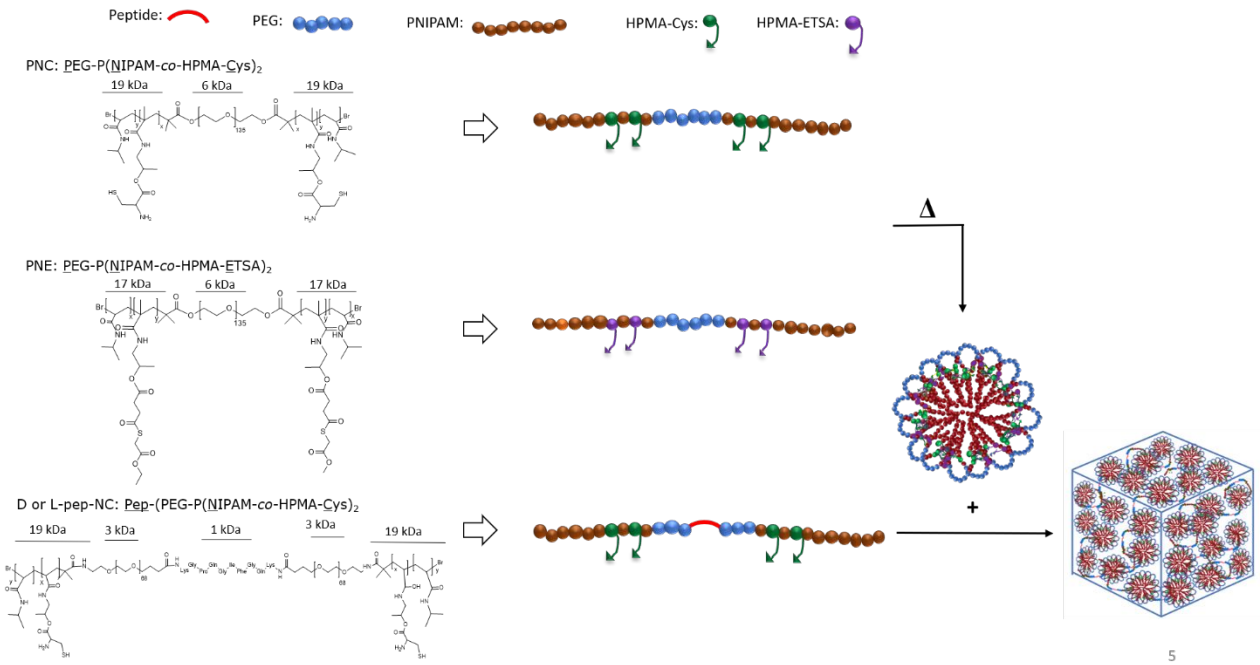
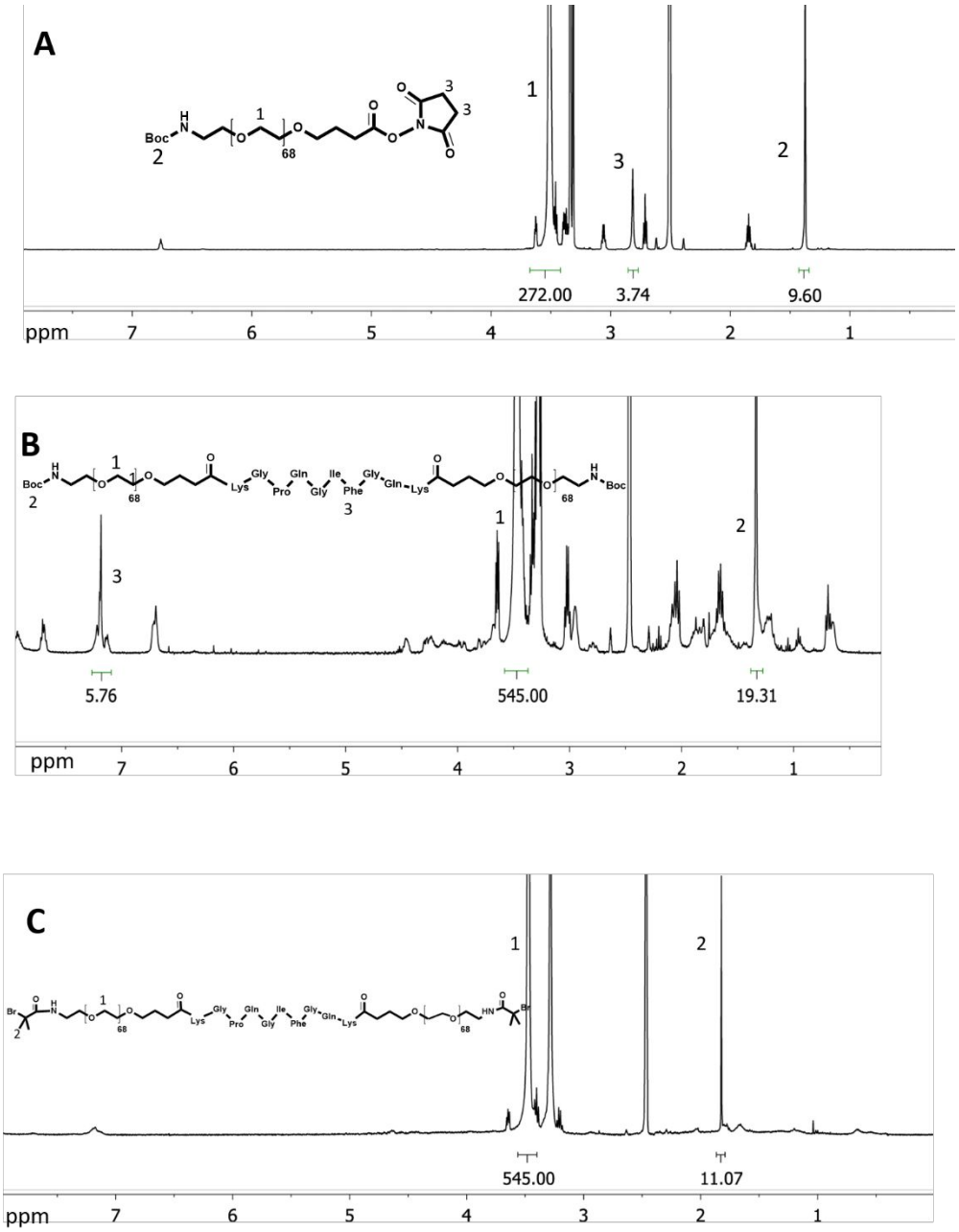
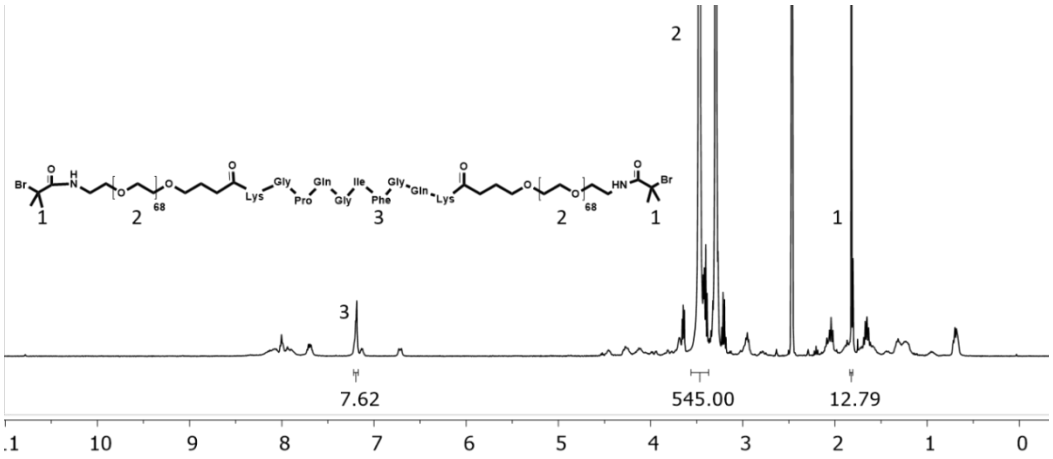
Supporting information



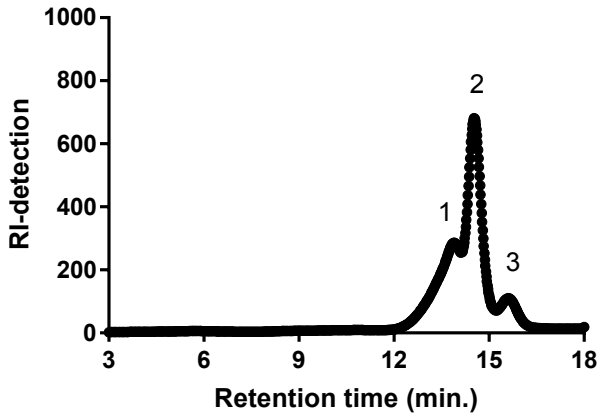
SI-figure 1: The structures of PNC, PNE, and Pep-NC. Core crosslinked flower-like micelles made from PNC and PNE linked via Pep-NC to yield a macroscopic hydrogel based on CCL crosslinked with an enzymatically cleavable spacer.



SI-Figure 2: ^{1}H-NMR spectra of A) starting material of alpha-*t*-butyloxycarbonylamino-ω-carboxy succinimidyl ester poly(ethylene glycol) (Boc-NH-PEG-NHS) (PEG-M_n 3 kDa), B) L-Pep-PEG conjugate before deprotection of boc group, C) L-Pep-PEG ATRP macroinitiator. The integrations are normalized based on the number of hydrogens in the corresponding PEG molecules. Deuterated DMSO was used as solvent.

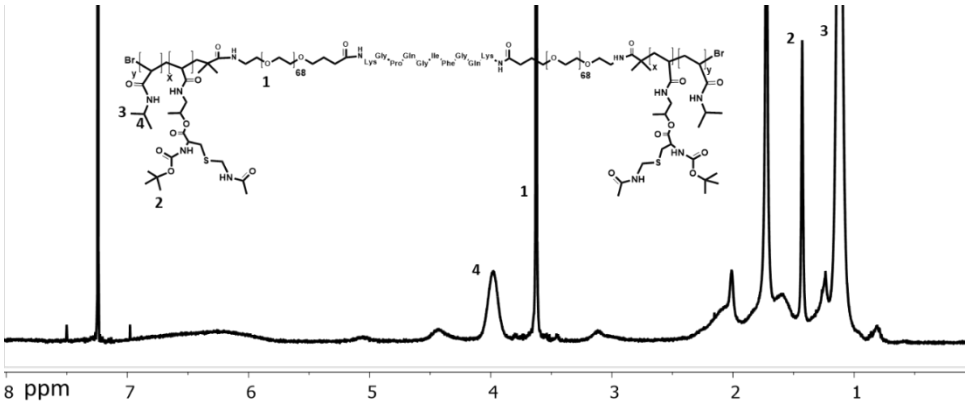


SI-Figure 3: ^{1}H-NMR spectrum of D-Pep-PEG ATRP macroinitiator. The integrations are normalized based on the number of hydrogens in the corresponding PEG molecules. Deuterated DMSO was used as solvent.

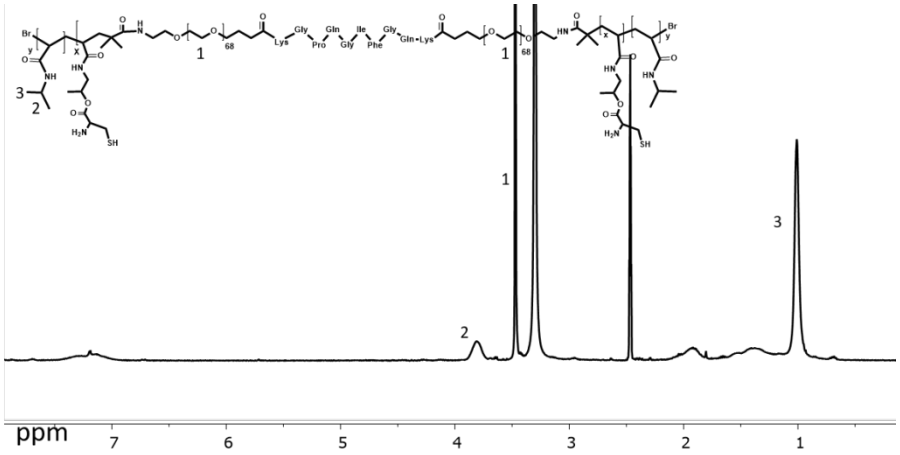


SI-Figure 4: GPC chromatogram of D-Pep-PEG ATRP macroinitiator in DMF containing 10 mM LiCl. Peak 1 corresponds to conjugation of peptide to the higher M_n PEG derivative present in the commercial starting compound 2 (see Fig. 1.), peak 2 confirms formation of PEG-D-Pep-PEG with a M_n of 7.9 kDa , and peak 3 belongs to non-conjugated PEG (M_n: 3.4 kDa).

A

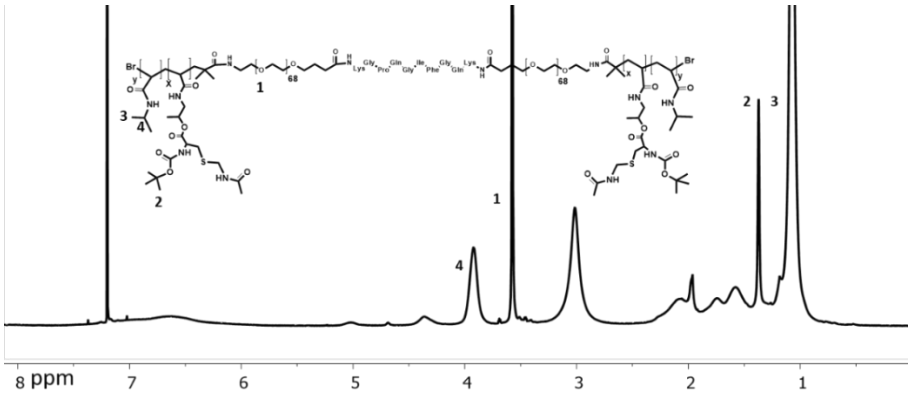


B

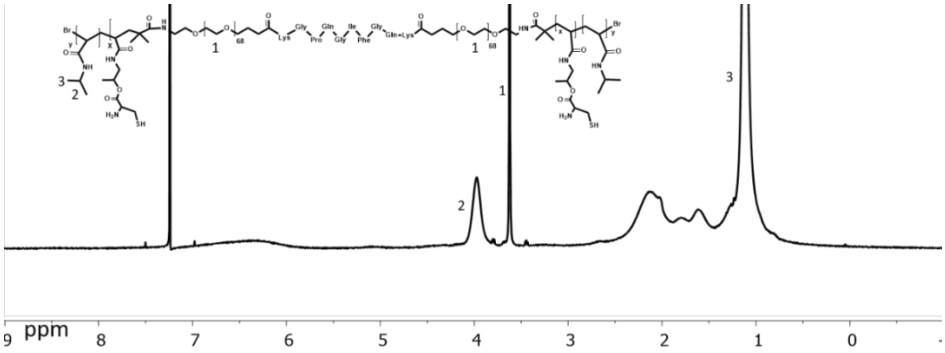


SI-Figure 5: A) ^{1}H-NMR spectrum of protected L-Pep-NC in $CDCl_3$, B) ^{1}H-NMR spectrum of L-Pep-NC in deuterated DMSO.

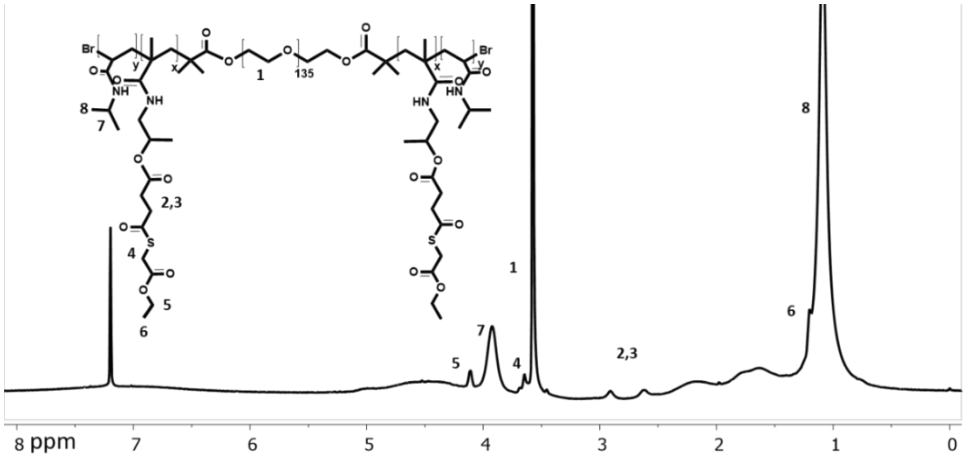
A



B

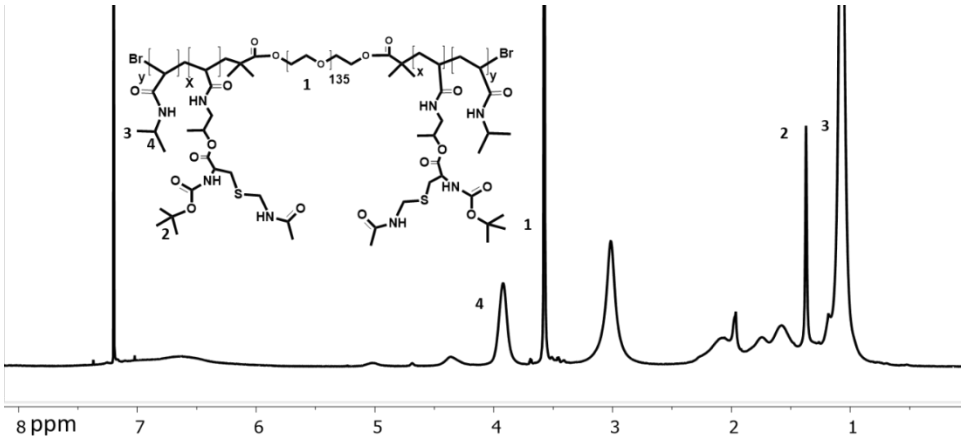


SI-Figure 6: A) ^{1}H-NMR spectrum of protected D-Pep-NC in $CDCl_3$ B) ^{1}H-NMR spectrum of D-Pep-NC in $CDCl_3$.

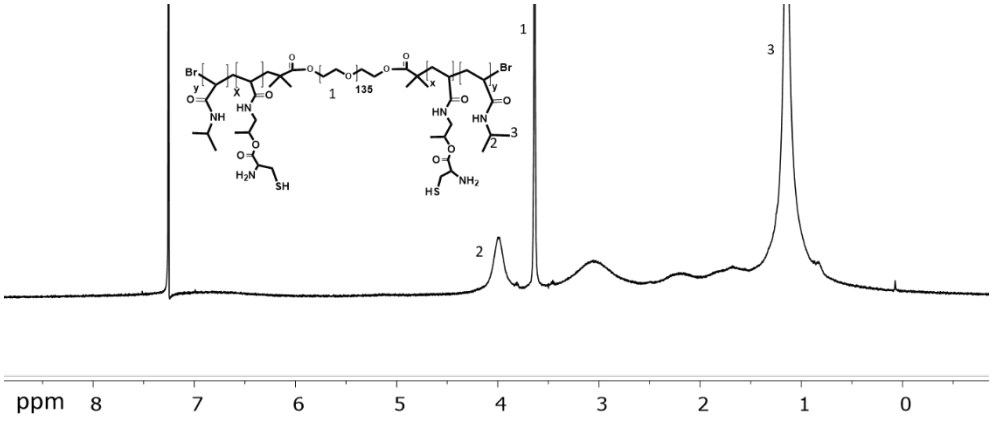


SI-Figure 7*:* ^{1}H-NMR spectrum of PNE in $CDCl_3$.

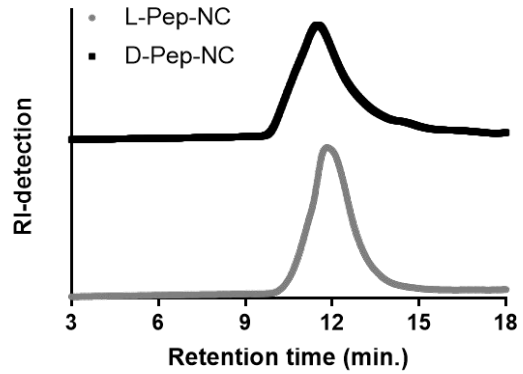
A



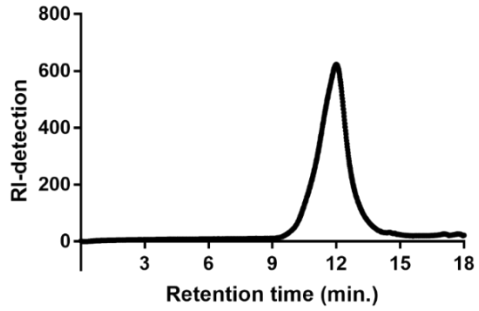
B



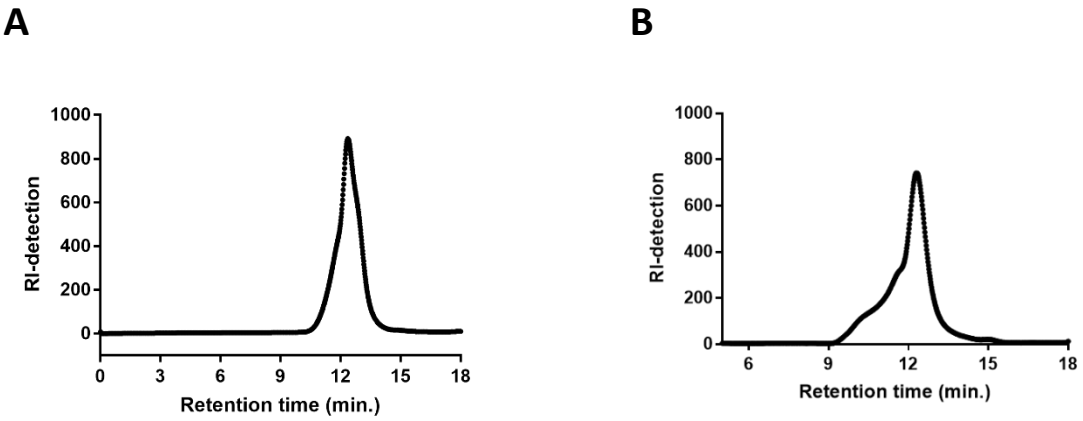
SI-Figure 8: A) ^{1}H-NMR spectrum of protected PNC in $CDCl_3$, B) ^{1}H-NMR spectrum of PNC in $CDCl_3$.



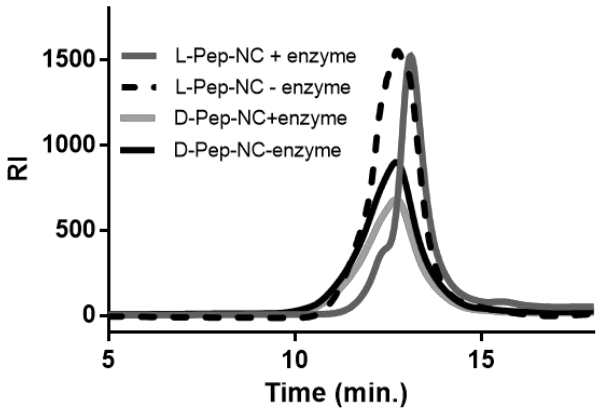
SI-Figure 9: GPC chromatogrammes of L-Pep-NC and D-Pep-NC in DMF containing 10 mM LiCl.



SI-Figure 10: GPC chromatogram of PNE in DMF containing 10 mM LiCl.

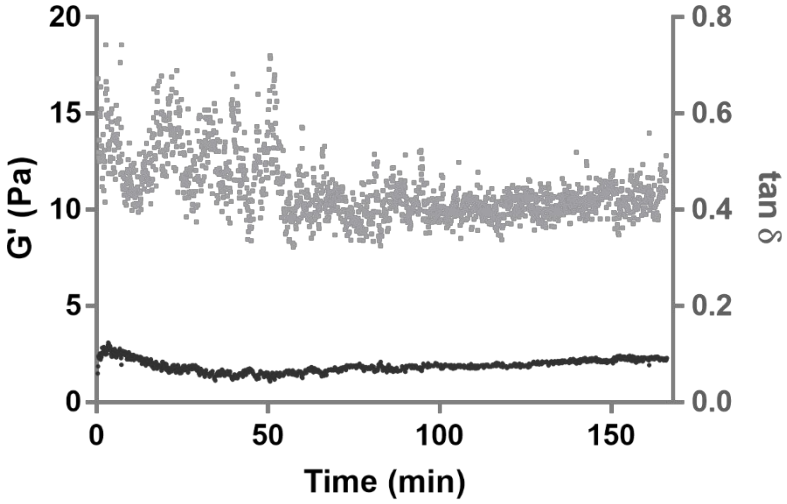


SI-Figure 11: GPC chromatograms of A) protected PNC B) PNC in DMF containing 10 mM LiCl.



Polymer	M_n (kDa)	
	- enzyme	+ enzyme
L-pep-NC	62.3	32.8
D-pep-NC	63.7	64.0

SI-Figure 12: GPC chromatograms of L-Pep-NC and D-Pep-NC before and after incubation with collagenase at a concentration of 30 units.mL^{-1} for 24 hours at 37°C.



SI-figure 13: Storage modulus (G') and tan δ as a function of time for micelles at 37 °C.