090204 Quiz 4 Introduction to Polymers

I class we synthesized Glyptal, swelled and deswelled hydrogels and made and reversed a PVA network.

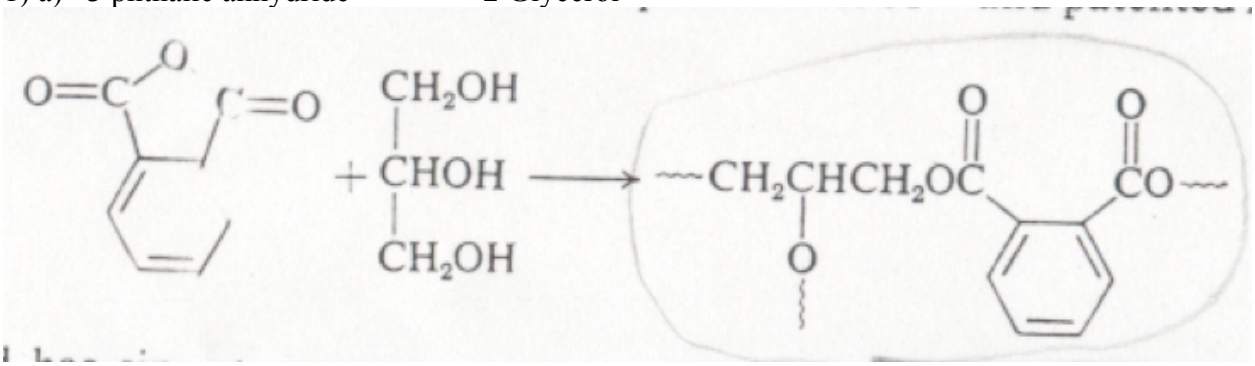
1) The synthesis of glyptal involves a trifunctional and a difunctional reactant in a condensation reaction.
   a) Give the monomers involved in glyptal in a stoichiometric chemical reaction equation. (Draw the structure and give the number of these monomers involved in a stoichiometrically balanced reaction.)
   b) What solvent is used to make glyptal?
   c) Draw the structure of sodium acetate and explain why it was used in this reaction.
   d) Give a sequence of events that occur chronologically in the reaction to form Glyptal.
   e) Give the structure of glyptal and the structure of PET (PETE) and comment on the difference in properties between these two similar polyesters based on the difference in chemical structure.

2) a) Give the structure of PMMA and the structure of the polyacrylate used in the hydrogel. Compare the two and explain the differences in properties between PMMA and polyacrylate associated with this structural difference, i.e. why isn't PMMA a superabsorbent?
   b) What happened when uncrosslinked polyacrylate was added to water? Explain this.
   c) The swelling ratio Q for the hydrogel was about 100 to 500. Write an equation for the swelling ration as a function of the interaction parameter, χ, and the molecular weight between crosslinks, n.
   d) If you wanted a more robust gel what n would you choose.
   e) What happens to χ when salt is added to the hydrogel? Explain what happens to the hydrogel.

3) a) Draw the structure of PVA and boric acid.
   b) The combination of PVA and boric acid yields slime, but when NaOH is added a rubbery elastomer results. Explain this in terms of the percolation model for gelation.
   c) What happens to the molecular weight between crosslinks when NaOH is added? What about when HCl is added?
   d) Gellation occurs at a fixed value of the extent of reaction, p_c, where c indicates the critical extent of reaction. A critical point is where some feature of the system goes to infinity. What feature of a gelling system goes to infinity at p_c, the gel point? Make a rough plot.
   e) Give a function that relates the critical extent of reaction with the structure of a stoichiometric network and calculate p_c for the glyptal system using this function.

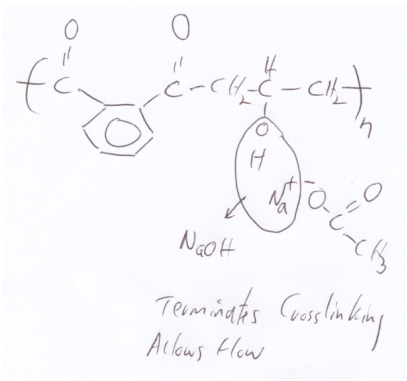
ANSWERS: 090204 Quiz 4 Introduction to Polymers

1) a) **3** phthalic anhydride + **2** Glycerol

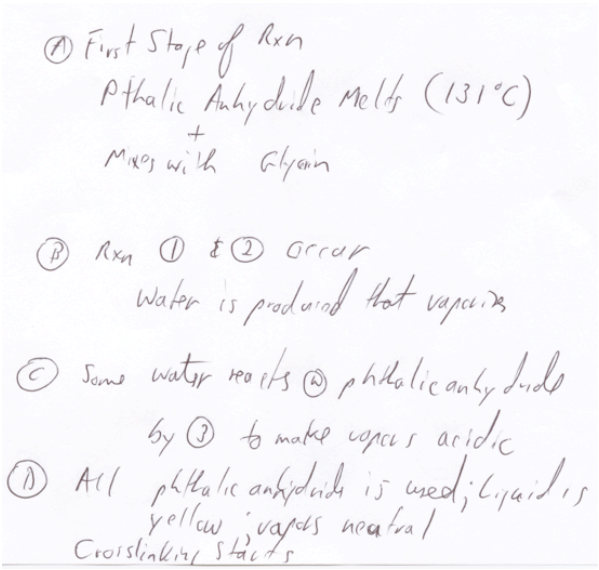


b) The reaction is fun neat (no solvent).

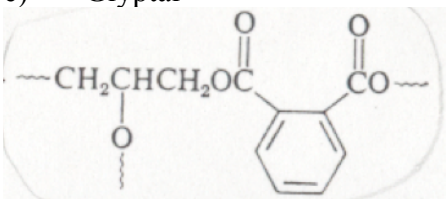
c) The overall extent of reaction relies on the functionality of the monomers and the viscosity (kinetics) of the reacting system. If the system forms a glass too early the reaction ends since molecular mobility is needed for the reaction to occur. Sodium Acetate is used to decrease the functionality of the system to make the system less viscous during the reaction and yielding an overall higher extent of reaction.



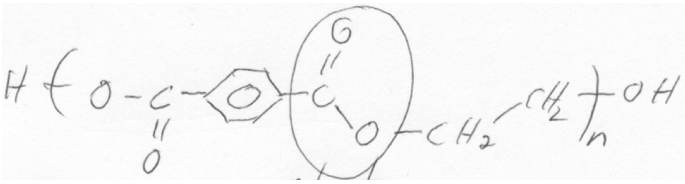
d)



e) Glyptal

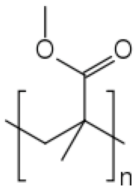


PET (PETE)

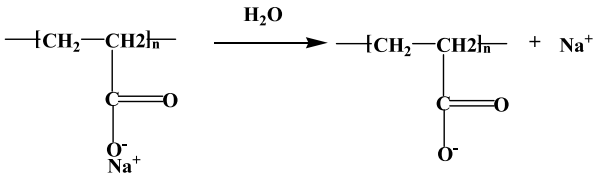


Glyptal has di ortho carboxylic substutited aromatic group and PET has di para substituted aromatic group. This makes PET more flexible than glyptal. Also, the trifunctionality of glycerin versus the difunctionality of ethylene glycol leads to a network structure that is more rigid compared to PET.

2) a) PMMA



Sodium Polyacrylate



PMMA doesn't have an ioniazable group and it has a more bulky structure that allows it to form a glass. Polyacrylate has a more flexible structure and a highly ionizable group that will have a highly negative interaction parameter with water.

b) The uncrosslinked sodium polyacrylate just dissolved in water and formed a viscous solution. Crosslinked polyacrylate swelled because the network structure opposed the solvation. The network structure retains a solid form for the gel despite the polymers desire to dissolve.

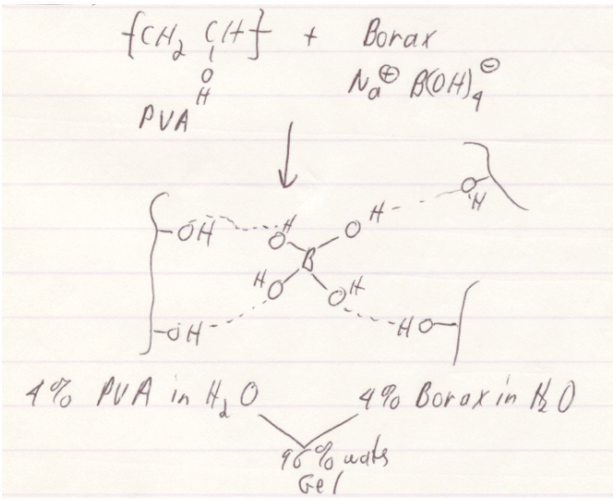
c) V_1 is the molar volume of the solvent.

$$Q = \frac{1}{v_2} \sim \left[\frac{-n\chi}{V_1} \right]^{3/5}$$

d) A more robust gel would be formed with a lower n because the gel modulus is proportional to kT/n following rubber elasticity theory.

e) Salt increases the value of χ (chi parameter) making the swelling ratio drop. If sufficient salt is added χ become positive and the gel desorbs water (the gel collapses).

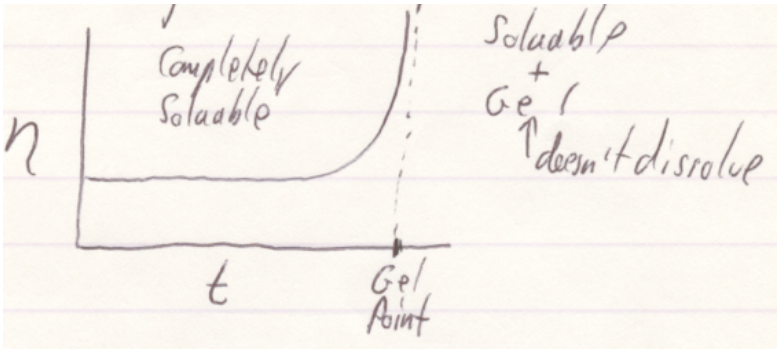
3) a)



b) The Na ion forms a bridge between OH groups in boric acid and in PVA. When only a few Na ions are present a loose network forms that is still a liquid, that is percolation has not occurred, that is, there is no connecting pathway through the entire system. When NaOH is added there are sufficient Na ions to link PVA molecules through boric acid groups to percolate across the gel.

c) As NaOH is added the molecular weight between crosslinks decreases and the gel becomes more rigid. As HCl is added this molecular weight becomes larger and the gel loosens.

d) The viscosity goes to infinity at the gel point. The viscous liquid becomes a solid at the gel point.



e) $p_c = 2/f_{avg}$ define f_{avg}