Kinetics of Free Radical Chain Polymerization-3

Radical chain polymerization is a chain reaction consisting of a sequence of three steps—initiation, propagation, and, termination. The initiation step involves two reactions. The first is the production of free radicals by homolytic dissociation of an initiator species I to yield a pair of radicals R

$$I \xrightarrow{k_d} 2R\cdot$$

where kd is the rate constant for the catalyst dissociation. The second part of the initiation involves the addition of this radical to the first monomer molecule to produce radical M1

$$R\cdot + M \xrightarrow{k_i} M_1\cdot$$

Propagation consists of the growth of Mn by the successive additions of large numbers of monomer molecules. Each addition creates a new radical that has the same identity.

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot$$

Monomer disappears by the initiation reaction as well as by the propagation. The rate of monomer disappearance, also called the rate of polymerization, is given by

$$-\frac{d[M]}{dt} = R_i + R_p$$

The rate of propagation, and therefore the rate of polymerization, is the sum of many individual propagation steps. Since the rate constants for all the propagation steps are the same, one can express the polymerization rate by

$$-\frac{d[M]}{dt} = R_p = k_p[M\cdot][M]$$

In order to do this, one can use steady-state assumption: the concentration of radicals increases initially, but almost instantaneously reaches a constant, steady-state value. That means the rate of change of the concentration of radicals is zero during the course of the polymerization. Therefore, the rates of initiation Ri and termination Rt of radicals are equal

$$R_t = R_i = 2k_t[M\cdot]^2$$

$$[M\cdot] = \left(\frac{R_i}{2k_t}\right)^{1/2}$$

These equations substitute from above equations yields the rate of polymerization equation.

$$R_p = k_p[M](R_i/2k_t)^{1/2}$$

$$-\frac{d[M]}{dt} = R_p = k_p[M\cdot][M]$$

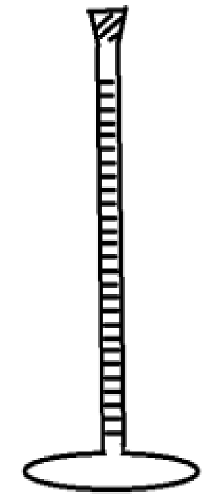
where $[M]$ is the monomer concentration and $[M\cdot]$ is the total concentration of all chain radicals, that is, all radicals of size $M_1\cdot$ and larger.

$$R_t = R_i = 2k_t[M\cdot]^2$$

$$[M\cdot] = \left(\frac{R_i}{2k_t}\right)^{1/2}$$

Dilatometric method

Polymerization kinetics are tracked by using dilatometry. In this experiment the rate of polymerization will be measured by the use of dilatometry. Dilatometry is not useful for most step polymerizations where there is a small molecule by-product that results in no appreciable volume change upon polymerization.



Dilatometers are placed in precisely temperature controlled water bath.

Calibration of dilatometer: The volume of dilatometer (Vd) is determined by the difference of weight of empty dilatometer and dilatometer filled with distilled water upto top level of capillary.

Calculate and compare the gravimetric conversion with the one you assume based on reaction mixture volume decrease. Then wash the dilatometer thoroughly (repeatedly) by toluene followed by acetone and drying as during its calibration. All glassware and syringes that were in contact with styrene should be washed finally by acetone and dried. Data evaluation:

The data are evaluated from the dependence of ln $(V_0-V_f)/(V_t-V_f)$ on time (in s). where Vo is initial volume of feed, Vf-final volume after polymerization at 100% conversion and Vtvolume at given time t. Differences in volumes can be expressed by difference of capillary level L_0, L_f and L_t that are measured in the experiment.

$$\Delta V_{\text{total fract}} = \frac{\left(\frac{W_1}{d_1}\right) - \left(\frac{W_1}{d_2}\right)}{\left(\frac{W_1}{d_1}\right)}$$

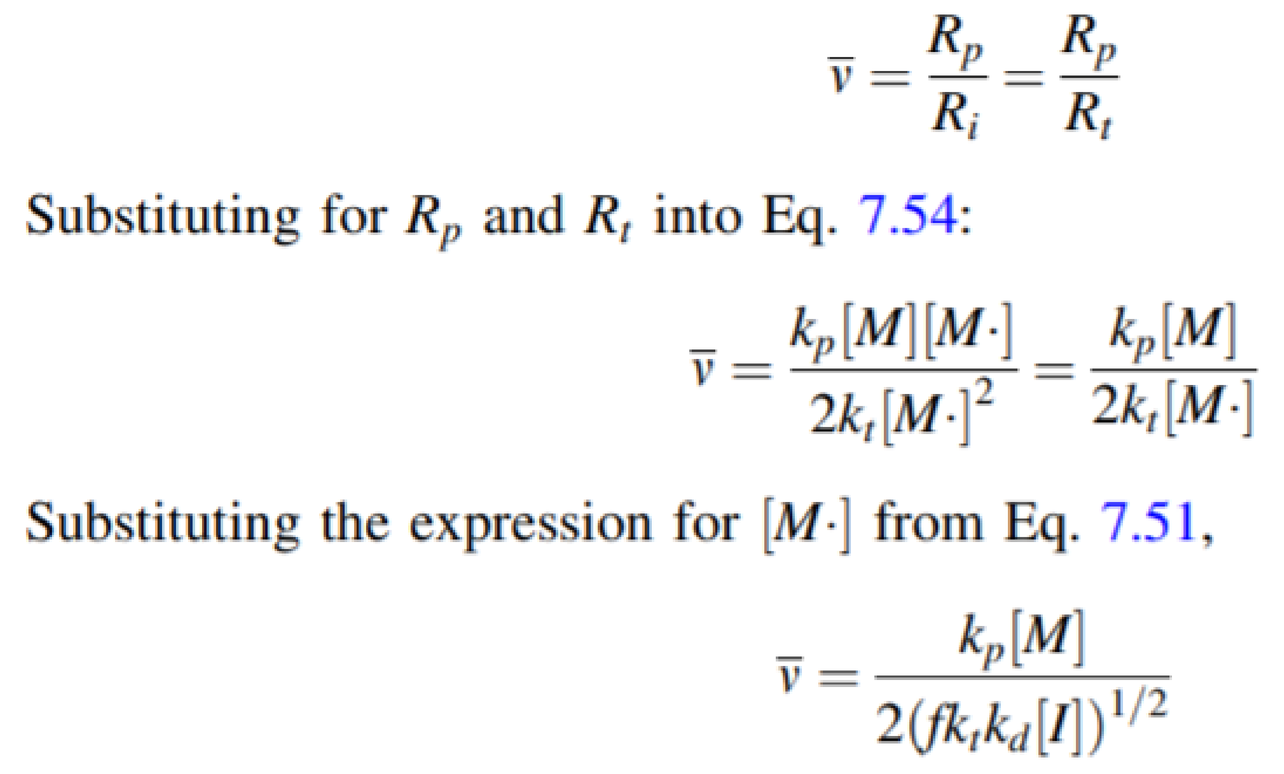
$$\frac{\Delta[M]}{\Delta t} = \frac{\left(\frac{\Delta V}{\Delta t}\right) \text{ x } \left(\frac{[M]}{V_0}\right)}{\left(\frac{d_2 - d_1}{d_2}\right)} = \frac{[M]d_2}{V_0(d_2 - d_1)} \; \frac{\Delta V}{\Delta t}$$

$$\Delta V_{\text{total fract}} = \frac{d_2 - d_1}{d_2}$$

Average Kinetic Chain Length

Another important parameter related to polymerization rate is the average kinetic chain length, m, which is defined as the average number of monomer units polymerized per chain initiated, which is equal to the rate of polymerization per rate of initiation. Since Ri = Rt under steady-state conditions,

Kinetic chain length is related to a variety of rate and concentration parameters. It will decrease as both of initiator concentration and initiator efficiency increase.



$$\bar{\nu} = \frac{R_p}{R_i} = \frac{R_p}{R_t}$$

Substituting for R_p and R_t into Eq. 7.54:

$$\bar{\nu} = \frac{k_p[M][M\cdot]}{2k_t[M\cdot]^2} = \frac{k_p[M]}{2k_t[M\cdot]}$$

Substituting the expression for $[M\cdot]$ from Eq. 7.51,

$$\bar{\nu} = \frac{k_p[M]}{2(fk_tk_d[I])^{1/2}}$$