FACULTY OF **ENGINEERING AND ARCHITECTURE**

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First principles based design of radical (co)polymerization

Aim

Explore the use of quantum chemical calculations to obtain reliable rate coefficients for propagation and side reactions involved in (controlled) radical (co)polymerization processes. The calculated rate coefficients are to be implemented in available microkinetic models and validated by comparison of simulation results with experimental data from pulsed laser polymerization (PLP) and (co)polymerization. A user-friendly database with validated rate coefficients will be established.

Justification

The fundamental understanding and in-silico guided design of controlled and free radical polymerization processes and the development of new functional polymer materials remains a tremendous challenge. At the molecular level, the outcome of a radical polymerization process is determined by the interplay of a multitude of discrete elementary reactions. The relation between the resulting polymer microstructure and the polymerization conditions is obscured due to the inherent complex nature of this interplay between these reactions. Knowledge of the underlying reaction mechanism and the intrinsic chemical rate coefficients of the elementary reactions involved is thus critical to optimize polymerization processes and to design new functional polymer materials.

In general, the experimental study of an elementary reaction in a radical polymerization process in isolation is almost impossible. Moreover, the experimental determination of intrinsic rate coefficients is not always straightforward and requires dedicated experimental studies. One of the most established experimental techniques to measure propagation rate coefficients is pulsed laser polymerization (PLP). However, the occurrence of side reactions can complicate or even prevent the accurate determination of the propagation rate coefficient. Alternatively, reliable parameter fitting by regression to experimental polymerization data is possible but this can become very tedious for more complex polymerization systems.

Instead of applying the aforementioned experimental techniques, intrinsic rate coefficients can also be obtained from quantum chemical calculations in combination with textbook statistical thermodynamic formulae and conventional transition state theory. The last decades there has been a fast-paced development of quantum chemical methods and the application of computational chemistry as a complement to experiment opens up the possibility to accelerate the optimization of polymerization processes and the in-silico design of functional polymer material.

Program

First, an appropriate computational method is to be selected to calculate reliable propagation rate coefficients for a limited range of well-established vinylmonomers (e.g. styrene, MMA).

In a second step, this method will be applied to calculate rate coefficients for propagation and side reactions (e.g. transfer to monomer, thermal initiation, etc.) involved in the (controlled) radical (co)polymerization of a broad range of vinylmonomers. Attention will be focussed on vinylmonomers relevant for the synthesis of polymers with high-tech and biomedical applications. Next to that, an evaluation of the effect of the chain length and the solvent on the intrinsic rate coefficient is to be performed.

Validation of the calculated rate coefficients will be performed in close collaboration with the ongoing experimental and model development work in the group. In a first stage, the calculated rate coefficients will be implemented in available microkinetic models to compare model predictions with experimental data. In a second stage, the rate coefficients will be used to design experimental recipes for (controlled) (co)polymerization of a selected set of (co)monomers that are to be validated by experiment.

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