

The synergy of experiments and modeling to identify all monomer sequences and functional groups in copolymerization processes

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A design of copolymerization products requires a control of the monomer sequences, ideally per macrospecies present and this along the whole synthesis procedure.¹ Next to that information on the nature of all end-groups is crucial, in particular in view of precision control.

In the present work, it is demonstrated that advanced matrix-based kinetic Monte Carlo (*kMC*) simulations allow to visualize all monomer sequences from one chain end to the other, including a differentiation according to the different end-groups (*cf.* Figure 1).²⁻⁴ Focus is on all major controlled radical polymerization (CRP) techniques to highlight the generic nature of the developed methodology. All simulations account for a detailed reaction scheme and possible diffusional limitations due to viscosity increases. Model validation is extensively performed with respect to average CRP characteristics such as the monomer conversion, number average chain length, and dispersity.

The models are subsequently used to design the copolymerization processes investigated with respect to the identification of the most suited mediating agent and reaction conditions, including a differentiation between batch and fed-batch approaches.

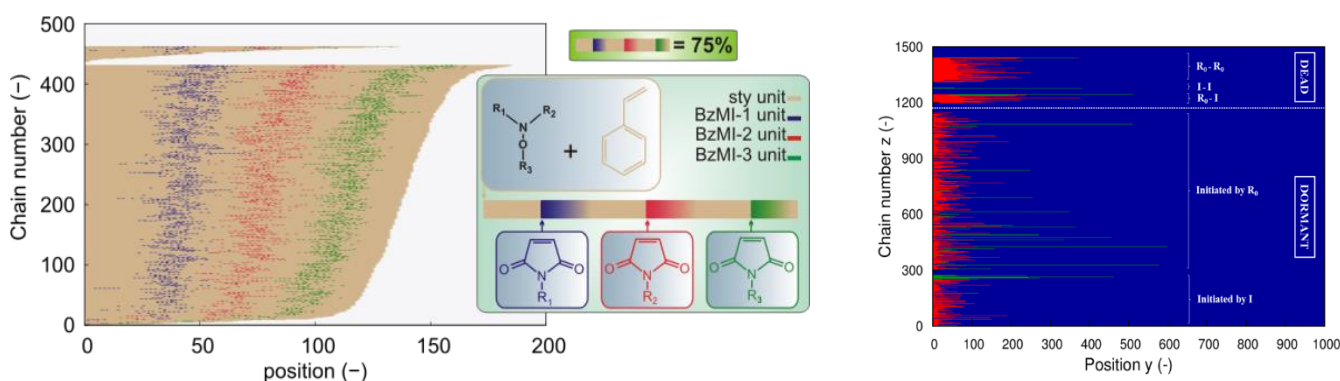


Figure 1. Monomer sequences for two major controlled radical copolymerizations: left: nitroxide mediated polymerization aiming at sequence controlled polymers³; right: reversible addition fragmentation chain transfer polymerization or macromolecular design via the interchange of xanthates, aiming at block copolymers.⁴

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