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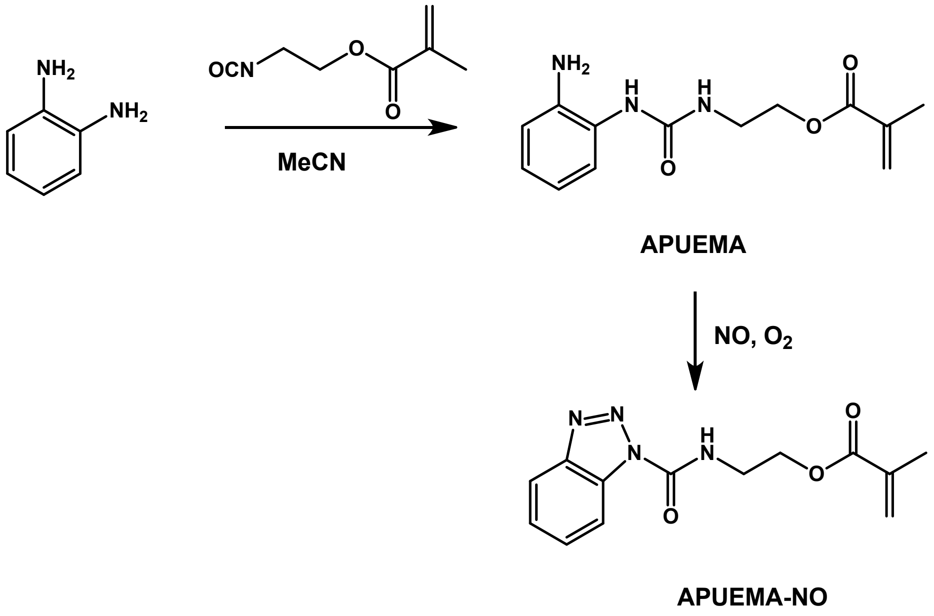
Supporting Information

The use of endogenous gaseous molecules (NO and CO_2) to regulate the self-assembly of a dual-responsive triblock copolymer

Jinming Hu, [†] **Michael R Whittaker,** [†] **Yang Li,** [†] **John F Quinn,***[†] **and Thomas P Davis***[†‡]

[†]*ARC Centre of Excellence in Convergent Bio-Nano Science & Technology, Monash Institute of Pharmaceutical Sciences, Monash University, Parkville Campus, Royal Parade, Melbourne, VIC 3052;* [‡] *Department of Chemistry, University of Warwick, Gibbet Hill, Coventry, CV4 7AL*

To whom the correspondence should be addressed. Email: Thomas.P.Davis@monash.edu or John.F.Quinn@monash.edu



Scheme S1. Synthetic route for the preparation of the NO-responsive monomer, 2-(3-(2-aminophenyl)ureido)ethyl methacrylate (APUEMA), and the subsequent formation of benzotriazole-derivates (APUEMA-NO) in the presence of nitric oxide.

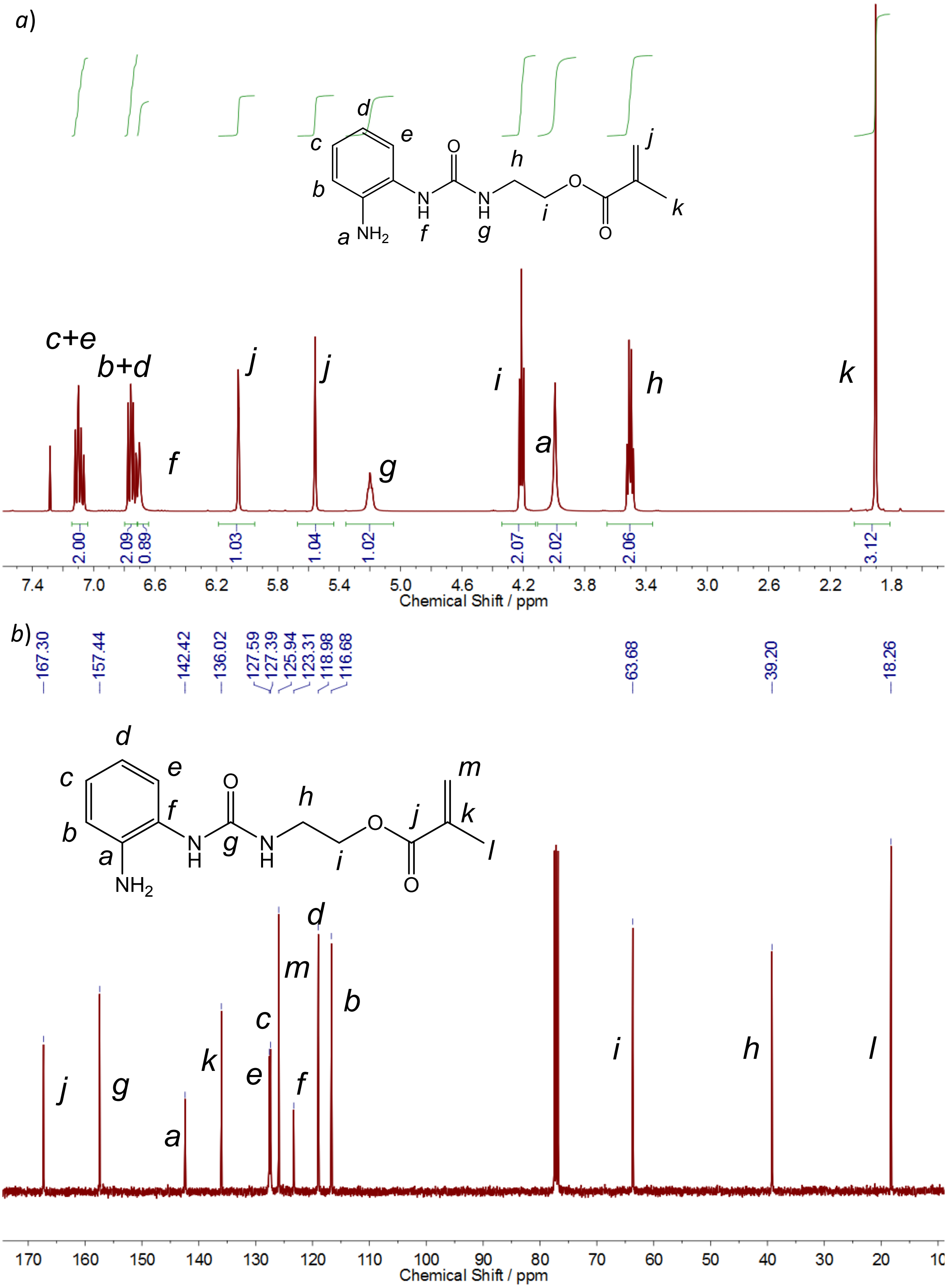


Figure S1. (a) ^{1}H and (b) ^{13}C NMR spectra recorded in $CDCl_3$ for APUEMA monomer, respectively.

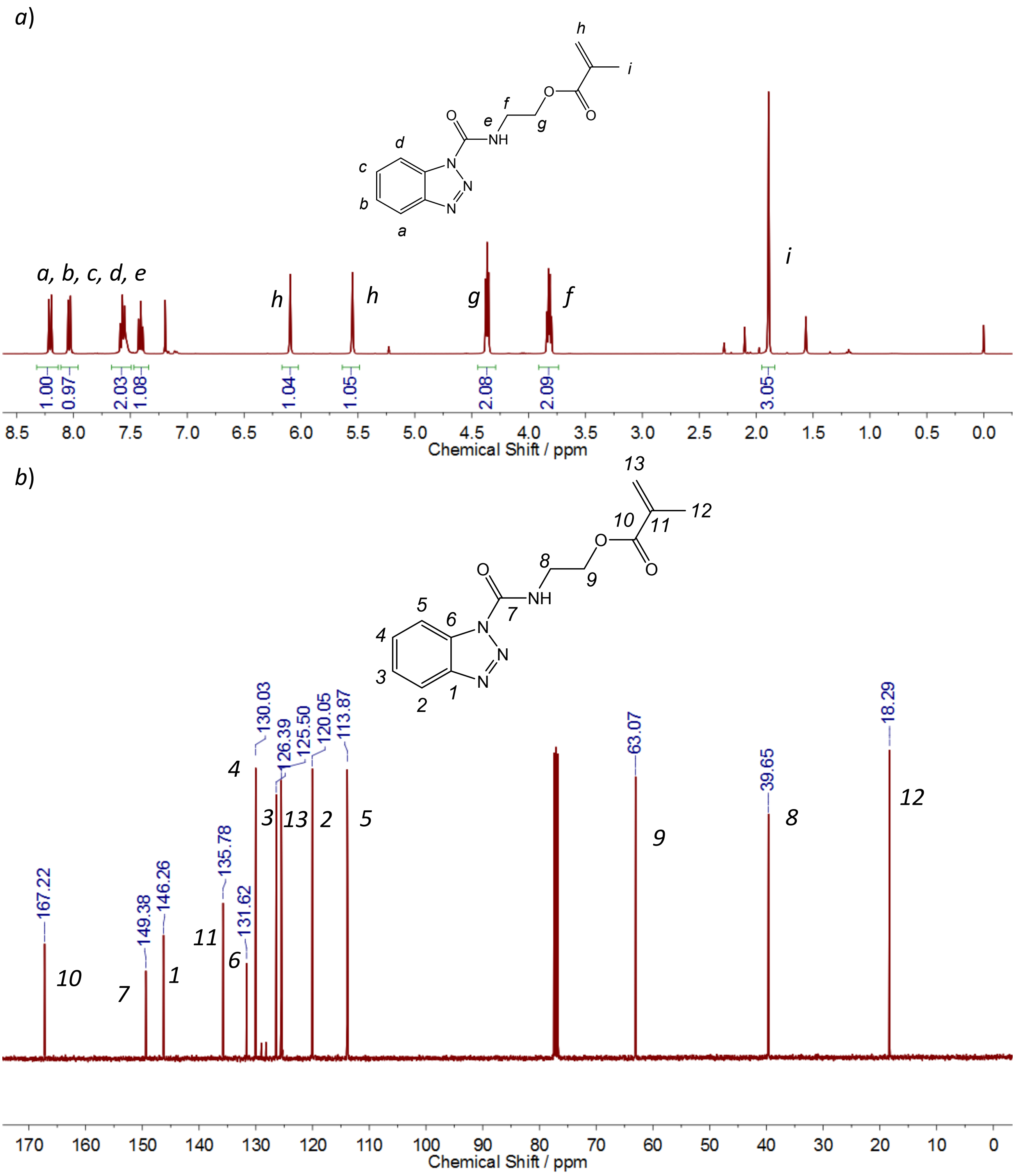


Figure S2. (a) ^{1}H and (b) ^{13}C NMR spectra recorded in $CDCl_3$ for APUEMA monomer after reaction with NO (APUEMA-NO), respectively.

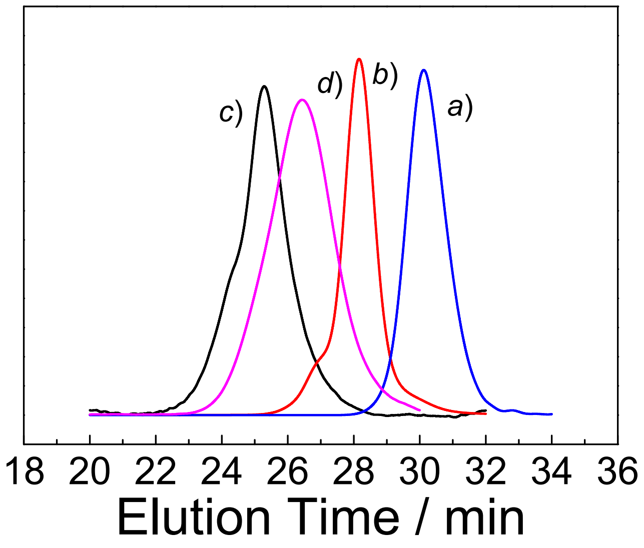


Figure S3. GPC traces recorded for (a) POEGMA macroRAFT agent, (b) OD diblock precursor, (c) ODA triblock copolymer, and (d) ODA triblock copolymer after reaction with NO.

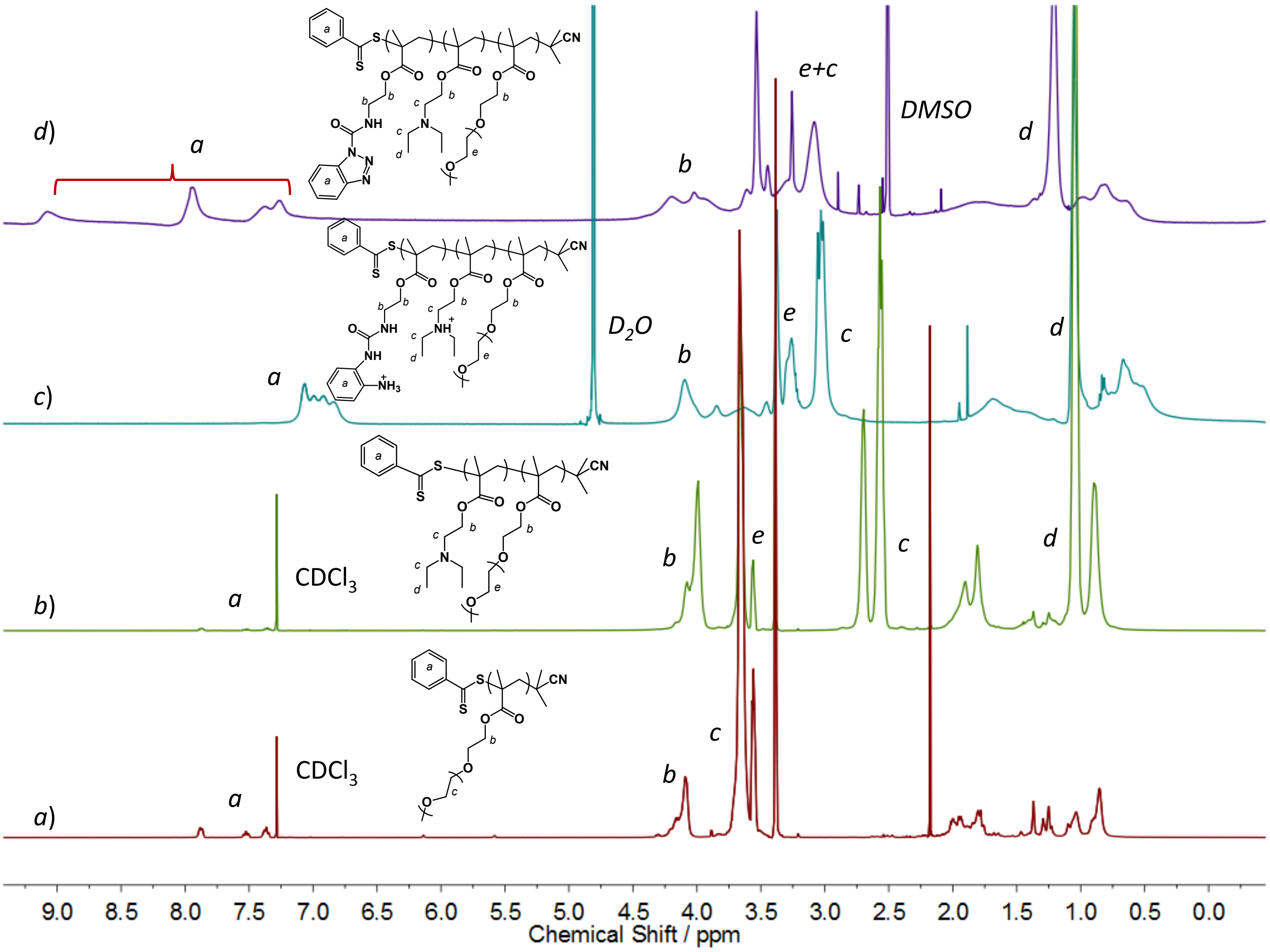


Figure S4. ^{1}H NMR spectra recorded for (a) POEGMA macroRAFT agent, (b) OD diblock precursor in $CDCl_3$, (c) ODA triblock copolymer in D_2O/DCl (pH = 1), and (d) ODA triblock copolymer after reaction with NO in DMSO-d_6.

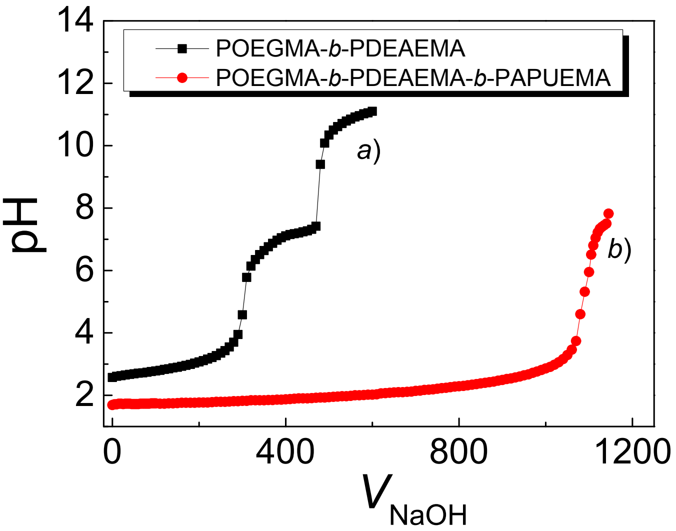


Figure S5. Potentiometric titration curves obtained for an aqueous solution (1.0 g/L) of (a) OD diblock precursor and (b) ODA triblock copolymer, respectively.

Note: the potentiometric titration was performed as follows: 20 mg polymer was dissolved in 20 ml diluted HCl solution to provide1.0 mg/ml polymer stock solutions without filtration. The pH of the polymer solutions was then tuned by gradual addition of 1.0 M NaOH solution.

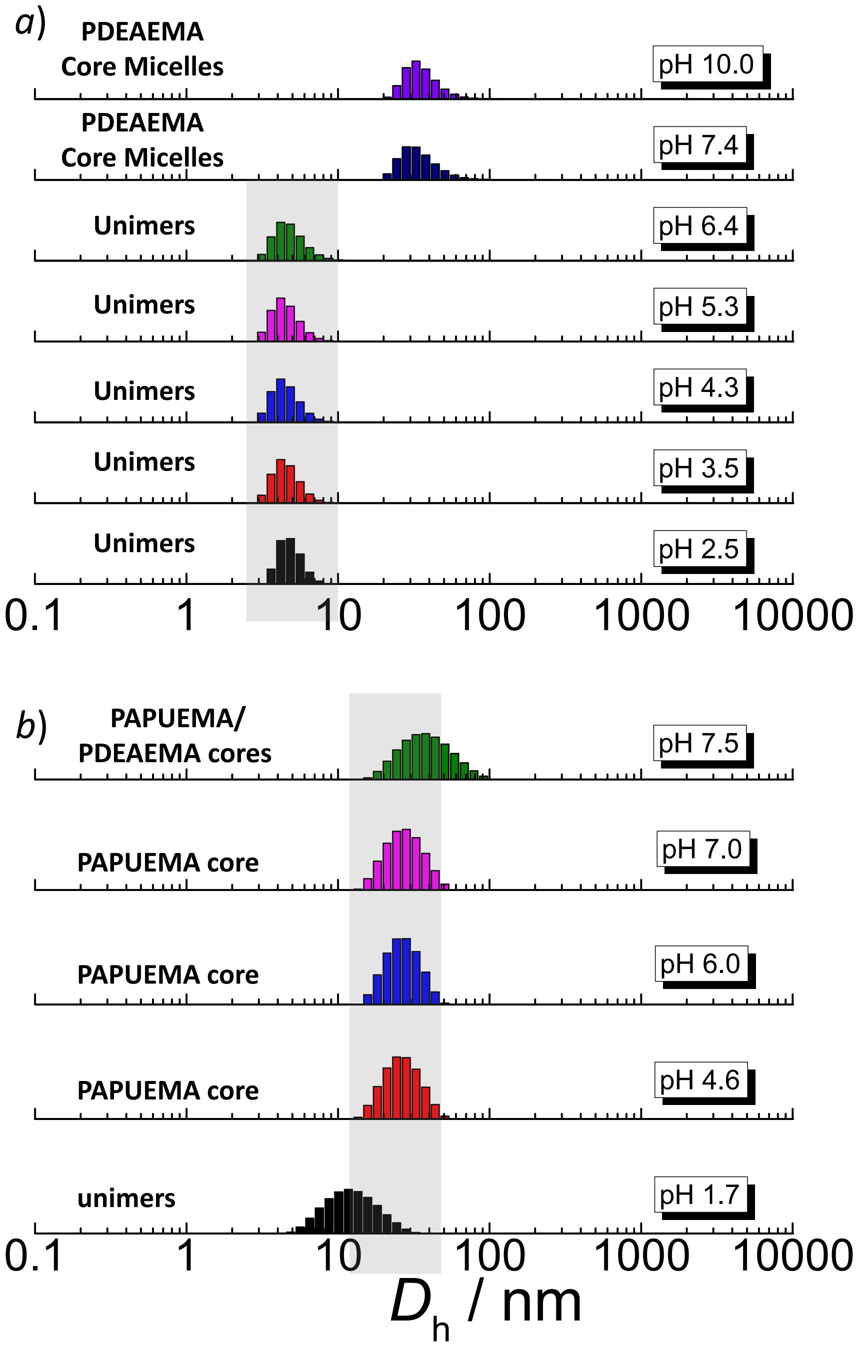


Figure S6. Variation of number-average hydrodynamic distribution, $f(D_h)$, for an aqueous solution of (a) OD diblock precursor and (b) ODA triblock copolymer (1.0 g/L) with pH. The data represent a single experiment performed in triplicate. Note: the pH-induced self-assembly was performed as follows: 20 mg polymer was dissolved in 20 ml diluted HCl solution to provide polymer stock solutions (1.0 mg/ml). The pH of the polymer solutions was then tuned by gradual addition of 1.0 M NaOH solution. The aqueous solutions were filtrated by passing through a cellulose membrane (pore size: 0.45 μm) prior to DLS measurements.

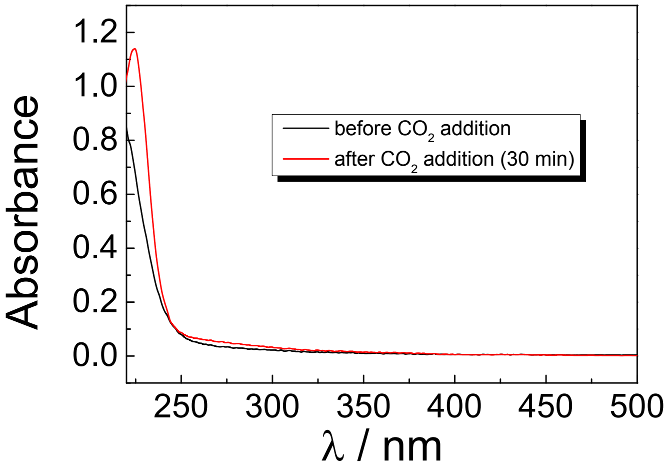


Figure S7. Absorbance spectra of aqueous solutions (0.05 g/L) of OD diblock copolymer in the absence and presence of CO_2 addition. Note: The RAFT chain terminus was removed in the presence of an excess amount of AIBN.