Supporting Information for "Coupled Stochastic Simulation of the Chain Length and Particle Size Distribution in Miniemulsion Radical Copolymerization of Styrene and N-Vinylcaprolactam"

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S1 Additional modeling details

S1.1 Calculation of (macroscopic) apparent chain length and monomer conversion dependent termination rate coefficients

Apparent chain length and monomer conversion dependent termination rate coefficients are calculated via the composite k_t model[1] as accessible via reversible addition fragmentation chain transfer – chain length dependent – termination (RAFT-CLD-T) experiments. The apparent (macroscopic) termination rate coefficient for termination between two radicals of chain length i, $k_{t,app}(i,i)$, is calculated via:

$i < i_{gel}$

$$k_{t,app}(i,i) = k_t(1,1)i^{-\alpha_S} \qquad i < i_{SL} \qquad \text{(S1)}$$

$$k_{t,app}(i,i) = k_t(1,1){i_{SL}}^{\alpha_L-\alpha_S}i^{-\alpha_L} \qquad i \geq i_{SL} \qquad \text{(S2)}$$

$i \geq i_{gel}$

$$k_{t,app}(i,i) = k_t(1,1){i_{gel}}^{\alpha_{gel}-\alpha_S}i^{-\alpha_{gel}} \qquad i < i_{SL} \qquad \text{(S3)}$$

$$k_{t,app}(i,i) = k_t(1,1){i_{SL}}^{\alpha_L-\alpha_S}{i_{gel}}^{\alpha_{gel}-\alpha_L}i^{-\alpha_{gel}} \qquad i \geq i_{SL} \qquad \text{(S4)}$$

Due to the lack of CLD-T model parameters for VCL radicals, model parameters pertaining to styrenic radicals[2] are used irrespective of the terminal unit (m_p: mass fraction of the polymer):

$\alpha_S = 0.53$

$\alpha_L = 0.15$

$\alpha_{gel} = 1.22m_p - 0.11$

$i_{SL} = 30$

$i_{gel} = 3.30{m_p}^{-2.13}$

The apparent termination rate coefficient for termination between a radical of chain length i and chain length j, $k_{t,app}(i,j)$, is approximated via:[3]

$$k_{t,app}(i,j) = \left(k_{t,app}(i,i)\, k_{t,app}(j,j)\right)^{0.5} \tag{S5}$$

It is worthwhile to highlight that in the *k*MC model no lumping of the termination possibilities is performed and an average $<k_{t,app}>$ is thus not used. Instead each termination possibility is considered individually. Indeed, for each termination possibility $k_{t,app}(i,j)$ is calculated based on the chain length of the two radicals and the polymer mass fraction and volume of the reaction locus (*i.e.* the aqueous phase or a specific particle) in which the two radicals of the termination possibility are present.

S1.2 Calculation of chain length dependent diffusion coefficients for entry and exit of oligomers

The diffusion coefficient of oligoradicals having a chain length i, $D_R(i)$, is assessed via:[4]

$$D_R(i) = \frac{D_M}{i^{0.664+2.2m_p}} \tag{S6}$$

in which D_M is the diffusion coefficient of a styrene molecule and m_p the polymer mass fraction of the reaction locus (*i.e.* the aqueous phase or a specific particle) in which the radical is present. For the calculation of the diffusion coefficient in the aqueous phase, m_p is taken equal to zero.

S1.3 Entry and exit of initiator and monomer molecules: only lumped update

In contrast to entry and exit events of radicals, which are sampled one by one, in agreement with Marien *et al.*,[5] entry and exit phenomena of the initiator (AIBN) and the comonomers (styrene and VCL) are sampled via lumped events, *i.e.* they are only taken into account after a certain number of events (*e.g.* 1000) has taken place. If this is the case, the number of I_2, styrene and VCL molecules at the current time t_i (t_{i-1} is the time of the previous update) is updated at follows:

$$X_{I_2}(i,t_i) = X_{I_2}(i,t_{i-1}) + \left[R_{entry,I_2}(i,t_{i-1}) - R_{exit,I_2}(i,t_{i-1})\right][t_i - t_{i-1}],\ i = 1,..N_p \tag{S7}$$

$$X_S(i,t_i) = X_S(i,t_{i-1}) + \left[R_{entry,S}(i,t_{i-1}) - R_{exit,S}(i,t_{i-1})\right][t_i - t_{i-1}],\ i = 1,..N_p \tag{S8}$$

$$X_V(i,t_i) = X_V(i,t_{i-1}) + \left[R_{entry,V}(i,t_{i-1}) - R_{exit,V}(i,t_{i-1})\right][t_i - t_{i-1}],\ i = 1,..N_p \tag{S9}$$

$$X_{I_2,aq}(t_i) = X_{I_2,aq}(t_{i-1}) + \left[\sum_{i=1}^{N_p} R_{exit,I_2}(i,t_{i-1}) - \sum_{i=1}^{N_p} R_{entry,I_2}(i,t_{i-1})\right][t_i - t_{i-1}] \tag{S10}$$

$$X_{s,aq}(t_i) = X_{s,aq}(t_{i-1}) + \left[\sum_{i=1}^{N_p} R_{exit,s}(i,t_{i-1}) - \sum_{i=1}^{N_p} R_{entry,s}(i,t_{i-1})\right][t_i - t_{i-1}] \tag{S11}$$

$$X_{V,aq}(t_i) = X_{V,aq}(t_{i-1}) + \left[\sum_{i=1}^{N_p} R_{exit,V}(i,t_{i-1}) - \sum_{i=1}^{N_p} R_{entry,V}(i,t_{i-1})\right][t_i - t_{i-1}] \tag{S12}$$

with $X_{I_2}(i,t_i)$, $X_S(i,t_i)$ and $X_V(i,t_i)$ the number of I_2, styrene and VCL molecules in particle i (N_p particles in total) at time t_i, $X_{I_{2,aq}}(t_i)$, $X_{S,aq}(t_i)$ and $X_{V,aq}(t_i)$ the number of I_2, styrene and VCL molecules in the aqueous phase at time t_i, $R_{entry,I_2;S;V}(i,t_{i-1})$ the entry rate (in s^{-1}) of I_2/styrene/VCL to particle i at time t_{i-1} and $R_{exit,I_2;S;V}(i,t_{i-1})$ the exit rate (in s^{-1}) of I_2/styrene/VCL from particle i at time t_{i-1}. Note that $R_{entry,I_2;S;V}(i,t_{i-1})$ and $R_{exit,I_2;S;V}(i,t_{i-1})$ follow from:

$$R_{entry,Z}(i,t_{i-1}) = k_{entry,Z}(i,t_{i-1})\ [Z]_{aq}(t_{i-1}) \tag{S13}$$

$$R_{exit,Z}(i,t_{i-1}) = k_{exit}(i,t_{i-1}) X_Z(i,t_{i-1}) \tag{S14}$$

with $Z = I_2$, styrene or VCL and $k_{\mathrm{entry},Z}(i,t_{i-1})$ and $k_{\mathrm{exit},Z}(i,t_{i-1})$ the entry/exit rate coefficient for species Z and particle i at time t_{i-1}, so calculated using its diameter $d_{p,i}$ at time t_{i-1}.

S1.4 Entry and exit rate coefficients corresponding to a particle diameter of 200 nm

To allow a comparison with the entry/exit rate coefficients corresponding to a particle diameter at 100 nm (listed in Table 1 in the main text) the values corresponding to a particle diameter of 200 nm are listed in Table S1. For all other particle sizes the reader is referred to formulas in the footnotes of Table 1 (main text) for the calculation of the corresponding entry/exit rate coefficients.

Table S1. Entry and exit rate coefficients corresponding to a particle diameter of 200 nm.

Event	**Equation**	**k for d_p = 200 nm**
Entry of I_2	$I_{2,w} \xrightarrow{k_{entry,I}} I_{2,p}$	1.2×10^{7} L mol^{-1} s^{-1}
Entry of I	$I_w \xrightarrow{k_{entry,I}} I_p$	1.2×10^{7} L mol^{-1} s^{-1}
Entry of M_A	$M_{A,w} \xrightarrow{k_{entry,M_A}} M_{A,p}$	1.2×10^{7} L mol^{-1} s^{-1}
Entry of M_B	$M_{B,w} \xrightarrow{k_{entry,M_B}} M_{B,p}$	1.2×10^{7} L mol^{-1} s^{-1}
Entry of $M_A{}^*$	$M^*_{A,w} \xrightarrow{k_{entry,M^*_A}} M^*_{A,p}$	1.2×10^{7} L mol^{-1} s^{-1}
Entry of $M_B{}^*$	$M^*_{B,w} \xrightarrow{k_{entry,M^*_B}} M^*_{B,p}$	1.2×10^{7} L mol^{-1} s^{-1}
Entry of R_i	$R_{i,w} \xrightarrow{k_{entry,R}} R_{i,p}$	1.2×10^{7} L mol^{-1} s^{-1}
Exit of I_2	$I_{2,p} \xrightarrow{k_{exit,I_2}} I_{2,w}$	4.2×10^{-2} s^{-1}
Exit of I	$I_p \xrightarrow{k_{exit,I}} I_w$	6.0×10^{-1} s^{-1}
Exit of M_A	$M_{A,p} \xrightarrow{k_{exit,M_A}} M_{A,w}$	1.7×10^{-2} s^{-1}
Exit of $M_A{}^*$	$M^*_{A,p} \xrightarrow{k_{exit,M^*_A}} M^*_{A,w}$	1.7×10^{-2} s^{-1}
Exit of M_B	$M_{B,p} \xrightarrow{k_{exit,M_B}} M_{B,w}$	1.9×10^{-1} s^{-1}
Exit of $M_B{}^*$	$M^*_{B,p} \xrightarrow{k_{exit,M^*_B}} M^*_{B,w}$	1.9×10^{-1} s^{-1}
Exit of R_i ($i \leq i_{sol}$)	$R_{i,p} \xrightarrow{k_{exit,R}} R_{i,w}$	6.0×10^{-1} s^{-1} [c]

S2 Additional results supporting the main text

Evolution of the fraction of particles having zero, one, or two or more macroradicals (corresponding to Figure 3 in the main text)

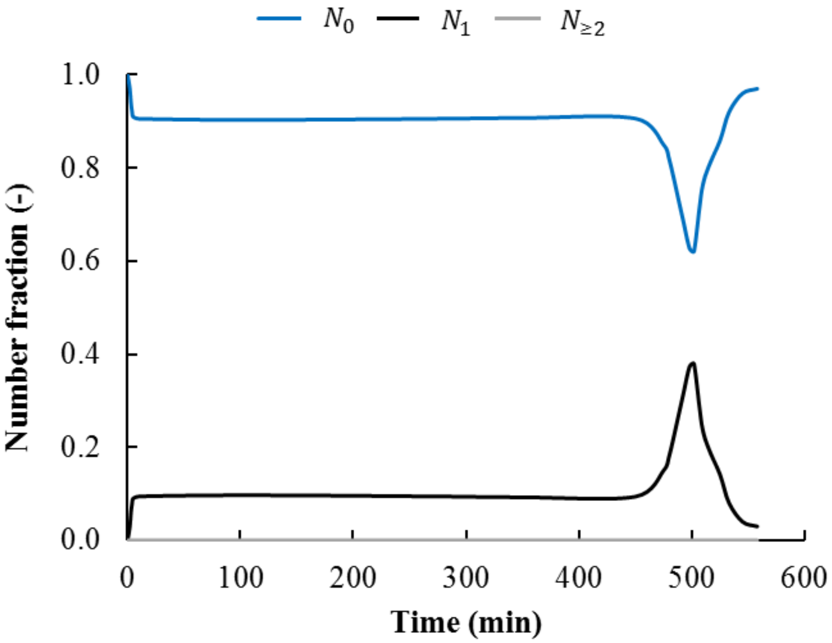

Figure S1. Evolution of the fraction of particles possessing zero (N_0; blue line), one (N_1; black line), or two or more macroradicals ($N_{\geq 2}$; grey line) corresponding to the $\bar{n}_R$ profile in Figure 3 in the main text; initial conditions: caption Figure 2 (main text); model parameters: Table 1 (main text); smoothed lines.

Evolution of the average number of macroradicals per particle for the case $\bar{d}_{p,0}$ *= 200 nm*

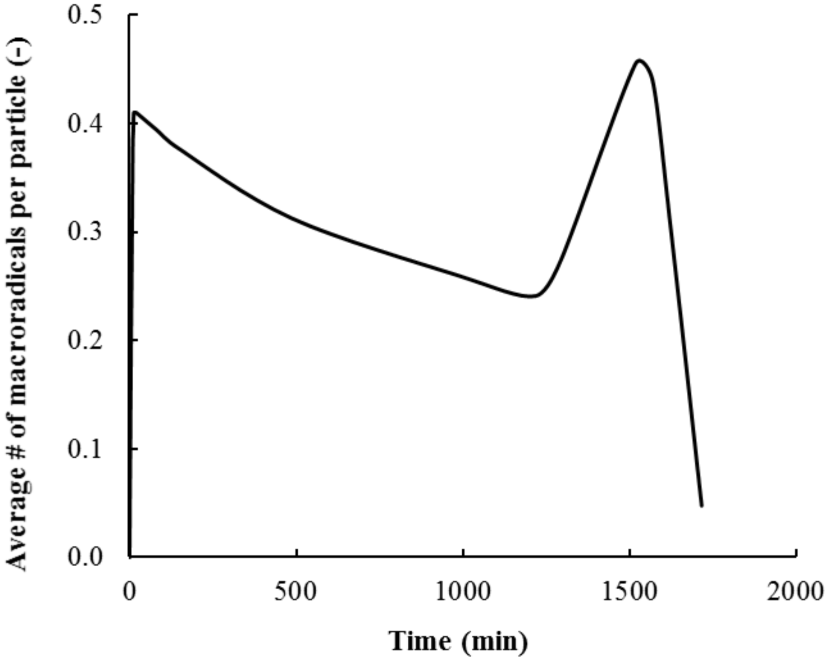

Figure S2. Evolution of the average number of macroradicals per particle corresponding to Figure 7 (main text); initial conditions: caption Figure 7 (main text); model parameters: Table 1 (main text); smoothed lines.

Evolution of the fraction of particles possessing zero, one, or two or more macroradicals for the case $\bar{d}_{p,0}$ *= 200 nm*

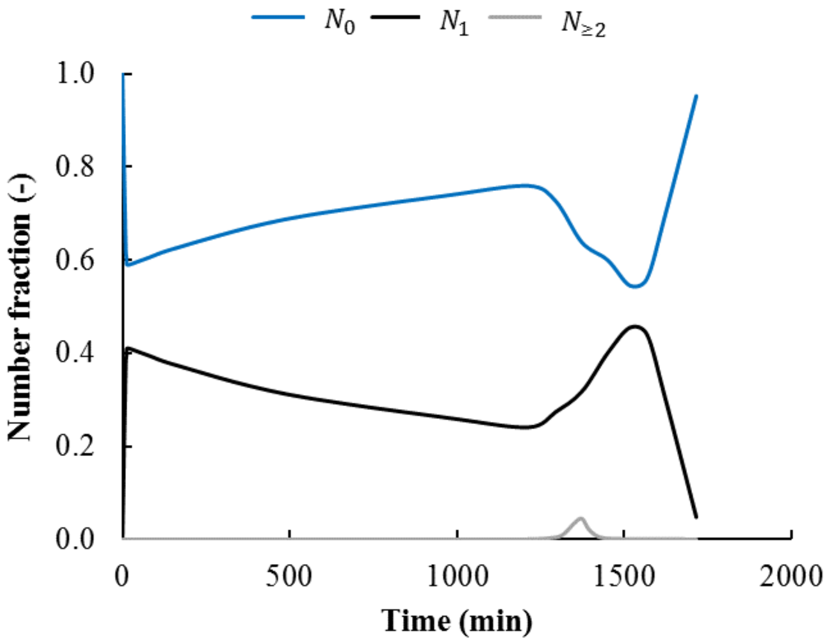

Figure S3. Evolution of the fraction of particles possessing zero (blue line), one (black line) or two or more (grey line) macroradicals corresponding to Figure 7 (main text); initial conditions: Figure 7 (main text); model parameters: Table 1 (main text); smoothed lines.

S3 References

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