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Coach	Supervisor(s)	Funding
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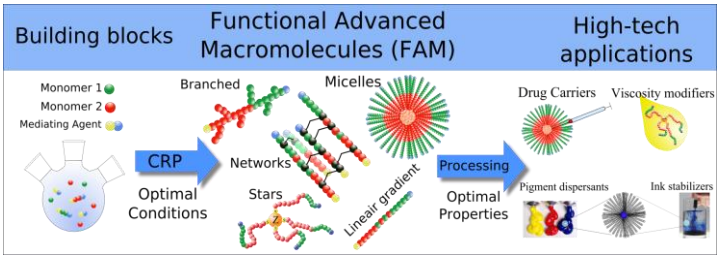
First principles design of RAFT mediating agents for controlled radical polymerization

Aim

Obtain reliable kinetics for the reactions involved in RAFT controlled radical polymerization using quantum chemical calculations, in order to assess the influence of the chemical structure on the performance of a range of RAFT mediating agents, which allows to formulate optimal combinations of mediating agent and polymerization conditions.

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 macro radicals in a dormant state preventing the uncontrolled growth that is typical for conventional free radical polymerization (FRP).
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.
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 design of functional polymer material.

Program

1) Computationally evaluate rate coefficients for addition, fragmentation, and possible side reactions for potentially interesting RAFT agents, focussing on different monomer combinations relevant for the synthesis of polymers with high-tech and biomedical applications.
2) Validation of the calculated rate coefficients in close collaboration with the ongoing experimental and model development work. Evaluation of the performance of the candidate RAFT mediating agents
3) Design optimal combinations of promising mediating agents, monomer and polymerization conditions to synthesize targeted functional (co)polymers that are to be validated by experiment.