

Name: ANSWER KEY [printed]

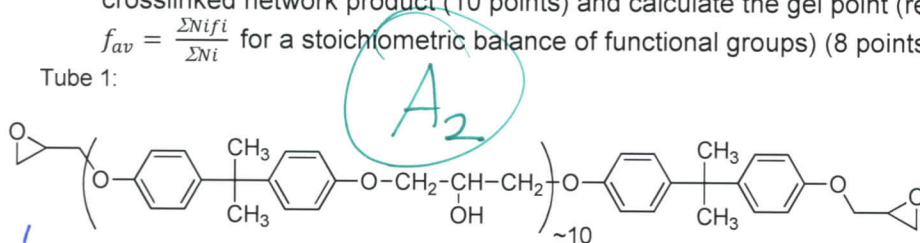
"On my honor, as an Aggie, I have neither given nor received unauthorized aid on this academic work."

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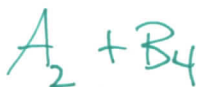
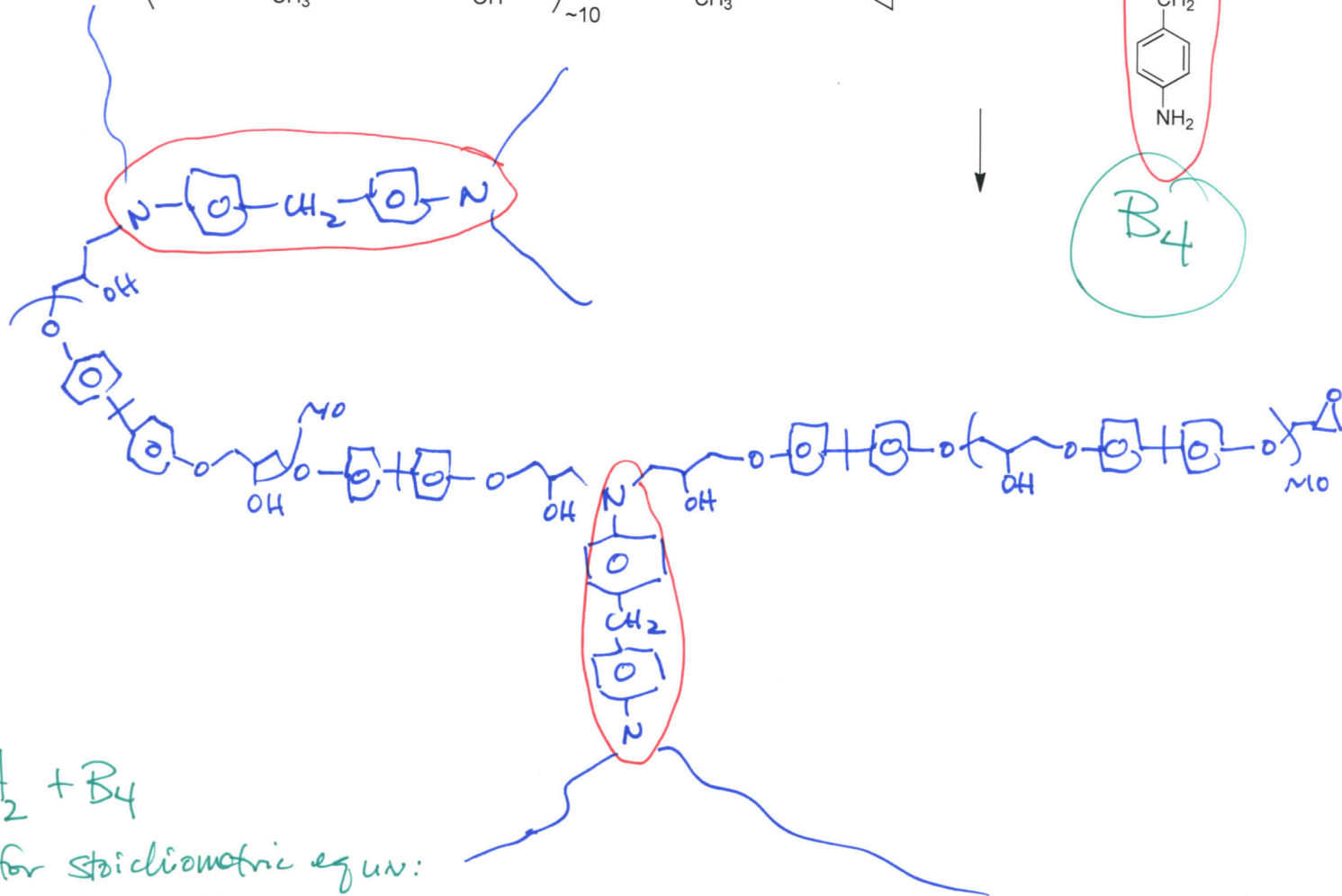
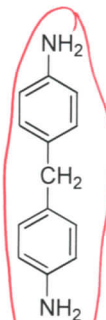
Exam II, February 28, 2012, 100 pts
 Polymer Chemistry, CHEM 466, Spring 2012
 Texas A&M University, College Station, TX, USA

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 $f_{av} = \frac{\sum Ni f_i}{\sum Ni}$ for a stoichiometric balance of functional groups) (8 points).

Tube 1:



Tube 2:



for stoichiometric equn:



$$f_{av} = \frac{2 \cdot 2 + 1 \cdot 4}{2 + 1} = \frac{8}{3}$$

$$p_c = \frac{2}{8/3} = \frac{6}{8} = \frac{3}{4} \Rightarrow \text{gel pt. @ 75\% conversion}$$

2. For the chemical structure shown below, a block copolymer composition that is known as Spandex:

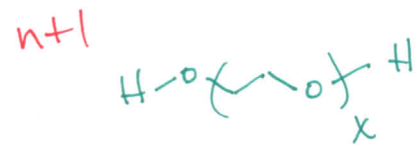
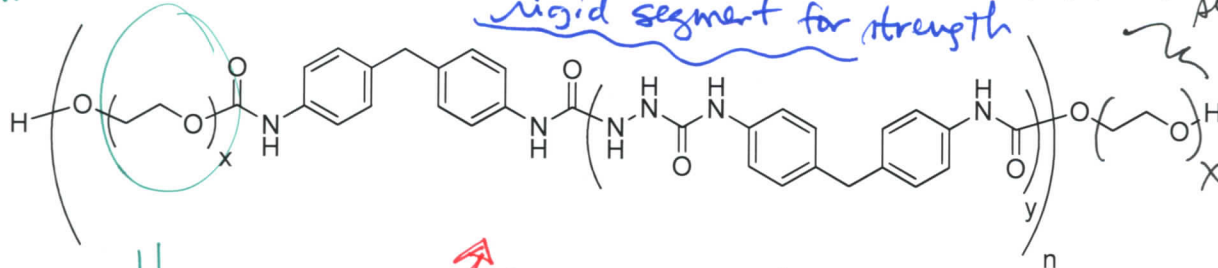
- (i) Provide a retrosynthetic analysis that works backwards to small molecule monomer starting materials. (10 points)
- (ii) Provide the forward reaction sequences that would be followed to build up the block copolymer structure. (5 points)
- (iii) On the polymer structure given, label the functional 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)

Soft, rubbery segment, also semi-crystalline w/low T_m

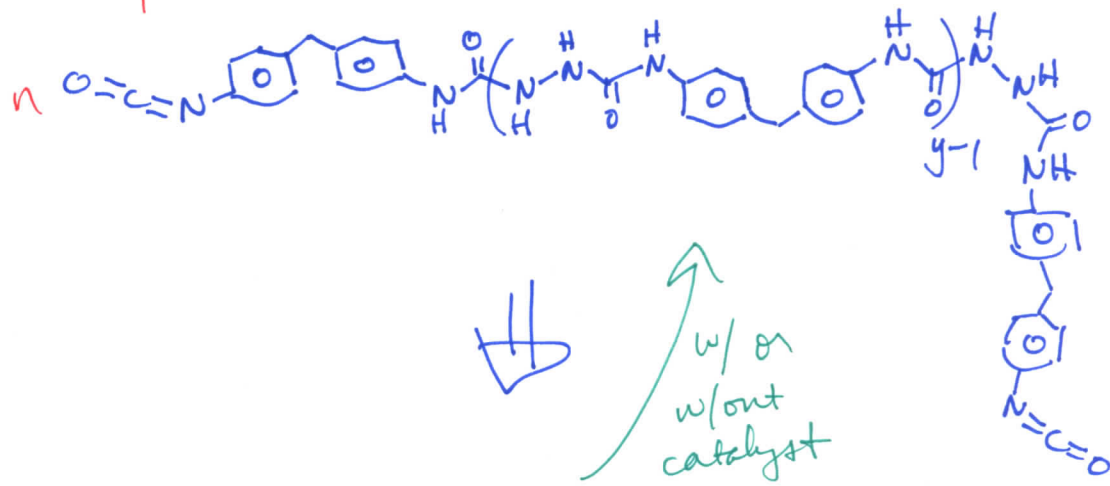
for elasticity

rigid segment for strength

sorry, this ()_x was not drawn, so grading was lenient/generous

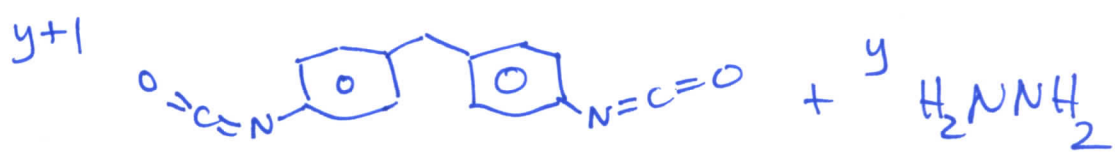


w/ or w/out catalyst

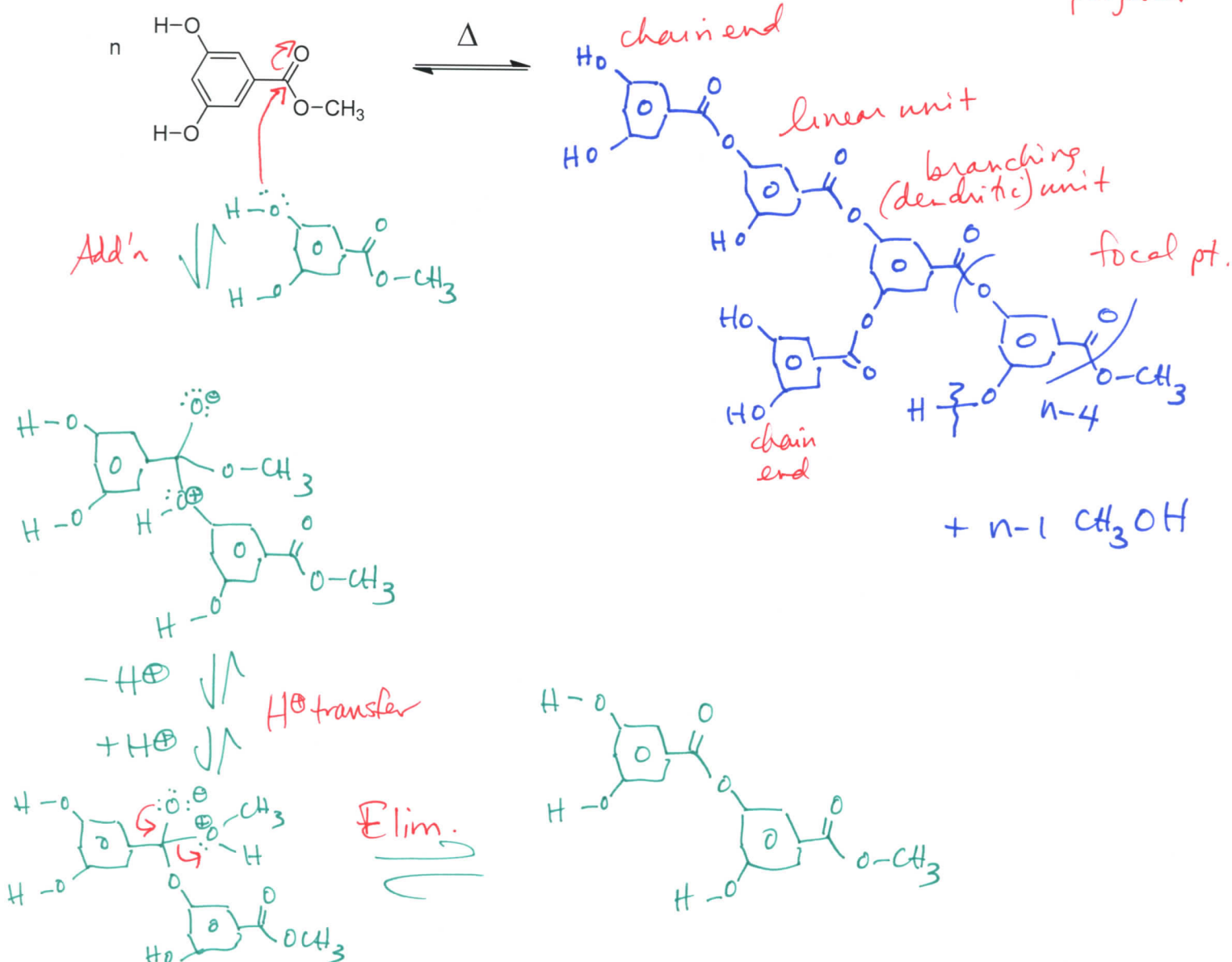


1) HO⁻ Na⁺
2) H⁺

w/ or w/out catalyst



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) *hyperbranched polyester*
 (iii) Draw the electron arrow-pushing reaction mechanism. (8 points)

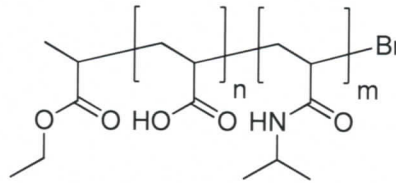


(iv) List three applications that have been or are being pursued for hyperbranched polymers or dendritic macromolecules and state which primary characteristic of the polymer is utilized for each particular application (e.g., as discussed in Froehling, P. J. Polym. Sci., Part A: Polym. Chem. **2004**,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

- crosslinkers, high chain end func. groups
- viscosity modifiers, high degree of branching
- crystallization suppressants in gas hydrates, high branching + func groups
- dye carriers for fibers, etc., internal vs. external globular structure
- nanolithography resist materials, compact size + globular shape
- drug delivery devices, globular shape + internal vs. external chem. etc.

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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)



Answer: The PAA block segment will comprise the shell.

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

Answer: The block polymer will assemble to micelles above the lower critical solution temperature (LCST) of PNIPAM block, which is 32 °C

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)

Any answer between 440-450 nm is correct

- (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)

This tells you that the film was not permeable to molecule A

- (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)

This tells you that the film is permeable to molecule A (2 pts)

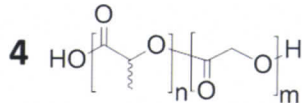
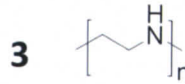
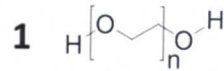
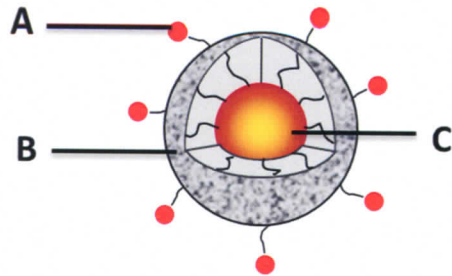
This also tells you that the saturation time for molecule A in your polymer films is 5 minutes - Stating that the permeability half-life was 2 ½ is also correct. (1 pt)

- (iv) Is there any benefit to observing emission at 525 nm? (3 points)

Yes (2 pts)

Observing emission at 525 nm is a second way to observe FRET to the dye B and should have similar kinetics to the rise in emission from dye B. (1 pt)

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. Smart component or targeting ligand or endosomolytic agent or imaging probe: Enhance selectivity, enhance the cellular uptake, escape the endosomes, active targeting, reduce toxicity or can be used for imaging and diagnosis.

B. Shell or corona: Prolong the circulation, allow passive targeting *via* the enhanced permeability and retention effect, reduce opsonization, reduce the toxicity or protect the drug against degradation.

C. Core: Solubilize hydrophobic drugs or complex charged drugs and can provide protection for the drug against degradation.

(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. Poly(ethylene glycol): Shell

2. Disulfide linkage: Between shell and targeting ligand or between shell and core or as a crosslinker in the shell and/or the core.

3. Polyethyleneimine: Core

4. Poly(D, L-lactide-co-glycolide): Core