NSWER KF Name: [printed]

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

[signature]

## Exam I, February 6, 2014, 100 pts Polymer Chemistry, CHEM 466, Spring 2014 Texas A&M University, College Station, TX, USA

 Nylon 6 can be, theoretically, produced by either condensation, step-growth polymerization or by addition, chain-growth polymerization. From retrosynthetic analyses, provide one (1) <u>monomer</u> that could be employed and list three (3) of the <u>basic points</u> that we had discussed as characteristics for <u>each</u> of these two (2) types of polymerization. [30 points]



Condensation, step-growth polymerization

Addition, chain-growth polymerization

Monomer

Ð NH, 40

Monomer 0

**Basic** points

i) monomers undergo rxn Wead other + poly chain ends ii) poly chain ends can react w/each other iii) broad PDI

iv) often a small molecule by-product (condensate) is produced

U) high DPn a chieved only a high 20 conversion

**Basic** points initiator required terminator required ii) iii) monomers react only W/ mit ator or propagating poly chain end iv) high DP, at high or low to conversion

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 The polyester shown below, which is either poly(ε-caprolactone) or poly(6-hydroxycaproic acid), depending on the monomer used for its synthesis, can undergo intra- and intermolecular transesterification reactions, which may be catalyzed by acids, bases, transition metal catalysts, etc.

ANSWER KEY

(a) Draw the electron arrow-pushing mechanism for one intramolecular "back-biting" transesterification reaction of this polymer under acid-catalyzed conditions and another under non-catalyzed conditions, giving the products for your mechanisms in each case. (You may prefer to draw-out more than one repeat unit structure to represent the polymer chain). [20 points]



Name: ANSWER KEY

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(b) Figure 2.4 of the textbook includes four data plots that were used to illustrate the relative rates of increase in polymer chain length ( $N_n$ ) and reduction of monomer concentration ([A]/[A]<sub>0</sub>) vs. time for catalyzed and non-catalyzed polymerization conditions. In part (a) above, intramolecular "back-biting" reactions can be considered to be the opposite of ring-opening polymerizations, producing monomer (in the case that the backbiting proceeds for the terminal repeat unit, which is kinetically favored) while shortening the polymerization, indicate which data below were plotted for intramolecular back-biting depolymerization, indicate which data would represent [A]/[A]<sub>0</sub> vs. time and N<sub>n</sub> (also called DP<sub>n</sub>) vs. time for the acid-catalyzed intramolecular transesterification reaction and which data would result from [A]/[A]<sub>0</sub> vs. time and N<sub>n</sub> vs. time for the non-catalyzed reaction. [8 points]



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3. Nylon 6 and poly(ε-caprolactone) have similar polymer backbone structures, with one carbonyl, five methylenes and a heteroatom, nitrogen or oxygen, respectively. Each is able to undergo crystallization. However, their thermal transition temperatures differ significantly. The glass transition temperature (T<sub>g</sub>) for nylon 6 is 52 °C, whereas the T<sub>g</sub> for poly(ε-caprolactone) is 112 degrees lower at -60 °C. Similarly, the melting transition temperature (T<sub>m</sub>) for nylon 6 is 225 °C, whereas the T<sub>m</sub> of poly(ε-caprolactone) is 60 °C. Briefly explain in words and provide a molecular structure diagram that explains the significant differences in thermal properties for these two polymers. [10 points]

Name: ANSWER KEY

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Name: ANSWER KEY [printed]

For the polyurethane-urea-ether copolymer discussed during the 01/30/2014 lecture: wethane nea methane ma a) Label the urethane, urea and ether functionalities provide a retrosynthetic pathway for its preparation and provide the conditions for the forward reaction(s). The retrosynthesis should proceed back to small molecules, except that you may use a pre-established polyether. [20 points] H-0 ( ~ of H EN WN-N H H H 01 0 0 L'catalist, establishment of urea linhager OT N=C=0 + 4 H2N-NH2 y+1 0

ntl

b) List two (2) compositional/structural components and their properties that contribute to the polymer material overall exhibiting a combination of flexibility and rigidity that allows for it to serve as elastic fibers. [4 points]

i) soft, rubberg + semi-crystalline polyether segments ii) u/low Ig + Ton values

rigid aromatic polyunea segments iii) H-bondity of usea + wethane groups

5

Name: ANSWER KEY [printed]

5. (a) Calculate the values of M<sub>n</sub>, M<sub>w</sub> and PDI for a polymer mixture having equivalent moles of two polymers with exact molecular weights being 2.0 kDa and 10 kDa. [6 points]

$$M_{n} = \frac{\sum N_{x} M_{x}}{\sum N_{x}} = \frac{1 \cdot 2000 \text{ Da} + 1 \cdot 10000 \text{ Da}}{1 + 1} = 6.0 \text{ kDa}$$

$$M_{w} = \frac{\sum N_{x} M_{x}^{2}}{\sum N_{x} M_{x}} = \frac{1 \cdot 2000 \text{ Da}^{2} + 1 \cdot 10000 \text{ Da}^{2}}{1 \cdot 2000 \text{ Da}^{2} + 1 \cdot 10000 \text{ Da}^{2}} = 8.7 \text{ kDa}$$

$$1 \cdot 2000 \text{ Da} + 1 \cdot 10000 \text{ Da} = 8.7 \text{ kDa}$$

 $PDI = \frac{Mw}{M_n} = \frac{8.7 \text{ kDa}}{60 \text{ kDa}} = 1.5 (2 \text{ sig Ayr})$ 

- (b) There are two interesting observations that you should consider and comment on:
- The M<sub>n</sub> falls at an interesting absolute value and relative to M<sub>w</sub>. [1 point] M<sub>n</sub> is at the midpt. b/c equal # is of 2 + 10 kDa polys M<sub>w</sub> is greater b/c equal # of 10 kDa poly has greater mass M<sub>w</sub> is greater b/c equal # of 2 kDa poly has greater mass The PDI value may seem unusually large or small relative to the molecular weights of the (i)
- (ii) polymers in the mixture. [1 point]

surprisingly small PDI, given that there is a 5x difference in the poly mol. wts.