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

1. ***Inicialization***

$I \xrightarrow{k_d} 2R\bullet$ $R\bullet + M \xrightarrow{k_i} P_1\bullet$	$r_d = k_d c_I$ $r_{init} = k_i c_{R\bullet} c_M$

2. *Propagation*

$P_1\bullet + M \xrightarrow{k_p} P_2\bullet$	$r_1 = k_p c_{P_1\bullet} c_M$
$P_2\bullet + M \xrightarrow{k_p} P_3\bullet$	$r_2 = k_p c_{P_2\bullet} c_M$
.	.
.	.
$P_{i-1}\bullet + M \xrightarrow{k_p} P_i\bullet$	$r_{i-1} = k_p c_{P_{i-1}\bullet} c_M$
.	.

3.

4. *Termination*

$P_k\bullet + P_l\bullet \xrightarrow{k_t} P_{k+l}$	$r_{t,k+l} = k_t c_{P_k\bullet} c_{P_l\bullet}$

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

$$\frac{dc_{R\bullet}}{dt} = 2r_d - r_{init} = 0$$

$$2k_d c_I = k_i c_{R\bullet} c_M$$

$$c_{R\bullet} = \frac{2k_d c_I}{k_i c_M}$$

Balance of the first active polymer radical $P_1\bullet$ (the radical $P_1\bullet$ undergoes the termination sequence by addition $P_1\bullet + P_j\bullet \xrightarrow{k_t} P_{1+j},\ j = 1, 2, ...\infty$) 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 $P_k \bullet, k = 2, 3, \ldots\infty$

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

By summing the last equation from k=2 to k=∞, we obtain

$$k_p c_M \sum_{k=2}^{\infty} c_{P_{k-1}\bullet} - k_p c_M \sum_{k=2}^{\infty} c_{P_k\bullet} - k_t \sum_{k=2}^{\infty} c_{P_k\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} =$$

$$= k_p c_M \sum_{k=1}^{\infty} c_{P_k\bullet} - k_p c_M \sum_{k=1}^{\infty} c_{P_k\bullet} + k_p c_M c_{P_1\bullet} - k_t \sum_{k=1}^{\infty} c_{P_k\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} + k_t c_{P_1\bullet} \sum_{j=1}^{\infty} c_{P_j\bullet} = 0$$

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)

$$R_M = -r_{init} - k_p c_M \sum_{j=1}^{\infty} c_{P_j\bullet} = -\left(k_i c_{R\bullet} c_M + k_p c_M \sum_{j=1}^{\infty} c_{P_j\bullet} \right) =$$

$$= -\left(2k_d c_I + k_p \sqrt{\frac{2k_d c_I}{k_t}} c_M \right) \cong -k_p \sqrt{\frac{2k_d c_I}{k_t}} c_M$$

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

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

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

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

Last equation represents a recurrence relation which can be used repeatitively

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

$$= c_{P_1\bullet} \left(\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right)^{k-1}$$

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

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

Now the rate of polymer P_n production is

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

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

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

Modeling an Isothermic Batch Polymerization Reactor (V_R~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

$$\frac{\mathrm{d}c_I}{\mathrm{d}t} = -k_d c_I$$

$$\frac{\mathrm{d}c_M}{\mathrm{d}t} = -k_p \sqrt{\frac{2k_d c_I}{k_t}} c_M$$

$$\frac{\mathrm{d}c_{P_n}}{\mathrm{d}t} = \frac{(n-1)k_t}{2} \left(\frac{2k_d c_I}{k_p c_M + \sqrt{2k_t k_d c_I}} \right)^2 \left(\frac{k_p c_M}{k_p c_M + \sqrt{2k_t k_d c_I}} \right)^{n-2}$$

Initial conditions

$t = 0$

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

$c_M = 3$ mol/dm^3

$c_{P_n} = 0$

Data (80 ^{o}C)

k_d [s^{-1}]	**1.45x10^{-5}**	**k_t [$dm^3.mol^{-1}.s^{-1}$]**	**1.2x10^6**
k_p [$dm^3.mol^{-1}.s^{-1}$]	**4.4x10^2**		