Modelling insights into the nitroxide-mediated radical polymerization of styrene

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Reaction Mechanism and Moments

Description	Step
Chemical initiation	$I \xrightarrow{k_d} 2R_{in}^{\bullet}$
Nitroxyl ether decomposition	$NO_E \underset{k_{d2}}{\overset{k_{a2}}{\rightleftharpoons}} R_{in}^{\bullet} + NO_x^{\bullet}$
Mayo dimerization	$M + M \xrightarrow{k_{dim}} D$
Thermal initiation	$M + D \xrightarrow{k_{ia}} D^{\bullet} + M^{\bullet}$
First propagation (primary radicals)	$R_{in}^{\bullet} + M \xrightarrow{k_p} R_1^{\bullet}$
First propagation (monomeric radicals)	$M^{\bullet} + M \xrightarrow{k_p} R_1^{\bullet}$
First propagation (dimeric radicals)	$D^{\bullet} + M \xrightarrow{k_p} R_1^{\bullet}$
Propagation	$R_r^{\bullet} + M \xrightarrow{k_p} R_{r+1}^{\bullet}$

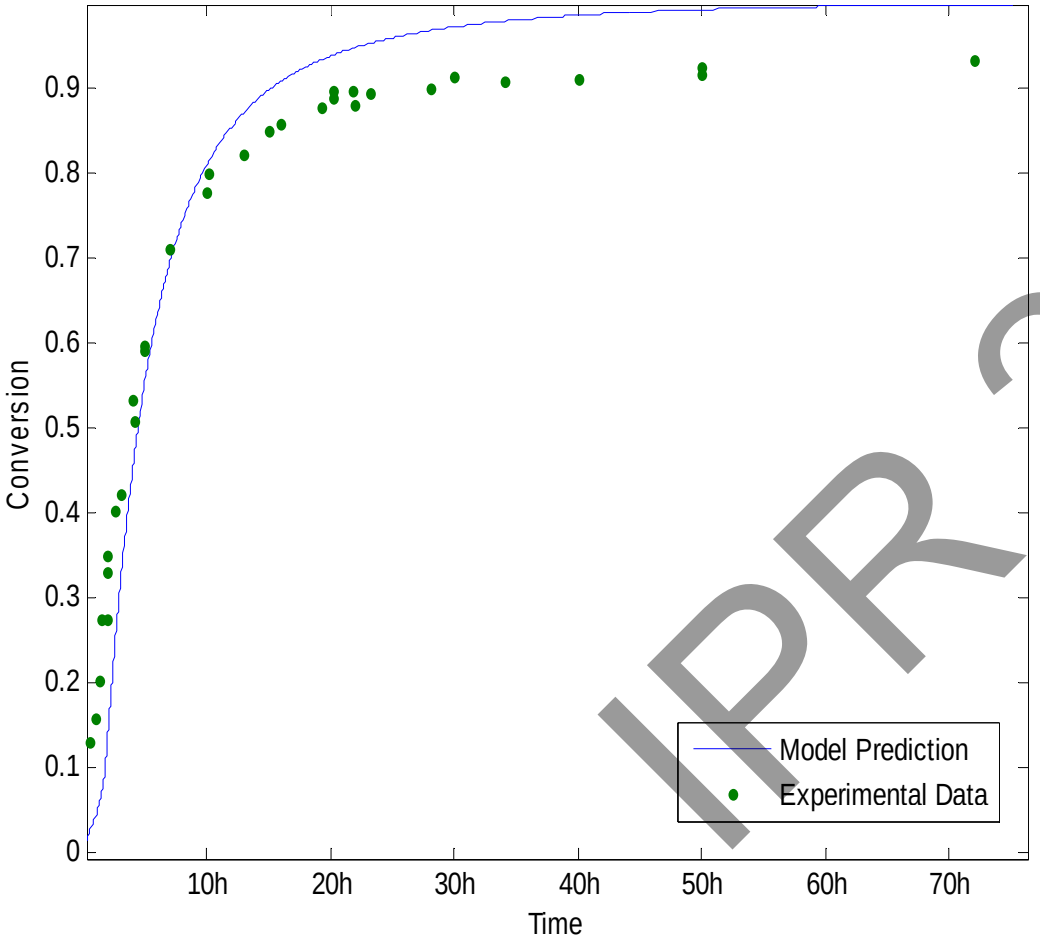
Dormant living exchange (monomeric alkoxyamine)	$M^{\bullet} + NO_x^{\bullet} \underset{k_{da}}{\overset{k_a}{\rightleftharpoons}} MNO_x$
Dormant living exchange (polymeric alkoxyamine)	$R_r^{\bullet} + NO_x^{\bullet} \underset{k_{da}}{\overset{k_a}{\rightleftharpoons}} R_r NO_x$
Alkoxyamine decomposition	$MNO_x \xrightarrow{k_{decomp}} M + HNO_x$
Rate enhancement reaction	$D + NO_x^{\bullet} \xrightarrow{k_{h3}} D^{\bullet} + HNO_x$
Termination by combination	$R_r^{\bullet} + R_s^{\bullet} \xrightarrow{k_{tc}} P_{r+s}$
Termination by disproportionation	$R_r^{\bullet} + R_s^{\bullet} \xrightarrow{k_{td}} P_r + P_s$
Transfer to monomer	$R_r^{\bullet} + M \xrightarrow{k_{fM}} P_r + M^{\bullet}$
Transfer to dimer	$R_r^{\bullet} + D \xrightarrow{k_{fD}} P_r + D^{\bullet}$

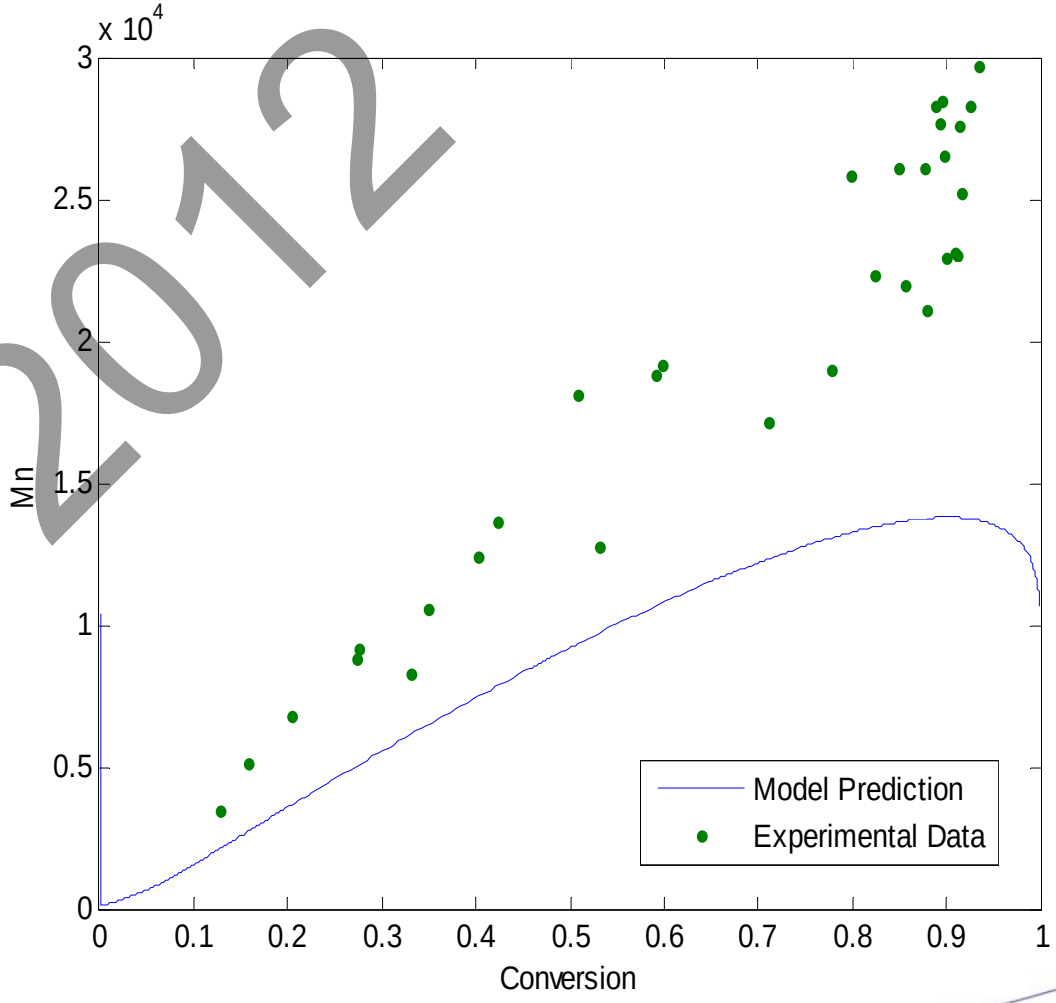
Moments used for MW estimation:

$$\lambda_i = \sum_r r^i R_r \quad \delta_i = \sum_r r^i R_r ON_x \quad \mu_i = \sum_r r^i P_r$$

Fully Mechanistic Model (FMM)

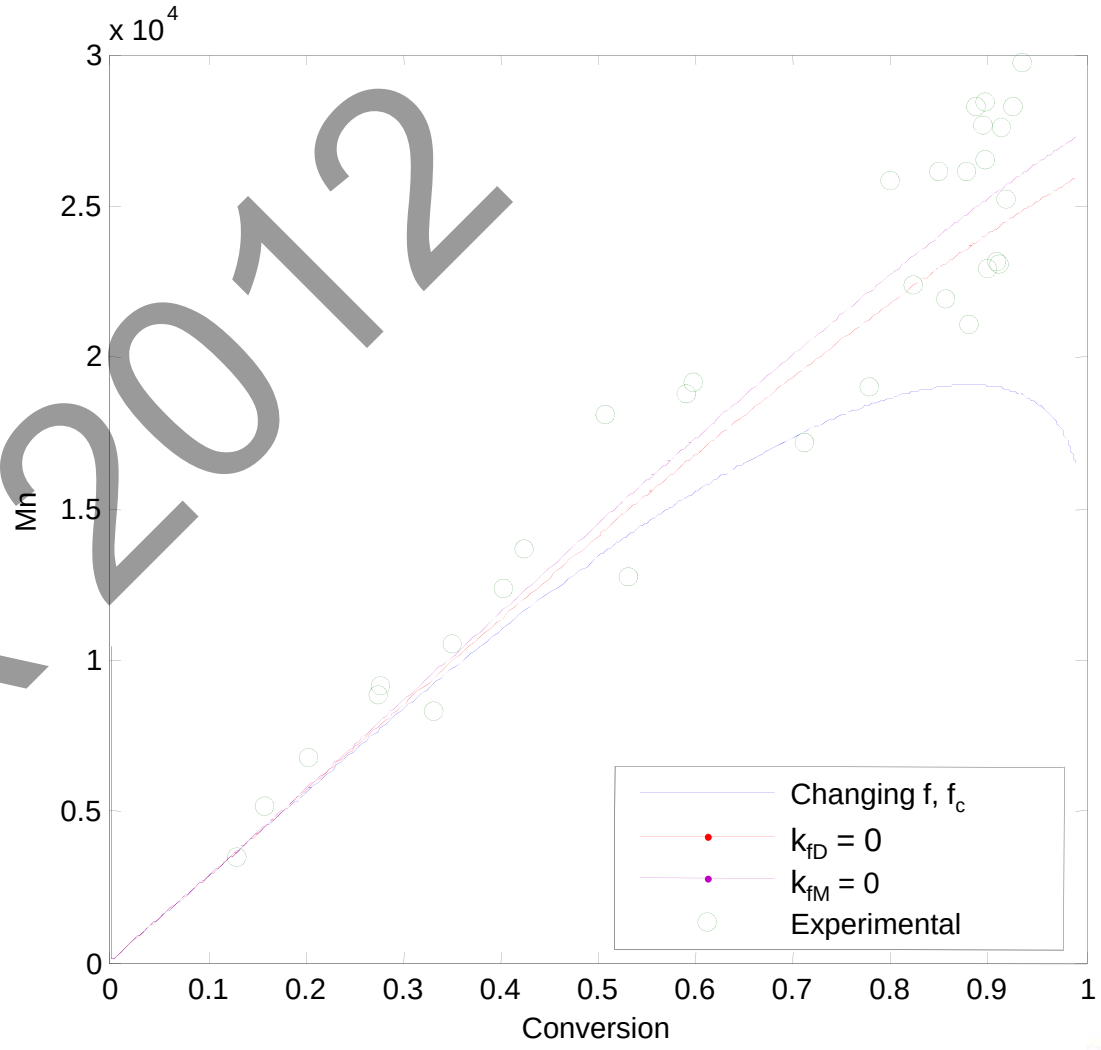
Prior state of the art





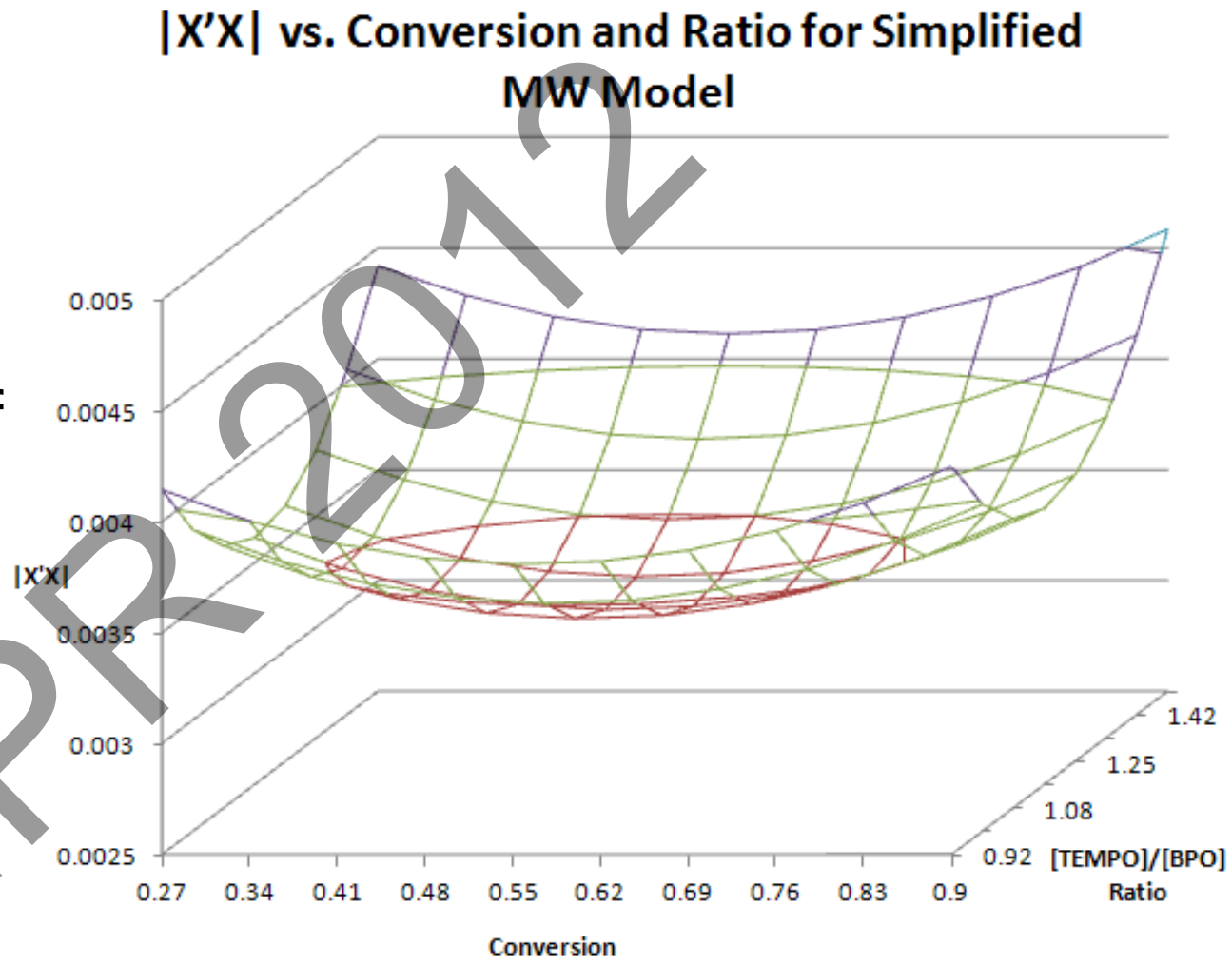
FMM Updates and Improvements

- Added controller efficiency f_c, allowed for f and f_c to change with conversion
- Removal of chain transfer to dimer and then monomer reactions
- These changes led to improved agreement with experimental data



D-Optimal Design Applications

- The D-optimality criterion (i.e., maximization of the determinant of X'X) can be used to select the next best experiments to be run for a process



Model and Design Applications

- Based on prior experimental trials

Level	T (°C)	$[I]_0$ (M)	$[N]_0$ (M)
Low	120	0.036	0.058
High	130	0.072	0.086

- Previous Bayesian approach compared with D-optimality results (with decoded $[N]_0/[I]_0$ Ratio)

Experiment		Bayesian Design				D-Optimal Design			
		T	[I]	[N]	Ratio	T	[I]	[N]	Ratio
First Sequence of Two Runs	1	-1	1	-1	0.81	-1	1	-1	0.81
	2	1	1	-1	0.81	1	1	-1	0.81
Second Sequence of Two Runs	3	-1	1	1	1.19	-0.6	1	1	1.19
	4	1	1	1	1.19	0.2	0.6	0.4	1.19