

Supporting Information

Method of Moments Applied to Most-Likely High-Temperature Free-radical Polymerization Reactions

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Rate Equations for the Other Reactions

1. Propagation by tertiary radicals of type R_n^{***}

In this kind of propagation reaction, one monomer is added to a tertiary radical of the type R_n^{***} , generating a secondary radical that is one monomer unit longer than the tertiary radical. This reaction forms long branches along the backbone.



$$r_M = -k_p^t [M] \sum [R_n^{***}] = -k_p^t [M] \rho_0^{***} \quad (S2)$$

$$r_{\rho_0^{**}} = k_p^t [M] \sum (n+1)^0 [R_n^{***}] = k_p^t [M] \rho_0^{***} \quad (S3)$$

$$r_{\rho_1^{**}} = k_p^t [M] \sum (n+1)^1 [R_n^{***}] = k_p^t [M] (\rho_1^{***} + \rho_0^{***}) \quad (S4)$$

$$r_{\rho_2^{**}} = k_p^t [M] \sum (n+1)^2 [R_n^{***}] = k_p^t [M] (\rho_2^{***} + 2\rho_1^{***} + \rho_0^{***}) \quad (S5)$$

$$r_{\rho_0^{***}} = -k_p^t [M] \sum n^0 [R_n^{***}] = -k_p^t [M] \rho_0^{***} \quad (S6)$$

$$r_{\rho_1^{***}} = -k_p^t [M] \sum n^1 [R_n^{***}] = -k_p^t [M] \rho_1^{***} \quad (S7)$$

$$r_{\rho_2^{***}} = -k_p^t [M] \sum n^2 [R_n^{***}] = -k_p^t [M] \rho_2^{***} \quad (S8)$$

Here $(n+1)$ in Eqs.(S3)-(S5) reflects the fact that the reaction generates a secondary radical with length $(n+1)$ monomer units, where n in Eqs.(S6)-(S8) reflects the fact that the reaction consumes a tertiary radical of the type R_n^{***} with length n monomer units. Note that these rate equations satisfy $r_M + r_{\rho_1^{**}} + r_{\rho_1^{***}} = 0$, confirming that this reaction does not change the total number of monomer units in the system.

2. Propagation by tertiary radicals of type \tilde{R}_n^{***}

In this kind of propagation reaction, one monomer is added to a tertiary radical of the type \tilde{R}_n^{***} , generating a secondary radical that is one monomer unit longer than the tertiary radical:



The occurrence of this reaction leads to the formation of a short chain branch. The contributions of this reaction to the production rates of different species as well as rates of moments are as follows:

$$r_M = -k_p^t [M] \sum [\tilde{R}_n^{***}] = -k_p^t [M] \tilde{\rho}_0^{***} \quad (S10)$$

$$r_{\rho_0^{**}} = k_p^t [M] \sum (n+1)^0 [\tilde{R}_n^{***}] = k_p^t [M] \tilde{\rho}_0^{***} \quad (S11)$$

$$r_{\rho_1^{**}} = k_p^t [M] \sum (n+1)^1 [\tilde{R}_n^{***}] = k_p^t [M] (\tilde{\rho}_1^{***} + \tilde{\rho}_0^{***}) \quad (S12)$$

$$r_{\rho_2^{**}} = k_p^t [M] \sum (n+1)^2 [\tilde{R}_n^{***}] = k_p^t [M] (\tilde{\rho}_2^{***} + 2\tilde{\rho}_1^{***} + \tilde{\rho}_0^{***}) \quad (S13)$$

$$r_{\tilde{\rho}_0^{***}} = -k_p^t [M] \sum n^0 [\tilde{R}_n^{***}] = -k_p^t [M] \tilde{\rho}_0^{***} \quad (S14)$$

$$r_{\tilde{\rho}_1^{***}} = -k_p^t [M] \sum n^1 [\tilde{R}_n^{***}] = -k_p^t [M] \tilde{\rho}_1^{***} \quad (S15)$$

$$r_{\tilde{\rho}_2^{***}} = -k_p^t [M] \sum n^2 [\tilde{R}_n^{***}] = -k_p^t [M] \tilde{\rho}_2^{***} \quad (S16)$$

Note that the rate equations satisfy $r_M + r_{\rho_1^{**}} + r_{\tilde{\rho}_1^{***}} = 0$, confirming that the reaction does not change the total number of monomer units in the system.

3. β -Scission reaction from the left hand side of tertiary radical type R_n^{***}

In this kind of β -scission reaction, there are $(n-2)$ possible sites for scission. Like other β -scission reactions, it produces a secondary radical and a macromonomer.

$$r_{\rho_{0,L}^{***}} = -\sum \frac{1}{2} \frac{1}{n-2} k_\beta [R_n^{***}] (n-2) = -\frac{1}{2} k_\beta \rho_0^{***} \quad (S17)$$

$$r_{\rho_{1,L}^{***}} = -\sum \frac{1}{2} \frac{1}{n-2} k_\beta [R_n^{***}] n(n-2) = -\frac{1}{2} k_\beta \rho_1^{***} \quad (S18)$$

$$r_{\rho_{2,L}^{***}} = -\sum \frac{1}{2} \frac{1}{n-2} k_\beta [R_n^{***}] n^2(n-2) = -\frac{1}{2} k_\beta \rho_2^{***} \quad (S19)$$

$$r_{\rho_{0,L}^{**}} = \sum \frac{1}{2} \frac{1}{n-2} k_\beta [R_n^{***}] (n-2) = \frac{1}{2} k_\beta \rho_0^{***} \quad (S20)$$

$$r_{\rho_{1,L}^{**}} = \sum \frac{1}{2} \frac{1}{n-2} k_\beta [R_n^{***}] (1 + \dots + (n-2)) = \sum \frac{1}{2} \frac{1}{n-2} k_\beta [R_n^{***}] \frac{1}{2} (n-2)(n-1) = \frac{1}{4} k_\beta (\rho_1^{***} - \rho_0^{***}) \quad (S21)$$

$$r_{\rho_{2,L}^{**}} = \sum \frac{1}{2} \frac{1}{n-2} k_\beta [R_n^{***}] (1^2 + \dots + (n-2)^2) = \sum \frac{1}{2} k_\beta [R_n^{***}] \frac{(n-2)(n-1)(2n-3)}{6(n-2)} = \frac{1}{12} k_\beta (2\rho_2^{***} - 5\rho_1^{***} + 3\rho_0^{***}) \quad (S22)$$

$$r_{\epsilon_{0,L}} = \sum \frac{1}{2} \frac{1}{n-2} k_\beta [R_n^{***}] (n-2) = \frac{1}{2} k_\beta \rho_0^{***} \quad (S23)$$

$$r_{\epsilon_{1,L}} = \sum \frac{1}{2} \frac{1}{n-2} k_\beta [R_n^{***}] (2 + \dots + (n-1)) =$$

$$\sum \frac{1}{2} \frac{1}{n-2} k_{\beta} [R_n^{***}] \frac{1}{2} (n-2)(n+1) = \frac{1}{4} k_{\beta} (\rho_1^{***} + \rho_0^{***}) \quad (\text{S24})$$

$$r_{\epsilon_{2,L}} = \sum \frac{1}{2} \frac{1}{n-2} k_{\beta} [R_n^{***}] (2^2 + \dots + (n-1)^2) =$$

$$\sum \frac{1}{2} k_{\beta} [R_n^{***}] \frac{(n-2)(2n^2+n+3)}{6(n-2)} = \frac{1}{12} k_{\beta} (2\rho_2^{***} + \rho_1^{***} + 3\rho_0^{***}) \quad (\text{S25})$$

These equations satisfy $r_{\rho_1^{***}} + r_{\rho_1^{**}} + r_{\epsilon_1} = 0$, confirming that this reaction does not change the total number of monomer units.

4. Chain transfer from a tertiary radical type R_n^{***} to a solvent

In this reaction, a tertiary radical formed by transfer to polymer abstracts a hydrogen from a solvent molecule, leading to the formation of a dead polymer chain and an active solvent-based radical:



The following rate equations describe the contributions of this reaction to the production and consumption of different species as well as the relevant moments:

$$r_s = -k_{tr,s}^t [S] \rho_0^{***} \quad (\text{S27})$$

$$r_{R_0^*} = k_{tr,s}^t [S] \rho_0^{***} \quad (\text{S28})$$

$$r_{\rho_0^{**}} = r_{\rho_1^{**}} = r_{\rho_2^{**}} = 0 \quad (\text{S29})$$

$$r_{\rho_0^{***}} = -k_{tr,s}^t [S] \rho_0^{***} \quad (\text{S30})$$

$$r_{\rho_1^{***}} = -k_{tr,s}^t [S] \rho_1^{***} \quad (\text{S31})$$

$$r_{\rho_2^{***}} = -k_{tr,s}^t [S] \rho_2^{***} \quad (\text{S32})$$

$$r_{\delta_0} = k_{tr,s}^t [S] \rho_0^{***} \quad (\text{S33})$$

$$r_{\delta_1} = k_{tr,s}^t [S] \rho_1^{***} \quad (\text{S34})$$

$$r_{\delta_2} = k_{tr,s}^t [S] \rho_2^{***} \quad (\text{S35})$$

5. Chain transfer from a tertiary radical type \tilde{R}_n^{***} to a solvent

In this reaction, a tertiary radical formed through backbiting abstracts a hydrogen from a solvent molecule, resulting in the formation of a dead polymer chain and an active solvent-based radical:



$$r_s = -k_{tr,s}^t [S] \tilde{\rho}_0^{***} \quad (\text{S37})$$

$$r_{\rho_0^{**}} = r_{\rho_1^{**}} = r_{\rho_2^{**}} = 0 \quad (\text{S38})$$

$$r_{\tilde{\rho}_0^{***}} = -k_{tr,s}^t [S] \tilde{\rho}_0^{***} \quad (\text{S39})$$

$$r_{\tilde{\rho}_1^{***}} = -k_{tr,s}^t [S] \tilde{\rho}_1^{***} \quad (S40)$$

$$r_{\tilde{\rho}_2^{***}} = -k_{tr,s}^t [S] \tilde{\rho}_2^{***} \quad (S41)$$

$$r_{\delta_0} = k_{tr,s}^t [S] \tilde{\rho}_0^{***} \quad (S42)$$

$$r_{\delta_1} = k_{tr,s}^t [S] \tilde{\rho}_1^{***} \quad (S43)$$

$$r_{\delta_2} = k_{tr,s}^t [S] \tilde{\rho}_2^{***} \quad (S44)$$

$$r_{R_0^*} = k_{tr,s}^t [S] \tilde{\rho}_0^{***} \quad (S45)$$

6. Chain transfer from a tertiary radical type R_n^{***} to a monomer

In this transfer to monomer reaction, a macroradical of type R_n^{***} abstracts a hydrogen from a monomer leading to the formation of a dead polymer chain with the same number of monomer units and the generation of a secondary radical with one monomer unit:



The following rate equations describe the contributions of this reaction to the production and consumption of different species as well as the relevant moments:

$$r_{R_1^{**}} = k_{tr,M}^t [M] \rho_0^{***} \quad (S47)$$

$$r_M = -k_{tr,M}^t [M] \rho_0^{***} \quad (S48)$$

$$r_{\rho_0^{**}} = r_{\rho_1^{**}} = r_{\rho_2^{**}} = k_{tr,M}^t [M] \rho_0^{***} \quad (S49)$$

$$r_{\rho_0^{***}} = -k_{tr,M}^t [M] \rho_0^{***} \quad (S50)$$

$$r_{\rho_1^{***}} = -k_{tr,M}^t [M] \rho_1^{***} \quad (S51)$$

$$r_{\rho_2^{***}} = -k_{tr,M}^t [M] \rho_2^{***} \quad (S52)$$

$$r_{\delta_0} = k_{tr,M}^t [M] \rho_0^{***} \quad (S53)$$

$$r_{\delta_1} = k_{tr,M}^t [M] \rho_1^{***} \quad (S54)$$

$$r_{\delta_2} = k_{tr,M}^t [M] \rho_2^{***} \quad (S55)$$

This reaction should does not change the total number of monomer units in the system; $r_M + r_{\rho_1^{**}} + r_{\rho_1^{***}} + r_{\delta_1} = 0$ holds.

7. Chain transfer from a tertiary radical type \tilde{R}_n^{***} to a monomer

In this transfer to monomer reaction, a macroradical of type \tilde{R}_n^{***} abstracts a hydrogen from a monomer leading to the formation of a dead polymer chain with the same number of monomer units and the generation of a secondary radical with one monomer unit:



The following rate equations describe the contributions of this reaction to the production and consumption of different species as well as the relevant moments:

$$r_{R_1^{***}} = k_{tr,M}^t [M] \tilde{\rho}_0^{***} \quad (S57)$$

$$r_M = -k_{tr,M}^t [M] \tilde{\rho}_0^{***} \quad (S58)$$

$$r_{\rho_0^{***}} = r_{\rho_1^{***}} = r_{\rho_2^{***}} = k_{tr,M}^t [M] \tilde{\rho}_0^{***} \quad (S59)$$

$$r_{\tilde{\rho}_0^{***}} = -k_{tr,M}^t [M] \tilde{\rho}_0^{***} \quad (S60)$$

$$r_{\tilde{\rho}_1^{***}} = -k_{tr,M}^t [M] \tilde{\rho}_1^{***} \quad (S61)$$

$$r_{\tilde{\rho}_2^{***}} = -k_{tr,M}^t [M] \tilde{\rho}_2^{***} \quad (S62)$$

$$r_{\delta_0} = k_{tr,M}^t [M] \tilde{\rho}_0^{***} \quad (S63)$$

$$r_{\delta_1} = k_{tr,M}^t [M] \tilde{\rho}_1^{***} \quad (S64)$$

$$r_{\delta_2} = k_{tr,M}^t [M] \tilde{\rho}_2^{***} \quad (S65)$$

As expected, this reaction does not change the total number of monomer units: $r_M + r_{\rho_1^{***}} + r_{\tilde{\rho}_1^{***}} + r_{\delta_1} = 0$.

8. Chain transfer from a tertiary radical type R_n^{***} to a dead polymer chain

In this reaction, a tertiary radical of type R_n^{***} abstracts a hydrogen from a dead polymer chain, leading to the formation of a new dead polymer chain and a new tertiary radical of type R_m^{***} :



This reaction has a reactant monoradical that is different from its counterpart in reaction (120). The reactions (S66) and (120) also differ in their rate coefficients; the rate of the reaction (S66) is around three orders of magnitude lower than that of the reaction (120). The following rate equations describe the contributions of this reaction to the production and consumption of different species as well as the relevant moments:

$$r_{\rho_0^{***}} = 0 \quad (S67)$$

$$r_{\rho_1^{***}} = -k_{tr,P}^t \rho_1^{***} \delta_1 + k_{tr,P}^t \delta_2 \rho_0^{***} \quad (S68)$$

$$r_{\rho_2^{***}} = -k_{tr,P}^t \rho_2^{***} \delta_1 + k_{tr,P}^t \delta_3 \rho_0^{***} \quad (S69)$$

$$r_{\delta_0} = 0 \quad (S70)$$

$$r_{\delta_1} = -k_{tr,P}^t \rho_0^{***} \delta_2 + k_{tr,P}^t \delta_1 \rho_1^{***} \quad (S71)$$

$$r_{\delta_2} = -k_{tr,P}^t \rho_0^{***} \delta_3 + k_{tr,P}^t \delta_1 \rho_2^{***} \quad (S72)$$

Again, the sum of the first moments here is zero, which confirms this reaction does not change the total number of monomer units in the system.

9. Chain transfer from a tertiary radical type \tilde{R}_n^{***} to a dead polymer chain

In this reaction, a tertiary radical of type \tilde{R}_n^{***} abstracts a hydrogen from a dead polymer chain, leading to the formation of a new dead polymer chain and a new tertiary radical of type R_m^{***} :



The following rate equations describe the contributions of this reaction to the production and consumption of different species as well as the relevant moments:

$$r_{\tilde{\rho}_0^{***}} = -k_{tr,p}^t \tilde{\rho}_0^{***} \delta_1 \quad (S74)$$

$$r_{\tilde{\rho}_1^{***}} = -k_{tr,p}^t \tilde{\rho}_1^{***} \delta_1 \quad (S75)$$

$$r_{\tilde{\rho}_2^{***}} = -k_{tr,p}^t \tilde{\rho}_2^{***} \delta_1 \quad (S76)$$

$$r_{\rho_0^{***}} = k_{tr,p}^t \tilde{\rho}_0^{***} \delta_1 \quad (S77)$$

$$r_{\rho_1^{***}} = k_{tr,p}^t \tilde{\rho}_0^{***} \delta_2 \quad (S78)$$

$$r_{\rho_2^{***}} = k_{tr,p}^t \tilde{\rho}_0^{***} \delta_3 \quad (S79)$$

$$r_{\delta_0} = 0 \quad (S80)$$

$$r_{\delta_1} = -k_{tr,p}^t \tilde{\rho}_0^{***} \delta_2 + k_{tr,p}^t \delta_1 \tilde{\rho}_1^{***} \quad (S81)$$

$$r_{\delta_2} = -k_{tr,p}^t \tilde{\rho}_0^{***} \delta_3 + k_{tr,p}^t \delta_1 \tilde{\rho}_2^{***} \quad (S82)$$

This reaction does not change the total number of monomer units in the system either; $r_{\tilde{\rho}_1^{***}} + r_{\rho_1^{***}} + r_{\delta_1} = 0$ holds.

10. Chain transfer from a tertiary radical type R_n^{***} to a macromonomer

This is a chain transfer reaction to a macromonomer by a macroradical containing a tertiary radical of type R_n^{***} . The occurrence of the reaction causes the generation of the same type of tertiary radical, R_m^{***} , and a dead saturated polymer chain:



The following rate equations describe the contributions of this reaction to the production and consumption of different species as well as the relevant moments:

$$r_{\rho_0^{***}} = 0 \quad (S84)$$

$$r_{\rho_1^{***}} = -k_{tr,p}^t \rho_1^{***} (\epsilon_1 - \epsilon_0) + k_{tr,p}^t \rho_0^{***} (\epsilon_2 - \epsilon_1) \quad (S85)$$

$$r_{\rho_2^{***}} = -k_{tr,p}^t \rho_2^{***} (\epsilon_1 - \epsilon_0) + k_{tr,p}^t \rho_0^{***} (\epsilon_3 - \epsilon_2) \quad (S86)$$

$$r_{\delta_0} = k_{tr,p}^t \rho_0^{***} (\epsilon_1 - \epsilon_0) \quad (S87)$$

$$r_{\delta_1} = k_{tr,p}^t \rho_1^{***} (\epsilon_1 - \epsilon_0) \quad (S88)$$

$$r_{\delta_2} = k_{tr,p}^t \rho_2^{***} (\epsilon_1 - \epsilon_0) \quad (S89)$$

$$r_{\epsilon_0} = -k_{tr,p}^t \rho_0^{***} (\epsilon_1 - \epsilon_0) \quad (S90)$$

$$r_{\epsilon_1} = -k_{tr,p}^t \rho_0^{***} (\epsilon_2 - \epsilon_1) \quad (S91)$$

$$r_{\epsilon_2} = -k_{tr,p}^t \rho_0^{***} (\epsilon_3 - \epsilon_2) \quad (S92)$$

The sum of the first moments is zero here, which confirms that this reaction does not change the total number of monomer units in the system.

11. Chain transfer from a tertiary radical type \tilde{R}_n^{***} to a macromonomer

This reaction involves the abstraction of a tertiary hydrogen by a tertiary radical of type \tilde{R}_n^{***} from a macromonomer, leading to the generation of an R_m^{***} -type tertiary radical and a dead saturated polymer chain:



The following rate equations describe the contributions of this reaction to the production and consumption of different species as well as the relevant moments:

$$r_{\rho_0^{***}} = k_{tr,p}^t \tilde{\rho}_0^{***} (\epsilon_1 - \epsilon_0) \quad (S94)$$

$$r_{\rho_1^{***}} = k_{tr,p}^t \tilde{\rho}_0^{***} (\epsilon_2 - \epsilon_1) \quad (S95)$$

$$r_{\rho_2^{***}} = k_{tr,p}^t \tilde{\rho}_0^{***} (\epsilon_3 - \epsilon_2) \quad (S96)$$

$$r_{\tilde{\rho}_0^{***}} = -k_{tr,p}^t \tilde{\rho}_0^{***} (\epsilon_1 - \epsilon_0) \quad (S97)$$

$$r_{\tilde{\rho}_1^{***}} = -k_{tr,p}^t \tilde{\rho}_1^{***} (\epsilon_1 - \epsilon_0) \quad (S98)$$

$$r_{\tilde{\rho}_2^{***}} = -k_{tr,p}^t \tilde{\rho}_2^{***} (\epsilon_1 - \epsilon_0) \quad (S99)$$

$$r_{\delta_0} = k_{tr,p}^t \tilde{\rho}_0^{***} (\epsilon_1 - \epsilon_0) \quad (S100)$$

$$r_{\delta_1} = k_{tr,p}^t \tilde{\rho}_1^{***} (\epsilon_1 - \epsilon_0) \quad (S101)$$

$$r_{\delta_2} = k_{tr,p}^t \tilde{\rho}_2^{***} (\epsilon_1 - \epsilon_0) \quad (S102)$$

$$r_{\epsilon_0} = -k_{tr,p}^t \tilde{\rho}_0^{***} (\epsilon_1 - \epsilon_0) \quad (S103)$$

$$r_{\epsilon_1} = -k_{tr,p}^t \tilde{\rho}_0^{***} (\epsilon_2 - \epsilon_1) \quad (S104)$$

$$r_{\epsilon_2} = -k_{tr,p}^t \tilde{\rho}_0^{***} (\epsilon_3 - \epsilon_2) \quad (S105)$$

The sum of the first moments is zero here, which confirms that this reaction does not change the total number of monomer units in the system.

12. Termination by combination of a secondary radical and a tertiary radical type R_m^{***}

In this reaction, a secondary radical and a tertiary radical of the type R_m^{***} combine and form a saturated dead polymer chain that includes the monomer units of both radicals:



The following rate equations describe the contributions of this reaction to the production and consumption of different species as well as the relevant moments:

$$r_{R_0^*} = -2k_{tc}^t [R_0^*] \rho_0^{***} \quad (S107)$$

$$r_{R_1^{**}} = -2k_{tc}^t [R_1^{**}] \rho_0^{***} \quad (S108)$$

$$r_{R_2^{**}} = -2k_{tc}^t [R_2^{**}] \rho_0^{***} \quad (S109)$$

$$r_{\rho_0^{**}} = -2k_{tc}^t \rho_0^{**} \rho_0^{***} \quad (S110)$$

$$r_{\rho_1^{**}} = -2k_{tc}^t \rho_1^{**} \rho_0^{***} \quad (S111)$$

$$r_{\rho_2^{**}} = -2k_{tc}^t \rho_2^{**} \rho_0^{***} \quad (S112)$$

$$r_{\rho_0^{***}} = -2k_{tc}^t \rho_0^{**} \rho_0^{***} \quad (S113)$$

$$r_{\rho_1^{***}} = -2k_{tc}^t \rho_0^{**} \rho_1^{***} \quad (S114)$$

$$r_{\rho_2^{***}} = -2k_{tc}^t \rho_0^{**} \rho_2^{***} \quad (S115)$$

$$r_{\delta_0} = 2k_{tc}^t \rho_0^{**} \rho_0^{***} \quad (S116)$$

$$r_{\delta_1} = 2k_{tc}^t (\rho_1^{**} \rho_0^{***} + \rho_0^{**} \rho_1^{***}) \quad (S117)$$

$$r_{\delta_2} = 2k_{tc}^t (\rho_2^{**} \rho_0^{***} + \rho_0^{**} \rho_2^{***} + 2\rho_1^{**} \rho_1^{***}) \quad (S118)$$

Here, $r_{\rho_1^{**}} + r_{\rho_1^{***}} + r_{\delta_1} = 0$, confirming that this reaction does not change the total number of monomer units, as it should not.

13. Termination by combination of a secondary radical and a tertiary radical type \tilde{R}_m^{***}

In this reaction, a secondary radical and a tertiary radical of the type \tilde{R}_m^{***} combine and form a saturated dead polymer chain that includes the monomer units of both radicals:



The following rate equations describe the contributions of this reaction to the production and consumption of different species as well as the relevant moments:

$$r_{R_0^*} = -2k_{tc}^t [R_0^*] \tilde{\rho}_0^{***} \quad (S120)$$

$$r_{R_1^{**}} = -2k_{tc}^t [R_1^{**}] \tilde{\rho}_0^{***} \quad (S121)$$

$$r_{R_2^{**}} = -2k_{tc}^t [R_2^{**}] \tilde{\rho}_0^{***} \quad (S122)$$

$$r_{\rho_0^{**}} = -2k_{tc}^t \rho_0^{**} \tilde{\rho}_0^{***} \quad (S123)$$

$$r_{\rho_1^{**}} = -2k_{tc}^t \rho_1^{**} \tilde{\rho}_0^{***} \quad (S124)$$

$$r_{\rho_2^{**}} = -2k_{tc}^t \rho_2^{**} \tilde{\rho}_0^{***} \quad (S125)$$

$$r_{\tilde{\rho}_0^{***}} = -2k_{tc}^t \rho_0^{**} \tilde{\rho}_0^{***} \quad (S126)$$

$$r_{\tilde{\rho}_1^{***}} = -2k_{tc}^t \rho_0^{**} \tilde{\rho}_1^{***} \quad (S127)$$

$$r_{\tilde{\rho}_2^{***}} = -2k_{tc}^t \rho_0^{**} \tilde{\rho}_2^{***} \quad (S128)$$

$$r_{\delta_0} = 2k_{tc}^t \rho_0^{**} \tilde{\rho}_0^{***} \quad (S129)$$

$$r_{\delta_1} = 2k_{tc}^t (\rho_1^{**} \tilde{\rho}_0^{***} + \rho_0^{**} \tilde{\rho}_1^{***}) \quad (S130)$$

$$r_{\delta_2} = 2k_{tc}^t(\rho_2^{**}\tilde{\rho}_0^{***} + \rho_0^{**}\tilde{\rho}_2^{***} + 2\rho_1^{**}\tilde{\rho}_1^{***}) \quad (S131)$$

Here, $r_{\rho_1^{**}} + r_{\tilde{\rho}_1^{***}} + r_{\delta_1} = 0$, confirming that this reaction does not change the total number of monomer units, as it should not.

14. Termination by combination of two tertiary radicals of the types R_n^{**} and \tilde{R}_m^{***}

In this reaction, a tertiary radical of the type R_n^{**} and a tertiary radical of the type \tilde{R}_m^{***} combine and form a saturated dead polymer chain that includes the monomer units of both radicals. The following rate equations describe the contributions of this reaction to the production and consumption of different species as well as the relevant moments:



$$r_{\rho_0^{**}} = -2k_{tc}^{tt}\rho_0^{**}\tilde{\rho}_0^{***} \quad (S133)$$

$$r_{\rho_1^{**}} = -2k_{tc}^{tt}\rho_1^{**}\tilde{\rho}_0^{***} \quad (S134)$$

$$r_{\rho_2^{**}} = -2k_{tc}^{tt}\rho_2^{**}\tilde{\rho}_0^{***} \quad (S135)$$

$$r_{\tilde{\rho}_0^{***}} = -2k_{tc}^{tt}\rho_0^{**}\tilde{\rho}_0^{***} \quad (S136)$$

$$r_{\tilde{\rho}_1^{***}} = -2k_{tc}^{tt}\rho_0^{**}\tilde{\rho}_1^{***} \quad (S137)$$

$$r_{\tilde{\rho}_2^{***}} = -2k_{tc}^{tt}\rho_0^{**}\tilde{\rho}_2^{***} \quad (S138)$$

$$r_{\delta_0} = 2k_{tc}^{tt}\rho_0^{**}\tilde{\rho}_0^{***} \quad (S139)$$

$$r_{\delta_1} = 2k_{tc}^{tt}(\rho_1^{**}\tilde{\rho}_0^{***} + \rho_0^{**}\tilde{\rho}_1^{***}) \quad (S140)$$

$$r_{\delta_2} = 2k_{tc}^{tt}(\rho_2^{**}\tilde{\rho}_0^{***} + \rho_0^{**}\tilde{\rho}_2^{***} + 2\rho_1^{**}\tilde{\rho}_1^{***}) \quad (S141)$$

The sum of the first moments is zero, confirming that there is no change in the total number of monomer units upon the occurrence of this reaction.

15. Termination by disproportionation of a secondary radical and a tertiary radical of the type R_m^{**}

In these reactions, a secondary radical abstracts a hydrogen from or donates a hydrogen to a tertiary radical of type R_m^{**} , leading to the formation of a saturated and an unsaturated dead chain:



Relations to calculate k_{td}^t from k_t and k_t^{tt} have been reported in Ref. [1]. The following rate equations describe the contributions of this reaction of (S142) to the production and consumption of different species as well as the relevant moments:

$$r_{R_0^{**}} = -k_{td}^t[R_0^{**}]\rho_0^{**} \quad (S144)$$

$$r_{R_1^{**}} = -k_{td}^t[R_1^{**}]\rho_0^{**} \quad (S145)$$

$$r_{R_2^{**}} = -k_{td}^t[R_2^{**}]\rho_0^{**} \quad (S146)$$

$$r_{\rho_0^{**}} = -k_{td}^t \rho_0^{**} \rho_0^{***} \quad (S147)$$

$$r_{\rho_1^{**}} = -k_{td}^t \rho_1^{**} \rho_0^{***} \quad (S148)$$

$$r_{\rho_2^{**}} = -k_{td}^t \rho_2^{**} \rho_0^{***} \quad (S149)$$

$$r_{\rho_0^{***}} = -k_{td}^t \rho_0^{**} \rho_0^{***} \quad (S150)$$

$$r_{\rho_1^{***}} = -k_{td}^t \rho_0^{**} \rho_1^{***} \quad (S151)$$

$$r_{\rho_2^{***}} = -k_{td}^t \rho_0^{**} \rho_2^{***} \quad (S152)$$

$$r_{\delta_0} = k_{td}^t \rho_0^{**} \rho_0^{***} \quad (S153)$$

$$r_{\delta_1} = k_{td}^t \rho_1^{**} \rho_0^{***} \quad (S154)$$

$$r_{\delta_2} = k_{td}^t \rho_2^{**} \rho_0^{***} \quad (S155)$$

$$r_{\epsilon_0} = k_{td}^t \rho_0^{**} \rho_0^{***} \quad (S156)$$

$$r_{\epsilon_1} = k_{td}^t \rho_0^{**} \rho_1^{***} \quad (S157)$$

$$r_{\epsilon_2} = k_{td}^t \rho_0^{**} \rho_2^{***} \quad (S158)$$

As in the case of the other reactions, for the reaction of (S142), the sum of the first moments is zero here too. For the reaction of (S143), the rate equations of (S144) to (S154) are applicable. However, the following rate equations are different:

$$r_{\delta_1} = k_{td}^t \rho_0^{**} \rho_1^{***} \quad (S159)$$

$$r_{\delta_2} = k_{td}^t \rho_0^{**} \rho_2^{***} \quad (S160)$$

$$r_{\epsilon_0} = k_{td}^t \rho_0^{**} \rho_0^{***} \quad (S161)$$

$$r_{\epsilon_1} = k_{td}^t \rho_1^{**} \rho_0^{***} \quad (S162)$$

$$r_{\epsilon_2} = k_{td}^t \rho_2^{**} \rho_0^{***} \quad (S163)$$

16. Termination by disproportionation of a secondary and a tertiary radical of the type \tilde{R}_m^{***}

In these reactions, a secondary radical abstracts a hydrogen from or donates a hydrogen to a tertiary radical of the type \tilde{R}_m^{***} , leading to the formation of a saturated and an unsaturated dead chain:



The following rate equations describe the contributions of the reaction (S164) to the production and consumption of different species as well as the relevant moments:

$$r_{R_0^*} = -k_{td}^t [R_0^*] \tilde{\rho}_0^{***} \quad (S166)$$

$$r_{R_1^{**}} = -k_{td}^t [R_1^{**}] \tilde{\rho}_0^{***} \quad (S167)$$

$$r_{R_2^{**}} = -k_{td}^t [R_2^{**}] \tilde{\rho}_0^{***} \quad (S168)$$

$$r_{\rho_0^{**}} = -k_{td}^t \rho_0^{**} \tilde{\rho}_0^{***} \quad (S169)$$

$$r_{\rho_1^{**}} = -k_{td}^t \rho_1^{**} \tilde{\rho}_0^{***} \quad (S170)$$

$$r_{\rho_2^{**}} = -k_{td}^t \rho_2^{**} \tilde{\rho}_0^{***} \quad (S171)$$

$$r_{\tilde{\rho}_0^{***}} = -k_{td}^t \rho_0^{**} \tilde{\rho}_0^{***} \quad (S172)$$

$$r_{\tilde{\rho}_1^{***}} = -k_{td}^t \rho_0^{**} \tilde{\rho}_1^{***} \quad (S173)$$

$$r_{\tilde{\rho}_2^{***}} = -k_{td}^t \rho_0^{**} \tilde{\rho}_2^{***} \quad (S174)$$

$$r_{\delta_0} = k_{td}^t \rho_0^{**} \tilde{\rho}_0^{***} \quad (S175)$$

$$r_{\delta_1} = k_{td}^t \rho_0^{**} \tilde{\rho}_1^{***} \quad (S176)$$

$$r_{\delta_2} = k_{td}^t \rho_0^{**} \tilde{\rho}_2^{***} \quad (S177)$$

$$r_{\epsilon_0} = k_{td}^t \rho_0^{**} \tilde{\rho}_0^{***} \quad (S178)$$

$$r_{\epsilon_1} = k_{td}^t \rho_1^{**} \tilde{\rho}_0^{***} \quad (S179)$$

$$r_{\epsilon_2} = k_{td}^t \rho_2^{**} \tilde{\rho}_0^{***} \quad (S180)$$

Again, the sum of all rates of the first moments is zero, confirming this reaction does not change the total number of monomer units in the system. For the reaction of (S165), the rate equations of (S166) to (S175) are applicable. However, the following rate equations are different:

$$r_{\delta_1} = k_{td}^t \rho_1^{**} \tilde{\rho}_0^{***} \quad (S181)$$

$$r_{\delta_2} = k_{td}^t \rho_2^{**} \tilde{\rho}_0^{***} \quad (S182)$$

$$r_{\epsilon_0} = k_{td}^t \rho_0^{**} \tilde{\rho}_0^{***} \quad (S183)$$

$$r_{\epsilon_1} = k_{td}^t \rho_0^{**} \tilde{\rho}_1^{***} \quad (S184)$$

$$r_{\epsilon_2} = k_{td}^t \rho_0^{**} \tilde{\rho}_2^{***} \quad (S185)$$

17. Termination by disproportionation between two tertiary radicals; (R_m^{***}) and (\tilde{R}_n^{***})

In these reactions, a tertiary radical of the type R_m^{***} abstracts a hydrogen from or donates a hydrogen to a tertiary radical of the type \tilde{R}_n^{***} , leading to the formation of a saturated and an unsaturated dead chain:



The following rate equations describe the contributions of the reaction of (S186) to the production and consumption of different species as well as the relevant moments:

$$r_{\rho_0^{***}} = -k_{td}^{tt} \rho_0^{***} \tilde{\rho}_0^{***} \quad (S188)$$

$$r_{\rho_1^{***}} = -k_{td}^{tt} \rho_1^{***} \tilde{\rho}_0^{***} \quad (S189)$$

$$r_{\rho_2^{***}} = -k_{td}^{tt} \rho_2^{***} \tilde{\rho}_0^{***} \quad (S190)$$

$$r_{\tilde{\rho}_0^{***}} = -k_{td}^{tt} \rho_0^{***} \tilde{\rho}_0^{***} \quad (S191)$$

$$r_{\tilde{\rho}_1^{***}} = -k_{td}^{tt} \rho_0^{***} \tilde{\rho}_1^{***} \quad (S192)$$

$$r_{\tilde{\rho}_2^{***}} = -k_{td}^{tt} \rho_0^{***} \tilde{\rho}_2^{***} \quad (S193)$$

$$r_{\delta_0} = k_{td}^{tt} \rho_0^{***} \tilde{\rho}_0^{***} \quad (S194)$$

$$r_{\delta_1} = k_{td}^{tt} \rho_0^{***} \tilde{\rho}_1^{***} \quad (S195)$$

$$r_{\delta_2} = k_{td}^{tt} \rho_0^{***} \tilde{\rho}_2^{***} \quad (S196)$$

$$r_{\epsilon_0} = k_{td}^{tt} \rho_0^{***} \tilde{\rho}_0^{***} \quad (S197)$$

$$r_{\epsilon_1} = k_{td}^{tt} \rho_1^{***} \tilde{\rho}_0^{***} \quad (S198)$$

$$r_{\epsilon_2} = k_{td}^{tt} \rho_2^{***} \tilde{\rho}_0^{***} \quad (S199)$$

The sum of rates of all first moments is zero here, which confirms that the reaction does not change the total number of monomer units in the system. For the reaction of (S187), the rate equations of (S188) to (S194) are applicable. However, the following rate equations are different:

$$r_{\delta_1} = k_{td}^{tt} \rho_1^{***} \tilde{\rho}_0^{***} \quad (S200)$$

$$r_{\delta_2} = k_{td}^{tt} \rho_2^{***} \tilde{\rho}_0^{***} \quad (S201)$$

$$r_{\epsilon_0} = k_{td}^{tt} \rho_0^{***} \tilde{\rho}_0^{***} \quad (S202)$$

$$r_{\epsilon_1} = k_{td}^{tt} \rho_0^{***} \tilde{\rho}_1^{***} \quad (S203)$$

$$r_{\epsilon_2} = k_{td}^{tt} \rho_0^{***} \tilde{\rho}_2^{***} \quad (S204)$$

18. Propagation of a tertiary radical of the type R_n^{***} by reacting with a macromonomer

In this reaction, a tertiary radical of the type R_n^{***} reacts with a macromonomer (unsaturated dead polymer) and propagates (forms a longer branched growing chain):



The following rate equations describe the contributions of this reaction to the production and consumption of different species as well as the relevant moments:

$$r_{\rho_0^{***}} = 0 \quad (S206)$$

$$r_{\rho_1^{***}} = k_{mac}^t \rho_0^{***} \epsilon_1 \quad (S207)$$

$$r_{\rho_2^{***}} = k_{mac}^t (\rho_0^{***} \epsilon_2 + 2\rho_1^{***} \epsilon_1) \quad (S208)$$

$$r_{\epsilon_0} = -k_{mac}^t \rho_0^{***} \epsilon_0 \quad (S209)$$

$$r_{\epsilon_1} = -k_{mac}^t \rho_0^{***} \epsilon_1 \quad (S210)$$

$$r_{\epsilon_2} = -k_{mac}^t \rho_0^{***} \epsilon_2 \quad (S211)$$

Here, $r_{\epsilon_1} + r_{\rho_1^{***}} = 0$, confirming that the reaction does not alter the total number of monomer units in the system.

19. Propagation of a tertiary radical of type \tilde{R}_n^{***} by reacting with a macromonomer

In this kind of propagation, a tertiary live chain \tilde{R}_n^{***} reacts with a macromonomer (dead polymer chain with a double bond) and forms a tertiary radical of the type R_{n+m}^{***} :



The contributions of this reaction to the rates of the moments are as follows.

$$r_{\tilde{\rho}_0^{***}} = -k_{mac}^t \tilde{\rho}_0^{***} \epsilon_0 \quad (S213)$$

$$r_{\tilde{\rho}_1^{***}} = -k_{mac}^t \tilde{\rho}_1^{***} \epsilon_0 \quad (S214)$$

$$r_{\tilde{\rho}_2^{***}} = -k_{mac}^t \tilde{\rho}_2^{***} \epsilon_0 \quad (S215)$$

$$r_{\rho_0^{***}} = k_{mac}^t \tilde{\rho}_0^{***} \epsilon_0 \quad (S216)$$

$$r_{\rho_1^{***}} = k_{mac}^t (\tilde{\rho}_1^{***} \epsilon_0 + \tilde{\rho}_0^{***} \epsilon_1) \quad (S217)$$

$$r_{\rho_2^{***}} = k_{mac}^t (\tilde{\rho}_2^{***} \epsilon_0 + \tilde{\rho}_0^{***} \epsilon_2 + 2\tilde{\rho}_1^{***} \epsilon_1) \quad (S218)$$

$$r_{\epsilon_0} = -k_{mac}^t \tilde{\rho}_0^{***} \epsilon_0 \quad (S219)$$

$$r_{\epsilon_1} = -k_{mac}^t \tilde{\rho}_0^{***} \epsilon_1 \quad (S220)$$

$$r_{\epsilon_2} = -k_{mac}^t \tilde{\rho}_0^{***} \epsilon_2 \quad (S221)$$

20. Ranges of unavailble MA rate coefficients based on the family-type-behavior

To use the family-type behavior [2,3], one needs to find a scale factor, which in this case, is the ratio of the propagation rate coefficient of MA to that of n BA or the ratio of their termination rate coefficients. As different rate coefficients have been reported for the propagation reaction of n BA (Table S2), several scale factors can be obtained [3]. Furthermore, for other n BA secondary reactions such as backbiting and β -scission reactions, various rate coefficients have been reported. Using the steps described below we calculated ranges for the activation energy and frequency factor of MA β -scission rate coefficients. We used the same steps to calculate the same ranges for the MA backbiting reaction.

1. Based on family-type-behavior:

$$k_{\beta SMA} = \frac{k_{pMA}}{k_{pBA}} * k_{\beta SBA} \quad (S222)$$

where $k_{\beta S_{MA}}$, $k_{p_{MA}}$, $k_{p_{BA}}$ and $k_{\beta S_{BA}}$ are the β -scission rate coefficient of MA, the propagation rate coefficient of MA, the propagation rate coefficient of n BA, and the β -Scission rate coefficient of n BA, respectively. Therefore:

$$k_{\beta S_{MA}} = \frac{z_{p_{MA}} \exp\left(\frac{-E_{p_{MA}}}{RT}\right)}{z_{p_{BA}} \exp\left(\frac{-E_{p_{BA}}}{RT}\right)} * z_{\beta S_{BA}} * \exp\left(-\frac{E_{\beta S_{BA}}}{RT}\right) = \frac{z_{p_{MA}} * z_{\beta S_{BA}}}{z_{p_{BA}}} \exp\left(\frac{-E_{p_{MA}} - E_{\beta S_{BA}} + E_{p_{BA}}}{RT}\right) \quad (S223)$$

$$k_{\beta S_{MA}} = \frac{z_{p_{MA}} * z_{\beta S_{BA}}}{z_{p_{BA}}} \exp\left(\frac{-(E_{p_{MA}} + E_{\beta S_{BA}} - E_{p_{BA}})}{RT}\right) = z_{\beta S_{MA}} * \exp\left(\frac{-E_{\beta S_{MA}}}{RT}\right) \quad (S224)$$

2. Calculate the upper and lower limits using:

$$\text{Upper limit of } z_{\beta S_{MA}} = \frac{z_{p_{MA}} \times \text{highest reported } z_{\beta S_{BA}}}{\text{lowest reported } z_{p_{BA}}} \quad (S225)$$

$$\text{Lower limit of } z_{\beta S_{MA}} = \frac{z_{p_{MA}} \times \text{lowest reported } z_{\beta S_{BA}}}{\text{highest reported } z_{p_{BA}}} \quad (S226)$$

$$\text{Upper limit of } E_{\beta S_{MA}} = \text{highest reported } E_{\beta S_{BA}} + E_{p_{MA}} - \text{lowest reported } E_{p_{BA}} \quad (S227)$$

$$\text{Lower limit of } E_{\beta S_{MA}} = E_{p_{MA}} + \text{lowest reported } E_{\beta S_{BA}} - \text{highest reported } E_{p_{BA}} \quad (S228)$$

The *ga* command of MATLAB searches within these ranges to find the optimum values of unavailable MA rate coefficients at each temperature. The gel effect parameters [3] are also estimated by *ga* command and the values are reported in Table S3. The estimated reaction kinetic parameters are then used in our polymerization reactor model to predict monomer conversion and average molecular weights.

Table S1: Most-Likely Reactions in High-Temperature Polymerization of Alkyl Acrylates.

Monomer self-initiation $3M \xrightarrow{k_i} R_1^{**} + R_2^{**}$	Backbiting $R_n^{**} \xrightarrow{k_{bb}} \tilde{R}_n^{***}$	Chain transfer to polymer $R_n^{**} + D_m \xrightarrow{m k_{tr,p}} D_n + R_m^{***}$ $R_n^{***} + D_m \xrightarrow{m k_{tr,p}^*} D_n + R_m^{***}$ $\tilde{R}_n^{***} + D_m \xrightarrow{m k_{tr,p}^*} D_n + R_m^{***}$
Propagation $R_n^{**} + M \xrightarrow{k_p} R_{n+1}^{**}$ $R_n^{***} + M \xrightarrow{k_p^*} R_{n+1}^{***}$ $\tilde{R}_n^{***} + M \xrightarrow{k_p^*} R_{n+1}^{***}$ $R_n^{**} + U_m \xrightarrow{k_{mac}} R_{n+m}^{**}$ $R_n^{***} + U_m \xrightarrow{k_{mac}^*} R_{n+m}^{***}$ $\tilde{R}_n^{***} + U_m \xrightarrow{k_{mac}^*} R_{n+m}^{***}$	β -Scission $\tilde{R}_n^{***} \xrightarrow{k_\beta} R_2^{**} + U_{n-2}$ $\tilde{R}_n^{***} \xrightarrow{k_\beta} R_{n-3}^{**} + U_3$ $R_n^{***} \xrightarrow{k_\beta} R_m^{**} + U_{n-m}$ $R_n^{***} \xrightarrow{k_\beta} R_{n-m}^{**} + U_m$ Migration $\tilde{R}_n^{***} \xrightarrow{k_{mig}} R_n^{***}$	Termination by disproportionation $R_n^{**} + R_m^{**} \xrightarrow{k_{td}} D_n + U_m$ $R_n^{**} + R_m^{**} \xrightarrow{k_{td}^*} D_m + U_n$ $R_n^{**} + R_m^{**} \xrightarrow{k_{td}^*} D_n + U_m$ $R_n^{**} + R_m^{**} \xrightarrow{k_{td}^*} D_m + U_n$ $R_n^{**} + \tilde{R}_m^{***} \xrightarrow{k_{td}^*} D_m + U_n$ $R_n^{**} + \tilde{R}_m^{***} \xrightarrow{k_{td}^*} D_n + U_m$ $R_n^{***} + R_m^{***} \xrightarrow{k_{td}^{**}} D_n + U_m$ $R_n^{***} + R_m^{***} \xrightarrow{k_{td}^{**}} D_m + U_n$ $R_n^{***} + \tilde{R}_m^{***} \xrightarrow{k_{td}^{**}} D_m + U_n$ $R_n^{***} + \tilde{R}_m^{***} \xrightarrow{k_{td}^{**}} D_n + U_m$ $\tilde{R}_n^{***} + \tilde{R}_m^{***} \xrightarrow{k_{td}^{**}} D_n + U_m$ $\tilde{R}_n^{***} + \tilde{R}_m^{***} \xrightarrow{k_{td}^{**}} D_m + U_n$

Chain transfer to monomer $R_n^{**} + M \xrightarrow{k_{tr,m}} D_n + R_1^{**}$ $R_n^{***} + M \xrightarrow{k_{tr,M}^t} D_n + R_1^{**}$ $\tilde{R}_n^{***} + M \xrightarrow{k_{tr,M}^t} D_n + R_1^{**}$	Termination by combination $R_n^{**} + R_m^{**} \xrightarrow{k_{tc}} D_{n+m}$ $R_n^{**} + R_m^{***} \xrightarrow{2k_{tc}^t} D_{n+m}$ $R_n^{**} + \tilde{R}_m^{***} \xrightarrow{2k_{tc}^t} D_{n+m}$ $R_n^{***} + R_m^{***} \xrightarrow{k_{tc}^{tt}} D_{n+m}$ $R_n^{***} + \tilde{R}_m^{***} \xrightarrow{2k_{tc}^{tt}} D_{n+m}$ $\tilde{R}_n^{***} + \tilde{R}_m^{***} \xrightarrow{k_{tc}^{tt}} D_{n+m}$	De-propagation $R_{n+1}^{**} \xrightarrow{k_{-p}} R_n^{**} + M$
Chain transfer to macromonomer $R_n^{**} + U_m \xrightarrow{(m-1)k_{tr,p}} D_n + R_m^{***}$ $R_n^{***} + U_m \xrightarrow{(m-1)k_{tr,p}^t} D_n + R_m^{***}$ $\tilde{R}_n^{***} + U_m \xrightarrow{(m-1)k_{tr,p}^t} D_n + R_m^{***}$		Chain transfer to solvent $R_n^{**} + S \xrightarrow{k_{tr,s}} D_n + R_0^*$ $R_n^{***} + S \xrightarrow{k_{tr,s}^t} D_n + R_0^*$ $\tilde{R}_n^{***} + S \xrightarrow{k_{tr,s}^t} D_n + R_0^*$

Table S2: Kinetic Parameter Values Reported for nBA in the Literature.

Propagation by secondary	Activation Energy (kJ.mol ⁻¹)	Frequency Factor (L.mol ⁻¹ .s ⁻¹)	Temp. (°C)	Polymerization Medium	Polymerization Mechanism	Publication Year
Ref. [1]	17.90	2.21E7	140-220	Bulk	Free-Radical	2016
Ref. [4]	17.80	2.05E7	40	NA	Free-Radical	2003
Ref. [5]	17.90	2.21E7	-10-30	Bulk	Free-Radical	2007
Ref. [6]	17.40	1.80E7	138	Xylene	Free-Radical	2004
Ref. [7]	17.90	2.21E7	80-170	Xylene/Ethyl Benzene	Free-Radical	2010
Ref. [8]	17.90	2.21E7	60	Toluene	RAFT	2016
Ref. [9]	17.90	2.21E7	60-140	Bulk/Xylene	Free-Radical	2016
Ref. [10]	17.90	2.21E7	60	THF	Free-Radical	2015
Ref. [11]	17.90	2.21E7	70	Xylene	Free-Radical	2014
Ref. [12]	17.90	2.21E7	50	Bulk	Free-Radical	2016
Ref. [12]	17.98	2.19E7	50	Toluene	Free-Radical	2016
Ref. [13]	17.24	1.80E7	138	Xylene	Free-Radical	2010
Ref. [14]	18.10	2.31E7	90-120	DMF/DMSO	NMP	2011
Propagation by Tertiary	Activation Energy (kJ.mol ⁻¹)	Frequency Factor (L.mol ⁻¹ .s ⁻¹)	Temp. (°C)	Polymerization Medium	Polymerization Mechanism	Publication Year
Ref. [1]	28.60	1.20E6	140-220	Bulk	Free-Radical	2016
Ref. [4]	29.50	1.25E6	40	NA	Free-Radical	2003
Ref. [5]	28.90	1.52E6	-10 - 30	Bulk	Free-Radical	2007
Ref. [7]	28.60	1.20E6	80-170	Xylene/Ethyl Benzene	Free-Radical	2010
Ref. [8]	28.90	1.58E6	60	Toluene	RAFT	2016
Ref. [9]	28.90	1.58E6	60-140	Bulk/Xylene	Free-Radical	2016
Ref. [10]	28.60	1.20E6	60	THF	Free-Radical	2015
Ref. [11]	28.90	1.58E6	70	Xylene	Free-Radical	2014
Ref. [15]	28.30	9.20E5	60	Toluene	Free-Radical	2010
Ref. [14]	28.90	1.52E6	90-120	DMF/DMSO	NMP	2011
Backbiting	Activation Energy (kJ.mol ⁻¹)	Frequency Factor (s ⁻¹)	Temp. (°C)	Polymerization Medium	Polymerization Mechanism	Publication Year
Ref. [1]	32.70	7.41E7	140-220	Bulk	Free-Radical	2016
Ref. [4]	29.80	4.31E7	40	NA	Free-Radical	2003
Ref. [5]	31.70	4.84E7	-10 - 30	Bulk	Free-Radical	2007
Ref. [7]	32.70	7.41E7	80-170	Xylene/Ethyl Benzene	Free-Radical	2010

Ref. [8]	52.30	3.2E10	60	Toluene	RAFT	2016
Ref. [9]	52.30	3.2E10	60-140	Bulk/Xylene	Free-Radical	2016
Ref. [10]	32.70	7.41E7	60	THF	Free-Radical	2015
Ref. [15]	34.70	1.60E8	60	Toluene	Free-Radical	2010
Ref. [14]	29.30	3.50E7	90-120	DMSO/DMF	NMP	2011
Ref. [16]	30.6±5.4	Ln(17.8±2.1)	30-50	Bulk/Propionate	Free-Radical	2019
β-Scission	Activation Energy (kJ.mol⁻¹)	Frequency Factor (s⁻¹)	Temp. (°C)	Polymerization Medium	Polymerization Mechanism	Publication Year
Ref. [1]	63.90	1.49E9	140-220	Bulk	Free-Radical	2016
Ref. [16]	81.10±18.2	Ln(29.7±5.5)	110-140	Bulk/Propionate	Free radical	2019
Ref. [7]	63.90	1.49E9	80-170	Xylene/Ethyl Benzene	Free-Radical	2010
Ref. [8]	55.40	1.47E9	60	Toluene	RAFT	2016
Ref. [9]	55.40	1.47E9	60-140	Bulk/Xylene	Free-Radical	2016
Ref. [14]	71.50	8.60E10	90-120	DMSO/DMF	NMP	2011
Transfer to Polymer	Activation Energy (kJ.mol⁻¹)	Frequency Factor (L.mol⁻¹.s⁻¹)	Temp. (°C)	Polymerization Medium	Polymerization Mechanism	Publication Year
Ref. [1]	29.00	4.01E3	140-220	Bulk	Free-Radical	2016
Ref. [4]	29.00	4.01E3	40	NA	Free-Radical	2003
Ref. [7]	29.00	4.01E3	80-170	Xylene/Ethyl Benzene	Free-Radical	2010
Ref. [8]	43.30	6.70E7	60	Toluene	RAFT	2016
Ref. [9]	27.70	2.48E3	60-140	Bulk/Xylene	Free-Radical	2016
Ref. [10]	29.00	4.01E3	60	THF	Free-Radical	2015
Ref. [11]	27.70	2.48E3	70	Xylene	Free-Radical	2014
Transfer to monomer	Activation Energy (kJ.mol⁻¹)	Frequency Factor (L.mol⁻¹.s⁻¹)	Temp. (°C)	Polymerization Medium	Polymerization Mechanism	Publication Year
Ref. [1]	32.60	2.9E5	140-220	Bulk	Free-Radical	2016
Ref. [4]	32.60	2.9E5	40	NA	Free-Radical	2003
Ref. [4] (by tertiary radical)	46.10	2.0E5	40	NA	Free-Radical	2003
Ref. [5]	32.60	2.9E5	-10 - 30	Bulk	Free-Radical	2007
Ref. [5] (by tertiary radical)	46.10	2.0E5	-10 - 30	Bulk	Free-Radical	2007
Ref. [7]	32.60	2.9E5	80-170	Xylene/Ethyl Benzene	Free-Radical	2010
Ref. [8]	32.60	2.88E5	60	Toluene	RAFT	2016
Ref. [9]	32.60	2.88E5	60-140	Bulk/Xylene	Free-Radical	2016
Ref. [10]	32.60	2.90E5	60	THF	Free-Radical	2015
Ref. [11]	32.60	2.88E5	70	Xylene	Free-Radical	2014
Ref. [10] (by tertiary radical)	46.10	2.00E5	60	THF	Free-Radical	2015
Ref. [13]	32.60	2.88E5	138	Xylene	Free-Radical	2010
Termination by Secondary	Activation Energy (kJ.mol⁻¹)	Frequency Factor (L.mol⁻¹.s⁻¹)	Temp. (°C)	Polymerization Medium	Polymerization Mechanism	Publication Year

Ref. [1]	8.40	3.89E9	140-220	Bulk	Free-Radical	2016
Ref. [4]	5.58	2.50E8	40	NA	Free-Radical	2003
Ref. [5]	5.60	1.34E9	-10 - 30	Bulk	Free-Radical	2007
Ref. [6]	2.40	2.57E8	138	Xylene	Free-Radical	2004
Ref. [7]	8.40	3.89E9	80-170	Xylene/Ethyl Benzene	Free-Radical	2010
Ref. [8]	8.40	1.30E10	60	Toluene	RAFT	2016
Ref. [9]	3.50	1.32E10	60-140	Bulk/Xylene	Free-Radical	2016
Ref. [10]	8.40	1.30E10	60	THF	Free-Radical	2015
Ref. [11]	8.40	1.30E10	70	Xylene	Free-Radical	2014
Ref. [15]	8.40	1.30E10	60	Toluene	Free-Radical	2010
Ref. [13]	3.98	5.14E8	138	Xylene	Free-Radical	2010
Termination by Tertiary	Activation Energy (kJ.mol⁻¹)	Frequency Factor (L.mol⁻¹.s⁻¹)	Temp. (°C)	Polymerization Medium	Polymerization Mechanism	Publication Year
Ref. [1]	19.60	5.30E9	140-220	Bulk	Free-Radical	2016
Ref. [4]	5.56	2.10E8	40	NA	Free-Radical	2003
Ref. [5]	5.60	1.80E7	-10 - 30	Bulk	Free-Radical	2007
Ref. [7]	19.60	5.30E9	80-170	Xylene/Ethyl Benzene	Free-Radical	2010
Ref. [8]	19.60	5.30E9	60	Toluene	RAFT	2016
Ref. [9]	4.00	1.29E7	60-140	Bulk/Xylene	Free-Radical	2016
Ref. [10]	5.60	1.80E7	60	THF	Free-Radical	2015

Table S3: Estimated parameters of the gel effect model [3]

i	b_i	c_i
1	49.805	0.600
2	-10.380	1.750
3	26.140	-0.042

Table S4: Equations, initial conditions, and other MA rate coefficients

Reaction	Rate equation	Comment
Propagation of tertiary radicals (k_p^t)	$k_p^t = k_p/1000$	Three orders of magnitude less than propagation by secondary radicals [2]
Chain transfer to monomer from secondary radicals ($k_{tr,M}$)	$k_{tr,M} = b * k_{tr,M}$ of <i>n</i> -BA	b is a scaling factor defined in ref. [3]
Chain transfer to monomer from tertiary radicals ($k_{tr,M}^t$)	$k_{tr,M}^t = b * k_{tr,M}^t$ of <i>n</i> -BA	b is a scaling factor defined in ref. [3]
Chain transfer to polymer from secondary radical ($k_{tr,p}$)	$k_{tr,p} = b * k_{tr,p}$ of <i>n</i> -BA	b is a scaling factor defined in ref. [3]
Chain transfer to polymer from tertiary radical ($k_{tr,p}^t$)	$k_{tr,p}^t = k_{tr,p}/1000$	Three orders of magnitude less than corresponding secondary radical rate coefficient
Termination of secondary radicals (k_t)	$\log k_t = 9.48 - \frac{454}{T}$	Reported in [17]

Termination of tertiary radicals (k_t^t)	$k_t^t = a * k_t^t$ of n-BA	a is a scaling factor defined in ref. [3]
Other equations		
$k_t^{tt} = k_{td}^{tt} + k_{tc}^{tt}$	$k_t^t = k_{td}^t + k_{tc}^t$	$k_t = k_{td} + k_{tc}$
$k_{td} = \delta_t k_t$	$k_{td}^{tt} = \delta_t k_t^{tt}$	$k_{td}^t = \delta_{st} \sqrt{k_t k_t^{tt}}$
$k_{tc} = (1 - \delta_s) k_t$	$k_{tc}^{tt} = (1 - \delta_t) k_t^{tt}$	$k_{tc}^t = (1 - \delta_{st}) \sqrt{k_t k_t^{tt}}$
$k_{mac} = \gamma k_p$	$\delta_s = 0.1$	$\delta_{st} = 0.7$
$\delta_t = 0.9$	$\gamma = 0.5$	
Reactor initial conditions		
Initial monomer concentration = $11.03 \frac{mol}{L}$	Polymerization time = 250 min	All other concentrations = 0

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