

# The Interaction Between the Chain Length and Particle Size Distribution in Radical Miniemulsion (Co)Polymerization: Going Beyond the Smith-Ewart Approach

Yoshi W. Marien,<sup>1,2</sup> Paul H.M. Van Steenberge,<sup>1</sup> Andrij Pich,<sup>2,3</sup> Dagmar R. D'hooge<sup>1,4</sup>

<sup>1</sup>Laboratory for Chemical Technology (LCT), Ghent University, Ghent, Belgium

<sup>2</sup>DWI – Leibniz Institute for Interactive Materials e.V. and RWTH Aachen University, Aachen, Germany

<sup>3</sup>Aachen-Maastricht Institute for Biobased Materials (AMIBM), Geleen, The Netherlands

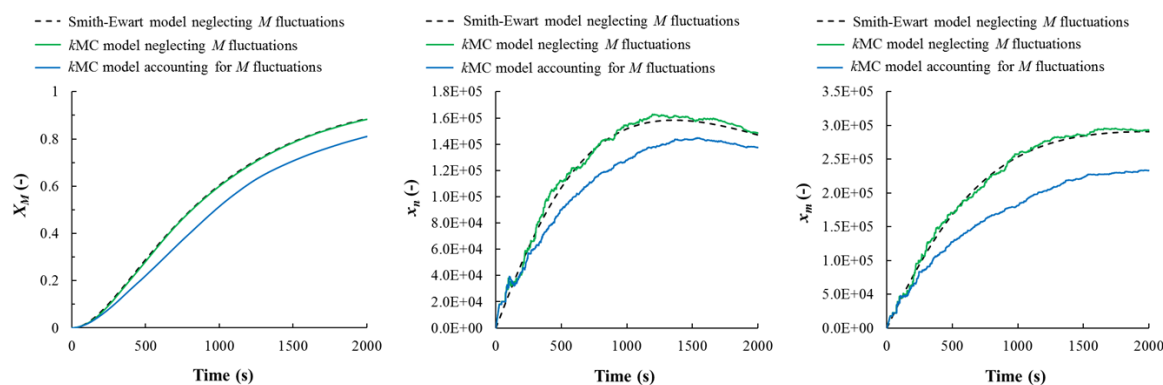
<sup>4</sup>Centre for Textile Science and Engineering (CTSE), Ghent University, Ghent, Belgium

Most studies on emulsion polymerization and in particular the ones using the Smith-Ewart approach assume an average particle size and monomer concentration. Moreover, the zero-one or pseudo-bulk approximation is often employed. Using a novel kinetic Monte Carlo (*k*MCM) model in which reaction and interphase mass transfer events are tracked for each particle and diffusional limitations on termination and exit/entry are taken into account it is demonstrated that differences in the number of radicals and monomer concentration between particles need to be acknowledged. For the first time, the coupled simulation of the evolution of the chain length distribution (CLD) and particle size distribution (PSD) in miniemulsion (co)polymerization is highlighted.<sup>1,2</sup>

First, a downgraded *k*MCM model in which only the average particle size instead of the entire PSD is considered and in which the actual particle monomer concentrations are assumed to be equal to the average one is successfully benchmarked to a conventional Smith-Ewart model for miniemulsion homopolymerization (**Fig. 1: full green vs. dashed black line**). Notably, if the full *k*MCM model is used (**Fig. 1: full blue line**), *i.e.* fluctuations in the monomer concentration over the particles are taken into account, a different evolution of the miniemulsion characteristics is obtained, illustrating the relevance of the developed modelling strategy.<sup>1</sup>

Next, the *k*MCM model is applied to radical miniemulsion copolymerization of styrene and N-vinylcaprolactam (VCL). The disparate terminal monomer reactivity ratios are shown to induce a consecutive dominant incorporation of styrene and VCL. Moreover, the initial comonomer fractions are demonstrated to affect the exit and entry pattern, thereby affecting the evolution of the CLD. A strong effect of the initial PSD on the miniemulsion kinetics is also highlighted. A very dynamic PSD is simulated, with a negative skewing of the PSD at low monomer conversions and a uniformization of the PSD as the monomer conversion further increases.

Overall, the developed modelling tool allows to overcome the shortcomings of the Smith-Ewart approach and unveils unique insights for radical miniemulsion (co)polymerizations, enabling the model-guided design of copolymer nanoparticles for *e.g.* controlled drug delivery applications.<sup>2</sup>



**Figure 1.** Importance of monomer fluctuations over the particles for the calculation of the evolution of the monomer conversion ( $X_M$ ; left) and number ( $x_n$ ; middle) and mass ( $x_m$ ; right) average chain length.

<sup>1</sup> Y. W. Marien, P. H.M. Van Steenberge, D. R. D'hooge, G. B. Marin, *Macromolecules* **2019**, *52*, 1408-1423.

<sup>2</sup> Y. W. Marien, P. H.M. Van Steenberge, A. Pich, D. R. D'hooge, *React. Chem. Eng.* **2019**, *4*, 1935-1947.

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## Dr. Yoshi W. Marien

Affiliation: Laboratory for Chemical Technology (LCT), Ghent University, Belgium

E-mail: Yoshi.Marien@UGent.be

Personal History:

2015-2019     Doctoral researcher at LCT; research stays at DWI/RWTH Aachen University and the Centre for Advanced Macromolecular Design (CAMD; University of New South Wales; Australia)

Since 2019     Postdoctoral researcher at LCT

Research interests: emulsion polymerization, nanoparticles for drug delivery, polymerization kinetics