080505 Introduction to Polymer Science, Polymer Chemistry Quiz 4

1) In class we synthesized nylon using a Schotten-Baumann interfacial polymerization method. According to wikipedia:

The name "Schotten-Baumann reaction conditions" is often used to indicate the use of a two-phase solvent system, consisting of water and an organic solvent. The base within the water phase neutralizes the acid, generated in the reaction, while the starting materials and product remain in the organic phase...

a) How does the nylon synthesis used in class reflect Schotten-Baumann conditions?

-Give details of the organic solvent and base that are used and specify what acid is neutralized.

-Does the product remain in the organic phase?

-Do the the starting materials remain in the organic phase?

b) Give an advantage and a disadvantage for the interfacial reaction used to make nylon compared to the glyptal reaction.

c) What determines the rate of reaction in an interfacial reaction? (e.g. concentration, reaction rate constants, transport, byproduct or product removal etc.)

2) We also synthesized glyptal polyester in class which has some similarities to the condensation synthesis of polyethylene terephthalate (PET or PETE, i.e. water bottles).

a) Why is phthalic anhydride used rather than phthalic acid in the glyptal synthesis?

b) Give two reactions that phthalic anhydride undergoes in the polymerization and 3 ways that it can be incorporated into the growing polyester chain.

c) Give two reactions that sodium acetate can undergo in this reaction.

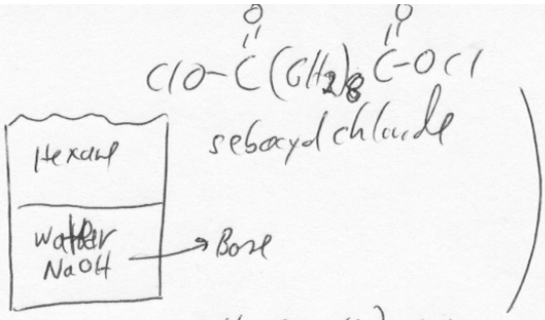
3) In addition to inventing nylon, polyesters, and neoprene, Carothers developed a method to calculate the number and weight average molecular weight for step growth polymerization using the extent of reaction p, as well as a method to predict the gel point in terms of the critical extent of reaction p_c for multifunctional reactants.

a) Give Carothers' equation for the number average degree of polymerization, M_n, in step growth polymerization and sketch a plot of M_n versus p from this equation. (The number average molecular weight is this value times the molecular weight of a monomer, M_0.)

b) The number average degree of polymerization, M_n, is given by the number of monomers in the reacting system, $N(0)$, divided by the number of polymer chains and monomers at time t, $N(t)$. Show how you can obtain the equation of part a) by defining p in terms of $N(0)$ and $N(t)$ and then substituting M_n for $N(0)/N(t)$ and rearranging.

c) Write an expression for p for a system with an average functionality f_{avg} and show that when M_n goes to infinity, p goes to $p_c = 2/f_{avg}$.

ANSWERS: 080505 Introduction to Polymer Science, Polymer Chemistry Quiz 4

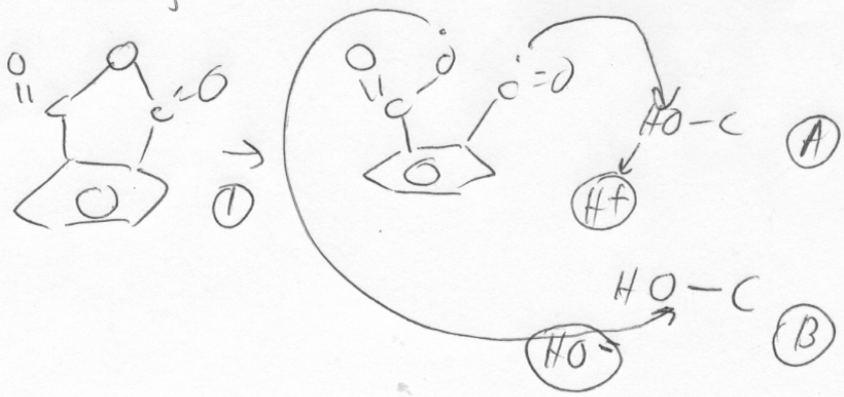
1) a) 

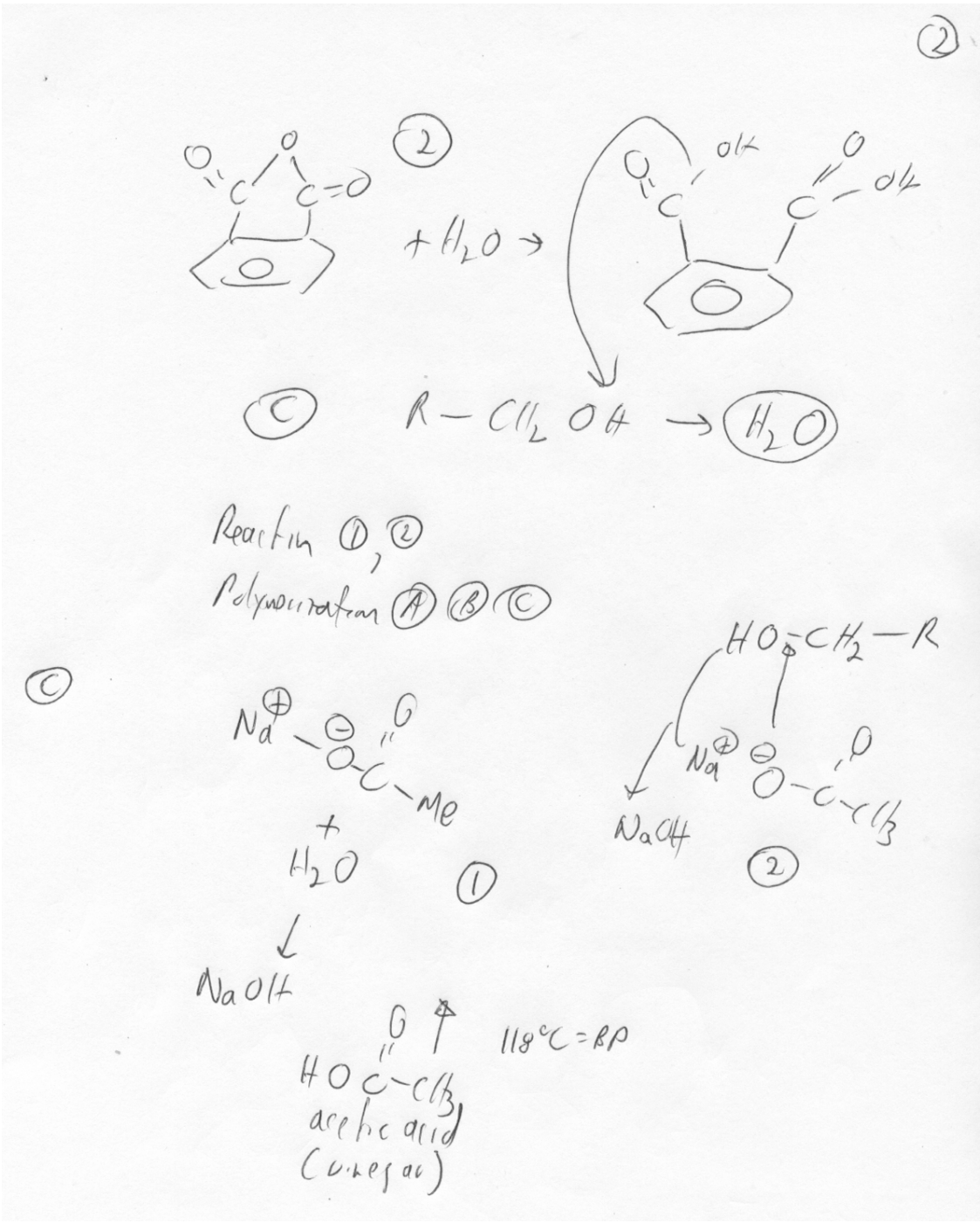
① Starting materials are in each of the two phases rather than remaining in the organic phase Product is removed from system as a solid.

b) Advantages
Low temperature
Rapid Reaction
Disadvantages
Solvent waste

c) Diffusion of reactants to the interface + interfacial area govern rate.

2) a) Tm 131°C vs. 210°C
Ring + Strain ⇒ polymer formation

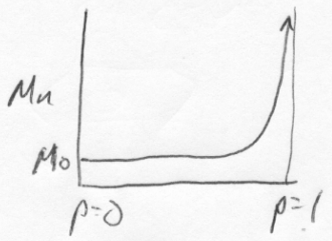
b) 


②
②
+ H_2O →
OH
OH
Ⓒ $R-CH_2OH$ → H_2O
Reaction ①, ②
Polymerization Ⓐ Ⓑ Ⓒ
Ⓒ
$Na^{\oplus}$
Me
+
H_2O
①
NaOH
$HO-CH_2-R$
$Na^{\oplus}$
CH_3
NaOH
②
118°C = BP
$HO-C-CH_3$
acetic acid
(vinegar)

(3) (3)

(3) $\frac{1}{1-p} = M_n$

a)



b) $M_n = \frac{N(0)}{N(t)}$

$$p = \frac{N(0) - N(t)}{N(0)} = 1 - \frac{1}{M_n}$$

so

$$M_n = \frac{1}{1-p}$$

c) for functionality f_{avg}

$$p = \frac{2\,(N(0) - N(t))}{f_{avg}\, N(0)}$$

$$= \frac{2}{f_{avg}} \left(1 - \frac{1}{M_n}\right) \to 0 \text{ at } M_n \to \infty$$

$$p_c = \frac{2}{f_{avg}}$$