UNIVERSITEIT GENT

FACULTY OF **ENGINEERING AND ARCHITECTURE**

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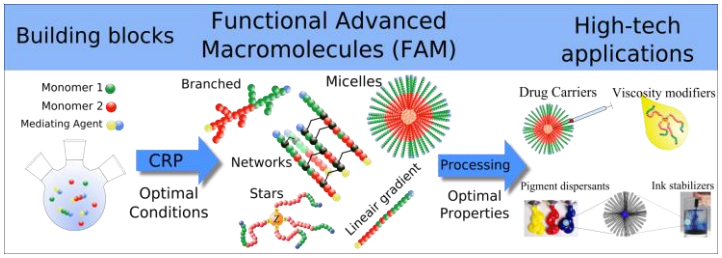
First principles design of mediating agents for controlled radical (co)polymerization

Aim

Explore the use of quantum chemical calculations to obtain reliable rate coefficients for RAFT and NMP specific reactions involved in controlled radical (co)polymerization. The influence of the chemical structure on the performance of a range of RAFT and NMP mediating agents will be assessed. Optimal combinations of mediating agent and polymerization conditions to synthesize a range of targeted functional (co)polymers will be specified. A user-friendly database with validated rate coefficients will be established.

Justification

Sophisticated macromolecular architectures that meet predefined end-use properties have a tremendous potential for a variety of high-tech applications and can, in principle, be synthesized using controlled radical polymerization (CRP) techniques that do not require industrially unattractive stringent oxygen or water free environments or highly purified reagents. In CRP, a mediating agent is added to reversibly capture macroradicals in a dormant state preventing the uncontrolled growth that is typical for conventional free radical polymerization (FRP). Despite intense research efforts, however, industrial application has remained elusive, since a commercially viable CRP product must possess the unique pre-defined properties dictated by the targeted application.



Full control of the detailed chemical structure of the individual macromolecules can only be accomplished within a very narrow window of process conditions since it requires that throughout the polymerization the rates of the various elementary reactions are carefully balanced which introduces the need for dynamic synthesis protocols that allow an instantaneous control of reactant concentrations and temperature. This rate control pertains not only to initiation, propagation and termination reactions but more importantly also includes activation/deactivation reactions involving the mediating agent. Possible side reactions leading to structural defects in the polymer chain have also to be accounted for.

To elucidate and quantify the effect of the molecular structure of the monomer and the mediating agent on the chemistry and the reactions rates, cutting edge quantum chemical techniques can be used to assist in obtaining intrinsic rate coefficients as a complement to experiment and, hence, to contribute to an accelerated optimization of controlled polymerization processes and the in-silico design of functional polymer material.

Program

First, an appropriate computational method is to be selected to calculate reliable activation/deactivation rate coefficients for a limited range of well-established vinylmonomers (e.g. styrene, MMA). In a second step, this method will be applied to evaluate rate coefficients for activation/deactivation and possible side reactions for a broad range of potential RAFT and NMP mediating agents and vinylmonomers. Attention will be focussed on vinylmonomers relevant for the synthesis of polymers with high-tech and biomedical applications. Evaluation of the performance of the candidate RAFT and NMP mediating agents will be performed by implementing the calculated rate coefficients in available microkinetic models to simulate conversion and (co)polymer microstructural characteristics. In a second stage, the rate coefficients will be used to design optimal combinations of promising mediating agent, monomer and polymerization conditions to synthesize targeted functional (co)polymers that are to be validated by experiment.

Advisors: Prof. Marie-Françoise Reyniers, Prof. Maarten Sabbe

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