Experimental & Modelling Digital Twin Approach for Polymer Synthesis via Re-initiated Oxygen inhibited RAFT Polymerization

Emil Pashayev, Felix Kandelhard & Prokopios Georgopanos
Helmholtz-Zentrum Hereon, Institute of Membrane Research, Geesthacht, Germany
Contact: emil.pashayev@hereon.de

Introduction

Controlled polymerization techniques like the reversible-addition fragmentation chain transfer polymerization (RAFT) are sensitive to impurities such as oxygen [1]. In this work, a kinetic model describing the oxygen inhibited RAFT dispersion polymerization for the synthesis of poly(4-vinylpyridine)-b-polystyrene (P4VP-b-PS) [2-3] is developed and using the model, the effect of the re-initiation on the inhibited RAFT polymerization is predicted. Based on the prediction, re-initiation is applied as a tool to enhance monomer conversion, which leads to:

- More sustainable polymerisation process
- Prevention of loss of valuable material
- Easier purification of final product

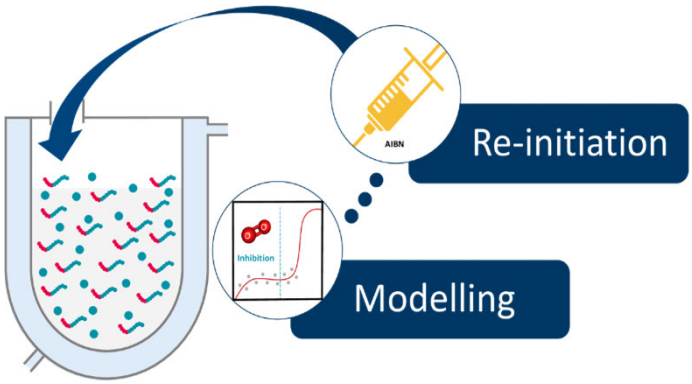

Figure 1. Digital twin approach for polymer synthesis via re-initiated oxygen-inhibited RAFT polymerization. [1]

Modeling Approach

Table 1. Kinetic model describing reaction steps of inhibition process. [1]

Inhibition by Oxygen

$$P_n^* + O_2 \xrightarrow{k_{in,O_2,1}} P_n(O_2)_1^*$$

$$P_n(O_2)_l M^* + O_2 \xrightarrow{k_{in,O_2,1}} P_{n+1}(O_2)_{l+1}^*$$

$$P_n(O_2)_l M^* + M \xrightarrow{k_p} P_{n+1}(O_2)_l M^*$$

$$P_n(O_2)_l^* + M \xrightarrow{k_{in,O_2,2}} P_n(O_2)_l M^*$$

$$P_{n_1}(O_2)_{l_1}^* + P_{n_2}(O_2)_{l_2}^* \xrightarrow{k_{in,O_2,3}} M_{n_1}(O_2)_{l_1-1}OH + M_{n_2}(O_2)_{l_2-1} = O + O_2$$

$$P_{n_1}(O_2)_{l_1}^* + P_{n_2}(O_2)_{l_2} M^* \xrightarrow{k_{td}} M_{n_1}(O_2)_{l_1-1} + M_{n_2}(O_2)_{l_2} M$$

$$P_{n_1}(O_2)_{l_1}^* + P_{n_2} \xrightarrow{k_{td}} M_{n_1}(O_2)_{l_1} + M_{n_2}$$

$$P_{n_1}(O_2)_{l_1} M^* + P_{n_2} \xrightarrow{k_{td}} M_{n_1}(O_2)_{l_1} M + M_{n_2}$$

$$P_{n_1}(O_2)_{l_1} M^* + P_{n_2}(O_2)_{l_2} M^* \xrightarrow{k_{td}} M_{n_1}(O_2)_{l_1} M + M_{n_2}(O_2)_{l_2} M$$

Results

❖ Experiment vs. Simulation

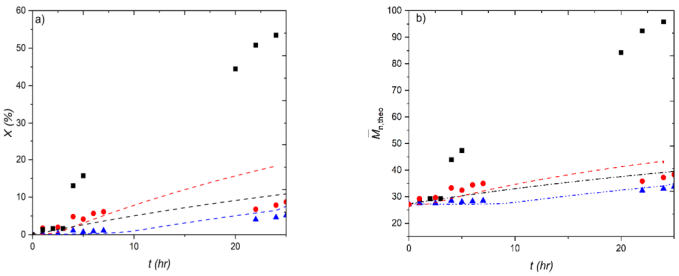

Figure 2. Evolution of simulated (dashed line) and experimental (points) styrene conversion X (a) and number average molar mass $\bar{M}_{n,theo}$ (b) within the period of 24 h for three different RAFT : Initiator ratios of 10:1 in oxygen-free solution (■), 10:1 (▲) and 10:4 (●) in oxygen-exposed solutions. [1]

❖ Parameter Estimation & Model Prediction

Table 2. Results of parameter estimation for the reaction coefficients $k_{in,O_2,1}$, $k_{in,O_2,2}$ and $k_{in,O_2,3}$ are reaction rate coefficient of oxygen molecule with growing radicals at 60 °C, of monomer with peroxy radicals and of the termination of the peroxy radicals, respectively. [1]

$k_{in,O_2,1}(L\ mol^{-1}\ s^{-1})$	$k_{in,O_2,2}(L\ mol^{-1}\ s^{-1})$	$k_{in,O_2,3}(L\ mol^{-1}\ s^{-1})$
$3.4 \cdot 10^6$	$1.00 \cdot 10^{-3}$	$1.94 \cdot 10^{10}$

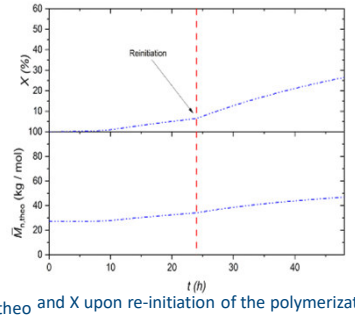

Figure 3. Simulated $\bar{M}_{n,theo}$ and X upon re-initiation of the polymerization. [1]

❖ Re-initiation

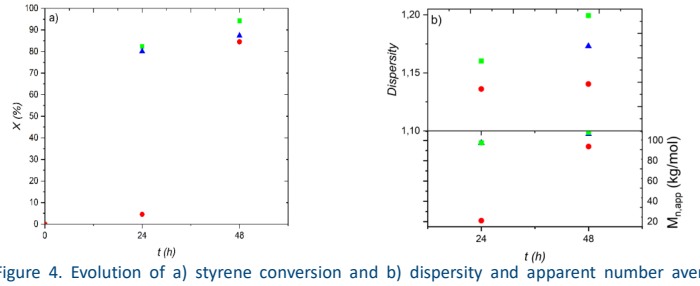

Figure 4. Evolution of a) styrene conversion and b) dispersity and apparent number average molar mass of the (■) oxygen-free initiated and (▲) oxygen-free and re-initiated as well as (●) oxygen-exposed and re-initiated experiments. [1]

Summary

Model & Re-initiation

- ❖ High ***X*** (>96 %)
- ❖ Good ***Đ*** (≤1.2)

- ❖ Easier purification
- ❖ Reduction of material waste
- ❖ More sustainable process

Literature

[1] E. Pashayev, et al., *Macromol. React. Eng.*, **2022**, 17, 2, DOI: 10.1002/mren.202200068.

[2] K. Nieswandt, et. al., *Polym.* , **2022**, 14, 62, DOI: 10.3390/polym14010062.

[3] F. Kandelhard, et al., *Ind. Eng. Chem. Res.*, **2023**, DOI: 10.1021/acs.iecr.3c00607.

[4] R. Li, et. al., *Ind. Eng. Chem. Res.*, **2006**, 45, 3001, DOI: 10.1021/ie0512439.