Electronic Supplementary Material (ESI) for Biomaterials Science.

Table S1. Summary of PEG hydrogel groups (Total: 21 groups).

Group Abbreviation	**Monomer**	**MW*** (kDa)	**Conc.** (% (w/v))
Chain-growth-polymerized hydrogels (MW 2 kDa)	PEGDA (2 kDa)	2	10,15,20
Chain-growth-polymerized hydrogels (MW 4 kDa)	PEGDA (4 kDa)	4	
Chain-growth-polymerized hydrogels (MW 5 kDa)	PEGDA (5 kDa)	5	
Step-growth-polymerized hydrogels (4arm PEG, MW 2.5 kDa)	4arm PEG-NB (5 kDa), 4arm PEG-SH (5 kDa)	2.5	
Step-growth-polymerized hydrogels (4arm PEG, MW 4 kDa)	4arm PEG-NB (5 kDa), PEG-diSH (1.5 kDa)	4	
Step-growth-polymerized hydrogels (8arm PEG, MW 2.5 kDa)	8arm PEG-NB (10 kDa), 8arm PEG-SH (10 kDa)	2.5	
Step-growth-polymerized hydrogels (8arm PEG, MW 4 kDa)	8arm PEG-NB (10 kDa), PEG-diSH (1.5 kDa)	4	

***** MW is defined as molecular weight between adjacent crosslinking points.

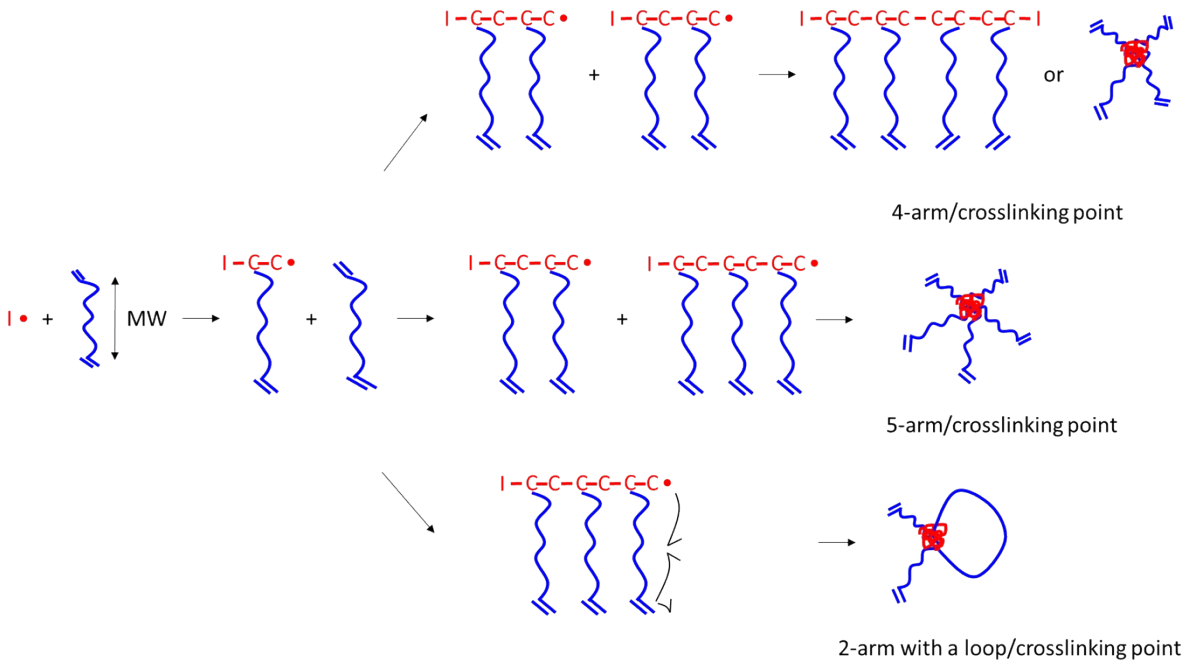

Figure S1. Possible crosslink functionalities in chain-growth-polymerized hydrogel. Crosslink functionality is defined as the number of arms per crosslinking point. Due to random nature of radical propagation and termination in chain-growth-polymerization, crosslink functionality is not fixed across the hydrogel. (Red represents a crosslinking point and blue represents PEGDA monomer. I and C stand for initiator and carbon respectively. Red dots represent radicals.)

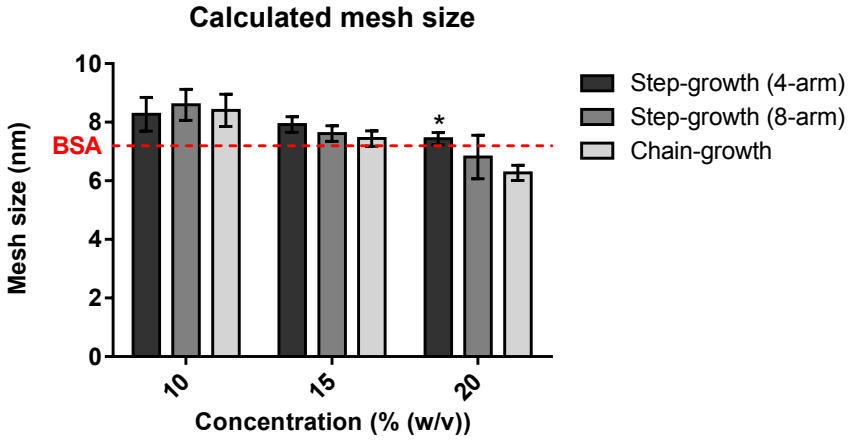

Figure S2. Calculated network mesh size of chain-growth- and step-growth-polymerized hydrogels. Chain-growth-polymerized hydrogels (light grey) were constructed from 4 kDa PEGDA and step-growth-polymerized hydrogels were constructed from 4 kDa 4-arm (black) or 8-arm (dark grey) PEG. Hydrogel network mesh size was calculated according to Flory-Rehner theory as previously described [1]. Hydrodynamic diameter of BSA is 7.2 nm. *$p<0.05$ compared to chain-growth-polymerized hydrogels.

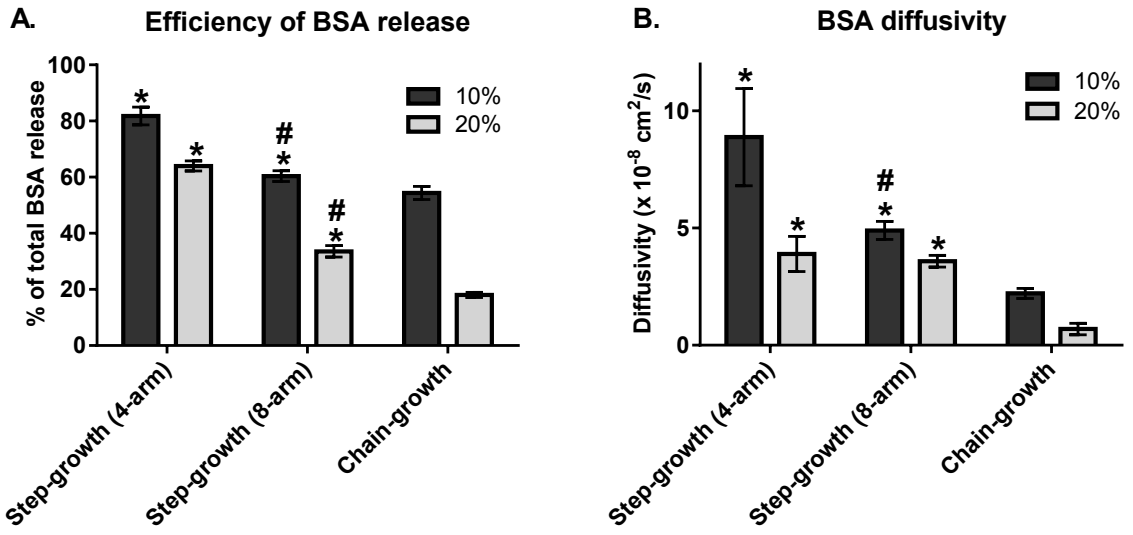

Figure S3. Effects of crosslinking mechanism and crosslink functionality on BSA release. Chain-growth-polymerized hydrogels were constructed from 4 kDa PEGDA and step-growth-polymerized hydrogels were constructed from 4 kDa 4-arm or 8-arm PEG (10, 20% (w/v)). (A) Effects of crosslinking mechanism and crosslink functionality on BSA release efficiency (M_t/M_{Load} x 100%). (B) Effects of crosslinking mechanism and crosslink functionality on BSA diffusivity. Data are presented as mean ± standard deviation (n=4). *$p<0.05$ compared to chain-growth-polymerized hydrogels; #$p<0.05$ compared to step-growth-polymerized hydrogels constructed from 4-arm PEG.

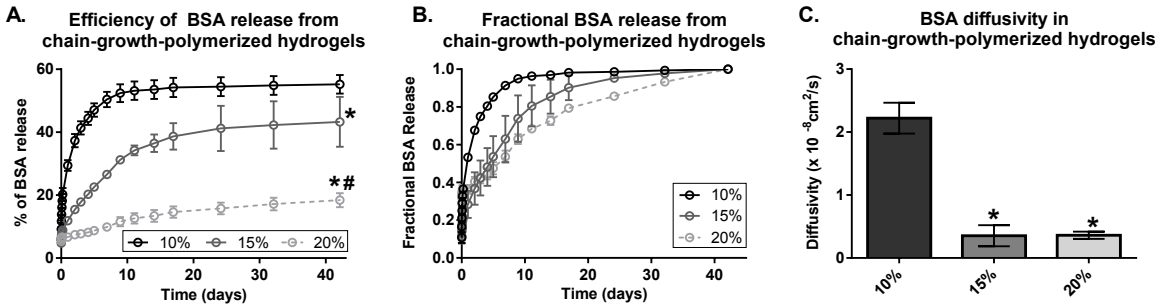

Figure S4. Effect of varying PEG concentration on BSA release from chain-growth-polymerized hydrogels. All chain-growth-polymerized hydrogels are MW 2 kDa with PEGDA concentrations of 10% (black), 15% (dark grey), or 20% (light grey) (w/v). (A) Effect of varying PEG concentration on BSA release efficiency (M_t/M_{Load} x 100%). (B) Effect of varying PEG concentration on fractional BSA release (M_t/M_∞). (C) Effect of varying PEG concentration on BSA diffusivity. Data are presented as mean ± standard deviation (n=4). *$p<0.05$ compared to the corresponding 10% gels; #$p<0.05$ compared to the corresponding 15% gels.

(1) Lee, S.; Tong, X.; Yang, F. The effects of varying poly(ethylene glycol) hydrogel crosslinking density and the crosslinking mechanism on protein accumulation in three-dimensional hydrogels. *Acta biomaterialia* **2014**, *10*, (10), 4167-74, DOI: 10.1016/j.actbio.2014.05.023.