Chemistry/MatSci 5223W Wednesday, January 18

Assignment 2
Due: *In Lab,* Thursday, January 19/Friday, January 20

1. (You should read the instructions for Lab 1 before attempting this assignment.) In Lab 1, you will be polymerizing styrene via free-radical polymerization, with the intention of determining the rate constant for polymerization (k_p) under your bulk polymerization conditions. During the initial stages of free-radical polymerization, the rate of polymerization (R_p) can be calculated by the equation

$$R_p = -\frac{d[\mathrm{M}]}{dt} = k_p\left(\frac{k_d f[\mathrm{I}]_0}{k_t}\right)^{1/2}[\mathrm{M}]_0 .$$

Given the rate constants, initiator efficiencies in the Lab 1 handout, a "molarity" for styrene dictated by ρ = 0.91 g/mL, and the quantities of initiators you plan to use, calculate how long you will have to run each styrene polymerization to achieve 10% conversion. (I.e., if $\Delta[M] = 0.1[M]_o$, then what is Δt?) Though the purpose of this lab is to determine k_p(styrene), you will have to assume a k_p to perform this calculation; you can find k_p values for of a wide range of monomers in the online Wiley Database of Polymer Properties (http://www.lib.umn.edu/cgi-bin/wil.cgi?res=dpp), which is identical to the bound *Polymer Handbook* (J. Brandrup, E. H. Immergut, and E. A. Grulke; 4th ed.; Wiley, New York, 1999; *Walter 2nd floor reference, QD388 .P65 1999*). Pick a value for styrene closest to your polymerization conditions (no solvent, 70 °C).

Δt(0.25 g peroxide): Δt(0.40 g peroxide):

Δt(0.55 g peroxide): Δt(0.70 g peroxide):

2. In Lab 1, you will be isolating your polystyrene from unreacted styrene monomer via precipitation, by adding a “nonsolvent” for polystyrene. This is an extremely common first step in obtaining pure polymer material from a polymerization mixture. But how do you know what solvents are “good” or “bad” for a particular polymer? We will be discussing solubility parameter calculations briefly in lecture, but a more common approach is to consult a listing of polymer-solvent compatibilities. One source for this information is James Mark’s *Polymer Data Handbook* (Oxford University Press, New York, 1999; *Available online, http://www.oup-usa.org/pdh/; login “pdh_user”, password “bigchain”.*)

   Below, list three “good” organic solvents for polystyrene that could be used to dissolve the polymer effectively, and list three “bad” organic solvents for polystyrene that could be used to precipitate the polymer from solution.