Problem Set 3 Model Solutions
Issued: 03/02/06
Due: 03/09/06
100 points total

20.462J/3.962J
Spring 2006

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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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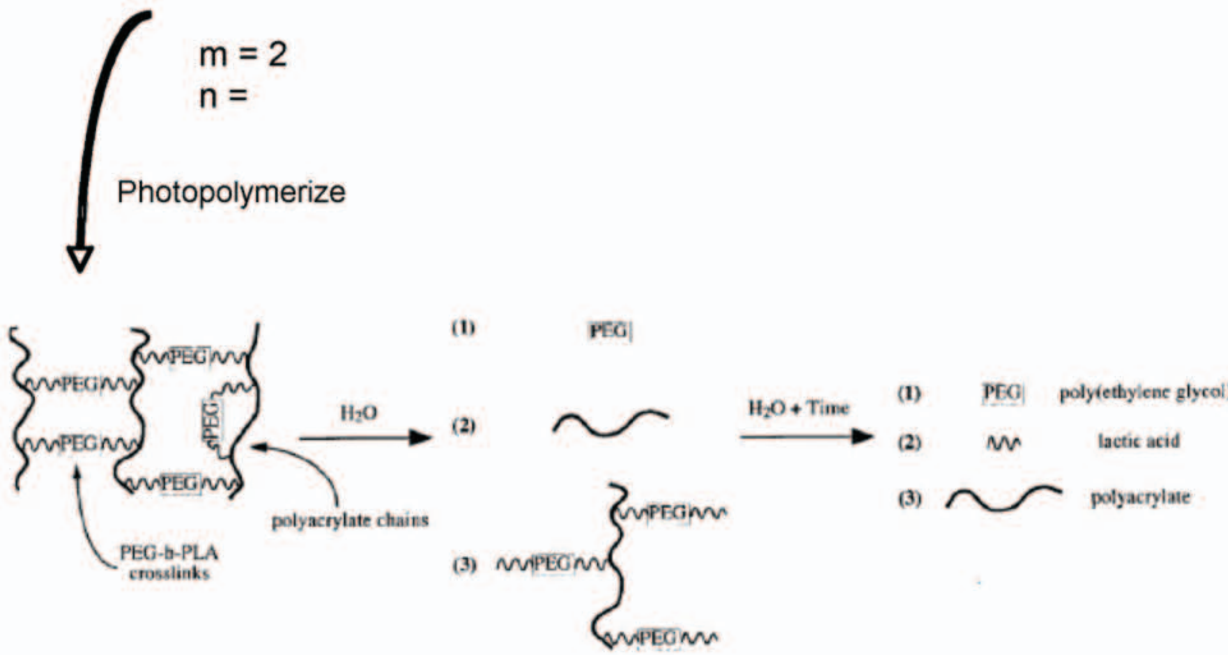
Please see:
Figure 1 in Mason, Mariah N., Andrew T. Metters, Christopher N. Bowman, and Kristi S. Anseth. "Predicting Controlled-Release Behavior of Degradable PLA-b-PEG-b-PLA Hydrogels." *Macromolecules* 34, no. 13 (2001): 4630-4635.



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

$$(i) \qquad \frac{dn_E}{dt} = -k' n_E$$

…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:

$$(ii) \qquad \upsilon = \frac{n_E}{2j}$$

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.

INTEGRATING (i): $n_e(t) = n_{E,0} e^{-k't}$ …WHERE $n_{E,0}$ IS THE INITIAL # OF ESTER LINKAGES PRESENT. PLUGGING THIS INTO (ii):

$$\nu(t) = \frac{n_{E,0}}{2j} e^{-kt} = \underbrace{C}_{\text{CONSTANT}} e^{-k't}$$

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

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

FROM THE NOTES ON HYDROGEL SWELLING THEORY, WE HAVE A RELATIONSHIP BETWEEN ν AND M_C:

$$\nu = \frac{\bar{V}_2 N_{AV}}{V_{sp,2} M_C} \quad \text{OR} \quad \nu \propto \frac{1}{M_C}$$

THUS: $\nu \propto e^{-k't} \propto \frac{1}{M_C}$ OR: $M_C \propto e^{k't}$

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

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

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:

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

FIRST, WE LOOK AT THE $\ln(1-\Phi_{2,s})$ TERM. NOTE THAT WE CAN'T JUST ASSUME THIS TERM IS NEGLIGIBLE RELATIVE TO THE $\Phi_{2,s}$ TERM. INSTEAD, WE EXPAND IT:

$$\ln(1+x) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n+1} x^{n+1} \quad \text{FOR } |x| < 1$$

$$\therefore \ln(1-\Phi_{2,s}) \simeq -\Phi_{2,s} - \frac{\Phi_{2,s}^2}{2} + \underbrace{\cdots}_{\text{NEGLECT HIGHER-ORDER (VERY SMALL) TERMS}}$$

WE THEN HAVE:

$$\frac{1}{M_C} = \underbrace{\cancel{\frac{1}{M}}}_{\simeq 0 \text{ IF } M \text{ VERY LARGE}} - \frac{V_{sp,2}}{\bar{V}_1 \Phi_{2,r}} \left[\frac{\cancel{-\Phi_{2,s}} - \frac{\Phi_{2,s}^2}{2} + \cancel{\Phi_{2,s}} + \chi\Phi_{2,s}^2}{\left[\left(\frac{\Phi_{2,s}}{\Phi_{2,r}}\right)^{1/3} - \underbrace{\cancel{\frac{1}{2}\left(\frac{\Phi_{2,s}}{\Phi_{2,r}}\right)}}_{\text{NEGLIGIBLE NEXT TO } (\cdots)^{1/3} \text{ TERM FOR } \Phi_{2,s} \text{ SMALL}}\right]}\right]$$

$$\boxed{\frac{1}{M_C} \simeq -\frac{V_{sp,2}}{\bar{V}_1 \Phi_{2,r}} \frac{(-\Phi_{2,s}^2)\left(\frac{1}{2}-\chi\right)}{\left(\frac{\Phi_{2,s}}{\Phi_{2,r}}\right)^{1/3}} = \frac{V_{sp,2}\left(\frac{1}{2}-\chi\right)\Phi_{2,s}^{5/3}}{\bar{V}_1 \Phi_{2,r}^{2/3}}}$$

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:

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

$$Q = \frac{1}{\phi_{2,s}}$$

$$\frac{1}{M_c} \propto e^{-k't} \propto \phi_{2,s}^{5/3} \propto Q^{-5/3}$$

$$\therefore \boxed{Q \propto e^{k'\left(\frac{3}{5}t\right)}}$$

... THIS EXPONENTIAL DEPENDENCE OF Q W/ TIME MATCHES ~~EX~~ EXPERIMENTAL DATA REASONABLY WELL.