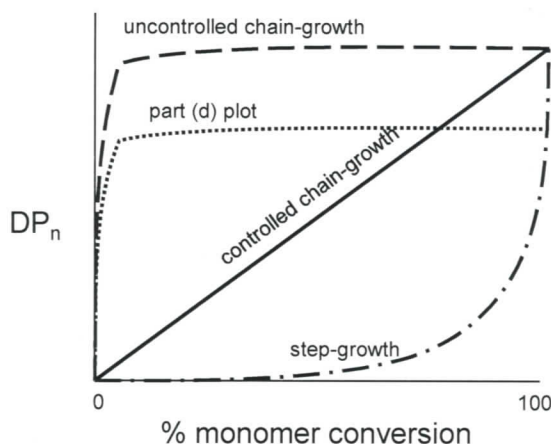


"On my honor, as an Aggie, I have neither given nor received unauthorized aid on this academic work."

_____ [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]

polymer: monomer ratio increases with increasing % monomer conversion — the % polymer would be 10, 50 + 90% at monomer conversions of 10, 50 + 90%

- (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]

The polymer DP_n values would be the same at 10, 50 + 90 % monomer conversions

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

- i. initiation
- ii. propagation
- iii. termination

(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]

increasing k_t relative to k_p would result in lowering of DP_n — this could be accomplished by adding a terminating species

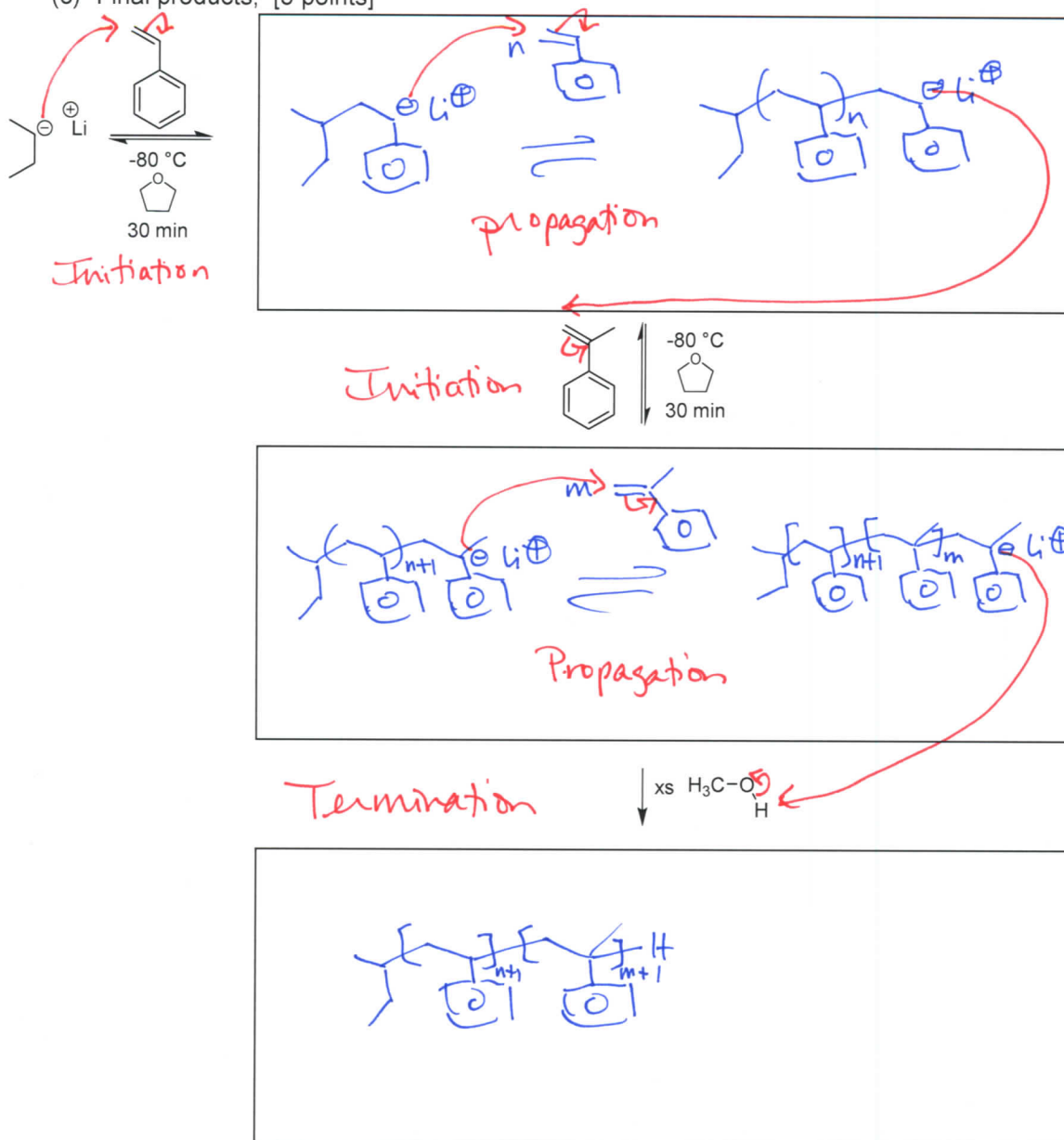
(e) List the three mechanistic steps involved in controlled chain-growth polymerizations. [3 points]

- i. initiation
- ii. propagation
- iii. reversible termination (ultimately anionic (+ cationic) polymerizations are usually terminated irreversibly (although cationic polymer termination by halogen is reversible))

(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]

add a reversible terminator to gain control

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

$$\Delta G = \Delta H - T\Delta S$$

setting $\Delta G = 0$

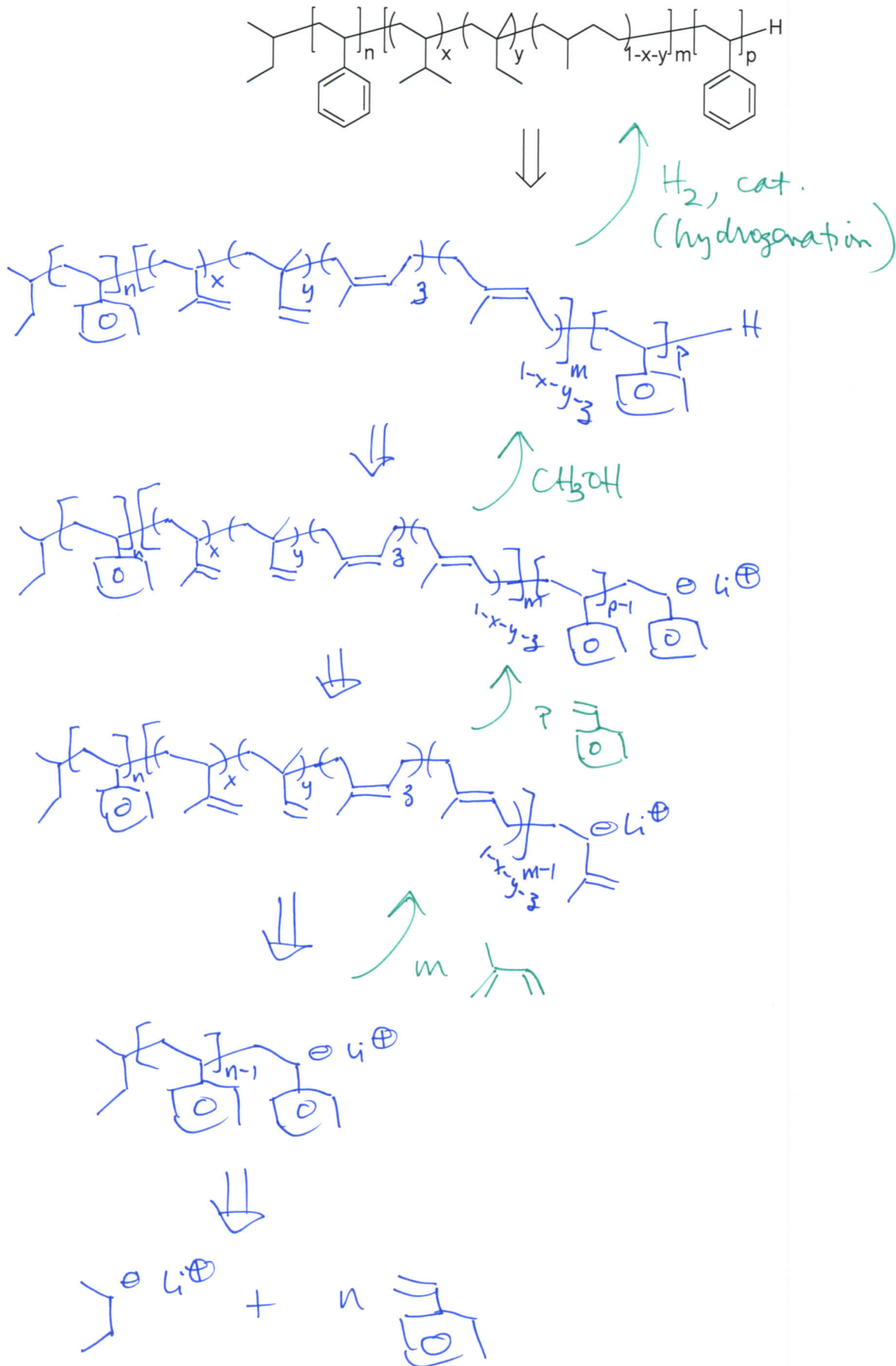
$$\Rightarrow 0 = \Delta H - T_c \Delta S$$

$$\Rightarrow T_c = \frac{\Delta H}{\Delta S} = \text{ceiling temp.}$$

using $\Delta H = -35 \text{ kJ/mol}$ + $\Delta S = -0.104 \text{ kJ/K.mol}$
 for α -methyl styrene, $T_c = 337 \text{ K} = 64^\circ\text{C}$
 $\therefore 80^\circ\text{C}$ is above T_c , so polymer is disfavored
 + block copolymer will not proceed
 T_c styrene is 429°C + its polymer will proceed

final product

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]

Kraton

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

Houston, TX

- (d) List three advantages to the hydrogenated SIS triblock copolymer vs. its unsaturated precursor. [3 points] *removal of reactive C=C groups gives:*

- i. increased compatibility with polyolefins + oil
- ii. increased UV stability
- iii. increased thermal stability

(also "oxidation + weather resistance, processing stability, etc.)

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

elastic components of disposable diapers, bags, gloves, intravenous products, medical film, tubing + many others...

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

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

Frank Caruso

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

University of Melbourne, Australia

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

Layer-by-layer assembly of nanoparticles/capsules for therapeutics

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

Karl Haider

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

Bayer Material Science products/technologies + careers in industry

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

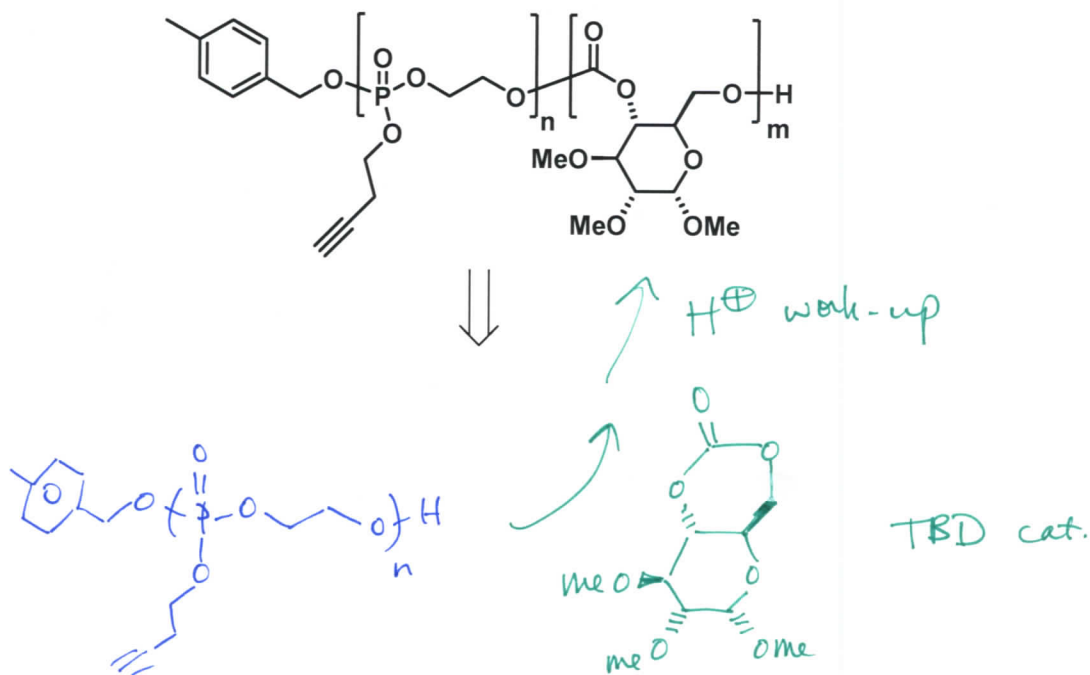
polycarbonates, polyurethanes, etc.

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

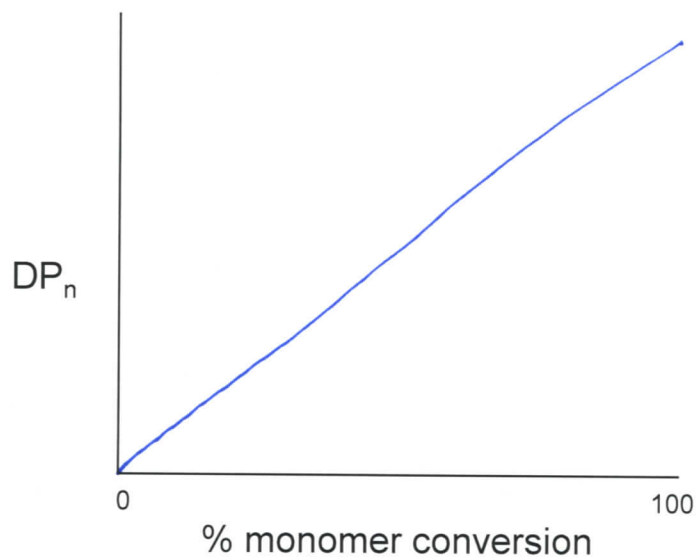
poly(bisphenol A carbonate) is found in DVDs, eyeglasses, etc.

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.

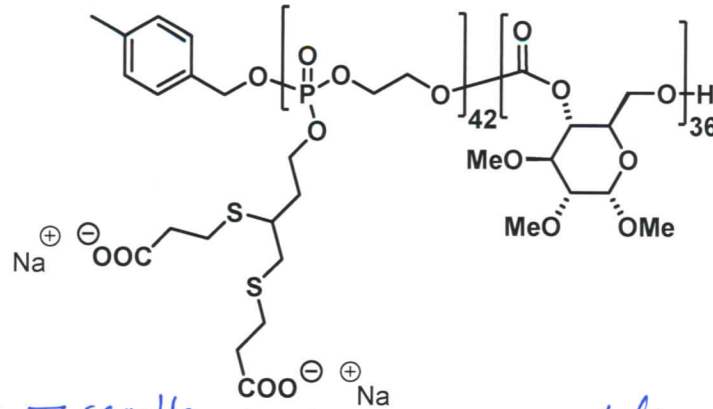
(a) Provide a retrosynthetic pathway for the preparation of this polymer, by ring opening polymerization from a macroinitiator (*i.e.*, only growth of the second block needs to be shown). [6 points]



(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]



- 1) amphiphilic — capable of forming nanoparticles in H_2O
 - 2) hydrolytically degradable
 - 3) exhibits an LCST
- ... other answers possible ...

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

when assembled into nanoparticles in H_2O ,
 the polymer nanostructures are capable
 of packaging + transporting imaging agents
 +/or therapeutics for nanomedicine
 applications

... other answers possible ...

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:

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

For styrene polymerization: $\Delta H = -73 \text{ kJ/mol}$, $\Delta S = -0.104 \text{ kJ/K}\cdot\text{mol}$ For α -methyl styrene polymerization: $\Delta H = -35 \text{ kJ/mol}$, $\Delta S = -0.104 \text{ kJ/K}\cdot\text{mol}$ **Textbook:**Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*, 2nd Edition; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2007