Model-based design of reaction conditions for segmented copolymer synthesis by combining step- and chain-growth polymerization L De Keer <dies.dekeer@ugent.be>, PHM Van Steenberge <paul.vansteenberge@ugent.be>, MF Reyniers <mariefrancoise.reyniers@ugent.be> and Dr. D’hooge*<dagmar.dhooge@ugent.be>, LCT, Ghent University; T Gegenhuber <thomas.gegenhuber@kit.edu>, A J*a <a.goldmann@qut.edu.au> and C. Barner-Kowollik*b <christopher.barnerkowollik@qut.edu.au>, *Queensland University of Technology; bKarlsruhe Institute of Technology

Model-based design using bivariate kinetic Monte Carlo (kMC) simulations is applied to identify suited reaction conditions to obtain high molar mass segmented copolymers, employing a unique combination of light driven Diels-Alder based step-growth and reversible addition fragmentation chain transfer (RAFT) polymerisation. For the step-growth precursor polymer synthesis, off-stoichiometric conditions (r = [AA]0/[BB]0 = 1.5) need to be used to ensure the optimal compensation for unexpected AA homopolymer formation. The optimal r value is based on a detailed product distribution analysis using a kMC model comprising of over 200 reactions and approximately 20 macrospecies types and taking into account practical constraints such as the reaction time and solubility limits. For the RAFT polymerization, it is demonstrated in silico that the optimized conditions at 60°C allow to incorporate well defined polystyrene segments (on average 100 monomer units) in the BB units of the original step-growth polymer and the disturbance of unwanted AA homopolymer segments is very low.