Supporting information for

Simulation time analysis of kinetic Monte Carlo algorithmic steps for basic radical (de)polymerization kinetics of linear polymers

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1. Kinetic parameters for the studied polymerization processes

In this section, we show the kinetic parameters used in the Arrhenius chemical rate coefficient for the three polymerization processes under study: free radical polymerization (FRP) of methyl methacrylate (Table S1), nitroxide mediated polymerization (NMP) of styrene (Table S2), and radical depolymerization of poly(methyl methacrylate) (Table S3).

Table S1. Kinetic parameters for the free radical polymerization (FRP) of methyl methacrylate

Reaction Channel	A ((L mol^{-1}) s^{-1})	E_a (kJ mol^{-1})	Reference
Conventional radical dissociation	$5.88 \cdot 10^5$	133.0	[1-5]
Chain Initiation	$2.67 \cdot 10^6$	22.4	[6, 7]
Propagation	$2.67 \cdot 10^6$	22.4	[8-12]
Termination by disproportionation [a]	$8 \cdot 10^6$	0	
Termination by recombination [a]	$2 \cdot 10^6$	0	
Chain transfer to monomer	$3.54 \cdot 10^6$	55.1	[13]

[a] Average constant value

Table S2. Kinetic parameters for the nitroxide mediated polymerization (NMP) of styrene

Reaction Channel	A ((L mol^{-1}) s^{-1})	E_a (kJ mol^{-1})	Reference
Activation			
from nitroxide + initiator radical	$1.16 \cdot 10^{13}$	105.3	[14]
from radical	$4.04 \cdot 10^{17}$	148.7	[14]
Deactivation			
from nitroxide + initiator radical	$2.80 \cdot 10^{6}$	0	[14]
from radical	$1.09 \cdot 10^{6}$	0	[14]
Chain initiation			
from fragment of Type I	$1.55 \cdot 10^{6}$	16.5	[15]
from fragment of Type II	$4.24 \cdot 10^{7}$	32.5	[16]
Propagation	$4.24 \cdot 10^{7}$	32.5	[16]
Chain transfer to monomer [a]	$2.3 \cdot 10^{6}$	53	[17]
Recombination [a,b]	$1 \cdot 10^{8}$	0	[18]

[a] The same value is used for all the possible combinations shown in Figure 6 in the main text

[b] Average constant value

Table S3. Kinetic parameters for the radical depolymerization of poly(methyl methacrylate)

Reaction Channel	A ((L mol^{-1}) s^{-1})	E_a (kJ mol^{-1})	Reference
Fission	$2.0 \cdot 10^{-2}$	0	[7]
Radical unzipping via β-scission	$5.0 \cdot 10^{3}$	0	[7]
Recombination [a]	$1 \cdot 10^{4}$	0	[7]

[a] average constant value

2. Reaction event frequency analysis of the studied processes

In this section, we present the results for the reaction event frequency for each of the three polymerization processes under study: free radical polymerization (FRP) of methyl methacrylate (Fig. S.1), nitroxide mediated polymerization (NMP) of styrene (Figure S.2), and radical depolymerization of poly(methyl methacrylate) (Figure S.4). For each of the processes, specific reactions are considerably more frequent than others by orders of magnitude, for which special care should be taken in terms of time optimization strategies.

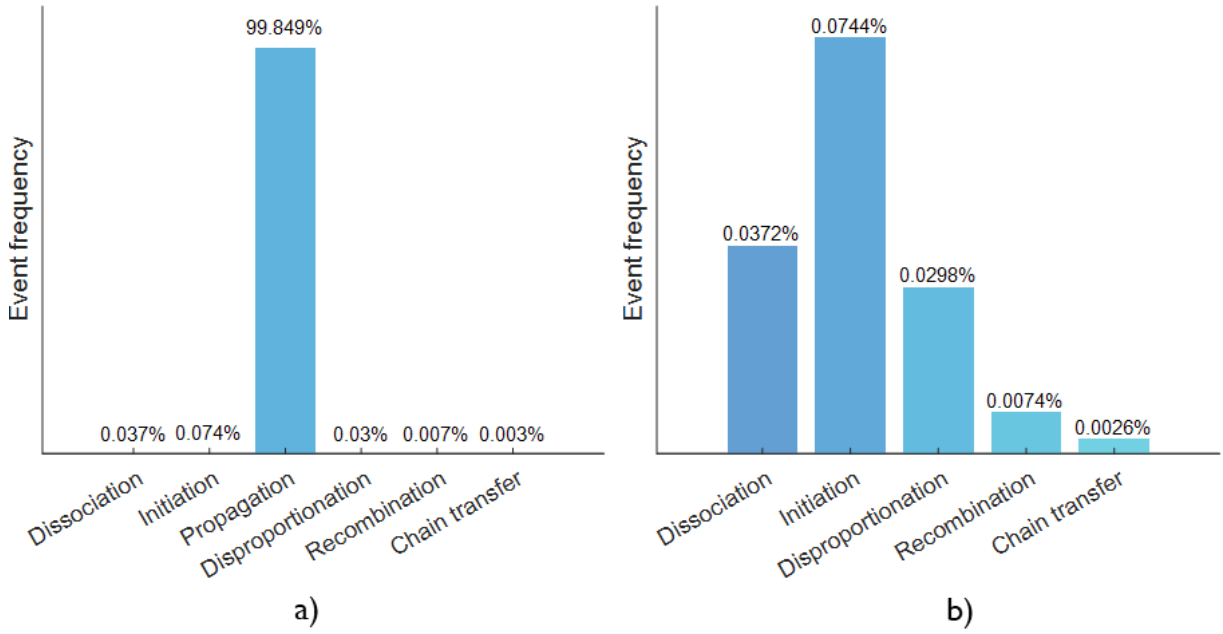

Figure S1. Reaction channel frequency for FRP of methyl methacrylate. In (a), the relative frequencies for all the reaction channels are presented, while in (b) the most frequent reaction channel, the one corresponding to propagation, is excluded.

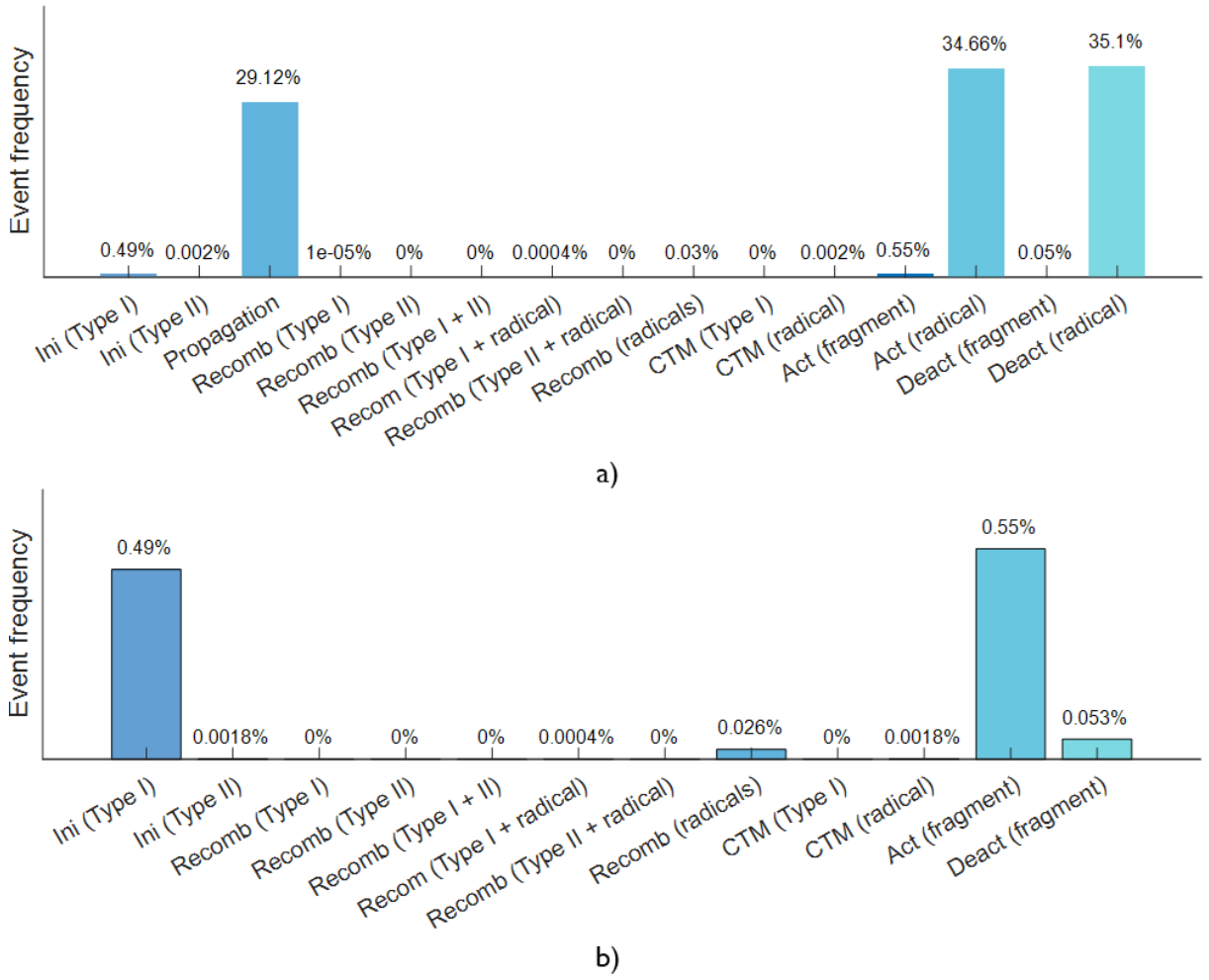

Figure S2. Reaction channel frequency for NMP of styrene. In (a), the relative frequencies for all the reaction channels are presented, while in (b) the most frequent reaction channels, the ones corresponding to propagation and the (de)activation via polymer radical, are excluded. The following abbreviations were used: Ini: initiation, Recomb: recombination, CTM: chain transfer to monomer, Act: activation, Deact: deactivation.

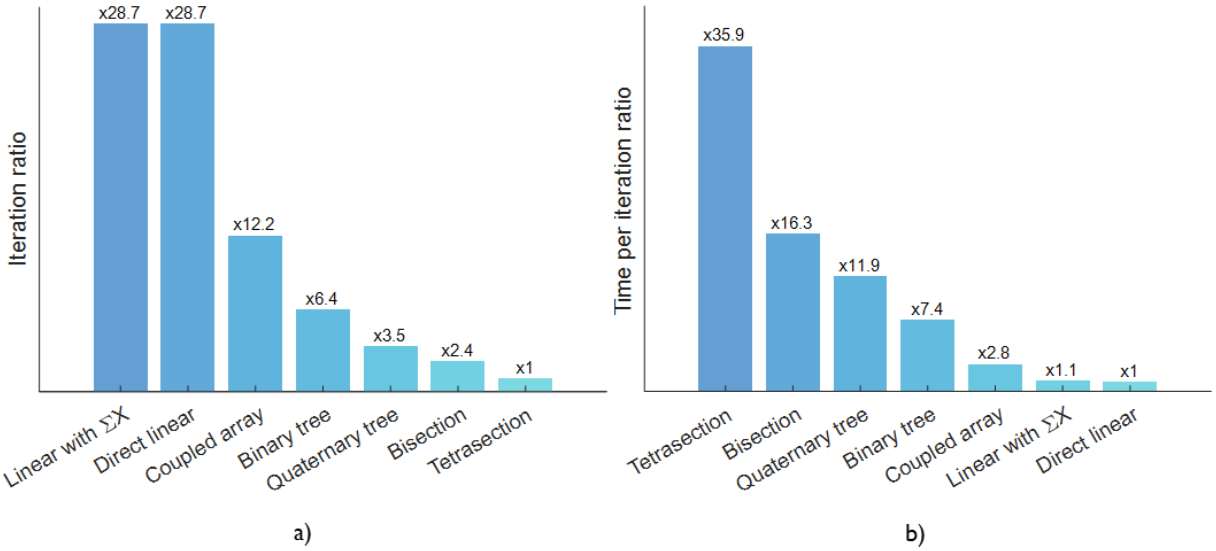

Figure S3. Iteration results for NMP showing (a) the number of iterations used per method and (b) the ratio between the simulation time and the number of iterations. Contrary to the *q*-search and *d*-tree search methods, the linear searches require more iterations but are algorithmically simpler, hence the time per iteration is considerably shorter.

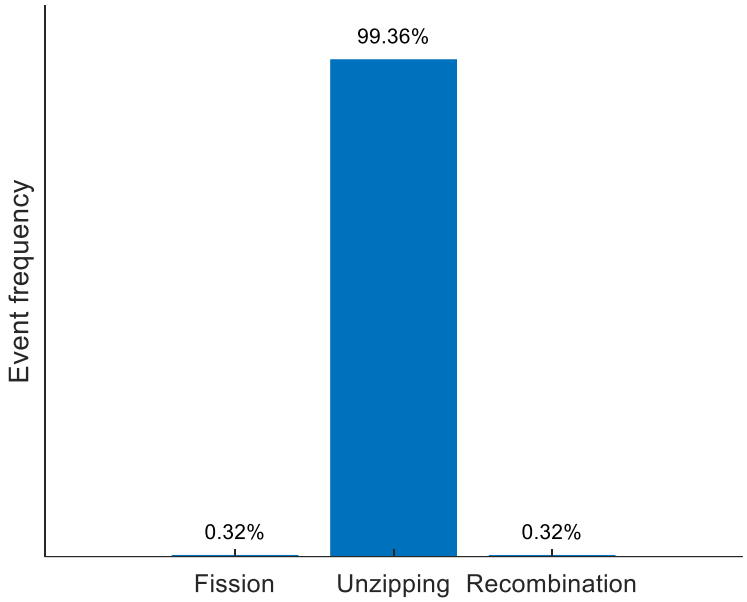

Figure S4. Reaction channel frequency for depolymerization of poly(methyl methacrylate). In (a), the relative frequencies for all the reaction channels are presented, while in (b) the most frequent reaction channel, the one corresponding to Unzipping via □-scission, is excluded.

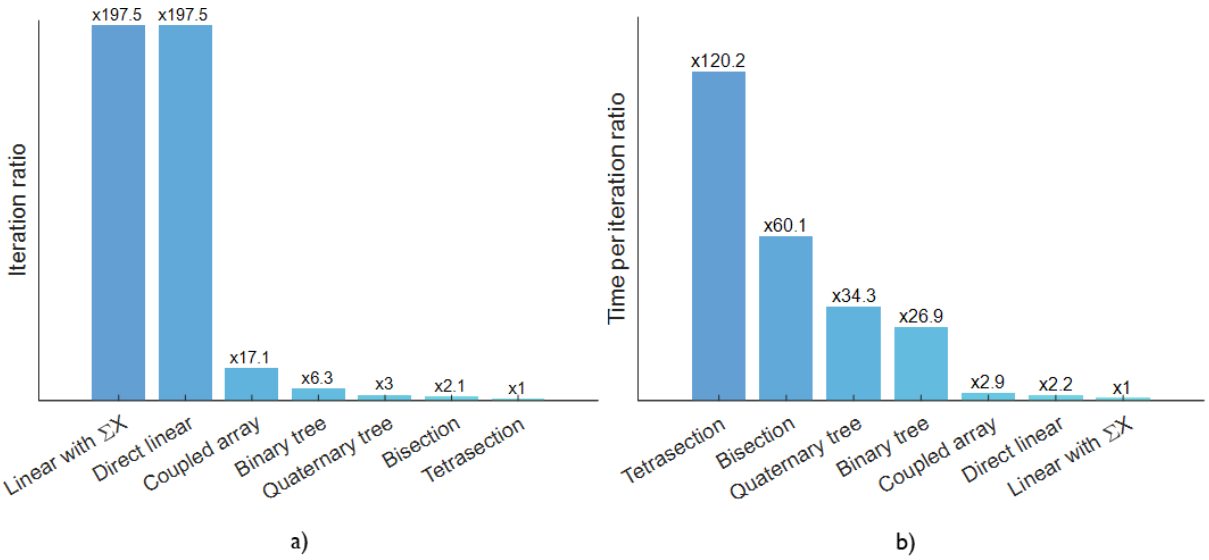

Figure S5. Iteration results for depolymerization showing (a) the number of iterations used per method and (b) the ratio between the simulation time and the number of iterations. Contrary to the *q*-search and *d*-tree search methods, the linear searches require more iterations but are algorithmically simpler, hence the time per iteration is considerably shorter.

3. References

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