CHEM/MATS/CHEN 5221/8221 **Fall 2005**

Problem Set #3

24-26. Hiemenz and Lodge, Chapter 2, Problems 3, 5, 7

27. A polyester is prepared under conditions of stoichiometric balance, but no attempt is made to remove water. Eventually, the reaction comes to equilibrium with equilibrium constant K. If $[COOH]_o$ is the initial concentration of carboxylic acid groups, show that the equilibrium water concentration is

$$[H_2O] = K \frac{[COOH]_o}{DP_n(DP_n - 1)}$$

28. In class we considered the acid (HA) catalyzed reaction of RCOOH and R'OH, and came up with the result that $R_p = k_f K_{eq} [HA] [COOH] [OH]$, where k_f is the rate constant for formation of the active complex $RC(OH)_2OR'H^+$ and K_{eq} is the equilibrium constant for the reaction of HA with RCOOH.

Do a more thorough derivation, considering explicity k_d, the rate constant of dissociation of the complex back to R'OH and $RC(OH)_2^+$, and k_r, the rate constant of dissociation of the complex to ester RCOOR' and byproducts. Use a steady state approximation on $[RC(OH)_2OR'H^+]$. Under what limiting condition is the answer we obtained in class correct?

29. For the Most Probable Distribution it is clear that there is always more i-mer present than (i+1)-mer, at any $0 < p < 1$. However, the absolute amount of an i-mer should go through a maximum with time, as the reaction progresses; there is zero to start, but at late enough stages i-mer will have mostly reacted to contribute to all the larger species. Use the chain rule and any suitable simplifications ($k[A]_o t >> 1$?) to find the degrees of conversion at which the mole fraction and the absolute concentration of i-mer have their maximum in time. Compare to the number average degree of polymerization at the same conversion; does the answer this make sense?

30. For the polymerization of succinic acid and 1,4-butanediol under stoichiometric balance in xylene:

(a) Draw the chemical structures of the reactants, products, and important intermediates for both the strong-acid-catalyzed and self-catalyzed case.

(b) Generate a quantitative plot of DP_n versus time for the self-catalyzed case up to 28,000 s, given $k = 6 \times 10^{-3}$ mol^{-2} L^2 s^{-2} and 3 mol L^{-1} starting concentration of each monomer. How many hours would it take to make a polymer with $DP_n = 300$?

(c) Do the same for the catalyzed case, with $k = 6 \times 10^{-2}$ mol^{-1} L s^{-1} and the same starting concentration. How many hours would it take to make a polymer with $DP_n = 300$?

(d) Qualitatively explain the origin of the different shapes of the curves in the two plots.