

Spring 2008

Preparation and Reactions of Polymers

PTFE/CHE/CHEM 6750

Instructor: Anselm C. Griffin
Polymer, Textile & Fiber Engineering
Room 3508 MRDC
e-mail: Anselm.Griffin@ptfe.gatech.edu

This course presents a detailed treatment of the reactions involved in the synthesis of both man-made and natural polymers, including preparation and degradative reactions of polymer systems.

Text: "Principles of Polymerization", 4th ed., by G. Odian

Topical Outline

- Introduction to Polymers
- Step-Growth Polymerization and Step-Growth Polymers
- Free-Radical Chain-Growth Polymerization
- Ionic Chain-Growth Polymerization
- Ring-Opening Polymerization
- Common Chain-Growth Polymers
- Naturally Occurring Polymers
- Reactions of Polymers
- Degradation of Polymers

Attendance: You are expected to attend all class meetings.

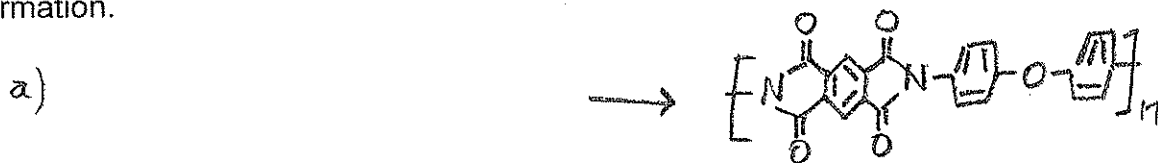
Grading: There will be three examinations during the semester. Each will count 33% of your final grade. In addition to readings from the textbook, there will be assignments made in class. Part of the course requirement will be a topical report which may involve a short presentation to the class.

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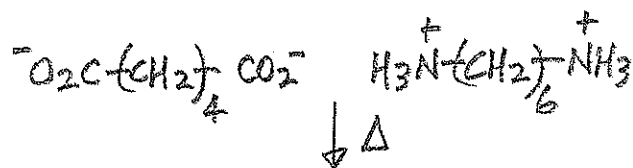
PTFE 6750 Exam I Spring 2008

- (12 pts) 1. Give the chemical structure for the repeating unit of a specific:
- polyamide
 - polyester
 - polyurethane
 - polycarbonate
- (8 pts) 2. For step-growth polymers the molecular weight (average DP) achieves a high value only at very high conversion – late in the polymerization. Explain.
- (10 pts) 3. Phase transfer catalysts (PTC) are often used in polymer synthesis. Describe a typical PTC and explain (in detail) how it functions in promoting polymerization.

(42 pts) 4. For each of the polymers below, give a reasonable set of reactant(s) for its formation.

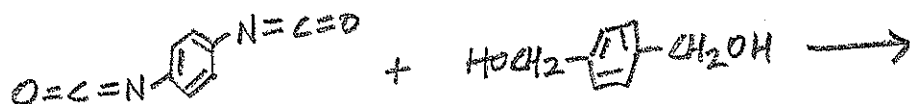


(6 pts) 5. Nylon salts were used by Carothers in the early days of polymer chemistry to insure the exact 1:1 match of carboxylic acid and amine groups in the formation of nylons. Provide the repeat structure of the polymer formed from heating the 'nylon salt' below.



- (8 pts) 6. The Carothers equation is useful in many ways. It can help explain the need for high purity in our monomers for a step-growth polymerization. Using the Carothers equation, explain the possibilities for achieving an average DP of 60 in a polyesterification in which one component (the diacid) has a purity of 98%? of 99%?

- (8 pts) 7. Consider the reaction of a bis isocyanate with a diol (below) to produce a polymer. This is an 'addition' reaction, yet this polymerization has all of the characteristics of a step-growth reaction. Explain this seeming discrepancy.



- (6 pts) 8. For conversion of a carboxylic acid to an ester (or polyester), one could treat the carboxylic with SOCl_2 to first form the acid chloride. Another method uses the methyl or ethyl esters as reactants for polymerization. a) Why are the acids themselves not used directly? b) What do the acid chloride and the short-chain esters have in common as monomers for polyesterification?

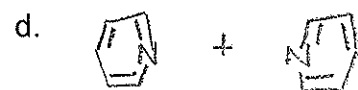
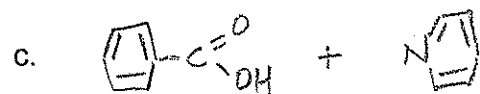
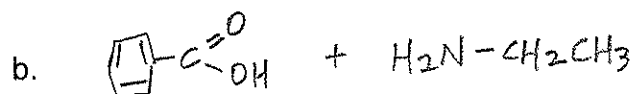
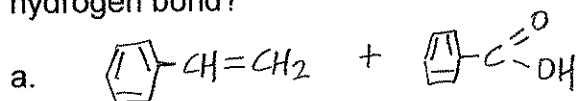
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Exam 2

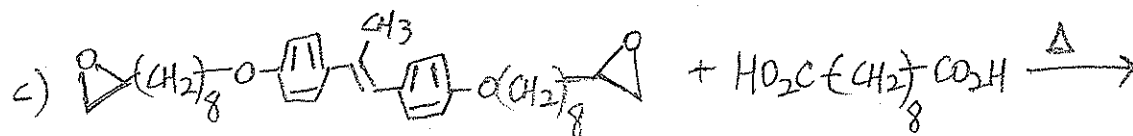
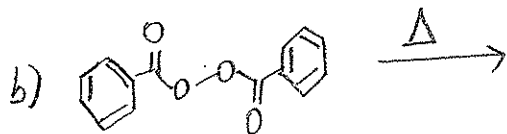
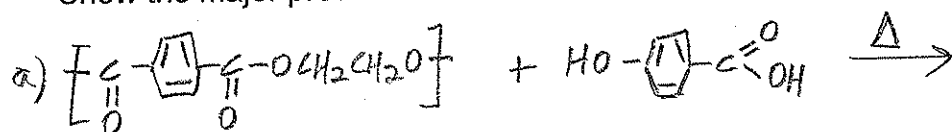
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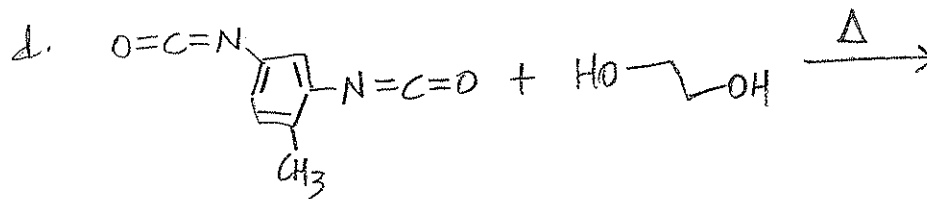
- (6 pts) 1. Chain association polymers can be connected through hydrogen bonds. Which one of the following pairs is most likely to form a hydrogen bond?



- (8 pts) 2. For a given association chain polymer, fibers can be drawn at low temperatures, but not at high temperatures. Explain.

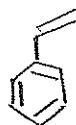
- (24 pts) 3. Show the major product from each of the reactions below.





- (8 pts) 4. For preparation of step-growth polymers, solution polymerization is an attractive method, but it is not without its drawbacks. Give two limitations for use of this technique.

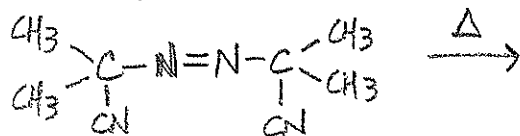
- (8 pts) 5. In the propagation step of the polymerization of styrene, a growing chain end can add to a styrene monomer. Show the structure of the two possible free radicals that can be formed and indicate the more stable one.



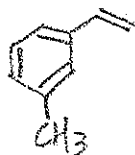
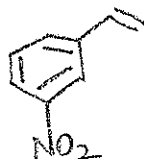
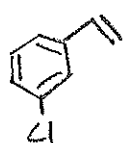
Styrene

- (8 pts) 6. The rate of termination of growing radical chain ends is reduced due to increased viscosity of the reaction medium for which one of the following:
- Cannizaro effect
 - supramolecular effect
 - gel effect
 - initiator effect
 - liquid crystal effect

- (6 pts) 7. For the free radical initiator AIBN, show the free radical (initiator) formed upon thermal decomposition of AIBN.



- (8 pts) 8. Consider the three styrenic monomers below. Which one would have the least difficulty in undergoing a 'clean' free radical polymerization? Circle it.



- (8 pts) 9. In free radical polymerizations, chain transfer to polymer can lead to 'backbiting'. Illustrate this process with a simple drawing.

- (8 pts) 10. Consider the four radical polymerization techniques: bulk, solution, suspension, and emulsion. Circle the one that involves polymerization inside micelles.

- (8 pts) 11. In free radical copolymerization, if the reactivity ratios of the two monomers are both near zero, what type of internal structure would you expect for the copolymer?

- random copolymer
- alternating copolymer
- no reaction occurs
- homopolymerization of each monomer separately

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Exam 3

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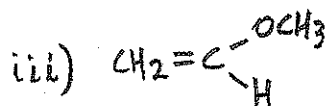
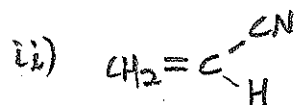
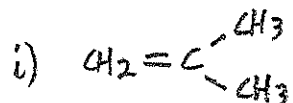
(8 pts)

1. Metallocene catalysts are used for which one of the following:
- a) nylon synthesis
 - b) olefin polymerization
 - c) transesterification
 - d) ADMET polymerization
 - e) Merrifield peptide synthesis

Circle the correct answer.

(18 pts)

2. For each of the monomers below tell whether anionic or cationic polymerization would be preferred for its polymerization.

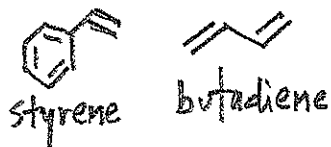


(10 pts)

3. In the Merrifield solid phase peptide synthesis method, the efficiency of each step is critical to the successful production of the desired peptide. (a) If a specific pentapeptide is desired, estimate the amount (% yield) of the pure pentapeptide if each amino acid incorporation proceeded with a 98% yield? (b) What is the purpose of the dicyclohexylcarbodiimide used in this synthesis method?

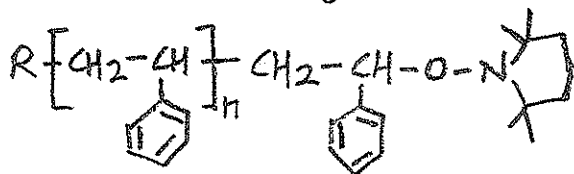
(10 pts) 4.

An A-B block co-polymer can be made from styrene and butadiene using n-butyl lithium. Show the chemical structure of this block co-polymer.



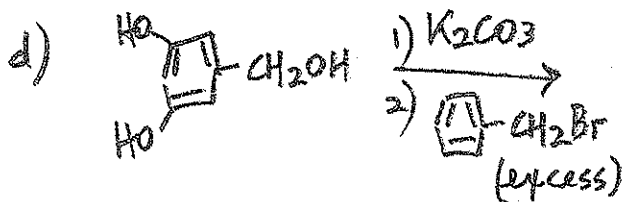
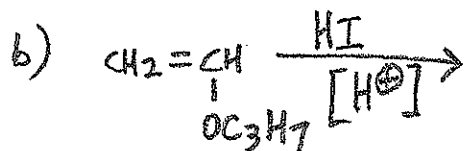
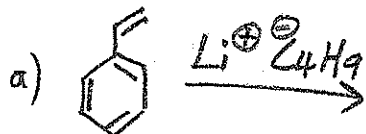
(10 pts) 5.

For living radical polymerizations a structure such as that below can be formed. Although there is no radical chain end shown, a longer chain structure can be obtained when this species is exposed to additional monomer. Show using chemical structures how this can occur.



(24 pts) 6.

Show the polymer formed from each of the reactions below:

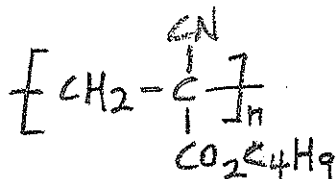


(10 pts) 7.

(a) Is it possible to make a dendrimer with an exact (high) molecular weight? Defend your answer. (b) Would it be best to use a 'convergent' or a 'divergent' approach in making a dendrimer if you wanted the dendritic polymer to have a surface with different properties at various locations on the surface? Explain.

(8 pts) 8.

The polymer shown below is an example of a cyanoacrylate studied for medical applications in wound closure. Show the monomer and describe how this reaction occurs with living tissue.



(bonus
4 pts) 9.

Which one of the following is associated with Suzuki coupling of aromatic rings and can lead to polymers having aryl-aryl bonds?

- a) phenylboronic acids
- b) butadiene
- c) metallocenes
- d) arborols
- e) photoacid generators