

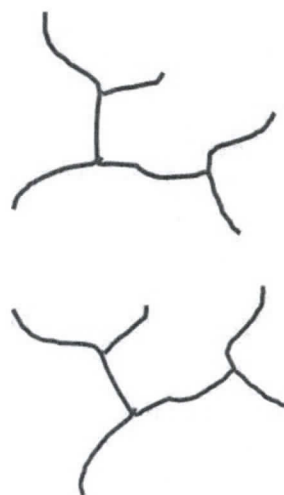
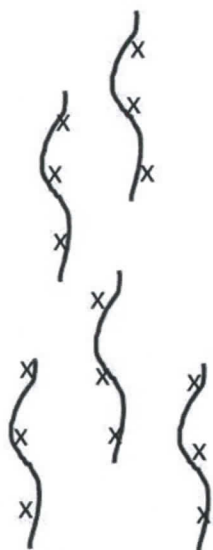
Name: KEY [printed]

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

_____ [signature]

Exam I, February 3, 2011, 125 pts
Polymer Chemistry, CHEM 466, Spring 2011
Texas A&M University, College Station, TX, USA

1. For either covalent or supramolecular polymers, we discussed general structural parameters (each of which is illustrated schematically below) that influence the physical and mechanical properties, list four. [8 points]



1. molecular weight
2. molecular weight distribution
3. architecture / topology
4. composition

also
stereochemistry

2. Give three properties of (macro)molecules that are influenced by the (macro)molecular size (i.e., the degree of polymerization and molecular weight), and describe briefly how the property changes with size. [12 points]

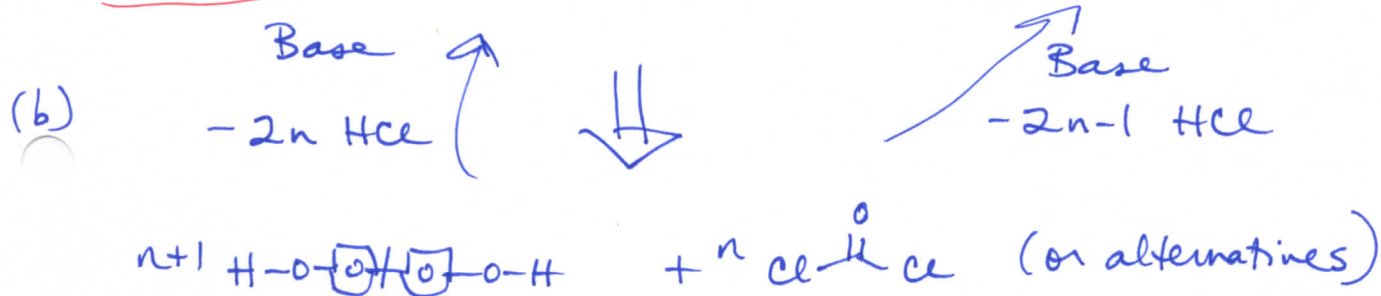
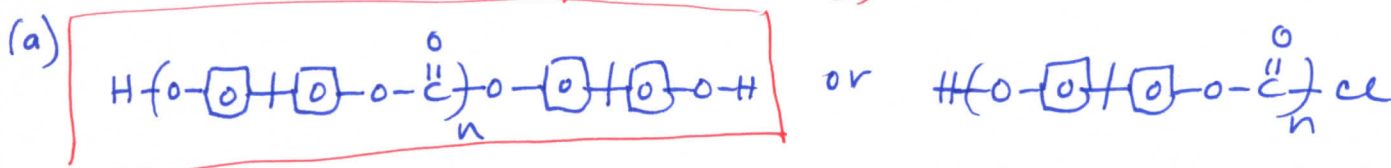
Property	Effect, as size increases
1. solubility	decreases as size increases
2. viscosity	increases as size increases
3. thermal transition temperatures (T_g , T_m , bp)	increase as size increases

also mechanical properties
(strength, toughness, modulus)

increase as size increases

3. For the CD shown on the table at the front of the room:
- Draw the polymer structure (we also discussed this polymer being used in drinking cups, eyeglasses and other applications). [10 points]
 - Provide a retrosynthetic pathway for its preparation. [10 points]
 - If the polymerization were to be performed with 0.95 equivalents and 1.00 equivalents of the two monomers, calculate the maximum degree of polymerization that could be obtained. [10 points]
 - Do you predict that these conditions would result in the formation of a polymer? [2 points]
 - For your retrosynthetic analysis, identify which monomer would be present at 0.95 equivalents, being certain that your assignment agrees with your polymer structure. [3 points]
 - Calculate the number-average molecular weight (M_n), the weight-average molecular weight (M_w) and the polydispersity index (PDI) for this polymerization, given a sample having a 1:2:1 ratio of the number of moles of polymer chains of exact molecular weights 482, 2768 and 5308 g/mol, respectively. [15 points]

structure, based on ~~(d)~~ (e) information



(c) w/ stoichiometric imbalance, use Egn. 2.7.7 of text

$$N_n = \frac{1+r}{1+r-2pr} \quad \text{where } N_n = DP_n \quad r = \frac{V_1^0}{V_2^0} < 1 \quad \Rightarrow \quad DP_n = \frac{1+0.95}{1+0.95-2(1)(0.95)} \quad @ 100\% \text{ conv. A}$$

$$P = C_A \quad = 39$$

(d) yes, $n \geq 10$ is considered to be a polymer

(e) at 0.95 equiv. of $\text{Cl}-\overset{\text{O}}{\parallel}\text{C}-\text{Cl}$, the structure on the left would be obtained

(f) on next page

Name: KEY [printed]

Equations, which may be of use:

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

N_x = # moles of polymer chains having molecular weight, M_x

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

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

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

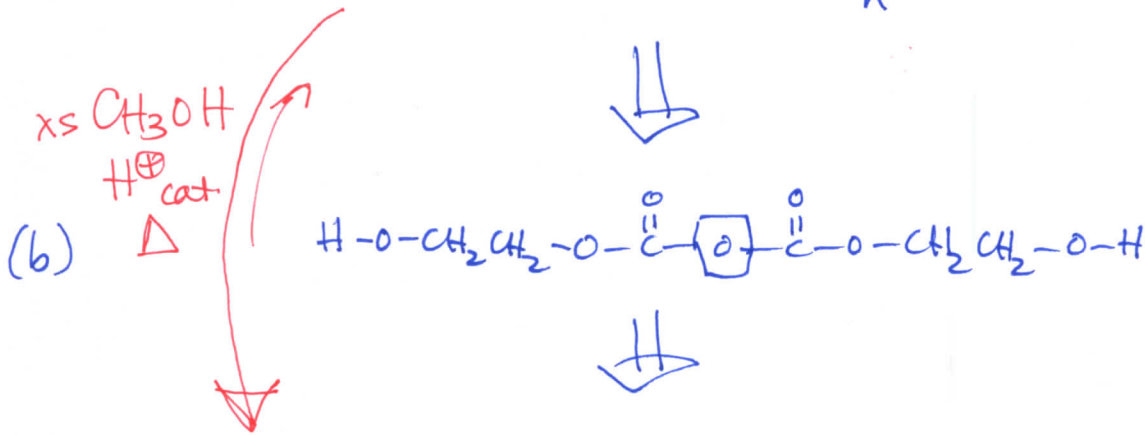
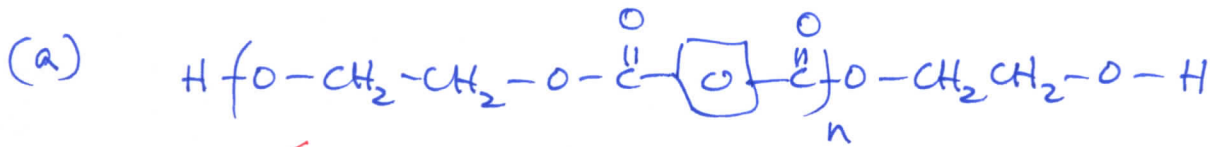
#3 (f)

$$M_n = \frac{\sum N_x m_x}{\sum N_x} = \frac{1 \text{ mol} (482 \text{ g/mol}) + 2 \text{ mol} (2768 \text{ g/mol}) + 1 \text{ mol} (5308 \text{ g/mol})}{1 \text{ mol} + 2 \text{ mol} + 1 \text{ mol}}$$
$$= \underline{\underline{2832 \text{ g/mol}}}$$

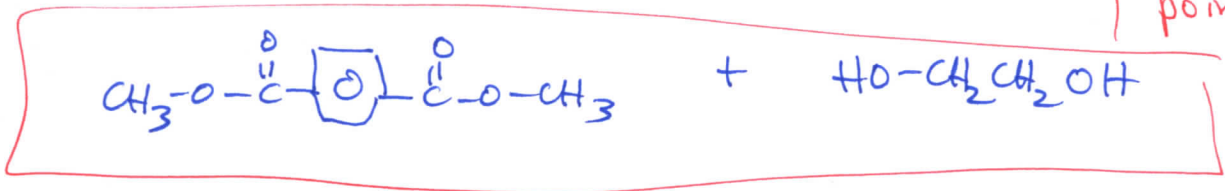
$$M_w = \frac{\sum N_x m_x^2}{\sum N_x m_x} = \frac{1 \text{ mol} (482 \text{ g/mol})^2 + 2 \text{ mol} (2768 \text{ g/mol})^2 + 1 \text{ mol} (5308 \text{ g/mol})^2}{1 \text{ mol} (482 \text{ g/mol}) + 2 \text{ mol} (2768 \text{ g/mol}) + 1 \text{ mol} (5308 \text{ g/mol})}$$
$$= \underline{\underline{3861 \text{ g/mol}}}$$

$$PDI = \frac{M_w}{M_n} = \frac{3861 \text{ g/mol}}{2832 \text{ g/mol}} = \underline{\underline{1.363}}$$

4. For the water bottle shown on the table at the front of the room:
- Draw the polymer structure. [10 points]
 - We discussed the importance of transesterification reactions and also equilibria during condensation, step-growth polymerizations. Provide chemical reaction conditions that could be used to revert the polymer structure of part (a) back to the industrially-applied monomers (which might be useful, for instance in recycling processes). [10 points]
 - Provide an electron arrow-pushing mechanism for the chemistry that you propose in part (b). [10 points]



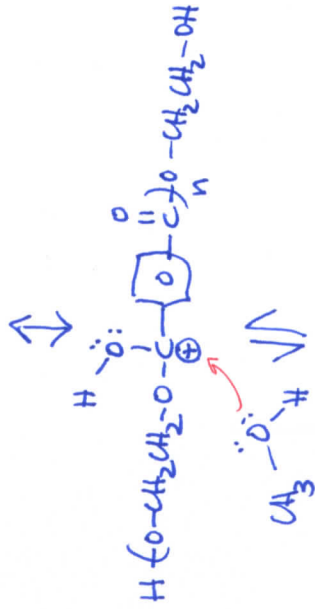
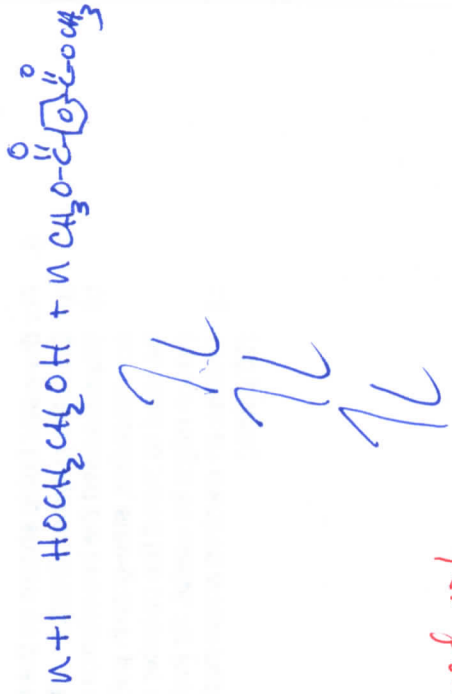
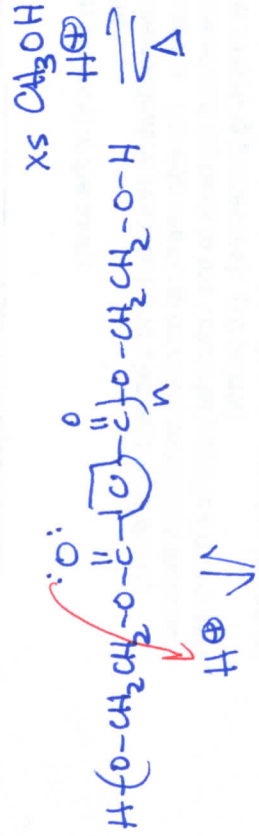
evaluation of the retrosynthetic analysis leads to these two monomers as the starting point



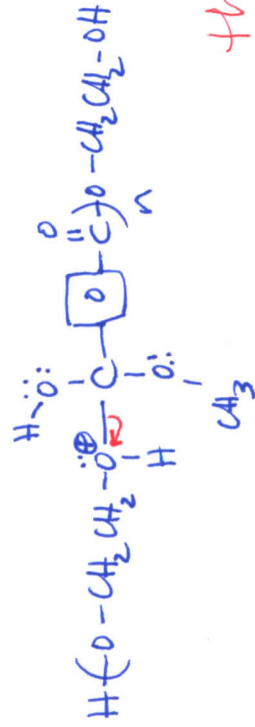
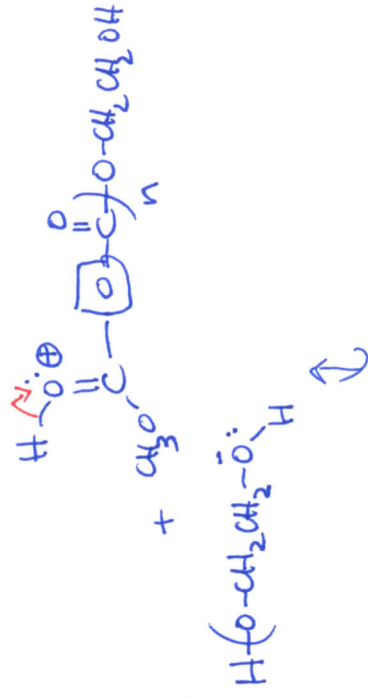
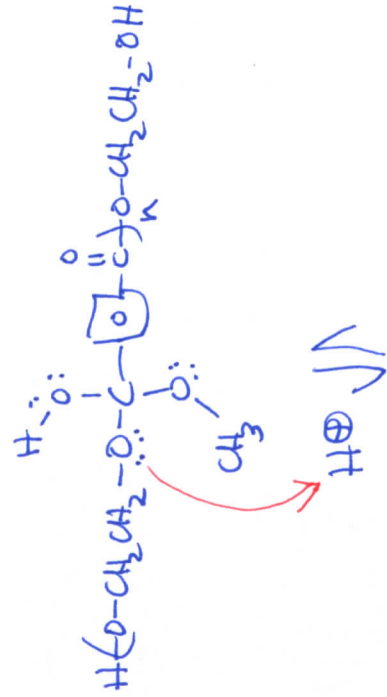
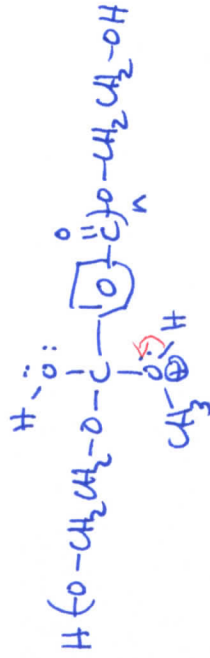
therefore, in answer to (b) the conditions would include rxn with xs CH₃OH, in the presence of an acid catalyst, at elevated temperature

(c) on a separate page

4C



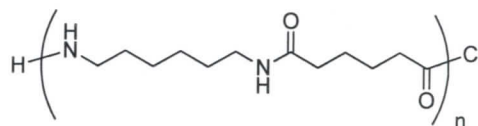
cleaved poly chain w/ alcohol + methyl ester chain ends



this step gives chain cleavage

Name: KEY [printed]

5. Within the diagram below (Figure 2.7 from your textbook, Hiemenz, P. C.; Lodge, T. P. *Polymer Chemistry*, 2nd Edition; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2007):
- Draw the reagents, placed within the appropriate locations of the reaction vessel, that would lead to the preparation of Nylon 6,6 via interfacial polymerization. [10 points]
 - Provide an electron arrow-pushing mechanism for the polymerization. [10 points]
 - Give one object or product in which Nylon 6,6 may be found and identify the primary characteristic of the amide linkages along the backbone of Nylon 6,6 that provide the physical and mechanical properties for its application in that object/product. [5 points]



Nylon 6,6

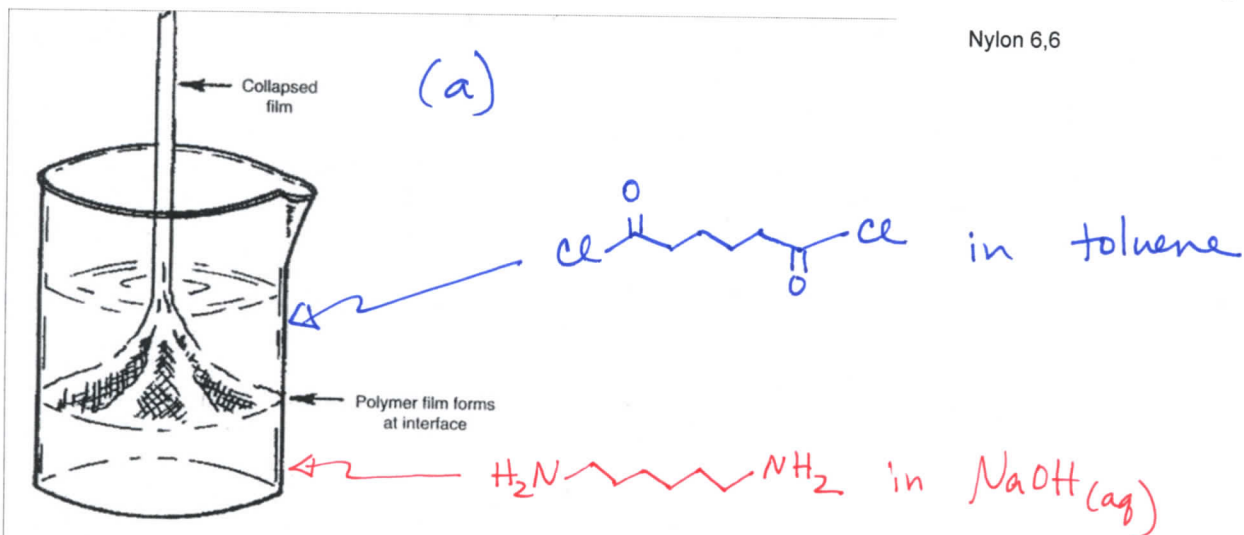
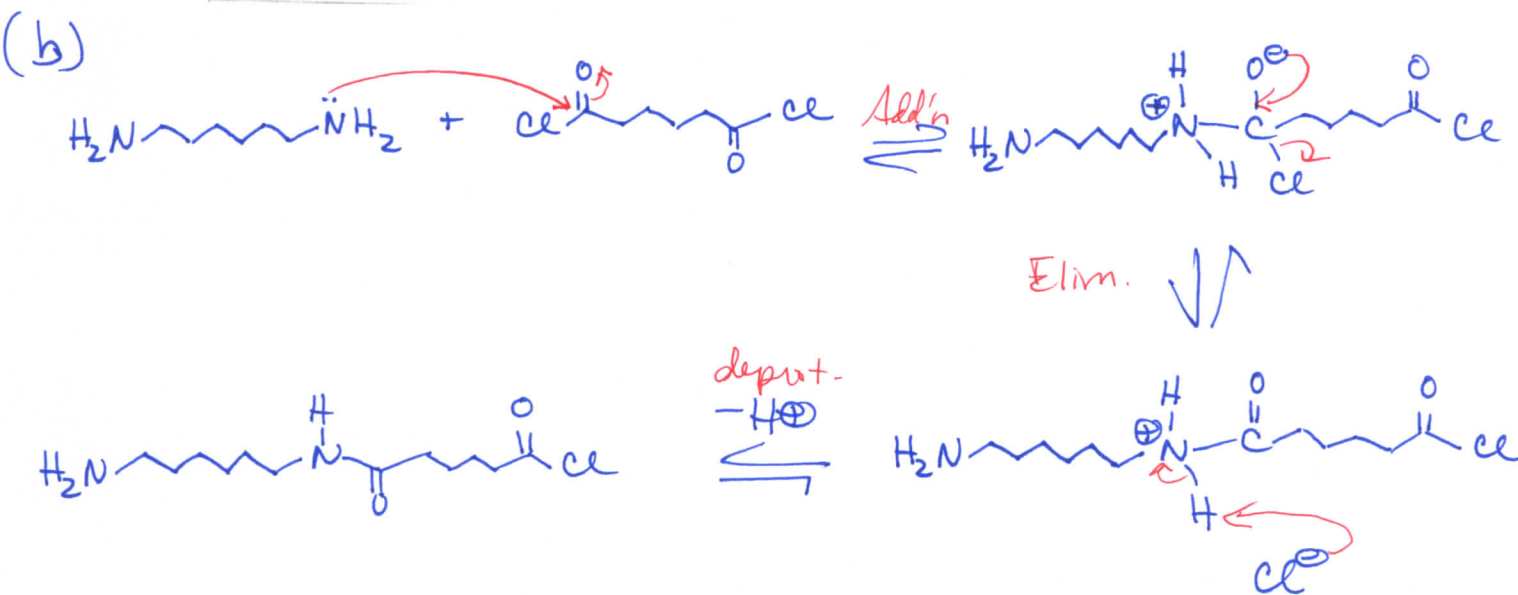


Figure 2.7 Sketch of an interfacial polymerization with the collapsed polymer film being withdrawn from the surface between the immiscible phases. (From Morgan, P.W. and Kwolek, S.L. *J. Chem. Educ.*, 36, 182, 1959. With permission.)



(c) ropes, tents, clothing, etc.; H-bonding (intra- + inter-chain) interactions provide pseudo crosslinks (supramolecularly)