Supporting Material for **Mathematical Modeling of the Production of Elastomers by Emulsion Polymerization in Trains of Continuous Reactors**

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SM1. Detailed Expressions for Radical Entry and Exit and Mass Balances for Species

Note. Notice that, for clarity and to interconnect with the main text, some of the equations are repeated from the main text and their numbers in the main text are kept here.

For the entry rate coefficient of radicals in particles, the collision model (proportional to r^2), as opposed to the diffusion model (proportional to r), is used:

$$\rho = N_A\, V_w\, k_{mp}\, 4\pi\, r^2\, [P]_w \tag{S1a}$$

where ρ is in $\mathrm{Ls^{-1}}$; k_{mp} is an entry coefficient for radicals in particles ($\mathrm{m/s^{-1}}$); r is the radius of an average particle; $[P]_w$ is the radical concentration in the aqueous phase.

For radical entry to micelles, a similar expression is used:

$$\rho_{mic} = N_A\, V_w\, k_{mm}\, a_m\, [P]_w \tag{S1b}$$

where k_{mm}, $\mathrm{m/s^{-1}}$, is the entry coefficient for radicals in micelles, and a_m is the total micellar surface area.

Radical exit coefficient

This is given by the following expressions:

$$k_{des} = V_{\mathrm{w}}\,(g\Psi + g^T\, \Psi^T) \tag{S1c}$$

with chain transfer frequencies g and g^T:

$$g = \overline{k_{tr_M}}\,[M]_p \tag{S1d}$$

$$g^T = \overline{k_{tr_T}}\,[T]_p \tag{S1e}$$

where $[\boldsymbol{T_p}]$ is the chain transfer agent concentration in particles, mol/L, and exit probabilities Ψ and Ψ^T:

$$\Psi = \frac{k_o}{k_o + \overline{k_p}[M]_p} \qquad \Psi^T = \frac{{k_o}^T}{{k_o}^T + \overline{k_p}[M]_p}$$

(S1f) (S1g)

where

$$k_o = \frac{12}{d_p^2\, m_d} \quad \frac{D_w\, D_p}{D_p + 2D_w} \qquad\qquad k_o{}^T = \frac{12}{d_p^2\, m_{d_T}} \frac{D_{wT}\, D_{pT}}{D_{pT} + 2D_{wT}}$$

(S1h) (S1i)

D_w and D_p are the diffusion coefficients (m^2/s) of monomeric radicals in water and particles, respectively; D_{wT} and D_{pT} are diffusion coefficients of CTA in water and particles, respectively; m_d and m_{dT} are the partition coefficients between particles and water of monomeric and CTA radicals, respectively; d_p is the average particle diameter. The exit coefficient k_{des}, has units of Ls^{-1}.

Equations (S1d, S1e) require the use of pseudo-homopolymer chain transfer constants. The following expressions are proposed to this end:

$$\overline{k_{tr_M}} = \sum_{i=1}^{2} \sum_{j=1}^{2} p_i \emptyset_j k_{trM_{ij}} \tag{S1j}$$

$$k_{trM_{ii}} = C_{M_i} k_{p_{ii}} \tag{S1k}$$

$$C_{M_{12}} = \sqrt{C_{M_1} C_{M_2}} \tag{S1l}$$

$$k_{trM_{ij}}\,(i \neq j) = C_{M_{12}} k_{p_{ij}} \tag{S1m}$$

$$\overline{k_{tr_T}} = \sum_{i=1}^{2} p_i k_{trT_i} \tag{S1n}$$

$$k_{trT_i} = C_{T_i} k_{p_{ii}} \tag{S1o}$$

where the C_{M_i} and the C_{T_i} are the chain transfer constants implicitly defined by Equations (S1k) and (S1o), respectively.

Initiator I_w

$$\frac{dI_w}{dt} = -k_{d1} Y_1^r\, I_w / V_w \; + F_{in} \frac{w_{I,in}}{M_I} - \frac{I_w\, F_{out}}{M_T} \tag{12}$$

Reducing Agents Y_1 and Y_2

$$\frac{dY_1}{dt} = \frac{F_{in} w_{y1,in}}{M_{y1}} - \frac{Y_1\, F_{out}}{M_T} \tag{13}$$

$$\frac{dY_2}{dt} = \frac{F_{in} w_{y2,in}}{M_{y2}} - \frac{Y_2 F_{out}}{M_T} - k_{d2} Y_1^o Y_2 / V_w \tag{14}$$

$$Y_1 = Y_1^r + Y_1^o \tag{S1p}$$

Neglecting flow terms for Y_1^r and using Eq. (S1p):

$$\frac{dY_1^r}{dt} = (-k_{d1} I_w Y_1^r + k_{d2}(Y_1 - Y_1^r) Y_2)/V_w \tag{S1q}$$

and assuming the quasi-steady state (QSSA) for Y_1^r:

$$Y_1^r = \frac{k_{d2} Y_1 Y_2}{k_{d1} I_w + k_{d2} Y_2} \tag{S1r}$$

Primary Radicals R_w and Polymeric Radicals P_w (aqueous phase)

$$\frac{d\,R_w}{d_t} = k_{d1} f Y_1^r\, I_w/V_w \; - \; k_i\, R_w M_{aq}\,/\,V_w \tag{S1s}$$

M_{aq} is the molar amount of monomer in the aqueous phase. In Eq. (S1s) it has been assumed that there is no entry of primary radicals into micelles or particles.

$$\frac{dP_w}{dt} = k_i\, R_w M_{aq}\,/\,V_w - k_t {P_w}^2/\,V_w \text{ - } k_{mp}\, 4\pi r^2\, P_w\, \sum_{n=0}^{2} F_n - \, k_{mm} a_m\, M_{ic}\, P_w + \frac{K_{des}}{N_A} \sum_{n=0}^{2} F_n \tag{S1t}$$

Taking the QSSA for R_w and P_w, and combining the resulting equations, a simple quadratic equation for P_w is obtained:

$$-\,k_t\, P_w^2/\,V_w - \, k_{mp} 4\pi\, r^2\, P_w\, \sum_{n=0}^{2} F_n - \, k_{mm} a_m\, M_{ic}\, P_w + \frac{K_{des}}{N_A} \sum_{n=0}^{2} F_n + k_{d1} f Y_1^r\, I_w/V_w = 0 \tag{21}$$

The micelle concentration, M_{ic}, (L^{-1}) can be calculated from the surfactant balance as shown below.

Surfactant S

$$\frac{dS}{dt} = \frac{F_{in} w_{s,in}}{M_s} - \, F_{out} \frac{S}{M_T} \tag{15}$$

It is assumed that the surfactant rapidly reaches thermodynamic equilibrium and is partitioned between surfactant adsorbed in particles, S_a, in monomer droplets, S_d, or free, S_f, which can be in solution or forming micelles, depending on its concentration (all quantities in moles).

$$S = S_a + S_d + S_f \approx S_a + S_f \tag{S1u}$$

Neglecting the amount of surfactant adsorbed in monomer droplets, S_a can be represented by a Langmuir isotherm:

$$S_a = \frac{A_p \, \Gamma_\infty \, b \, S_f \, / \, V_w}{1 + b \, S_f \, / \, V_w} \tag{S1v}$$

where the particle surface area A_p, is given by:

$$A_p = 4\pi V_w \sum_{n=0}^{2} F_n \; r_h^2 \tag{S1w}$$

with r_h being the radius of a monomer swollen particle. Combining (S1u) and (S1v), a quadratic equation for S_f can be derived:

$$S + SbS_f / \; V_w \; - \; A_p \, \Gamma_\infty \, b \, S_f / V_w \; - (\, S_f + b \, S_f^2 / V_w) \; = 0 \tag{S1x}$$

Once Eq. (S1x) is solved for S_f, the micelle concentration can be determined as follows:

$$M_{ic} = \frac{(S_f \, / \, V_w - [S]^{cmc}) N_A a_{em}}{4\pi \, r_m^2} \qquad \text{if} \qquad S_f / V_w \geq [S]^{cmc} \tag{16}$$

$$M_{ic} = 0 \qquad \text{if} \qquad S_f / V_w < [S]^{cmc} \tag{17}$$

Where $[S]^{cmc}$ is the critical micelle concentration of the surfactant (mol L^{-1}); a_{em} is the surface area per surfactant molecule, and r_m is the radius of a micelle.

Chain Transfer Agent (Tr)

$$\frac{dT_r}{dt} = \frac{F_{in} w_{Tr,in}}{M_{Tr}} - \frac{F_{out} T_r}{M_T} - k_{trT} [T_r]_p \; \frac{\sum_{n=1}^{2} n F_n}{N_A} \; V_w + \frac{F_{ri,Tr}}{M_{Tr}} \tag{18}$$

$$[T_r]_p = \frac{T_r}{V_p} \tag{S1y}$$

where $F_{r,Tr}$ is a side feed stream (mass flow) of CTA to reactor *ri*.

Although the CTA employed in the process is usually a long-chain molecule (dodecyl mercaptan), which is not water soluble, for generality it is considered here that the CTA can partition between the aqueous and the particle phase.

Besides the total mass balance of the CTA, it is considered that this component partitions between the particles and the aqueous phase. Defining $[Tr]_p$ and $[Tr]_w$ as the concentrations of CTA in the particle and aqueous phase, respectively, the total amount of CTA satisfies the relationship:

$$Tr = [Tr]_p V_p + [Tr]_w \tag{S1z}$$

And the concentrations in the two phases are assumed to follow the partition coefficient defined as:

$$K_T = \frac{[Tr]_p}{[Tr]_w} \tag{19}$$

Resulting in:

$$[Tr]_p = \frac{K_T Tr}{K_T V_p + V_w} \tag{S1aa}$$

This concentration is used to calculate the kinetics and the desorption term in the particle balances (see SM).

Water (in mass units)

$$\frac{dW}{dt} = F_{in} w_{w1\,in} - \frac{F_{out}\,W}{M_T} \tag{20}$$

SM2. Monomer Partitioning Equations

Based on the definition of the equivalent conversion, x, (Eq. 22 in main text):

If $x \leq x_{sat}$ (intervals 1 and 2)

In this case $[M]_p$ is calculated by first considering the mass of monomer (M) and polymer (P) contained in a hypothetical particle of unit mass, $(M + P) = 1$, from which Eqs. (S2a)-(S2c) and (23) follow:

$$\frac{P}{M+P} = x_{sat} \tag{S2a}$$

$$P = x_{sat} \tag{S2b}$$

$$M = 1 - x_{sat} \tag{S2c}$$

$$[M]_p = [M]_{psat} = \frac{(M_1 \,/\, M_{w1}) + (M_2 \,/\, M_{w2})}{V_p'} \tag{23}$$

V_p' is the volume of this hypothetical particle, which is calculated assuming volume additivity:

$$V_p' = \frac{M_1}{\rho_1} + \frac{M_2}{\rho_2} + \frac{P_1}{\rho_{p1}} + \frac{P_2}{\rho_{p2}} \tag{24}$$

and M_{wi} = molecular weight of monomer *i*.

P_1 and P_2 are the amounts of type 1 and 2 monomer units, respectively, in the polymer $(P = P_1 + P_2)$ present in the hypothetical particle. These are easily calculated, since the copolymer composition, and therefore the ratio P_1/P_2, are known at any given time. Similarly, M_1, M_2 can be calculated based on the proportion of the remaining monomers taking into account that a known fraction of the monomer 2 can be present in the aqueous phase in the NBR case.

ρ_i, ρ_{pi}, (i=1,2) are the densities of monomer *i* and homopolymer *i*, respectively.

If $x > x_{sat}$ $(mass\ conversion\ x,$ interval 3), $[M]_p$ is calculated assuming that all the remaining monomer, except for the possible presence of AN in the water phase (NBR case), is in the particles:

$$[M]_p = \frac{(M_1^m \,/\, M_{w1}) + ((M_2^m - M_{2w}^m) \,/\, M_{w2})}{V_p} \tag{25}$$

$$\text{where} \quad V_p = \frac{M_1^m}{\rho_1} + \frac{M_2^m - M_{2w}^m}{\rho_2} + \frac{H_1^m}{\rho_{p1}} + \frac{H_2^m}{\rho_{p2}} \tag{26}$$

and the superindex *m* indicates mass units.

An approximate way of estimating the amount of AN in the water phase (M_{2w}) in the NBR case is based on a partition coefficient, defined as the ratio of mass concentrations of monomer 2 in the particles and the water phase:

$$\chi_{AN} = \frac{[(M_2^m]_p}{[(M_2^m]_w}$$

(27)

which can be written as:

$$\chi_{AN} = \frac{(M_2^m - M_{2w}^m)/V_p}{M_{2w}^m/V_w} \tag{S2d}$$

V_p above is the total volume of the particle phase. Replacing (26) in (S2d) and rearranging, a quadratic equation can be obtained for M_{2w}, resulting in:

$$\frac{\chi_{AN}}{\rho_2} M_{2w}^2 - \left[\chi_{AN}\left(\frac{M_1^m}{\rho_1} + \frac{M_2^m}{\rho_2} + \frac{P_1^m}{\rho_{p1}} + \frac{P_2^m}{\rho_{p2}}\right) + V_w\right] M_{2w} + M_2^m V_w = 0 \qquad (28)$$

SM3. Dimensionless version of the Population Balance Equations for Particles and Original Polymer Moments Equations

Defining $\overline{F_{j,r}} = F_{j,r}/N_{dim}$, where N_{dim} is a characteristic number of particles per L of water, Equations (7)-(9) become

$$\frac{dV_w\overline{F_{0,r}}}{dt} = -\rho\overline{F_{0,r}} + k_{des}\overline{F_{1,r}} + \frac{2k_t'}{v}\overline{F_{2,r}} + Q\overline{F_{0,r-1}} - Q\overline{F_{0,r}} \qquad \text{(S3a)}$$

$$\frac{dV_w\overline{F_{1,r}}}{dt} = \rho\overline{F_{0,r}} - (\rho + k_{des})\overline{F_{1,r}} + (\rho + 2k_{des})\overline{F_{2,r}} + \frac{\rho_{mic}M_{ic}}{N_{dim}} + Q\overline{F_{1,r-1}} - Q\overline{F_{1,r}} \qquad \text{(S3b)}$$

$$\frac{dV_w\overline{F_{2,r}}}{dt} = \rho\overline{F_{1,r}} - (\rho + 2k_{des} + \frac{2k_t'}{v})\overline{F_{2,r}} + Q\overline{F_{2,r-1}} - Q\overline{F_{2,r}} \qquad \text{(S3c)}$$

Polymer Moments Equations

PBE's for Live Polymer Moments

$$\mu_{K,n} = \sum_{r=1}^{\infty} r^K N_n^r \qquad n = 1, 2, \quad K = 0, 1, 2 \qquad (32)$$

Zeroth Moments ($K = 0$)

$\boldsymbol{n = 1}$

$$\frac{dV_w \sum_{r=1}^{\infty} N_1^r}{dt} = \frac{dV_w \mu_{0,1}}{dt} = k_{des}\mu_{0,2} + \rho N_0 + \rho_{mic}M_{ic} - k_{des}N_1 - \rho\mu_{0,1} + \frac{\rho\mu_{0,2}}{2} + FIN\mu_{0,1}^f - FOUT\mu_{0,1} \qquad \text{(S3d)}$$

where

FIN = $F_{in,ri} w_w^f / \rho_w$

FOUT=$\frac{V_w Q_{out,ri} \rho_{ri}}{M_T}$

Note that $N_1 \equiv F_{1,ri} \equiv \mu_{0,1}$, $\mu_{0,2} \equiv 2N_2 \ \equiv \ 2F_{2,ri}$, and Eq. (S2a) is equivalent to (Eq. 8)

$\boldsymbol{n=2}$

$$\frac{dV_w \mu_{0,2}}{dt} = -k_{des}\mu_{0,2} + \rho(\mu_{0,1} - \mu_{0,2}/2) - \frac{k_t V_w}{N_A v}\mu_{0,2} + FIN\mu_{0,2}^f - FOUT\mu_{0,2} \tag{S3e}$$

Since $\mu_{0,2} \equiv 2N_2 \ \equiv \ 2F_{2,ri}$, Eq. (S3e) is equivalent to Eq. (9).

First Moments ($\boldsymbol{K=1}$)

$\boldsymbol{n=1}$

$$\frac{dV_w \sum_{r=1}^{\infty} rN_1^r}{dt} = \frac{dV_w \mu_{1,1}}{dt} = k_p[M]_p V_w \mu_{0,1}$$
$$-k_{trM}[M]_p \mu_{1,1} V_w + k_{des}\mu_{1,2} - k_{trT}[Tr]_p \mu_{1,1} V_w + \rho N_0 + \rho_{mic} Mic$$
$$-k_{des}\mu_{0,1} - \rho\mu_{1,1} + k_{trT}[Tr]_p \mu_{0,1} V_w + k_{trM}[M]_p \mu_{0,1} V_w + \frac{\rho\mu_{1,2}}{2} + FIN\mu_{1,1}^f - FOUT\mu_{1,1} \tag{S3f}$$

$\boldsymbol{n=2}$

$$\frac{dV_w \mu_{1,2}}{dt} = k_p[M]_p V_w \mu_{0,2} - k_{trM}[M]_p \mu_{1,2} V_w$$
$$-k_{des}\mu_{1,2} - k_{trT}[Tr]_p \mu_{1,2} V_w + \rho\mu_{1,1} - \rho\mu_{1,2}/2 + \frac{k_t V_w}{2N_A v}(-2\mu_{1,2})$$
$$+k_{trT}[Tr]_p \mu_{0,2} V_w + k_{trM}[M]_p \mu_{0,2} V_w + FIN\mu_{1,2}^f - FOUT\mu_{1,2} \tag{S3g}$$

Second Moments (K=2)

$\boldsymbol{n=1}$

$$\frac{dV_w \sum_{r=1}^{\infty} r^2 N_1^r}{dt} = \frac{dV_w \mu_{2,1}}{dt} = k_p[M]_p V_w(2\mu_{1,1} + \mu_{0,1})$$

$$-k_{trM}[M]_p V_w \mu_{2,1} + k_{des}\mu_{2,2} - k_{trT}[Tr]_p \mu_{2,1} V_w + \rho N_0 + \rho_{mic} Mic$$

$$-k_{des}\mu_{0,1} - \rho\mu_{2,1} + k_{trT}[Tr]_p V_w \mu_{0,1} + k_{trM}[M]_p V_w \mu_{0,1} + \rho\mu_{2,2}/2 + FIN\mu_{2,1}^f - FOUT\mu_{2,1} \qquad \text{(S3h)}$$

$\boldsymbol{n = 2}$

$$\frac{dV_w \mu_{2,2}}{dt} = k_p[M]_p V_w(2\mu_{1,2} + \mu_{0,2}) - k_{trM}[M]_p V_w \mu_{2,2}$$

$$-k_{des}\mu_{2,2} - k_{trT}[Tr]_p V_w \mu_{2,2} + \rho\mu_{2,1} - \rho\mu_{2,2}/2 - \frac{k_t V_w}{2N_A v}\mu_{2,2}$$

$$+k_{trT}[Tr]_p \mu_{0,2} V_w + k_{trM}[M]_p \mu_{0,2} V_w + FIN\mu_{2,2}^f - FOUT\mu_{2,2} \qquad \text{(S3i)}$$

The following definitions are also applicable:

$N_n = \sum_{r=1}^{\infty} N_n^r$ = Total number of particles having *n* radicals, per L of water (*n*=1,2).

$N = \sum_{n=1}^{2} \sum_{r=1}^{\infty} N_n^r$ = Total number of particles per L of water.

PBE's for Dead Polymer Moments

$\lambda_{K,n} = \sum_{r=1}^{\infty} r^K D_n^r, \;\; K = 0,1,2 \quad n = 0,1,2$

Zeroth Moments (K=0)

$\boldsymbol{n = 0}$

$$\frac{dV_w \lambda_{0,0}}{dt} = -\rho\lambda_{0,0} + k_{des}\lambda_{0,1} + \frac{V_w k_t}{N_A v}\lambda_{0,2}$$

$$\frac{+k_{td}V_w}{N_A v}\mu_{0,2} + \frac{F_{in,ri} w^F}{\rho_w}\lambda_{0,0}^f - \frac{V_w Q_{out,ri}\rho_{ri}}{M_T}\lambda_{0,0}$$

$$+\frac{k_{tc}V_w}{N_A v} 2N_2 \qquad \text{(S3j)}$$

$\boldsymbol{n = 1}$

$$\begin{aligned}\frac{dV_w\lambda_{0,1}}{dt} &= \rho\lambda_{0,0} - \rho\lambda_{0,1} + 2k_{des}\lambda_{0,2} - k_{des}\lambda_{0,1}\\ &+V_w k_{trM}[M]_p\mu_{0,1} + V_w k_{trT}[Tr]_p\mu_{0,1} + \rho\lambda_{0,2}\\ &+F_{in,ri}w^F\lambda_{0,1}^f/\rho_w - \frac{\lambda_{0,1}V_wQ_{out,ri}}{M_T}\rho_{ri}\end{aligned}\tag{S3k}$$

$\boldsymbol{n = 2}$

$$\begin{aligned}\frac{dV_w\lambda_{0,2}}{dt} &= \rho\lambda_{0,1} - \rho\lambda_{0,2} - 2k_{des}\lambda_{0,2} + V_w k_{trM}[M]_p\mu_{0,2}\\ &+V_w k_{trT}[Tr]_p\mu_{0,2} - \frac{V_w}{N_A v}k_t\lambda_{0,2} + F_{in,ri}w_w^f\lambda_{0,2}^f/\rho_w - \frac{\lambda_{0,2}V_wQ_{out,ri}}{M_T}\rho_{ri}\end{aligned}\tag{S3l}$$

First Moments (K=1)

$\boldsymbol{n = 0}$

$$\begin{aligned}\frac{dV_w\lambda_{1,0}}{dt} &= -\rho\lambda_{1,0} + k_{des}\lambda_{1,1} + \frac{V_w}{N_A v}k_t\lambda_{1,2}\\ &+\frac{k_{td}V_w}{N_A v}\mu_{1,2} + \frac{k_{tc}V_w}{N_A v}(2\mu_{1,2}) + F_{in,ri}w_w^f\lambda_{1,0}^f/\rho_w - \lambda_{1,0}V_w\frac{Q_{out,ri}}{M_T}\rho_{ri}\end{aligned}\tag{S3m}$$

$\boldsymbol{n = 1}$

$$\begin{aligned}\frac{dV_w\lambda_{1,1}}{dt} &= \rho\lambda_{1,0} - \rho\lambda_{1,1} + 2k_{des}\lambda_{1,2} - k_{des}\lambda_{1,1}\\ &+V_w k_{trM}[M]_p\mu_{1,1} + V_w k_{trT}[Tr]_p\mu_{1,1} + \rho\lambda_{1,2}\\ &+F_{in,ri}w_w^f\lambda_{1,1}^f/\rho_w - \frac{\lambda_{1,1}V_wQ_{out,ri}}{M_T}\rho_{ri}\end{aligned}\tag{S3n}$$

$\boldsymbol{n = 2}$

$$\frac{dV_w\lambda_{1,2}}{dt} = \rho\lambda_{1,1} - \rho\lambda_{1,2} - 2k_{des}\lambda_{1,2} + V_w k_{trM}[M]_p\mu_{1,2}$$

$$+V_w k_{trT}[Tr]_p\mu_{1,2} - \frac{V_w}{N_A v}k_t\lambda_{1,2} + F_{in,ri}w_w^f\lambda_{1,2}^f/\rho_w - \lambda_{1,2}\frac{V_w Q_{out,ri}}{M_T}\rho_{ri} \qquad \text{(S3o)}$$

Second Moments (K=2)

$\boldsymbol{n} = \mathbf{0}$

$$\frac{dV_w\lambda_{2,0}}{dt} = -\rho\lambda_{2,0} + k_{des}\lambda_{2,1} + \frac{V_w}{N_A v}k_t\lambda_{2,2}$$

$$+\frac{k_{td}V_w}{N_A v}\mu_{2,2} + \frac{k_{tc}V_w}{N_A v\mu_{0,2}/2}\left[\mu_{0,2}\mu_{2,2} + \mu_{1,2}^2\right]$$

$$+F_{in,ri}w_w^f\frac{\lambda_{2,0}^f}{\rho_w} - \lambda_{2,0}\frac{V_w Q_{out,ri}}{M_T}\rho_{ri}$$

(S3p)

$\boldsymbol{n} = \mathbf{1}$

$$\frac{dV_w\lambda_{2,1}}{dt} = \rho\lambda_{2,0} - \rho\lambda_{2,1} + 2k_{des}\lambda_{2,2} - k_{des}\lambda_{2,1}$$

$$+V_w k_{trM}[M]_p\mu_{2,1} + V_w k_{trT}[Tr]_p\mu_{2,1} + \rho\lambda_{2,2}$$

$$+F_{in,ri}w_w^f\frac{\lambda_{2,1}^f}{\rho_w} - \frac{\lambda_{2,1}V_w Q_{out,ri}}{M_T}\rho_{ri} \qquad \text{(S3q)}$$

$\boldsymbol{n} = \mathbf{2}$

$$\frac{dV_w\lambda_{2,2}}{dt} = \rho\lambda_{2,1} - \rho\lambda_{2,2} - 2k_{des}\lambda_{2,2} + V_w k_{trM}[M]_p\mu_{2,2} + V_w k_{trT}[Tr]_p\mu_{2,2} - \frac{V_w}{N_A v}k_t\lambda_{2,2}$$

$$+F_{in,ri}w_w^f\frac{\lambda_{2,2}^f}{\rho_w} - \frac{\lambda_{2,2}V_w Q_{out,ri}}{M_T}\rho_{ri} \qquad \text{(S3r)}$$

Transfer to Polymer and Double Bond Polymerization Terms

In the previous equations, the transfer-to-polymer and double bond polymerization terms have not been included. They are explained next and described as additional terms to be incorporated in the previous equations. To indicate the corresponding modifications to the previous equations the notation =…+ will be used. For example, the following equation:

$$\frac{dV_w\lambda_{1,0}}{dt} = \cdots + additional\ terms$$

indicates that the *additional terms* have to be added to the right-hand side of Eq. (S3m).

Live Polymer

To derive the corresponding terms, the following reaction schemes are considered:

$$N_n^r + D_n^j \xrightarrow{j\,k_{trp}} D_n^r + N_n^j$$

$$N_n^r + D_n^j \xrightarrow{F_{1,mo}^c r k_{db}} N_n^{r+j}$$

The general balance for live polymer, Eq. (62) is modified as (in the following equations $F_{1,mo}^c$ is written as F_1 for simplicity.

$$\frac{dV_w N_n^r}{d_t} = \cdots \left[-k_{trp}\left(\sum_{j=1}^{\infty} jD_n^j\right)N_n^r + k_{trp} r D_n^r \sum_{j=1}^{\infty} N_n^j - k_{db}F_1\left(\sum_{j=1}^{\infty} jD_n^j\right)N_n^r + k_{db}F_1 \sum_{j=1}^{r} jN_n^{r-j} D_n^j\right] \frac{nV_w}{N_n N_A v} \tag{S3s}$$

From which the moment equations are modified as:

Live Polymer Moments **K=0,1,2** for $\boldsymbol{n} = \mathbf{1}$

$$\frac{dV_w\mu_{0,1}}{dt} = \cdots + 0 \tag{S3t}$$

$$\frac{dV_w\mu_{1,1}}{dt} = \cdots + \left[-k_{trp}\lambda_{1,1}\mu_{1,1} + k_{trp}\lambda_{2,1}\mu_{0,1} + k_{db}F_1\lambda_{2,1}\mu_{0,1}\right]\frac{1}{N_1}\frac{V_w}{N_A v} \tag{S3u}$$

$$\frac{dV_w\mu_{2,1}}{dt} = \cdots + \left[-k_{trp}\lambda_{1,1}\mu_{2,1} + k_{trp}\lambda_{3,1}\mu_{0,1} + k_{db}F_1\lambda_{3,1}\mu_{0,1} + 2k_{db}F_1\lambda_{2,1}\mu_{1,1}\right]\frac{1}{N_1}\frac{V_w}{N_A v} \tag{S3v}$$

Live Polymer Moments **K=0,1,2** for $\boldsymbol{n} = \mathbf{2}$

$$\frac{dV_w\mu_{0,2}}{dt} = \cdots + 0 \tag{S3w}$$

$$\frac{dV_w\mu_{1,2}}{dt} = \cdots + \left[-k_{trp}\lambda_{1,2}\mu_{1,2} + k_{trp}\lambda_{2,2}\mu_{0,2} + k_{db}F_1\lambda_{2,2}\mu_{0,2}\right]\frac{2}{N_2}\frac{V_w}{N_A v} \tag{S3x}$$

$$\frac{dV_w\mu_{2,2}}{dt} = \cdots + \left[-k_{trp}\lambda_{1,2}\mu_{2,2} + k_{trp}\lambda_{3,2}\mu_{0,2} + k_{db}F_1\lambda_{3,2}\mu_{0,2} + 2k_{db}F_1\lambda_{2,2}\mu_{1,2}\right]\frac{2}{N_2}\frac{V_w}{N_A v} \tag{S3y}$$

Dead Polymer

To derive the dead polymer terms, the kinetic scheme is better re-written as:

$$N_n^j + D_n^r \xrightarrow{r\,k_{trp}} D_n^j + N_n^r$$

$$N_n^j + D_n^r \xrightarrow{F_{1,mo}^c r k_{db}} N_n^{r+j}$$

$$\frac{dV_w D_n^r}{d_t} = \left[-k_{trp} r D_n^r \sum_{j=1}^{\infty} N_n^j + k_{trp} N_n^r \sum_{j=1}^{\infty} j D_n^j - k_{db}F_1\left(\sum_{j=1}^{\infty} j D_n^j\right)N_n^r\right]\frac{nV_w}{N_n N_A v} \tag{S3z}$$

Dead Polymer Moments **K=0,1,2** for $\boldsymbol{n} = \mathbf{1}$

$$\frac{dV_w\lambda_{0,1}}{d_t} = \cdots - k_{db}F_1\mu_{0,1}\lambda_{1,1} \tag{S3aa}$$

$$\frac{dV_w\lambda_{1,1}}{d_t} = \cdots + \left\{k_{trp}\left[-\lambda_{2,1}\mu_{0,1} + \mu_{1,1}\lambda_{1,1}\right] - k_{db}F_1\mu_{0,1}\lambda_{2,1}\right\}\frac{V_w}{N_1 N_A v} \tag{S3ab}$$

$$\frac{dV_w\lambda_{2,1}}{d_t} = \cdots + \left\{k_{trp}\left[-\lambda_{3,1}\mu_{0,1} + \mu_{2,1}\lambda_{1,1}\right] - k_{db}F_1\mu_{0,1}\lambda_{3,1}\right\}\frac{V_w}{N_1 N_A v} \tag{S3ac}$$

Dead Polymer Moments **K=0,1,2** for $\boldsymbol{n} = \mathbf{2}$

$$\frac{dV_w\lambda_{0,2}}{d_t} = \cdots + \left\{k_{trp}\left[-\lambda_{1,2}\mu_{0,2} + \mu_{0,2}\lambda_{1,2}\right] - k_{db}F_1\mu_{0,2}\lambda_{1,2}\right\}\frac{2V_w}{N_2N_Av} \tag{S3ad}$$

$$\frac{dV_w\lambda_{1,2}}{d_t} = \cdots + \left\{k_{trp}\left[-\lambda_{2,2}\mu_{0,2} + \mu_{1,2}\lambda_{1,2}\right] - k_{db}F_1\mu_{0,2}\lambda_{2,2}\right\}\frac{2V_w}{N_2N_Av} \tag{S3ae}$$

$$\frac{dV_w\lambda_{2,2}}{d_t} = \cdots + \left\{k_{trp}\left[-\lambda_{3,2}\mu_{0,2} + \mu_{2,2}\lambda_{1,2}\right] - k_{db}F_1\mu_{0,2}\lambda_{2,2}\right\}\frac{2V_w}{N_2N_Av} \tag{S3af}$$

Notice that these reactions do not contribute terms for particles with *n=0* since these particles contain no live polymer to react with.

On the other hand, since some of the previous terms introduce the moment closure problem (the first moment depends on the 2nd moment; the 2nd moment depends on the third moment, and so on) the Hulburt and Katz approximation is used:

$$\lambda_{3,n} = \frac{\lambda_{2,n}}{\lambda_{0,n}\lambda_{1,n}}\left(2\lambda_{2,n}\lambda_{0,n} - \lambda_{1,n}^2\right) \quad \text{n} = 0,1,2 \tag{S3ag}$$

* H. M. Hulburt, S. Katz, *Chem. Eng. Sci*, **1964**, *19*, 555.

Dimensionless Versions of the Live Polymer Moments Equations

$$\overline{\mu_{K,n}} = \frac{\sum_{r=1}^{\infty} rN_n^r}{Mf_d}, K, n = 1,2$$

Mf_d is a characteristic value (10^{17}) for the live polymer moments.

$$\frac{dV_w\bar{\mu}_{1,1}}{dt} = k_p[M]_pV_w\bar{\mu}_{0,1}$$
$$-k_{trM}[M]_p\bar{\mu}_{1,1}V_w + k_{des}\bar{\mu}_{1,2} - k_{trT}[Tr]_p\bar{\mu}_{1,1}V_w + \rho\overline{N_0} + \rho_{mic}\overline{M\iota c}$$
$$-k_{des}\bar{\mu}_{0,1} - \rho\bar{\mu}_{1,1} + k_{trT}[Tr]_p\bar{\mu}_{0,1}V_w + k_{trM}[M]_p\bar{\mu}_{0,1}V_w + \frac{\rho\bar{\mu}_{1,2}}{2}$$
$$+F_{IN}\bar{\mu}_{1,1}^{f} - F_{OUT}\bar{\mu}_{1,1} \tag{S3ah}$$

where $\overline{M\iota c} = Mic\ /Mf_d$

$$\frac{dV_w\bar{\mu}_{1,2}}{dt} = k_p[M]_p V_w\left(\bar{\mu}_{0,2}\right) - k_{trM}[M]_p\bar{\mu}_{1,2}V_w$$

$$-k_{des}\bar{\mu}_{1,2} - k_{trT}[Tr]_p\bar{\mu}_{1,2}V_w + \rho\bar{\mu}_{1,1} - \frac{\rho\bar{\mu}_{1,2}}{2} + \frac{k_t V_w}{2N_A v}(-2\bar{\mu}_{1,2})$$

$$+ k_{trT}[Tr]_p\bar{\mu}_{0,2}V_w + k_{trM}[M]_p\bar{\mu}_{0,2}V_w + F_{IN}\bar{\mu}^f_{1,2} - F_{OUT}\bar{\mu}_{1,2} \tag{S3i}$$

$$\frac{dV_w\bar{\mu}_{2,1}}{dt} = k_p[M]_p V_w\left(2\bar{\mu}_{1,1} + \bar{\mu}_{0,1}\right) - k_{trM}[M]_p V_w\bar{\mu}_{2,1} + k_{des}\bar{\mu}_{2,2}$$

$$-k_{trT}[Tr]_p\bar{\mu}_{2,1}V_w + \rho\overline{N_0} + \rho_{mic}\overline{M\iota c}$$

$$-k_{des}\bar{\mu}_{0,1} - \rho\bar{\mu}_{2,1} + k_{trT}[Tr]_p V_w\bar{\mu}_{0,1} + k_{trM}[M]_p V_w\bar{\mu}_{0,1} + \frac{\rho\bar{\mu}_{2,2}}{2} + F_{IN}\bar{\mu}^f_{2,1} - F_{OUT}\bar{\mu}_{2,1} \tag{S3j}$$

$$\frac{dV_w\bar{\mu}_{2,2}}{dt} = k_p[M]_p V_w\left(2\bar{\mu}_{1,2} + \bar{\mu}_{0,2}\right) - k_{trM}[M]_p V_w\bar{\mu}_{2,2}$$

$$-k_{des}\bar{\mu}_{2,2} - k_{trT}[Tr]_p V_w\bar{\mu}_{2,2} + \rho\bar{\mu}_{2,1} - \frac{\rho\bar{\mu}_{2,2}}{2} - \frac{k_t V_w}{2N_A v}\bar{\mu}_{2,2}$$

$$+k_{trT}[Tr]_p\bar{\mu}_{0,2}V_w + k_{trM}[M]_p\bar{\mu}_{0,2}V_w + F_{IN}\bar{\mu}^f_{2,2} - F_{OUT}\bar{\mu}_{2,2} \tag{S3k}$$

Dimensionless Versions of the Dead Polymer Moments Equations

Only those equations that are modified in their dimensionless version are included here. In the rest of the equations it is possible to replace the original moments by their dimensionless versions. For example, Equation S3al below is the dimensionless version of Eq. S3k (similarly for Equations S3j and S3l)

$$\frac{dV_w\overline{\lambda_{0,1}}}{dt} = \rho\overline{\lambda_{0,0}} - \rho\overline{\lambda_{0,1}} + 2k_{des}\overline{\lambda_{0,2}} - k_{des}\overline{\lambda_{0,1}}$$

$$+V_w k_{trM}[M]_p\overline{\mu_{0,1}} + V_w k_{trT}[Tr]_p\overline{\mu_{0,1}} + \rho\overline{\lambda_{0,2}}$$

$$+F_{in,ri}w^F\overline{\lambda^f_{0,1}}/\rho_w - \frac{\overline{\lambda_{0,1}}V_w Q_{out,ri}}{M_T}\rho_{ri} \tag{S3al}$$

1st Moments

$$n = 0 \qquad \overline{\lambda_{1,0}} = \sum_{r=1}^{\infty} rD_o^r\,/Mf_1$$

Mf_1, Mf_2 are characteristic values (10^{20} and 10^{23}, respectively) for the dead polymer moments

$$\frac{dV_w\overline{\lambda_{1,0}}}{dt} = -\rho\overline{\lambda_{1,0}} + k_{des}\overline{\lambda_{1,1}} + \frac{V_w}{N_A v}k_t\overline{\lambda_{1,2}}$$

$$+\frac{k_{td}V_w}{N_A v}\overline{\mu_{1,2}} + \frac{k_{tc}V_w(2\overline{\mu_{1,2}})}{2N_A v}\frac{Mf_d}{Mf_1} + F_{in,ri}w_w^f\overline{\lambda_{1,0}^f}/\rho_w - \overline{\lambda_{1,0}}V_w\frac{Q_{out,ri}}{M_T}\rho_{ri} \qquad \text{(S3am)}$$

$n = 1$ $\qquad \overline{\lambda_{1,1}} = \sum rD_1^r\,/Mf_1$

$$\frac{dV_w\overline{\lambda_{1,1}}}{dt} = \rho\overline{\lambda_{1,0}} - \rho\overline{\lambda_{1,1}} + 2k_{des}\overline{\lambda_{1,2}} - k_{des}\overline{\lambda_{1,1}}$$

$$+(V_w k_{trM}[M]_p\overline{\mu_{1,1}} + V_w k_{trT}[Tr]_p\overline{\mu_{1,1}})\frac{Mf_d}{Mf_1} + \rho\overline{\lambda_{1,2}}$$

$$+F_{in,ri}w_w^f\overline{\lambda_{1,1}^f}/\rho_w - \frac{\overline{\lambda_{1,1}}V_w Q_{out,ri}}{M_T}\rho_{ri} \qquad \text{(S3an)}$$

$n = 2$ $\qquad \lambda_{1,2} = \sum rD_2^r/\,Mf_1$

$$\frac{dV_w\overline{\lambda_{1,2}}}{dt} = \rho\overline{\lambda_{1,1}} - \rho\overline{\lambda_{1,2}} - 2k_{des}\overline{\lambda_{1,2}} + (V_w k_{trM}[M]_p\overline{\mu_{1,2}}$$

$$+V_w k_{trT}[Tr]_p\overline{\mu_{1,2}})\frac{Mf_d}{Mf_1} - \frac{V_w}{N_A v}k_t\overline{\lambda_{1,2}} + F_{in,ri}w_w^f\overline{\lambda_{1,2}^f}/\rho_w - \overline{\lambda_{1,2}}\frac{V_w Q_{out,ri}}{M_T}\rho_{ri} \qquad \text{(S3ao)}$$

2nd Moments

$n = 0$ $\qquad \overline{\lambda_{2,0}} = \sum_{r=1}^{\infty} r^2 D_o^r\,/Mf_2$

$$\frac{dV_w\overline{\lambda_{2,0}}}{dt} = -\rho\overline{\lambda_{2,0}} + k_{des}\overline{\lambda_{2,1}} + \frac{V_w}{N_A v}k_t\overline{\lambda_{2,2}}$$

$$+\frac{k_{td}V_w}{N_A v}\overline{\mu_{2,2}}\frac{Mf_d}{Mf_2} + \frac{k_{tc}V_w}{N_A v\mu_{0,2}/2}\left[\overline{\mu_{0,2}\mu_{2,2}} + \overline{\mu_{1,2}^2}\right]\frac{Mf_d}{Mf_2}$$

$$+F_{in,ri}w_w^f\frac{\lambda_{2,0}^f}{\rho_w} - \lambda_{2,0}\frac{V_w Q_{out,ri}}{M_T}\rho_{ri} \qquad \text{(S3ap)}$$

$n = 1$ $\qquad \overline{\lambda_{2,1}} = \sum_{r=1}^{\infty} r^2 D_1^r\,/Mf_2$

$$\frac{dV_w\overline{\lambda_{2,1}}}{dt} = \rho\overline{\lambda_{2,0}} - \rho\overline{\lambda_{2,1}} + 2k_{des}\overline{\lambda_{2,2}} - k_{des}\overline{\lambda_{2,1}}$$

$$+(V_w k_{trM}[M]_p\overline{\mu_{2,1}} + V_w k_{trT}[Tr]_p\overline{\mu_{2,1}})\frac{Mf_d}{Mf_2} + \rho\overline{\lambda_{2,2}}$$

$$+F_{in,ri}w_w^f\frac{\overline{\lambda_{2,1}^f}}{\rho_w} - \frac{\overline{\lambda_{2,1}}V_wQ_{out,ri}}{M_T}\rho_{ri} \qquad \text{(S3aq)}$$

$n = 2$ $\qquad \overline{\lambda_{2,2}} = \sum_{r=1}^{\infty} r^2 D_2^r\ /Mf_2$

$$\frac{dV_w\overline{\lambda_{2,2}}}{dt} = \rho\overline{\lambda_{2,1}} - \rho\overline{\lambda_{2,2}} - 2k_{des}\overline{\lambda_{2,2}} + (V_w k_{trM}[M]_p\overline{\mu_{2,2}} + V_w k_{trT}[Tr]_p\overline{\mu_{2,2}})\frac{Mf_d}{Mf_2} - \frac{V_w}{N_A v}k_t\overline{\lambda_{2,2}}$$

$$+F_{in,ri}w_w^f\frac{\overline{\lambda_{2,2}^f}}{\rho_w} - \frac{\overline{\lambda_{2,2}}V_wQ_{out,ri}}{M_T}\rho_{ri} \qquad \text{(S3ar)}$$

Dimensionless versions of the additional transfer to polymer and double bond polymerization terms

Live Polymer

$\bar{\mu}_{1,1}$

$$\frac{dV_w\bar{\mu}_{1,1}}{dt} = \cdots + \left[-k_{trp}\bar{\lambda}_{1,1}\ \bar{\mu}_{1,1}Mf_1 + k_{trp}\bar{\lambda}_{2,1}\bar{\mu}_{0,1}Mf_2 + k_{db}F_1\bar{\lambda}_{2,1}\bar{\mu}_{0,1}Mf_2\right]\frac{1}{\overline{N_1}*Mf_d}\frac{V_w}{N_A v} \qquad \text{(S3as)}$$

$\bar{\mu}_{2,1}$

$$\frac{dV_w\bar{\mu}_{2,1}}{dt} = \cdots + \left[-k_{trp}\bar{\lambda}_{1,1}\bar{\mu}_{2,1}Mf_1 + k_{trp}\bar{\lambda}_{3,1}\bar{\mu}_{0,1}Mf_2 + k_{db}F_1\bar{\lambda}_{3,1}\bar{\mu}_{0,1}Mf_2 + 2k_{db}F_1\bar{\lambda}_{2,1}\bar{\mu}_{1,1}Mf_2\right]\frac{1}{\overline{N_1}*Mf_d}\frac{V_w}{N_A v} \qquad \text{(S3at)}$$

$\bar{\mu}_{1,2}$

$$\frac{dV_w\bar{\mu}_{1,2}}{dt} = \cdots + \left[-k_{trp}\bar{\lambda}_{1,2}\bar{\mu}_{1,2}Mf_1 + k_{trp}\bar{\lambda}_{2,2}\bar{\mu}_{0,2}Mf_2 + k_{db}F_1\bar{\lambda}_{2,2}\bar{\mu}_{0,2}Mf_2\right]\frac{2}{\overline{N_2}Mf_d}\frac{V_w}{N_A v} \qquad \text{(S3au)}$$

$\bar{\mu}_{2,2}$

$$\frac{dV_w\bar{\mu}_{2,2}}{dt} = \cdots + \Big[-k_{trp}\bar{\lambda}_{1,2}\bar{\mu}_{2,2}Mf_1 + k_{trp}\bar{\lambda}_{3,2}\bar{\mu}_{0,2} + k_{db}F_1\bar{\lambda}_{3,2}\bar{\mu}_{0,2}Mf_2 + 2k_{db}F_1\bar{\lambda}_{2,2}\bar{\mu}_{1,2}Mf_2\Big]\frac{2}{\overline{N_2}Mf_d}\frac{V_w}{N_A v} \qquad \text{(S3av)}$$

Dead Polymer

Notice that

$$\overline{\lambda_{0,n}} = \sum_{r=1}^{\infty} D_n^r \;/Mf_d$$

$\overline{\lambda_{0,1}}$

$$\frac{dV_w\overline{\lambda_{0,1}}}{d_t} = \ldots + -k_{db}F_1\overline{\lambda_{1,1}}\overline{\mu_{0,1}}\frac{Mf_1}{Mf_d}\frac{V_w}{\overline{N_1}N_A v} \qquad \text{(S3aw)}$$

$\overline{\lambda_{1,1}}$

$$\frac{dV_w\overline{\lambda_{1,1}}}{d_t} = \cdots + \left\{k_{trp}\left[-\overline{\lambda_{2,1}}\overline{\mu_{0,1}}\frac{Mf_2}{Mf_1} + \overline{\mu_{1,1}}\overline{\lambda_{1,1}}\right] - k_{db}F_1\overline{\lambda_{2,1}}\overline{\mu_{0,1}}\frac{Mf_2}{Mf_1}\right\}\frac{V_w}{\overline{N_1}N_A v} \qquad \text{(S3ax)}$$

$\overline{\lambda_{2,1}}$

$$\frac{dV_w\overline{\lambda_{2,1}}}{d_t} = \cdots + \left\{k_{trp}\left[-\frac{\lambda_{3,1}\overline{\mu_{0,1}}}{Mf_2} + \overline{\mu_{2,1}}\overline{\lambda_{1,1}}\frac{Mf_1}{Mf_2}\right] - k_{db}F_1\overline{\lambda_{3,1}}\overline{\mu_{0,1}}\frac{Mf_2}{Mf_1}\right\}\frac{V_w}{\overline{N_1}N_A v} \qquad \text{(S3ay)}$$

$\overline{\lambda_{0,2}}$

$$\frac{dV_w\overline{\lambda_{0,2}}}{d_t} = \cdots + -k_{db}F_1\overline{\lambda_{1,2}}\overline{\mu_{0,2}}\frac{Mf_1}{Mf_d}\frac{V_w}{\overline{N_1}N_A v} \qquad \text{(S3az)}$$

$\overline{\lambda_{1,2}}$

$$\frac{dV_w\overline{\lambda_{1,2}}}{d_t} = \cdots + \left\{k_{trp}\left[-\overline{\lambda_{2,2}}\overline{\mu_{0,2}}\frac{Mf_2}{Mf_1} + \overline{\mu_{1,2}}\overline{\lambda_{1,2}}\right] - k_{db}F_1\overline{\lambda_{2,2}}\overline{\mu_{0,2}}\frac{Mf_2}{Mf_1}\right\}\frac{2V_w}{\overline{N_2}N_A v} \tag{S3ba}$$

$\overline{\lambda_{2,2}}$

$$\frac{dV_w\overline{\lambda_{2,2}}}{d_t} = \cdots + \left\{k_{trp}\left[-\frac{\lambda_{3,2}\overline{\mu_{0,2}}}{Mf_2} + \overline{\mu_{2,2}}\overline{\lambda_{1,2}}\frac{Mf_1}{Mf_2}\right] - k_{db}F_1\overline{\lambda_{3,2}}\overline{\mu_{0,2}}\frac{Mf_2}{Mf_1}\right\}\frac{2V_w}{\overline{N_2}N_A v} \tag{S3bb}$$

SM4. Effects of changes on the initiator and activator concentrations in the SBR case

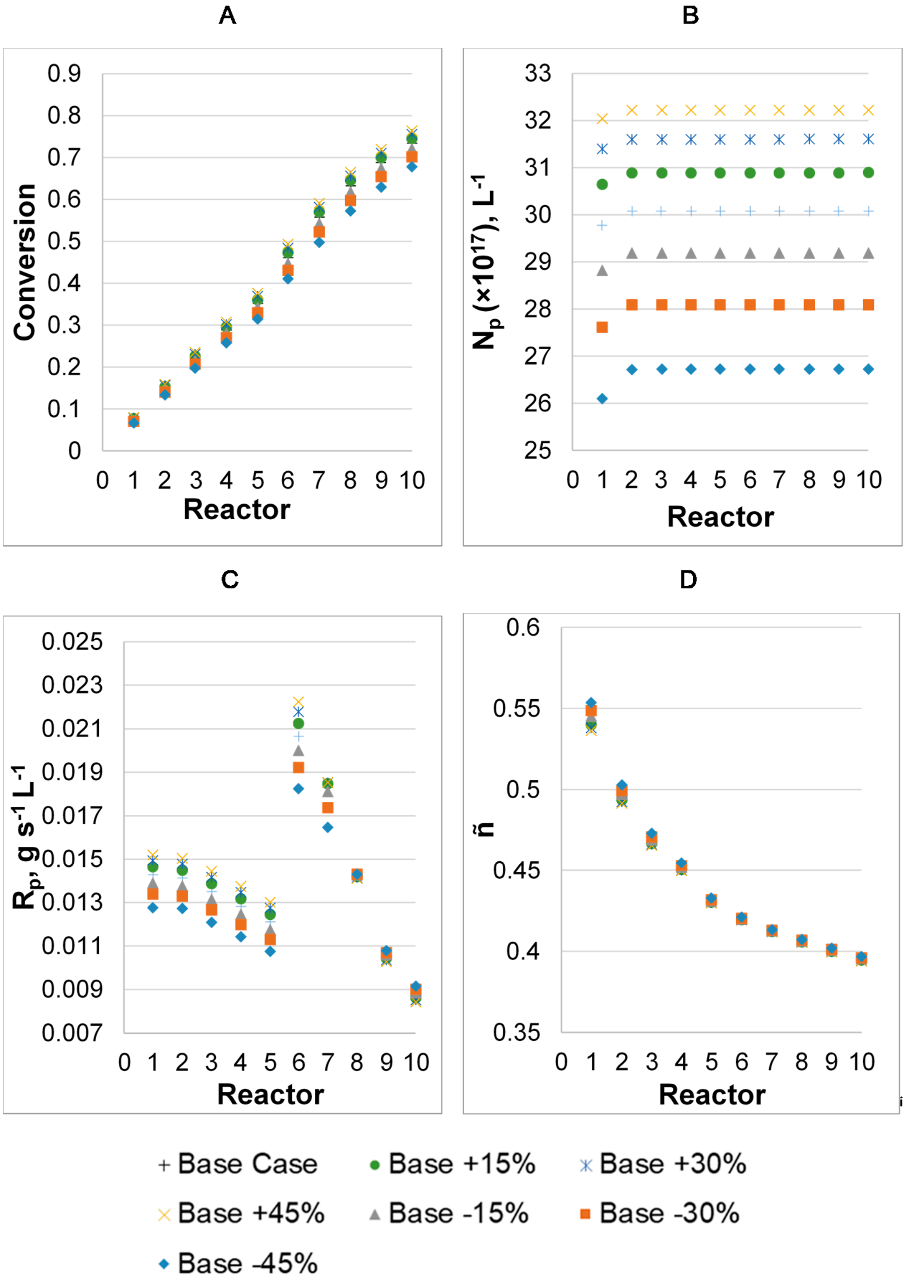

Figure S.1. Effect of the simultaneous variation of initiator and activator 1 (from -45% to +45%) on conversion (A), number of particles N_{p} (B), rate of polymerization R_{p} (C), and average number of radicals per particle $\bar{n}$ (D), along the reactor train with respect to the base case in SBR production.

SM5. Mayo-Lewis plot of F_1 vs f_1 for the NBR case

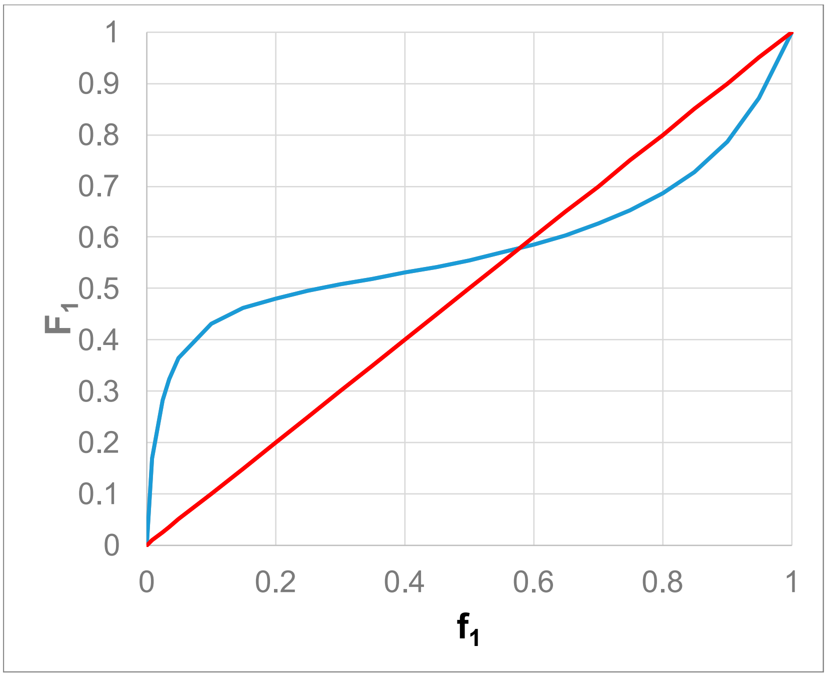

Figure S.2 Mayo-Lewis plot (blue line) of the instantaneous copolymer composition F_1 vs. monomer feed composition f_1 for the butadiene (1) – acrylonitrile (2) system using reactivity ratios $r_1 = 0.30$, $r_2=0.04$. The red line is only a reference to locate the azeotropic composition.