Supplementary Information for:

Simulation of the RAFT polymerization in 3D: steric restrictions and incompatibility between species

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A. Comparison of the chain length distributions obtained within the "full" and simplified kinetic models.

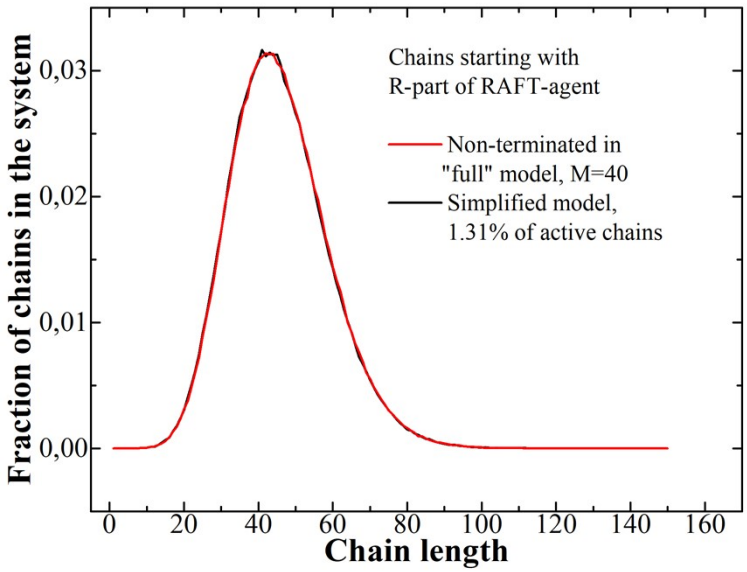

Fig.S1 Comparison of the chain length distributions obtained within the "full" and simplified kinetic models. For the full model, non-terminated chain starting with R-part of the RAFT agent are shown as the main desired product of the polymerization.

B. Influence of the termination type

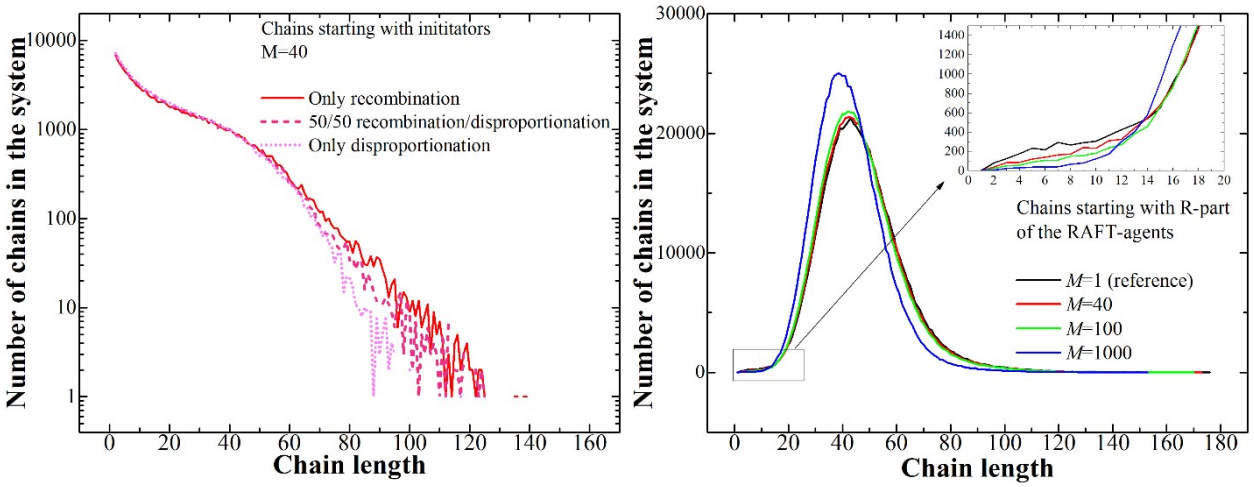

Fig.S2 Chain length distributions obtained within the kinetic model for different types of the termination reactions: starting with initiators (left); starting with R-parts of the RAFT agents (right).

C. Investigation of the reaction speed leading to a kinetically controlled exchange reaction in DPD

In order to find the maximum p_t value below which the resulting chain-length distributions do not depend on it when C_{ex} is fixed, the following system was studied: RAFT agent fraction is 0.006 (in the DPD model, each RAFT agent consists of 2 beads), monomer beads fraction is 0.1434, and the rest ~0.85 is solvent. The initiator fraction was varied; since the initiation is immediate and there is no termination, the fraction of active chains f_a in the system is equal to the number of initiators divided by the total number of chains. We studied several p_t values as well as the fractions of active chains f_a to cover different situations, and the C_{ex} value was fixed at 17.5 in all cases; the results are shown in Fig.S3.

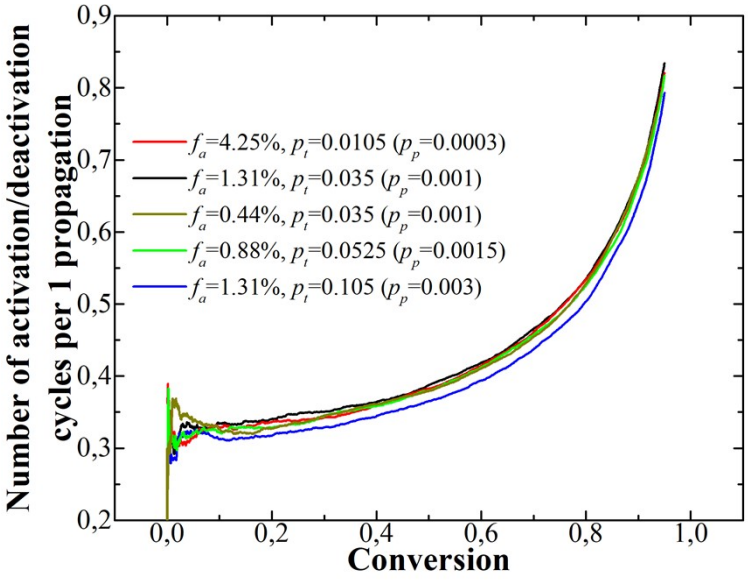

Fig.S3 Dependences of the average total number of activation/deactivation cycles per every propagation event on conversion for different fractions of active chains f_a and probability of the addition to the RAFT end group reaction p_t obtained using DPD.

The system with f_a=4.25% and p_t=0.0105 (p_p=0.0003) has the least influence of diffusion as it has the lowest reaction probabilities and, at the same time, the highest number of active chains. We see that the p_t=0.0525 (p_p<=0.0015) for all studied values of f_a the curves coincide. When the value of p_t becomes as high as 0.105 (corresponds to p_p=0.03) the number of activation/deactivation cycles starts to slightly decrease, indicating that at such probabilities the exchange reaction becomes diffusion controlled.

D. Investigation of the reaction parameters for the case of PISA

In order to test the reliability of the results obtained for non-zero χ-values, we additionally tested slower reaction speed, different fractions of active chains as well as the behavior within the "full" model for the case when the RAFT end groups had affinity to the solvent (χ_{B-Reg}=1.8, for which very wide chain-length distribution was observed). The following cases were compared:

0. Simplified model, f_a=1.31% and p_p=0.001. Identical to the system studied in the main text.
1. Simplified model, f_a=4.25% and p_p=0.0001. Compared to the system studied in the main text (case 0), this case has ~3.33 more active ends, but the reaction probabilities are 10 times smaller. This means that the reaction is significantly slower, giving the chains more time to diffuse. Also, larger number of active chains could lead to the reduction of the dispersity.
2. "Full" model with $p_i=4\times10^{-7}$, p_t=0.001, p_p=0.001, [MacroRAFT]/[initiator]=5. In this case we found that the maximum fraction of simultaneously active chains is roughly equal to that in the case 0. The presence of the termination reaction inside the micelles could stop the growth of the longer chains forming them, and the slow radical formation from the initiators (which occurs in the solution) provides new radicals outside the micelles.
3. "Full" model with $p_i=1.33\times10^{-7}$, p_t=0.003, p_p=0.001. In this case the simultaneous number of active chains is ~3 times smaller than in the case 2.

PISA for these 4 cases was studied in a larger simulation box of the size 100^3 for better statistics; the obtained chain-length dependences at 50% conversion (which is well above the onset of the micelles formation, see Fig.9 of the main text) are shown in Fig. S4.

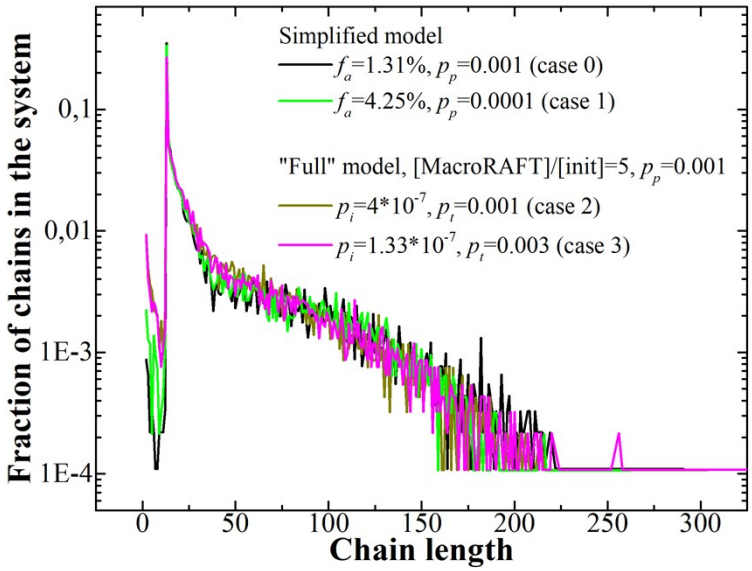

Fig. S4 Chain length distributions at 50% conversion obtained during PISA for the case when the RAFT end groups had affinity to the solvent (χ_{B-Reg}=1.8) under different conditions.

We do not see any significant differences between the distributions (apart from those expected due to the apparent changes in the models).