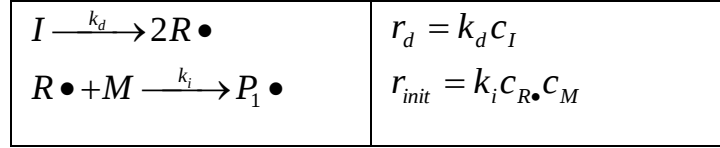
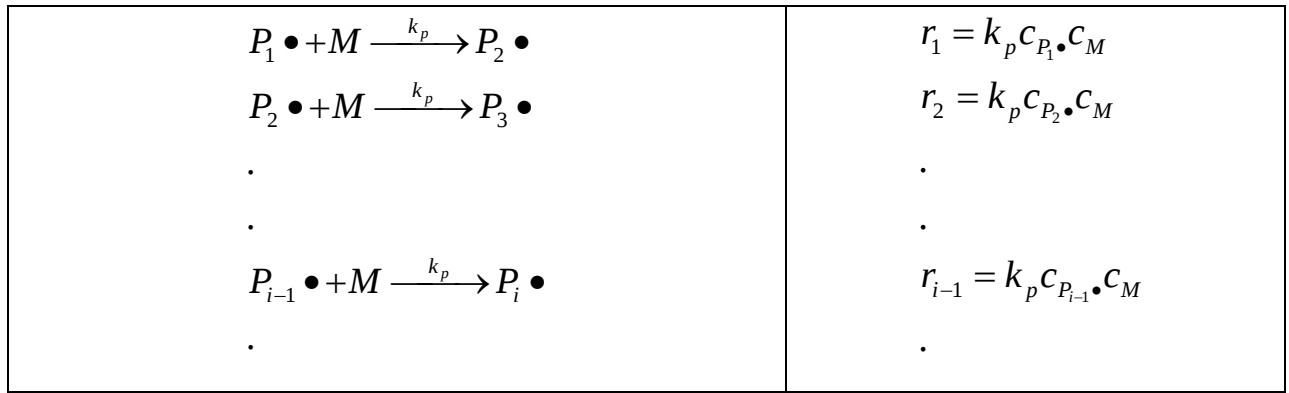


Chains (i.e., addition) polymerization requires an initiator (I) and proceeds by three steps mechanism:

1. *Initialization*



2. *Propagation*



3.

4. *Termination*



Using the SSH (Steady State Hypothesis) for the initiator free radical $R\bullet$, we have

$$\begin{aligned}\frac{dc_{R\bullet}}{dt} &= 2r_d - r_{init} = 0 \\ 2k_d c_I &= k_i c_{R\bullet} c_M \\ c_{R\bullet} &= \frac{2k_d c_I}{k_i c_M}\end{aligned}$$

Balance of the first active polymer radical $P_1\bullet$ (the radical $P_1\bullet$ undergoes the termination sequence by addition $P_1\bullet + P_j\bullet \xrightarrow{k_t} P_{1+j}, j=1, 2, \dots, \infty$) can be written as

$$R_{P_1\bullet} = r_{init} - r_1 - r_{t,1} = k_i c_{R\bullet} c_M - k_p c_{P_1\bullet} c_M - k_t c_{P_1\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} = 0$$

Thus the concentration of $P_1\bullet$ is given by

$$c_{P_1\bullet} = \frac{k_i c_{R\bullet} c_M}{k_p c_M + k_t \sum_{j=1}^{\infty} c_{P_j\bullet}} = \frac{k_i \frac{2k_d c_I}{k_i c_M} c_M}{k_p c_M + k_t \sum_{j=1}^{\infty} c_{P_j\bullet}} = \frac{2k_d c_I}{k_p c_M + k_t \sum_{j=1}^{\infty} c_{P_j\bullet}}$$

Balance of active polymer radical $P_k\bullet, k = 2, 3, \dots, \infty$

$$R_{P_k\bullet} = k_p c_{P_{k-1}\bullet} c_M - k_p c_{P_k\bullet} c_M - k_t c_{P_k\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} = 0$$

By summing the last equation from $k=2$ to $k=\infty$, we obtain

$$\begin{aligned} k_p c_M \sum_{k=2}^{\infty} c_{P_{k-1}\bullet} - k_p c_M \sum_{k=2}^{\infty} c_{P_k\bullet} - k_t \sum_{k=2}^{\infty} c_{P_k\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} &= \\ = k_p c_M \sum_{k=1}^{\infty} c_{P_k\bullet} - k_p c_M \sum_{k=1}^{\infty} c_{P_k\bullet} + k_p c_M c_{P_1\bullet} - k_t \sum_{k=1}^{\infty} c_{P_k\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} + k_t c_{P_1\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} &= 0 \end{aligned}$$

Taking into account the balance equation for $P_1\bullet$

$$k_i c_{R\bullet} c_M - k_p c_{P_1\bullet} c_M - k_t c_{P_1\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} = 0$$

and using expression for $c_{R\bullet} = \frac{2k_d c_I}{k_i c_M}$ we have

$$k_t \left(\sum_{j=1}^{\infty} c_{P_j\bullet} \right)^2 = k_i c_{R\bullet} c_M \Rightarrow \sum_{j=1}^{\infty} c_{P_j\bullet} = \sqrt{\frac{k_i c_{R\bullet} c_M}{k_t}} = \sqrt{\frac{2k_d c_I}{k_t}}$$

The equation for concentration of $P_1\bullet$ becomes

$$c_{P_1\bullet} = \frac{2k_d c_I}{k_p c_M + k_t \sum_{j=1}^{\infty} c_{P_j\bullet}} = \frac{2k_d c_I}{k_p c_M + \sqrt{2k_t k_d c_I}}$$

Now the equation for the rate of monomer consumption is (monomer reacts in initialization and propagation steps)

$$\begin{aligned} R_M &= -r_{init} - k_p c_M \sum_{j=1}^{\infty} c_{P_j\bullet} = - \left(k_i c_{R\bullet} c_M + k_p c_M \sum_{j=1}^{\infty} c_{P_j\bullet} \right) = \\ &= - \left(2k_d c_I + k_p \sqrt{\frac{2k_d c_I}{k_t}} c_M \right) \cong -k_p \sqrt{\frac{2k_d c_I}{k_t}} c_M \end{aligned}$$

The equations for the rate of polymer P_n production (P_n denotes the macromolecule having n monomeric units) is given by

$$R_{P_n} = \frac{1}{2} \sum_{k=1}^{n-1} k_t c_{P_{n-k}} \cdot c_{P_k} \cdot$$

From balance equation for active polymer radical $P_k \cdot$ we have

$$c_{P_k \cdot} = \frac{k_p c_{P_{k-1}} \cdot c_M}{k_p c_M + k_t \sum_{j=1}^{\infty} c_{P_j} \cdot} = \frac{k_p c_{P_{k-1}} \cdot c_M}{k_p c_M + \sqrt{2k_t k_d c_I}}$$

Last equation represents a recurrence relation which can be used repetitively

$$\begin{aligned} c_{P_k \cdot} &= \frac{k_p c_{P_{k-1}} \cdot c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} = \frac{k_p \left(\frac{k_p c_{P_{k-2}} \cdot c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right) c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} = c_{P_{k-2}} \cdot \left(\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right)^2 = \dots = \\ &= c_{P_1} \cdot \left(\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right)^{k-1} \end{aligned}$$

Substituting for $c_{P_1} \cdot$ we get

$$c_{P_k \cdot} = \frac{2k_d c_I}{k_p c_M + \sqrt{2k_t k_d c_I}} \left(\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right)^{k-1}$$

Now the rate of polymer P_n production is

$$\begin{aligned} R_{P_n} &= \frac{1}{2} \sum_{k=1}^{n-1} k_t c_{P_{n-k}} \cdot c_{P_k} \cdot = \\ &= \frac{k_t}{2} \sum_{k=1}^{n-1} \frac{2k_d c_I}{k_p c_M + \sqrt{2k_t k_d c_I}} \left(\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right)^{n-k-1} \frac{2k_d c_I}{k_p c_M + \sqrt{2k_t k_d c_I}} \left(\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right)^{k-1} = \\ &= \frac{(n-1)k_t}{2} \left(\frac{2k_d c_I}{k_p c_M + \sqrt{2k_t k_d c_I}} \right)^2 \left(\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right)^{n-2} \end{aligned}$$

Modeling an Isothermic Batch Polymerization Reactor ($V_R \sim \text{const.}$)

We determine the concentration of initiator (I), monomer (M - styrene) and polymer (P_n , $n = 5, 10, 20, 50, 100, 500$) as a function of time in an isothermic constant volume batch reactor. A balance on the initiator, the monomer and the polymers are

$$\frac{dc_I}{dt} = -k_d c_I$$

$$\frac{dc_M}{dt} = -k_p \sqrt{\frac{2k_d c_I}{k_t}} c_M$$

$$\frac{dc_{P_n}}{dt} = \frac{(n-1)k_t}{2} \left(\frac{2k_d c_I}{k_p c_M + \sqrt{2k_t k_d c_I}} \right)^2 \left(\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right)^{n-2}$$

Initial conditions

$$t = 0$$

$$c_I = 10^{-2} \text{ mol/dm}^3$$

$$c_M = 3 \text{ mol/dm}^3$$

$$c_{P_n} = 0$$

Data (80 °C)

$k_d \text{ [s}^{-1}\text{]}$	1.45×10^{-5}	$k_t \text{ [dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\text{]}$	1.2×10^6
$k_p \text{ [dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}\text{]}$	4.4×10^2		