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

Problem Set #5

39.-44. Hiemenz and Lodge, Chapter 3, Problems 1, 3, 5, 7 (note A = α), 8, 11.

45. Draw the mechanisms for the following processes in the radical polymerization of styrene in toluene: (a) initiation by cumyl peroxide; (b) propagation; (c) termination by disproportionation; (d) transfer to solvent.

46. Show the mechanisms of addition of a butadiene monomer to a poly(butadienyl) radical, to give each of the three possible geometric isomers.

47. Consider the polymerization of styrene in toluene initiated by di-*t*-butylperoxide for a solution containing 0.04 moles of initiator and 2 moles of monomer per liter. The initial rates of initiation, R_i, and propagation, R_p, are found to be 1.6×10^{-10} $M \cdot s^{-1}$ and 6.4×10^{-7} $M \cdot s^{-1}$, respectively.

    (a) Calculate fk_d and $k_p/k_t^{1/2}$.

    (b) Assuming no chain transfer, calculate the initial kinetic chain length.

    (c) Assuming only disproportionation and under the conditions stated, the transfer constant of styrene, C_M, is 0.85×10^{-4}. How much does this transfer affect the molecular weight of the polymer?

    (d) The molecular weight of this polymer is too high. The desired molecular weight of this polymer is 40,000 $g \cdot mol^{-1}$. How much CCl_4 (in g/L) should be added to the reaction medium to attain the desired molecular weight? C_T of CCl_4 is 9×10^{-3}.

    (e) Under the conditions stated, the polymerization is too slow. What is the initial rate of polymerization if the temperature is raised to 100 °C?

    (f) Calculate the conversion attained after the reaction has gone for 5 h at 100 °C. Assume volume expansion doesn't change concentration significantly and that the initiator concentration is constant through the entire reaction.

The following problems are adapted from Odian, Chapter 3:

48. Using ^{14}C-labeled AIBN as initiator, a sample of styrene is polymerized to $N_n = 1.52 \times 10^4$. The AIBN has an activity of 9.81×10^7 counts min^{-1} mol^{-1} in a scintillation counter. If 3.22 g of the polystyrene has an activity of 203 counts min^{-1}, what is the mode of termination?

49. Poly(vinyl acetate) with N_n = 100,000 is hydrolyzed to poly(vinyl alcohol). Subsequent oxidation of the later with periodic acid to cleave all 1,2 diol linkages yields a poly(vinyl alcohol) with N_n = 200. Calculate the percentages of head-to-head and head-to-tail linkages in the original poly(vinyl acetate).

50. A polymer produced by radical polymerization in the absence of transfer reactions is shown to contain 1.4 initiator fragments per polymer. Calculate the relative amounts of termination by disproportionation and combination.