Kinetic Monte Carlo modeling of precursor route synthesis for conjugated polymers

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Precursor routes for conjugated polymers

Conjugated materials such as Poly(phenylene vinylene)s (PPVs) are used in light-emitting diodes, photovoltaic cells, thin film transistors, biosensors and field effect transistors. PPVs may be synthesized in numerous ways, including the base induced formation of para-quinoxidimethanes M from para-xylene derivatives HML (shown for the sulfanyl route). The para-quinoxidimethane M, which is the true monomer in this process, auto-initiates a radical polymerization. The resulting precursor polymer is soluble in organic solvents, which constitutes the main advantage of using a precursor route for the synthesis of PPV. After processing, the rigid PPV is obtained by a final elimination step.

Validation in concentrated reaction conditions ([HML]₀ = 0.1 M)

Validation in diluted reaction conditions ([HML]₀ = 10⁻⁴ M)

Developing and validating kinetic Monte Carlo technique

Monte Carlo simulations are suitable for modeling polymerization processes since they allow to simulate populations of macromolecules in complete molecular detail, which is difficult using deterministic solvers. In addition, they do not rely on the use of quasi steady state approximations, which are often used to solve the reaction rate equations with deterministic solvers. The Gibson and Bruck variant of Gillespie’s stochastic simulation algorithm is implemented. Specifically for modeling polymerization reaction systems, optimized data structures and arithmetic operations are used as outlined by Chaffey-Miller et al. (Macromol. Theory Simul. 2007, 16, 575-592). Resulting chain length distributions (CLDs) are compared with a h-p-Galerkin finite element method implemented in the commercial software package PREDICI®, which uses grid-lumped data for the chain length domain (see figure bottom left).

Simulation of optimized reaction conditions

Theoretical influence of termination by recombination on CLD

Conclusions

The use of mathematical-model guided polymer design is illustrated for PPV precursor synthesis for the sulfanyl route. Termination by recombination can be neglected and optimal reaction conditions are obtained when [RO⁻]/[HML]₀ = 1 (i.e. maximum polymer yield and chain length and minimal defect content).

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