Supplementary Information for "Coupled matrix kinetic Monte Carlo simulations applied for advanced understanding of polymer grafting kinetics"

Freddy L. Figueira,[1] Yi-Yang Wu,[2] Yin-Ning Zhou,[2*] Zheng-Hong Luo,[2*] Paul H.M. Van Steenberge,[1] and Dagmar R. D'hooge[1,3*]

[1]Ghent University, Laboratory for Chemical Technology (LCT), Technologiepark 125, B-9052 Gent, Belgium1

[2]Department of Chemical Engineering, School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, P. R. China

[3]Ghent University, Centre for Textile Science and Engineering, Technologiepark 70a, B-9052 Gent, Belgium

Corresponding authors: dagmar.dhooge@ugent.be zhouyn@sjtu.edu.cn; luozh@sjtu.edu.cn.

S1 Explanation for Figure 2 in the main text

From a helicopter point of view 4 matrix/array groups, which are depicted as boxes in Fig. 2 in the main text, can be identified that all give information on a specific part/fragment of the macrospecies for which labels (e.g. "20" "2050") are considered. In the bottom left box the molecular information/history of the precursor BB's thus in the present work linear Bd based parts is included ("green units"), whereas in the top left box emphasis is on additional structural elements being in the present work styrene-based parts ("blue" units) thus conventional ("free") chains, grafts and the grafts from which bridges are formed. The top right box gives the information of the connections for the top and bottom left box, and the bottom right box addresses the positions of all radical types.

For the two left boxes extra labels are introduced as well to enable further internal classifications and to map sequences of events. A label can for instance correspond to an initiator fragment type, a monomer sequence (*e.g.* a series of St units), a recombination event, a hydrogen abstraction (on the precursor BB), graft initiation or double bond addition, with examples at the bottom of Fig. 2 in the main text and with a full list of labels for the case study provided in Section S2. Auxiliaries arrays are employed as well to track for instance the segment and chain length in order to facilitate updates of the matrix data structure during the *k*MC simulation.

In the top right box of Fig. 2 in the main text the connection points are originating from recombination of two conventional radical chains or graft chain initiation, each row indicating the labels and the positions of the involved structural elements and precursor chains. In order to distinguish between precursor chains on one hand and linear/grafted elements on the other, the formers are stored with positive values and the latter with negative values. For instance, in the third row of the connectivity matrix it is depicted that the third St unit of the side element "-2030" is attached to the ninth Bd unit of the precursor chain "50", corresponding to a termination by recombination of a conventional linear ECR and a Bd radical unit thus MCR of a precursor chain. Another example is given in row seven, displaying the recombination of the labels "-2010" and "-2020", which corresponds to the termination by recombination of two graft ECRs. Furthermore, in the bottom right

box for the conventional living species and the living grafts the radical position corresponds to the last attached unit, but in the case of a precursor BB the radical unit can be along the chain so that the position of the (mid-chain) radical unit must be also stored.

More in detail it can be deduced from Fig. 2 in the main text that by coupling the four boxes the side element with the label "2030" has been formed because of a chain initiation by a chemical initiator fragment (sequence label 1), 3 conventional propagations (sequence label 11; segment label 3) and a termination by recombination with a precursor radical unit (sequence label 14). On the other hand, the precursor chain with label "20" has been modified because of the following reaction events: a hydrogen abstraction by a chemical initiator radical (label 26), a graft initiation (label 10) and a double bond addition of a conventional ECR (label 24). The precursor chain considered thus modified during FRIG in a way that is composed of three segments of 5 Bd units, 2 Bd units and 1 Bd unit, with in general the precursor unit that underwent an event defined as the last unit of the segment and potentially one extra segment.

Hence, the concept of Fig. 2 in the main text allows the identification of the molecular structure of conventional linear chains and GC structural elements such as T-grafts, H-grafts, and crosslinks in Fig. 1. It should be further emphasized that although for the selected case study the precursor macrospecies, the conventional chains and the grafts contain only one monomer unit type (Bd or St) this coupled matrix driven data structure is also capable of mapping copolymeric precursor chains, side elements and conventional chains. The capabilities of this concept, but for linear copolymerization, has for instance been proved in recent matrix-based *k*MC work on radical copolymerization of methyl methacrylate and 2-methylene-1,3-dioxepane.[1]

S2 Extra input for the data structure for the coupled matrix Monte Carlo (CMMC) algorithm

In this section, we first present the complete list of events and segment labels utilized in the main matrices of the data structure show, in Fig. 2 in the main text and then the basic concepts of our chain identification procedure used in the postprocessing module of the Coupled Matrix Monte Carlo (CMMC) concept introduced in this work, Fig 3 in the main text. In both cases the labels refer to the selected case study, the free radical induced grafting (FRIG) of polybutadiene (PB) with Styrene (St) using benzoyl peroxide (BPO) as chemical initiator.

Table S1 presents the labels for conventional (free) and graft chain initiation. These labels not only identify the different (small) radicals involved in the chain initiation: benzoyloxy, styryl, 1-phenyl-ethen-1-yl, 1-phenyltetralyl, but also their origin: chemical initiator dissociation, monomer thermal self-initiation or chain transfer reactions. Table S2 shows the list of events associated to conventional (free) and grafted chain propagation (which exact number of occurrences stored in the "Segment Length" array), termination by recombination and chain transfer. In Table S3 the events related to the precursor backbones are listed.

Table S1 List of labels for conventional (free) and grafted chain initiation for the FRIG of PB with St and BPO as chemical initiator.

Label	*Event description*
1	benzoyloxy radical from benzoyl peroxide dissociation ($R^{\bullet}_{0,1}$)
2	Styryl radical from styrene thermal self-initiation ($R^{\bullet}_{0,2}$)
3	1-phenyl-ethen-1-yl radical from free PS end-chain radical (ECR) transfer to monomer ($R^{\bullet}_{0,4}$)
4	1-phenyl-ethen-1-yl radical from transfer from precursor MCR to monomer ($R^{\bullet}_{0,4}$)
5	1-phenyl-ethen-1-yl radical from grafted ECR transfer to monomer ($R^{\bullet}_{0,4}$)
6	1-phenyltetralyl radical from styrene thermal self-initiation ($R^{\bullet}_{0,3}$)
7	1-phenyltetralyl radical from free PS ECR transfer to dimer ($R^{\bullet}_{0,3}$)
8	1-phenyltetralyl radical from transfer from precursor MCR to Dimer ($R^{\bullet}_{0,3}$)
9	1-phenyltetralyl radical from grafted ECR transfer to Dimer ($R^{\bullet}_{0,3}$)
10	Precursor mid-chain radical (MCR) (graft initiation)

Table S2 List of labels for chain propagation events, termination by recombination and chain transfer for the FRIG of PB with St and BPO as chemical initiator.

Label	*Event description*
11	Conventional chain propagation
12	Grafted chain propagation
13	Recombination between conventional PS ECRs (producing dead conventional PS chain)
14	Recombination between conventional PS ECR and precursor MCR (producing a T-graft)
15	Recombination between conventional PS and grafted St ECRs (producing a T-graft)
16	Recombination between grafted St ECR and precursor MCR (producing a H-graft)
17	Recombination between grafted St ECR (producing a H-graft)
18	Chain transfer from conventional PS ECR to monomer (producing 1-phenyl-ethen-1-yl radical, $R_{0,2}$)
19	Chain transfer from grafted St ECR to monomer (producing 1-phenyl-ethen-1-yl radical, $R_{0,2}$)
20	Chain transfer from conventional PS ECR to precursor unit (producing a precursor MCR)
21	Chain transfer from grafted St ECR to precursor unit (producing a precursor MCR)
22	Chain transfer from conventional PS ECR to dimer (producing 1-phenyltetralyl radical $R_{0,3}$)
23	Chain transfer from grafted St ECR to dimer (producing 1-phenyltetralyl radical $R_{0,3}$)
24	Double bond addition of conventional PS ECR to precursors unit (producing a T-Graft)
25	Double bond addition of grafted radical chain to precursors sites (producing a H-Graft)

Table S3 List of labels for events where a butadiene (Bd) unit of the PB precursor backbone is involved.

Label	*Event description*
26	Precursor hydrogen abstraction by a conventional chemical initiator radical ($R_{0,1}$)
27	Precursor hydrogen abstraction by a styryl radical ($R_{0,2}$)
28	Precursor hydrogen abstraction by a 1-phenyltetralyl radical ($R_{0,3}$)
29	Precursor hydrogen abstraction by a 1-phenyl-ethen-1-yl radical ($R_{0,4}$)
30	Recombination of precursor MCRs (producing a pure crosslink)
31	Chain transfer from precursor MCR to monomer (producing 1-phenyl-ethen-1-yl radical, $R_{0,4}$)
32	Chain transfer from precursor MCR to precursor unit (producing precursor MCRs)
33	Chain transfer from precursor MCR to dimer (producing 1-phenyltetralyl radical $R_{0,3}$)
34	Double bond addition of precursor MCR to precursor unit (producing a pure crosslink)

In a next step, in this section, we focus on postprocessing (related to last figure in the main text). Figure S1 depicts one graft copolymer (GC) chain and 2 conventional polystyrene (PS) chains. The GC chain is composed of 4 PB primary elements, 5 St primary elements, 3 T-grafts, and 2 H-grafts. The information on segments is here essential input. Since the labels of the structural elements are also known (but not shown for clarity here) the type of event specifically leading to recombinations can be traced and then the nature of the elements involved can be identified. For instance. the label "17" indicates the recombination of two grafted ECRs, then both "blue" elements are part of a H-graft in a GC; the precursor backbone "green" elements to which that blue elements are connected can be identified searching for their connection points in the connectivity matrix; the rest of elements of the GC can be identified in a similar fashion.

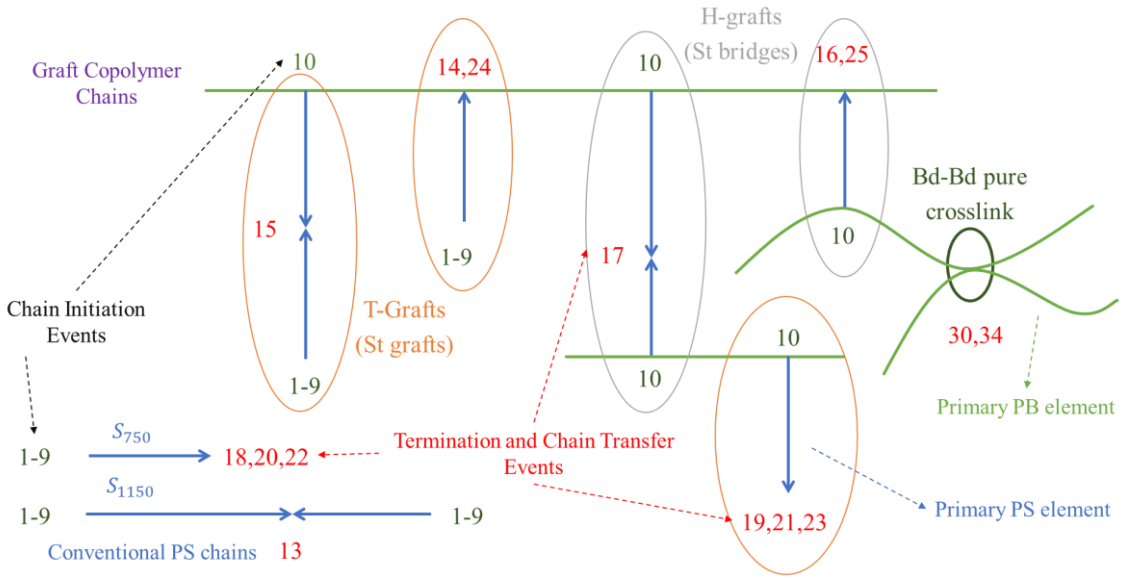


Figure S1 Identification of complex structures performed during CMMC postprocessing. The combination of the connectivity information and the sequence of events for each structural element stored in the data structure permits the identification of complex structures produced during the FRIG of PB with St and BPO as chemical initiator.

S3 Additional simulation output

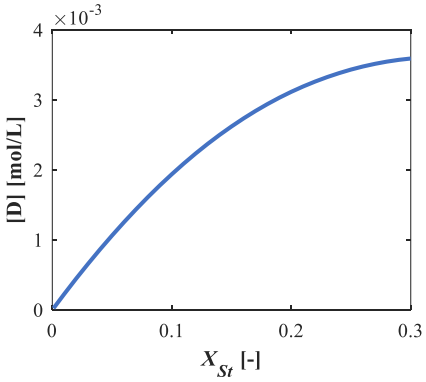


Figure S2. Variation of the molar concentration 1-phenyl-1,2,3,9-tetrahydronaphtalene, referred elsewhere as dimer (D), with styrene conversion (X_{St}). Results for the kinetic Monte Carlo using the kinetic parameters of Table 1 and reaction conditions defined by Case A in Table 2 of the main text.

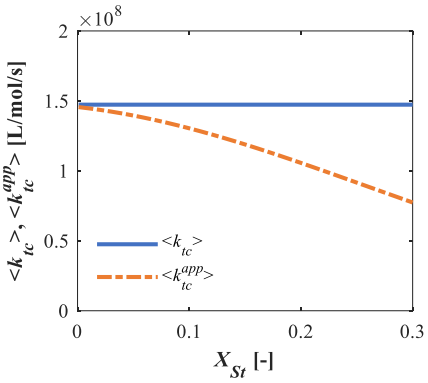


Figure S3 Variation of the apparent termination by recombination rate coefficient with styrene conversion (X_{St}) alongside the case with no such variation. Results for the kinetic Monte Carlo using the kinetic parameters of Table 1 and reaction conditions defined by Case A in Table 2 of the main text.

S4 Numerical convergence of CMMC algorithm for the FRIG of PB with St and BPO as chemical initiator.

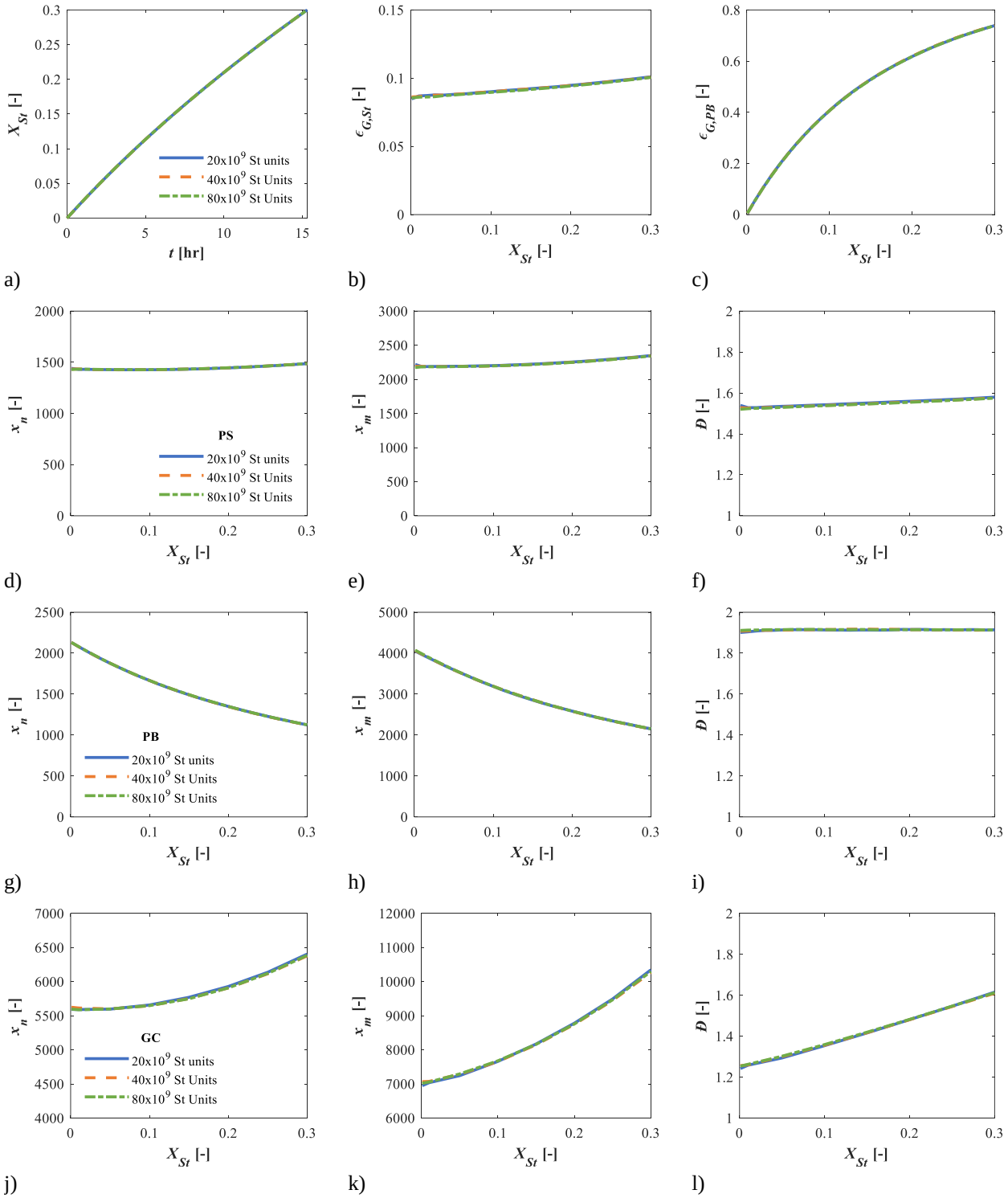


Figure S4 Numerical convergence of the CMMC simulation of the FRIG of PB with St and BPO as chemical initiator. (a) variation of St conversion (X_{St}) with time (t); variation with X_{St} of (b) St graft efficiency; (c) PB graft efficiency; (d)-(e) number/mass average chain length of polystyrene (PS); (f) dispersity of PS; (g)-(h) number/mass average chain length of polybutadiene (BP); (i) dispersity of PB; (j)-(k) number/mass average chain length of graft copolymer (GC); (l) dispersity of GC; kinetic parameters of Table 1 and reaction conditions defined by Case A in Table 2 of the main text for 20 billion, 40 billion and 80 billion starting St units.

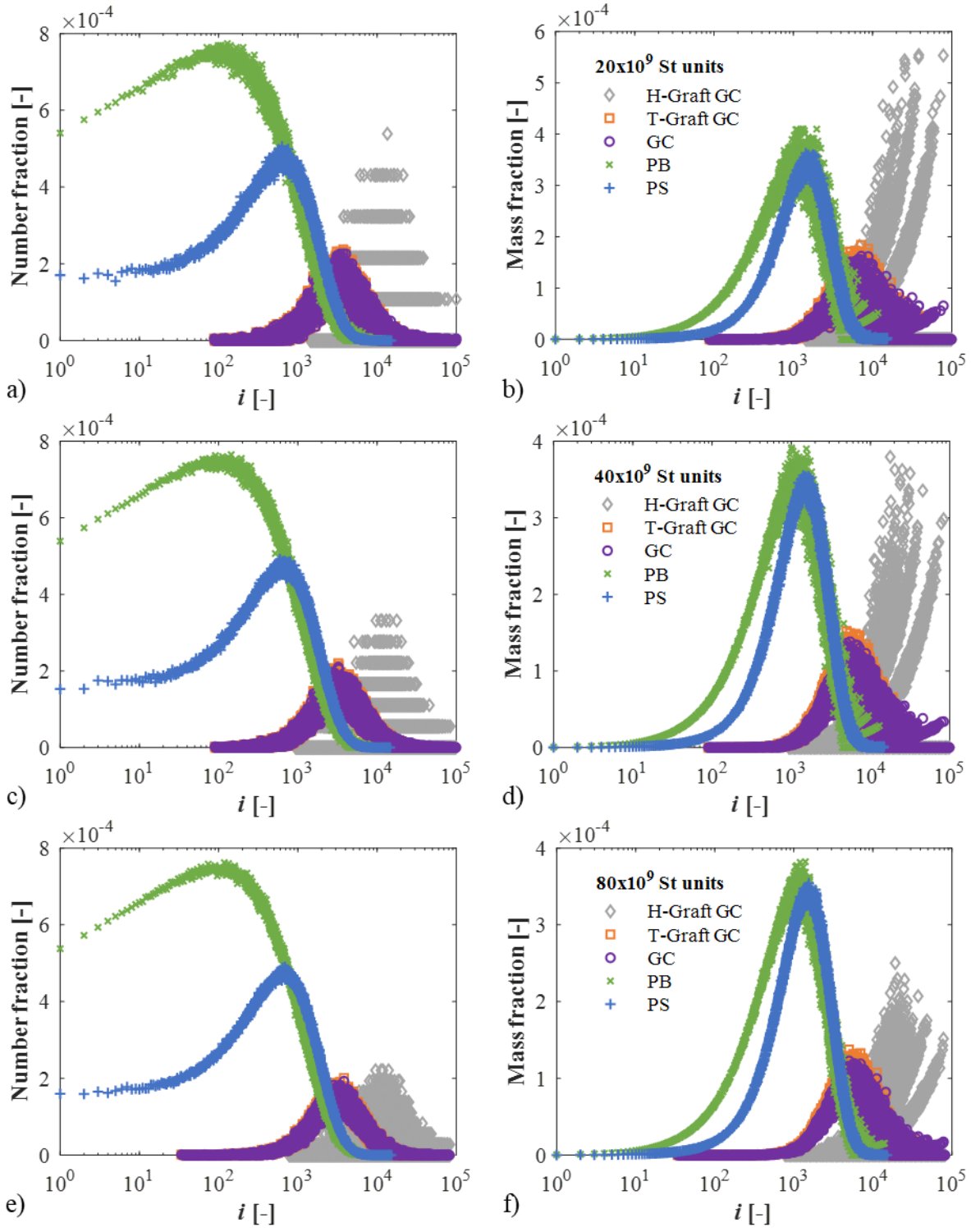


Figure S5. Number/mass chain length distributions (CLDs; always normalized) at 30% St conversion focus is on PB, PS, and graft copolymer (GC) molecules alongside the split-up in molecules with only T-grafts and with at least one H-Graft; Simulation started with (a)/(b) 20 billion initial St units; (c)/(d) 40 billion initial St units; (e)/(f) 80 billion initial St units; kinetic parameters of Table 1 and reaction conditions defined by Case A in Table 2 of the main text.

S5 Benchmarking kMC with method of moments simulations for FRIG of PB with St and BPO as chemical initiator

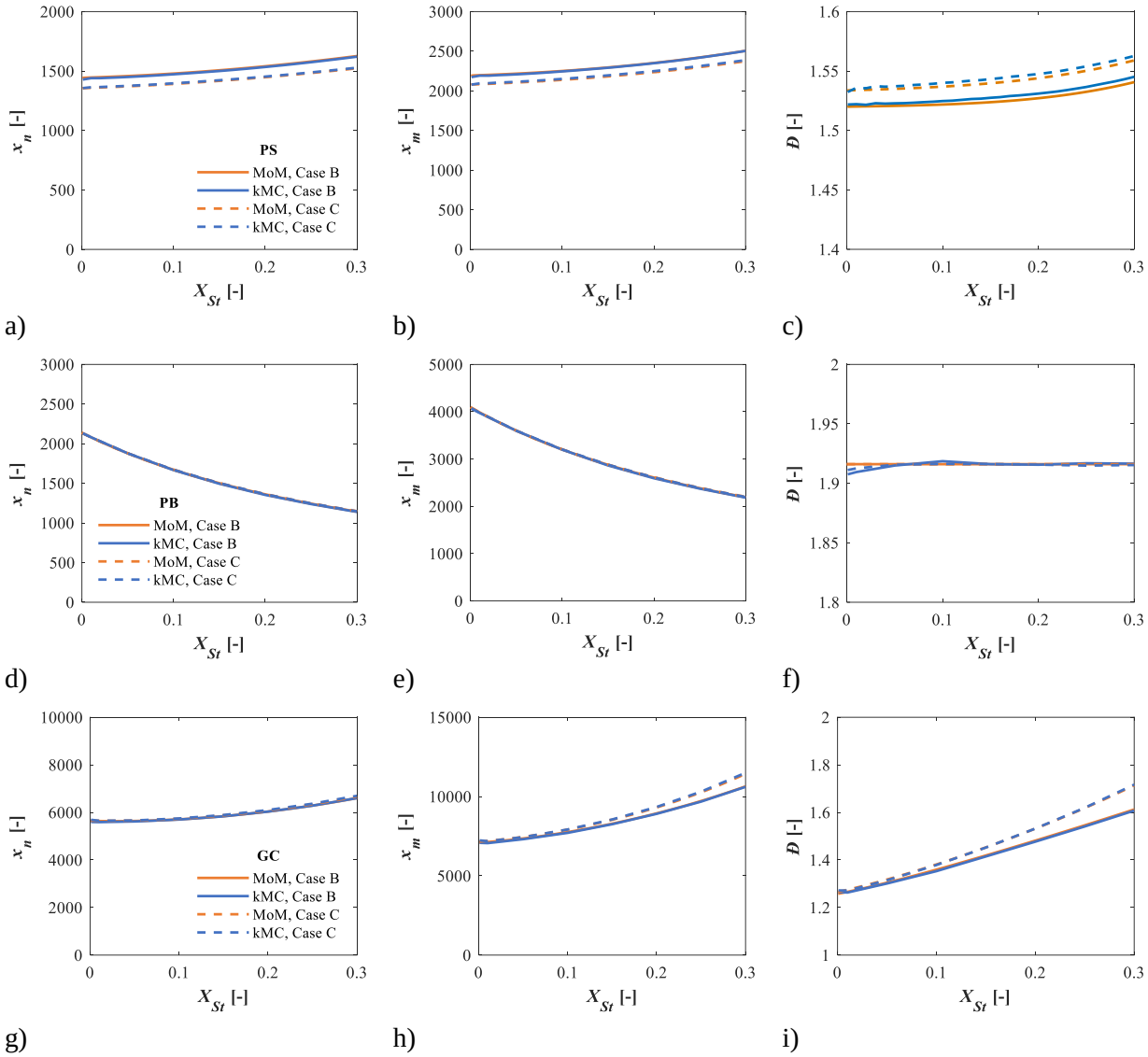
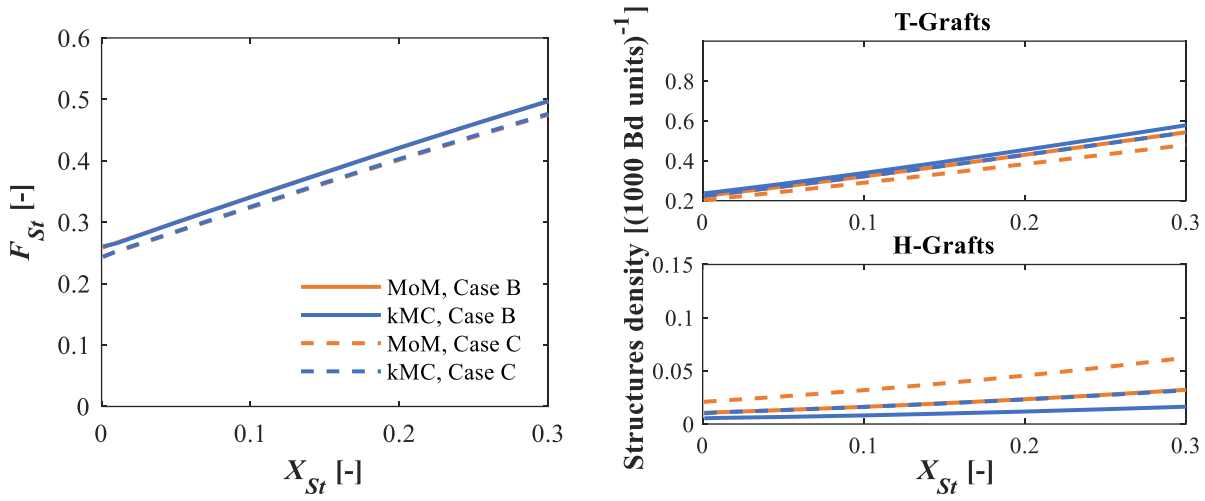


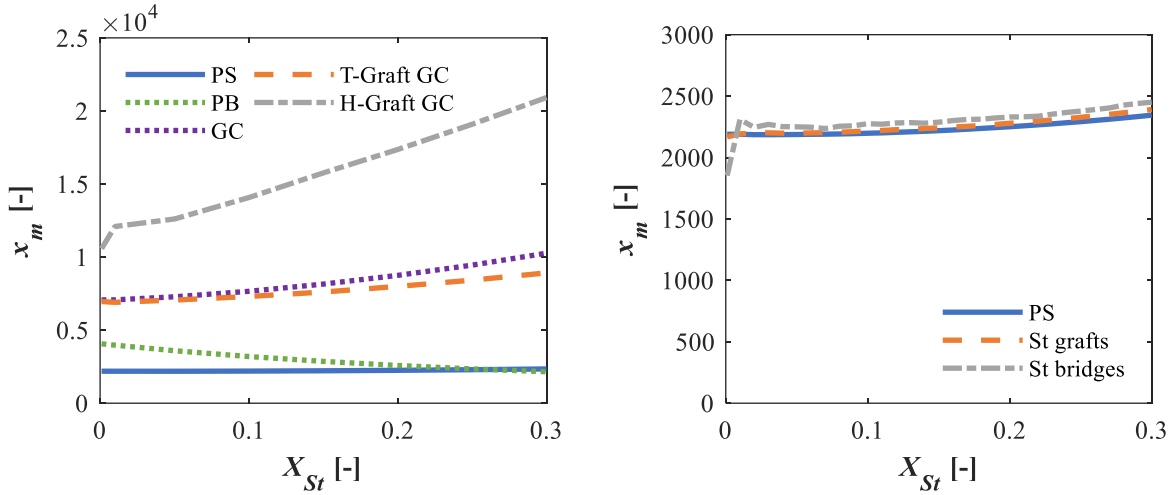
Figure S6. Benchmark with method of moments (MoM) simulations for Case B and C in Table 2 in the main text, without thermal self-initiation and macropropagation (kinetic parameters in Table 1 in the main text): variation with Styrene (St) conversion of (a)-(b) number/mass average chain length of polystyrene (PS); (c) dispersity of PS; (d)-(e) number/mass average chain length of polybutadiene (BP); (e) dispersity of PB; (g)-(h) number/mass average chain length of graft copolymer (GC); (i) dispersity of GC. MoM simulations are inherently characterized by simplifications for average chain length characteristics so that preference should be given to the CMMC results.



a) b)

Figure S7 Benchmark with method of moments (MoM) simulations for Case B and C in Table 2 in the main text, without thermal self-initiation and macropropagation (kinetic parameters in Table 1 in the main text): variation with Styrene (St) conversion of (a) content of St units in the graft copolymer and (b) Density of T-Grafts and H-Grafts in the graft copolymer, expressed per thousand Bd units.

S6 Additional average properties



a) b)

Figure S8 (a) Mass average chain lengths of macrospecies types in free radical induced grafting (FRIG) of polybutadiene (PB) with styrene (St). Focus on main macrospecies types conventional polystyrene (PS) and PB and graft copolymer (GC) with a distinction made between GC with only T-Grafts and GC with at least one H-Graft; (b) analogous plot for repeating the PS result and including also data regarding St grafts and bridges as such; kinetic parameters of Table 1 and reaction conditions Case A in Table 2 in the main text.

S7 Additional Distributions

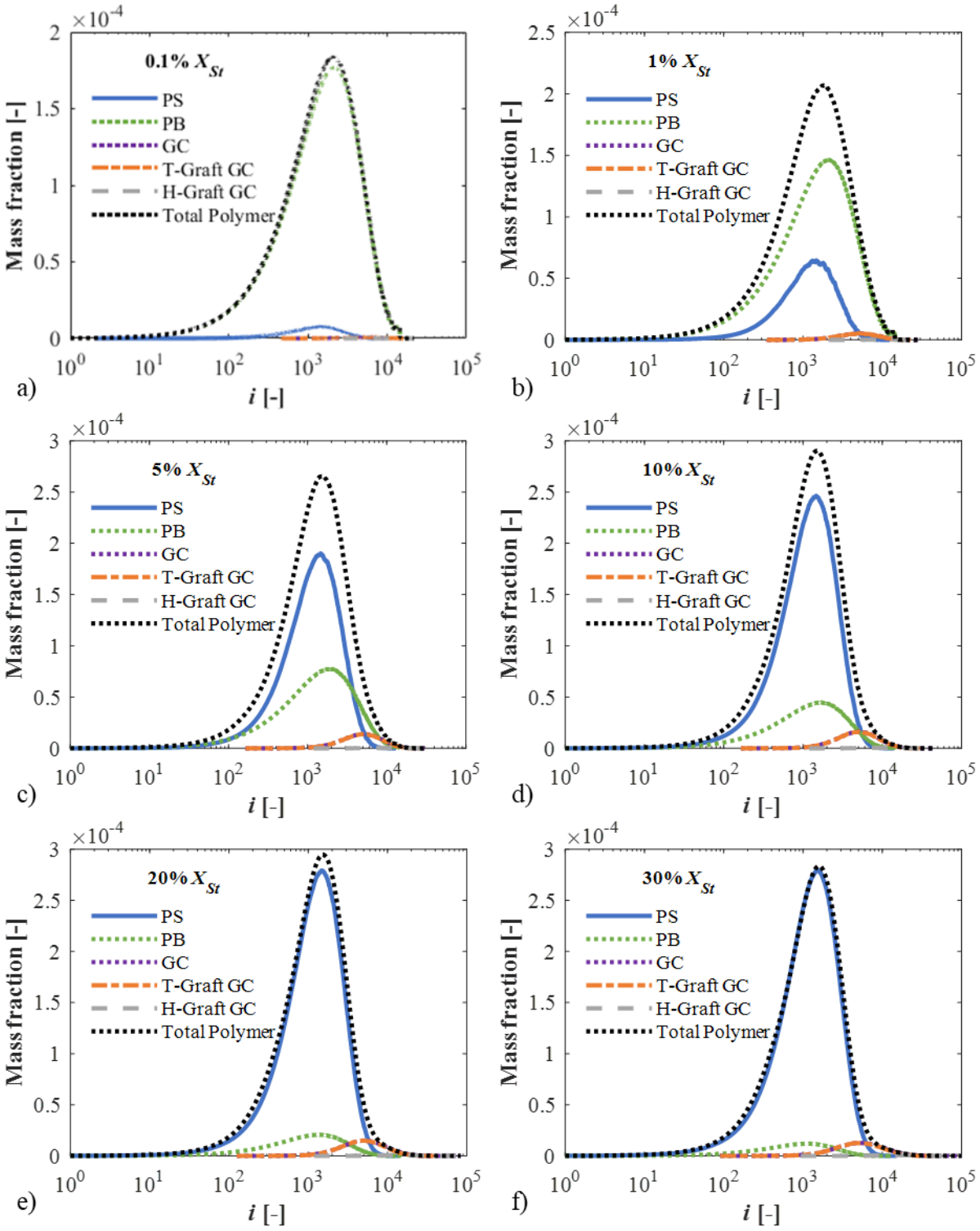


Figure S9 Kinetic Monte Carlo simulated mass average chain length distributions (CLDs; normalized by the total polymer content) at various St conversions; focus on PB, PS, and graft copolymer (GC) molecules at (a) 0,1 %; (b) 1%; (c) 5%, (d) 10%; (e) 20%; (f) 30%. Kinetic parameters of Table 1 and reaction conditions defined by Case A in Table 2 of the main text, 40 billion starting St units.

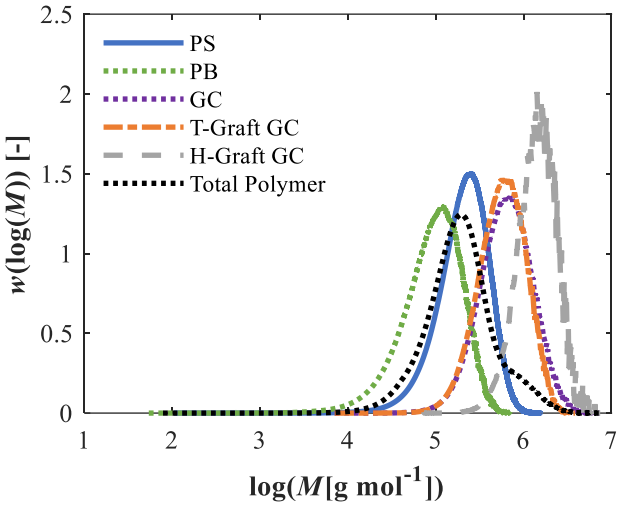


Fig. S10 Kinetic Monte Carlo simulated log-MMD for macrospecies types in free radical induced grafting (FRIG) of polybutadiene (PB) with styrene (St) at 30% St conversion; focus is on PB, PS, and graft copolymer (GC) molecules alongside the split-up in molecules with only T-grafts and with at least one H-Graft; also the total polymer is depicted; kinetic parameters of Table 1 and reaction conditions Case A in Table 2; smoothing by moving average method.

S8 References

1. K. De Smit, Y. W. Marien, K. M. Van Geem, P. H. M. Van Steenberge and D. R. D'Hooge, *React. Chem. Eng.*, 2020, **5**, 1909-1928.