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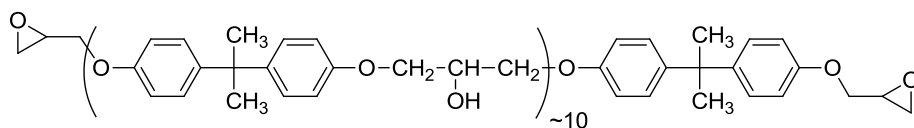
“On my honor, as an Aggie, I have neither given nor received
unauthorized aid on this academic work.”

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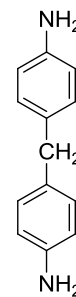
Exam II, February 28, 2012, 100 pts
Polymer Chemistry, CHEM 466, Spring 2012
Texas A&M University, College Station, TX, USA

1. For the reaction of the epoxy components shown below, draw the chemical structure for the crosslinked network product (10 points) and calculate the gel point (reminder: $p_c = 2/f_{av}$ and $f_{av} = \frac{\sum N_i f_i}{\sum N_i}$ for a stoichiometric balance of functional groups) (8 points).

Tube 1:



Tube 2:

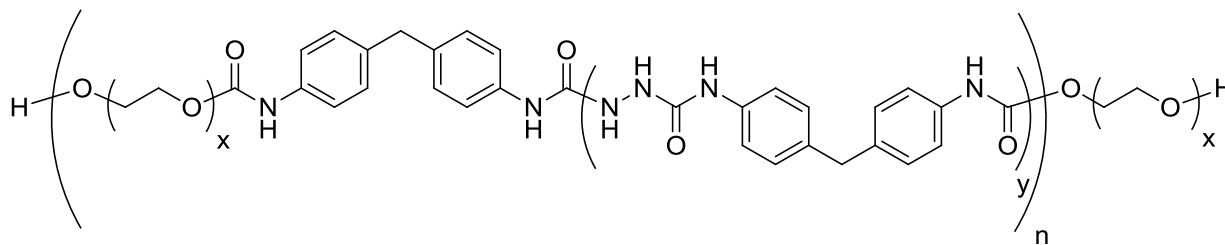


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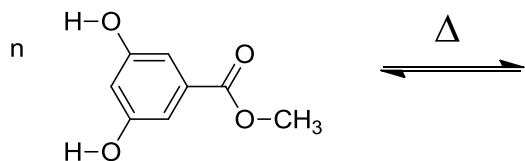


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2. For the chemical structure shown below, a block copolymer composition that is known as Spandex:
- Provide a retrosynthetic analysis that works backwards to small molecule monomer starting materials. (10 points)
 - Provide the forward reaction sequences that would be followed to build up the block copolymer structure. (5 points)
 - On the polymer structure given, label the functional groups and segment types, and the properties of each that lead to the physical and mechanical properties that allow for this polymer to be utilized in applications that require strength and elasticity. (5 points)



3. (i) Provide the products from the following reaction, showing and labeling each type of repeat unit in the polymer structure. (10 points)
(ii) State what kind of polymer is produced (architecture and composition). (2 points)
(iii) Draw the electron arrow-pushing reaction mechanism. (8 points)

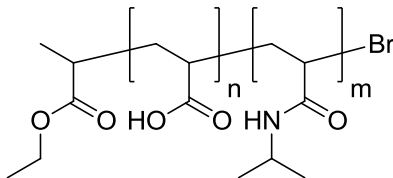


(iv) List three applications that have been or are being pursued for hyperbranched polymers or dendritic macromolecules and state which primary characteristic of the polymer is utilized for each particular application (e.g., as discussed in Froehling, P. J. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3110-3115 or Fréchet, J. M. J. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3713-3725). (3 points)

- 1.
- 2.
- 3.

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4. If a block copolymer of acrylic acid and N-isopropylacrylamide, PAA₅₀-*b*-PNIPAM₅₀ (shown below, with $n = m = 50$), is assembled into micelles in water, which block segment will comprise the shell? (5 points)



Over which temperature range will the supramolecular-assembly will take place? (5 points)

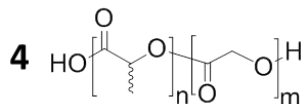
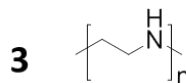
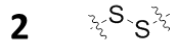
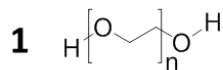
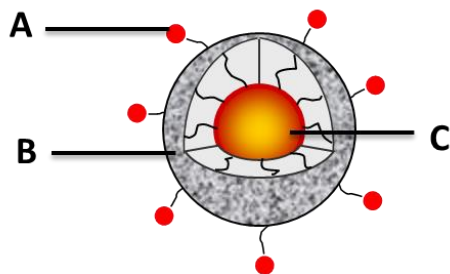
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5. You have a polymer film that may or may not be permeable to a molecule A (absorbs 440-450 nm – emits 525 nm). The bottom surface of the polymer film has been covalently bonded to dye B (absorbs 520-560 nm - emits 580 nm). You intend to expose the top surface to a solution of A.

Assuming you intend on using FRET studies to determine permeability:

- (i) What would be a reasonable wavelength for excitation? (3 points)
- (ii) Using this excitation, if you collected fluorescence at 580 nm and found that no emission was observed after exposure, what would this tell you? (3 points)
- (iii) If you collected fluorescence at 580 nm and found that the emission rose from zero to a maximum after 5 minutes, what would this tell you? (3 points)
- (iv) Is there any benefit to observing emission at 525 nm? (3 points)

6. Considering the general features of nanoparticles:



(i) Identify A, B and C components illustrated on the graph, and explain briefly the role of each component in circumventing the biological barriers and hurdles towards efficient drug delivery. (9 points)

A.

B.

C.

(ii) What are the structures (1, 2, 3 and 4) illustrated in the figure and where can they be located into the nanoparticle structure? (8 points)

1.

2.

3.

4.

Equations, which may be of use:

Number-average molecular weight:

$$M_n = \frac{\sum N_x M_x}{\sum N_x}$$

 $N_x = \# \text{ moles of polymer chains having molecular weight, } M_x$

Weight-average molecular weight:

$$M_w = \sum w_x M_x = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

 $w_x = \text{wt fraction of polymer chains having molecular weight, } M_x = \frac{N_x M_x}{\sum N_x M_x}$

Degree of polymerization:

$$DP_n = \frac{1}{1 - c}$$

 $c = \text{extent of conversion of functional groups}$

Polydispersity index:

$$PDI = \frac{M_w}{M_n}$$

Critical extent of reaction:

$$p_c = \frac{2}{f_{av}}$$

Average degree of monomer functionality:

$$f_{av} = \frac{\sum N_i f_i}{\sum N_i}$$