Supplementary Material

Theoretical kinetic model

The reaction mechanism followed in this work is summarized in Table 1.

Table A1. Typical simple kinetic mechanism of free-radical polymerization

Initiation

$$I \xrightarrow{k_d} 2PR^{\bullet}$$

$$PR^{\bullet} + M \xrightarrow{k_I} P_1^{\bullet}$$

Propagation

$$P_n^{\bullet} + M \xrightarrow{k_p} P_{n+1}^{\bullet}$$

Depropagation

$$P_{n+1}^{\bullet} \xrightarrow{k_r} P_n^{\bullet} + M$$

Chain transfer to monomer

$$P_n^{\bullet} + M \xrightarrow{k_{fM}} D_n + M^{\bullet}$$
$$M^{\bullet} + M \xrightarrow{k_{pM}} P_1^{\bullet}$$

Termination by combination or disproportionation

$$P_n^{\bullet} + P_m^{\bullet} \begin{cases} \xrightarrow{k_{tc}} D_{n+m} \\ \xrightarrow{k_{td}} D_n + D_m \end{cases}$$

where, I denotes initiator, M monomer, PR^* primary radicals, P_n^* and D_n live radicals and polymer chains of length n, k_d, k_I, k_p, k_r, k_{fM}, k_{tc}, k_{td}, the rate constants for the initiator decomposition, chain initiation reaction, propagation, depropagation, chain transfer to monomer, termination by combination and disproportionation, respectively.

Based on the reaction mechanism illustrated in Table A1, the equations describing the mass balances of species in a batch isothermal reactor can be derived (Table A2).

Table A2. Species mass balance equations in an isothermal batch reactor

Initiator

$$\frac{1}{V}\frac{d(VI)}{dt} = -k_d I$$

Monomer

$$\frac{1}{V}\frac{d(VM)}{dt} = -\left(k_p + k_{fM}\right)MP_0$$

Macromolecular Species Balance

$$\frac{1}{V}\frac{d\left(VPR^{\bullet}\right)}{dt} = 2fk_d I - k_I PR^{\bullet} M = 0$$

$$\frac{1}{V}\frac{d(VP_n)}{dt} = \left(k_I PR^{*} M\right)\delta(n-1) + k_p M(P_{n-1} - P_n) - k_r(P_n - P_{n+1}) - \left(k_{fM} M + k_t P_0\right)P_n = 0$$

$$\frac{1}{V}\frac{d(VD_n)}{dt} = \left(k_{fM} M\right)P_n + \frac{1}{2}k_{tc}\sum_{r=1}^{n-1} P_r\, P_{n-r} + k_{td} P_0\, P_n$$

where : P_0 is the total concentration of “live” polymer: $P_0 = \sum_{r=0}^{\infty} P_r$ and $\delta(n)$ is the Kronecker delta

Following, the method of moments is employed to recast the infinite number of macromolecular chain population balance equations into a finite set of modeling equations. Moments of the chain length distribution (CLD) of the “live” radicals or “dead” polymer macromolecules are defined as:

$$\lambda_k = \sum_{n=0}^{\infty} n^k P_n \qquad ; \qquad \mu_k = \sum_{n=0}^{\infty} n^k D_n \qquad ; \qquad k=0,\, 1,\, 2$$