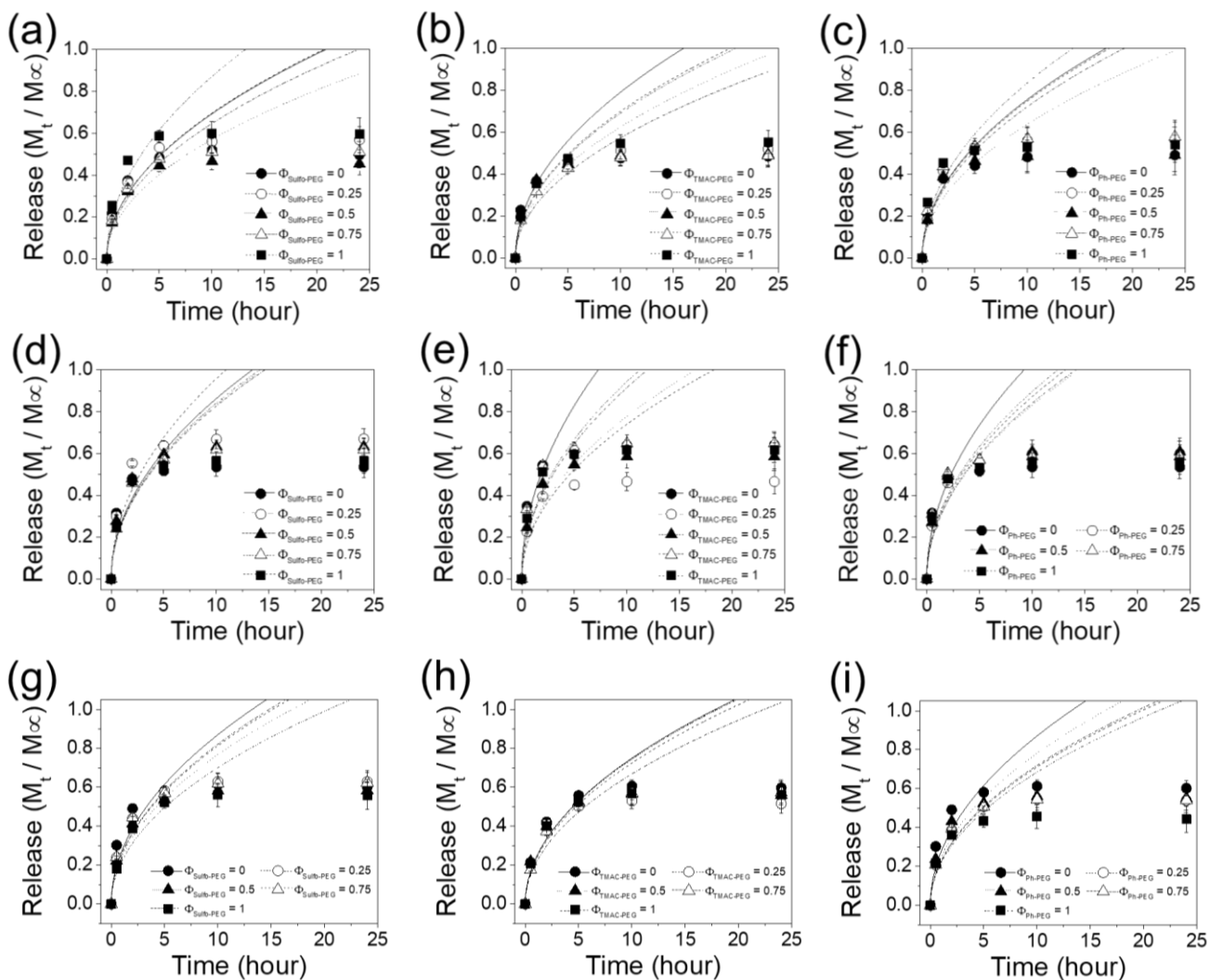




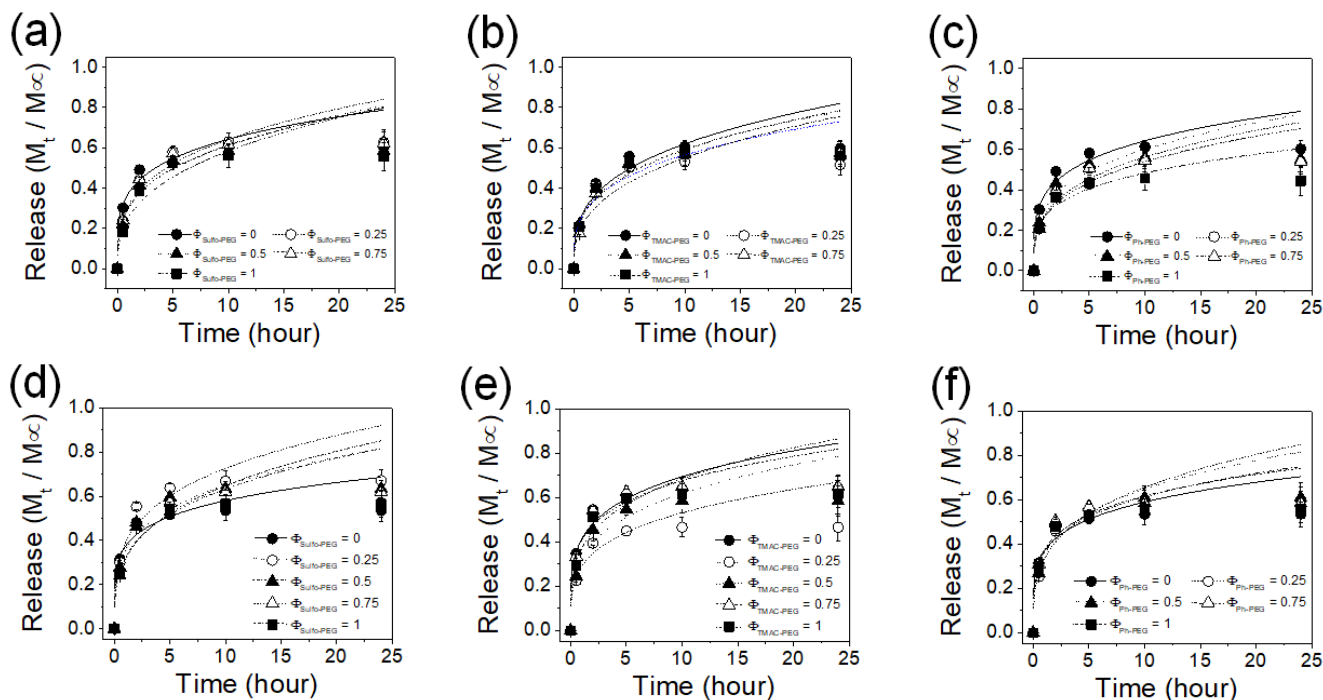
**FIGURE S9.** Release profiles of insulin from (a, d, g) Sulfo-PEG hydrogels, (b, e, h) TMAC-PEG hydrogels, and (c, f, i) Ph-PEG hydrogels. The profiles were fitted with Eq. (2). The PEGDA and PEGMA concentrations of the hydrogels were (a-c) 8 % and 4 %, (d-f) 10 % and 2 %, and (g-i) 6 % and 6 %.



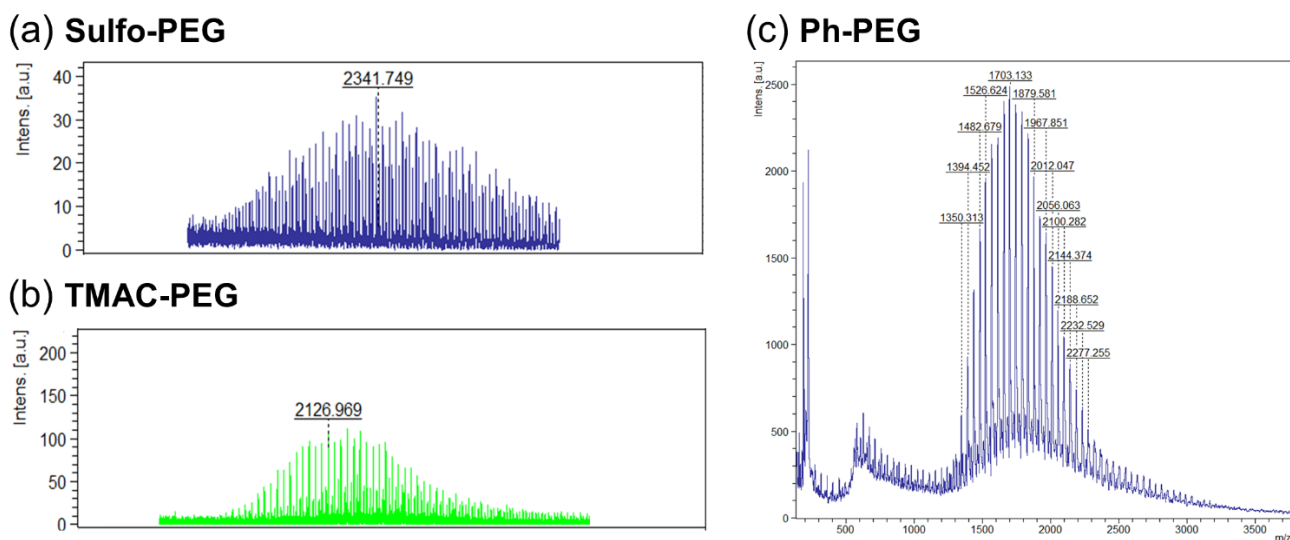
**FIGURE S10.** Release profiles of insulin from (a, d) Sulfo-PEG hydrogels, (b, e) TMAC-PEG hydrogels, and (c, f) Ph-PEG hydrogels. The profiles were fitted with Eq. (1). (a-c) 10% PEGDA and 2% PEGMA, (d-f) 6% PEGDA and 6% PEGMA.



**FIGURE S11.** Release profiles of trypsin from (a, d, g) Sulfo-PEG hydrogels, (b, e, h) TMAC-PEG hydrogels, and (c, f, i) Ph-PEG hydrogels. The profiles were fitted with Eq. (2). The PEGDA and PEGMA concentrations of the hydrogels were (a-c) 8 % and 4 %, (d-f) 10 % and 2 %, and (g-i) 6 % and 6 %.



**FIGURE S12.** Release profiles of trypsin from (a, d) Sulfo-PEG hydrogels, (b, e) TMAC-PEG hydrogels, and (c, f) Ph-PEG hydrogels. (a-c) 10% PEGDA and 2% PEGMA, (d-f) 6% PEGDA and 6% PEGMA.



**FIGURE S13.** The molecular weight distributions of (a) Sulfo-PEG, (b) TMAC-PEG, and (c) Ph-PEG, determined from MALDI-TOF mass spectrometry.