Polymers Course for Small Colleges and Universities

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Supporting Information

Useful Links/Resources

Useful textbooks/online resources for instructor preparation (Part 1 of course)

Hiemenz, P. C., & Lodge, T. P. (2007). Polymer chemistry; CRC Press: Boca Raton, Fl.

Cowie, J. M. G., & Arrighi, V. (2008). Polymers: chemistry and physics of modern materials; Taylor & Francis Goup: Boca Raton.

https://ocw.mit.edu/courses/chemical-engineering/10-569-synthesis-of-polymers-fall-2006/lecture-notes/

http://www.internetchemistry.com/chemistry/polymerization.htm

http://pslc.ws/macrog/maindir.htm

https://www.chem.tamu.edu/rgroup/wooley/chem466/lectures.php

Specific topics covered in Part I

Introduction to polymer chemistry

- What is a polymer?
- History
- Nobel Prizes

Step Growth Polymerizations

- Polyesters, polyamides, polyurethanes etc.
- Network polymers
- Limitations in relation to stability and molecular weight

Chain Growth Polymerizations

- Free Radical (initiation, propagation, termination)

- Polyethylene, polypropylene, polystyrene etc.
- Polymerization techniques (bulk, solution, suspension, emulsion)
- Limitations
- Controlled Polymerization methods (nitroxide mediated, RAFT etc.)
- Anionic and Cationic Polymerization
- Configurational isomers and tacticity (syndiotactic, atactic, isotactic)
- Metal catalyzed methods (Zeigler-Natta)
- Copolymers (block, alternating, statistical)
- Polymers for electronics (conjugated polymers: synthesis and properties)

Useful links for Instructor Preparation (Part 2 of course)

http://pubs.rsc.org Specifically Chemical Science, Chemical Communications, Polymer Chemistry, Journal of Materials Chemistry, Chemistry Education Research and Practice, RSC Advances

http://pubs.acs.org Specifically JACS, Macro Letters, Macromolecules, Biomacromolecules, ACS Applied Materials and Interfaces, C&EN.

http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1521-4095 Advanced Materials

https://www.nature.com Nature, Nature Materials

http://www.sciencemag.org

Primary literature from journals was the main source of part 2 course material and as such this kind of information advances regularly. Many of the journals listed above require subscription access, which may be a limitation for smaller schools, but many offer some open access articles free of charge.

Some good sources for open access polymers journals:

http://www.mdpi.com/journal/polymers

https://www.hindawi.com/journals/ijps/

http://www.scirp.org/journal/ojpchem/

https://www.nature.com/pj/

Some of the major topic areas and expectations in the course that was taught are included below for reference.

Organic photovoltaics

- Exciton formation and distances (thickness)
- Energy gaps and absorption of photons

- Performance criteria of solar cells (fill factor, annealing, etc.)
- Types of solar cell structure (blend, single, bulk heterojunction, ideal structure)

Silicon chemistry

- Applications of silsesquioxanes
- General synthesis methods (effect of water, temp, etc)
- Conjugation effects in SQs/solar cell performance
- Main points at bottom of slides
- Chiral separations background (3 interactions rule)
- Rice hull ash conversion to alkoxysilanes
- Substituted alkoxysilane synthesis

Peptoid/Peptide

- FRET analysis of kinetics to form ladders
- Parallel vs antiparallel conformation
- Reasons for using peptoids and peptides
- Sequence defined synthetic methods (solid support)
- DNA analogy to current system

Hydrogels

- Know swelling characteristic relationship to crosslinking
- LCST vs UCST and how to adjust it
- Uses/applications of hydrogels (i.e. tissue engineering)

Biodegradable polymers

- Process by which polymers degrade and how to adjust it
- Types of degradable polymers
- Factors that influence degradation rate

Surface adhesion

- Gecko and mussel examples (biomimetics), design requirements
- Non-fouling surface characteristics (charges, polarity, antimicrobial etc)

Tissue Engineering

- Materials and design parameters

Nylon Synthesis Demonstration

https://chemdemos.uoregon.edu/demos/Synthesis-of-Nylon

http://pslc.ws/macrog/nysyn.htm

Epoxy Resin Demonstration

http://www.loctiteproducts.com/tds/EPXY_QSET_S_tds.pdf

http://pslc.ws/macrog/eposyn.htm

Silicone Elastomers Demonstration

Many companies such as Wacker Chemical (Adrian, MI), Dow Corning (Midland, MI), and Gelest (Morrisville, PA) may offer samples of their different silicone products. It is good to show a silicone fluid and a cured silicone resin and discuss the structures of each. Silly putty can be used in a pinch, but it is a more complex formulation.

C&EN "What's That Stuff?"

https://cen.acs.org/collections/wts.html

Tech Briefs

http://www.techbriefs.com

Course Materials

5 Min Student Presentation Rubric

"Materials Minute"

Description: Lead a short 5-7 min presentation or discussion on a polymer topic important to society; similar to those we have done on Fix-A-Flat and Golf Balls. All presentations will take place June 9th 2016.

Topics: As long as it fits the category of an important polymeric material in society it can be from any era and nearly any source, it can be a news article, patent, magazine article, etc. You will need to have this article chosen and available for distribution by the June 7th class.

Presentation Style: You may choose to give a short 3-slide Powerpoint presentation, or give a chalk talk style presentation. Either way you will be required to lead the discussion amongst your peers, and the use of handouts is acceptable. You should point out the important polymer chemistry being portrayed including reactions and synthesis, why the material is useful, its history, and why it is important to society… for the past, present or future. Your presentation should not exceed 10 min or you will lose points, -1 for each additional minute.

Grading:

_____ Topic appropriate for the assignment (5 pts)

_____ Show a connection to and influence on society (5 pts)

_____ Highlight important points such as synthesis, history, and social and environmental impacts (5 pts)

_____ Effectiveness of leading group discussion on the topic (5 pts)

_____ Presentation is within the time requirements (5 pts)

_____/25 TOTAL

25 Min Student Presentation Rubric

"Topics in Polymer Chemistry, Function and Applications"

Description: Deliver a 20 min Powerpoint style presentation (5 min for questions) on a topic in polymers.

Topics: Your topic should be on an advancement or area of interest in polymer science. This can be based on a research article (advancement in a particular area, i.e. solar cell development), or a compilation of papers to teach a particular topic or technique used in polymer science (i.e. silsesquioxanes, or plasma polymerization, etc.).

Presentation Style: Your presentation should be a Powerpoint, and must include an *Introduction* section into the topic (Why is it important?), *Body* (recent findings, advancements and developments), *Conclusion* section, and *Recommendations:* (What you think should be done to advance the topic area!) Your presentation should not exceed 25 min or you will lose points, -1 for each additional minute.

You must use primary literature such as ACS journals for this project, with proper citation, (see the silsesquioxane slides for examples).

Grading:

_____ Topic appropriate for the assignment (5 pts)

_____ Introduction adequately defines the importance of the topic (5 pts)

_____ Body of presentation adequately discusses the findings, advancements and developments of the presentation area (10 pts)

_____ Conclusion gives representation of most important points (5 pts)

_____ Recommendations are well thought out and realistic (5 pts)

_____ References are properly referenced throughout the paper (5 pts)

_____ Slides are well organized and effectively presented (10 pts)

_____ Presentation is within the time requirements (5 pts)

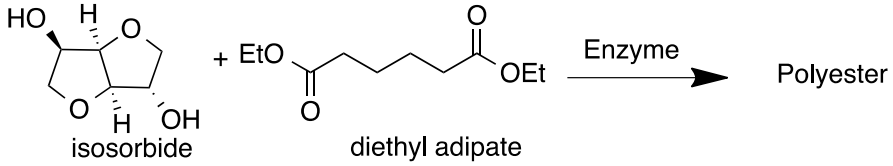
_____/50 TOTAL

Example Journals: Nature, Science, Nature Materials, Proceedings of the National Academy of Science USA (PNAS), Journal of the American Chemical Society (JACS), Biomaterials, Biomacromolecules, Advanced Materials, *Advanced Functional Materials, Angew. Chem. Inter. Ed., Applied Physics*

Example Exam 1 Questions and Topics

Short Answer

1. The polymer industry is searching for ways to replace petroleum-based feedstocks with renewable materials. Isosorbide is a biomass-derived monomer, synthesized from the dehydration of sorbitol. Catalani and co-workers recently reported the synthesis of isosorbide polyesters using enzymes as the catalysts (*Macromolecules* **2010**, *43*, 10315-10319). The poly(isosorbide adipate) produced with isosorbide are biodegradable, which is also a desired feature for the next-generation commodity materials.



a) Draw the chemical structure for the polyester that results from this step-growth polymerization? (10 pts)
b) Without any solvent present, the authors observed polymer molecular weights of about 2 kDa. In contrast, if the polymerization was run in cyclohexane:benzene mixtures, which forms an azeotrope with ethanol, the polymer molecular weights increase to about 20 kDa. Provide an explanation for this result. (10 pts)
c) The poly(isosorbide adipate) polymers have a T_g of 35 ^oC. What is T_g? Provide a complete explanation. (10 pts)

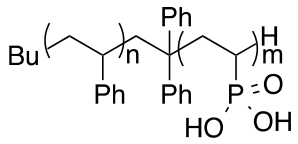
2. GPC is a very useful technique for measuring molecular weights.

a) What does GPC stand for? (5 pts)
b) What are two limitations of GPC? (10 pts)

c) Describe two other techniques that could be used to determine polymer molecular weights other than GPC, and their advantages. (10 pts)

3. Polymers can be classified either by their method of synthesis or by their properties. What are the two synthesis classifications and what defines each? (10 pts)

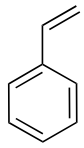
4. In class we discussed a case study on polymer proton exchange membrane fuel cells. We showed the synthesis of a PS-co-PVPA based polymer by anionic polymerization.



A B

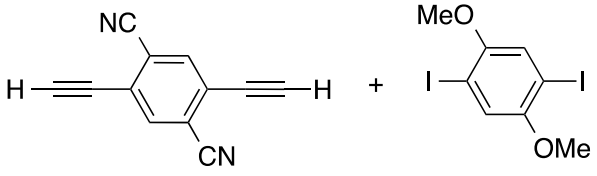
a) Draw a diagram showing the structure of the copolymer containing 20% block A and 80% block B. What is its structure type? (10 pts)
b) Though this polymer succeeded in offering ion exchange capacity superior to Nafion, what was its major drawback? (Remember Nafion is a fluorinated polymer). (5 pts)
c) Transformation reactions are often necessary when synthesizing block copolymers. Provide one specific example of a block copolymerization that requires a transformation reaction and show (with structures) how this is accomplished. (10 pts)

5. Show initiation (i.e. BPO), propagation, and termination (by chain combination) steps for the radical polymerization of styrene. (15 pts)



6. In general, in controlled radical polymerizations (CRP) (like ATRP), termination reactions are assumed to be essentially non-existent. Explain why this assumption is reasonable based on your understanding of CRP. (10 pts)

7. The following two monomers are copolymerized using metal catalysis (i.e. Sonogashira coupling).



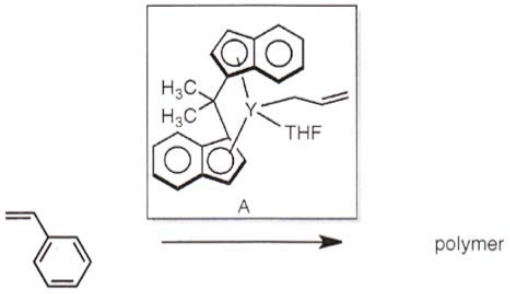
A B

a) What synthesis class does this polymer belong to, step-growth or chain-growth? (5 pts)
b) What type of catalyst should be used for this type of polymerization? (10 pts)

c) Draw the structure of the resulting polymer. (5 pts)
d) This class of polymers is called “conjugated polymers” because of the delocalized, π-conjugated backbone. These polymers are being widely explored for a number of different applications. Briefly describe one application and how the polymer could be used. (10 pts)

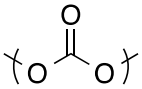
Multiple Choice (Circle Answer, 5 points each)

8. What type of polymer tacticity would be expected using Zieglar-Natta type polymerization with the following catalyst?



A. Atactic
B. Isotactic
C. Syndiotactic
D. Andiotactic

9. This structure represents what class of polymers?



A. Polyvinylchloride
B. Polyester
C. Polyamide
D. Polycarbonate

10. Which of the following does ROMP stand for?

A. Ring Opening Metathesis Polymerization
B. Ring Opening Metal-catalyzed Polymerization
C. Ring Olefin Metathesis Polymerization
D. Raney Olefin Metathesis Polymerization

11. Which of the following are major limitations to conductive polymers made by electropolymerization methods (i.e. polyacetylene)?

A. Insoluble (difficult to process)
B. Defects (disrupt conductivity)
C. Exist in both cis and trans (poor packing)
D. All of the above

12. The transfer of fluorescence energy from one molecule (fluorescent, higher energy), to another molecule of lower energy is a process known as:

A. Free Electron Transfer Dynamics (FETD)
B. Förster Electron Transfer Dynamics (FETD)
C. Förster Resonance Energy Transfer (FRET)
D. Förster Relocation Energy Transfer (FRET)

True/False (Circle Answer, 3 points each)

13. Step growth polymerizations are more efficient at achieving higher molecular weights than chain growth polymerizations. True False

14. Bakelite is an example of a thermoset polymer. True False

15. Suspension polymerization uses a large excess of surfactant and a water insoluble monomer. True False

16. Golf balls have an outer shell that is composed of a class of polymers made by step-growth polymerization called polyurethanes. True False

17. Excited state intramolecular proton transfer is a process by which a proton transfer occurs in the excited state from one form of a molecule to another, and may result in increased fluorescence. True False

18. The polymerization of thiophene using the Me-Grignard and Ni^0 catalyst approach is a step growth polymerization process. True False

19. In the TNT sensing application, fluorescence is turned off when TNT is associated with the polymer. True False

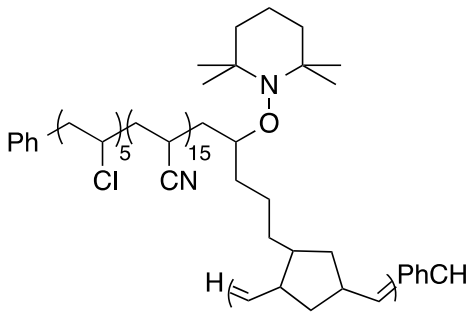
20. Lyotropic liquid crystals use solvent to induce layering and ordering. True False

21. The formation of an excimer between two polymers results in a broader and blue shifted emission. True False

22. Plastics are polymeric materials that are capable of changing shape when a stress is applied and retaining that shape when a stress is removed. True False

Extra Credit

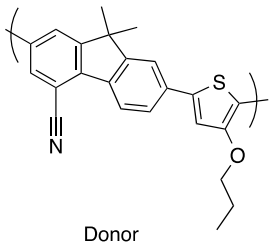
Devise a synthetic route to the following polymer. (10 points)



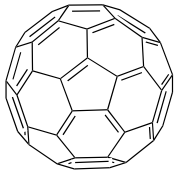
Exam 2 Example Questions

Short Answer

1. You build an organic solar cell using the polymer system shown below. You start with a bi-layer system (a layer of donor and a layer of acceptor material), and get a power conversion efficiency of 5%. You would like to increase the power conversion efficiency of the system. What parameters would you adjust and why (this may include morphology, chemical structure changes, etc.? What influence should adjusting these parameters have on the fill factor (FF) of the system? Be sure to use pictures/diagrams in your explanation. (15 pts)



Donor



Acceptor

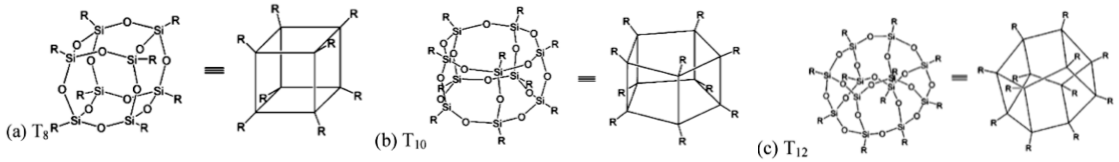
2. Phosphorescent phenomenon is very rare in pure organic molecules.

a) What are the reasons? (7 pts)
b) We discussed ways to make organic phosphorescent molecules, explain the design principle regarding your answer to part a. (7 pts)
c) What are some advantages LED has over LCD? (5 pts)

3. What is the definition of photochromism and what is the origin of the photochromism effect (light does what?)? (7 pts)

4. Silsesquioxanes are a class of well-defined silicon based inorganic polymer that can be synthesized by a variety of catalytic methods. We discussed in great detail how silsesquioxanes are formed using fluoride catalysis, and some of the conditions varied to

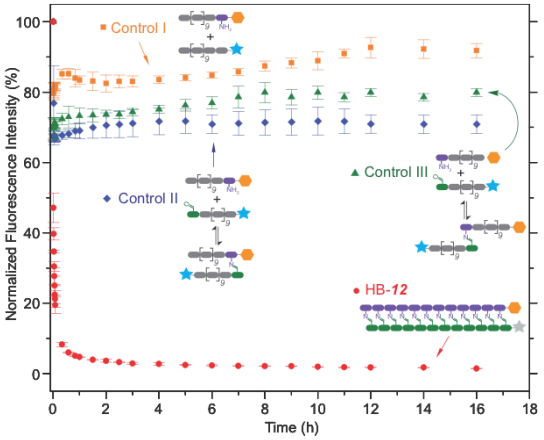
achieve a maximum yield of T_{10}, the most soluble cage system. You now want to increase the yield of T_8 (the kinetic product of cage formation, i.e. forms the fastest), while limiting the amount of T_{10} or T_{12}, both thermodynamic products formed by equilibration. What conditions and/or parameters would you suggest adjusting to achieve better conversion to T_8 and why (i.e. solvent, catalyst, temperature, etc.)? (15 pts) 'Use back of page if needed'



5. One of the major drawbacks to silicon chemistry is the intense amount of energy to break the Si-O bond (>500 kJ/mol).

a) What methods have scientists used to overcome this obstacle? (7 pts)
b) Draw an example of one of the types of molecules that can be formed by one of these techniques. (5 pts)
c) Draw a mechanism showing the reaction of the molecule in part b with phenylLi to form a mono-phenyl substituted alkoxysilane. (5 pts)

6. The plot below shows the results of a FRET hybridization fluorescence experiment with peptoids containing dynamic covalent groups to form ladders which can form by either a zipper mechanism, hand shake line, or a combination of both to reach their final ladder state. A series of controls, as shown were used to quantitatively determine the directionality and mechanism of this hybridization.



a) Based on this, what is the directionality of hybridization (parallel or anti-parallel) and mechanism (zipper, hand shake, or both) observed for the HB-**12** hybridization? Why did you come to this conclusion? (7 pts)

b) One of the major limitations of dynamic covalent molecular ladders is the limiting factor of the length of self assembly, a process known as kinetic trapping, where the ideal product length can no longer be achieved. Explain the method known as Vernier Templating and how it could be used to overcome this limitation. Use pictures as necessary. (10 pts)

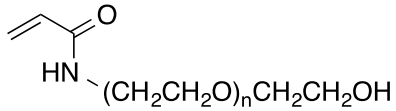
7. Briefly explain the effect of the following parameters on the degree of swelling of a hydrogel. Use pictures as necessary. (10 pts)

- Hydrophobicity

- Crosslinking density

- Distance between crosslinks (M_c)

8. The following new monomer was copolymerized with *N*-isopropyl acrylamide (PNIPAAM) monomers. Would the LCST increase or decrease from 32 °C in water? Explain your answer after considering all chemical factors of the new monomer. (7 pts)



9. The following drawing schematically describes a design strategy to make a smart drug delivery gel. Briefly explain how an antigen can trigger the gel to release the imbedded drug. (7 pts)

10. What is the meaning of biodegradation? Explain how we can design biodegradable polymers and control the degradation rate. (7 pts)

11. Why are non-fouling properties so important in certain bio-applications? How can we achieve anti-fouling properties in materials? (5 pts)

Multiple Choice (Circle Answer, 5 points each)

12. What is the ideal polymer thickness and maximum exciton diffusion distance in polymer solar cells?

E. 100 nm and 20 nm
F. 250 nm and 10 nm
G. 200 nm and 5 nm
H. 200 nm and 10 nm

13. What are the three components necessary for tissue engineering?

E. Growth factor, sugar, nitrocellulose
F. Growth factor, scaffold, cell
G. Scaffold, cell, cell food
H. All of the above

14. Chiral separation polymer stationary phases must have at least how many interactions with the analyte (i.e. hydrogen bonding)?

E. 1
F. 2
G. 3
H. 4

15. Why is it necessary to run the RLi substitution reactions on alkoxysilanes at low temperature?

E. More easily solubilize the starting materials
F. To make the product precipitate out of solution for easy purification
G. Limit the amount of multiple substitutions to favor one substitution
H. All of the above

16. Reversible organic reactions used in self-healing systems are a member of what area of chemistry:

E. Dynamic Conversion Chemistry (DCC)
F. Dynamic Covalent Chemistry (DCC)
G. Dynamic Combination Materials (DCM)
H. Dormant Reactivity Chemistry (DRC)

True/False (Circle Answer, 3 points each)

17. Hydrogen bonds are stronger than dynamic covalent bonds. True False

18. Silsesquioxanes are silicon–oxygen cage structures with the molecular formula $[RSiO_{1.5}]_n$. True False

19. Rice hull ash has a lower surface area than sand, and therefore requires less energy to convert to alkoxysilanes. True False

20. Geckos have extremely sticky feet due to secreted glue like substances from their setae. True False

21. Organic solar cells have achieved power conversion efficiencies of >20%.
True False

22. DNA is a biological information storage material that relies on hydrogen bonding for its unique double helix structure. True False

23. One of the main applications of hydrolysable/biodegradable polyesters (i.e. polyglycolide) is for degradable sutures. True False

24. Solar cells based on silsesquioxanes performed much better than solar cells that contained no silsesquioxane materials. True False

25. The synthesis of silsesquioxanes by fluoride catalysis essentially stops below 0°C due to the freezing of water, which is necessary as a co-catalyst. True False

26. Antimicrobial polymers are mostly made of very hydrophobic building blocks.
True False

Extra Credit (5 pts each)

A) Summarize (student X's…) presentation in a few sentences, what did you learn?

What is your overall favorite subject discussed in class?

Case Study and Other Course Notes Available Upon Request