Name: ANSWER KEY [printed]

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

_______________________[signature]

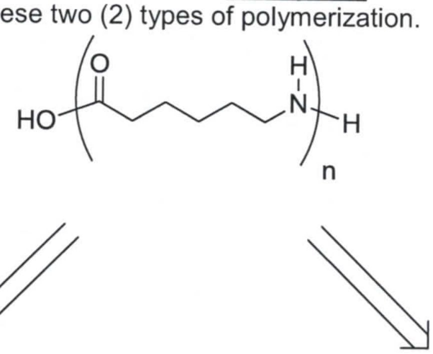
Exam I, February 2, 2012, 100 pts
Polymer Chemistry, CHEM 466, Spring 2012
Texas A&M University, College Station, TX, USA

1. We have discussed the importance of drawing full polymer structures, including the chain ends. Aside from a desire to be thorough, provide two reasons or explanations for why illustration of the chain end compositions is important. [10 points]

   i) the chain ends indicate how a polymer is synthesized

   ii) the chain ends can influence the polymer properties

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



Condensation, step-growth polymerization

Monomer

Basic points

i) monomers undergo rxn w/each other + poly chain ends

ii) poly chain ends react w/poly chain ends

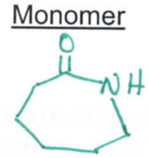
iii) broad PDI

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

(v) high degrees of polym. only at high monomer/func. grp. conversion

Addition, chain-growth polymerization

Monomer



Basic points

i) initiator required

ii) terminator required

iii) monomers react only w/initiator or propagating chain end of poly

(iv) high degrees of polym @ high or low degrees of monomer conversions

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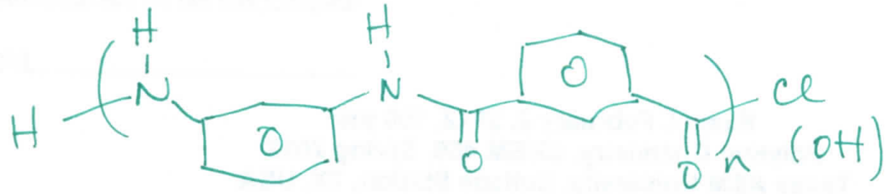
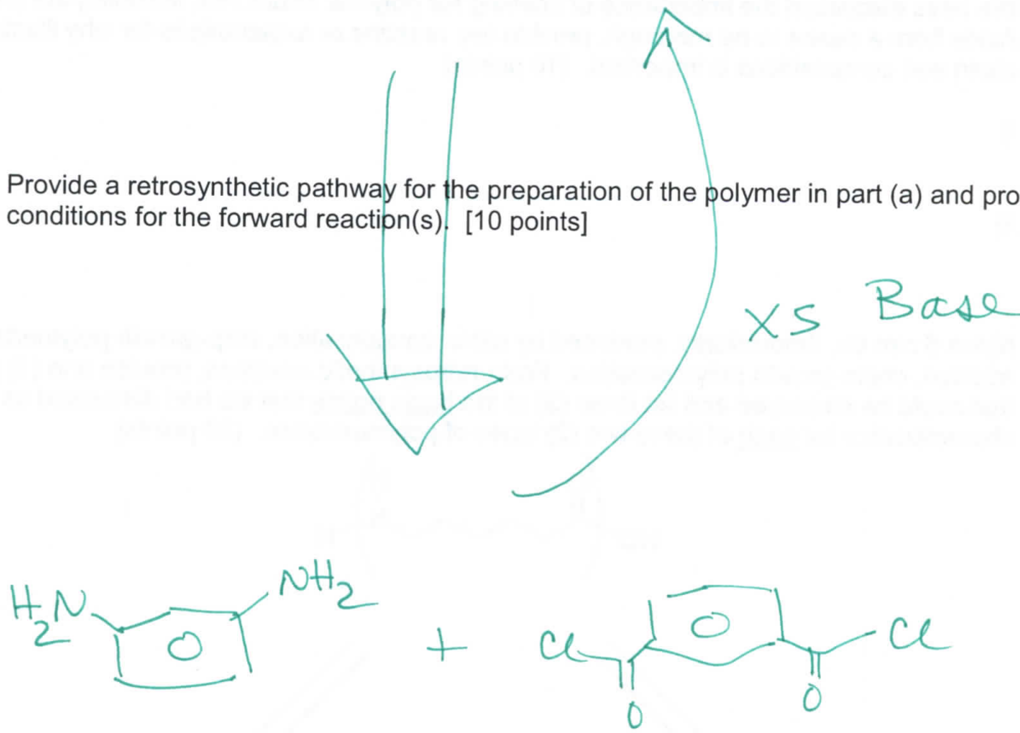
3. For the 'ove' glove shown during the 01/31/2012 lecture:
   a) Draw the structure for the polymer that is spun into fibers and woven to produce the glove. [6 points]



   b) Provide a retrosynthetic pathway for the preparation of the polymer in part (a) and provide the conditions for the forward reaction(s). [10 points]



   c) List three (3) features that contribute to the polymer of part (a) having remarkable thermal stability (no T_m and high T_{decomp}). [9 points]

i) rigid, stable aromatic rings

ii) no aliphatic groups

iii) intra- and inter-chain hydrogen bonding

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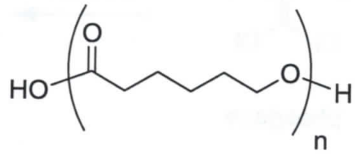
4. Below, you are given two sets of the numbers of moles and molecular weight data (a and b) for a poly(ε-caprolactone) sample before and after the sample underwent melt extrusion processing at elevated temperature. The data are not identified as being either before or after the processing. There are three significant figures valid for each value.



a		b	
N_x	M_x	N_x	M_x
1	5,000 g/mol	1	10,000 g/mol
3	15,000 g/mol	2	20,000 g/mol
3	25,000 g/mol	1	30,000 g/mol
1	35,000 g/mol		

a) Calculate the polydispersity index values for samples a and b. [10 points]

(a)

$$M_n = \frac{\sum N_x M_x}{\sum N_x} = \frac{(1\,mol)(5000\,g/mol) + (3\,mol)(15000\,g/mol) + (3\,mol)(25000\,g/mol) + (1\,mol)(35000\,g/mol)}{1\,mol + 3\,mol + 3\,mol + 1\,mol} = 20{,}000\ g/mol$$

$$M_w = \frac{\sum N_x M_x^2}{\sum N_x M_x} = \frac{(1\,mol)(5000\,g/mol)^2 + (3\,mol)(15000\,g/mol)^2 + (3\,mol)(25000\,g/mol)^2 + (1\,mol)(35000\,g/mol)^2}{(1\,mol)(5000\,g/mol) + (3\,mol)(15000\,g/mol) + (3\,mol)(25000\,g/mol) + (1\,mol)(35000\,g/mol)} = 23{,}800\ g/mol$$

$PDI = M_w/M_n = 1.19$

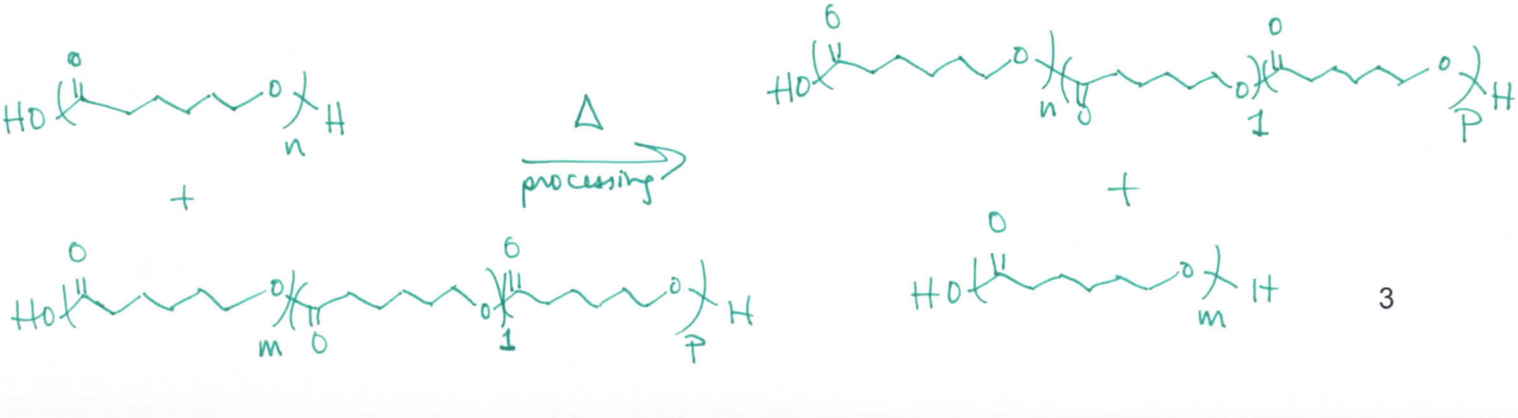
same calc.'s for (b) ⇒ $M_n = 20{,}000$ g/mol, $M_w = 22{,}500$ g/mol $PDI = \frac{M_w}{M_n} = 1.13$

b) State which data set is for the sample before processing and which is for the sample after processing. [5 points]

(a) is after processing
(b) is before processing

c) Show a chemical reaction that could have contributed to the <u>overall changes</u> in the sample during processing, drawing the starting material(s) and product(s). [10 points]

Transesterification – intermolecular rxns ⇒ higher + lower M_x
intramolecular back-biting only ⇒ lower M_x



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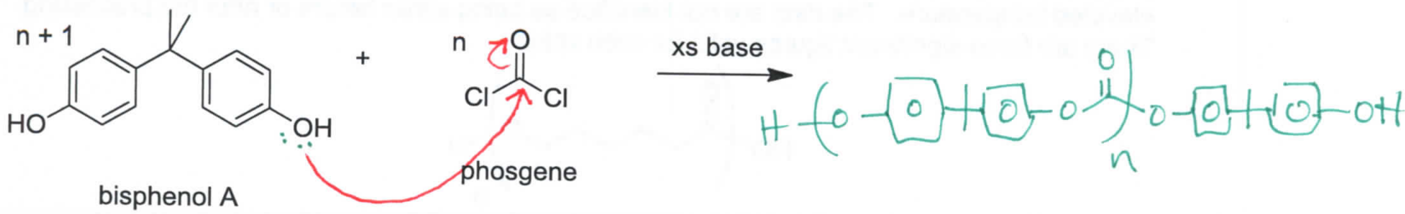
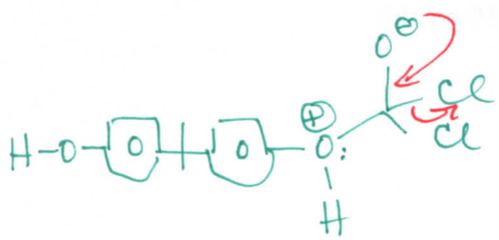
5. For the reaction of bisphenol A with phosgene, provide the electron arrow-pushing mechanism that leads to the formation of poly(bisphenol A carbonate), provide the structure of the polymer and state the most important characteristic that allows for this polymer to find application as an engineering material. [10 points]



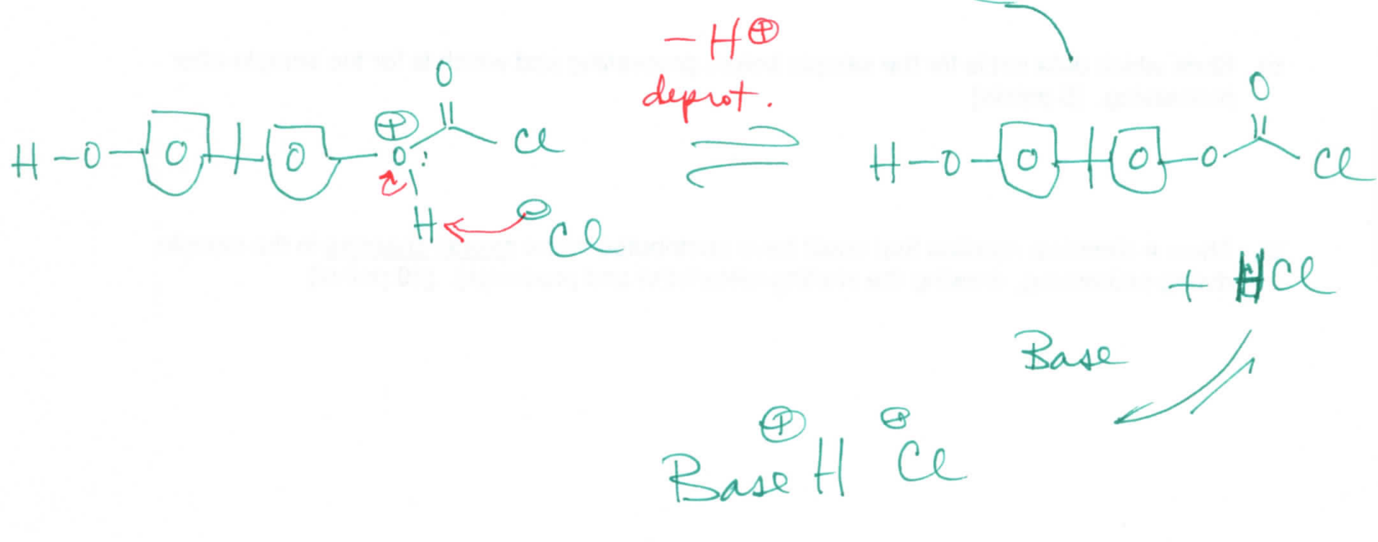
chain-chain packing and bundling results in blocking of Ar ring flips so that upon impact, the energy is dissipated through packing expansion and ring rotations

Add'n ⇅



Elim. ⇅

many times repeated w/ n HO–Ar–C–Ar–OH + n-1 Cl–C(=O)–Cl



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Equations, which may be of use:

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

$$N_x = \#\text{ moles of polymer chains having molecular weight, } M_x$$

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

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

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