Supporting information for

Kinetic Monte Carlo Convergence Demands for Thermochemical Recycling Kinetics of Vinyl Polymers with Dominant Depropagation

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S1. Polymerization conditions and feedstock characteristics

Three feedstocks have been synthesized in silico. For this two polymerization temperatures are formally chosen. Feedstock A and B are modeled at a lower temperature and feedstock C at a higher temperature. All three feedstocks are simulated with an initial initiator to monomer ratio of 0.0025 up to a monomer conversion of 0.2, according to the model of De smit et al. [1] but assuming intrinsic kinetics.

Table S1: Rate coefficients used for modelling the polymer feedstock A, B and C in Figure 2 of the main text; for simplicity no chain transfer to monomer.

Reaction	Equation	A	B	C	units
Initiator decomposition	$I_2 \rightarrow 2I^*$	1.2×10^{-4}	1.2×10^{-4}	3.8×10^{-7}	s^{-1}
Chain initiation	$I^* + M \rightarrow R_1^*$	2.0×10^{3}	2.0×10^{3}	5.0×10^{2}	L mol^{-1} s^{-1}
Propagation	$R_i^* + M \rightarrow R_{i+1}^*$	2.0×10^{3}	2.0×10^{3}	5.0×10^{2}	L mol^{-1} s^{-1}
Termination – Combination	$R_i^* + R_j^* \rightarrow P_{i+j}$	1.0×10^{9}	3.0×10^{8}	3.0×10^{7}	L mol^{-1} s^{-1}
Termination – Disproportionation	$R_i^* + R_j^* \rightarrow P_i + P_j$	0	7.0×10^{8}	7.0×10^{7}	L mol^{-1} s^{-1}

To confirm convergence was obtained at the chosen simulation volume for the polymerization of feedstock A, B and C an addition simulation was performed with a five times larger simulation volume.

This meant for feedstock A and B a $\sum_i i.X_{P_i}$ of 5 x10^9 and for feedstock C 5 x10^{10}. In Figure S1 a convergence of the polymerization results is shown for the three feedstocks for both simulation volumes (subplot a: conversion and subplot b number CLD).

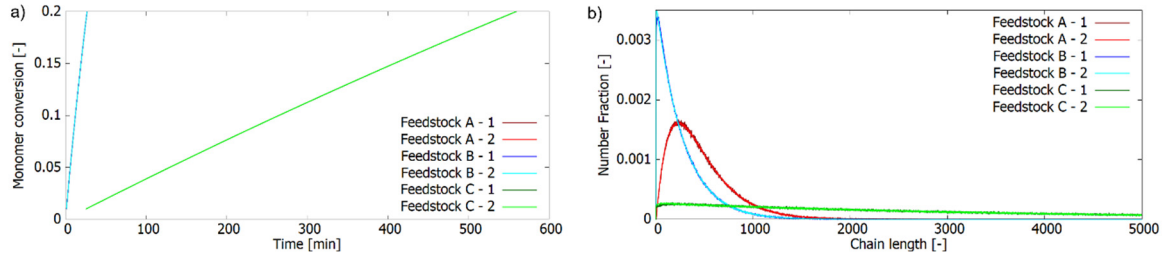

Figure S1: Convergence check of feedstock A, B and C at simulation volume 1 and 2 regarding monomer conversion (a) and CLD (b).

S2. Simulation times and volume

Table S2: Simulation duration of the thermochemical degradation of the three feedstocks at the defined cases in the main text (95% carbon-based conversion)

Case	$\sum_i i.X_{P_i}$	Feedstock A [min]	Feedstock B [min]	Feedstock C [min]
1	1.0 x10^5	2.30	2.45	2.34
2	1.0 x10^6	2.40	2.32	3.12
3	1.0 x10^7	3.05	3.91	3.80
4	5.0 x10^7	3.24	6.71	3.49
5	1.0 x10^8	3.48	6.91	3.45
6	5.0 x10^8	5.35	23.90	7.65
7	1.0 x10^9	10.01	76.89	8.29
8	5.0 x10^9	-	-	45.47
9	1.0 x10^{10}	-	-	95.89

Table S3: Simulation duration of the thermochemical degradation of the three feedstocks at the defined cases in the main text (50% carbon-based conversion)

Case	$\sum_i i.X_{P_i}$	Feedstock A [min]	Feedstock B [min]	Feedstock C [min]
1	1.0 x10^5	1.70	1.78	2.30
2	1.0 x10^6	2.17	1.97	2.48
3	1.0 x10^7	2.52	2.02	2.28
4	5.0 x10^7	1.90	2.25	2.34
5	1.0 x10^8	2.55	2.80	2.58
6	5.0 x10^8	2.68	8.34	5.10
7	1.0 x10^9	5.20	22.58	7.22
8	5.0 x10^9	-	-	36.15
9	1.0 x10^{10}	-	-	81.27

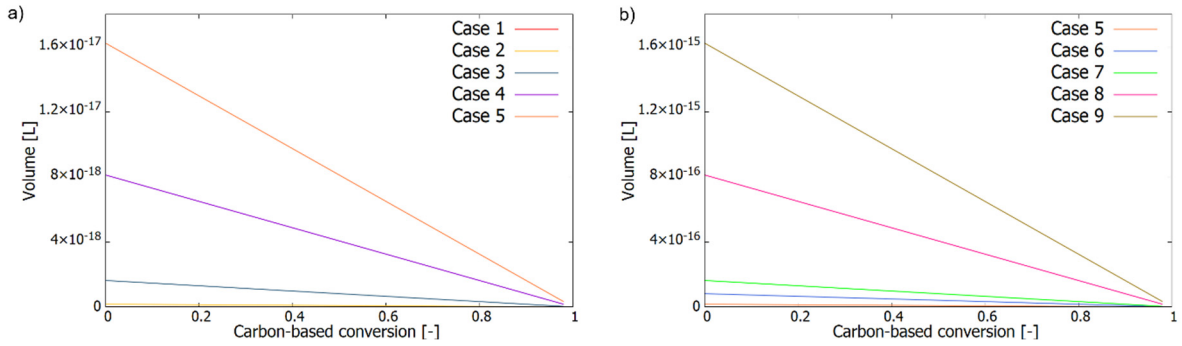

Figure S2: Evolution of the simulation volume as a f function of carbon-based conversion for case 1 to 5 on the left (a) and case 5 to 9 on the right (b) for feedstock C.

S3. Simulation results for Feedstock C

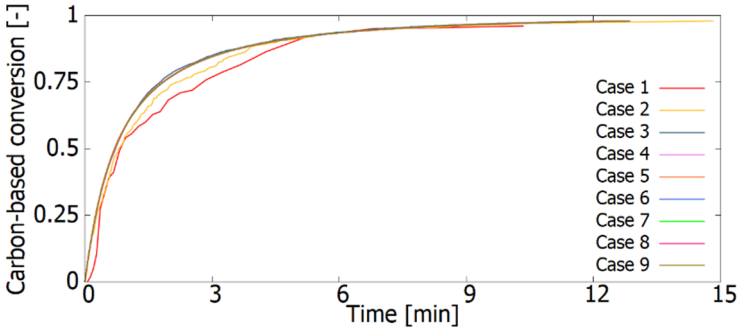

Figure S3: Effect of the MC control volume (Table 2) on the simulated carbon-based conversion profile for thermal degradation of feedstock C (Figure 1); kinetic parameters in Table 1.

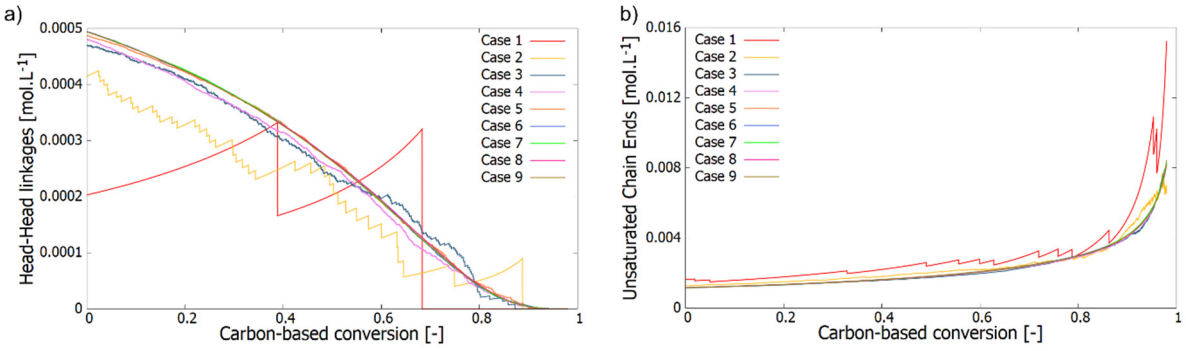

Figure S4: Effect of the MC control volume on the concentration of (a) Head-Head linkages during thermal degradation of feedstock C and (b) the unsaturated chain-ends expressed in mol.L^{-1} .

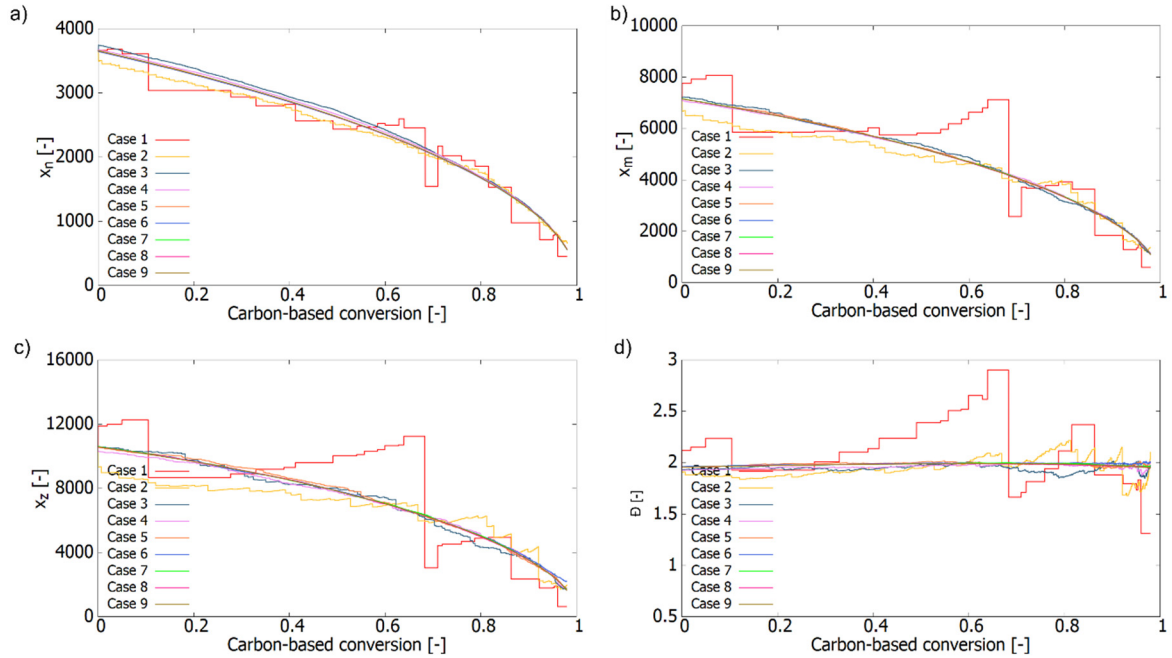

Figure S5: Effect of the MC control volume on the evolution of (a) the number average chain length (x_n), (b) the mass average chain length (x_m) , (c) the *z*-average chain length (x_z) and (d) dispersity (Đ) during thermal degradation of Feedstock C (Figure 12); model parameters: Table 1.

Table S4: Average relative error (%) (eq.7) for the carbon-based conversion ($\epsilon_{\mathrm{conv_C}}$) the number average chain length ($\epsilon_{\mathrm{x_n}}$), mass average chain length ($\epsilon_{\mathrm{x_m}}$), dispersity (Đ), and *z*-average chain length ($\epsilon_{\mathrm{x_z}}$) for feedstock C. In italic the starting point to reach the threshold (by default 1% but for ϵ_{x_z} 0.5%).

Cases	$\epsilon_{conversion}$ (%)	ϵ_{x_n} (%)	ϵ_{x_m} (%)	$\epsilon_{Đ}$ (%)	ϵ_{x_z} (%)
1 → 2	5.35	7.58	17.99	13.71	28.63
2 → 3	3.51	5.45	8.44	4.08	17.78
3 → 4	*0.71*	1.31	2.01	1.34	3.73
4 → 5	0.46	1.09	*0.92*	1.41	2.78
5 → 6	0.34	*0.27*	0.55	*0.50*	2.01
6 → 7	0.11	0.31	0.31	0.30	1.09
7 → 8	0.09	0.10	0.20	0.18	*0.39*
8 → 9	0.05	0.07	0.14	0.11	0.27

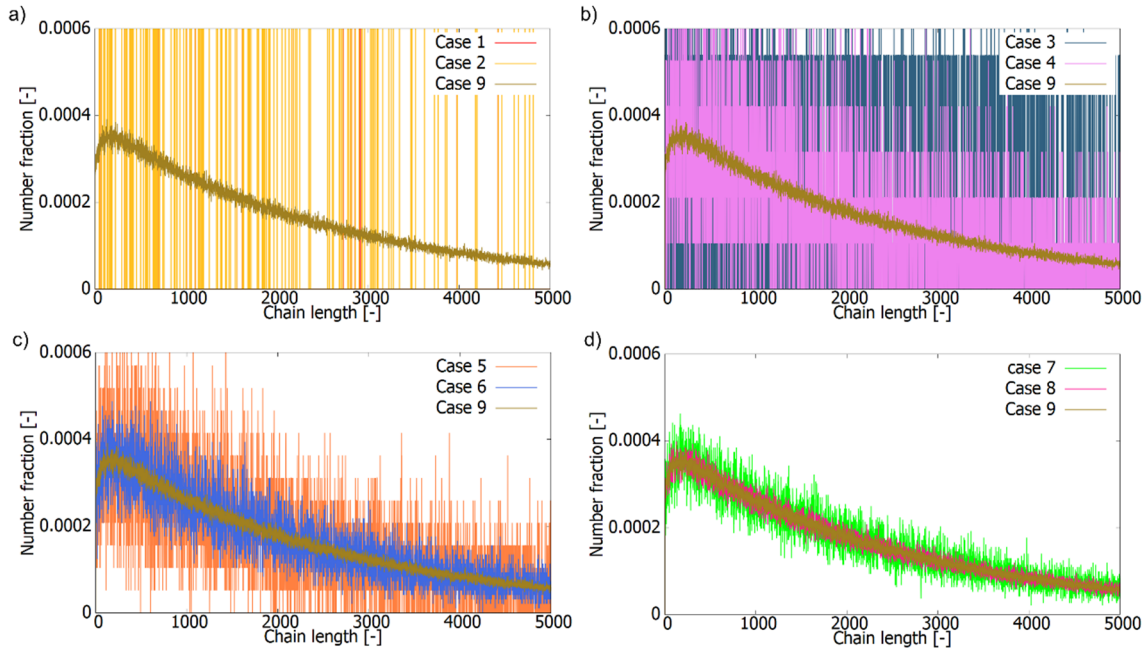

Figure S6: Number chain length distribution (CLD) at a carbon-based conversion of 50% for feedstock B for several cases with the CLD corresponding to Case 9 included in all subplots for comparison; (a) case 1 and 2, (b) case 3 and 4, (c) case 5 and 6, (c) case 7 and 8**. Practically case 7 can be selected as converged.**

S4. Radical concentration

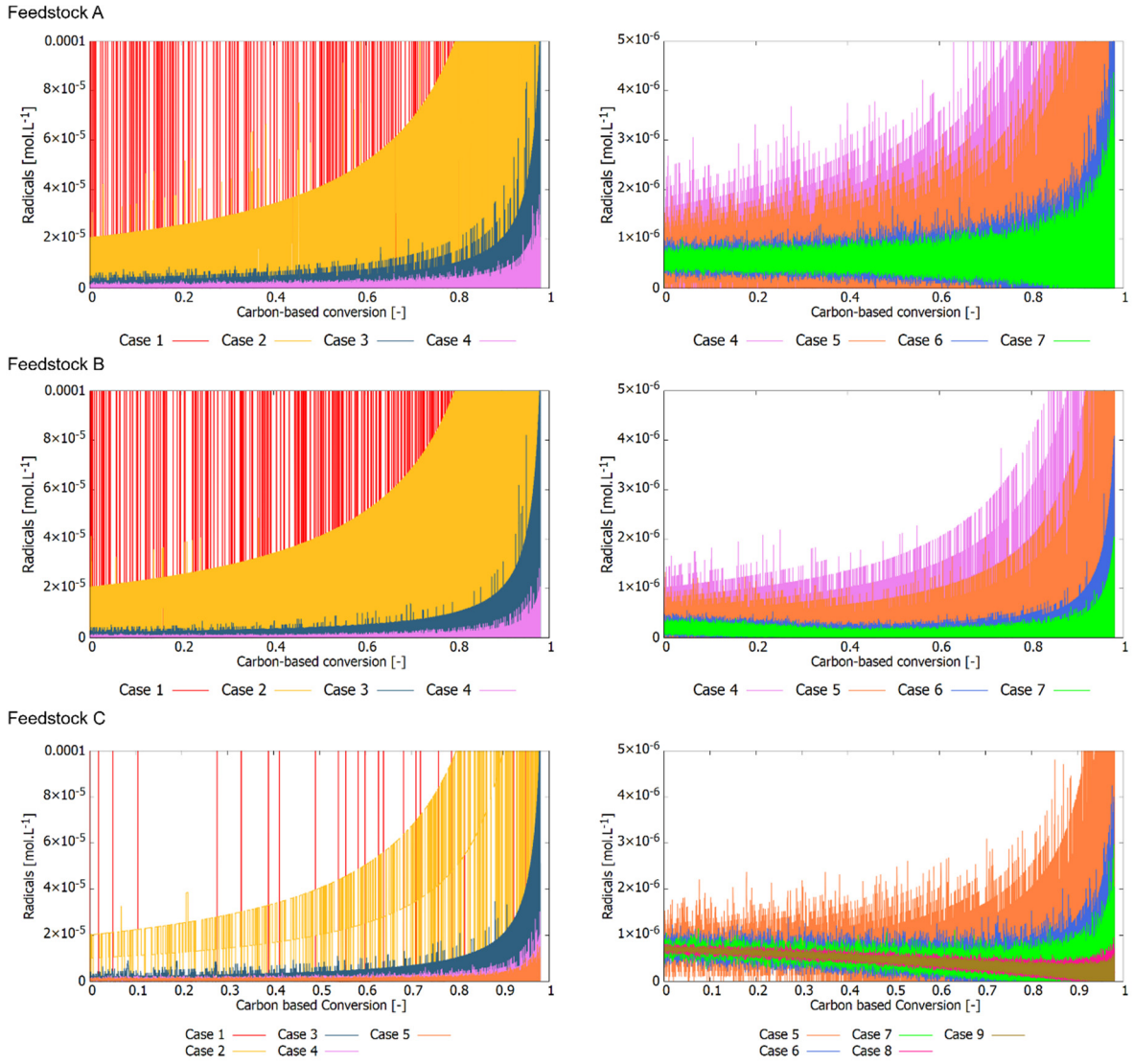

Figure S7: Radical concentration during the thermal degradation of feedstock A (cases 1 to 4 on the top left and 4 to 7 on the top right), feedstock B (cases 1 to 4 on the center left and 4 to 7 on the center right) and feedstock C (cases 1 to 5 on the bottom left)

S5. References

1. De Smit, K., et al., *Connecting polymer synthesis and chemical recycling on a chain-by-chain basis: a unified matrix-based kinetic Monte Carlo strategy.* Reaction Chemistry & Engineering, 2020. **5**(10): p. 1909-1928.