UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

MODEL BASED DETERMINATION OF LINEAR GRADIENT QUALITY OF ATRP COPOLYMERS

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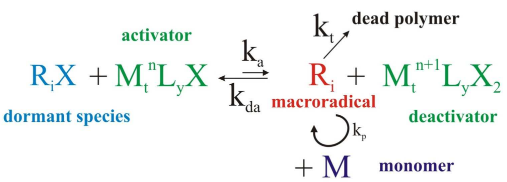
Atom transfer radical polymerization

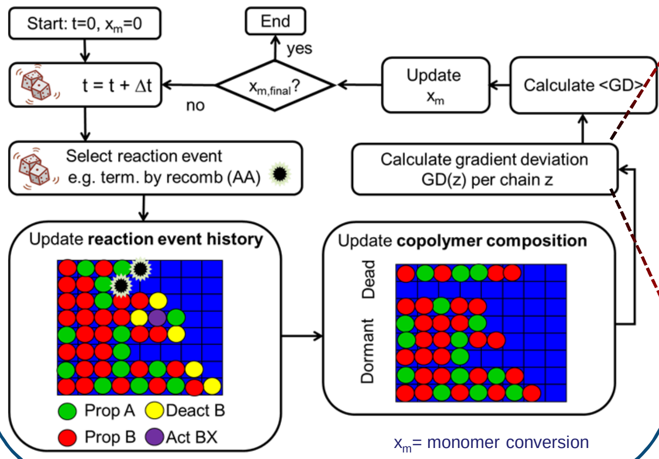
Controlled radical polymerization (CRP) allows the synthesis of macromolecules with predetermined chain length, low polydispersity, end-group functionality and controlled topology. Radicals are temporarily deactivated by a mediating agent. In atom transfer radical polymerization (ATRP), this activation/deactivation process is catalyzed by a transition metal complex. Under ideal conditions, all polymer chains grow concurrently and termination reactions are suppressed.



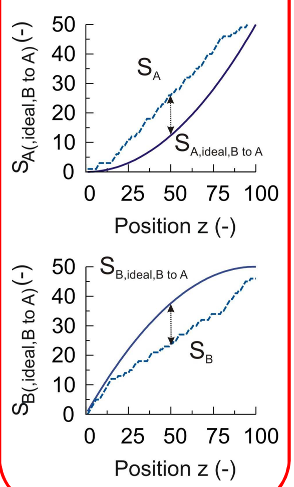
Linear gradient polymers

Linear gradient copolymers exhibit a gradual linear shift in the monomer composition from one chain end to the other:

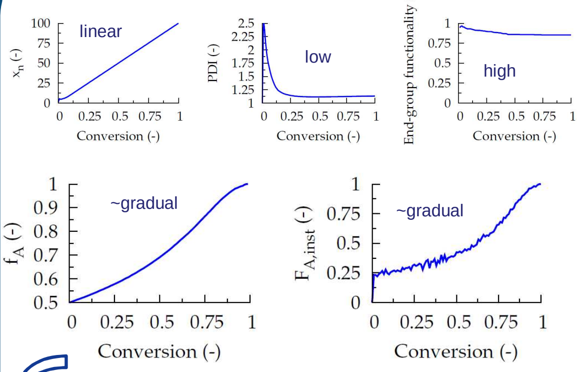
Kinetic Monte Carlo (kMC) simulation flow sheet



Gradient evaluation

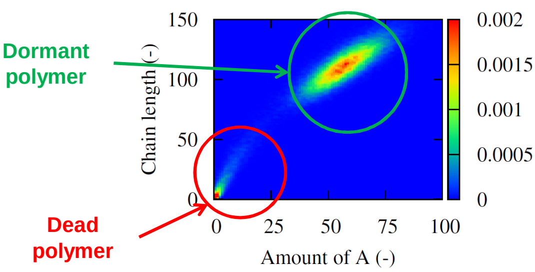


Conventional simulation: Average polymer properties

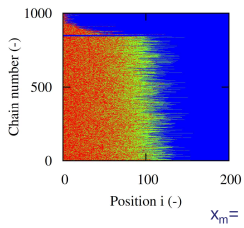


Methacrylates and acrylates *may* form gradient polymers

Chemical composition – chain length distribution

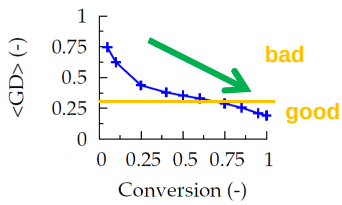


Detailed kMC simulation: sample of the polymer product



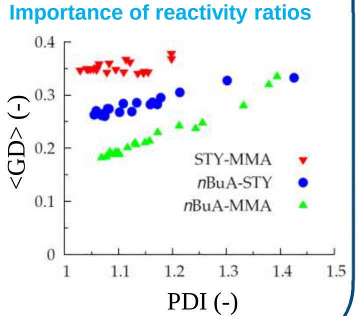
No reaction event
Propagation with methacrylate
Propagation with acrylate

Linear Gradient quality (x_m)

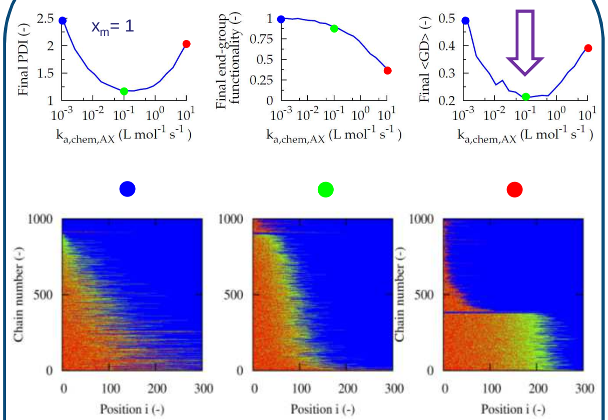


Deviation from ideal linear gradient decreases toward final conversion: relatively good linear gradient

Importance of reactivity ratios



Catalyst choice for optimal gradient quality



- Slow exchange => unwanted A and B dormant homopolymer
- Good exchange => optimal gradient
- Fast exchange => too much dead homopolymer A

Conclusions

A new copolymer property, i.e. the linear gradient deviation (<GD>) is introduced and applied to ATRP. For <GD> values lower than 0.3 the linear gradient quality is good. For the ATRP of methacrylates and acrylates, batch ATRP conditions allow to prepare copolymers with a good linear gradient quality in case an appropriate ATRP catalyst is chosen. The developed methodology can be also applied to other controlled radical polymerization techniques such as nitroxide mediated polymerization and reversible addition-fragmentation chain transfer polymerization.

Acknowledgments

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