Tuning the gradient quality via controlled radical polymerization

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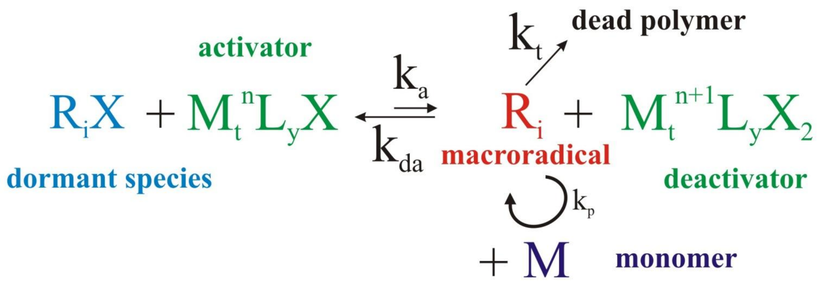
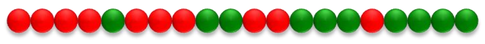
Atom transfer radical polymerization

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.

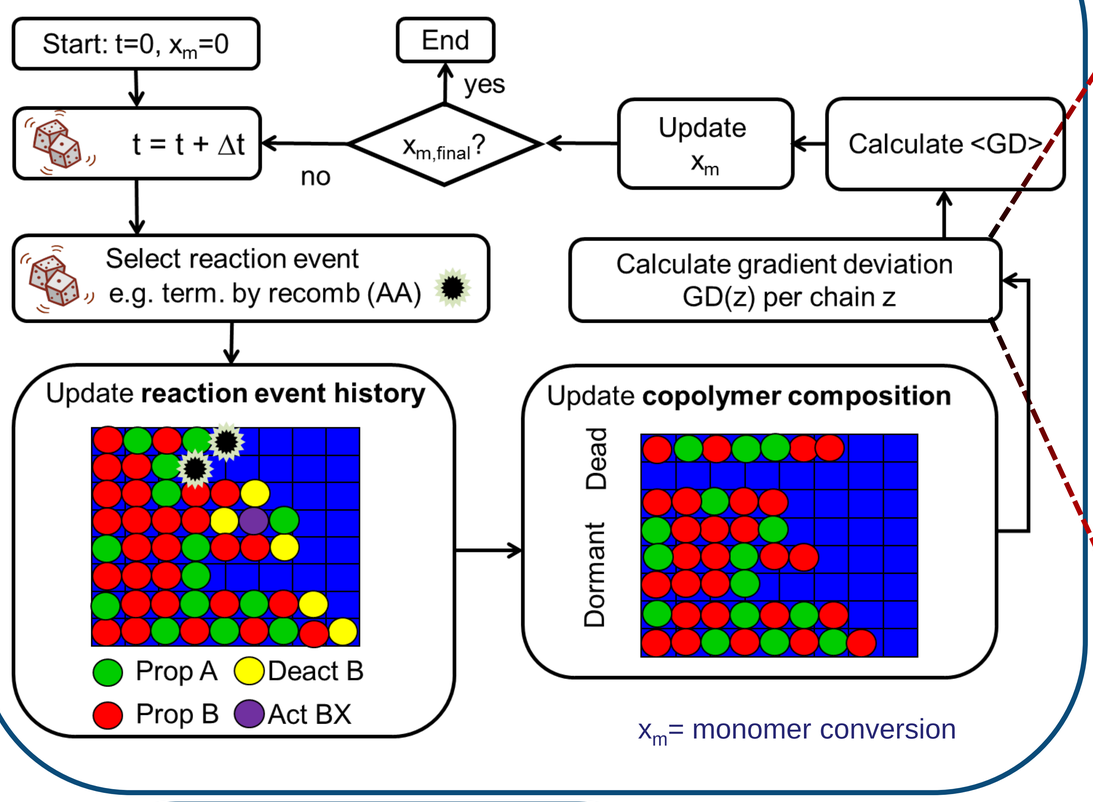


Linear gradient polymers

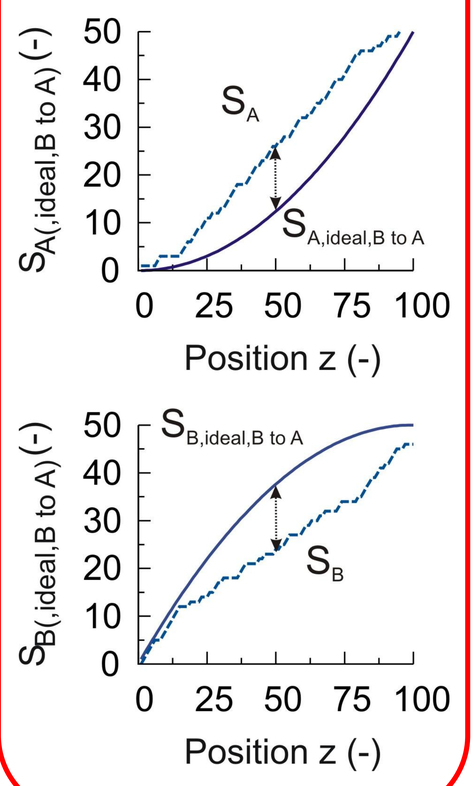
Linear gradient copolymers exhibit a gradual linear shift in the monomer composition from one chain end to the other:



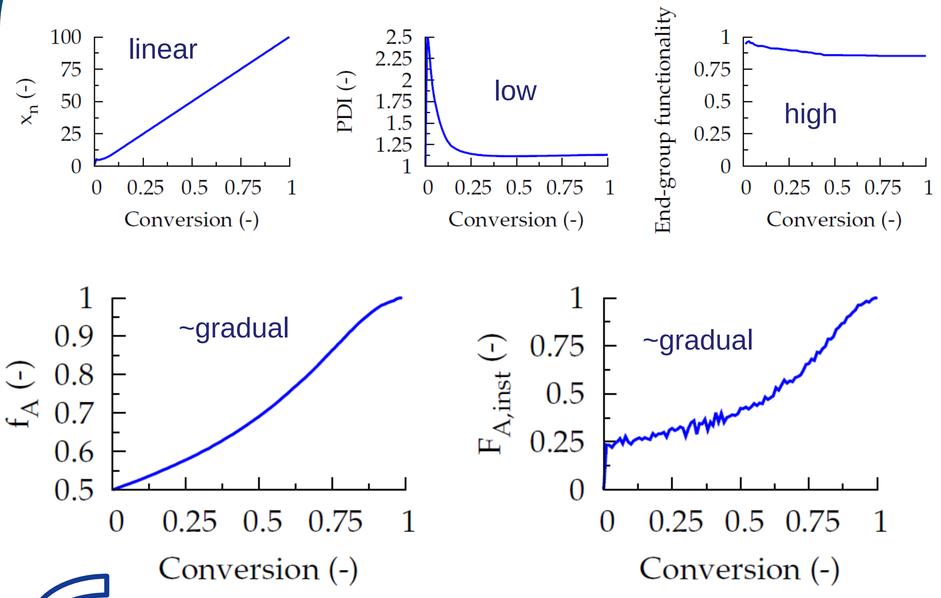
Kinetic Monte Carlo (kMC) simulation flow sheet



Gradient evaluation

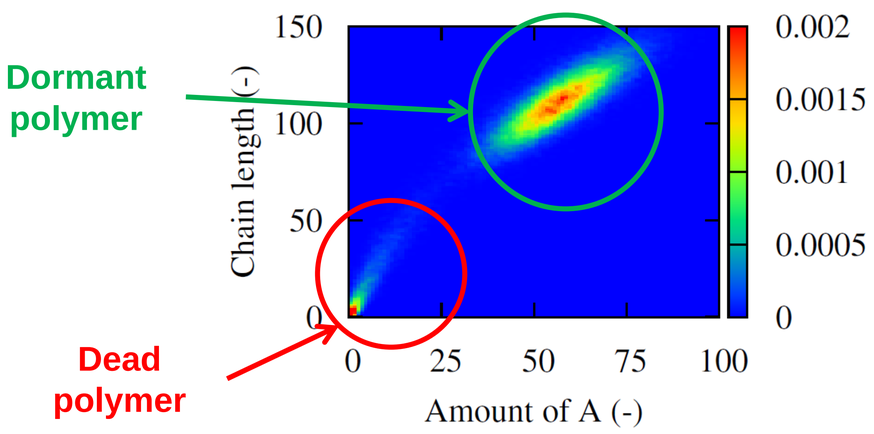


Conventional simulation: Average polymer properties



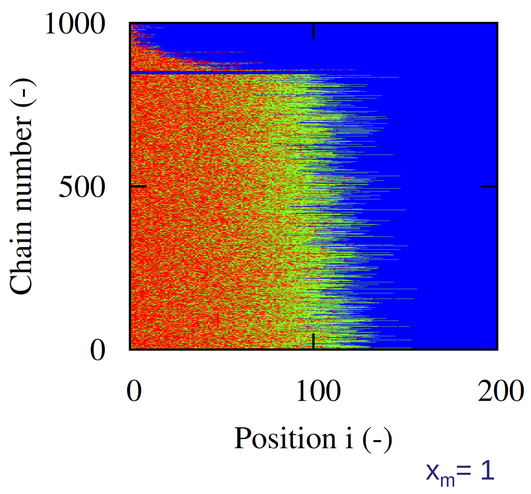
Methacrylates and acrylates ***may*** form gradient polymers

Chemical composition – chain length distribution



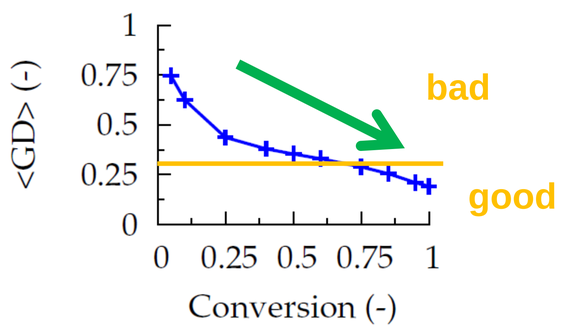
Detailed kMC simulation: sample of the polymer product

- Polymer chains organized horizontally
- Dead polymers at top (mostly methacrylate units)
- Dormant polymers at bottom (gradient character)
- Resemblance of the colour gradient and the $F_{A,inst}$ profile



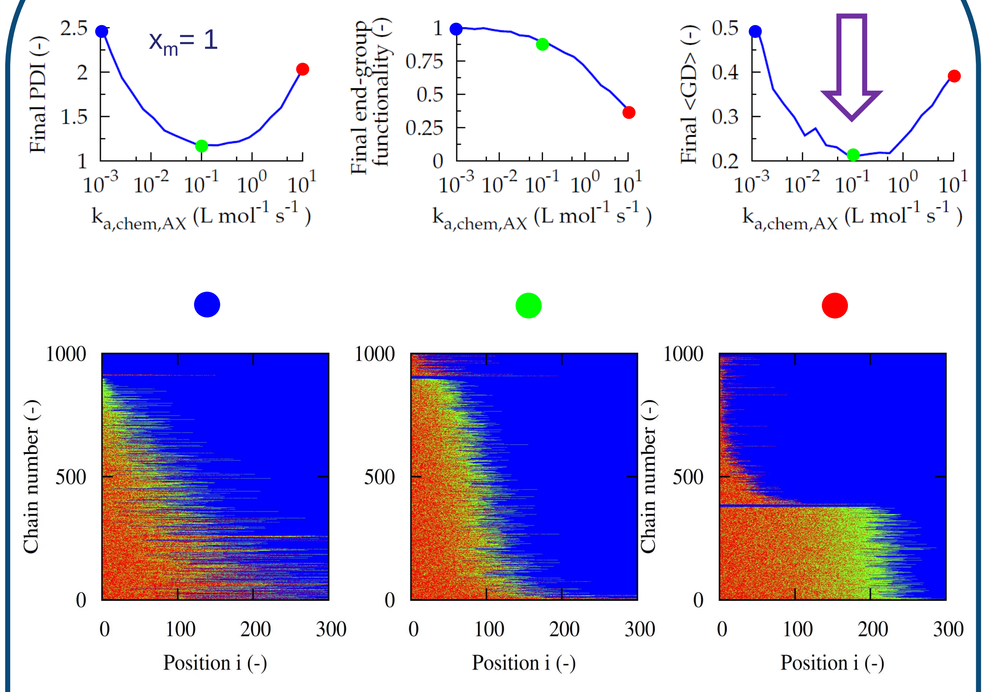
No reaction event
Propagation with methacrylate
Propagation with acrylate

Linear Gradient quality



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

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

This work is supported by the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT Vlaanderen), the 'Long Term Structural Methusalem Funding by the Flemish Government' and the Science Foundation (CHE 10-26060)