ETHzürich

Macromolecular Engineering: Networks and Gels

Lecture 12: Presentation description

Prof. Dr. Mark W. Tibbitt, 31. March 2021

Logistics:
   - Length: ~15 minutes including ?s/discussion
   - Present in groups: groups of ~4-6, ~15–20 groups total
   - Dates: 10.5, 12.5, 17.5, & 19.5
   - Pick a paper on a subject area of your interest!
     - I will suggest some papers in lecture before Easter break
     if you would like to select from those you can.

Desired structure:
   - Manuscript summary (1 slide)
   - Main content or application (2–4 slides)
   - Use of concepts from Networks & Gels (1–2 slides)
   - Summary/questions (1 slide)

Manuscript summary

Modeling Controlled Photodegradation in Optically Thick Hydrogels

Mark W. Tibbitt,[1] April M. Kloxin,[1,2] Kristi S. Anseth[1,2]

[1]Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado 80303
[2]Howard Hughes Medical Institute, University of Colorado Boulder, Boulder, Colorado 80303
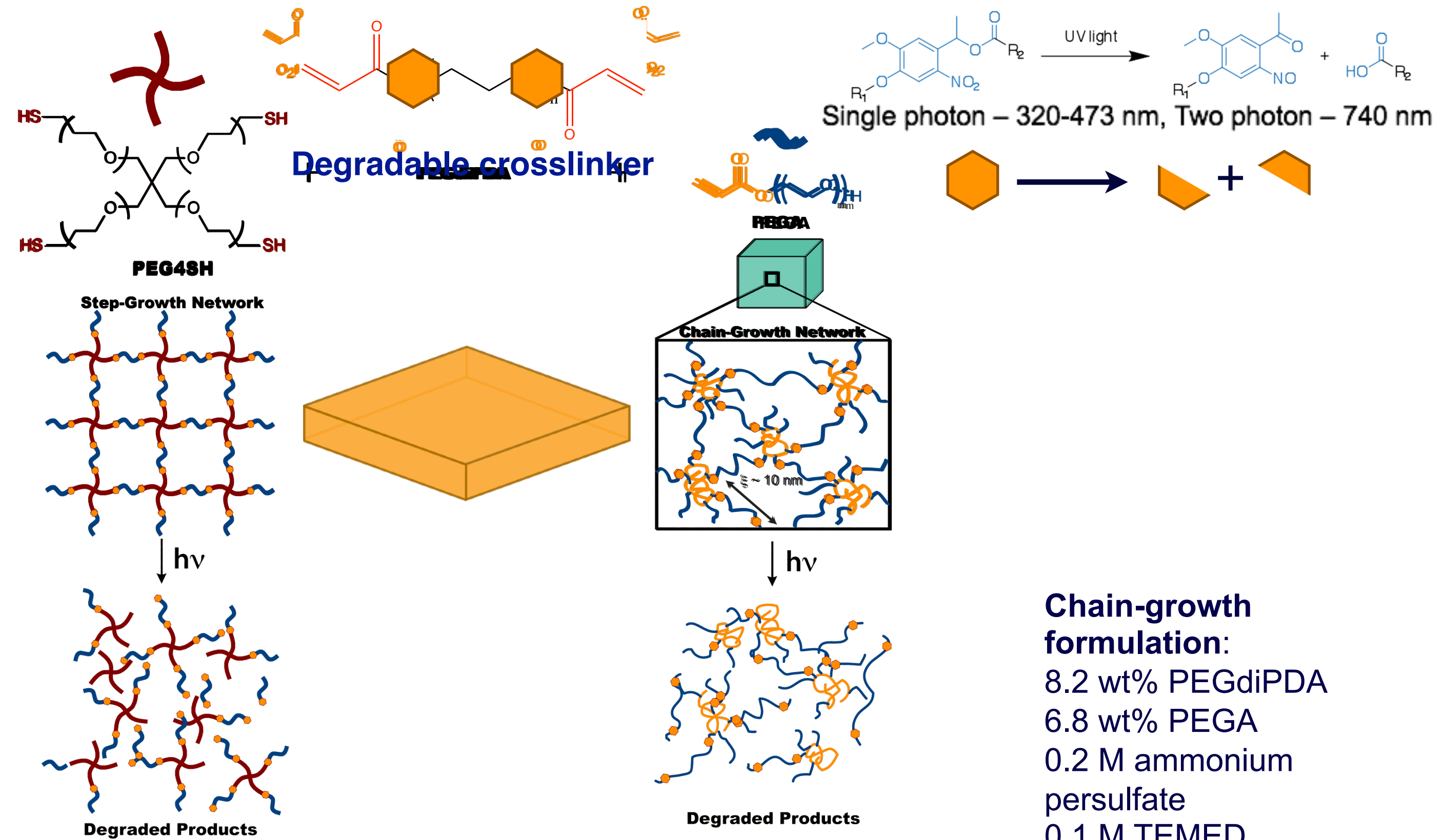Correspondence to: K. S. Anseth (E-mail: kristi.anseth@colorado.edu)

ABSTRACT: There is a growing interest in developing dynamically responsive hydrogels whose material properties are modulated by environmental cues, including with light. These photoresponsive hydrogels afford spatiotemporal control of material properties through an array of photoaddition and photodegradation reactions. For photoresponsive hydrogels to be utilized most effectively in a broad range of applications, the photoreaction behavior should be well understood, enabling the design of dynamic materials with uniform or anisotropic material properties. Here, a general statistical-kinetic model has been developed to describe controlled photodegradation in hydrogel polymer networks containing photolabile crosslinks. The heterogeneous reaction rates that necessarily accompany photochemical reactions were described by solving a system of partial differential equations that quantify the photoreaction kinetics in the material. The kinetics were coupled with statistical descriptions of network structure in chain polymerized hydrogels to model material property changes and mass loss that occur during the photodegradation process. Finally, the physical relevance of the model was demonstrated by comparing model predictions with experimental data of mass loss and material property changes in photodegradable, PEG-based hydrogels. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. 2013, 51, 1899–1911

KEYWORDS: biomaterials; degradation; hydrogels; modeling; photophysics

The authors developed a statistical-kinetic model of how light can be used in a controlled manner to dissolve photodegradable hydrogels.

UV light

Single photon – 320-473 nm, Two photon – 740 nm

Degradable crosslinker

PEGdiPDA

PEG4SH

PEGA

Step-Growth Network

Chain-Growth Network

ξ ~ 10 nm
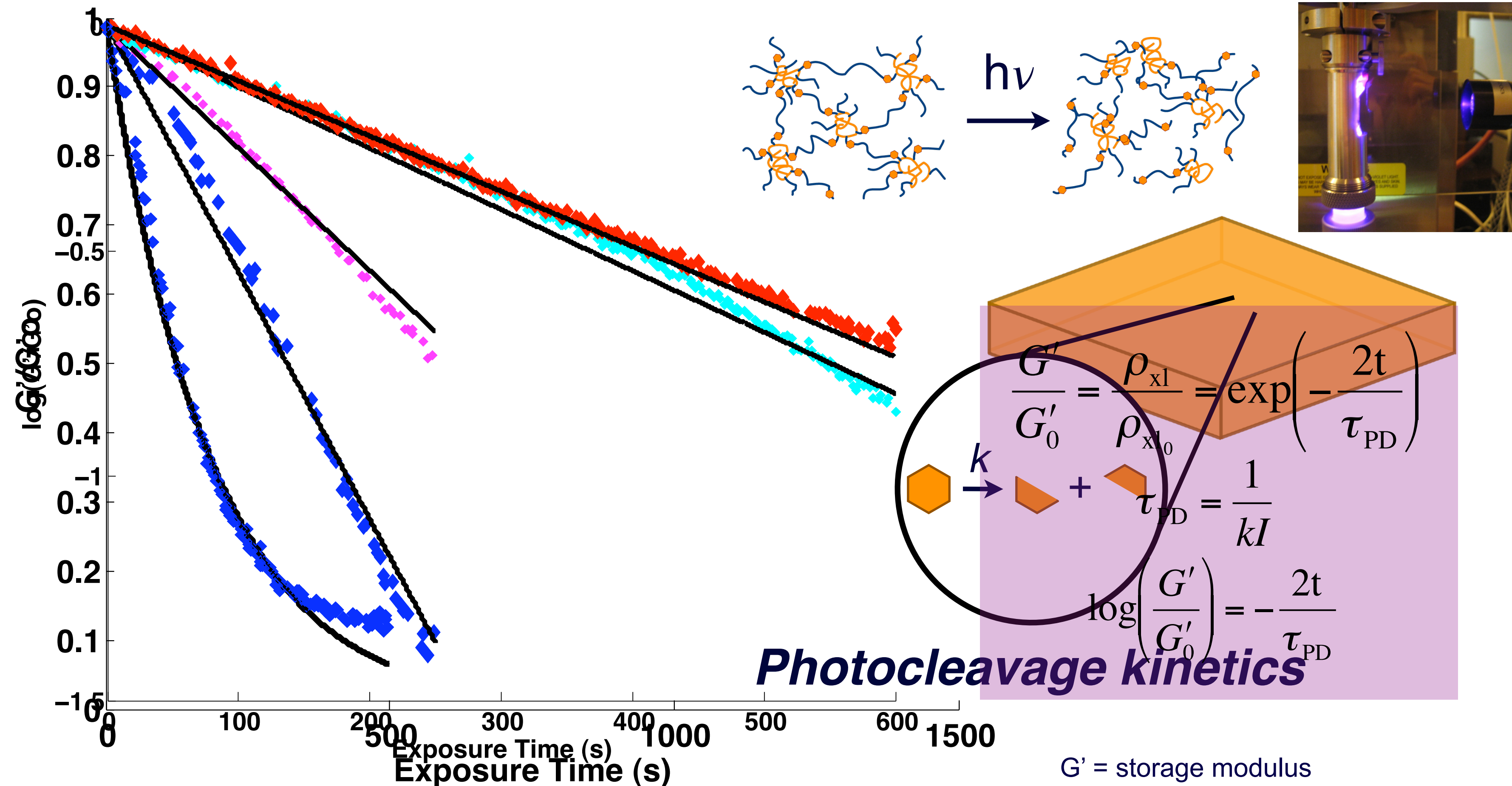
$h\nu$

$h\nu$

Degraded Products

Degraded Products

Step-growth formulation:
6.2 wt% PEGdiPDA
3.8 wt% PEG4SH 5K
300 mM triethanolamine
PBS pH 8.0
G' ~ 3.8 kPa

Chain-growth formulation:
8.2 wt% PEGdiPDA
6.8 wt% PEGA
0.2 M ammonium persulfate
0.1 M TEMED
PBS pH 8.0
G' ~ 10.6 kPa

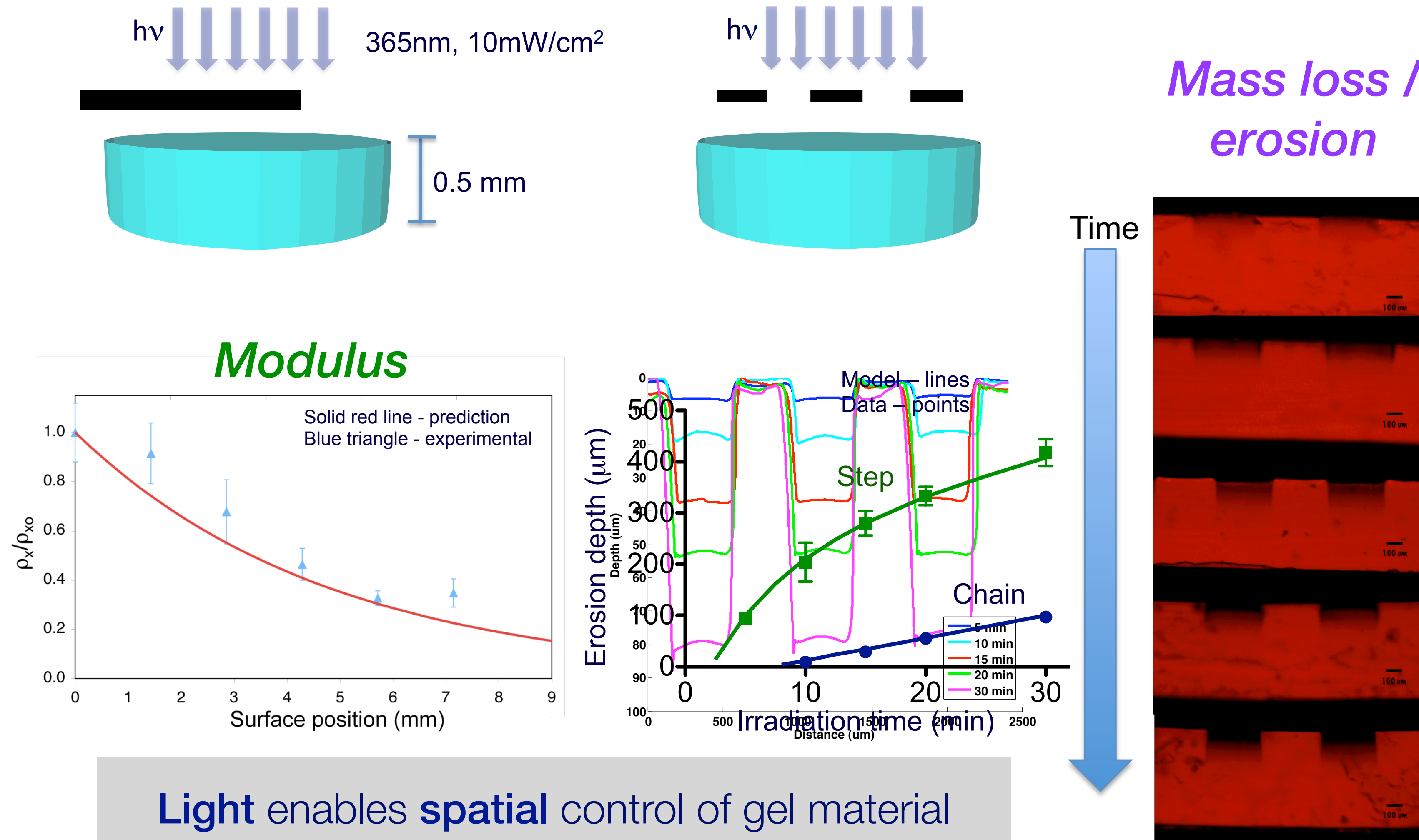**Decreased** crosslinking density (ν) leads to **increased** water swelling (Q) and mesh size (ξ) and **decreased** modulus (G, E).

Kloxin, A.M.; Kasko, A.M.; Salinas, C.N.; Anseth, K.S. *Science,* **2009**, *324*, 59.
Kloxin, A.M.; Tibbitt, M.W.; Anseth, K.S. *Nature Protocols,* **2010**, *5*, 1867.
Tibbitt, M.W.; Kloxin, A.M.; Sawicki, L.A.; Anseth, K.S. *Macromolecules,* **2013**, *46*, 2785.

$$\frac{G'}{G'_0} = \frac{\rho_{xl}}{\rho_{xl_0}} = \exp\left(-\frac{2t}{\tau_{PD}}\right)$$

$$k$$

$$\tau_{PD} = \frac{1}{kI}$$

$$\log\left(\frac{G'}{G'_0}\right) = -\frac{2t}{\tau_{PD}}$$

Photocleavage kinetics

log(G'/G'₀)
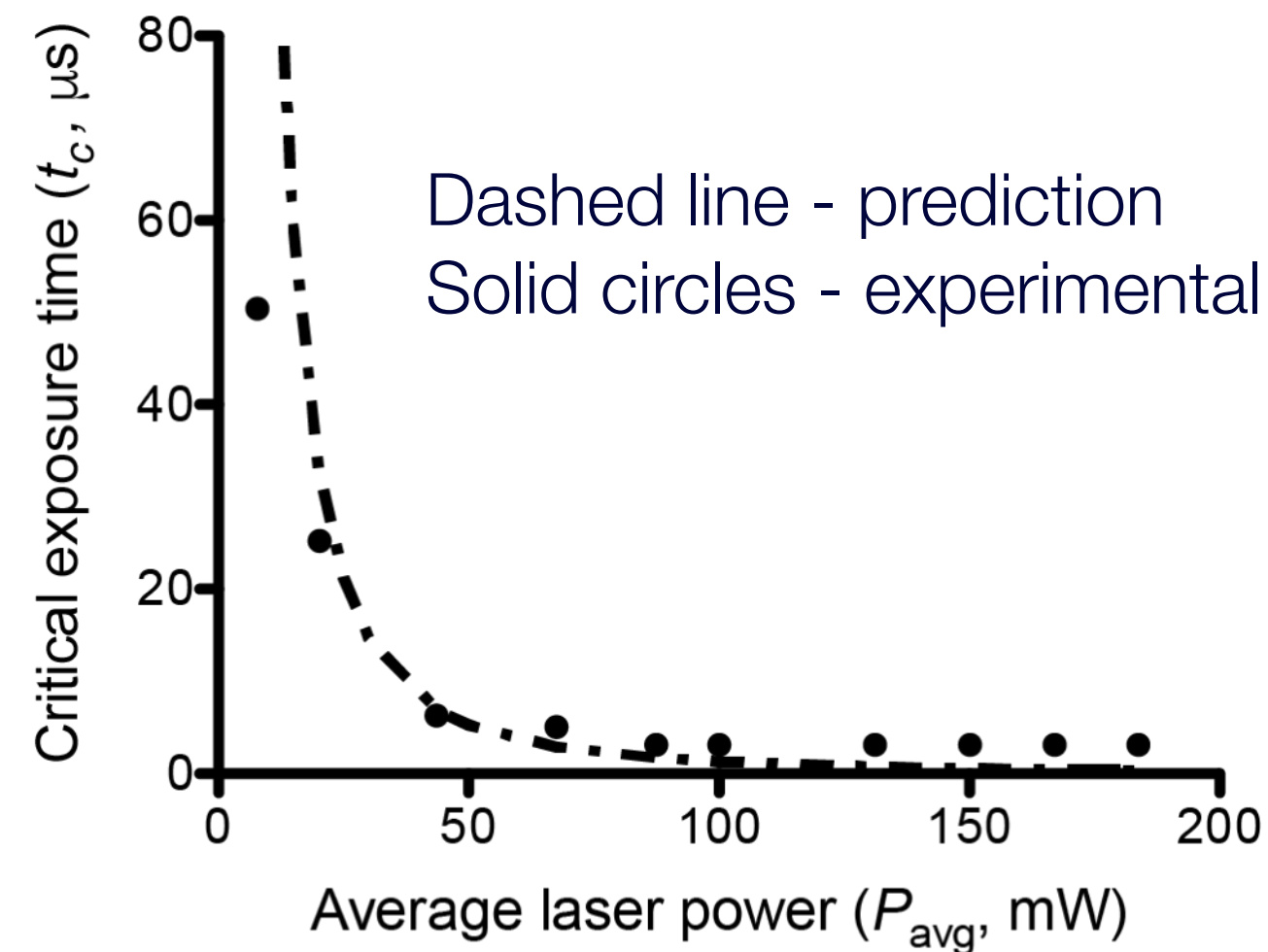
Exposure Time (s)

Exposure Time (s)

G' = storage modulus

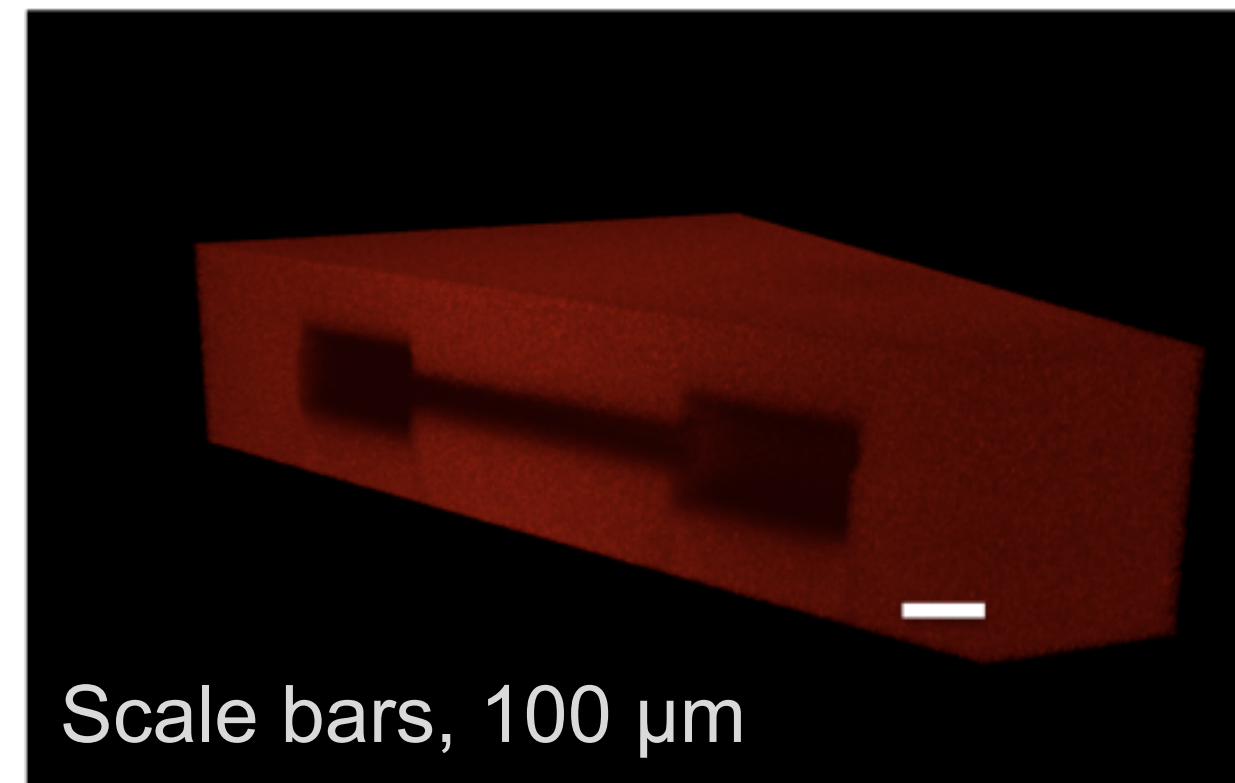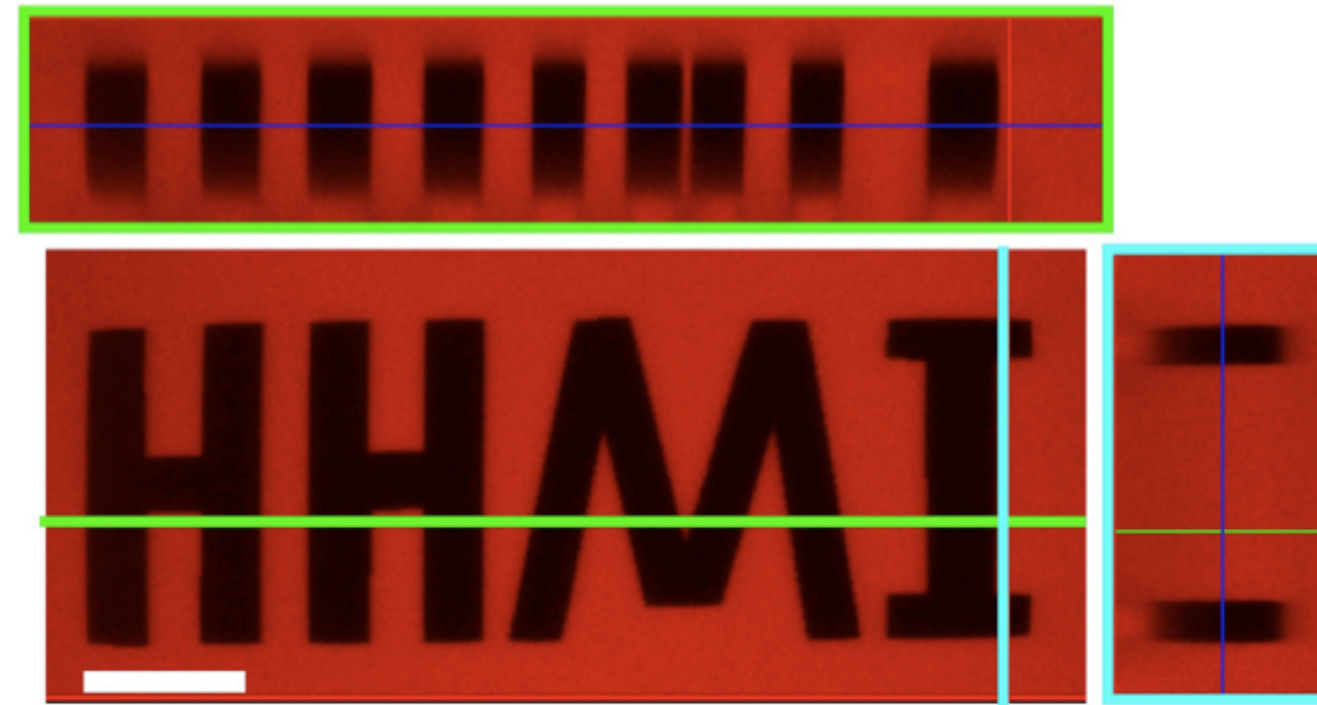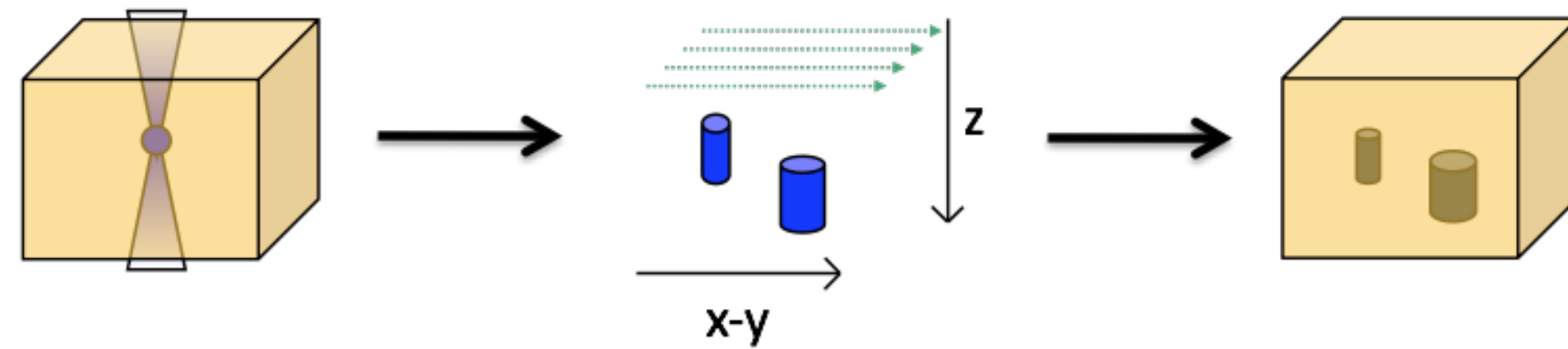Gels degrade in response to **light** in a **predictable** and **tunable** manner that is quantified with a **statistical-kinetic model**.

Kloxin, A.M.; Kasko, A.M.; Salinas, C.N.; Anseth, K.S. *Science,* **2009**, *324,* 59.
Kloxin, A.M.; Tibbitt, M.W.; Anseth, K.S. *Nature Protocols,* **2010**, 5, 1867.
Tibbitt, M.W.; Kloxin, A.M.; Sawicki, L.A.; Anseth, K.S. *Macromolecules,* **2013**, *46*, 2785.

hν   365nm, 10mW/cm^2

0.5 mm

hν

Mass loss / erosion

Time

Modulus

Solid red line - prediction
Blue triangle - experimental

ρ_x/ρ_{xo}

Surface position (mm)

Model — lines
Data — points

Erosion depth (µm)

Depth (µm)

Step

Chain

5 min
10 min
15 min
20 min
30 min

Irradiation time (min)

Distance (um)

Light enables **spatial** control of gel material properties via user-defined, *in situ* **patterning**.

Kloxin, A.M.; Tibbitt, M.W.; Kasko, A.M.; Fairbairn, J.A.; Anseth, K.S. *Advanced Materials*, **2010**, *22*, 61.
Tibbitt, M.W.; Kloxin, A.M.; Sawicki, L.A.; Anseth, K.S. *Macromolecules*, **2013**, *46*, 2785.
Tibbitt, M.W.; Kloxin, A.M.; Anseth, K.S. *Journal of Polymer Science Part A: Polymer Chemistry*, **2013**, *51*, 1899.

Scale bars, 100 µm

Dashed line - prediction
Solid circles - experimental

Focused light enables **precise** and **predictable** gel erosion on the micron-scale

Kloxin, A.M.; Tibbitt, M.W.; Kasko, A.M.; Fairbairn, J.A.; Anseth, K.S. *Advanced Materials,* **2010**, *22*, 61.
Tibbitt, M.W.; Kloxin, A.M.; Anseth, K.S. *Journal of Polymer Science Part A: Polymer Chemistry,* **2013**, *51*, 1899.
Tibbitt, M.W.; Kloxin, A.M.; Dyamenahalli, K.U.; Anseth, K.S. *Soft Matter,* **2010**, *4*, 5100.

Rubber elasticity theory:

$$\ln\left(\frac{G'}{G'_0}\right) = -2kt$$

$$G \equiv \nu k_B T$$

Mean-Field approach:

$$P(z,t) = 1 - \frac{[NBE](z,t)}{[NBE]_0}$$

Flory-Stockmayer equation:

$$P_{rg} = 1 - \frac{1}{\sqrt{N-1}}$$

$$P = \frac{1}{\sqrt{r(f_A - 1)(f_B - 1)}}$$

ETH *zürich*

Gelation theory and rubber elasticity were applied to develop a statistical-kinetic model of network degradation in photodegradable hydrogels.

Mean-field approaches similar to those used in class simplified the model framework.

Questions?