090304 Quiz 8 Introduction to Polymers (Chemistry)

This week we ran a suspension polymerization to make polystyrene, a solution polymerization to make polyacrylamide and we discussed Ziegler-Natta polymerization to make polypropylene.

1) Suspension polymerization is similar to emulsion polymerization.

a) Describe the importance of water to emulsion and suspension polymerization. Does water play an identical role in these two polymerizations? Is water a solvent?

b) Describe the initiator that we used in suspension polymerization. What condition is needed to initiate this reaction? Why was a different initiator used in the emulsion polymerization?

c) What is divinyl benzene and why is it included in this reaction?

d) What controls the size of the polymer beads (droplet size) that result from suspension polymerization?

e) What was the advantage of emulsion polymerization (over suspension polymerization) that lead to its development by Goodyear Tire and Rubber in the 1920's?

2) Polyacrylamide is soluble in water as is the monomer acrylamide therefore this is a solution polymerization.

a) Use the words *ferric* and *ferrous* to describe the initiator system for this polymerization. Why is this called a *redox system*?

b) When hydrogen peroxide was added to the reaction mixture it turned from a faint bluish green to red (rust color). Later the color seemed to fade. Why did it change color?

c) What temperature was needed to perform this polymerization? Why?

d) How was polymer separated from the viscous reaction mixture after polymerization?

e) Explain the disadvantage of solution polymerization compared to emulsion or suspension polymerization.

3) We looked at Ziegler-Natta polymerization briefly.

a) What two compounds would you mix to make a Ziegler-Natta catalyst system?

b) Why does one of these include a transition metal?

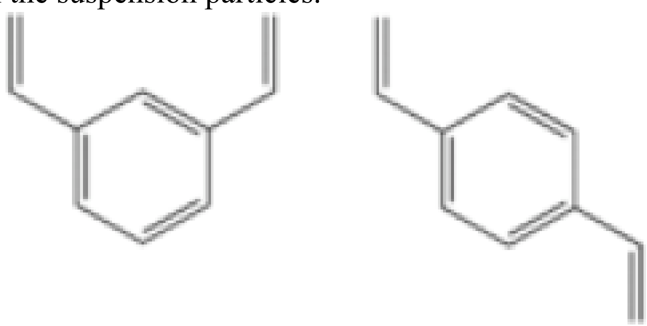
c) Is Ziegler-Natta polymerization carried out in the bulk or in solution? (You may need to guess an answer to this, ethylene monomer is a gas at STP.)

d) Why was there a problem with polymerization of propylene by free radical mechanisms?

e) Why does Ziegler-Natta polymerization result in isotactic polypropylene?

ANSWERS: **090304 Quiz 8 Introduction to Polymers (Chemistry)**

1) a) Bulk polymerization heats up to much so the idea in both emulsion and suspension polymerization is to disperse the bulk polymerization into small droplets where heat transfer is fast to a water phase. In emulsion polymerization the initiator is in the water phase and the water phase also contains reservoirs of monomer that feed the micellar reacting nano-droplets. In suspension polymerization the initiator is in the monomer phase so multiple initiated chains exist in each droplet. The kinetics of polymerization are the same for suspension and for bulk.
b) Benzoyl peroxide was used. It is initiated by heat at about 80C. BP goes into the monomer phase. In emulsion polymerization potassium persulfate was used as the initiator and it was in the water phase so it initiated the micelles only at the interface.
c) Divinyl benzene (below) acts as a tetrafunctional crosslinking agent making a network in the suspension particles.



d) The droplet size is controlled by the rate of mixing, the amount of polymer and the presence of polyvinylalcohol. The size is a balance between coalescence and breakup of the monomer/polymer droplets.
e) Emulsion polymerization allowed the production of sticky polymers such as polybutadiene and polyisoprene rubber.

2) a,b) To deionized water we added ferrous sulfate. Ferrous sulfate is a blue/green crystal so the solution became slightly blue/green. When hydrogen peroxide was added the solution immediately turned redish brown indicating the oxidation of ferrous sulfate, Fe+2 to Ferric sulfate, Fe+3 (or iron (III)). The hydrogen peroxide was reduced to produce two hydroxyl radicals and the iron (II) was oxidized to iron (III), Fe+3, or ferric sulfate. This is called a redox system because hydrogen peroxide is reduced (gains electrons) and iron is oxidized (loses electrons). The rust color fades later due to reduction of Fe+3 by –OH species in the aqueous solution.
c) The reaction occurred at room temperature. Heating was not an issue for this redox catalyst system.
d) Polymer was separated from the viscous polyacrylamide/water solution by pouring the polymer solution in acidified propanol which is a non-solvent for the polymer but is miscible with water. The acid terminates the remaining free radicals. The polymer is then filtered out.
e) The main disadvantage is that copious amounts of solvent are produced. Usually this is a toxic solvent mixture rather than water and propanol. In this reaction 1 gram of polymer was produced using about 300 ml of solvent so a 50 kilogram bag of polymer

would produce 15,000 liters of waste solvent. The polymerization rate is much slower in solution polymerization of high molecular weight polymers.

3) a) $TiCl_3$ and $Al(C_2H_5)_2Cl$ or $TiCl_4$ $Al(C_2H_5)_3$ or VCl_4 and $Al(C_2H_5)_2Cl$.
b) 6 bonding orbitals with only 5 filled leaves one for coordination with a vinyl bond. Transition metals have multiple oxidation states, this is why they are used as catalysts.
c) It is carried out in solution as described by the UBC web page, http://www.eng.uc.edu/~gbeaucag/Classes/IntrotoPolySci/UBCWassellExperiment%209.htm, although they do not give the solvent used. This is either p-xylene or dichlorobenzene at high temperature (135C).
d) Polypropylene can not propogate with a free radical mechanism because the methyl side group can hold a free radical more easily than the vinyl group.
e) The Cossee-Arlman mechanism is highly sterically restricted. The monmer only fits into the catalyst site in one orientation with respect to the growing chain.