Problem Set 3 **20.462J/3.962J**
Issued: 03/02/06 **Spring 2006**
Due: 03/09/06
100 points total

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1. Consider a hydrogel formed by polymerizing acrylate-encapped polylactide-b-poly(ethylene glycol)-b-polylactide, as illustrated below. The gel will break down to water-soluble products via hydrolysis of the PLA linkages in the crosslinks, releasing water-soluble PEG and polyacrylate chains. Also shown below is experimental data for the swelling ratio Q vs. time for a gel with 2 polylactide repeat units on each side of PEG in the crosslinks, and a best-fit line for an exponential dependence of swelling on time. Use this information to answer the questions below: our objective is to predict the exponential swelling behavior of these gels.

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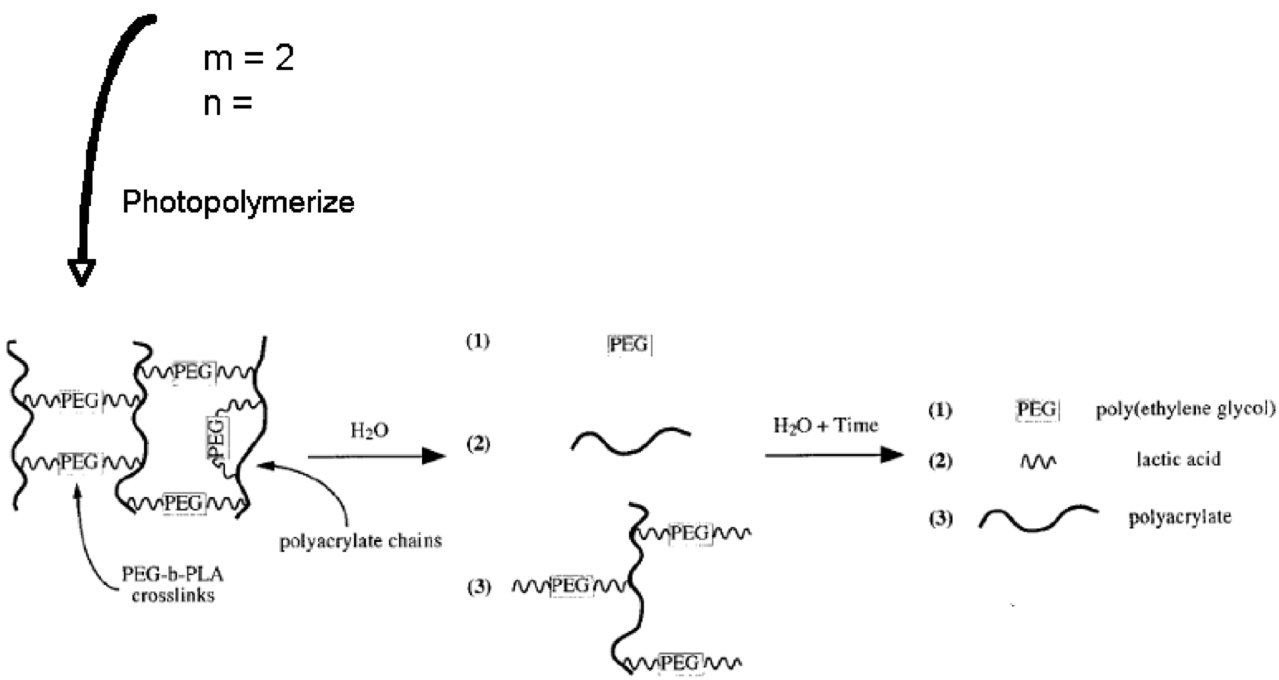
Please see:

Figure 2 in Mason, Mariah N., Andrew T. Metters, Christopher N. Bowman, and Kristi S. Anseth. "Predicting Controlled-Release Behavior of Degradable PLA-b-PEG-b-PLA Hydrogels." *Macromolecules* 34, no.13 (2001): 4630-4635.



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a. Assume that the PLA units in the crosslinks degrade by an autocatalytic mechanism, with the following kinetics:

$$\frac{dn_E}{dt} = -k' n_E$$

…where n_E is the number of intact ester linkages at any time. The number of ester linkages can be related to the number of network sub-chains by the following relationship:

$$\upsilon = \frac{n_E}{2j}$$

Where *j* is the number of PLA units in each degradable block of the crosslinks and the factor of two accounts for the 2 PLA blocks in each crosslink (one on each side of the center PEG linker). Using this information, write an equation for the number of network subchains as a function of time.

b. Using your result from part (a), show that the molecular weight between crosslinks, M_c, must have an exponential dependence on time:

$$M_c \propto e^{k' t}$$

c. Flory-Peppas theory gives us the relationship between M_C and the volume fractions of polymer in a swollen hydrogel:

$$\frac{1}{M_c} = \frac{2}{M} - \left(\frac{v_{sp,2}}{\overline{V}_1 \phi_{2,r}}\right) \frac{\left(\ln(1-\phi_{2,s}) + \phi_{2,s} + \chi \phi_{2,s}^2\right)}{\left[\left(\frac{\phi_{2,s}}{\phi_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{\phi_{2,s}}{\phi_{2,r}}\right)\right]}$$

Show that if $\phi_{2,s}$ is small (remember, the swelling ratio Q = $1/\phi_{2,s}$—small $\phi_{2,s}$ implies a swollen gel) and the molecular weight of the network chains *M* is very large, then this expression can be simplified to:

$$\frac{1}{M_c} \cong \frac{v_{sp,2}(1-\chi)\phi_{2,s}^{5/3}}{\overline{V}_1 \phi_{2,r}^{2/3}}$$

d. Show that by combining the results from parts (b) and (c), we have the result that the swelling ratio Q has an exponential dependence on time:

$$Q \propto e^{k'(3/5)t}$$