Lab 1
Free-Radical Bulk Polymerization

Introduction

Free-radical polymerization is used to synthesize a large fraction of the world's polymer output. Free-radical polymerized polystyrene, for example, has many familiar end uses (in items such as foam cups, plastic cutlery, and CD jewel cases). In this laboratory, you will analyze the free radical polymerization kinetics of styrene. In addition, you will prepare simple polymers from another monomer, butyl methacrylate. All of these polymerizations will be initiated using benzoyl peroxide as the radical initiator. In this experiment, you will evaluate the effect that initiator concentration has on both the molecular weight and rate for the polymerization of styrene. The chemical structure of the initiator and monomers are shown in Figure 1-1.
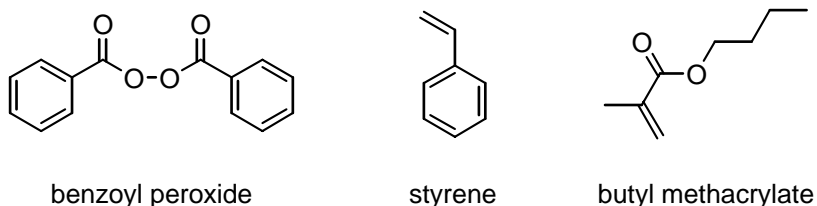

benzoyl peroxide   styrene   butyl methacrylate

Figure 1-1

Benzoyl peroxide slowly decomposes at temperatures above 50 ºC to give benzoyl (and other) radicals. The radicals will initiate polymerization of vinyl monomers such as styrene and alkyl acrylates. Free radical polymerizations proceed by a chain growth mechanism. Three fundamental processes are necessary to describe the polymerization mechanism: initiation, propagation, and termination.

Initiation begins with the thermal decomposition of benzoyl peroxide to give two benzoyl radicals. These radicals can add to the double bond of a vinyl monomer to generate another propagating radical. Assuming that the decomposition of the initiator is the rate limiting process, the overall rate of initiation can be expressed by equation 1.1,

$$(1.1) \qquad R_i = \frac{d[M_1\bullet]}{dt} = 2fk_d[I]$$

where R_i is the rate of formation of "primary" propagating radicals $M_1\bullet$ (the subscript refers to the molecule formed after the addition of one monomer: $M_1\bullet = I\text{-}M\bullet$), f is the initiator efficiency (the fraction of initiator that decomposes to give radicals that create polymer chains), and k_d is the first-order rate constant for the decomposition of initiator I.

Propagation is simply the addition of the more monomer, M, to the primary radical, $M_1\bullet$, to give the chain extended species $M_2\bullet$, or more generally for any number of additions, $M\bullet$. If the monomer consumed in the initiation step is ignored, the overall rate of polymerization is given by

(1.2) $$R_p = -\frac{d[M]}{dt} = k_p[M\bullet][M]$$

where k_p is the second-order rate constant for propagation.

Termination occurs either by coupling or disproportionation of the two $M\bullet$ species. Kinetically, these two processes are indistinguishable. Therefore, the rate of disappearance of $M\bullet$ can be expressed by the equation 1.3,

(1.3) $$R_t = -\frac{d[M\bullet]}{dt} = 2k_t[M\bullet]^2$$

where k_t is the second order rate constant for termination and is the simple sum of the rate constant termination by coupling and the rate constant for termination by disproportionation. The factor of 2 is generally accepted in the polymerization kinetics literature for reactions destroying radicals in pairs (though not all sources use this convention). The mode of termination is highly dependent on monomer structure. For the polymerization of styrene at 70 °C, for example, termination occurs by coupling alone. For methylmethacrylate, on the other hand, the rate constant for disproportionation is 7 times larger than the rate constant for termination by coupling.

The steady-state approximation maintains that the rates of initation and termination are equal; thus the rate of propagation (polymerization) can be expressed by equation 1.4.

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

For low conversions of monomer (<10%) we can safely assume that [M] and [I] are constant, and therefore the initial rate of polymerization is given by eq. 1.5,

(1.5) $$R_p = -\frac{\Delta[M]}{\Delta t} = k_p[M]_0[I]_0^{1/2}\left(\frac{k_d f}{k_t}\right)^{1/2}$$

where $[M]_o$ and $[I]_o$ are the initial concentration of monomer and initiator, respectively. In this experiment, you will vary $[I]_o$ and observe the effect on the amount of polymer formed over time. Assuming that all consumed monomer becomes polymer, the amount of polymer formed can be used to determine the change in monomer concentration ($\Delta[M]$) over a defined time interval (Δt).

The number average degree of polymerization X_n for polymers made by free radical polymerization can also be predicted from the kinetics. The kinetic chain length ν is defined as the average number of monomer units added to a chain per effective radical. Under steady state conditions, this is simply the

ratio of rate of propagation to the rate of termination (or initation, since the two are equated). Using the expressions given above, the kinetic chain length (at low conversion) can be given by:

$$(1.6) \qquad \nu = \frac{k_p^{\ 2}[M]^2}{2k_t R_p}$$

Chain termination events such as chain transfer will effect the kinetic chain length. If termination is solely by coupling, $X_n = 2\nu$. If termination is solely by disproportionation, $X_n = \nu$.

Table 1-1 has constants for the free radical polymerization of styrene at 70 °C taken from Odian's *Principles of Polymerization*. For the decomposition of benzoyl peroxide at 70 °C, $k_d = 1.0 \times 10^{-5}$ sec^{-1} and $f = 0.8$.

Table 1-1

| monomer	k_p(M^{-1} sec^{-1})	k_t(M^{-1} sec^{-1})	C_m	C_I	ρ (g/cm^3)
styrene	??	6×10^7	4.5×10^5	1.8×10^3	0.91

Experimental

Lab Check-In (Jan 19/20)

- Choose a lab partner. Your lab pair will occupy an entire bench side; find a free one.

- On your chosen bench, there should be some lab drawer checkout sheets. Each student should check out his/her own drawer. Check the listed contents of your drawer, and if anything is missing, please have one of the TA's sign off on the missing items and report them to the supply window. The check-in sheets also have a page on safety. Please read and obey these safety rules. When you are checked in, hand your sheet to the lab TAs.

Preparation of linear polymers by radical polymerization (Jan 19/20)

The goal of this experiment is to become familiar with manipulation of monomers and polymers.

- Pour approximately 5 mL of styrene into a 6" test tube, and add 0.05 g solid benzoyl peroxide. Swirl to dissolve. Use the styrene that has been provided by the TA's rather than from a reagent bottle; reagent grade monomer usually contains either *tert*-butylcatechol or monomethyl ether hydroquinone (MEHQ) as a self-initiated polymerization inhibitor, and these have been removed by the TA's.

OH
OH

OH

OCH₃
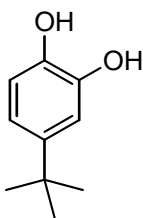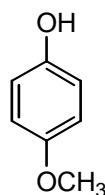
tert-butylcatechol   MEHQ

- In a separate test tube, repeat with 5 mL of butyl methacrylate.

- Spray 2 aluminum foil pans for 2-3 seconds with silicone mold release and allow to air dry for 10 min. Label the bottom of the pans with your name, the date and the monomer being polymerized.

- Carefully pour (with the aid of your stirring rod) the monomer and the monomer-initiator mixture into the aluminum pans. Cover the aluminum pans with aluminum foil. Make sure the foil is just larger than the pan to permit crimping of the edge, but do not fold the edges so that they are on the bottom of the pan after crimping.

- Place the pans in the room-pressure oven (not the vacuum oven), and heat at 70 °C for 2-3 days. The TA's will turn off the oven for you over the weekend.

- *Next week:* Remove your polymerized samples from their aluminum pans. How would you describe the samples? How do they compare to each other, and to the polymers prepared by other groups? Why might your samples have the physical properties they do?

- Save your samples. You will be using them in later labs.

Polymerization of styrene as a function of initiator concentration (Jan 19/20)

The goal of this experiment is to test the dependence of R_p on $[I]^{1/2}$, as per equation 1.5.

- Place 5 mL of styrene in a 6" test tube and add 0.10 g benzoyl peroxide. Swirl to dissolve. In four separate tubes repeat using 0.25 g, 0.40 g, 0.55 g, and 0.70 g of benzoyl peroxide.

- Loosely cork the test tubes, label them, and carefully place them in the 70 °C hot water bath. Make sure the test tube is secure in the water bath. Record the reaction time (the time you put the test tube into the water bath being $t = 0$) and temperature. Check the polymerization solution about every five minutes by swirling. Note any viscosity change. The liquid should start to become viscous at around 5-10% polymerization; you should have a good idea of how long to wait based on the calculations you made in the pre-lab assignment.

- As soon as it becomes viscous, remove the tube from the water bath and record the reaction time and temperature. Pour the solution into a 100 mL beaker, and add 50 mL of hexane to the beaker in 10 mL aliquots to precipitate the polymer as viscous goo. (You may find that cooling the beaker in an ice water bath helps precipitate the polymer.) After each hexane addition, try to work the precipitated polymer into a glob on the end of the spatula. At the end, once the glob is hardened a bit, decant the hexanes. If the polymer in your beaker looks dry of hexanes, dissolve the isolated polymer in as little methyl ethyl ketone as necessary to dissolve the material (a few drops), and reprecipitate with

hexanes. Be sure precipitation is complete. It can be difficult to recover all of the polymer, but do your best.

- Tare some aluminum foil pans, put each of your isolated polymer samples into its own pan, and place your samples in the vacuum oven for two days. (The TA's will also turn off this oven over the weekend.) Make sure each pan is marked with your name, the initiator amount used, and the tare value.

Polymer isolation (Jan 26/27)

- Determine the mass yield of your samples. If the yield is greater than 20%, or you isolate less than 150 mg of polymer (about 3%), you should disregard data from that polymerization run.

There is no lab writeup due for this lab; you will be evaluating your data in an Assignment.