Electronic Supplementary Material (ESI) for Soft Matter

Supporting Information:

pH-Triggered Shape Response of Cubical Ultrathin Hydrogel Capsules

Veronika Kozlovskaya, Yun Wang, William Higgins, Jun Chen, Yi Chen, Eugenia Kharlampieva*

University of Alabama at Birmingham, Department of Chemistry, Birmingham, Alabama, 35294

*The correspondence address: University of Alabama at Birmingham, Department of Chemistry, 901 14th Street South CHEM291, Birmingham, Alabama, USA. Tel: 12059340974; E-mail: ekharlam@uab.edu

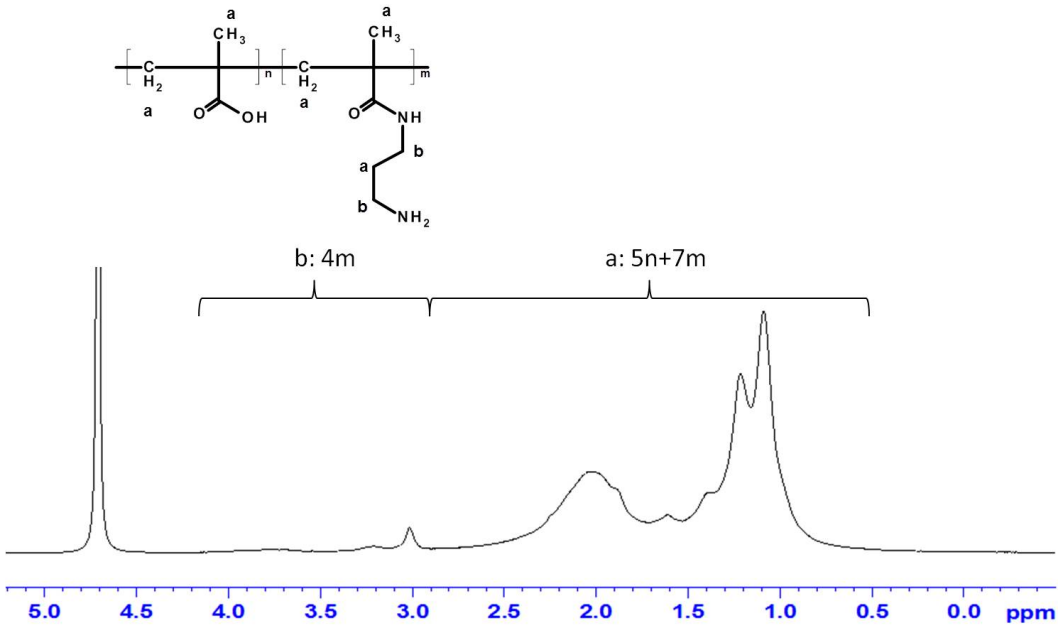

Fig. S1. ^{1}H NMR spectrum of poly(metacrylic acid-co-(aminopropyl)methacrylamide copolymer containing 6% of (aminopropyl)methacrylamide) units after hydrolysis of a *t*BOC protective group. The fraction of (aminopropyl)methacrylamide) -containing units was calculated as follows: f=m/(m+n), where m/n ratio was calculated from the integral intensities corresponding to $–CH_2N-$ protons (4m; δ: 2.9-4.2 ppm) and to $-CH_2-$ protons (5n+7m; δ: 0.5-2.9 ppm)

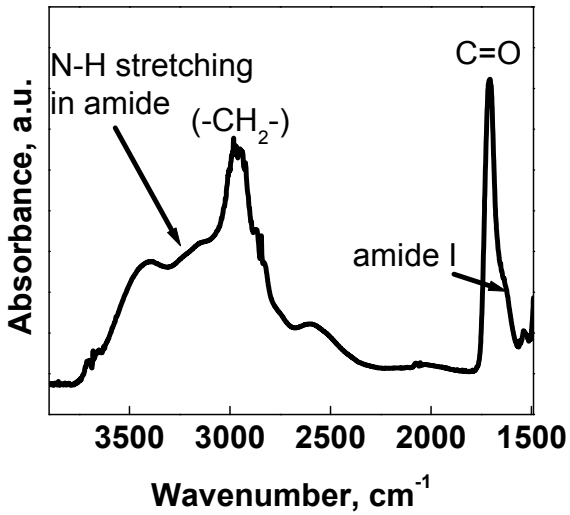

Fig. S2. FT-IR spectrum of poly(metacrylic acid-co-(aminopropyl)methacrylamide copolymer containing 6% of (aminopropyl)methacrylamide) units.

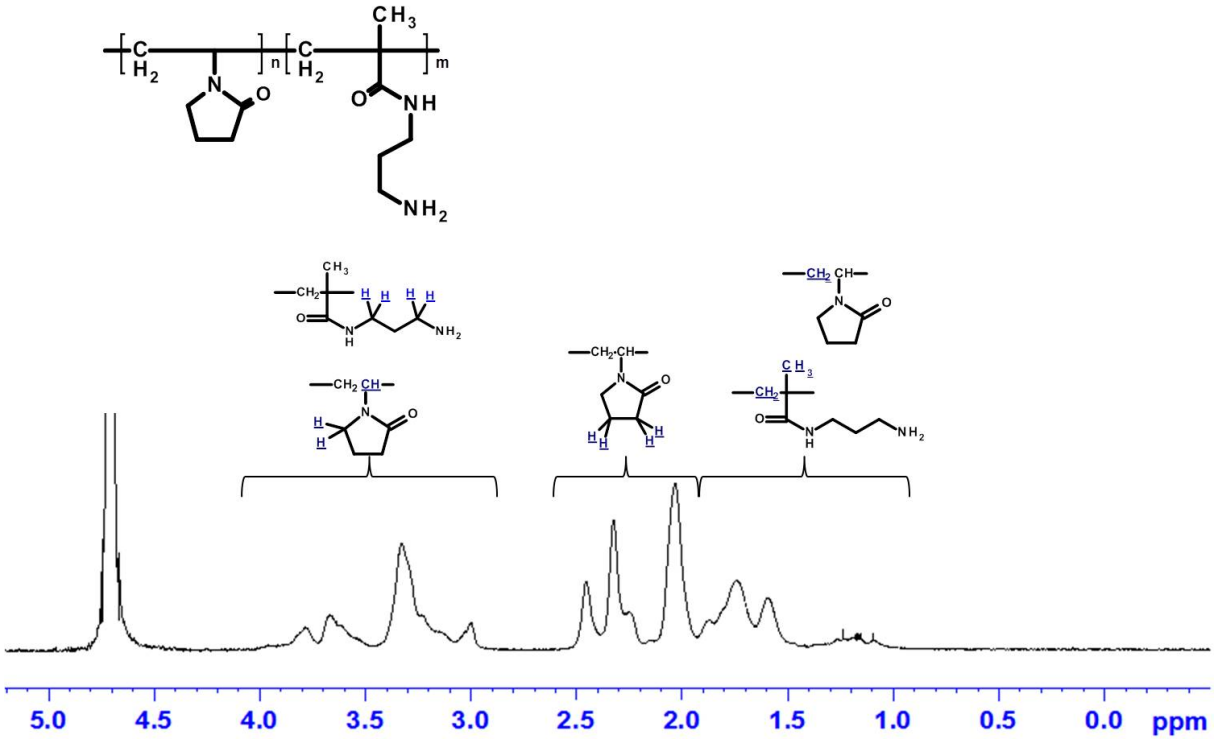

Fig. S3. ^{1}H NMR spectrum of poly(N-vinylpyrrolidone-co-(aminopropyl)methacrylamide copolymer containing 8% of (aminopropyl)methacrylamide) units after hydrolysis of a *t*BOC protective group. The fraction of (aminopropyl)methacrylamide) -containing units was calculated as follows: f=m/(m+n), where m/n ratio was calculated from the integral intensities corresponding to –CH_2N- protons (3n+4m; δ: 2.9-4.1 ppm) and to -C$\underline{H_2}$CO- protons (2n; δ: 2.2-2.6 ppm)

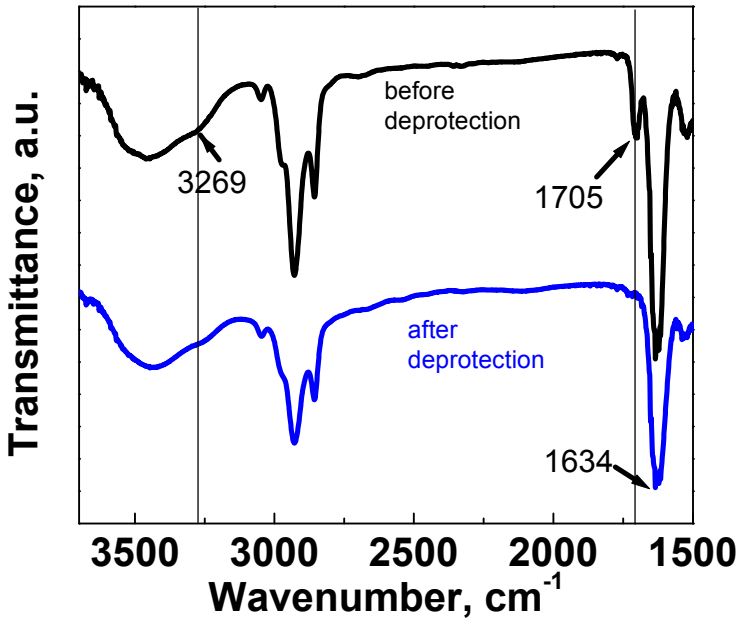

Fig. S4. FT-IR spectra of poly(N-vinylpyrrolidone-co-(aminopropyl)methacrylamide copolymer containing 14% of (aminopropyl)methacrylamide) units before and after hydrolysis of a *t*BOC protective group. The absorption band 3269 cm^{-1} corresponds to N-H stretching; The 1705 cm^{-1} peak corresponds to –C=O group in butoxycarbonyl protective group which is removed after acidic hydrolysis in methanol. The 1634 cm^{-1} band is due to the carbonyl groups in pyrrolidone ring and (aminopropyl)methacrylamide units.

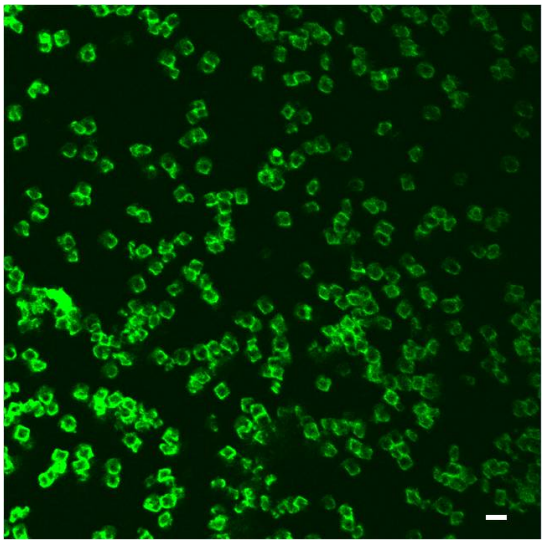

Fig. S5. CLSM image of hollow cubical $(PMAA)_{20}$ copolymer hydrogel capsules at pH=3. The scale bar is 5 μm.

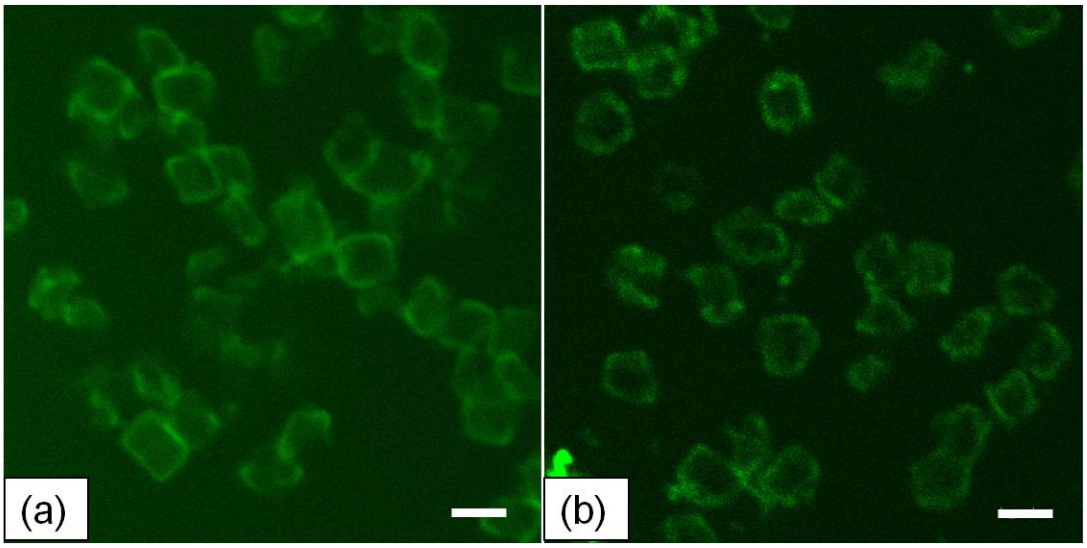

Fig. S6. CLSM images of hollow cubical $(PMAA\text{-}NH\text{-}PMAA)_{20}$ copolymer hydrogel capsules at pH=3 before exposure to pH=8 (a) and at pH=3 after the exposure (b). The scale bar is 3 μm in both images.

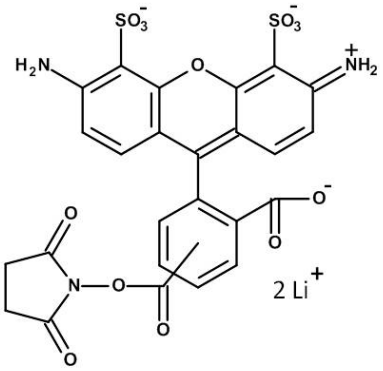

Fig. S7. Structure of Alexa Fluor 488 carboxylic acid, succinimidyl ester (Invitrogen)

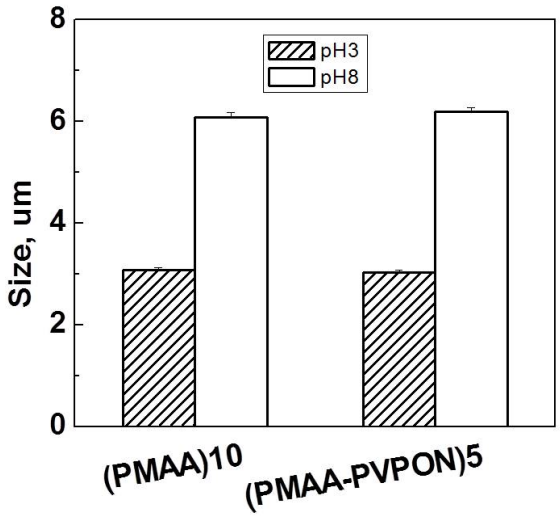

Fig. S8. pH-Dependent size variations of hollow $(PMAA)_{10}$ and $(PVPON\text{-}PMAA)_5$ capsules made using on spherical silica particles as sacrificial templates. Size analysis was performed using CLSM images of the capsules exposed to appropriate pH values. The $(PVPON\text{-}PMAA)_5$ capsules were made using PVPON-NH_2-14 copolymer.

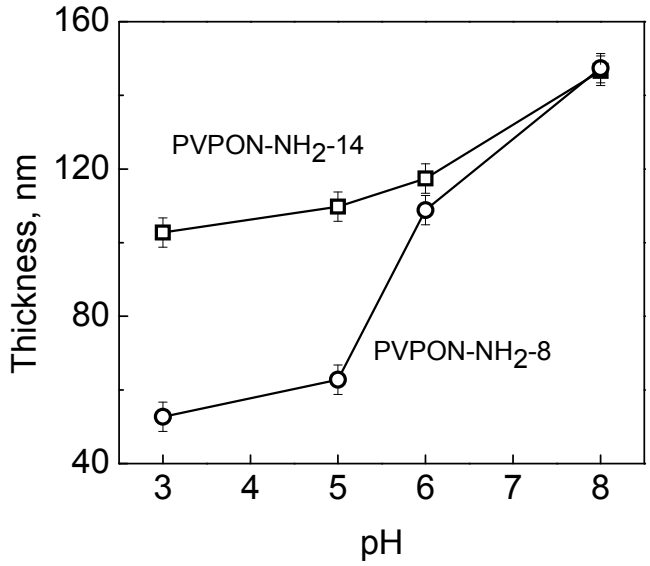

Fig. S9. pH-Dependent size variations of cross-linked $(PVPON\text{-}PMAA)_n$ films attached to surface of silicon wafer (in situ ellipsometry). Dry thicknesses are 45 nm and 33.5 nm for $(PVPON\text{-}PMAA)_n$ hydrogel films made of PVPON-NH_2-14 (n=5) and PVPON-NH_2-8 (n=6), respectively.

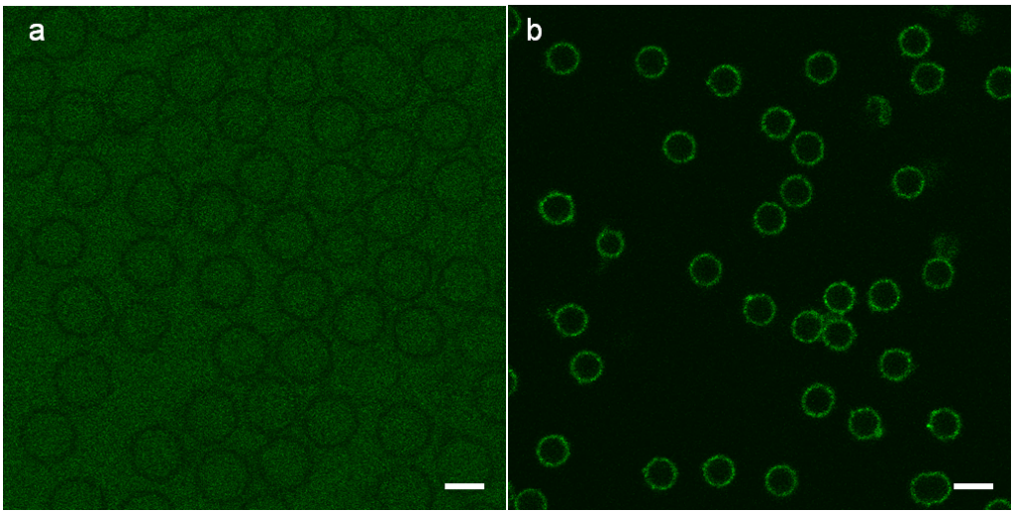

Fig. S10. Confocal images of $(PMAA)_{20}$ hollow spherical capsules at pH=8 (a) and pH=3 (b). The scale bar is 4 μm in both images.