Table of Contents

1. Materials

All amino acids used to prepare peptides by solid phase peptide synthesis (SPPS) were obtained from AAPPTec, Chem-Impex, and NovaBiochem. *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA, 99%), eosin Y disodium salt (dye content > 85%), *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (EDC•HCl, 99%), 4-(dimethylamino)pyridine (DMAP, 98%)), 6-Fmoc-amino hexanoic acid (97%), and acetate buffer (0.1 M, pH 5) were purchased from Sigma Aldrich and used without purification. 2-(Dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) was synthesized according to previous literature.[1] 4-((((2-Carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid (water-soluble RAFT agent, 95%) and 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl]pentanoic acid (CDTPA, 97%) was purchased from Combi-Blocks and used without further purification. Methacryloxyethyl thiocarbamoyl rhodamine B was purchased from Polysciences, Inc.

Thermolysin was purchased from Promega. LED strip light (450 nm) was purchased from Amazon.

2. Methods

^{1}H Nuclear Magnetic Resonance (1H NMR): ^{1}H NMR spectra were recorded on a Varian Inova spectrometer (500 MHz) in d_6-DMSO or $CDCl_3$. Chemical shifts are given in ppm downfield from tetramethylsilane TMS.

Analytical High-Performance Liquid Chromatography (HPLC): Analytical HPLC analysis of peptides was performed on a Jupiter 4μ Proteo 90Å Phenomenex column (150 x 4.60 mm) using a Hitachi-Elite LaChrom L-2130 pump equipped with UV-Vis detector (Hitachi-Elite LaChrom L2420).

Preparative HPLC: Armen Glider CPC preparatory HPLC was used to purify the peptides. The solvent system consists of (A) 0.1% TFA in water and (B) 0.1% TFA in acetonitrile

Electrospray Ionization Mass Spectrometry (ESI-MS): ESI-MS spectra of peptides were collected using a Bruker Amazon-SL spectrometer configured with an ESI source in both negative and positive ionization mode.

Transmission Electron Microscope (TEM): Twenty microliters of sample were applied onto a 400 mesh carbon grids (Ted Pella, INC.). The grids were observed on a Hitachi HT 7700 microscope operating at 120 kV. The images were recorded with a slow-scan charge-coupled device (CCD) camera (Veleta 2k × 2k).

Gel Permeation Chromatography (GPC): GPC measurements were performed on a set of Phenomenex Phenogel 5μ, 1K-75K, 300 x 7.80 mm in series with a Phenomex Phenogel 5μ, 10K-1000K, 300 x 7.80 mm columns with HPLC grade solvents as eluents: dimethylformamide (DMF) with 0.05M of LiBr at 60 °C. Detection consisted of a Wyatt Optilab T-rEX refractive index detector operating at 658 nm and a Wyatt DAWN® HELEOS® II light scattering detector operating at 659 nm. Absolute molecular weights and polydispersities were calculated using the Wyatt ASTRA software with dn/dc values determined by assuming 100% mass recovery during GPC analysis.

Dynamic Light Scattering (DLS): DLS analysis was conducted at room temperature on a Zetasizer Nano-ZS (Malvern). The laser for DLS was at a wavelength of 633 nm

Circular Dichroism Spectrophotometer (CD): CD spectra were measured using a Jasco J-815 spectrometer and each sample was measured from 190 to 260 nm with a slit width of 1 nm, scanning at 1 nm intervals with a 1s integration time. Measurements were taken 3× at 25°C and then averaged to give the spectra. Notably, the peptide and polymer were dissolved in DIW to a concentration of 100 μM (with respect to peptide concentration).

Atomic Force Microscope (AFM): Samples were prepared by pipetting 50 μl of 10x dilution in water onto 1 cm^2 freshly cleaved mica and incubated at room temperature for 1 minute before blot drying by holding the edge of the mica onto lint free tissue. AFM images were acquired using a Bruker Dimension FastScan AFM using Fastscan A tips and analyzed with Nanoscope V1.9 software. Images were acquired with a scan rate of 3.6Hz at 512 pixels by 512 pixels resolution. Images were plane flattened in XY simultaneously and then flattened using a 0 nm threshold.

Confocal Laser Scanning Microscopy (CLSM): Imaging was accomplished using LEICA SP5 II laser scanning confocal microscope with a 63x oil immersion objective at 1.5x optical zoom. All the images were Z-stack images. Slice thickness was 0.26 μm with a scan size of 1024 x 1024 pixels and a scan speed of 400 Hz. The cell nuclei (stained with DAPI) was accomplished using a 405 nm laser with a 15% laser power. The cell membrane (stained with Wheat Germ Agglutinin, Alexa Fluor 488 Conjugate) was accomplished using a 488 nm laser with a 12% laser power. Cell imaging for Rhodamine fluorescence was accomplished using a 543 nm laser with an 8% laser power.

Flow Cytometry: The cell uptake study was analyzed via flow cytometry using a BD FacsAria IIu 4-Laser flow cytometer (Becton Dickinson Inc., USA). Mean fluorescence intensity and PE-A-histogram data was prepared for presentation using FlowJo v10.

3. Experimental

3.1 Preparation of Peptide Monomers via Solid-Phase Peptide Synthesis (SPPS)

Peptides were synthesized on Rink resin (0.67 mmol/g) using standard FMOC SPPS procedures on an AAPPTec Focus XC automated synthesizer. A typical SPPS procedure included deprotection of the *N*-terminal Fmoc group with 20 % 4-methyl-piperidine in DMF (1 × 20 min, followed by 1 × 5 min), and 30 min amide couplings (twice) using 3.0 equiv. of the Fmoc-protected amino acid, 2.9 equiv. of HBTU and 6 equiv. of DIPEA. After that, peptide monomers were prepared by amide coupling to Fmoc-6-aminohexanoic acid, followed by Fmoc

deprotection and final amidation with acrylic acid (3 equiv.) in the presence of HBTU (2.9 equiv.), and DIPEA (6 equiv.).

3.2 Photo-Polymerization in DMSO

In a typical organic phase photo-induced polymerization (**P1**), peptide (GPLGLAGG) acrylamide monomer (30 mg, 50 equiv.) and DMA (3.7 mg, 50 equiv.) were dissolved in 150 µL of DMSO. Then 10 µL (1.0 equiv.) of DDMAT stock solution (2.7 mg in 100 µL of DMSO) was added into the reaction mixture. Following that, 10 µL (0.05 equiv.) of eosin Y disodium salt stock solution (2.6 mg in 1 mL of DMSO) and PMDETA (0.13 mg, 1.0 equiv.) were added. The solution was degassed by N_2 flow for 30 min and then placed into the photo-reactor (450 nm, 2.8 mW/cm^2) for 24 h. After polymerization, the polymer product was purified by dialysis into DIW, followed by lyophilization.

3.3 Photo-Polymerization in Aqueous Solution

In a typical aqueous photo-induced polymerization (**P14**), KLA peptide (KLAKLAKKLAKLAK) acrylamide monomer (30 mg, 25 equiv.) and DMA (1.8 mg, 25 equiv.) were dissolved in 150 µL of acetate buffer (0.1 M, pH 5). Then 10 µL (1.0 equiv.) of water-soluble RAFT agent stock solution (2.2 mg in 100 µL of acetate buffer) was added into the reaction mixture. Following that, 10 µL (0.05 equiv.) of eosin Y disodium salt stock solution (2.5 mg in 1 mL of acetate buffer) and PMDETA (0.12 mg, 1.0 equiv.) were added. The solution was degassed by N_2 flow for 30 min and then placed into the photo-reactor (450 nm, 2.8 mW/cm^2) for 24 h. After polymerization, the polymer product was purified by dialysis into DIW, followed by lyophilization.

3.4 Preparation of Rhodamine-Labeled Polymers

In all the cases of preparing rhodamine-labeled polymers, one equiv. of rhodamine B to RAFT agent was used, ensuring that on average one dye was attached to each polymer chain. In a typical polymerization (rhodamine-labeled **P14**), KLA peptide (KLAKLAKKLAKLAK) acrylamide monomer (30 mg, 25 equiv.), DMA (1.8 mg, 25 equiv.), and methacryloxyethyl thiocarbamoyl rhodamine B (0.48 mg, 1.0 equiv.) were dissolved in 150 µL of acetate buffer (0.1 M, pH 5). Then 10 µL (1.0 equiv.) of water-soluble RAFT agent stock solution (2.2 mg in 100 µL of acetate buffer) was added into the reaction mixture. Following that, 10 µL (0.05 equiv.) of eosin Y disodium salt stock solution (2.5 mg in 1 mL of acetate buffer) and PMDETA (0.12 mg, 1.0 equiv.) were added. The solution was degassed by N_2 flow for 30 min and then placed into the photo-reactor (450 nm, 2.8 mW/cm^2) for 24 h. After polymerization, the polymer product was purified by dialysis into DIW, followed by lyophilization.

3.5 *N*-Acetylation of poly(KLAAm-*co*-DMA)

In a typical procedure, poly(KLAAm-*co*-DMA) (1.0 equiv. with respect to free amines) was dissolved in DMF and then treated with 50 equiv. of acetic acid in the presence of 50 equiv. of EDC•HCl and 5 equiv. of 4-DMAP. The reaction mixture was stirred for 12 hours, followed by dialysis into DIW wand lyophilization.

3.6 Thermolysin-Induced Cleavage Experiments

For enzyme-triggered cleavage experiments, the molar ratio of thermolysin to peptide was set to 1 : 300. Moreover, the temperature was set to 55 °C to achieve the optimal activity of thermolysin. For example, poly(PepAm$_{21}$-*co*-DMA$_{24}$) (**P4**, 1 mg**,** 0.87 µmol with respect to peptides, 300 equiv.) was dissolved in 1 ml of DPBS solution. Then thermolysin (0.1 mg, 2.9 nmol, 1 equiv.) was added into the polymer solution which was stirred in a preheated oil bath at 55 °C. In the case of control experiments which involved using deactivated thermolysin, EDTA (100 equiv. to thermolysin) was utilized to capture the zinc and calcium ions, resulting in denaturing of thermolysin.

3.7 Cell Culture

Hela cells were purchased from ATCC. Cells were cultured at 37 ºC under 5% CO_2 in phenol-red containing Dulbecco`s Modified Eagle Medium (DMEM; Gibco Life Tech., cat. #11960-044) supplemented with 10% fetal bovine serum (Omega Scientific, cat. #11140-050), sodium pyruvate (Gibco Life Tech., cat. #35050-061), L-glutamine (Gibco Life Tech., cat. #35050-061), and the antibiotics penicillin/streptomycin (Corning Cellgro, cat. #30-002-C1). Cells were grown in T75 culture flasks and subcultured at ~75-80% confluency.

3.8 Cell Viability Assay

The cytotoxicity of materials was assessed using the CellTilter-Blue assay. HeLa cells were plated at a density of 5000 cells per well in a 96 well plate 18 hours prior to treatment. Materials were dissolved in DPBS at the desired concentration and added to the wells along with a 10% DMSO positive control. Cells were incubated for 72 hours at 37 ºC. Note that the concentration of all the materials is with respect to the peptide concentration to ensure that all peptides and polymers are fairly compared with respect to their therapeutic components. The media was removed and 80 µL of new media without phenol red was added followed by adding 20 µL of CellTilter-Blue reagent. The cells were incubated for 3 hours at 37 ºC. The fluorescence was measured at 560 nm excitation and 590 nm emission wavelength.

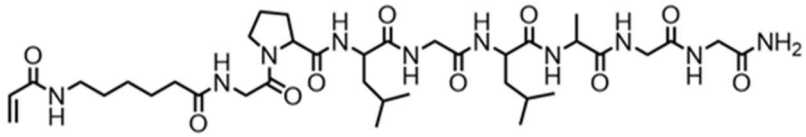
3.9 Confocal Laser Scanning Microscopy for Uptake in HeLa cells

HeLa cells were plated in a 4-chamber 35 mm round glass-bottom dishes at a density of 50,000 per well. Cells were incubated for 24 hours in a 5% CO_2 atmosphere at 37 °C. 500 µL of of KLA peptide, Poly(KLAAm$_{25}$-*co*-DMA$_{75}$), Poly(KLAAm$_{25}$-*co*-DMA$_{25}$), and Poly(KLAAm$_{10}$) (0.25 µM with respect to rhodamine for each material) in 10% FBS DMEM media without phenol red were incubated with the cells for 24 hours, respectively. After washing with DPBS to remove the residual peptides and polymers, 500 µL of Wheat Germ Agglutinin (5 µg/mL) conjugated with Alexa Fluor 488 was added to each well, then fixed with a 4% paraformaldehyde solution for 15 min at room temperature. The cells were washed with DPBS and stained by DAPI for 20 min at room temperature.

3.10 Flow Cytometry for Uptake Ability in HeLa cells

For cellular uptake measurements, HeLa cells were plated in 12-well plates at a density of 1,000,000 per well and incubated for 24 hours in a 5% CO_2 atmosphere at 37 °C. 500 µL of 0.25 µM (with respect to rhodamine) KLA peptide, poly(KLAAm$_{25}$-*co*-DMA$_{75}$), poly(KLAAm$_{25}$-*co*-DMA$_{25}$), and poly(KLAAm$_{10}$) in 10% FBS DMEM media without phenol red were incubated with the cells for 24 hours respectively. After triple washing with DPBS, 500 µL of 0.25% Trypsin-EDTA was added to each well for 10 min at 37 °C. Cells were fixed with a 4% paraformaldehyde solution for 15 min at room temperature.

4. Supporting figures, Schemes, and Tables



Molecular Weight: 806.96

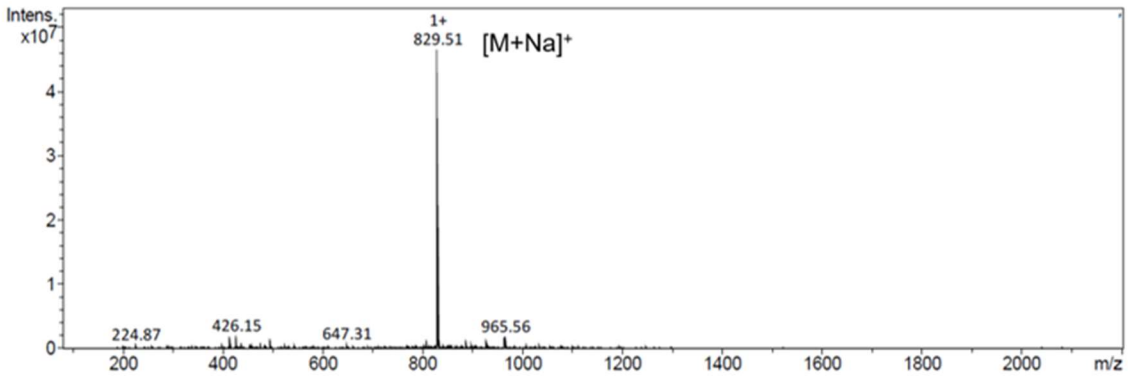


Figure S1. ESI-Mass spectrum of enzyme-responsive peptide monomer.

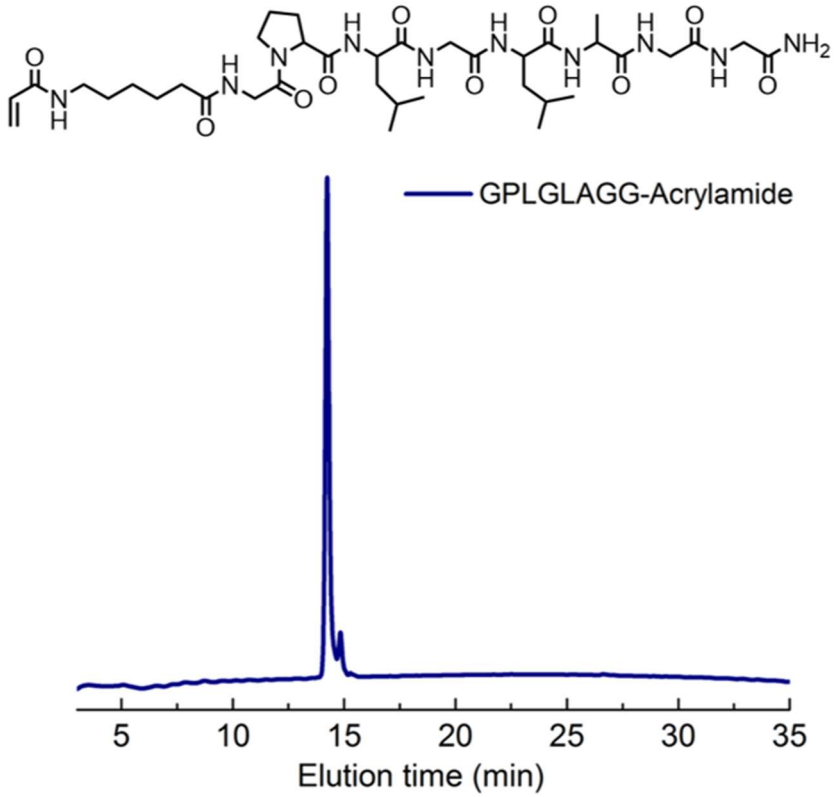


Figure S2. HPLC trace of enzyme-responsive peptide monomer.

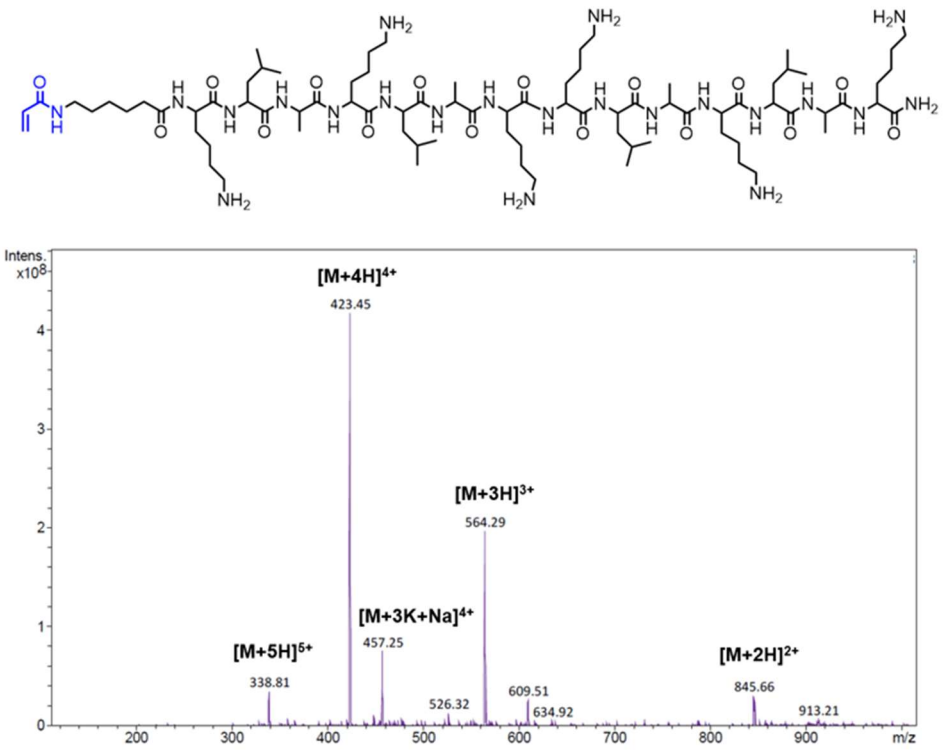


Figure S3. ESI-Mass spectrum of KLA peptide acrylamide monomer.

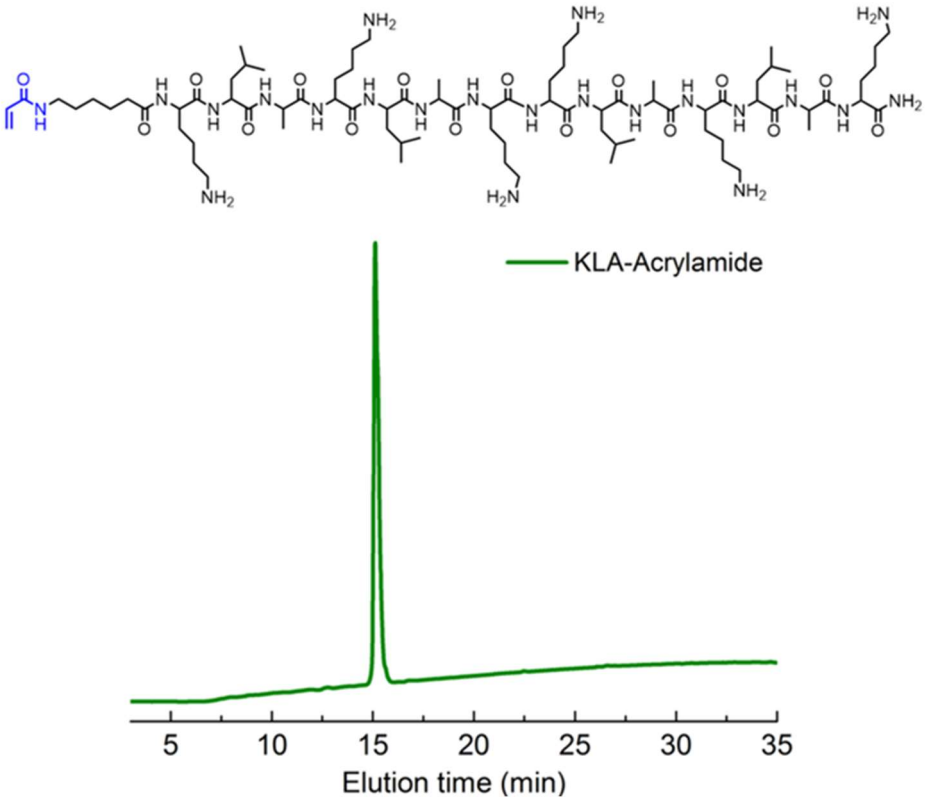


Figure S4. HPLC trace of KLA peptide acrylamide monomer.

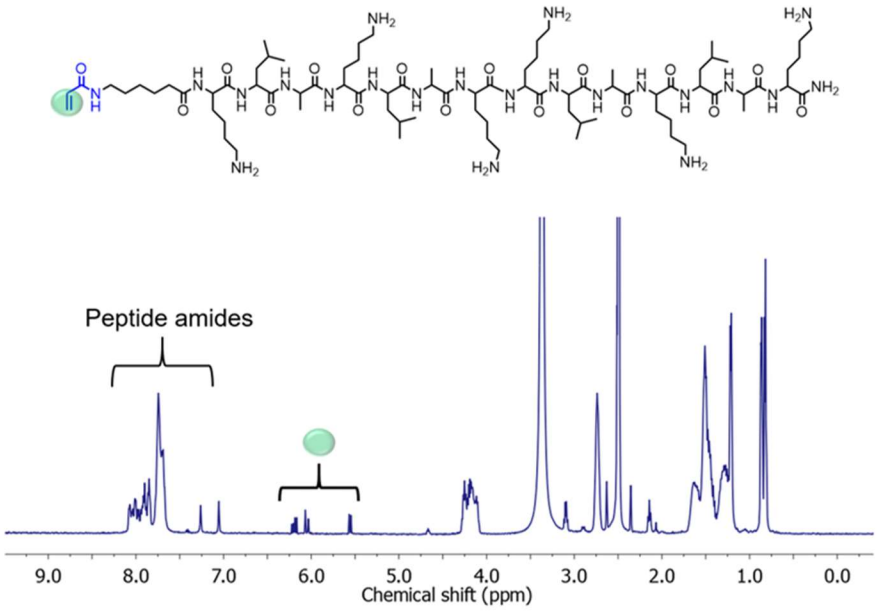


Figure S5. ^{1}H NMR spectrum of KLA peptide acrylamide monomer in d_6-DMSO at 25 °C.

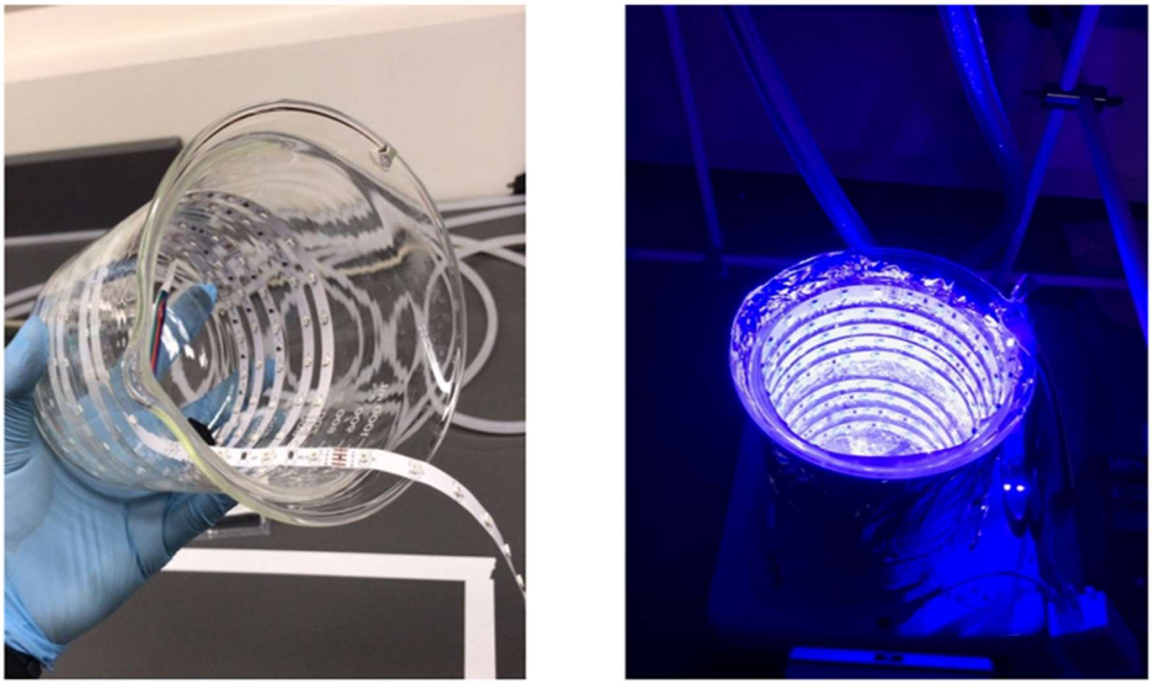


Figure S6. Assembly of photo-reactor by wrapping the LED strip light inside a beaker.

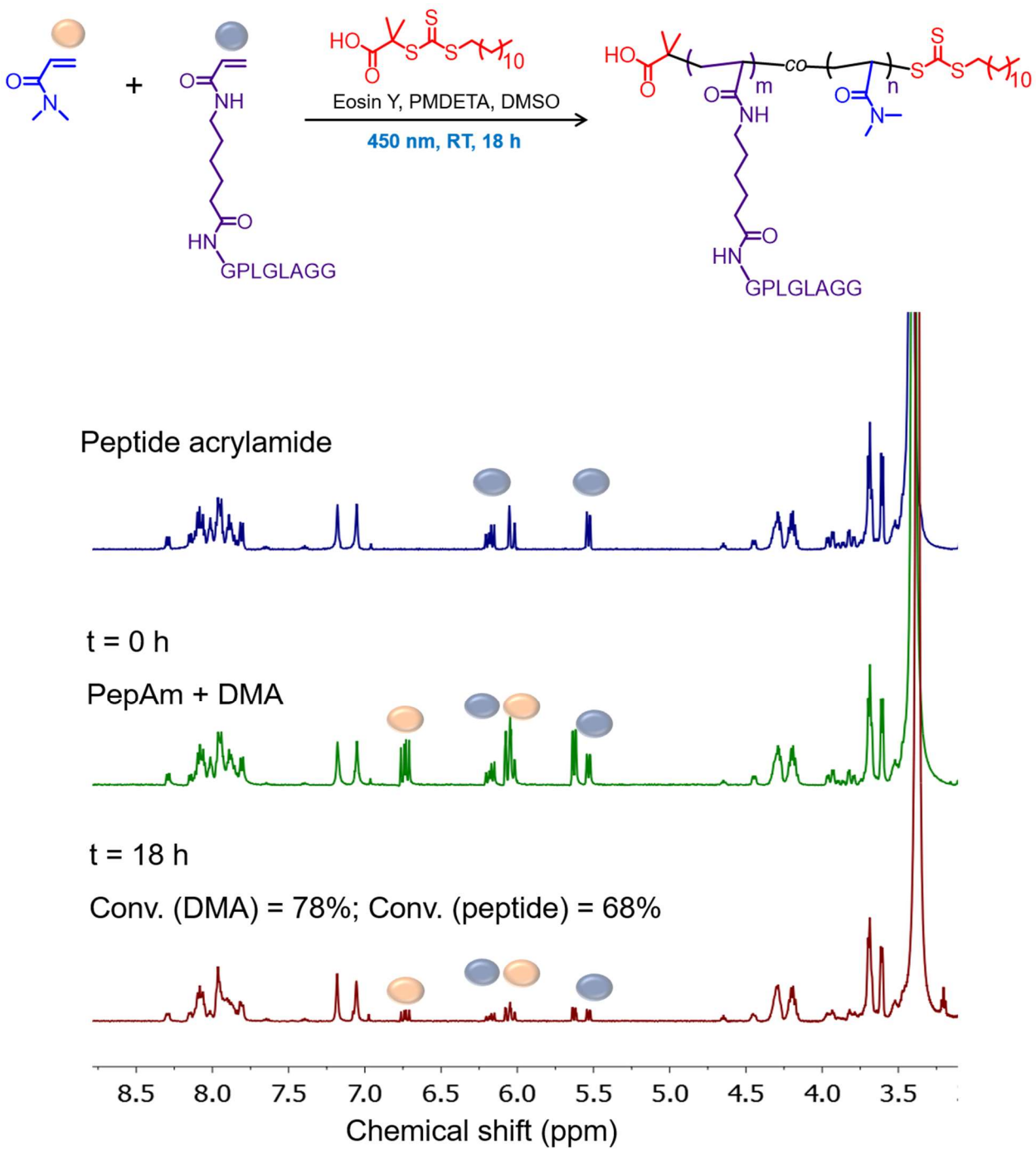


Figure S7. ^{1}H NMR spectra of enzyme-responsive peptide acrylamide (top blue), monomer mixtures before polymerization (middle green), and after polymerization for 18 h (bottom red);

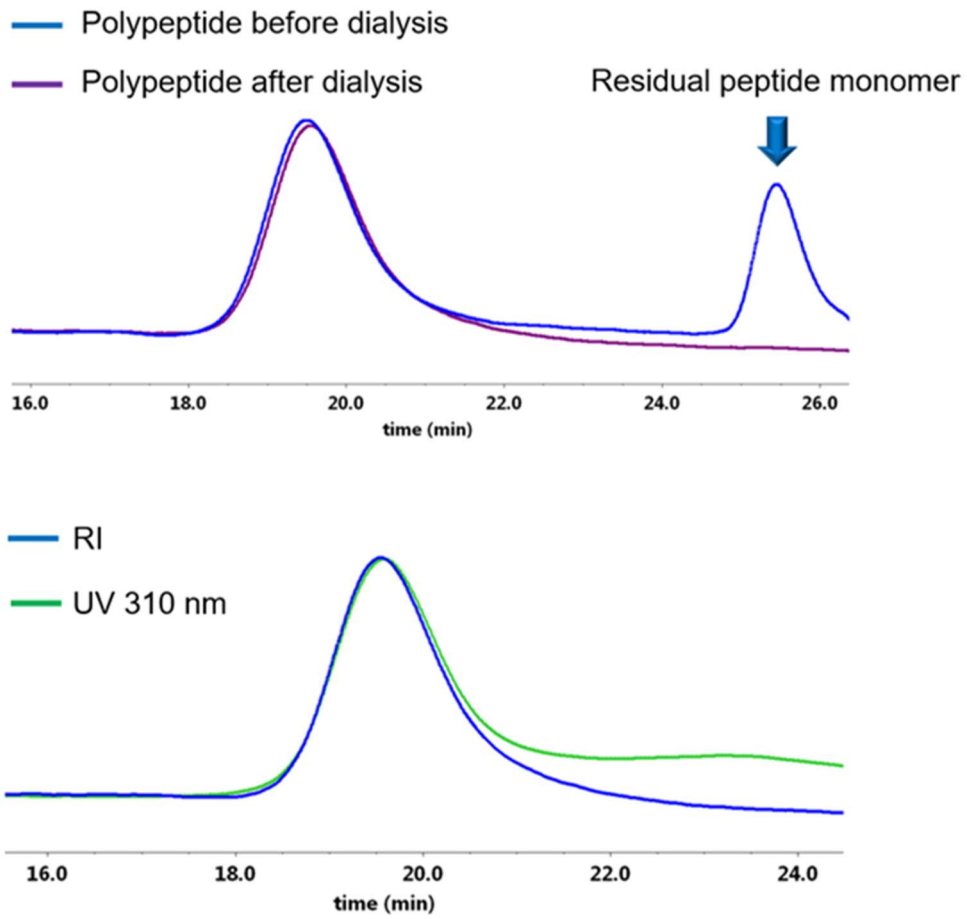


Figure S8. Top: GPC traces of P1 before and after dialysis (cut-off: 20,000 Da). The disappearance of peptide monomer peak clearly indicated that polypeptide was pure after dialysis; Bottom: GPC traces of P1 from both RI detector and UV detector (310 nm).

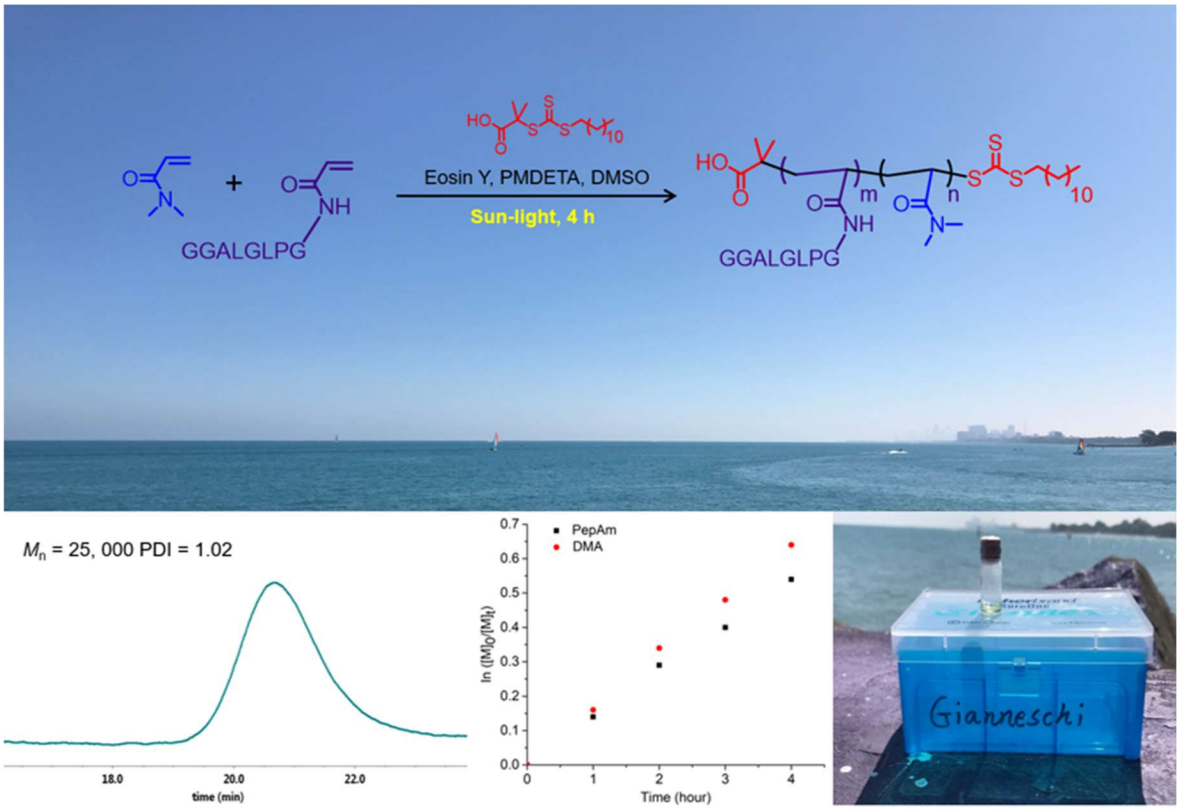


Figure S9. Sunlight-induced polymerization of peptide acrylamide in lakeshore at Northwestern University (Evanston campus, August 17th, 2018). ^{1}H NMR based kinetic study of polymerization demonstrated that peptide acrylamide possessed a propagation rate on par with that of the commoner DMA; SEC trace of the final product indicated that the polypeptide product is well-defined with a narrow polydispersity and number-average molecular weight similar to theoretical value (refer to P4 in Table S1).

Table S1. Photo-RDRP of peptide-acrylamide (PepAm) and DMA

Entry	Equiv. to CTA			Conv. (%)		$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol)	$Đ$
	PepAm	DMA	$[M]_0$	PepAm	DMA			
[a]**P0**	50	0	0.18 M	0%	N/A	N/A	N/A	N/A
[a]**P1**	50	50	0.36 M	12%	15%	5 600	4 900	1.08
[a]**P2**	50	100	0.54 M	30%	45%	16 500	10 800	1.15
[a]**P3**	50	150	0.72 M	68%	78%	39 900	46 000	1.01
[b]**P4**	50	150	0.72 M	42%	47%	24 200	25 000	1.02

Note: In each polymerization, 200 μL of DMSO was used. [M]/[CTA]/[EY]/[PMDETA] = X/1/0.05/1. [a]The polymerizations were triggered by blue LED (450 nm). [b]The polymerization was promoted under sunlight in Northwestern University.

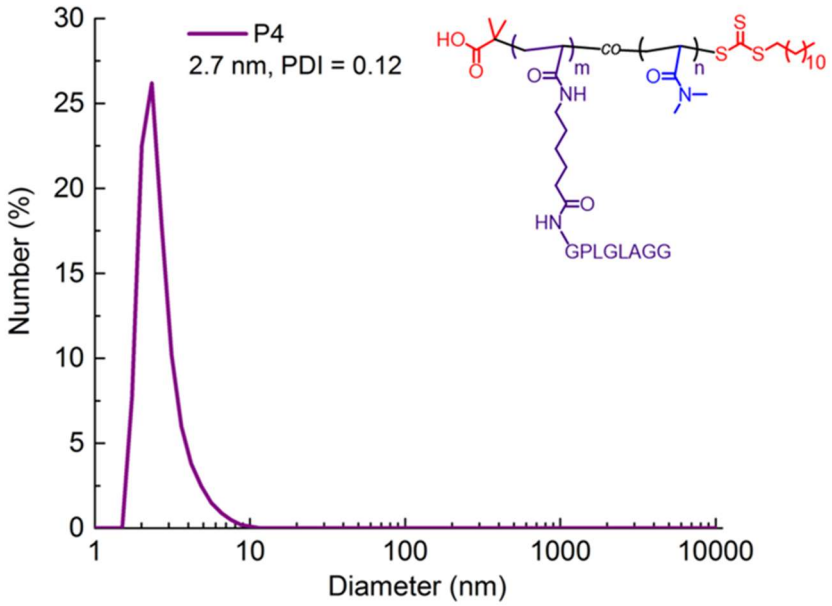


Figure S10. DLS trace of P4 in DIW. The small size (< 10 nm) of the polypeptide indicats that the polymer exists as free unimers in DIW.

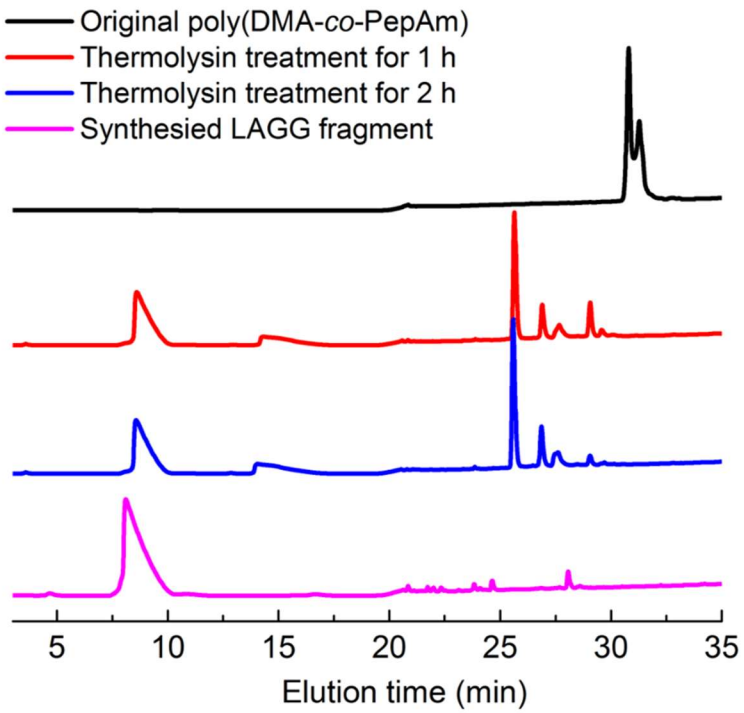


Figure S11. HPLC traces of P1 before and after being treated with thermolysin (1/300 equiv. to the number of peptides in the polymer). No further increase in the peak of the cleaved LAGG fragment was observed after 1 hour, suggesting that the enzyme-induced peptide cleavage was complete within one hour.

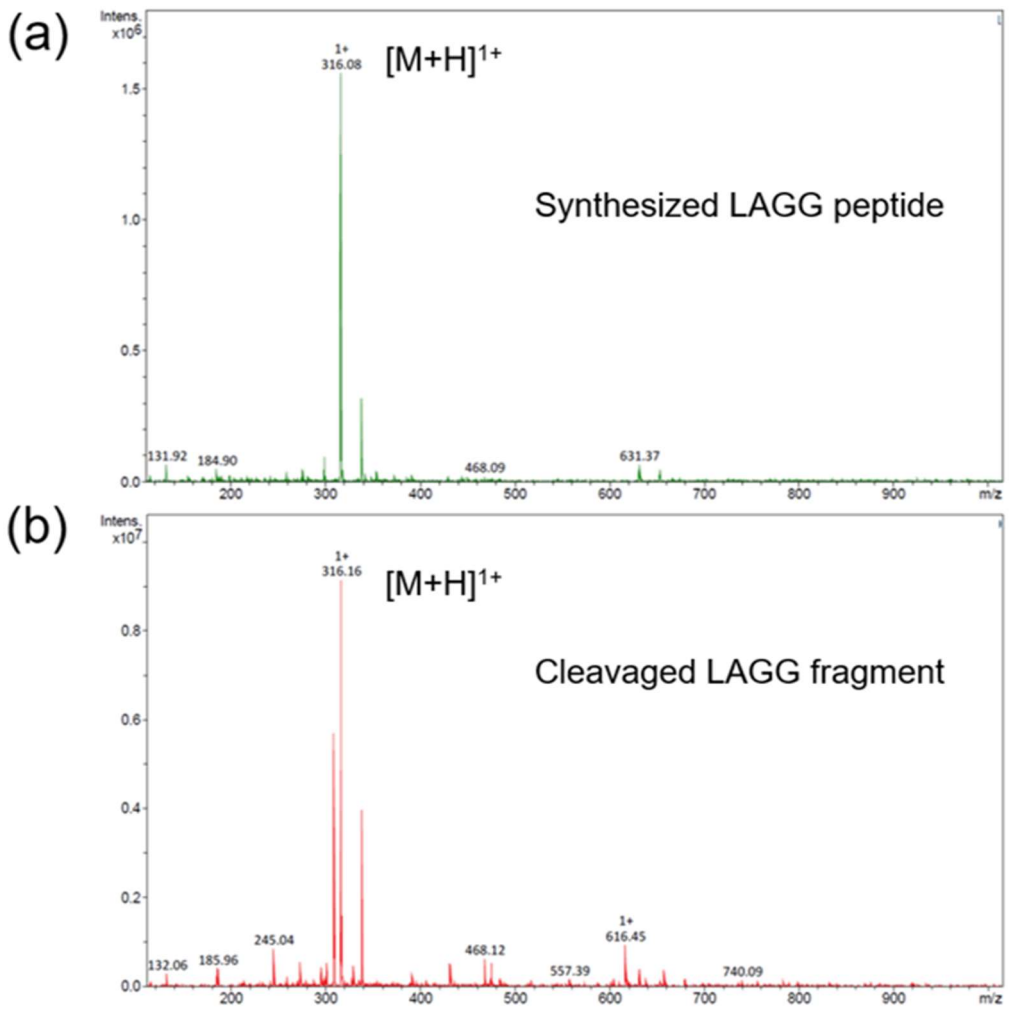


Figure S12. ESI-Mass spectra of synthetic LAGG fragment (a) and cleaved LAGG fragment (b) which was collected from HPLC separation. Notably, the cleaved LAGG was from P1 after treatment with thermolysin.

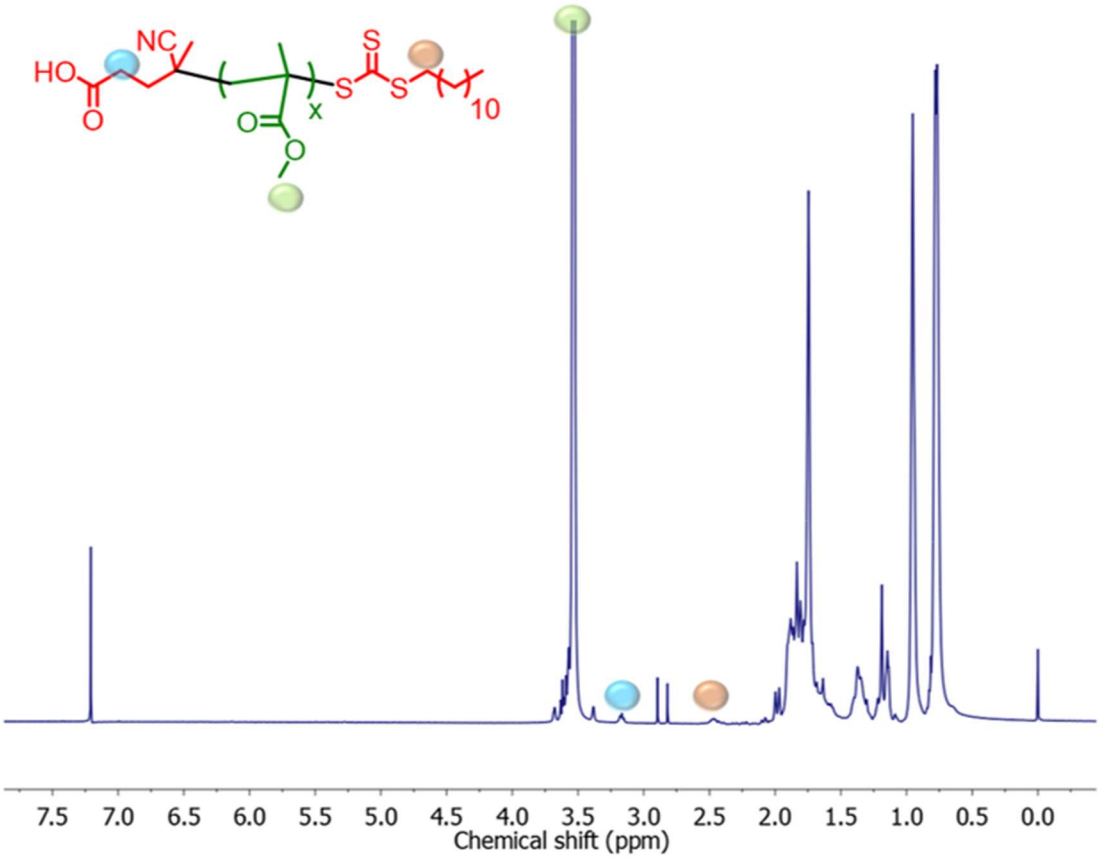
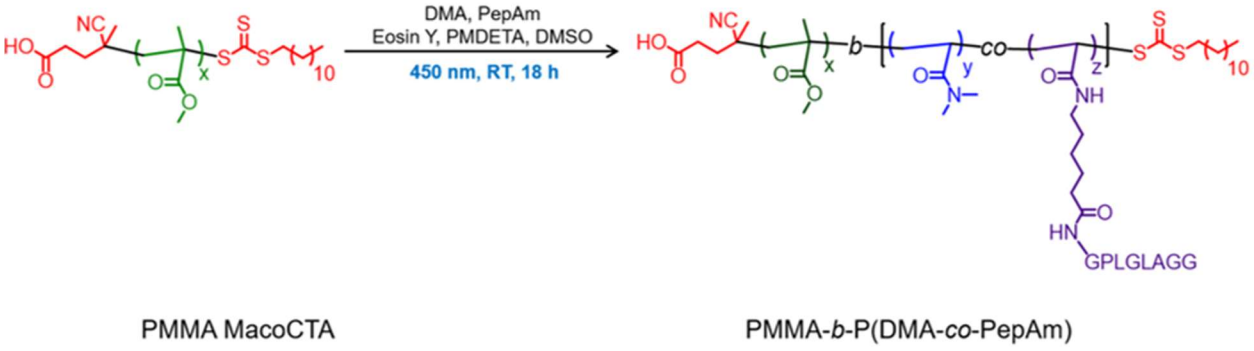


Figure S13. ^{1}H NMR spectrum of $PMMA_{90}$ macroCTA (P5) in $CDCl_3$ at 25 °C.



Scheme S1. Chain extension of PMMA macroCTA with DMA and PepAm.

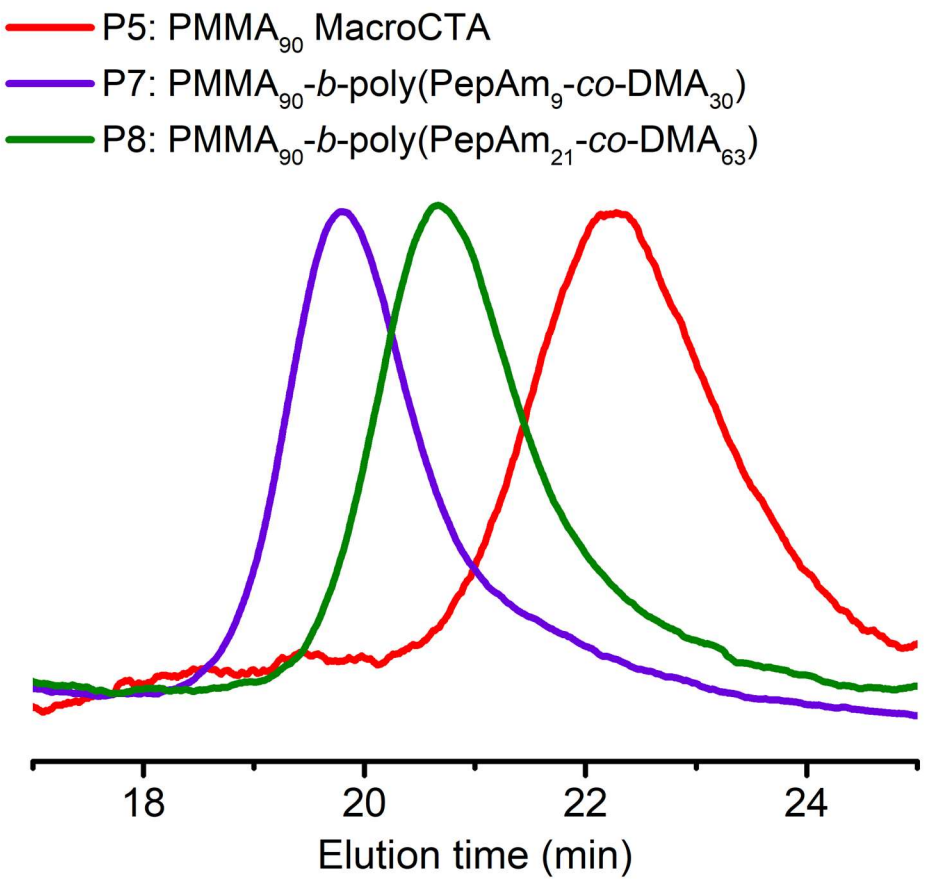


Figure S14. GPC traces of $PMMA_{90}$ macroCTA (P5), $PMMA_{90}$-*b*-poly($PepAm_9$-*co*-DMA_{30}) (**P7**), and $PMMA_{90}$-*b*-poly($PepAm_{21}$-*co*-DMA_{63}) (**P8**).

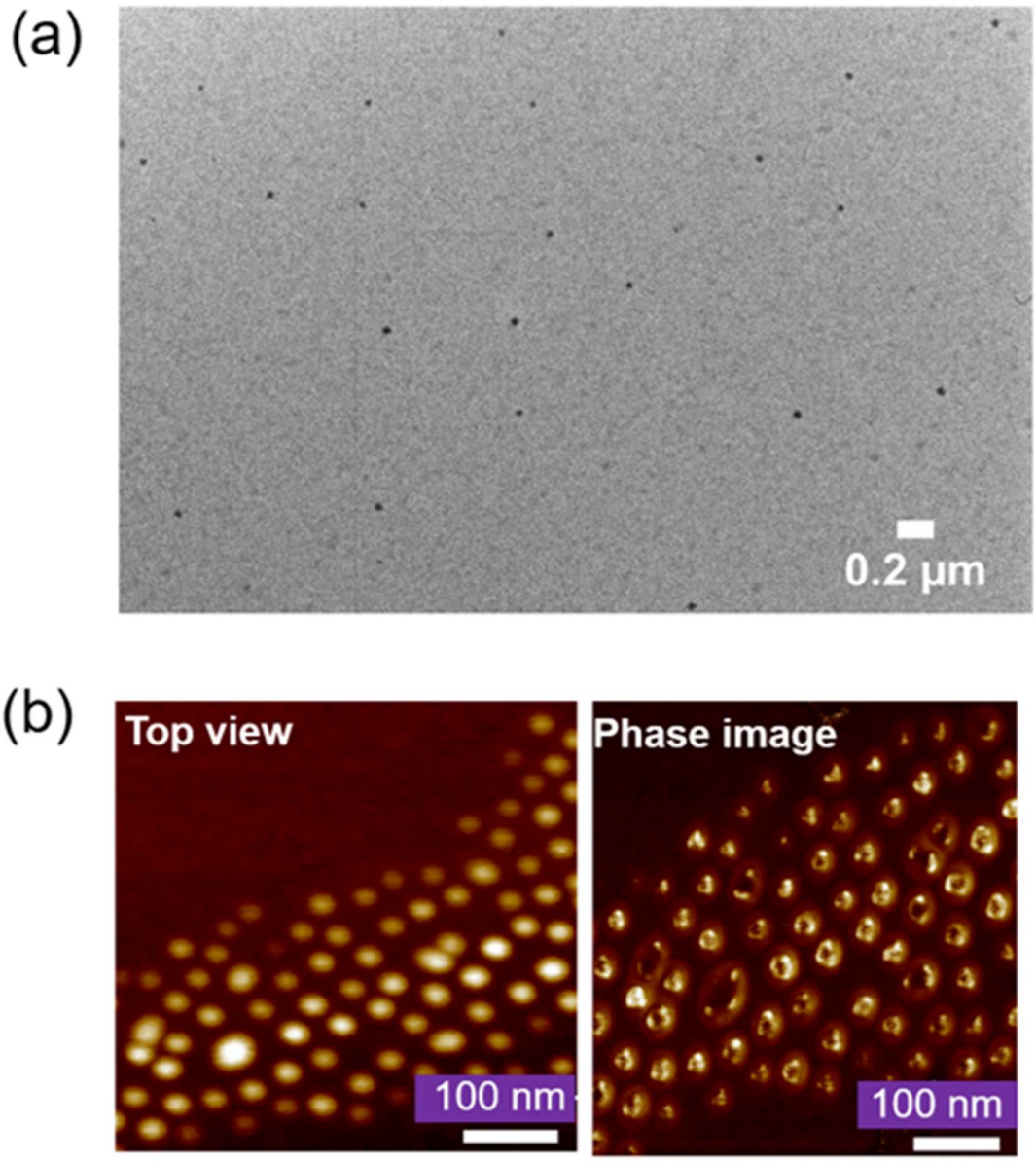


Figure S15. (a) TEM image of $PMMA_{90}$-*b*-poly($PepAm_9$-*co*-DMA_{30}) in DIW; (b) AFM micrographs of $PMMA_{90}$-*b*-poly($PepAm_9$-*co*-DMA_{30}) in DIW.

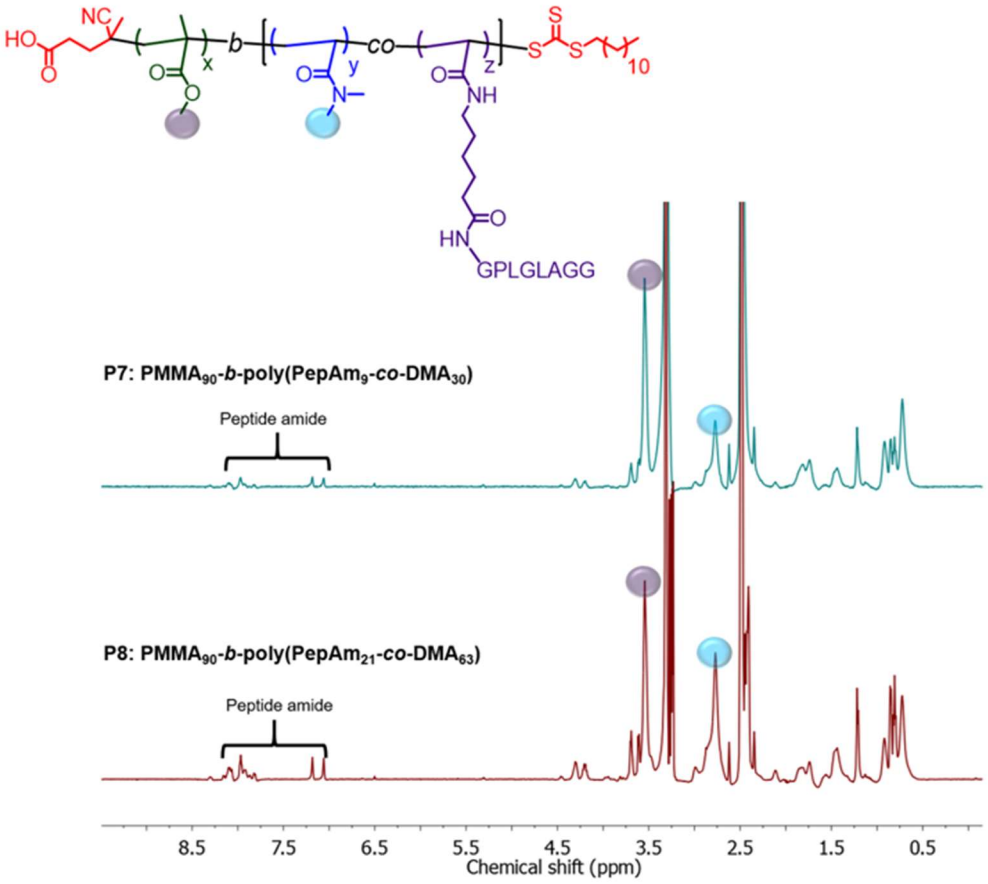


Figure S16. ^{1}H NMR spectrum of $PMMA_{90}$-*b*-poly($PepAm_{9}$-*co*-DMA_{30}) (**P7**), and $PMMA_{90}$-*b*-poly($PepAm_{21}$-*co*-DMA_{63}) (**P8**) in d_6-DMSO at 25 °C.

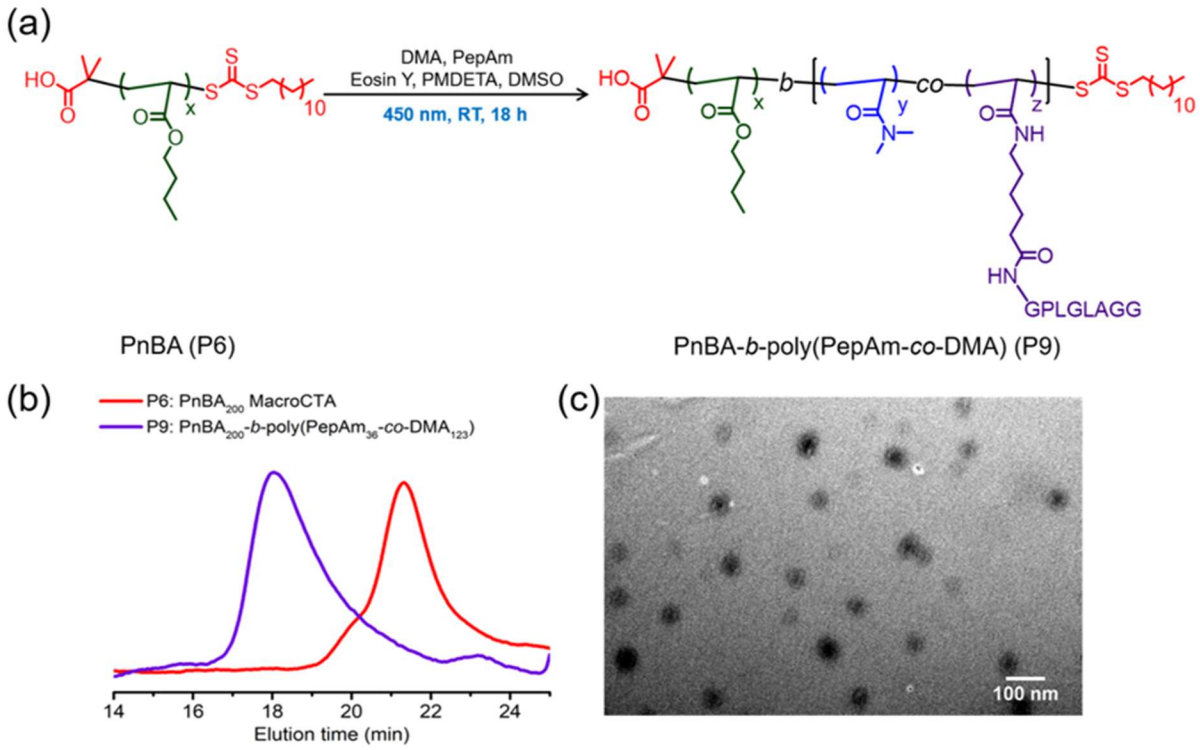


Figure S17. (a) Chain extension of PnBA macroCTA with peptide monomers and DMA spacers; (b) GPC traces of PnBA macroCTA (**P6**) and block copolymer $PnBA_{200}$-*b*-poly($PepAm_{36}$-*co*-DMA_{123}) (**P9**) indicated a successful chain extension; (c) TEM image confirmed the micellar structure of P9 in DIW.

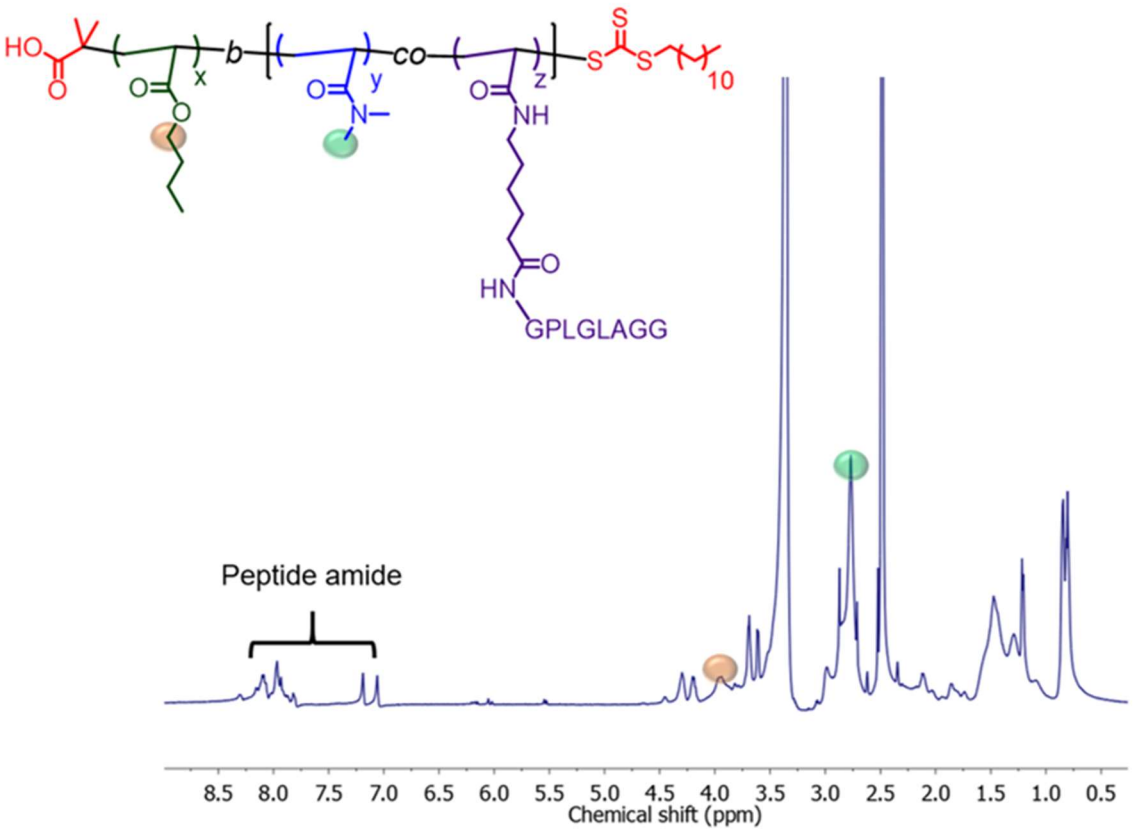


Figure S18. ^{1}H NMR spectrum of $PnBA_{200}$-*b*-poly($PepAm_{36}$-*co*-DMA_{123}) (**P9**) in d_6-DMSO.

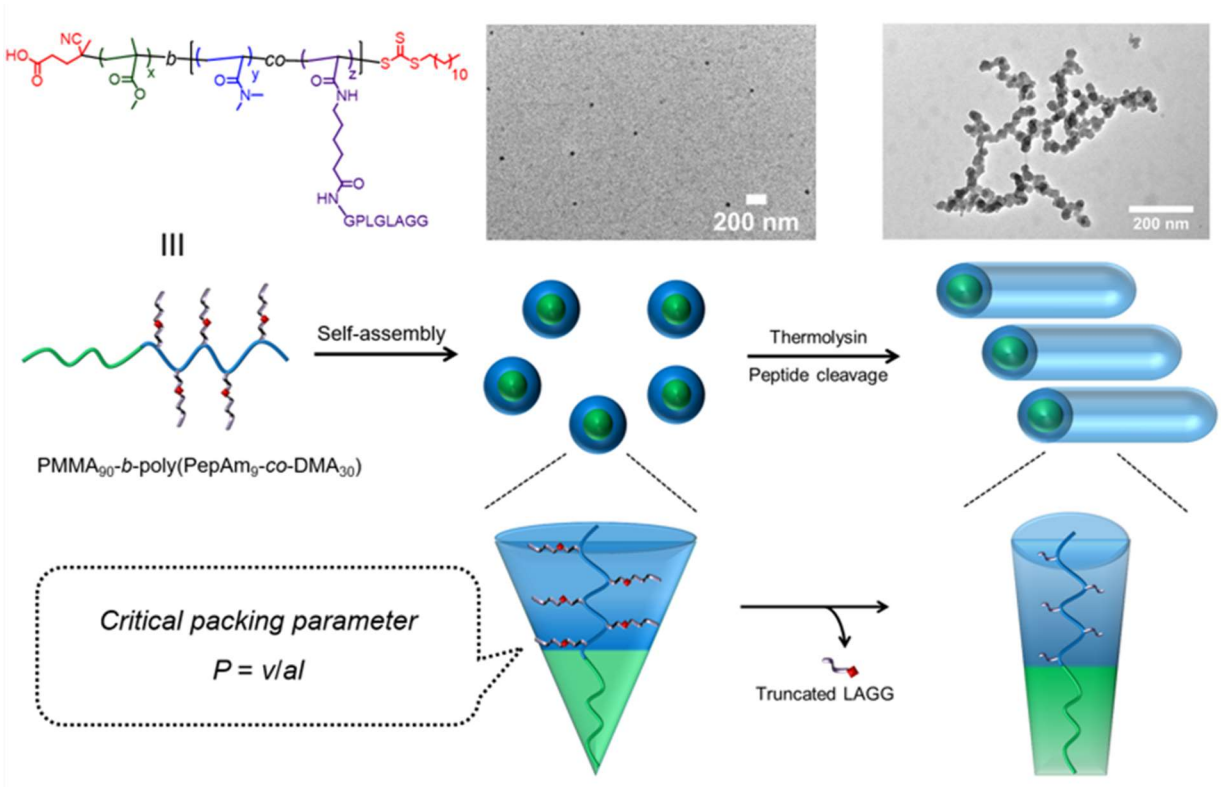


Figure S19. Enzyme-promoted shape transformation of $PMMA_{90}$-*b*-poly($PepAm_9$-*co*-DMA_{30}) (**P7**) based micelles. TEM elucidated a transition from spherical micelle to fused worm micelles after treatment with thermolysin.

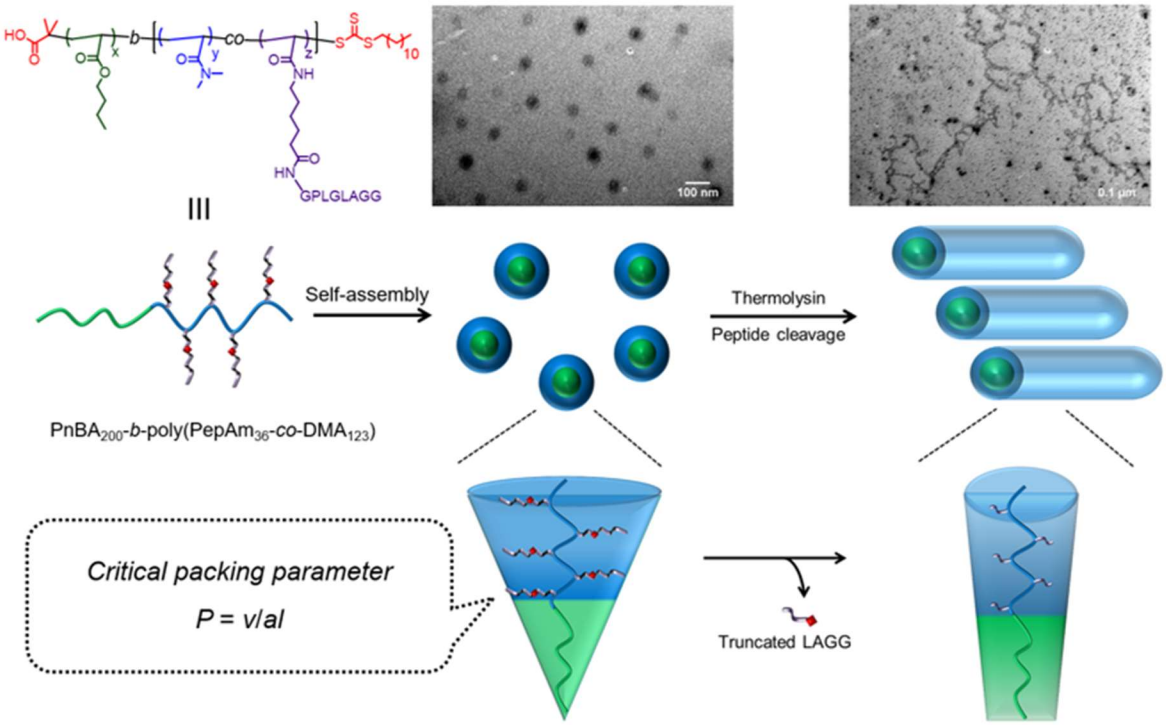


Figure S20. Enzyme-promoted shape transformation of $PnBA_{200}$-*b*-poly($PepAm_{36}$-*co*-DMA_{123}) (**P9**) based micelles. TEM elucidated a transition from spherical micelle to a mixture of micelles and fiber structure after treatment with thermolysin.

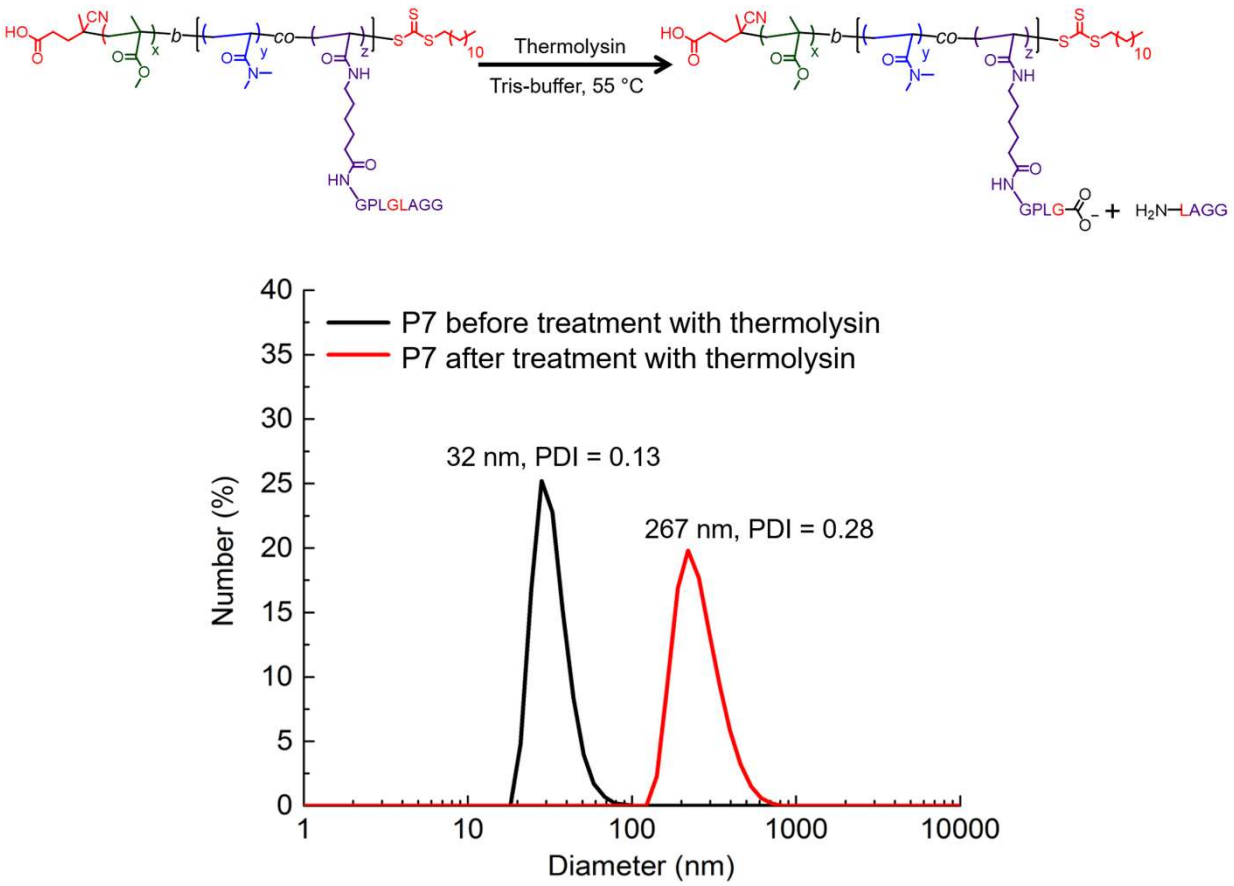


Figure S21. DLS traces of $PMMA_{90}$-*b*-poly($PepAm_{21}$-*co*-DMA_{63}) (P7) based nano-objects before and after thermolysin-promoted cleavage.

Table S2. Preparation of enzyme-responsive diblock copolymer

Entry	Equiv. to macroCTA			Conv. (%)		$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol)	$Đ$
	PepAm	DMA	$[M]_0$	PepAm	DMA			
[a]**P7**	13	37	0.72 M	72%	79%	19 900	16 200	1.04
[a]**P8**	25	75	0.72 M	82%	84%	31 800	27 000	1.06
[b]**P9**	50	150	0.72 M	71%	82%	68 000	66 400	1.17

Note: In each polymerization, 200 μL of DMSO was used. [M]/[CTA]/[EY]/[PMDETA] = X/1/0.05/1, RXN time = 18 h. [a]The chain extensions were performed using PMMA macroCTA (P5). [b]The chain extension was performed using PnBA macroCTA (P6).

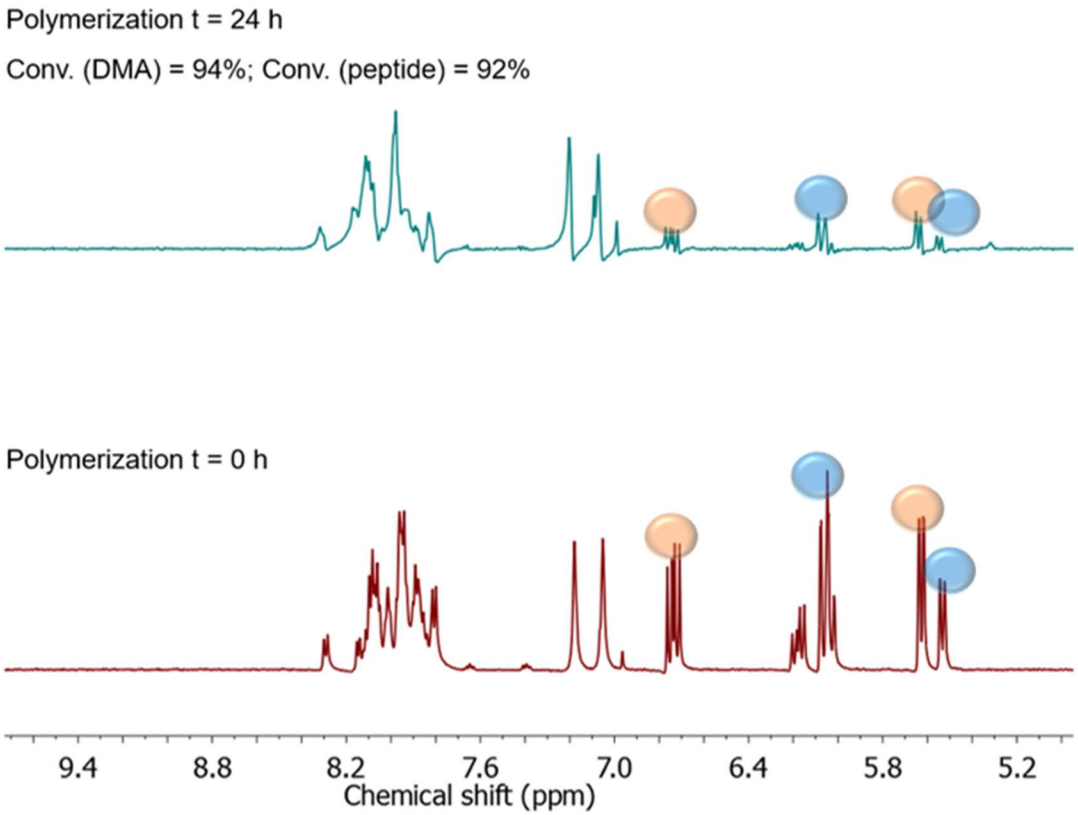


Figure S22. ^{1}H NMR spectra of reaction mixture (P10) before and after photo-polymerization in DIW. The dramatic reduction in vinyl proton signals (5.4 to 6.8 ppm) indicated a high monomer conversion.

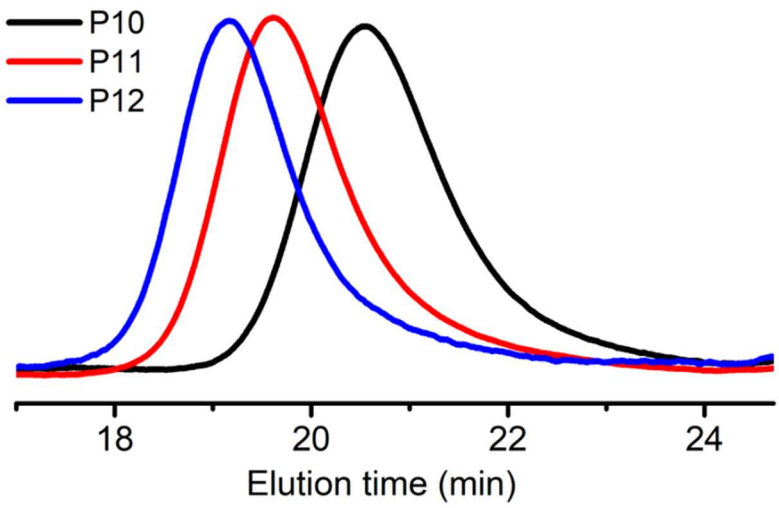


Figure S23. GPC traces of poly(PepAm-*co*-DMA) (**P10-P12**) prepared by aqueous photo-electron transfer RAFT polymerization. Please refer to Table S3 for the information of molecular weights and dispersity of each polymer.

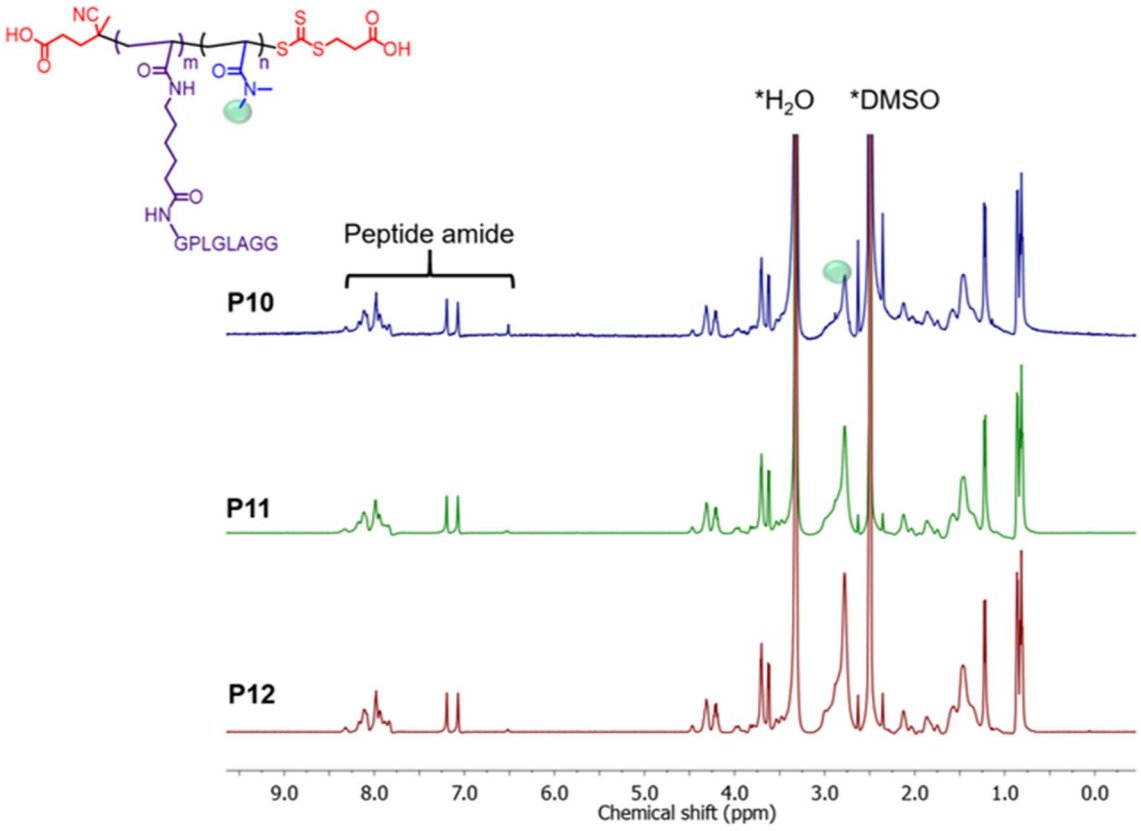


Figure S24. ^{1}H NMR spectra of poly(PepAm-*co*-DMA) (**P10-P12**) in d_6-DMSO at 25 °C.

Table S3. Aqueous photo-RDRP of PepAm and DMA.

Entry	Equiv. to CTA			Conv. (%)		$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol)	$Đ$
	PepAm	DMA	$[M]_0$	PepAm	DMA			
[a]**P10**	50	50	0.36 M	60%	64%	27 685	26 100	1.06
[a]**P11**	50	100	0.54 M	87%	85%	44 230	48 700	1.01
[a]**P12**	50	150	0.72 M	92%	94%	51 388	55 400	1.04

Note: In each polymerization, 200 μL of DIW was used. [M]/[CTA]/[EY]/[PMDETA] = X/1/0.05/1.
[a]The polymerizations were triggered by blue LED.

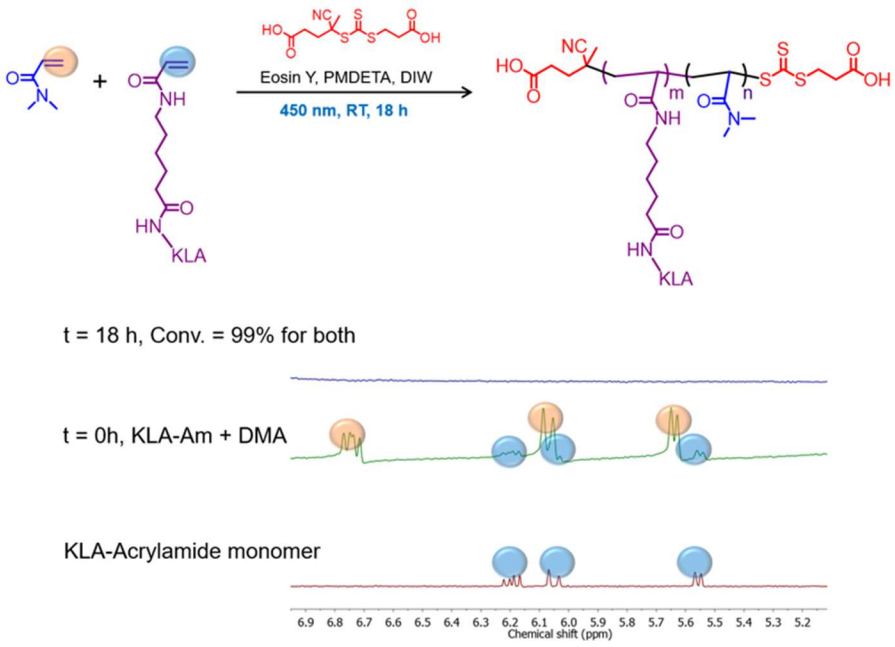


Figure S25. ^{1}H NMR spectra of reaction mixture (**P14**) before and after photo-polymerization in DIW. The full diminishment in vinyl proton signals (5.4 to 6.8 ppm) indicated quantitative monomer conversions were achieved for both KLA acrylamide and DMA.

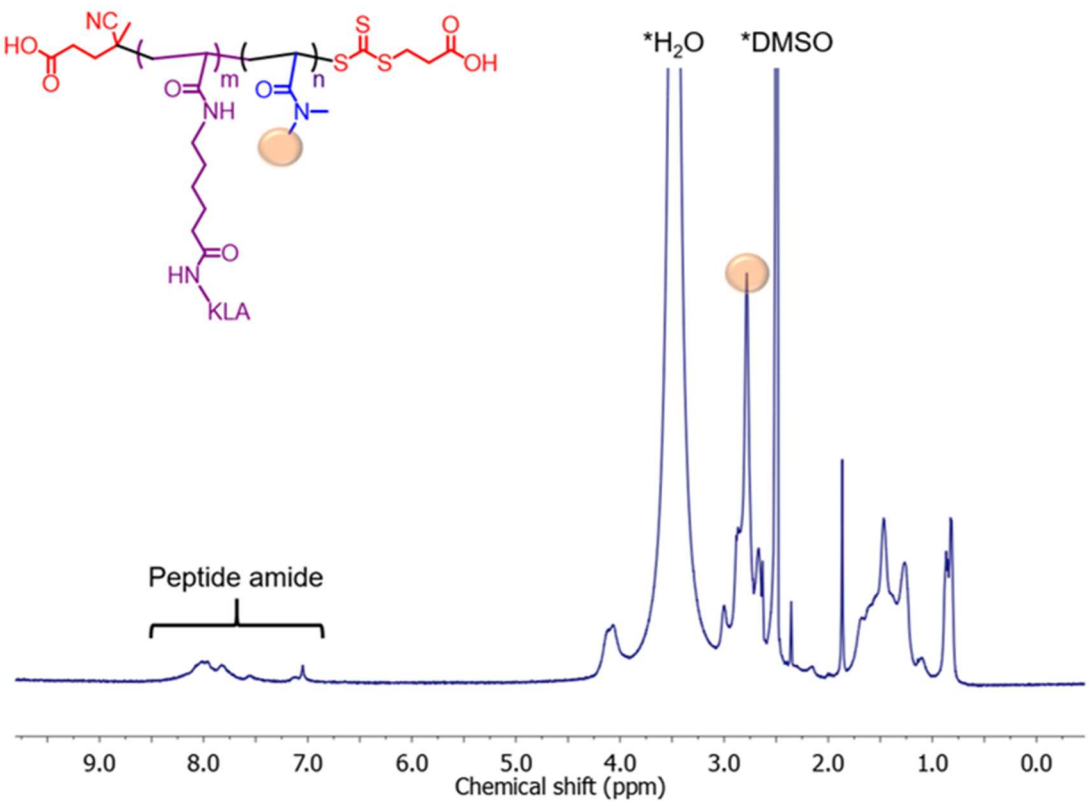
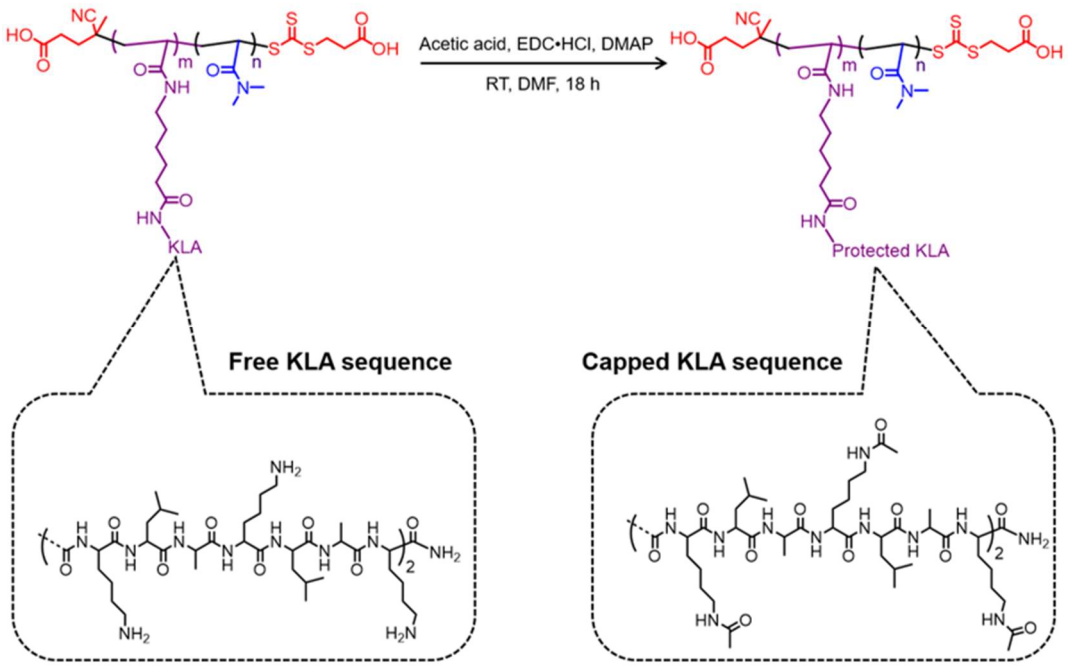


Figure S26. ^{1}H NMR spectrum of poly(KLAAm$_{25}$-*co*-DMA$_{25}$) (**P14**) in d$_6$-DMSO at 25 °C.



Scheme S2. Schematic of the *N*-acetylation of KLA based polypeptide brushes.

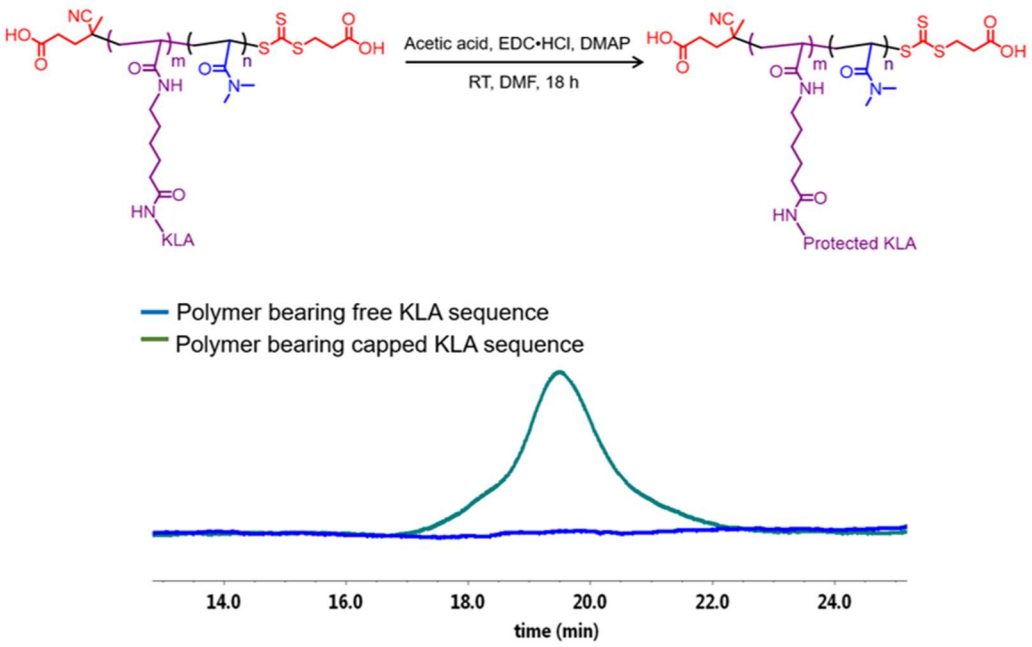


Figure S27. GPC traces of poly(KLAAm$_{25}$-*co*-DMA$_{150}$) (**P16**) before and after *N*-acetylation. The protection of amines eliminated the interactions between polymers and the GPC columns, allowing for accurate evaluation of the number-average molecular weights fro these amine-abundant polymers.

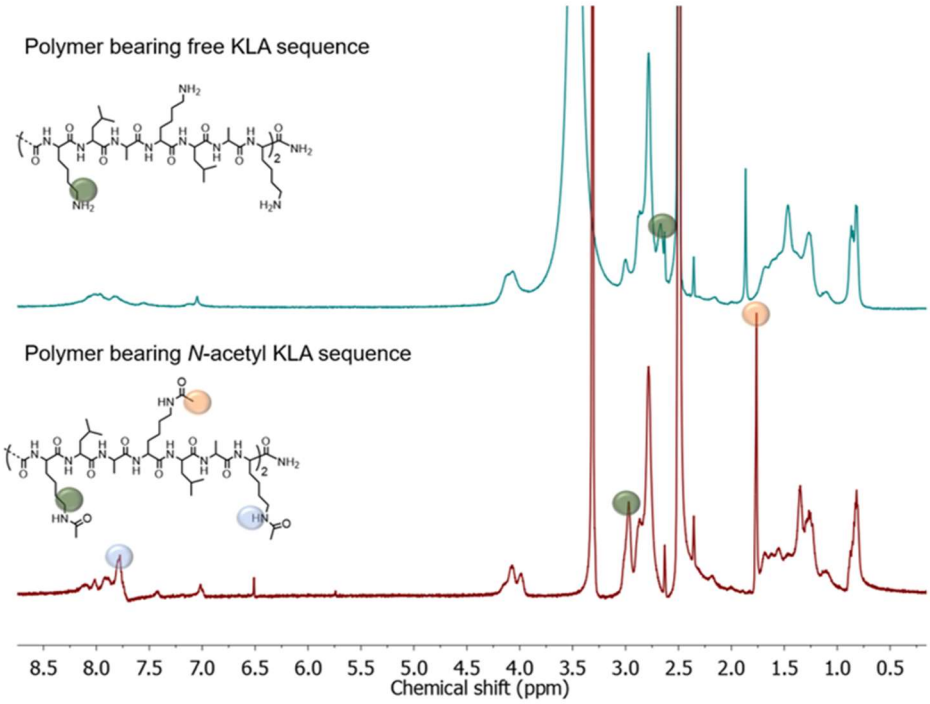


Figure S28. ^{1}H NMR spectra of poly(KLAAm$_{25}$-*co*-DMA$_{150}$) (**P16**) before and after *N*-acetylation.

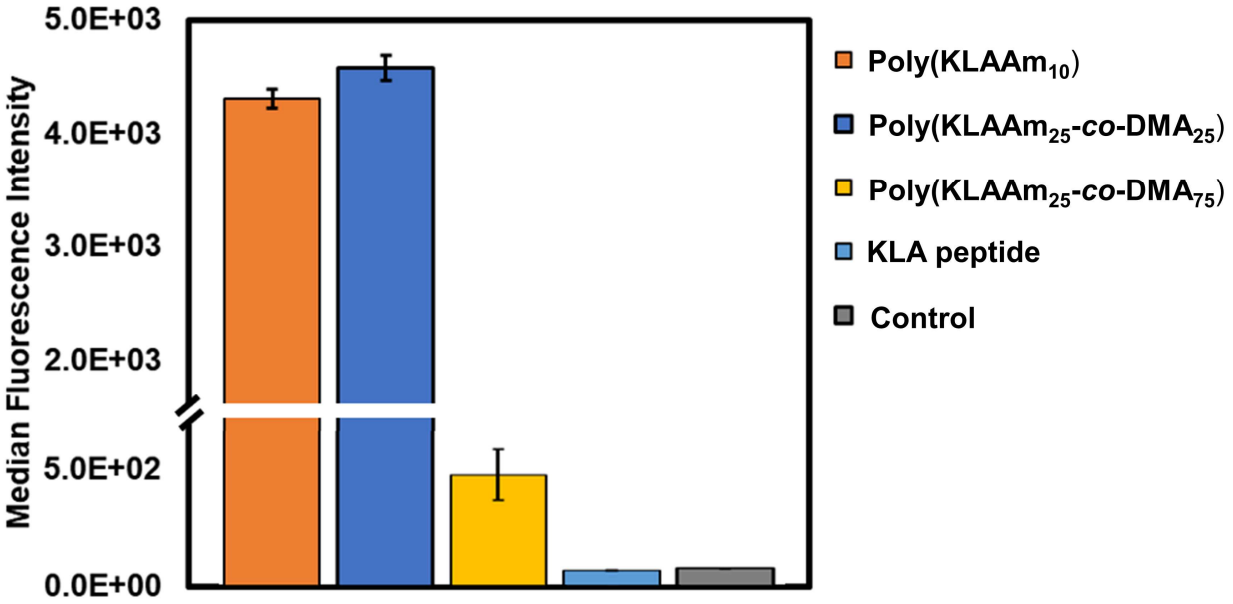


Figure S29. Evaluating cellular uptake ability of KLA based materials using flow cytometry: quantification of rhodamine fluorescence intensity of KLA based materials in Hela cells. The concentration of each material was set to 0.25 μM with respect to Rhodamine B. (data represent mean ± s.d., $n = 3$ independent experiments)

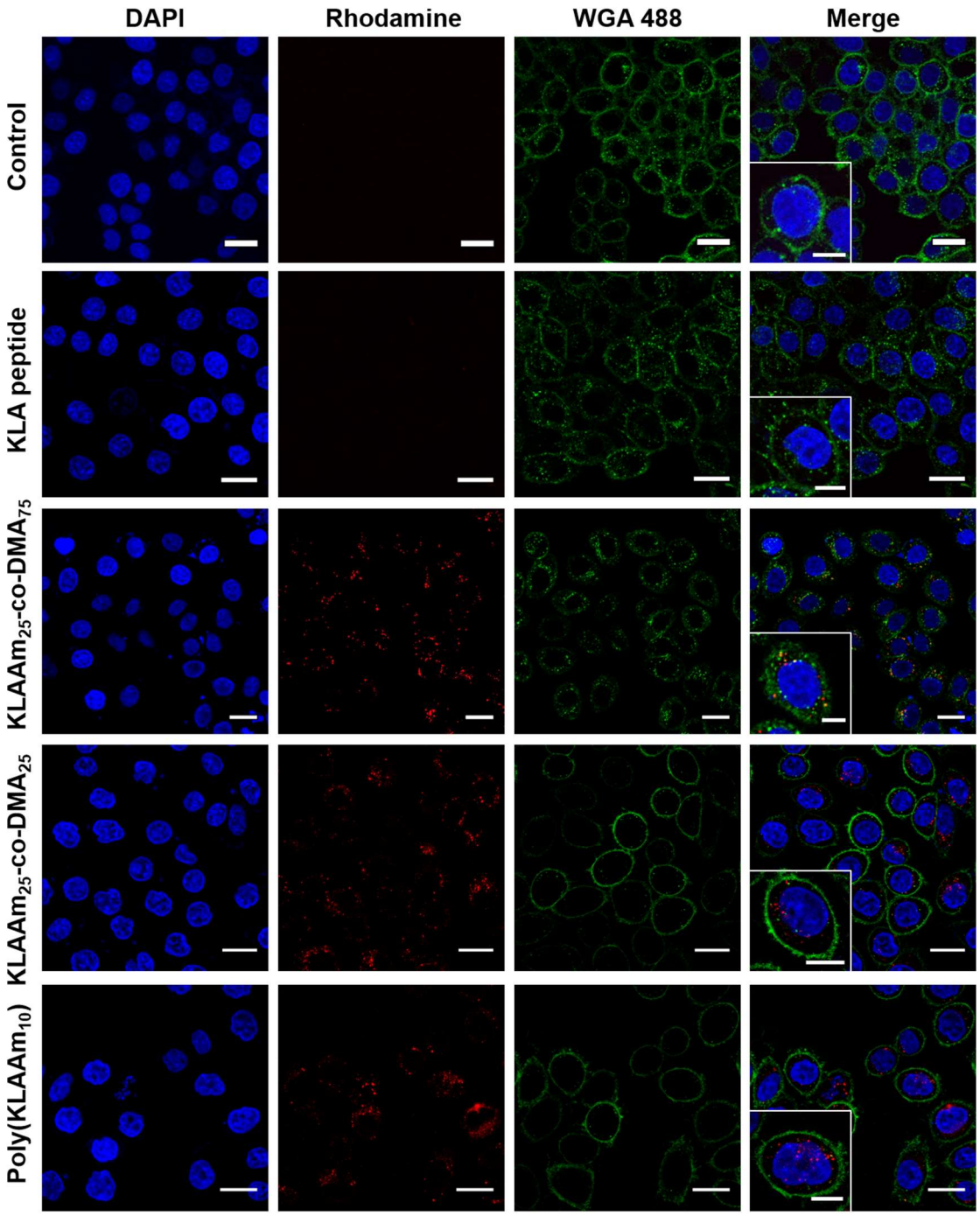


Figure S30. Confocal microscopy images of Hela cells incubated with rhodamine-labeled KLA peptide, poly(KLAAm$_{10}$), poly(KLAAm$_{25}$-*co*-DMA$_{25}$), and poly(KLAAm$_{25}$-*co*-DMA$_{75}$) at a concentration of 0.25 μM with respect to Rhodamine. Cell nuclei were stained with DAPI. Cell membrane was stained with WGA 488. Scale bar: 20 μm, insert scale bar 10 μm.

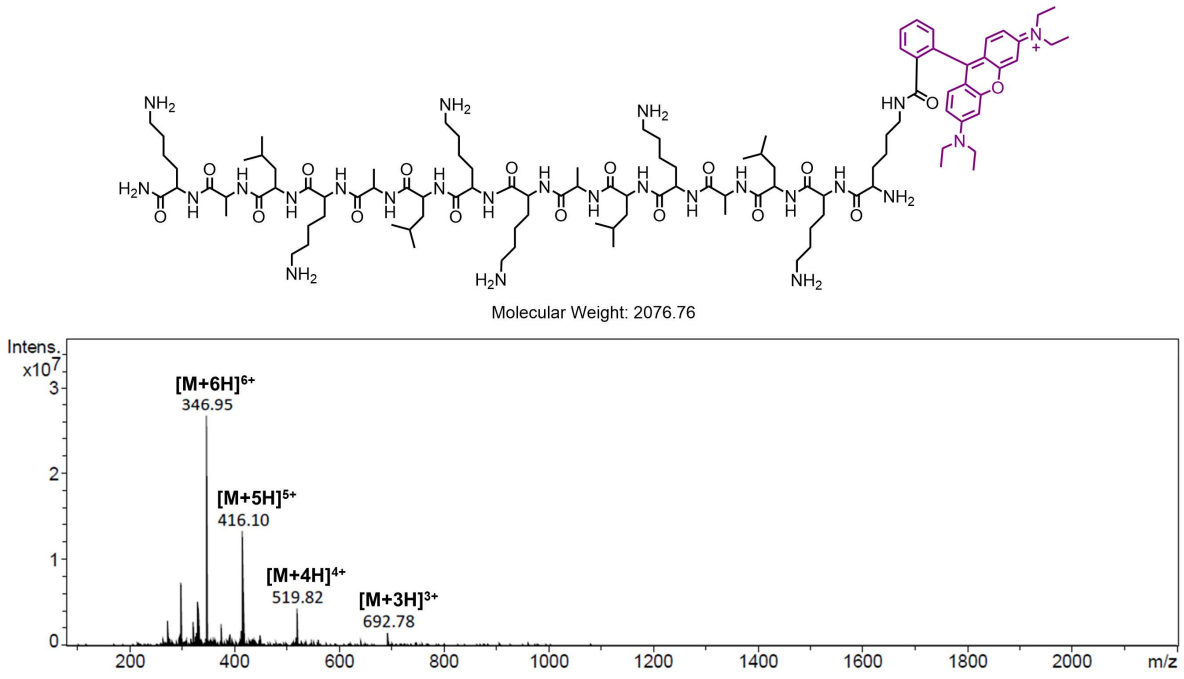


Figure S31. ESI-Mass spectrum of rhodamine B labeled KLA peptide (Rho-KLA).

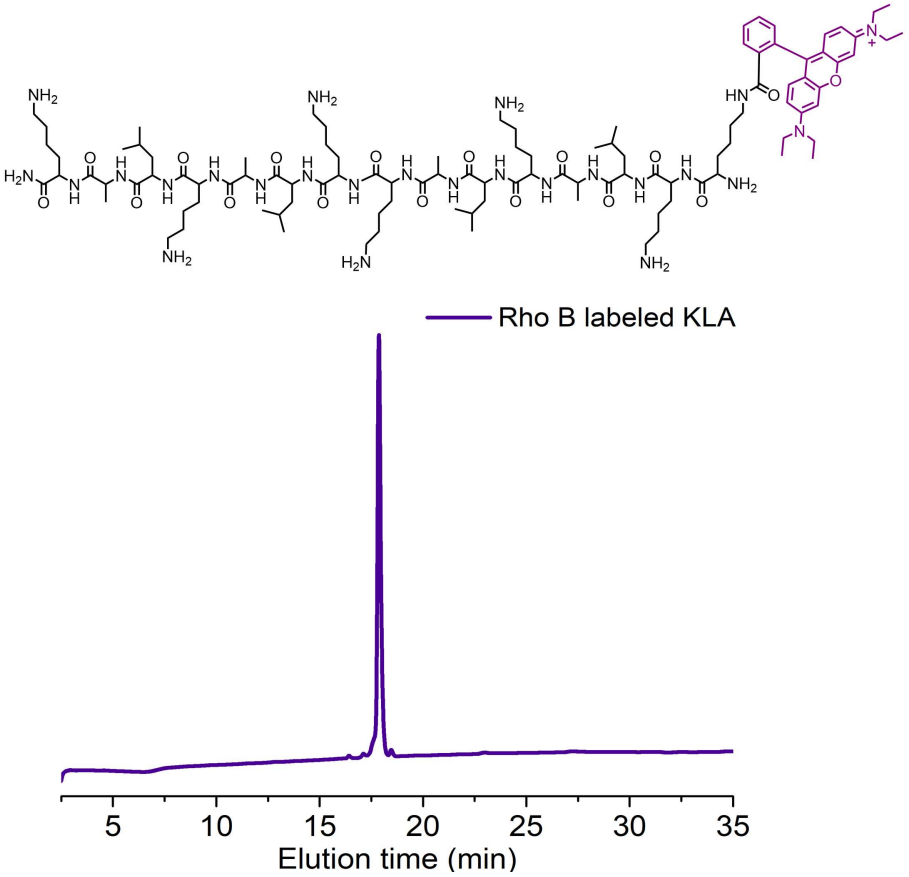


Figure S32. HPLC trace of rhodamine B labeled KLA peptide.

Table S4. Aqueous photo-RDRP of KLA-acrylamide (KLAAm) and DMA.

Entry	Equiv. to CTA			Conv. (%)				
	KLAAm	DMA	$[M]_0$	KLAAm	DMA	$M_{n,theo}$ (g/mol)	$M_{n,GPC}$ (g/mol)	$Đ$
[a]**P13**	25	0	0.09 M	40%	N/A	17 207	24 100	1.09
[a]**P14**	25	25	0.18 M	98%	99%	45 032	48 200	1.03
[a]**P15**	25	75	0.36 M	99%	99%	49 982	53 600	1.08
[a]**P16**	25	150	0.72 M	99%	99%	57 407	62 400	1.16

Note: In each polymerization, 200 µL of acetate buffer (0.1 M, pH 5) was used. [M]/[CTA]/[EY]/[PMDETA] = X/1/0.05/1. [a]The polymerizations were triggered by blue LED.

5. References

1. Xu, J. T.; Shanmugam, S.; Fu, C. K.; Aguey-Zinsou, K. F.; Boyer, C., Selective Photoactivation: From a Single Unit Monomer Insertion Reaction to Controlled Polymer Architectures. *J. Am. Chem. Soc.* **2016,** *138* (9), 3094-3106.