Model for The Bulk free radical polymerisation of Methyl Methacrylate.

- Semi-batch reactor.
- Non-Isothermal conditions
- Bulk free radical polymerisation scheme

Nomenclature

A_{i1} , A_{i2} : empirical parameters (i =1-4)

B_{i1}, B_{i2} : empirical parameters (i =1-4)

C_m , C_R $\left[\frac{mol}{m^3}\right]$: concentration of monomer and free radical

D : diffusivity of monomer in the monomer-polymer mixture

D_n : dead polymer molecule having n repeated units

f : initiator efficiency in the limiting case of zero diffusional resistance

I: initiator

$[I]_0$ $\left(\frac{mol}{m^3}\right)$: concentration of initiator at t=0

k_d $[s^{-1}]$: rate constant of for initiation in the presence of gel and glass effects

k_p , k_t , k_{tm} $\left[\frac{m^3}{mol\times s}\right]$: rate constants for propagation, termination and chain transfer to monomer in presence of gel and glass effects

k_{tc} , k_{td} $\left[\frac{m^3}{mol\times s}\right]$: rate constants for termination by combination and disproportion in presence of gel effects

$k_{td}^{0}, k_{p}^{0}, k_{tm}^{0}$ $\left[\frac{m^3}{mol\times s}\right]$: in absence of gel effects

$k_{td,o}, k_{po}^{0}, k_{tm,o}^{0}$ $\left[s^{-1}\ or\ \frac{m^3}{mol\times s}\right]$: frequency factors for the intrinsic rate constants

l_{chr} : length of chromosome

l_{str} : length of substring

$M\ [mol]$: monomer, moles of monomer in the liquid phase

M_w $\left[\frac{Kg}{Kmol}\right]$: weight average molecular weight [$\equiv \frac{(MW_m)(\lambda_2+\mu_2)}{\lambda_1+\mu_1}$

MW_m $\left[\frac{kg}{Kmol}\right]$: molecular weight of the monomer

n : number of parameters in the Simple Genetic Algorithm (SGA)

N_p : population size

P_c: probability of crossover

P_m : probability of mutation

P_n : growing polymer radical having n repeat units

r_m : radius of reaction sphere

R : primary radical

R_{li}, R_{lm} $\left[\frac{mol}{s}\right]$: rate of continuous addition of initiator and monomer

R_{vm} $\left[\frac{mol}{s}\right]$: rate of evaporation of monomer

$T(t)\ [K\ or\ ℃]$: temperature of the reaction mixture at time t

t : time (min)

$V_l\ [m^3]$: volume of the liquid at time t

$x_m(t)$: monomer conversion (molar) at time t $[\equiv 1-\left(\frac{M}{\varsigma_{m1}}\right)]$

α : fraction of monomer molecule undergoing chain transfer

$\dot{\gamma}\ [s^{-1}]$: shear rate

$\varsigma\ ,\varsigma_{m1}$: net monomer added to the reactor

$\eta\ [pa\ s]$: viscosity of the reaction mass

$\lambda_k\ [mol]$: k^{th} (k= 0, 1, 2…) moment of the live (P_n) polymer radicals $[\equiv \sum_{n=1}^{\infty} n^k P_n\ ]$

$\mu_k\ \ [mol]$: k^{th} $(k = 0,1,2..)$moment of the dead (D_n) polymer chains $[\equiv \sum_{n=1}^{\infty} n^k D_n]$

$\mu_n\ \ [mol]$: number average of chain length at time t $[\equiv \frac{\lambda_1+\mu_1}{\lambda_0+\mu_0}]$

$\rho_m\ ,\rho_p\ \ \left[\frac{kg}{m^3}\right]$: density of pure (liquid) monomer and polymer at temperature T

$\phi_m\ ,\phi_p$: volume fractions of monomer and polymer in liquid at time t

Model Equations

1. $\frac{\mathrm{dI}}{\mathrm{dt}} = -\mathrm{k_d I} + \mathrm{R_{li}(t)}$

2. $\frac{\mathrm{dM}}{\mathrm{dt}} = -(\mathrm{k_p} + \mathrm{k_{tm}})\left(\frac{\lambda_0 \mathrm{M}}{\mathrm{V_l}}\right) + \mathrm{R_{lm}(t)} - \mathrm{R_{vm}(t)} - \mathrm{k_i}\left(\frac{\mathrm{RM}}{\mathrm{V_l}}\right)$

3. $\frac{dR}{dt} = 2fk_dI - k_i(\frac{RM}{V_l})$

4. $\frac{d\lambda_0}{dt} = k_i\left(\frac{RM}{V_l}\right) - k_t\left(\frac{\lambda_o^2}{V_l}\right)$

5. $\frac{d\lambda_1}{dt} = k_i\left(\frac{RM}{V_l}\right) + k_pM\left(\frac{\lambda_0}{V_l}\right) - k_t\left(\frac{\lambda_0\lambda_1}{V_l}\right) + k_{tm}M\left(\frac{\lambda_o-\lambda_1}{V_l}\right)$

6. $\frac{d\lambda_2}{dt} = k_i\left(\frac{RM}{V_l}\right) + k_pM\left(\frac{\lambda_0+2\lambda_1}{V_l}\right) - k_t\left(\frac{\lambda_0\lambda_2}{V_l}\right) + k_{tm}M\left(\frac{\lambda_o-\lambda_2}{V_1}\right)$

7. $\frac{d\mu_0}{dt} = k_{tm}M\left(\frac{\lambda_0}{V_l}\right) + \left(k_{td} + \frac{1}{2}k_{tc}\right)\left(\frac{\lambda_0^2}{V_l}\right)$

8. $\frac{d\mu_1}{dt} = k_{tm}M\left(\frac{\lambda_1}{V_l}\right) + k_t\left(\frac{\lambda_o\lambda_1}{V_l}\right)$

9. $\frac{d\mu_2}{dt} = k_{tm}M\left(\frac{\lambda_2}{V_l}\right) + k_t\left(\frac{\lambda_0\lambda_2}{V_l}\right) + k_{tc}\left(\frac{\lambda_1^2}{V_l}\right)$

10. $\frac{d\varsigma_m}{dt} = R_{lm}(t) - R_{vm}(t)$

11. $\frac{d\varsigma_{m1}}{dt} = R_{lm}(t)$

12. $V_l = \left(\frac{M(MW_m)}{\rho_m}\right) + \left(\frac{(\varsigma_m - M)(MW_m)}{\rho_p}\right)$

13. $\phi_m = \frac{\left(\frac{M(MW_m)}{\rho_m}\right)}{\left(\frac{M(MW_m)}{\rho_m}\right)+\left(\frac{(\varsigma_m-M)(MW_m)}{\rho_p}\right)}$

14. $\phi_p = 1 - \phi_m$

15. $k_d = k_{d,o}\exp\left(-\frac{E_d}{RT}\right)$

16. $k_p^0 = k_{p,o}^0\exp\left(-\frac{E_p}{RT}\right)$

17. $k_{td}^0 = k_{td,o}^0 \exp\left(-\frac{E_{td}}{RT}\right)$

18. $k_t = k_t^0 \exp(A_1 \ + A_2 x_m + A_3 x_m^2 + A_4 x_m^3); \text{for } x_m > 0$

19. $k_p = k_p^0 \exp(B_1 + B_2 x_m + B_3 x_m^2 + B_4 x_m^3); \text{for } x_m > 0$

20. $A_i = A_{i1}(T - 273.15) + A_{i2} \ ; \ \ i = 1,2, \dots, 4$

21. $B_i = B_{i1}(T - 273.15) + B_{i2} \ ; \ \ i = 1,2, \dots ,4$

22. $X_m = 1 - \left(\frac{M(t)}{\varsigma_{m1}}\right)$

Initial conditions (t=0)

23. $\lambda_0 = \lambda_1 = \lambda_2 = \mu_0 = \mu_1 = \mu_2 = R = 0$

24. $I = I_0 \ ; \ \ M = \varsigma_m = \varsigma_{m1} = M_0$

Model Parameters

$\boldsymbol{\rho_m}$	$966.5 - 1.1(T\text{-}273.15)\ \frac{kg}{m^3}$
$\boldsymbol{\rho_p}$	$1200\ \frac{kg}{m^3}$
$\boldsymbol{f}$	0.58
$\boldsymbol{k_d}$	$f(k_{d,o}, E_d, T)$
$\boldsymbol{k_p}$	$f(k_p^0, B_1, B_2, B_3, B_4, x_m)$
$\boldsymbol{k_{tm}}$	$f(k_{tm}^0, E_p, T)$
$\boldsymbol{k_t}$	$f(k_t^0, A_1, A_2, A_3, A_4, x_m)$
$\boldsymbol{k_{td}^0}$	$f(k_{td,o}^0, E_{td})$
$\boldsymbol{A_i}$	$f(A_{i1}, A_{i2}, T)$
$\boldsymbol{B_i}$	$f(B_{i1}, B_{i2}, T)$

$\boldsymbol{k_d^0}$	$1.053 \times 10^{15}\ s^{-1}$
$\boldsymbol{k_{p,0}^0}$	$4.917 \times 10^{2}\ m^3 mol^{-1} s^{-1}$
$\boldsymbol{k_{td,0}^0}$	$9.800 \times 10^{4}\ m^3 mol^{-1} s^{-1}$
$\boldsymbol{k_{fm}^0}$	$4.66 \times 10^{6} m^3 mol^{-1} s^{-1}$
$\boldsymbol{k_{tc}}$	0.0
$\boldsymbol{k_t}$	k_d
$\boldsymbol{k_i}$	k_p
$\boldsymbol{k_{tm}/k_{tm}^0}$	k_p/k_p^0
$\boldsymbol{E_d}$	$128.45\ kJ\ mol^{-1}$
$\boldsymbol{E_p}$	$18.22\ kJ\ mol^{-1}$
$\boldsymbol{E_{td}}$	$2.937\ kJ\ mol^{-1}$
$(\boldsymbol{MW_m})$	$0.10013\ kg\ mol^{-1}$
$(\boldsymbol{MW_I})$	$0.06800\ kg\ mol^{-1}$
$\boldsymbol{A_{i1}, A_{i2}\ for\ i = 1\ to\ 4}$	$see\ ref$
$\boldsymbol{B_{i1}, B_{i2}\ for\ 1 = 1\ to\ 4}$	$see\ ref$

Ref: Sangwai, J.S., Bhat, S.A., Gupta, S., Saraf, D.N. and Gupta, S.K., 2005. Bulk free radical polymerizations of methyl methacrylateunder non-isothermal conditions and with intermediate additionof initiator: Experiments and modeling. *Polymer*, *46*(25), pp.11451-11462.