

Supplementary Information

In this Supporting Information addition, Tables, Schemes, and Figures are given relating to the discussion of following subjects in the main text:

- (i) a brief description of the mathematical model based on the method of moments;
- (ii) the genetic optimization algorithm NSGA-II;
- (iii) the multi-objective optimization results for ARGET ATRP of BMA; and
- (iv) the multi-objective optimization results for NMP of styrene.

Description of the Mathematical Model

In this work, a deterministic modeling approach is considered for the description of the evolution of polymerization kinetics. For simplicity, the method of moments is applied in which the chain length distribution (CLD) is described by a limited number of characteristic points. The CLD is namely represented by a discrete number of s -th ($s > 0$) order averages:

$$x_s = \frac{\sum_i i^s ([R_i] + [P_i] + [R_iX])}{\sum_i i^{s-1} ([R_i] + [P_i] + [R_iX])} \quad (1)$$

In this equation, $[R_i]$, $[P_i]$, and $[R_iX]$ are, respectively, the concentration of radicals, dead polymer molecules, and dormant polymer molecules with chain length i . Typically, for RDRP processes, the calculation is limited to the first and second ($s = 1,2$) order average. These two averages are also known as the number- and mass-averaged chain length (x_n and x_m). The relative position of these averages can be reflected by the dispersity, which allows assessing the broadness of the CLD:

$$D = \frac{x_m}{x_n} \quad (2)$$

For more details on the method of moments, the reader is referred to specialized literature [1,2].

Genetic Optimization Algorithm NSGA-II

In this work, several preliminary simulations were performed in order to select the optimal NSGA-II parameters and every simulation was performed multiple times using different random numbers sequences and checked for convergence.

Table S1. NSGA-II GA parameter values used [3].

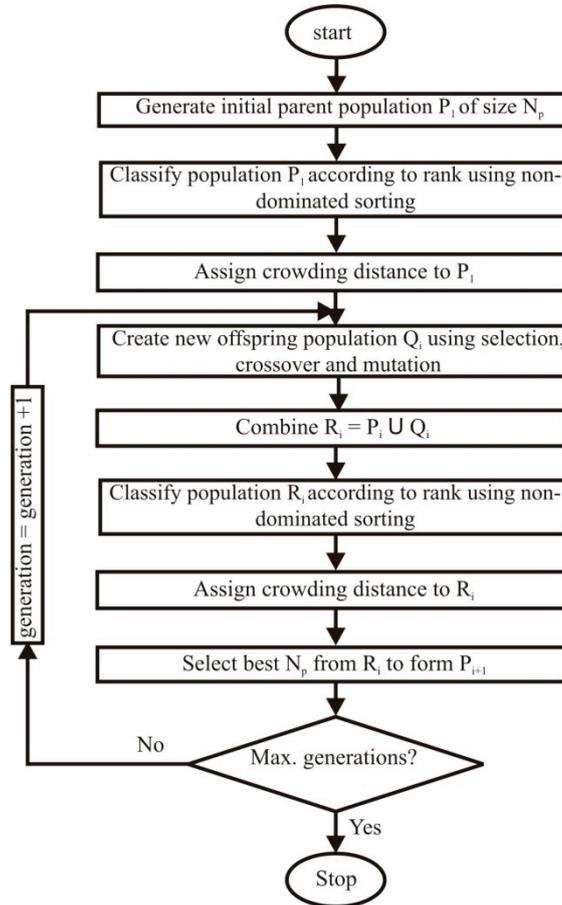
| Parent Population Size ^(a) | 200 */400 ** |
|---------------------------------------|----------------------------|
| Selection strategy | Binary tournament |
| Crossover type | Simulated binary crossover |
| Mutation type | Polynomial mutation |
| Crossover probability | 0.9 |
| Mutation probability (real) | 0.05 |
| Distribution index crossover | 5 |
| Distribution index mutation | 1 |
| Numbers of generations | 125 */150 ** |

^(a) Parent population size equal to offspring population size; * relates to single variation optimization studies, ** relates to multiple variation (combinations of individual optimization pathways) optimization studies.

Table S2. Overview of upper and lower boundaries of the variables used in the MOO-optimizations. For simultaneous variation of process conditions, identical boundaries were used as in the single variation studies; in all cases the final (overall) conversion is 0.75.

| Type of Optimization | Lower-Upper Boundary |
|--------------------------------------|----------------------|
| ARGET ATRP Temperature Profile | – |
| Var1-7 | 60–90 °C |
| ARGET ATRP Monomer Addition * | – |
| Var1 | 0.15–1 (-) |
| Var2-7 | 0–1 (-) |
| ARGET ATRP Reducing Agent Addition * | – |
| Var1-7 | 0–1 (-) |
| NMP Temperature Profile | – |
| Var1-7 | 80–120 °C |
| NMP Monomer Addition * | – |
| Var1 | 0.1–1 (-) |
| Var2-7 | 0–1 (-) |
| NMP Initial Nitroxide Loading | – |
| Var1 | 0–0.5 (-) |

* sum of fractions equal to 1.



Scheme S1. Flowchart of the NSGA-II algorithm.

Multi-Objective Optimization Results for ARGET ATRP of BMA

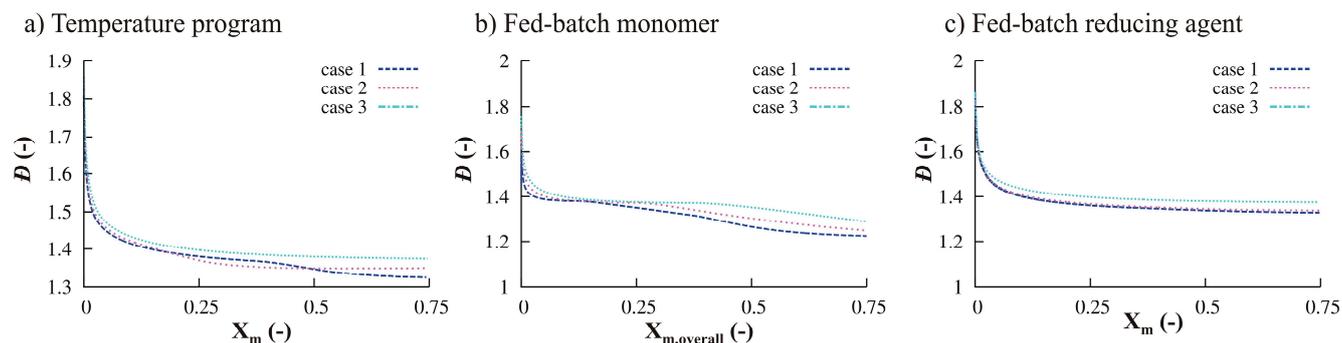


Figure S1. Dispersivity (D) profiles as a function of conversion for the three selected cases for the MOO-studies of the ARGET ATRP of BMA using (a) a piecewise linear temperature program (Figure 2; Main text); (b) a fed-batch monomer program (Figure 4; Main text); and (c) a fed-batch reducing agent program (Figure 5; Main text).

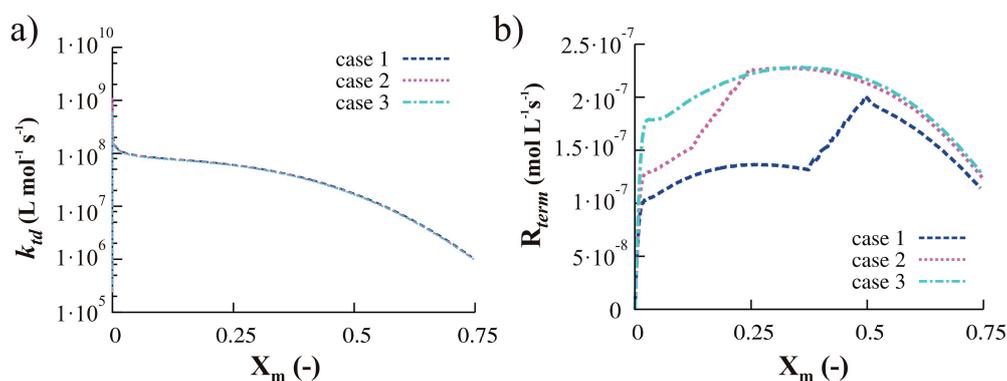


Figure S2. (a) Apparent rate coefficient for termination by disproportionation (recombination similar profile) as a function of conversion and (b) Termination rate as a function of conversion for the three selected cases for the MOO-studies of the ARGET ATRP of BMA using a piecewise linear temperature program (Figure 2; Main text).

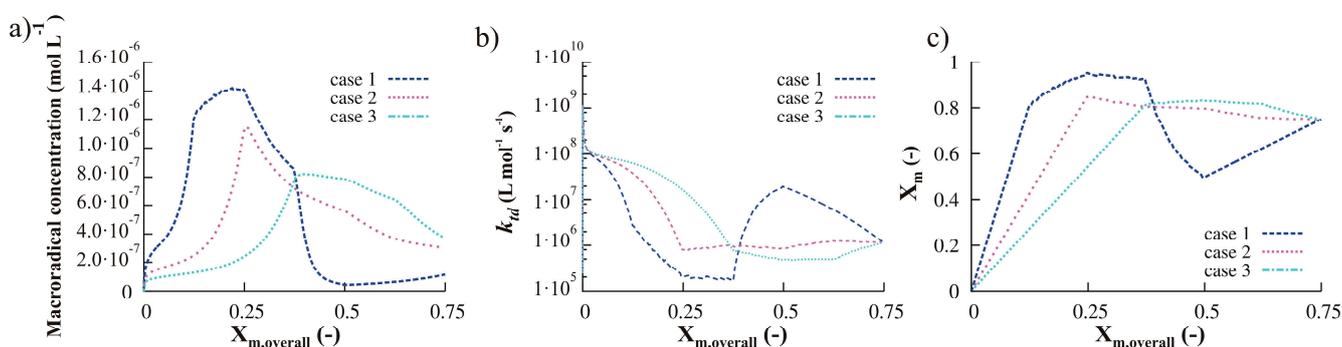


Figure S3. (a) Macroradical concentration as a function of the overall conversion; (b) Apparent rate coefficient for termination by disproportionation (recombination similar profile) as a function of the overall conversion; (c) *in situ* conversion as a function of the overall conversion for the three selected cases for the MOO-studies of the ARGET ATRP of BMA using a fed-batch monomer program (Figure 4; Main text).

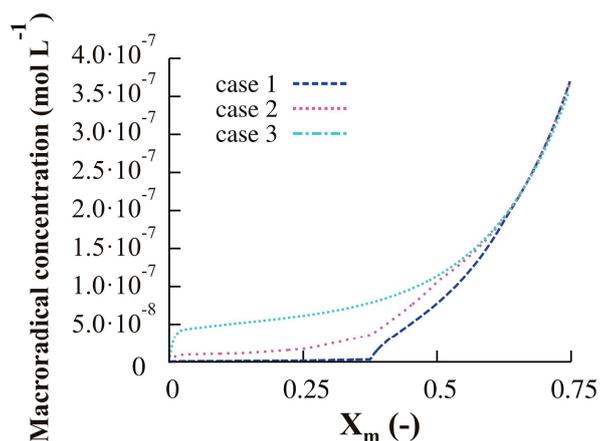


Figure S4. Macroradical concentration as a function of conversion for the three selected cases for the MOO-studies of the ARGET ATRP of BMA using a fed-batch reducing agent program (Figure 5; Main text).

Multi-Objective Optimization Results for NMP of Styrene

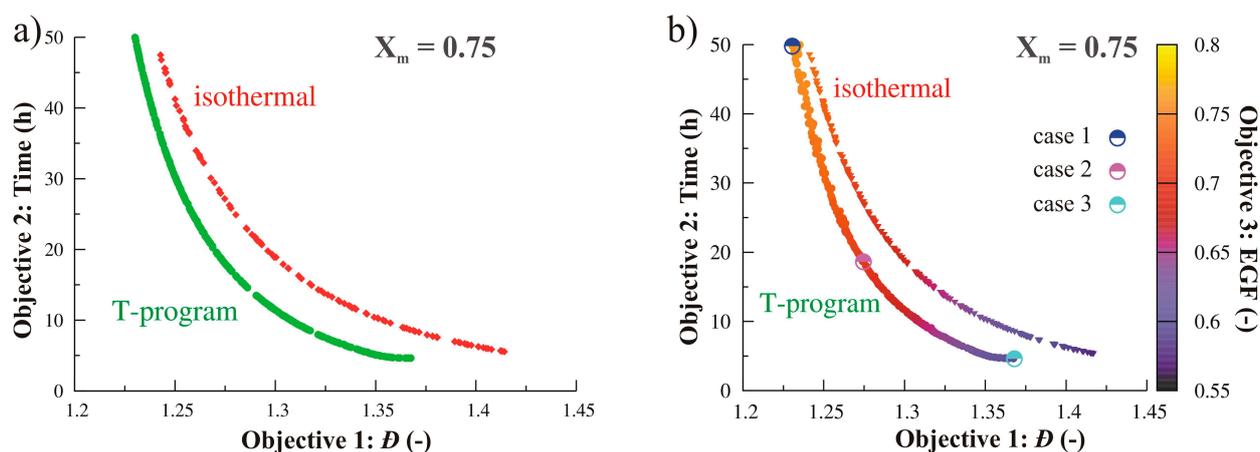


Figure S5. Multi-objective optimization (MOO) results for NMP of styrene using a piecewise linear temperature program with: (a) two objectives (*i.e.*, dispersity (D) and time to reach $X_m = 0.75$); and (b) three objectives (*i.e.*, dispersity (D), time to reach $X_m = 0.75$, and end-group functionality (EGF)).

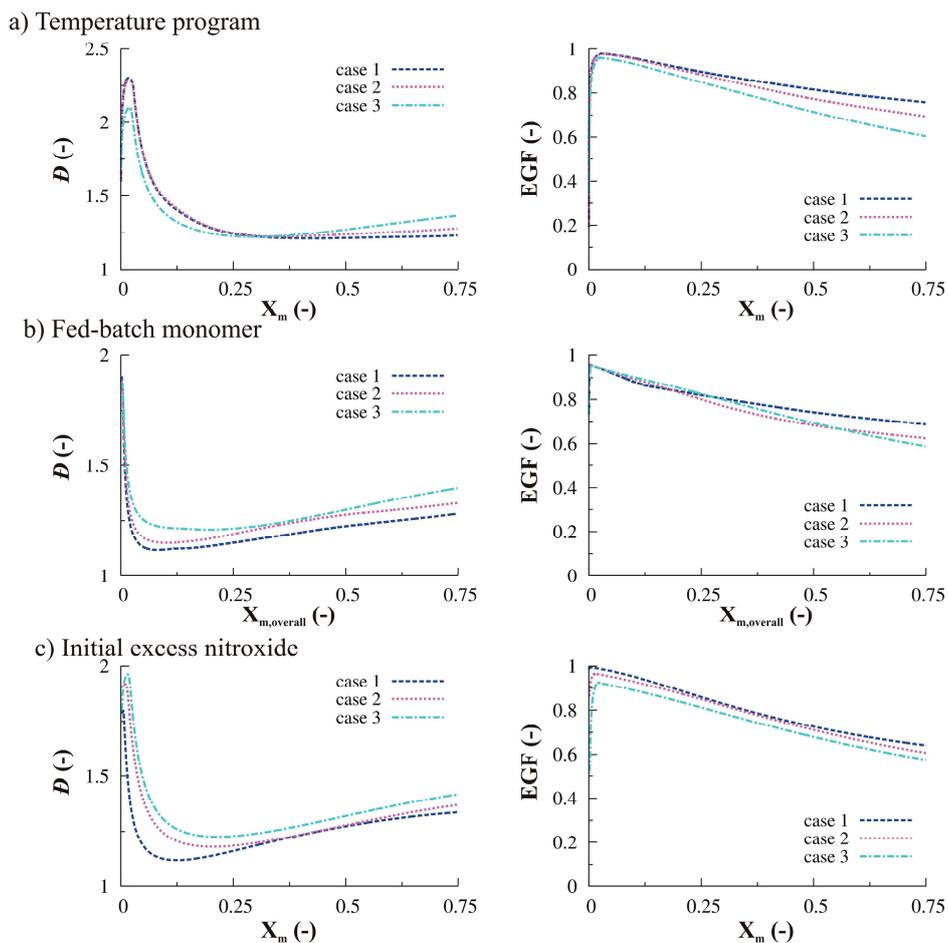


Figure S6. Dispersity (D) profiles as a function of conversion (**left** chart) and end-group functionality (EGF) profiles as a function of conversion (**right** chart) for the three selected cases for the MOO-studies of the NMP of styrene using: **(a)** a piecewise linear temperature program (Figure 7; Main text); **(b)** a fed-batch monomer program (Figure 8; Main text); and **(c)** an excess initial nitroxide loading (Figure 9; Main text).

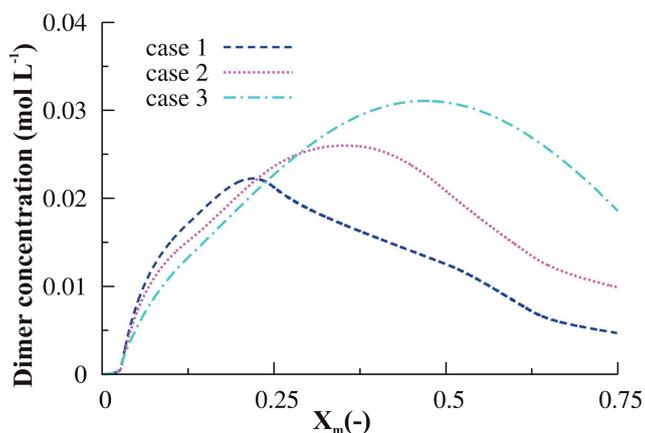


Figure S7. Dimer concentration profiles as a function of conversion for the three selected cases of the MOO of styrene using a piecewise linear temperature program (Figure 7; Main text).

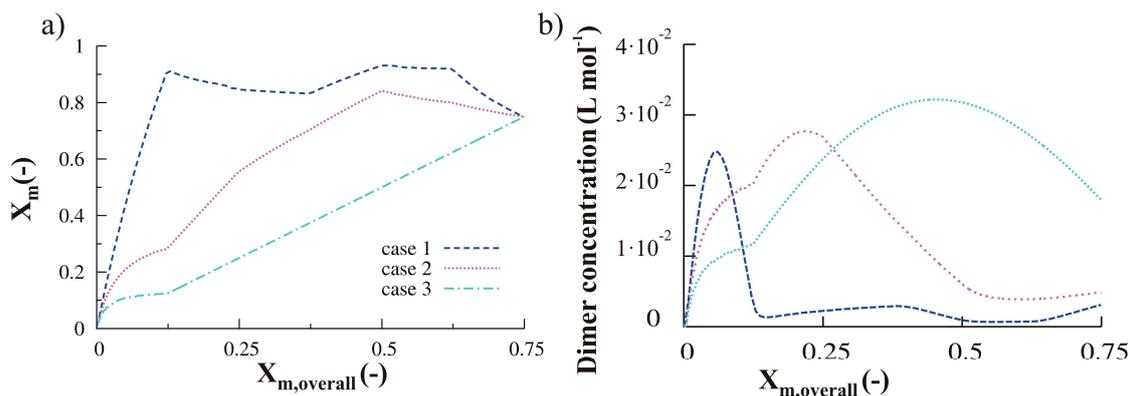


Figure S8. (a) *In situ* conversion (X_m) as a function of the overall conversion ($X_{m,overall}$) for the three selected cases and (b) dimer concentration as a function of $X_{m,overall}$ for the MOO of NMP of styrene using a fed-batch monomer program (Figure 8; Main text).

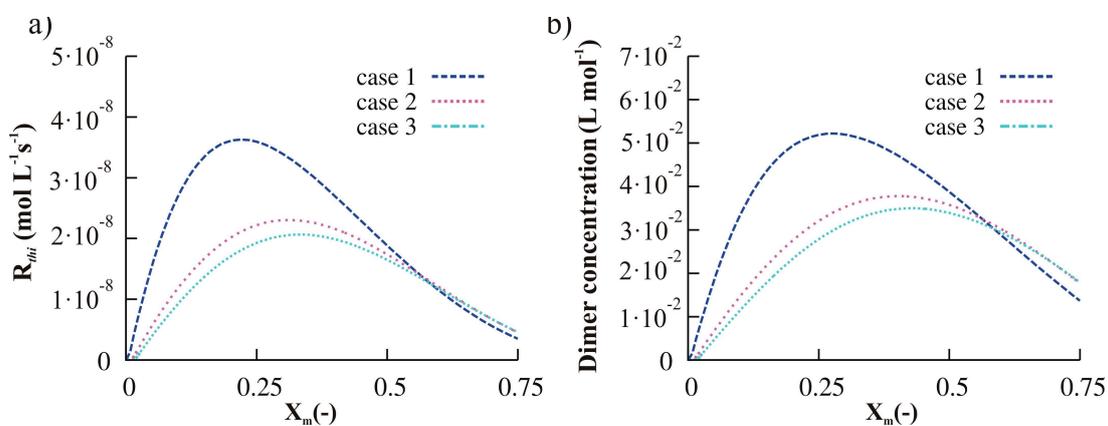


Figure S9. (a) Thermal initiation rate (R_{thi}) as a function of conversion (X_m) and (b) dimer concentration as a function of X_m for the three selected cases for the MOO of NMP of styrene using excess initial nitroxide (Figure 9; Main text).

References

1. Wang, A.R.; Zhu, S.P. Modeling the reversible addition-fragmentation transfer polymerization process. *J. Polym. Sci. Pol. Chem.* **2003**, *41*, 1553–1566.
2. Mastan, E.; Li, X.; Zhu, S. Modeling and theoretical development in controlled radical polymerization. *Progr. Polym. Sci.* **2015**, doi:10.1016/j.progpolymsci.2014.12.003.
3. Deb, K.; Pratap, A.; Agarwal, S.; Meyarivan, T. A fast and elitist multiobjective genetic algorithm: NSGA-II. *IEEE Trans. Evol. Comput.* **2002**, *6*, 182–197.