Name: ANSWER KEY [printed]

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

_____ [signature]

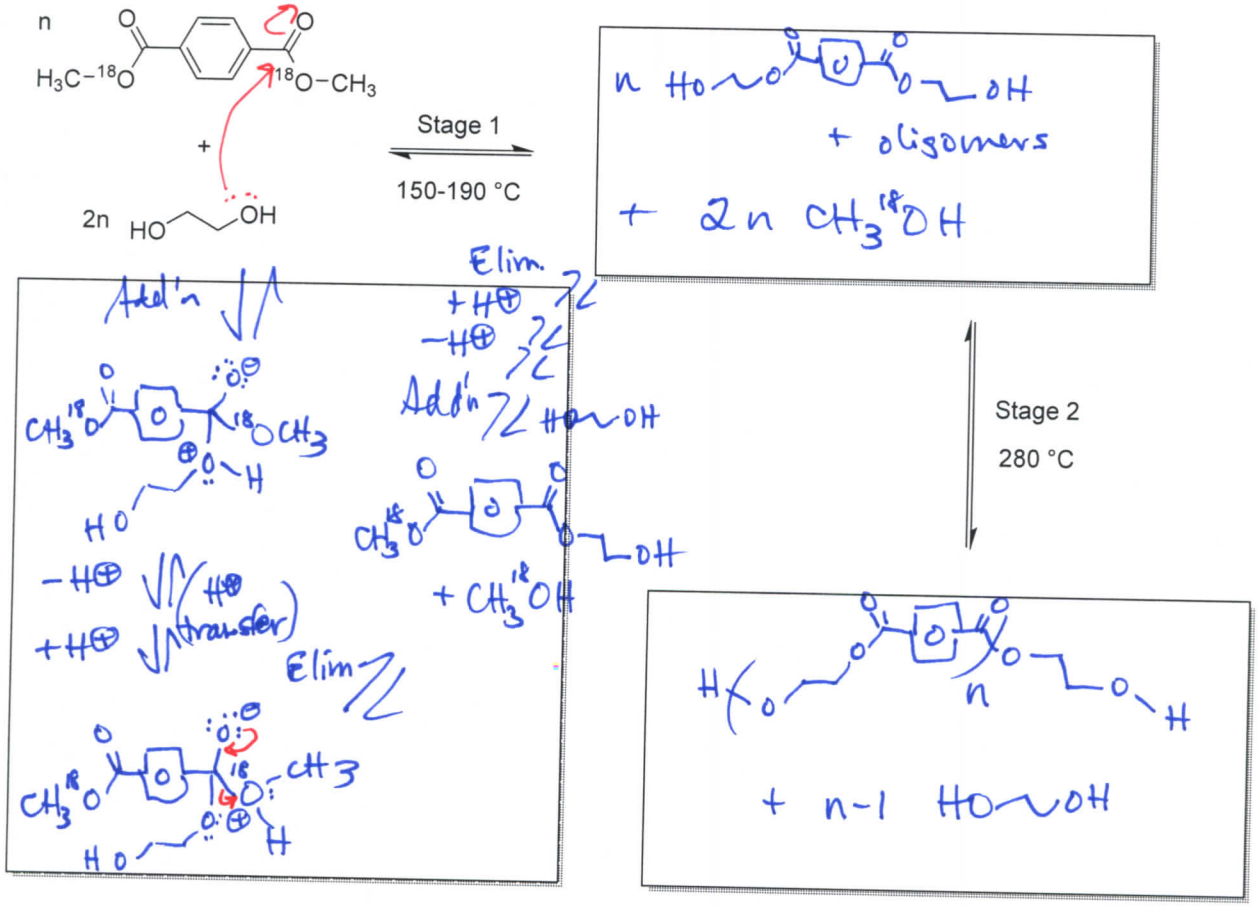
Exam I, February 7, 2013, 100 pts
Polymer Chemistry, CHEM 466, Spring 2013
Texas A&M University, College Station, TX, USA

1. The performance on quiz #3 was disappointing last week, therefore, this question provides another opportunity to demonstrate mastery of the material. However, with added expectations…

   (a) Draw the products that would predominate during the Stage 1 reaction conditions shown below, being certain to include all stoichiometries. [4 points]

   (b) Provide the electron arrow-pushing mechanism for the formation of the products during the Stage 1 reaction conditions. (It is necessary to show the mechanism only once, although it may be applied multiply to achieve the products.) [6 points]

   (c) Draw the products that would be produced during the Stage 2 reaction conditions shown below, being certain to include all stoichiometries. [4 points]



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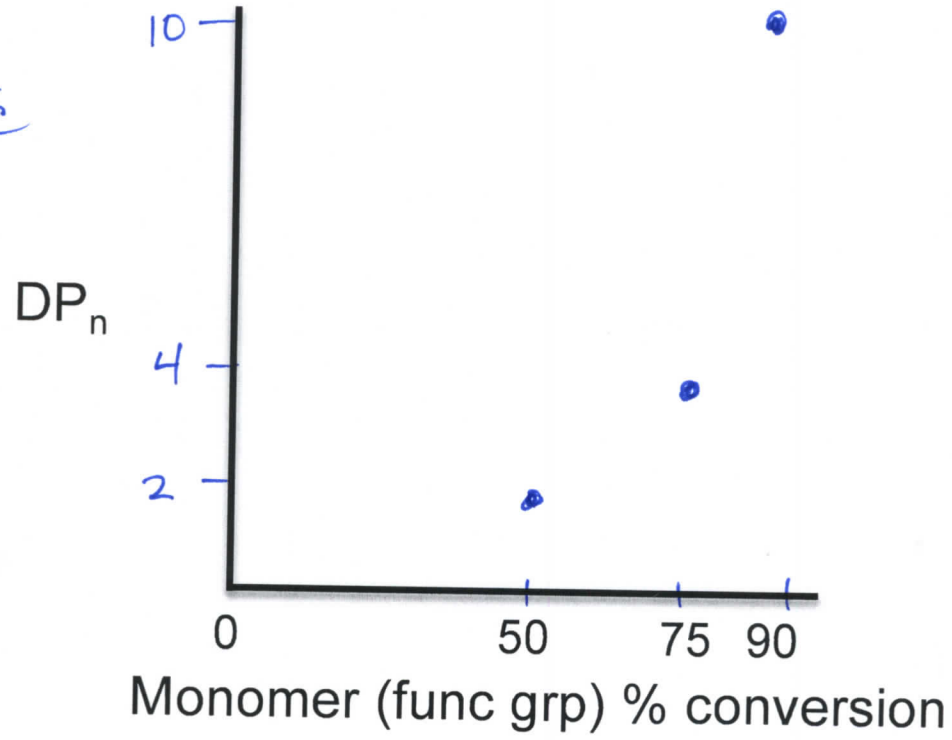
(d) State how the equilibria could be driven toward the products. [3 points]

remove the condensates ($CH_3^{15}OH$ + HO~OH) at each stage

(e) For the Stage 2 reaction, complete the data plot below, indicating the expected degrees of polymerization with AB monomer conversions of 50%, 75% and 90%. Be certain to label the y axis values. [6 points]

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



(f) If 100% conversion could be achieved, what would be the two possibilities for the products? [2 points]

Infinite DP_n

or

cyclic species

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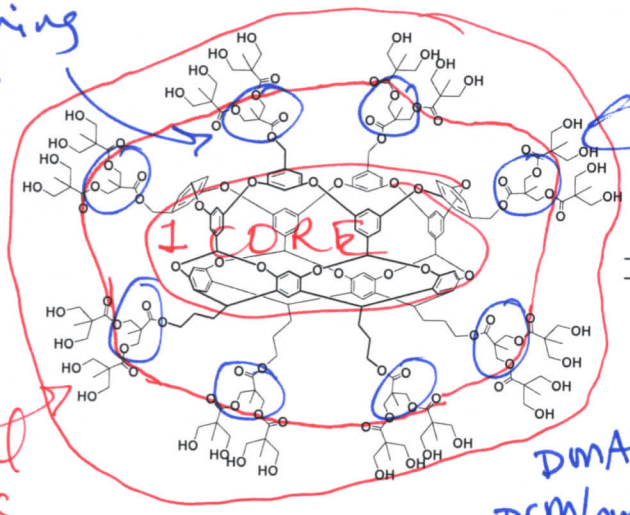
2. For the dendritic cavitand structure shown below:
   (a) State an application for which it was designed. [3 points]

⇒ To serve as a host for guest encapsulation (e.g. for drug delivery, solubility change + protection, environmental clean-up, etc.)

   (b) Directly on the structure, label the core, the branching units, and the terminal groups. [10 points]

   (c) Provide a retrosynthetic pathway for its preparation and provide reaction conditions for the forward reactions. For simplification, you may draw the core as an oval and draw the explicit chemical composition and structure for only one of the eight arms. [12 points]



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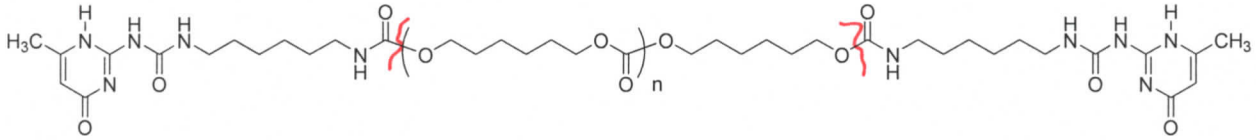
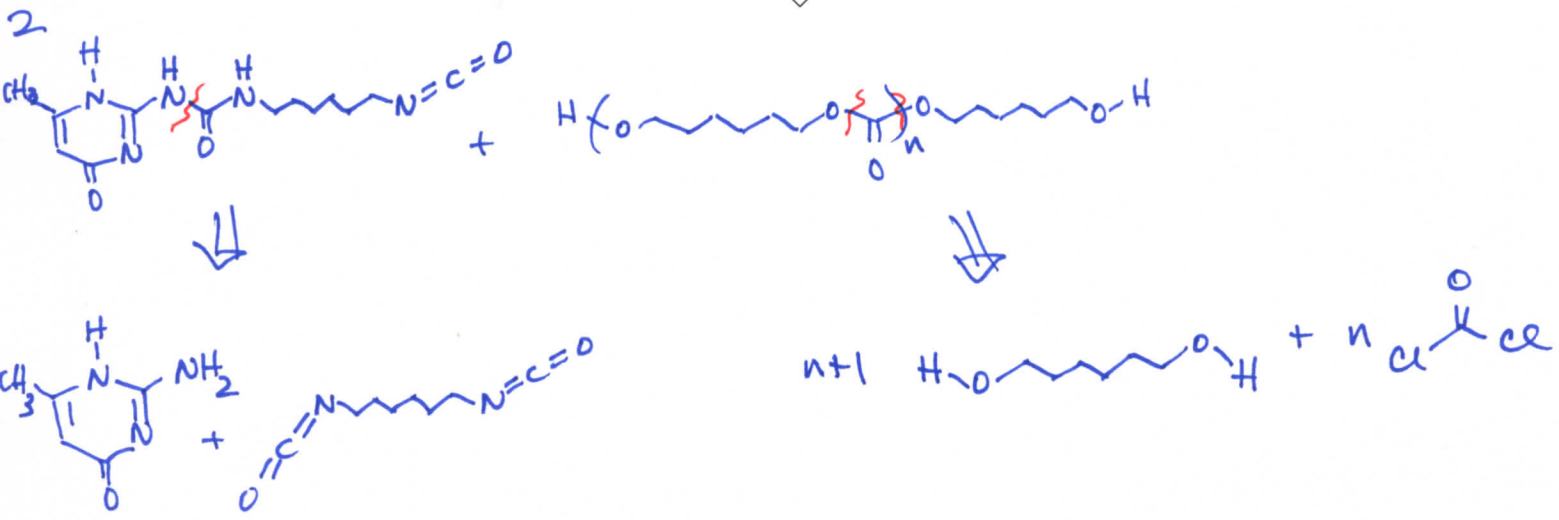
3. The following questions originate primarily from the article, B. J. B. Folmer, R. P. Sijbesma, R. M. Versteegen, J. A. J. van der Rijt, E. W. Meijer *Adv. Mater.* **2000**, *12*, 874-878.

(a) Provide a retrosynthetic pathway for the preparation of the following polycarbonate having UPy chain ends linked through a combination of urea and urethane linkages, working back to the point of all reagents being small molecules. [12 points]



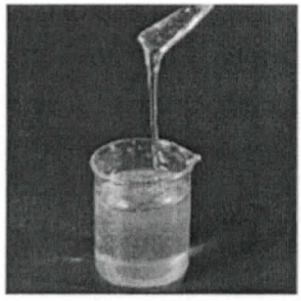


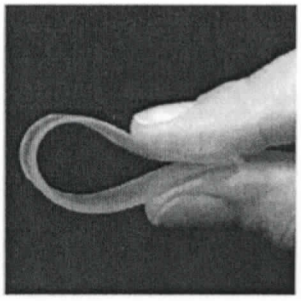
(b) Describe the role that the UPy groups have in modifying the composition, structure and properties of the polymers reported in this article. [4 points]

UPy as chain ends undergo quadrupolar H-bonding to establish supramolecular interactions between poly chains, effectively increasing the DP_n, MW, viscosity, + mechanical strength/toughness

(c) Label each of the following images as being a polymer sample that contains UPy chain ends or lacks UPy chain ends. [4 points]

lacks UPy chain ends





contains UPy chain ends

(d) What can be stated about the relative molecular weights or degrees of polymerization for a polystyrene sample having low viscosity and a poly(bisphenol A carbonate) having high viscosity? Explain your answer. [5 points]

nothing — comparisons of structure–property relationships must be made for polymers/molecules of the same composition

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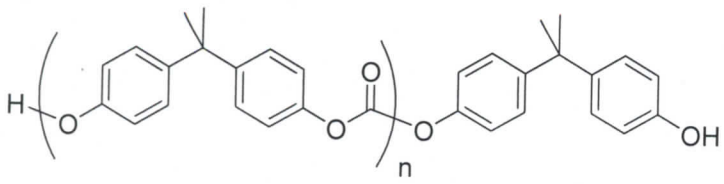
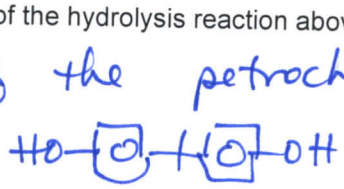
4. (a) Provide the products that would result from complete hydrolysis of the poly(bisphenol A carbonate) illustrated below. [9 points]



n+1

+ n CO_2

(b) Give one positive attribute of the hydrolysis reaction above. [5 points]

recyclability of the petrochemical-based monomer 

(c) Give one negative implication of the hydrolysis reaction above. [5 points]

potential carcinogenicity of BPA, + possibility for its generation when poly(bisphenol A carbonate) products are subjected to heat in presence of H_2O

(d) Describe two approaches that could avoid the hydrolysis products of poly(bisphenol A carbonate) and yet have access to robust engineering polymer materials. [6 points]

1) avoid heat +/or H_2O

2) produce alternative engineering polymers, e.g. derived from renewable resources or non-toxic monomers