Supplementary Material

Kinetic Monte Carlo simulation based detailed understanding of the transfer processes in semi-batch iodine transfer emulsion polymerizations of vinylidene fluoride

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Scheme S1: Transfer and propagation reactions included in the kMC model.

with I- : iodine end group;

D-: irreversibly deactivated end group

X, X': C_4F_8

reactions of I-X•

I-X•	+	I-X'-I	→	I-X-I	+	I-X'•
I-X•	+	D-X'-I	→	I-X-I	+	D-X'•
I-X•	+	I-X'P_m-I	→	I-X-I	+	I-X'P_m•
I-X•	+	I-X'P_m-I	→	I-X-I	+	I-P_mX'•
I-X•	+	D-X'P_m-I	→	I-X-I	+	D-X'P_m•
I-X•	+	I-X'P_m-D	→	I-X-I	+	D-P_mX'•
I-X•	+	D-P_mX'P_k-I	→	I-X-I	+	D-P_mX'P_k•
I-X•	+	I-P_mX'P_k-I	→	I-X-I	+	I-P_mX'P_k•
I-X•	+	M	→	I-XP_i•		

reactions of D-X•

D-X•	+	I-X'-I	→	D-X-I	+	I-X'•
D-X•	+	D-X'-I	→	D-X-I	+	D-X'•
D-X•	+	I-X'P_m-I	→	D-X-I	+	I-X'P_m•
D-X•	+	I-X'P_m-I	→	D-X-I	+	I- P_mX'•
D-X•	+	D-X'P_m-I	→	D-X-I	+	D-X'P_m•
D-X•	+	I-X'P_m-D	→	D-X-I	+	D-P_mX'•

$D\text{-}X^{\bullet} + D\text{-}P_mX'P_k\text{-}I \rightarrow D\text{-}X\text{-}I + D\text{-}P_mX'P_k^{\bullet}$

$D\text{-}X^{\bullet} + I\text{-}P_mX'P_k\text{-}I \rightarrow D\text{-}X\text{-}I + I\text{-}P_mX'P_k^{\bullet}$

$D\text{-}X^{\bullet} + M \rightarrow D\text{-}XP_1^{\bullet}$

reactions of $I\text{-}XP_n^{\bullet}$

$I\text{-}XP_n^{\bullet} + I\text{-}X'\text{-}I \rightarrow I\text{-}XP_n\text{-}I + I\text{-}X'^{\bullet}$

$I\text{-}XP_n^{\bullet} + D\text{-}X'\text{-}I \rightarrow I\text{-}XP_n\text{-}I + D\text{-}X'^{\bullet}$

$I\text{-}XP_n^{\bullet} + I\text{-}X'P_m\text{-}I \rightarrow I\text{-}XP_n\text{-}I + I\text{-}X'P_m^{\bullet}$

$I\text{-}XP_n^{\bullet} + I\text{-}X'P_m\text{-}I \rightarrow I\text{-}XP_n\text{-}I + I\text{-}P_mX'^{\bullet}$

$I\text{-}XP_n^{\bullet} + D\text{-}X'P_m\text{-}I \rightarrow I\text{-}X\text{-}P_n\text{-}I + D\text{-}X'P_m^{\bullet}$

$I\text{-}XP_n^{\bullet} + I\text{-}X'P_m\text{-}D \rightarrow I\text{-}X\text{-}P_n\text{-}I + D\text{-}P_mX'^{\bullet}$

$I\text{-}XP_n^{\bullet} + D\text{-}P_mX'P_k\text{-}I \rightarrow I\text{-}X\text{-}P_n\text{-}I + D\text{-}P_mX'P_k^{\bullet}$

$I\text{-}XP_n^{\bullet} + I\text{-}P_mX'P_k\text{-}I \rightarrow I\text{-}X\text{-}P_n\text{-}I + I\text{-}P_mX'P_k^{\bullet}$

$I\text{-}XP_n^{\bullet} + M \rightarrow I\text{-}XP_{n+1}^{\bullet}$

reactions of $I\text{-}P_nX^{\bullet}$

$I\text{-}P_nX^{\bullet} + I\text{-}X'\text{-}I \rightarrow I\text{-}XP_n\text{-}I + I\text{-}X'^{\bullet}$

$I\text{-}P_nX^{\bullet} + D\text{-}X'\text{-}I \rightarrow I\text{-}XP_n\text{-}I + D\text{-}X'^{\bullet}$

$I\text{-}P_nX^{\bullet} + I\text{-}X'P_m\text{-}I \rightarrow I\text{-}XP_n\text{-}I + I\text{-}X'P_m^{\bullet}$

$I\text{-}P_nX^{\bullet} + I\text{-}X'P_m\text{-}I \rightarrow I\text{-}XP_n\text{-}I + I\text{-}P_mX'^{\bullet}$

$I\text{-}P_nX^{\bullet} + D\text{-}X'P_m\text{-}I \rightarrow I\text{-}XP_n\text{-}I + D\text{-}X'P_m^{\bullet}$

$I\text{-}P_nX^{\bullet} + I\text{-}X'P_m\text{-}D \rightarrow I\text{-}XP_n\text{-}I + D\text{-}P_mX'^{\bullet}$

$I\text{-}P_nX^{\bullet} + D\text{-}P_mX'P_k\text{-}I \rightarrow I\text{-}XP_n\text{-}I + D\text{-}P_mX'P_k^{\bullet}$

$I\text{-}P_nX^{\bullet} + I\text{-}P_mX'P_k\text{-}I \rightarrow I\text{-}XP_n\text{-}I + I\text{-}P_mX'P_k^{\bullet}$

$I\text{-}P_nX^{\bullet} + M \rightarrow I\text{-}P_nXP_1^{\bullet}$

reactions of $D\text{-}P_nX^{\bullet}$

$D\text{-}XP_n^{\bullet} + I\text{-}X'\text{-}I \rightarrow D\text{-}XP_n\text{-}I + I\text{-}X'^{\bullet}$

$D\text{-}XP_n^{\bullet} + D\text{-}X'\text{-}I \rightarrow D\text{-}XP_n\text{-}I + D\text{-}X'^{\bullet}$

$D\text{-}XP_n^{\bullet} + I\text{-}X'P_m\text{-}I \rightarrow D\text{-}XP_n\text{-}I + I\text{-}X'P_m^{\bullet}$

$D\text{-}XP_n^{\bullet} + I\text{-}X'P_m\text{-}I \rightarrow D\text{-}XP_n\text{-}I + I\text{-}P_mX'^{\bullet}$

$D\text{-}XP_n^{\bullet} + D\text{-}X'P_m\text{-}I \rightarrow D\text{-}XP_n\text{-}I + D\text{-}X'P_m^{\bullet}$

$D\text{-}XP_n^{\bullet} + I\text{-}X'P_m\text{-}D \rightarrow D\text{-}XP_n\text{-}I + D\text{-}P_mX'^{\bullet}$

D-$XP_n^{\bullet}$	+	D-$P_mX'P_k$-I	→	D-XP_n-I	+	D-$P_mX'P_k^{\bullet}$
D-$XP_n^{\bullet}$	+	I-$P_mX'P_k$-I	→	D-XP_n-I	+	I-$P_mX'P_k^{\bullet}$
D-$XP_n^{\bullet}$	+	M	→	D-$XP_{n+1}^{\bullet}$		

reactions of D-$P_nXP_m^{\bullet}$

D-$P_nXP_m^{\bullet}$	+	I-X'-I	→	D-P_nXP_m-I	+	I-$X'^{\bullet}$
D-$P_nXP_m^{\bullet}$	+	D-X'-I	→	D-P_nXP_m-I	+	D-$X'^{\bullet}$
D-$P_nXP_m^{\bullet}$	+	I-$X'P_k$-I	→	D-P_nXP_m-I	+	I-$X'P_k^{\bullet}$
D-$P_nXP_m^{\bullet}$	+	I-$X'P_k$-I	→	D-P_nXP_m-I	+	I-$P_kX'^{\bullet}$
D-$P_nXP_m^{\bullet}$	+	D-$X'P_k$-I	→	D-P_nXP_m-I	+	D-$X'P_k^{\bullet}$
D-$P_nXP_m^{\bullet}$	+	I-$X'P_k$-D	→	D-P_nXP_m-I	+	D-$P_kX'^{\bullet}$
D-$P_nXP_m^{\bullet}$	+	D-$P_lX'P_k$-I	→	D-P_nXP_m-I	+	D-$P_lX'P_k^{\bullet}$
D-$P_nXP_m^{\bullet}$	+	I-$P_lX'P_k$-I	→	D-P_nXP_m-I	+	I-$P_lX'P_k^{\bullet}$
D-$P_nXP_m^{\bullet}$	+	M	→	D-$P_nXP_{m+1}^{\bullet}$		

reactions of I-$P_nXP_m^{\bullet}$

I-$P_nXP_m^{\bullet}$	+	I-X'-I	→	I-P_nXP_m-I	+	I-$X'^{\bullet}$
I-$P_nXP_m^{\bullet}$	+	D-X'-I	→	I-P_nXP_m-I	+	D-$X'^{\bullet}$
I-$P_nXP_m^{\bullet}$	+	I-$X'P_k$-I	→	I-P_nXP_m-I	+	I-X-$P_k^{\bullet}$
I-$P_nXP_m^{\bullet}$	+	I-$X'P_k$-I	→	I-P_nXP_m-I	+	I-$P_kX'^{\bullet}$
I-$P_nXP_m^{\bullet}$	+	D-$X'P_k$-I	→	I-P_nXP_m-I	+	D-$X'P_k^{\bullet}$
I-$P_nXP_m^{\bullet}$	+	I-$X'P_k$-D	→	I-P_nXP_m-I	+	D-$P_kX'^{\bullet}$
I-$P_nXP_m^{\bullet}$	+	D-$P_lX'P_k$-I	→	I-P_nXP_m-I	+	D-$P_lX'P_k^{\bullet}$
I-$P_nXP_m^{\bullet}$	+	I-$P_lX'P_k$-I	→	I-P_nXP_m-I	+	I-$P_lX'P_k^{\bullet}$
I-$P_nXP_m^{\bullet}$	+	M	→	I-$P_nXP_{m+1}^{\bullet}$		

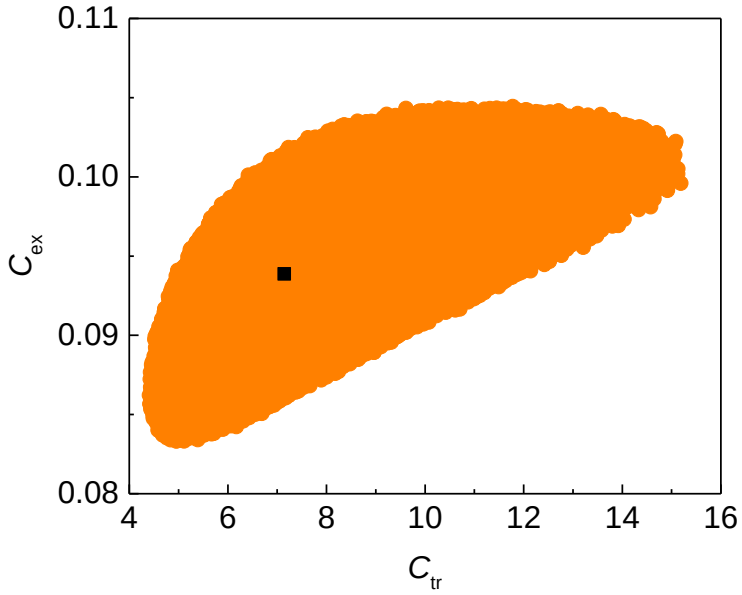

Figure S1: Confidence interval for the parameters C_{tr} and C_{ex} and optimum parameters (black).

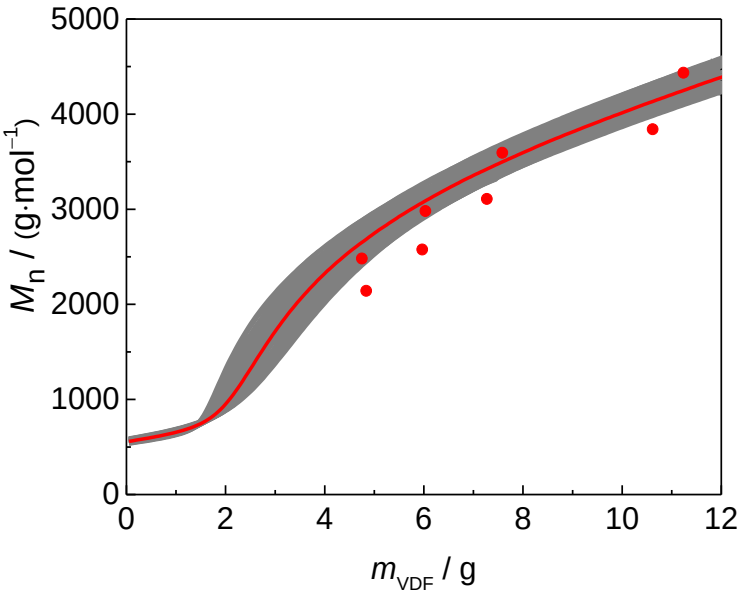

Figure S2: Sensitivity of the parameters C_{tr} and C_{ex}. The red line shows the simulation results with the optimum values and the red points the experimental data points (20 bar, 7.5 mmol I-C_4F_8-I (sample 5)). The grey band represents simulations carried out with 16 points taken from the outer sphere of the confidence interval, indicating that in all cases a good description of the experimental results is obtained.