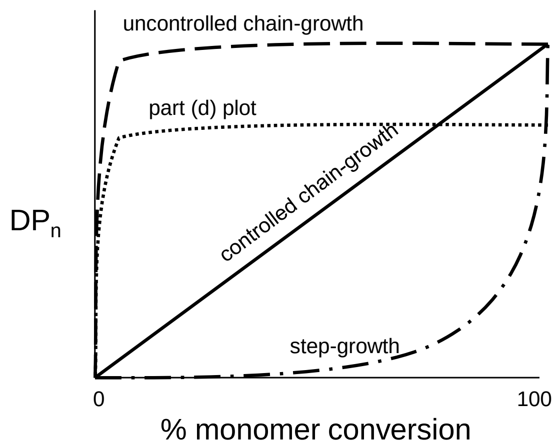
Name:____________________________[printed]

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

__________________________[signature]

Exam III, April 9, 2013, 100 pts
Polymer Chemistry, CHEM 466, Spring 2013
Texas A&M University, College Station, TX, USA

1. As question #2 of the 2012 Exam III, the following information was covered:
   i. Several key features of chain-growth, addition polymerizations include the requirement of an initiator, monomers undergo reaction with initiators and propagating chain ends, the reactions typically involve additions to unsaturated groups and proceed until monomer is consumed or termination occurs, and control over DP_n and PDI may be achieved (depending on the conditions).
   ii. Typical plots for degrees of polymerization *vs*. monomer conversions for uncontrolled chain-growth, controlled chain-growth and step-growth polymerizations differ significantly, as illustrated below.



As can be inferred from the plots above, the DP_n can be controlled by the extent to which monomer conversion is allowed to proceed, in the case of either controlled chain-growth or step-growth polymerization. In contrast, uncontrolled chain-growth polymerization, for which $k_i \sim k_p > k_t$, will result in the production of polymers having relatively high DP_n even at low % monomer conversion.

(a) For an uncontrolled chain-growth polymerization, in general, describe the relative proportions of polymer : monomer that would be present at 10, 50 and 90 % monomer conversions. [5 points]

(b) For an uncontrolled chain-growth polymerization, in general, describe the relative DP_n values of the polymers that would be present at 10, 50 and 90 % monomer conversions. [5 points]

(c) List the three mechanistic steps involved in uncontrolled chain-growth polymerizations. [3 points]

i.

ii.

iii.

(d) Based on your answers to parts (a)-(c) and also considering kinetics, how could the polymerization conditions be modified to produce a polymer having a similar DP_n *vs*. % monomer conversion profile to that shown for the uncontrolled chain-growth polymerization, but with an overall lower DP_n (i.e., the “part (d) plot”)? [5 points]

(e) List the three mechanistic steps involved in controlled chain-growth polymerizations. [3 points]

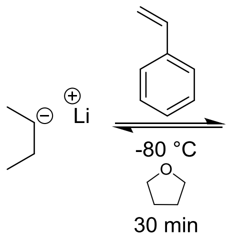
i.

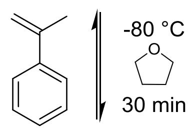
ii.

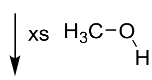
iii.

(f) How could the polymerization conditions be modified to alter the DP_n *vs*. % monomer conversion profile from that of an uncontrolled chain-growth polymerization to a controlled chain-growth polymerization? [5 points]

2. For the sequential anionic block copolymerizations of styrene and α-methyl styrene under the conditions given below, provide the:
   (a) Electron arrow-pushing mechanisms; [5 points]
   (b) Intermediates; [5 points]
   (c) Final products; [5 points]



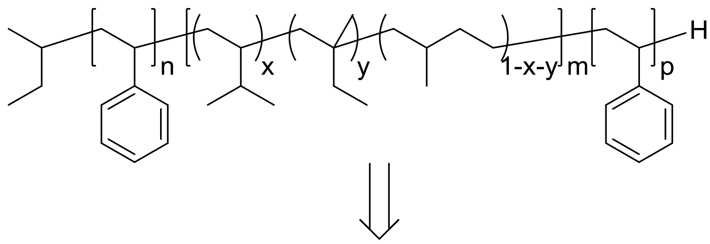




   (d) Imagine that the temperature for the polymerization was misread as 80 °C, which may seem like a minor oversight, what would be the final products of the polymerization (you may wish to consult the equations page, the last page of the exam)? [5 points]

Name:___________________________[printed]

3. (a) Provide a retrosynthesis for the hydrogenated SIS triblock copolymer shown below. [10 points]



(b) What is the name of the company that we discussed as a primary producer of the hydrogenated SIS triblock copolymer? [3 points]

(c) Where is that company's headquarters located? [3 points]

(d) List three advantages to the hydrogenated SIS triblock copolymer *vs*. its unsaturated precursor. [3 points]

i.

ii.

iii.

(e) Give one use for the hydrogenated SIS triblock copolymer, or one product type in which it can be found. [3 points]

4. For the Bayer Distinguished Lectures given on April 4 and 5:

(a) Who delivered the Bayer Distinguished Lectures? [2 points]

(b) From which institution is that person? [2 points]

(c) What was the topic(s) for the lectures? [2 points]

(d) Who is the Bayer scientist who also delivered a lecture? [2 points]

(e) What was the topic(s) of that lecture? [2 points]

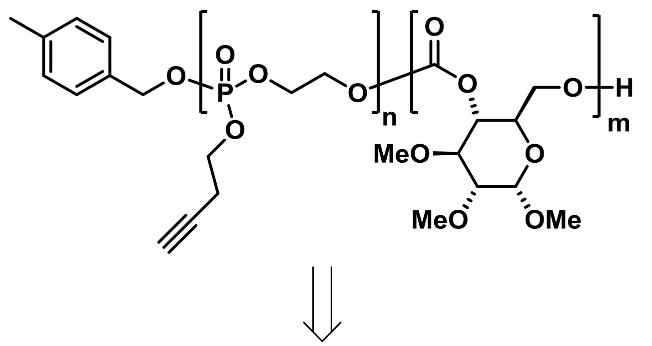
(f) What is one polymer-based material that Bayer manufactures? [2 points]

(g) In what objects/devices could it be found? [2 points]

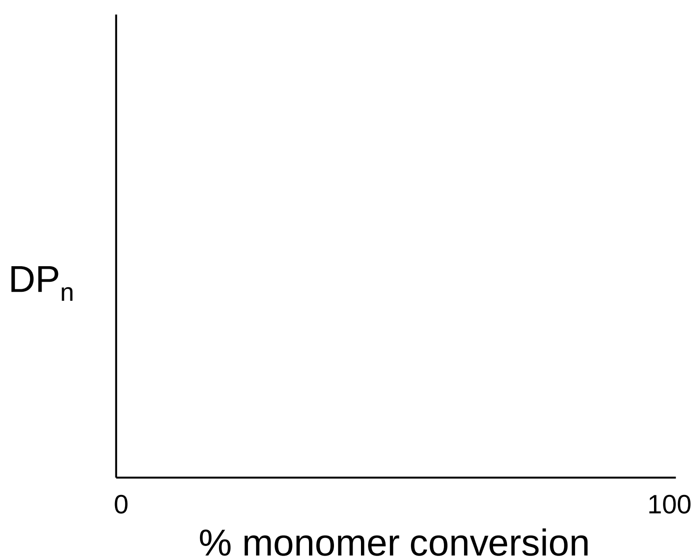
Name:__________________________[printed]

5. The following questions are related to the polyphosphoester-*b*-poly(glucose carbonate) diblock copolymer shown below that is prepared in the presence of the organocatalyst TBD, discussed during the guest lecture by Dr. Tiffany Gustafson.

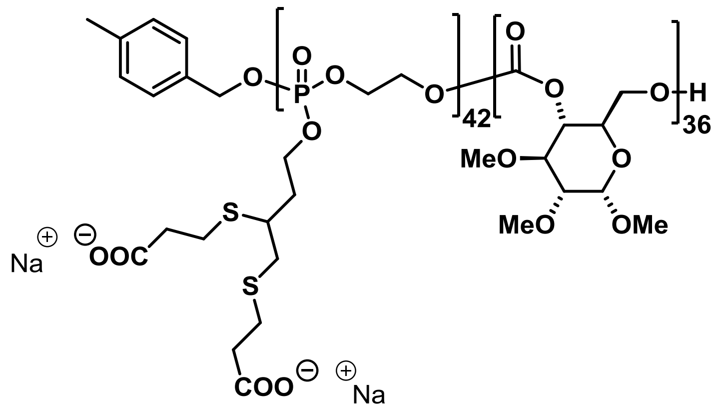
   (a) Provide a retrosynthetic pathway for the preparation of this polymer, by ring opening polymerization from a macroinitiator (*i.e.,* only growth of the second block needs to be shown). [6 points]



   (b) Draw a plot of DP_n *vs.* % conversion for this reaction. [4 points]



(c) Below is a functionalized version of this block copolymer. Describe two unique characteristics of this functionalized polymer. [4 points]



(d) Describe one application where this polymer could be utilized. [4 points]

Name:___________________________[printed]

Equations, which may be of use:

Number-average molecular weight:

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

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

Weight-average molecular weight:

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

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

Degree of polymerization:

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

c = 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:

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

For styrene polymerization: ΔH = -73 kJ/mol, ΔS = -0.104 kJ/K·mol

For α-methyl styrene polymerization: ΔH = -35 kJ/mol, ΔS = -0.104 kJ/K·mol

Textbook:
Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*, 2nd Edition; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2007