POLYMERS

SUPPLEMENTARY MATERIAL

1. Polymerization Rate Functions

Initiator

\[ r_i = -k_a I \]  
(S1)

Monomer- Fractional i-th Monomer Conversion (Y.)

\[ r_m = \sum_{j=1}^{2} (k_{pji} + k_{mji}) M_i R_{j,m}^i + k_a M_j^2 \delta(2 - i) \]  
(S2)

Macromolecular Species Balance

\[ r_{\text{mac}} = 2f k_a I - \sum_{j=1}^{2} k_j R^i \]  
(S3)

\[ r_{R_i,m} = \left( k_{a} R^i M_i + \sum_{j=1}^{2} k_{mji} R_{j,m}^i \right) \delta(n+i-2,m+1-i) + \sum_{j=1}^{2} k_{pji} M_i R_{j,n+i-2,m+1-i}^i + \sum_{j=1}^{2} k_{pji} M_j R_{j,n,m}^i - A_i R_{i,m}^i \]  
(S4)

\[ r_{D_{a,m}} = \sum_{i=1}^{2} \left( A_i - \frac{1}{2} \sum_{j=1}^{2} \sum_{k=1}^{2} k_{mji} R_{j,k}^i \right) R_{i,m}^i + \frac{1}{2} \sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{k=1}^{2} k_{mji} \sum_{r=1}^{m} \sum_{q=1}^{m} R_{i,r}^j R_{j,r,q}^i - \sum_{i=1}^{2} B_i \]  
(S5)

\[ A_i = \sum_{i=1}^{2} k_{mji} M_j + (k_{a} + k_{dji}) R_{j,0}^i + \sum_{i=1}^{2} k_{pji} \sum_{r=0}^{m} \sum_{q=0}^{m} \delta^{(i-j)} q^i \delta^{(2-i)} r^j D_{i,j}^i; i = 1,2 \]  
(S6)

\[ B_i = \sum_{i=1}^{2} k_{mji} R_{j,0}^i n^{(i-j)} m^{i-1} D_{a,m}; i = 1,2 \]  
(S7)

where : \( R_{0,0}^i \) is the total concentration of the i-th type radicals: \( R_{0,0}^i = \sum_{r=1}^{m} \sum_{q=0}^{m} R_{r,q}^i \)

and \( \delta(n,m) = \delta(n) \delta(m) \) is the Kronecker delta

2. Rate Functions for the Moment Equations of the Joint Chain Length-Copolymer Composition distribution

\[ r_{\lambda_m} = \left( k_{a} R^i M_i + \sum_{j=1}^{2} k_{mji} M_j \lambda_{0,0}^i \right) \delta(m) + \sum_{i=1}^{2} \sum_{j=1}^{2} k_{pji} M_i \left[ (2-i) \sum_{r=1}^{m} \sum_{m} \lambda_{r,m}^i + (i-1) \sum_{r=1}^{m} \sum_{m} \lambda_{r,m}^i \right] \]  
(S8)

\[-k_{mji} M_j \lambda_{0,0}^i + \sum_{j=1}^{2} k_{pji} M_j \lambda_{0,0}^i - \sum_{j=1}^{2} k_{mji} M_j \lambda_{0,0}^i + B_i + 3k_{a} M_j^2 \delta(n+i-2,m+1-i) ; n, m = 0,1 \]  
(S9)

\[ r_{\lambda_m} = \sum_{j=1}^{2} k_{pji} M_j \left[ (2-i) \sum_{r=1}^{m} \sum_{m} \lambda_{r,m}^j + (i-1) \sum_{r=1}^{m} \sum_{m} \lambda_{r,m}^j \right] - \sum_{j=1}^{2} k_{mji} M_j \lambda_{0,0}^j - \sum_{j=1}^{2} k_{mji} M_j \lambda_{0,0}^i \]  
(S10)

\[ A_i = \sum_{i=1}^{2} k_{mji} M_j + (k_{a} + k_{dji}) \lambda_{0,0}^i + \sum_{j=1}^{2} k_{pji} \sum_{r=0}^{m} \sum_{q=0}^{m} \delta^{(i-j)} q^i \delta^{(2-i)} r^j \mu_{0,0}^{j-1}; i = 1,2 \]
3. Variation of the reaction volume

The volume of the reacting mixture \((V)\) was calculated by the following equation:

\[
\frac{1}{V} \frac{dV}{dt} = -\varepsilon \left(\frac{dX_{\text{cum}}}{dt}\right) \frac{1}{1 - \varepsilon X_{\text{cum}}} \quad (S12)
\]

with \(\varepsilon = \frac{\rho_p - \rho_m}{\rho_p} \quad \text{and} \quad X_{\text{cum}} = \sum_{i=1}^{2} M_i \frac{V}{V} M_i \sum_{i=1}^{2} M_i \frac{V}{V} M_i \quad (S13)\)

Where \(\rho_p\) is the density of co-polymer, directly calculated from the homopolymers densities and the mean copolymer composition and \(\rho_m\) is the monomer’s mixture density calculated from the monomer’s densities by using a simple addition rule.