Name: ANSWER KEY [printed]

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

________________________[signature]

Final Exam, May 2, 2014, 100 pts
Polymer Chemistry, CHEM 466, Spring 2014
Texas A&M University, College Station, TX, USA

1. Choose a polymer that you find most interesting and answer the following questions.

   (a) Provide its chemical structure (don't forget to include the chain ends). **[5 points]**

   Many answers are possible, and the others w/in #1 are dependent on this part (a) answer

   (b) Provide a retrosynthetic pathway by which the polymer structure of part (a) could be prepared. **[5 points]**

   (c) State whether the polymerization step of your retrosynthesis in part (b) would proceed by a chain-growth or step-growth process. **[2 points]**

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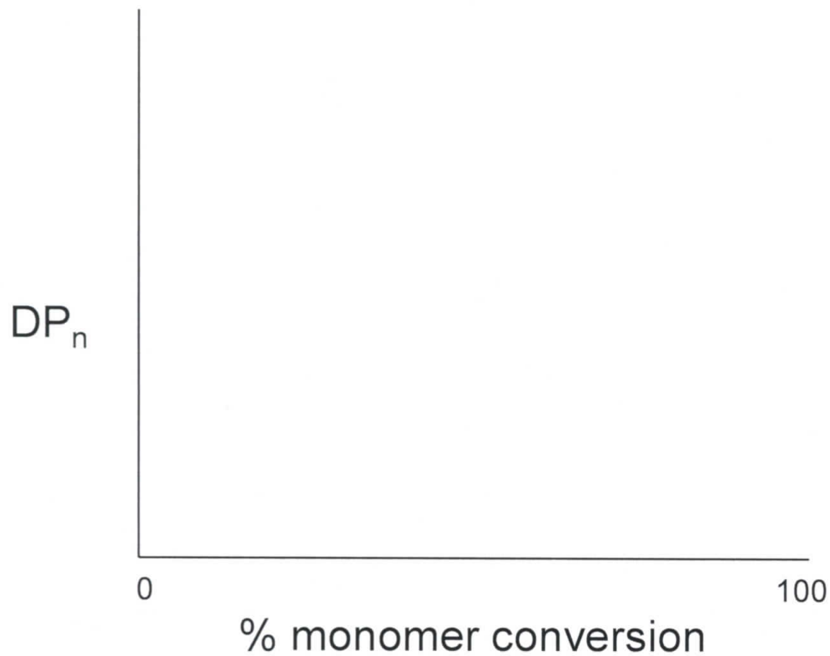
(d) State whether your polymerization would be controlled or un-controlled. **[2 points]**

(e) State whether the molecular weight distribution would be expected to be narrow or broad. **[2 points]**

(f) Draw the expected DP_n *vs.* % monomer conversion plot on the axes below. **[4 points]**



(g) Describe the physical and mechanical properties characteristics and how they relate to the polymer composition and structure. **[4 points]**

(h) State how this polymer is used or could be used. Indicate whether it is a component of current products or under research development. **[2 points]**

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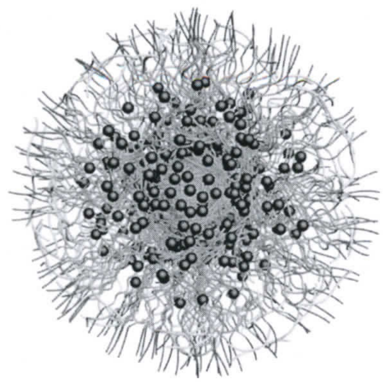
2. During the presentation of "Hybrid Magnetic Amphiphilic Block Copolymer Systems for Pollutant Remediation in Aqueous Environments":



(a) Why was the MSCK system crosslinked? **[5 points]**

Crosslinking prevents potential disassembly of the MSCKs during their implementation

(b) Who was the speaker? **[2 points]**

Adriana Pavia-Sanders

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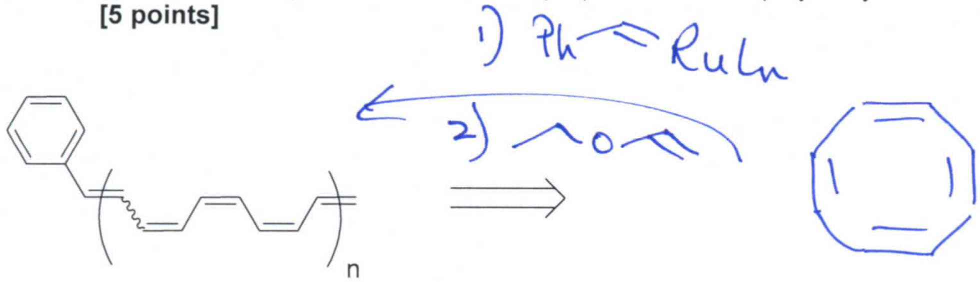
3. (a) Provide a retrosynthetic route for the preparation of the polyacetylene structure shown below. **[5 points]**



(b) As we had discussed in class, hydrogenation of this polymer could lead to a linear polyethylene. Provide the structure of the polymer that would result from hydrogenation of the polymer of part (a). **[5 points]**

(c) Industrially, however, linear polyethylene is produced using transition metal catalysts for the polymerization of ethylene. To tune the physical and mechanical properties of linear polyethylene, we discussed a process that was developed at Dow Chemical Company and involves copolymerization of ethylene with α-olefins, *e.g.* octene. Describe the key mechanistic features of the reaction system that were reported in the article, Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. *Science*, **2006**, *312*, 714-719, to obtain statistical olefin multi-block copolymers with alternating semicrystalline and amorphous segments. **[5 points]**

Two catalysts are used — one that is a poor incorporator of the α-olefin + gives crystalline polys comprised predominantly of linear polyethylene
— a second that is a good incorporator of the α-olefin + gives polys w/ low T_g

A chain shuttling agent provides reversible transfer of the growing polys between the catalysts
⇒ blocky polymer structures

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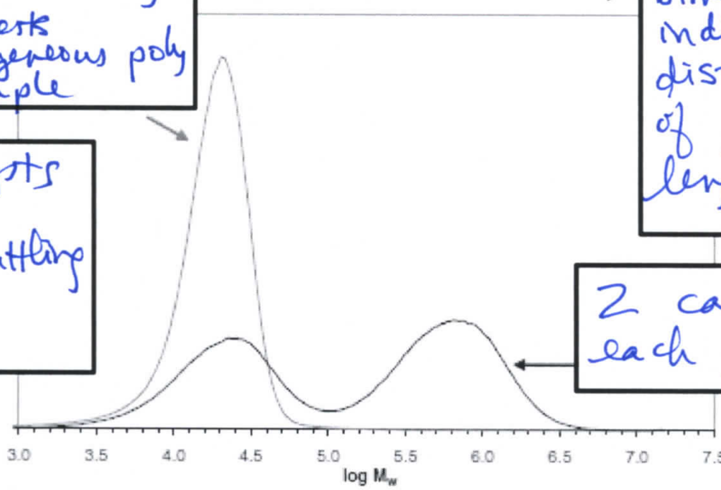
(c) In addition to ethylene and octene, predict the components (catalysts, *etc.*) that were employed during the copolymerizations that led to the molecular weight data obtained by GPC analysis (below), and explain the characteristics of the polymer/copolymer samples/mixtures. In agreement with the arrows, place each answer (for components and polymer characteristics) into a separate box—on the left for the GPC trace for one sample and on the right for the other. **[8 points]**

monomodality suggests homogeneous poly sample

2 catalysts + chain shuttling agent

effective production of multi-block copolymer structure



bimodality indicates two distinct populations of poly chain lengths; poly mixture

2 catalysts, each gives a different poly molecular weight

⇓

mixture of 2 types of polys — not uniform multi-block

(d) Give two advantages that were observed for the physical properties that resulted from the statistical multi-block copolymer structure. **[4 points]**

elastomeric character over broader range of conditions

optical transparency increased due to decreased dimensions of phase segregated, crystalline domains

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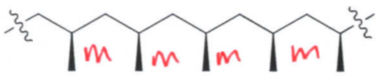
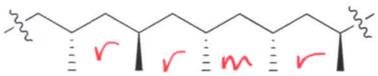
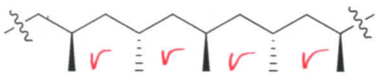
4. For the following polypropylene segments, label the meso and racemic diads, the polymer tacticities and predict whether they are likely to pack into crystalline or amorphous domains. **[15 points]**



isotactic — crystalline



atactic — amorphous



syndiotactic — crystalline

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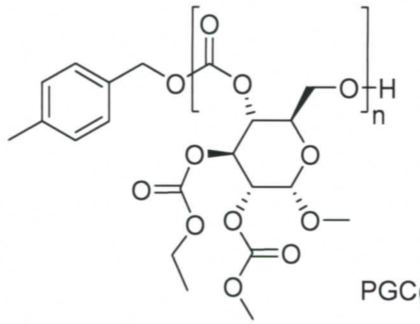
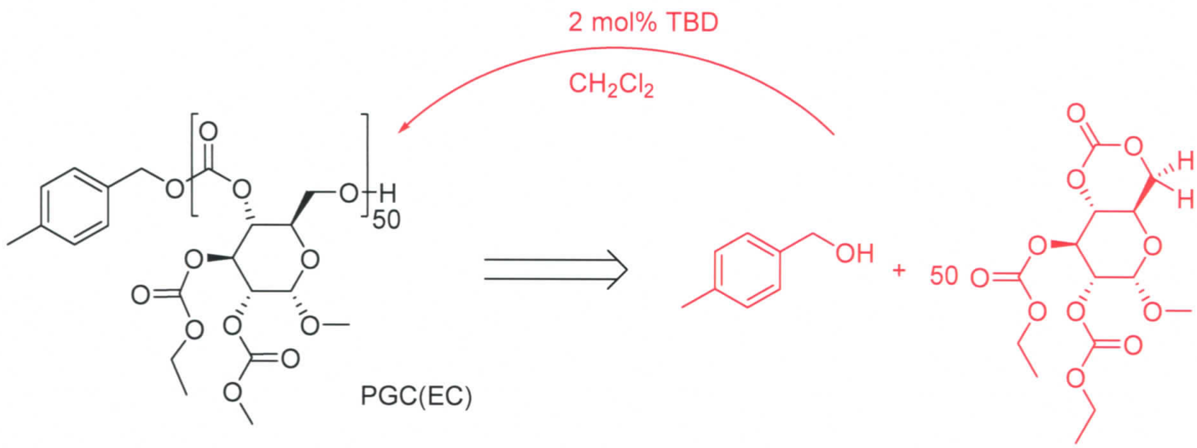
5. The following questions are related to the poly(glucose carbonate) polymer shown below (PGC(EC)) that is prepared in the presence of the organocatalyst TBD through ring opening polymerization of a cyclic carbonate monomer of glucose.

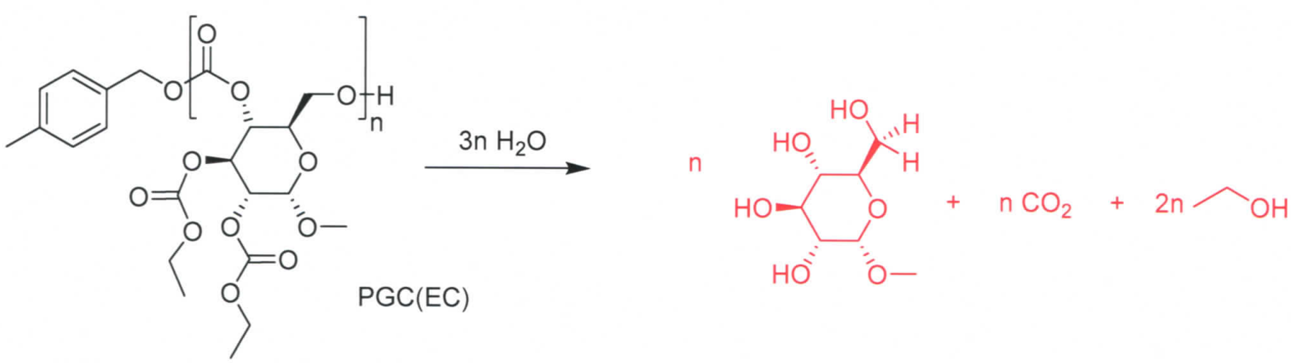


PGC(EC)

(a) Provide a retrosynthetic pathway for the preparation of this polymer (you need only to work back to the protected cyclic carbonate monomer). **[4 points]**



(b) Provide the expected products upon hydrolytic degradation of this polymer. **[4 points]**



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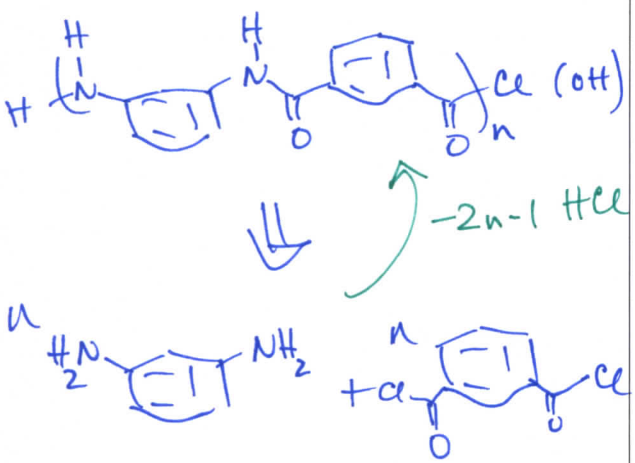
6. For quiz #10, several students expressed interest in the chemistries of the polymers used in 'ove' gloves and bullet-proof vests. Therefore,
   (a) Provide the structures of the polymers. **[5 points]**
   (b) Provide retrosyntheses for the polymers. **[5 points]**
   (c) Give their tradenames. **[2 points]**
   (d) Describe the characteristics of the polymer compositions and structures that lead to high temperatures for thermal transitions and decompositions, which allow for their utilization in these applications. **[5 points]**

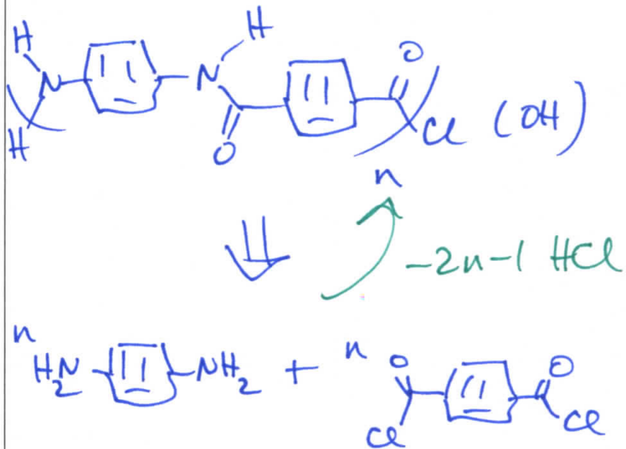
'ove' glove polymer:



Nomex

- no aliphatic C's
- rigid, stable aromatic rings
- H-bonding via amides
- meta-substituted Ar rings ⇒ inhibits xtallinity

Bullet-proof vest polymer:



Kevlar

} same

- para-substituted Ar rings ⇒ ↑ chain packing, ↑xtallinity, ↑ rigidity