Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

Particle Activation/Deactivation Effect in RAFT Emulsion Polymerization of Styrene

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1. Reactions in Aqueous Phase Reactions

The seeded RAFT emulsion polymerization begins with the decomposition of the water soluble initiator (potassium persulfate in the current case). Then the primary radicals ($I\cdot$) can react with the monomer in the aqueous phase (M). The generated polymer radicals ($IM_i\cdot$), which can undergo propagation, termination and entry into the particles.[1] Table S1 shows a schematic of the important aqueous phase reactions in the current case. $T\cdot$ is the sum of the initiator derived radicals and the desorbed monomer radicals. z represents the critical degree of polymerization, at which the oligomeric radical becomes surface-active and be able to enter the particle. The degree of polymerization was estimated to be 3 for styrene according to the semi-empirical thermodynamic model based on free energies of hydration.[2]

Table S1. Kinetic scheme for the aqueous phase reactions.

Primary radical initiation	$I - I \overset{k_d}{\rightarrow} 2I\cdot$
Polymer radical initiation	$I\cdot + M \overset{k_{PI}}{\rightarrow} IM\cdot$
Propagation	$IM_i\cdot + M \overset{k_{P,aq}^{i}}{\rightarrow} IM_{i+1}\cdot$
Termination	$IM_i\cdot + T\cdot \overset{k_{t,aq}}{\rightarrow} inactive\ oligomer$
	$E\cdot + T\cdot \overset{k_{t,aq}}{\rightarrow} inactive\ oligomer$
Radical entry into particle	$IM_z\cdot + particle \overset{k_e}{\rightarrow} entry$
Monomer radical entry and exit	$E\cdot + particle \underset{k_{dM}}{\overset{k_{eE}}{\rightleftarrows}} particle - E\cdot$

The following set of rate equations for the aqueous molecules can be derived based on the aqueous kinetic described above[2]:

$$\frac{d[I]}{dt} =- k_d[I] \tag{1}$$

$$\frac{d[I\cdot]}{dt} = 2k_d[I] - k_{PI}C_W[I\cdot] \tag{2}$$

$$\frac{d[IM_1 \cdot]}{dt} = k_{PI}C_W[I \cdot] - k_{p,aq}^{1}C_W[I \cdot] - k_{t,aq}[T \cdot][IM_1 \cdot] \tag{3}$$

$$\frac{d[IM_i \cdot]}{dt} = k_{p,aq}^{i-1}C_W[IM_{i-1} \cdot] - k_{p,aq}^{i}C_W[IM_i \cdot] - k_{t,aq}[T \cdot][IM_i \cdot], \quad i < z \tag{4}$$

$$\frac{d[IM_i \cdot]}{dt} = k_{p,aq}^{i-1}C_W[IM_{i-1} \cdot] - k_{p,aq}^{i}C_W[IM_i \cdot] - \qquad = z,...j_{crit} - 1 \tag{5}$$

$$\frac{d[E \cdot]}{dt} = k_{dM}\frac{N_1^m}{N_A} - k_{eE}[E \cdot]\frac{N_{tot}}{N_A} - k_{t,aq}[T \cdot][E \cdot] \tag{6}$$

where k_d is the decomposition rate coefficient of initiator, $k_{t,aq}$ is the termination rate coeffecient in the aqueous phase, $k_{p,aq}^{i}$ is the propagation rate coefficient of the oligomeric radical with the degree of i,[1] N_{tot} and N_1^m are the number concentration of the total latex particles and the particles with a monomer radical respectively.

2. Reactions in organic particle phase

In the particle phase, the polymeric radical ($P_n \cdot$) and the monomeric radical ($M \cdot$) can react with the monomer (M). The polymeric radical can react with the monomer, generating a monomeric radical and a dead polymer chain (D_n). The polymeric radical ($P_n \cdot$) can react with the dormant polymer chain ($TFAR - P_m$), generating a new polymeric radical ($P_m \cdot$) and a new dormant polymer chain ($RAFT - P_n$). The entry of a radical into a latex particle already containing a growing radical leads to instantaneous termination, genearting a dead polymer chain. The reactions in organic phase are listed in Table S2.

Table S2. Kinetic scheme for the organic particle phase reactions.

Propagation for polymeric radical	$P_n\cdot + M \overset{k_P}{\rightarrow} P_{n+1}\cdot$ (n ≥ 2)
Chain transfer to monomer	$P_n\cdot + M \overset{k_{tr}}{\rightarrow} D_n + M\cdot$ (n ≥ 2)
Propagation for monomeric radical	$M\cdot + M \overset{k_P}{\rightarrow} P_n\cdot$ (n = 2)
RAFT reaction	$P_n\cdot + RAFT - P_m \underset{k_{frag}}{\overset{k_{add}}{\rightleftarrows}} P_n\cdot - RAFT - P_m\cdot$ $\underset{k_{add}}{\overset{k_{frag}}{\rightleftarrows}} RAFT - P_n + P_m\cdot$ (n, m ≥ 2)
Termination	$P_n\cdot + entry\,radical \rightarrow dead\,polymer$ (n ≥ 1)

In Table S2, k_P is the propagation rate coefficient, k_{tr} is the rate coeffecient for chain transfer to monomer reaction, k_{add} is the addition rate coeffecient of RAFT reaction, k_{frag} is the fragmentation rate coeffecient of RAFT reaction, respectively.

3. Monte Carlo Simulation

After calculating the imaginary times of three events, the event with the shortest imaginary time is chosen as the real event, and the reaction time increases by $\Delta t = t_i$ (t_i represents t_{entry}, t_{des} and t_{prop}). With the reaction time increment Δt, the number of the reacted monomer units can be calculated by

$$\Delta N_M = N_M\left[1 - \exp\left(-\frac{k_P\Delta t}{V_S N_A}\right)\right] \tag{7}$$

where N_M is number of the unreacted monomer inside a particle, and related to the monomer concentration in the latex particle and the swollen particle volume by

$$N_M = C_P V_S N_A \tag{8}$$

The probability of an active polymer chain connecting a monomer unit is given by

$$p = \frac{k_P N_M}{k_P N_M + k_{add} N_{XP}} \tag{9}$$

where N_{XP} is the number of the RAFT agent inside a latex particle.

During an overall active period, the active radical could react with the RAFT agent and turn into an intermediate radical. This intermediate radical is capable of reverting to an active radical by fragmentation reaction. This process could repeat multiple times before a chain stop event like radical desorption happens. The overall connection probability for this repetition of the active periods is given by[3]

$$P = \frac{2p}{1+p} \tag{10}$$

The number fraction distribution of the chain length within a single overall active period is given by[3]

$$N(r) = P^{r-1}(1-P) \qquad \text{for } r \geq 1 \tag{11}$$

The random number that follows the above distribution can be calculated by[4]

$$r = ceiling[\ln(y)/lnP] \tag{12}$$

where the symbol of $ceiling$ is indicative of the closet integer.

The determined r is added to a randomly selected chain. Then P is recalculated to generate a new r to add to a random chain. This process is repeated until the sum of r reaches ΔN_M.

The probability of the radical inside a latex particle is active is given by

$$p_{R\cdot} = \bar{t}_{R\cdot} / (\bar{t}_{R\cdot} + \bar{t}_{PXP}) \quad (13)$$

where $\bar{t}_{R\cdot}$ and $\bar{t}_{PXP}$ are the average lifetime of an active radical ($R\cdot$) and an intermediate radical (PXP), calculated by

$$\bar{t}_{R\cdot} = 1/(k_{add} C_{XP}) \quad (14)$$

$$\bar{t}_{PXP} = 1/k_{frag} \quad (15)$$

A homogeneous random number y between 0 and 1 is generated by computer. If $y < p_{R\cdot}$, the radical is active. In this case, two chains are selected randomly to form a dead chain. Otherwise, the radical is in the intermediate state. Three chains are randomly selected to form a three-armed dead chain and the number of RAFT agent (N_{XP}) decreases by one. Either way the latex particle turns into dormant.

If radical desorption is chosen as the real event, a random chain is selected and turns into dead chain (generated from the radical transfer to monomer reaction) and the latex particle turns into dormant. If monomer radical propagation instead of desorption is chosen as the real event, a random chain is selected and turns into dead chain and the latex particle stays active.

4. Coefficient of variation for N_{ad}

The distributions of N_{ad} can be well fitted by Gaussian distribution as shown in the main text. The data-fitting results of Gaussian distribution are summerized in Table S3. The coefficient of variation for N_{ad} (CV) is a standardized measure of the dispersity of N_{ad}, which is defined as the ratio of the standard deviation (σ) to $\bar{N}_{ad}$.

Table S3. Data-fitting results of Gaussian distribution in Exps 1-5.

Exp	$\bar{N}_{ad}$	σ	R^2
1	53.29	5.57	0.98
2	23.04	3.72	0.96
3	13.88	3.11	0.97
4	9.24	2.82	0.95
5	6.54	2.61	0.97

Reference

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