

Supporting information for “Two-Compartment Kinetic Monte Carlo Modelling of Electrochemically Mediated ATRP”

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S1 Calculation of transport coefficients to describe the catalyst exchange between both compartments (detailed calculation of Equation (1) and (2) in the main text)

A two-film layer model is used in the present work to describe the exchange of catalyst type N from one compartment to the other (definitions compartments: Figure 3 in the main text). Figure S1 represents the general representation of this model, assuming a partitioning coefficient Γ_N at the interface. This interface must be seen as the “contact line” between both compartments. On both sides of this interface a solvent layer with a thickness d is assumed to reflect possible mass transport limitations (with all process parameters active, *e.g.* with stirring), with the associated mass transport coefficients $k_{N,i}$ ($i=1,2$; $\text{dm}_i \text{ s}^{-1}$) given by the ratio of the diffusion coefficient (D_i ; $i=1,2$; dm s^{-2}) to the solvent layer thickness.

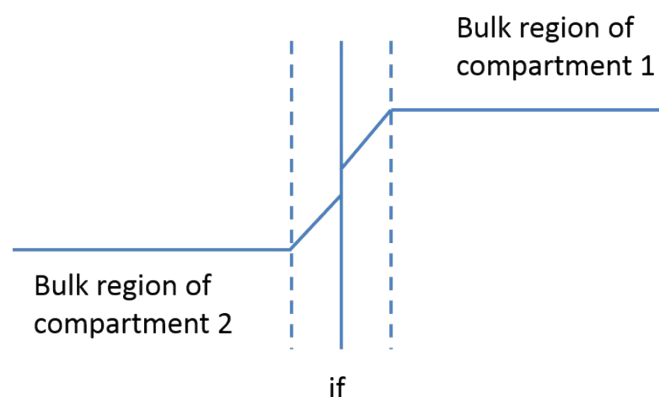


Figure S1: General representation of the two film layer model; if: interface (*cf.* Figure 2 in the main text; switch/border between compartments) for which a partitioning coefficient is used to obtain the concentrations (equilibrium conditions); in this work there is no interface resistance so that in the end one straight line is obtained from the bulk concentration in the one compartment to the one in the other compartment (see end of derivation).

The concentrations at the interfaces are denoted as $C_{N1,f}$ and $C_{N2,f}$ and Γ_N is defined as the ratio of the former to the latter (dimension: L_2/L_1), implicitly assuming equilibrium. In the present work, as explained in the main text Γ_N is assumed constant. To ensure continuity the (molar) flux for N ($\text{mol dm}^{-2} \text{ s}^{-1}$) is given by:^{1,2}

$$J_N = k_{N,1}(C_{N,1} - C_{N,1,f}) = -k_{N,2}(C_{N,2} - C_{N,2,f}) \quad (\text{S1})$$

Upon elimination of the interface concentration in the former equality, as explained in Wieme *et al.*,² this flux can be expressed based on the “bulk” compartment concentrations:

$$J_N = K_N(C_{N,1} - \Gamma_N C_{N,2}) \quad (\text{S2})$$

in which K_N is the overall transport coefficient for N (thus for both layers jointly; dm s^{-1}) defined based on the first phase:

$$K_N^{-1} = \left(\frac{1}{k_{N,1}} + \frac{\Gamma_N}{k_{N,2}} \right) \quad (\text{S3})$$

Defining the surface of one side of the electrode as S (dm^2), the number of N molecules that is being exchanged per second (J_N' ; $\# \text{ s}^{-1}$) becomes

$$J_N' = 2SN_A J_N = 2SN_A K_N (C_{N,1} - \Gamma_N C_{N,2}) \quad (\text{S4})$$

For kinetic Monte Carlo ($k\text{MC}$) simulations, the previous equation needs to be rewritten with respect to the “bulk” number of N molecules in each compartment ($X_{N,1}$ and $X_{N,2}$):

$$J_N' = 2SN_A K_N \left(\frac{X_{N,1}}{N_A V_1} - \Gamma_N \frac{X_{N,2}}{N_A V_2} \right) \quad (\text{S5})$$

Furthermore, so-called “microscopic” or kinetic Monte Carlo rate coefficients (k_{MC})^{3, 4} expressed in s^{-1} are formally needed, implying that following equation can be defined in parallel:

$$J_N' = k_{\text{MC},A,12} X_{N,1} - k_{\text{MC},A,21} X_{N,2} \quad (\text{S6})$$

with the subscript “ ij ” implying a movement from compartment i to compartment j .

To obtain a direct link with the conventional or so-called “macroscopic” rate coefficients (*cf.* main text; $\text{L mol}^{-1} \text{ s}^{-1}$) it can be additionally written that:

$$J'_N = k_{MC,A,12}X_{N,1} - k_{MC,A,21}X_{N,2} = k_{N,12} rt_{A,12} X_{N,1} - k_{N,21} rt_{A,21} X_{N,2} \quad (\text{S7})$$

in which “rt” formally represents the reaction type or the correction factor for volume effects to make a direct resemblance with the sampling of chemical reactions.³

Hence, the following relations are obtained:

$$k_{N,tr,12} = 2 SN_A K_N \quad (\text{S8})$$

$$k_{N,tr,21} = 2 SN_A K_N \Gamma_N = \Gamma_N k_{N,12} \quad (\text{S9})$$

$$rt_{N,tr,12} = \frac{1}{N_A V_1} \quad (\text{S10})$$

$$rt_{N,tr,21} = \frac{1}{N_A V_2} = \frac{rt_{N,tr,12}}{r_V} \quad (\text{S11})$$

in which r_V is volume ratio as defined in the main text.

As explained in the main text, in the present work, Γ_N is assumed constant: $\Gamma_N = \Gamma$. For simplicity it is given a value of one so that a straight line is obtained along the whole film as depicted in Figure 1 (right) in the main text.

S2 RAFT-CLD-T parameters

The RAFT-CLD parameters for termination involving secondary species are taken from the work of Johnston-Hall and Monteiro⁵ and are specified in Table S1. The values for the unimer radicals are specified in the main text.

Table S1: RAFT-CLD-T parameters to account for diffusional limitations on termination

i_{gel}	$6.9 m_p^{-2.2}$
α_s	0.78
α_l	0.15
α_{gel}	$0.8 w_p - 0.05$
i_{sl}	18

S3 Fraction of deactivator

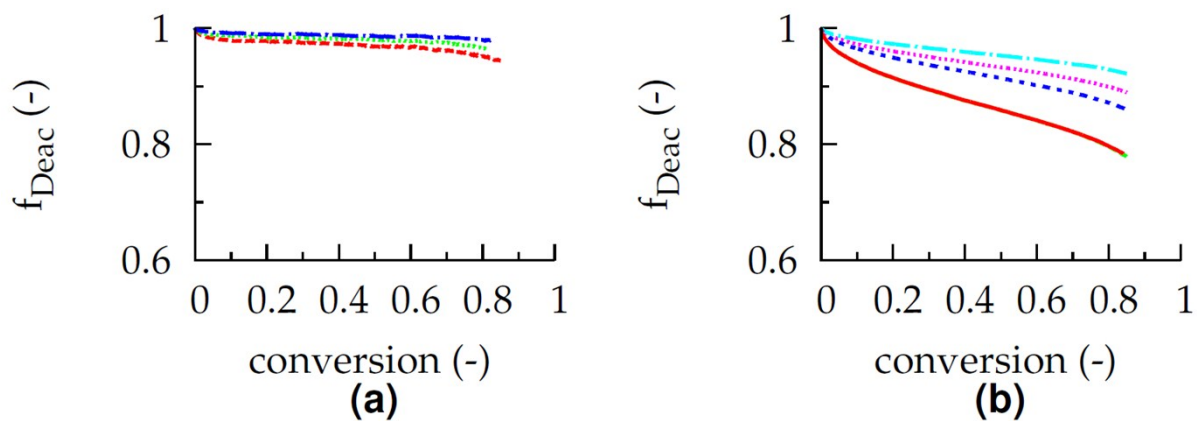


Figure S1: Fraction of deactivator in the large compartment (versus activator); left: MA/ME₆TREN case; right: *n*BuA/TPMA⁺ case; conditions in main text Figure 4 and 5.

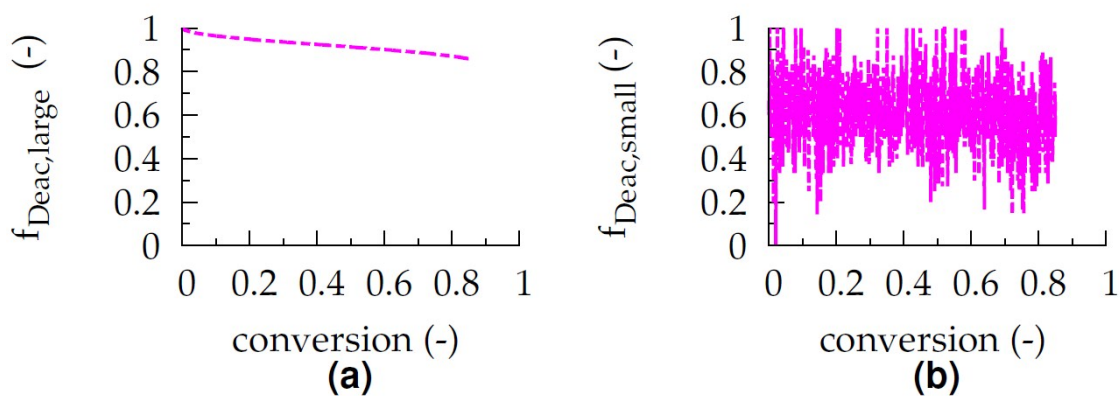


Figure S2: Fraction of deactivator in the large and small compartment (versus activator); *n*BuA/TPMA⁺ case; conditions in main text Figure 5; on average lower fractions are obtained in the small compartment.

S3 Simulation results in case diffusional limitations on termination are ignored ($\Delta E = -0.03$ V; red line from Figure 3 in the main text)

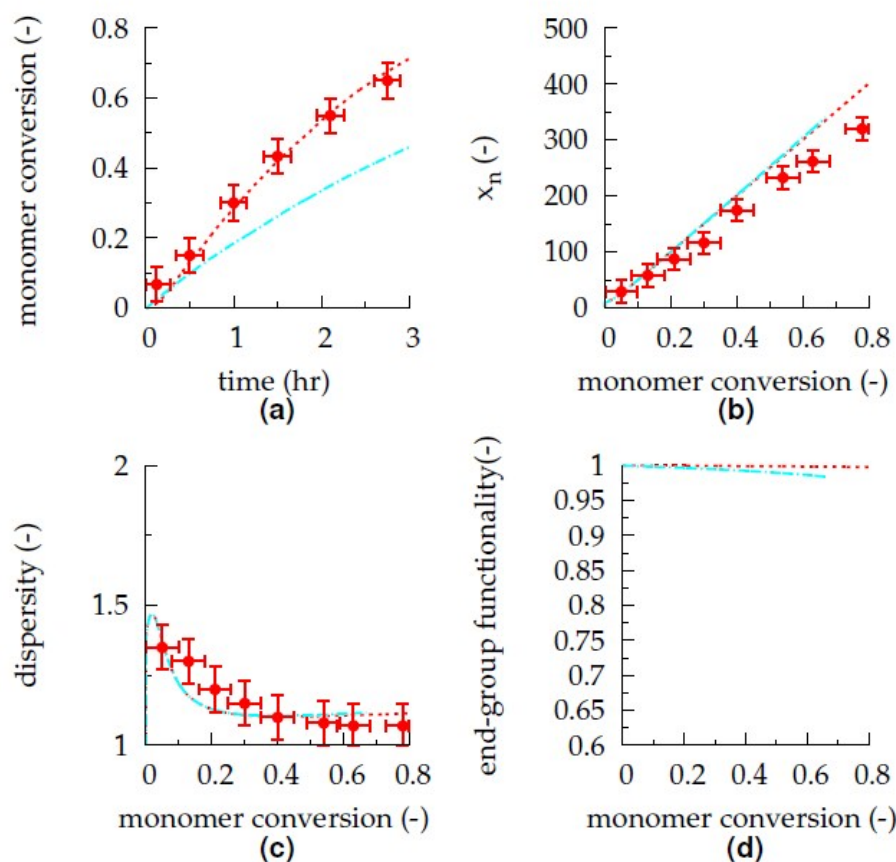


Figure S3: (a) Monomer conversion as a function of time; (b) number average chain length (x_n); (c) dispersity; (d) end-group functionality (EGF); as a function of (monomer) conversion; reaction conditions: $[M]_0:[R_0X]_0:[Deact]_0=300:1:0.025$; 50% solvent; $T=298$ K; $\Delta E = -0.03$ V (MA/ME₆TREN case). Red line: full model as in main text (Figure 4). Blue line: no diffusional limitations on termination

From Figure S3 it follows that it is crucial to account for diffusional limitation on termination. Strong deviations are obtained between both cases. Note that to counteract this shortcoming of a kinetic model neglecting diffusional limitations on termination one must formally change other kinetics parameters, which is not the preferred route both from a fundamental and design point of view. In particular in the present work focus is on the correct representation of the conversion profile in view of parameter tuning of the reduction rate coefficient k_{red} (discussion of Figure 4 in the main text). Only while accounting for diffusional limitations a correct determination of Equation (3) becomes possible (Figure S2(a)).

S4 References

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