LABORATORY FOR CHEMICAL TECHNOLOGY
Technologiepark 125, 9052 Gent, Belgium

Coach	**Supervisor(s)**	**Funding**
Farhan Siddiqui	Maarten Sabbe	

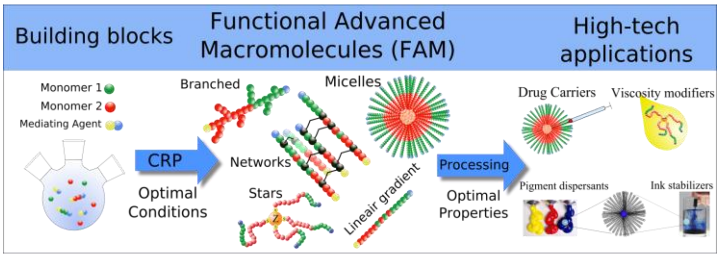
First principles design of RAFT mediating agents for controlled radical copolymerization

Aim

Ab Initio RAFT (reversible-addition fragmentation chain transfer) copolymerization of industrial relevance monomers.

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).



The polymerization of a wide range of functional monomers that are polymerizable by radical polymerization can be controlled by the reversible addition−fragmentation chain transfer (RAFT) process, in various reaction media along with its relative ease of use. Optimal control in RAFT polymerization requires choosing an appropriate RAFT agent (Z and R groups) for the monomer(s) to be polymerized and the reaction conditions. The Z and R groups both play critical roles in controlling efficiency of chain transfer and thereby determine the outcome of polymerization. Challenges still remain in the scaling and translation of this technique into industrial settings, as well as fully exploiting the mechanistic intricacies of RAFT to maximize control and versatility.
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) Improve existing and design new RAFT agents based on an ab-initio evaluation of the thermodynamics and rate coefficients for the addition-fragmentation reactions for different types of monomer (more activated monomers, MAM) and (low activated monomers, LAM) , focusing on the synthesis of polymers with high-tech and biomedical applications.

2) Design optimal combinations of promising RAFT agents, monomer and polymerization conditions to synthesize targeted functional (co) polymers that are to be validated by experiment.

3) Investigate termination kinetics in RAFT polymerization i.e. influence of termination of the radical intermediate formed by the RAFT process on controlled polymer synthesis.

GHENT UNIVERSITY

LCT DRIVING CHEMICAL TECHNOLOGY