polymers

MDPI

SUPPLEMENTARY MATERIAL

1. **Polymerization Rate Functions**

Initiator

$$\mathrm{r}_I = -k_d \mathrm{I} \qquad \text{(S1)}$$

Monomer- Fractional i-th Monomer Conversion (Y_i)

$$\mathrm{r}_{pi} = \sum_{j=1}^{2}\left(k_{pij} + k_{fmij}\right)\mathrm{M}_i \mathrm{R}^j_{0,0} + k_{th}\mathrm{M}_2^3 \delta(2-i) \qquad \text{(S2)}$$

Macromolecular Species Balance

$$\mathrm{r}_{R^\bullet} = 2\mathrm{fk_d I} - \sum_{j=1}^{2} k_{Ij}\mathrm{R}^\bullet \mathrm{M}_j = 0 \qquad \text{(S3)}$$

$$\mathrm{r}_{R^i_{n,m}} = \left(k_{iI}\mathrm{R}^\bullet \mathrm{M}_i + \sum_{j=1}^{2} k_{fmji}\mathrm{M}_i \mathrm{R}^i_{0,0}\right)\delta(n+i-2, m+1-i) + \sum_{j=1}^{2} k_{pji}\mathrm{M}_i \mathrm{R}^j_{n+i-2,m+1-i} + \sum_{j=1}^{2} k_{pji}\mathrm{M}_j \mathrm{R}^i_{n,m} - \mathrm{A}_i \mathrm{R}^i_{n,m} + \mathrm{B}_i + 3k_{th}\mathrm{M}_2^3 \delta(n+i-2, m+1-i) \qquad \text{(S4)}$$

$$\mathrm{r}_{D_{n.m}} = \sum_{i=1}^{2}\left(\mathrm{A}_i - \sum_{j=1}^{2} k_{tcij}\mathrm{R}^j_{0,0}\right)\mathrm{R}^i_{n,m} + \frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2} k_{tcij}\sum_{r=1}^{n-1}\sum_{q=1}^{m-1}\mathrm{R}^i_{r,q}\mathrm{R}^j_{n-r,m-q} - \sum_{i=1}^{2}\mathrm{B}_i \qquad \text{(S5)}$$

$$\mathrm{A}_i = \sum_{j=1}^{2} k_{fmij}\mathrm{M}_j + (k_{tcij} + k_{tdij})\mathrm{R}^j_{0,0} + \sum_{j=1}^{2} k_{fpij}\sum_{r=0}^{\infty}\sum_{q=0}^{\infty} r^{i\delta(i-1)} q^{i-1}\mathrm{D}_{r,q};\, i = 1,2 \qquad \text{(S6)}$$

$$\mathrm{B}_i = \sum_{j=1}^{2} k_{fpij}\mathrm{R}^j_{0,0} n^{i\delta(i-1)} m^{i-1}\mathrm{D}_{n,m};\, i = 1,2 \qquad \text{(S7)}$$

where : $\mathrm{R}^i_{0,0}$ is the total concentration of the i-th type radicals: $\mathrm{R}^i_{0,0} = \sum_{r=0}^{\infty}\sum_{q=0}^{\infty}\mathrm{R}^i_{r,q}$

and *δ(n,m)*= *δ(n) δ(m)* is the Kronecker delta

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

$$\mathrm{r}_{\lambda^i_{nm}} = \left(k_{iI}\mathrm{R}^\bullet \mathrm{M}_i + \sum_{j=1}^{2} k_{fmji}\mathrm{M}_i \lambda^i_{0,0}\right)\delta(m) + \sum_{j=1}^{2} k_{pji}\mathrm{M}_i\left[(2-i)\sum_{r}^{n}\binom{n}{r}\lambda^j_{rm} + (i-1)\sum_{r}^{m}\binom{r}{m}\lambda^j_{nr}\right] - \sum_{j=1}^{2} k_{pji}\mathrm{M}_j \lambda^i_{nm} - \mathrm{A}'_i \lambda^i_{nm} + \mathrm{B}_i + 3k_{th}\mathrm{M}_2^3 \delta(n+i-2, m+1-i) \quad ;\ n,m = 0,1 \qquad \text{(S8)}$$

$$\mathrm{r}_{\mu_{nm}} = \sum_{j=1}^{2} k_{pji}\mathrm{M}_i\left[(2-i)\sum_{r}^{n}\binom{n}{r}\lambda^j_{rm} + (i-1)\sum_{r}^{m}\binom{r}{m}\lambda^j_{nr}\right] - \sum_{j=1}^{2} k_{pji}\mathrm{M}_j \lambda^i_{nm} - \sum_{j=1}^{2}\sum_{i=1}^{2} k_{tcij}\lambda^j_{00}\lambda^i_{nm} + \frac{1}{2}\sum_{i=1}^{2}\sum_{j=1}^{2} k_{tcij}\sum_{r=1}^{n}\sum_{q=1}^{m}\binom{n}{r}\binom{m}{q}\lambda^i_{rq}\lambda^j_{n-r,m-q} \qquad \text{(S9)}$$

$$\mathrm{A}'_i = \sum_{j=1}^{2}\left(k_{fmij}\mathrm{M}_j + (k_{tcij} + k_{tdij})\lambda^j_{00}\right) + \sum_{j=1}^{2} k_{fpij}\sum_{r=0}^{\infty}\sum_{q=0}^{\infty}\mu_{10}{}^{i\delta(i-1)}\mu_{01}{}^{i-1};\, i = 1,2 \qquad \text{(S10)}$$

$$B_i = \sum_{j=1}^{2} k_{fpij} \lambda_{00}^{j} \mu_{n+1,m}^{i\delta(i-1)} \mu_{n,m+1}^{(i-1)}; i = 1,2 \quad \text{(S11)}$$

3. Variation of the reaction volume

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

$$\frac{1}{V}\frac{dV}{dt} = \frac{-\varepsilon(dX_{cum}/dt)}{1-\varepsilon X_{cum}} \quad \text{(S12)}$$

$$\text{with} \quad \varepsilon = \frac{\rho_p - \rho_m}{\rho_p} \quad X_{cum} = \sum_{i=1}^{2} M_i V MW_i \Big/ \sum_{i=1}^{2} M_{i0} V_0 MW_i \quad \text{(S13)}$$

Where ρ_p is the density of co-polymer, directly calculated from the homopolymers densities and the mean copolymer composition and ρ_m is the monomer's mixture density calculated from the monomer's densities by using a simple addition rule.