

Supporting Information to

Improved Mechanistic Insights into Radical Sulfinyl Precursor MDMO-PPV Synthesis by Combining Microflow Technology and Computer Simulations

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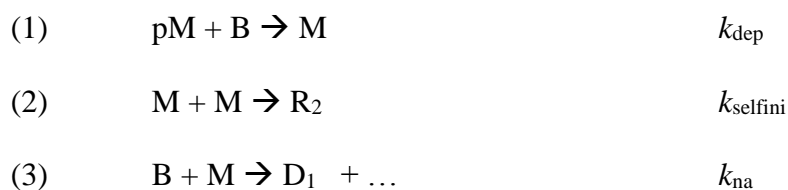
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1. Predici Model

Simulations have been carried out with Predici (CIT) version. 7.1.0 on an Intel i7 CPU running at 2.40 GHz. For all simulations, a Predici model comprising the following reaction steps and respective rate coefficients has been used:

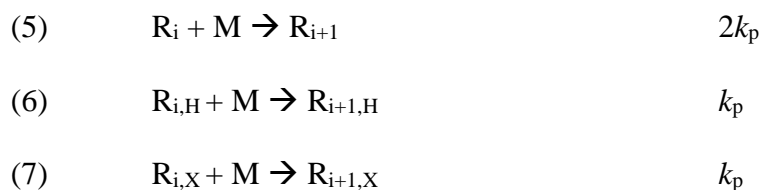
Monomer Formation



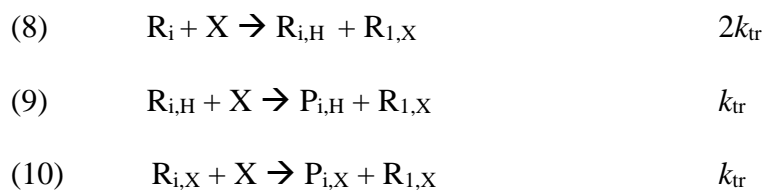
Chain Initiation



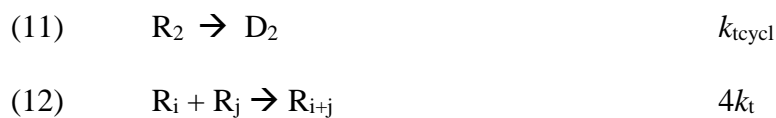
Propagation

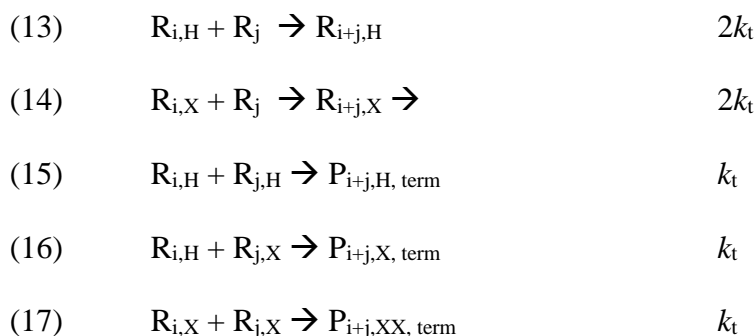


Transfer reactions



Termination





The above model describes the kinetics of the synthesis of MDMO-PPV via a radical sulfinyl pathway. A few assumptions and simplifications had to be made in order to arrive at a model that can be used on a practical level:

- Two models are designed in which chain reinitiation can either be excluded (**model 1**, inhibition model) or included (**model 2** non-inhibition model). As a placeholder, transfer to solvent (*sec*-BuOH) is assumed in the model, denoted as species X. Species X is defined as *s*-BuOH with an initial starting concentration of 10.5 M ($\rho = 0.808 \text{ g}\cdot\text{cm}^{-3}$ and $M_n = 74.12 \text{ g}\cdot\text{mol}^{-1}$). In general, species X could be seen as an additional (unknown) compound, susceptible to possible chain transfer.
- ESI-MS results indicate the presence of cyclic side products (dimers, trimers, tetramers and paracyclophane). As it is currently impossible to differentiate between these products quantitatively, all these reactions are placed together in one reaction in the model.
- Previous modelling work of *Van Steenberge et al.*¹ assumed the presence of a base induced product as well. Although not observed experimentally via ESI-MS, this reaction step is still considered in the model to verify its influence.
- Termination occurs via bimolecular combination. Due to the formation of biradical species, however, this reaction leads only to a reduction of overall radical concentrations, but not to dead polymer chains as termination products remain inherently biradicals. Still, polymer chains do not grow to infinite length indicating the

presence of an unknown chain stopping event. As a result a radical transfer reaction is implemented in the model as well.

Using the above reaction steps and rate coefficients as described above, simulations varying the individual kinetic parameters are monitored and compared to the experimental results obtained using MRT.

A differentiation between the different models needs to be made. Model 1 represents a model in which the X-species stemming from chain transfer is inactive. Model 2 represents the model where the same species can reinitiate polymerization.

2. Simulation results for variation of a single rate coefficient for model 1 (inhibition model) and model 2 (non-inhibition model) with other parameters as in Table 1 (initial conditions: 30°C.; $[\text{preM}]_i = 0.0325 \text{ mol}\cdot\text{L}^{-1}$ and $[\text{B}]_i = 0.0325 \text{ mol}\cdot\text{L}^{-1}$).

1. Deprotonation coefficient (k_{depr})

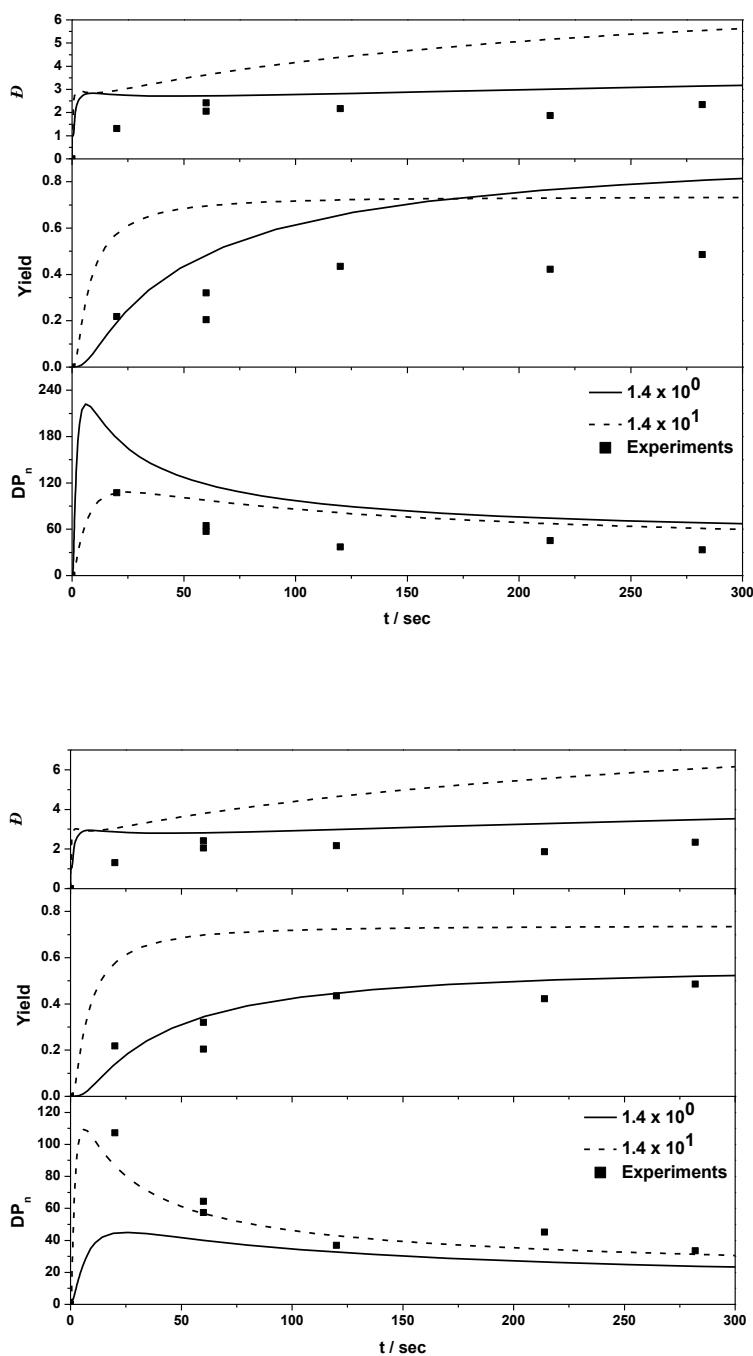


Figure S1: Influence on DP_n , D and yield upon varying the k_{deprot} value for model 1 (*top*) and model 2 (*bottom*).

2. Self-initiation coefficient (k_{selfini})

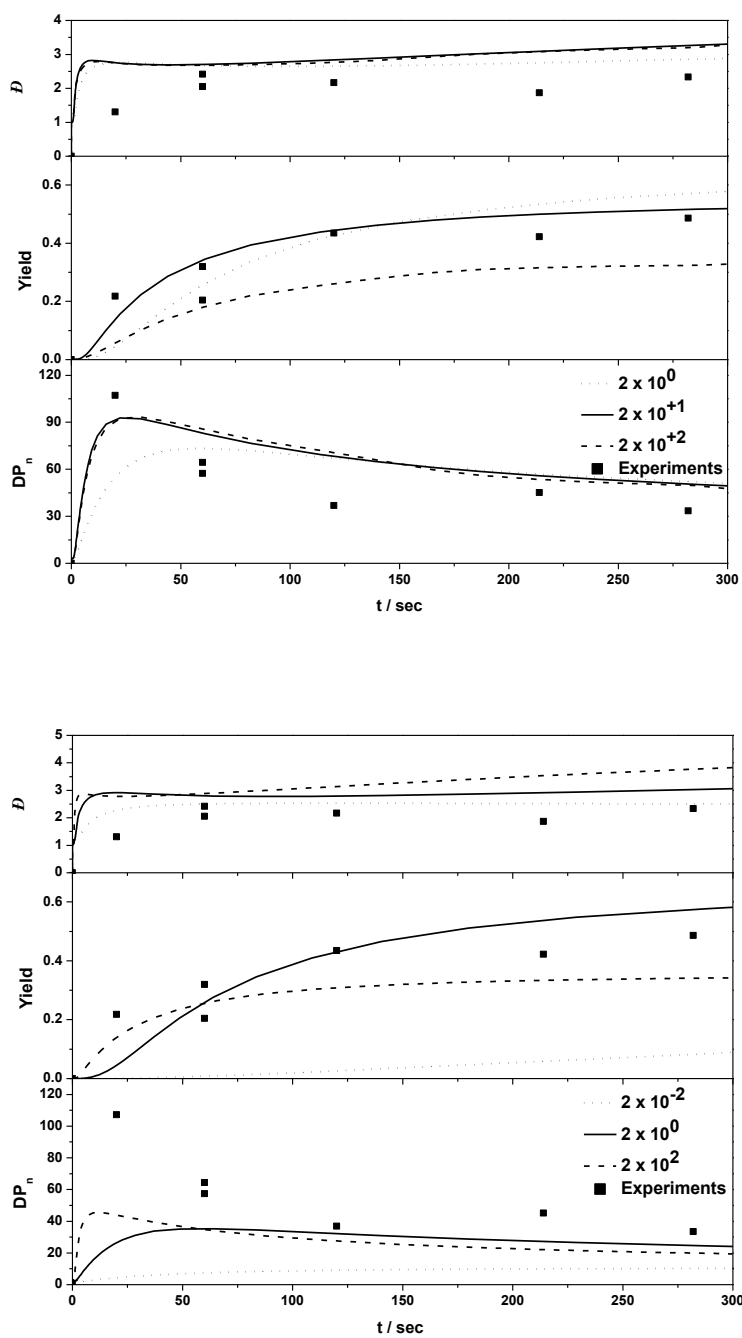


Figure S2: Influence on DP_n , D and yield upon varying the k_{selfini} value for model 1 (*top*) and model 2 (*bottom*).

3. Initiation and reinitiation coefficient (k_{ini} and $k_{ini,x}$)

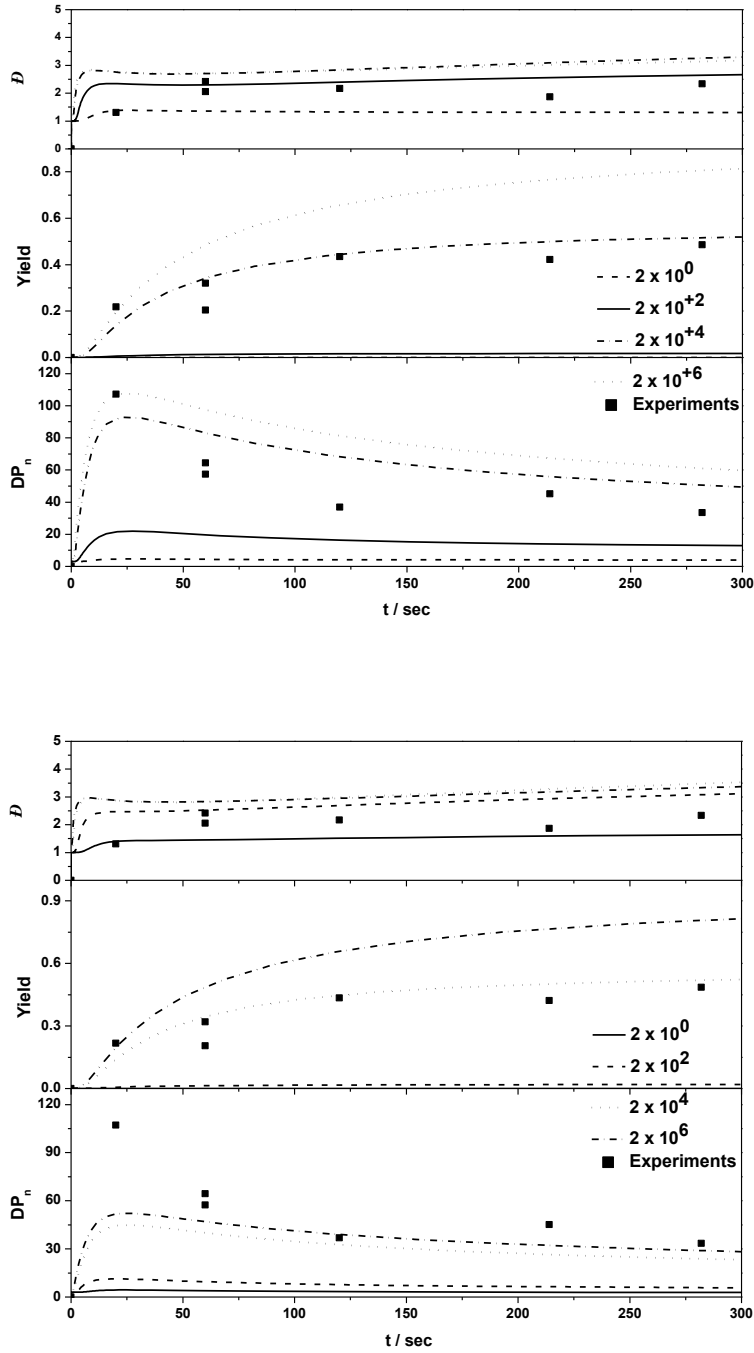


Figure S3: Influence on DP_n , D and yield upon varying the k_{ini} value for model 1 (*top*) and model 2 (*bottom*).

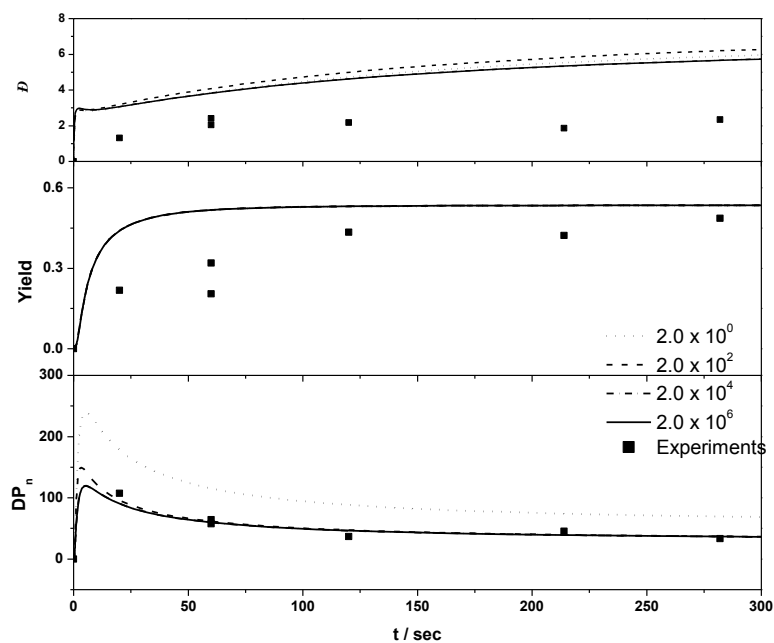


Figure S4: Influence on DP_n , D and yield upon varying the $k_{ini,x}$ value for model 2; in model 1 always zero value, hence, no additional plot.

4. Propagation coefficient (k_p)

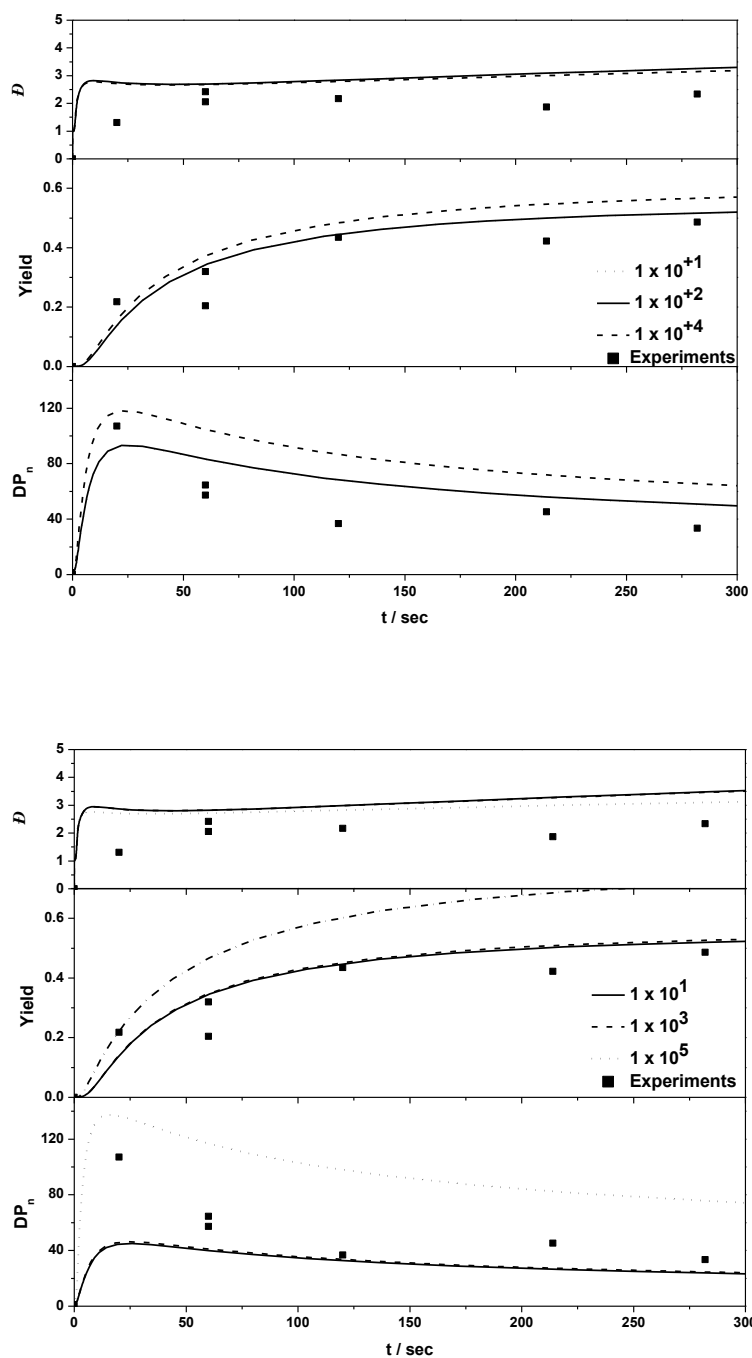


Figure S5: Influence on DP_n , D and yield upon varying the k_p value for model 1 (*top*) and model 2 (*bottom*).

5. Termination coefficient (k_t)

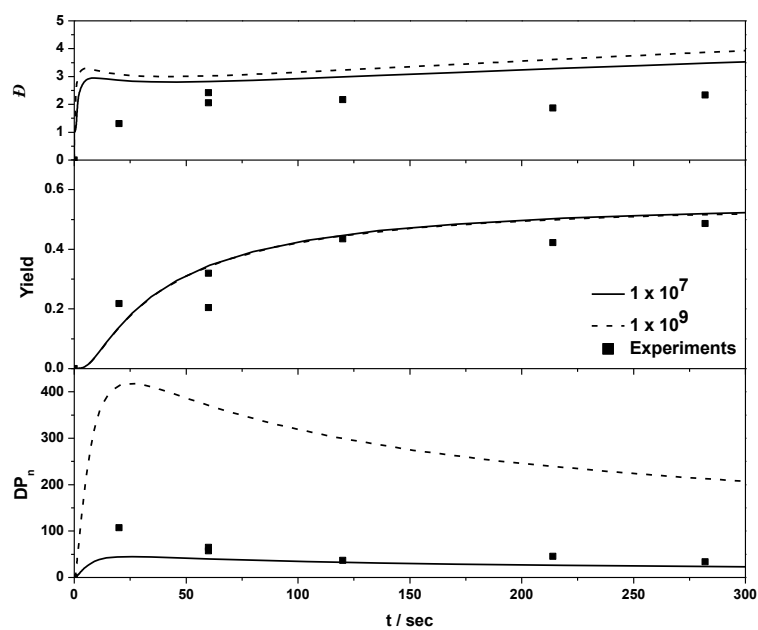
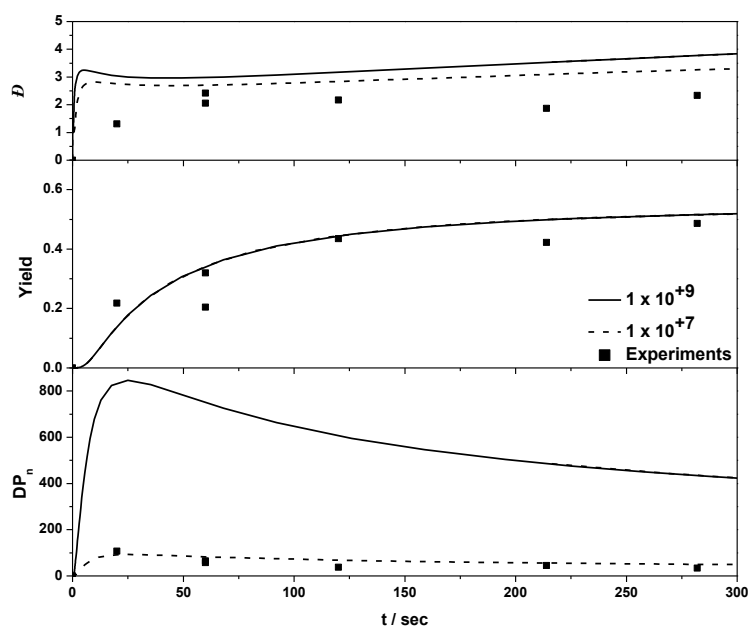


Figure S6: Influence on DP_n , D and yield upon varying the k_t value for model 1 (*top*) and model 2 (*bottom*).

6. Base elimination coefficient (k_{na})

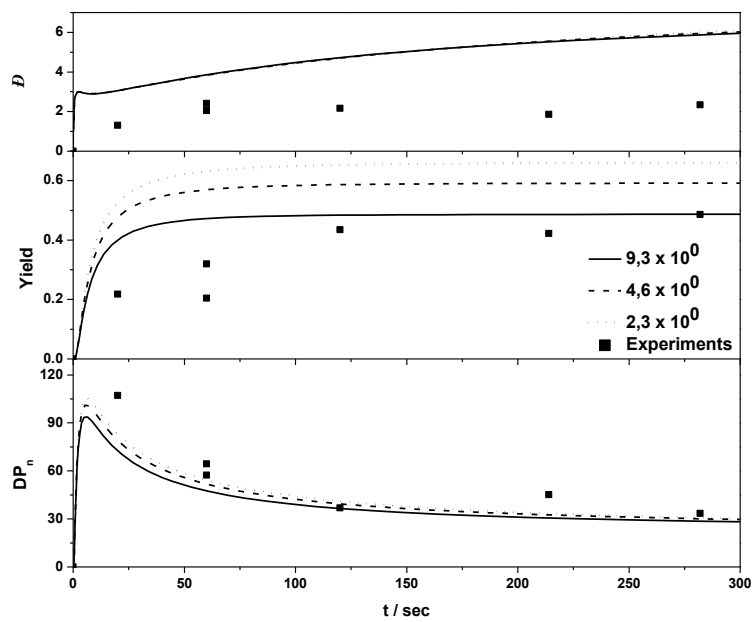


Figure S7: Influence on DP_n , D and yield upon varying the k_{na} value for model 2

7. Cyclization coefficient (k_{cycl})

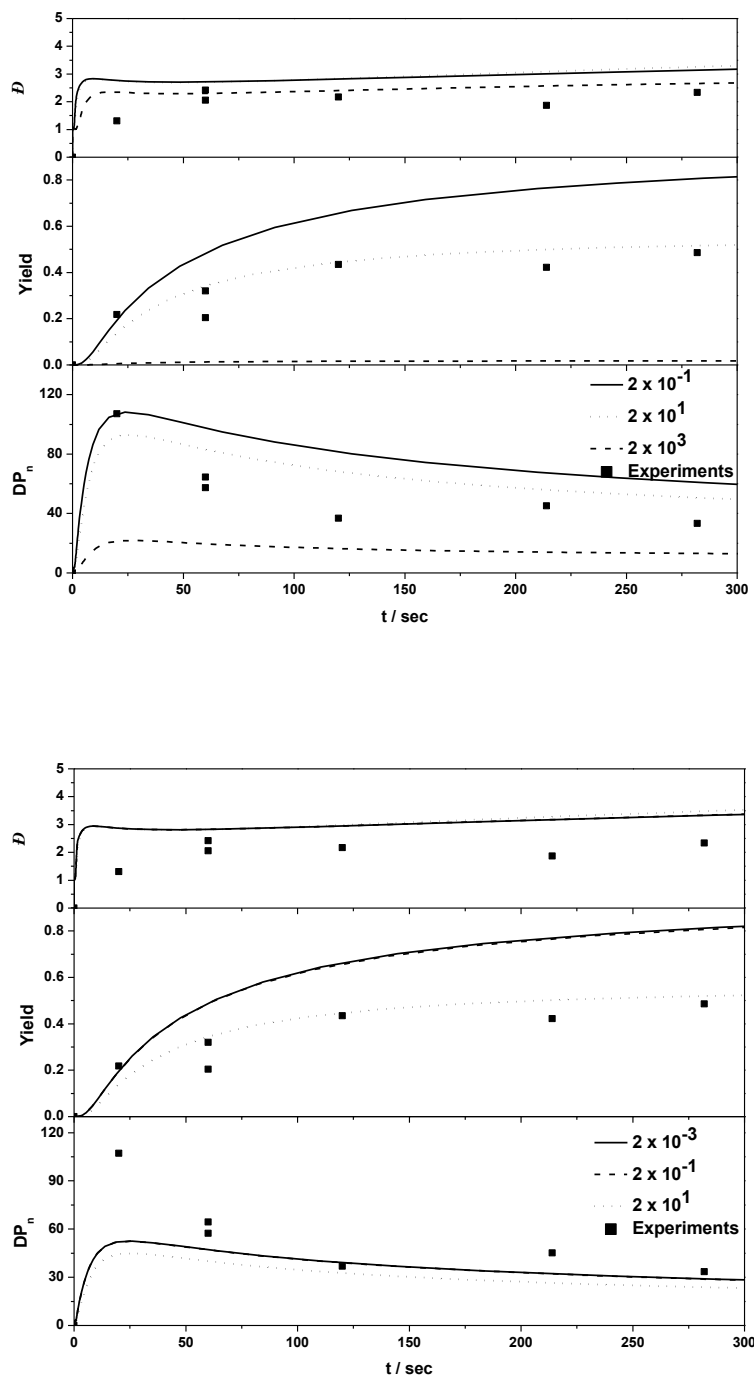


Figure S8: Influence on DP_n , D and yield upon varying the k_{cycl} value for model 1 (top) and model 2 (bottom).

References

- ¹ Van Steenberge, P.; Vandenberghe, J.; D'hooge, D.R.; Reyniers, M.-F.; Adriaenssens, P., Lutsen, L.; Vanderzande, D.; Marin, G.B., *Macromolecules*, **2011**, 44, 8716-8726.