# ESR 3/ ESPCI Paris

Larissa Hammer

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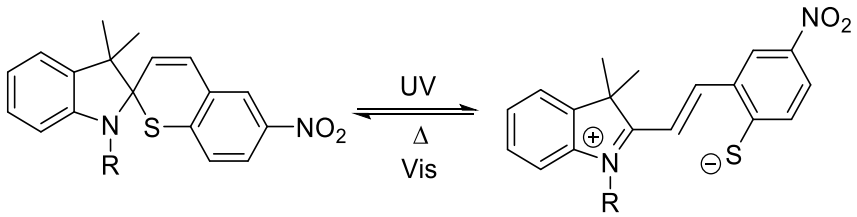
- Research internship at QUT in Brisbane/ AU in 2016
- Master graduation with specialization in polymer chemistry in 2017
- Industry internship at BASF/Ludwigshafen Germany

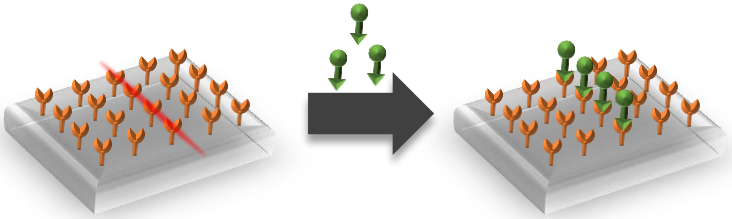

BASF
We create chemistry

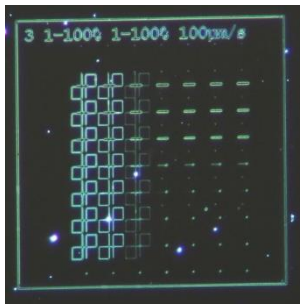
# Master Thesis

- Written in the group of Prof. Barner-Kowollik (KIT)
- ‘Spirothiopyrans as a Potential Platform for STED Lithography and the Formation of SCNPs’

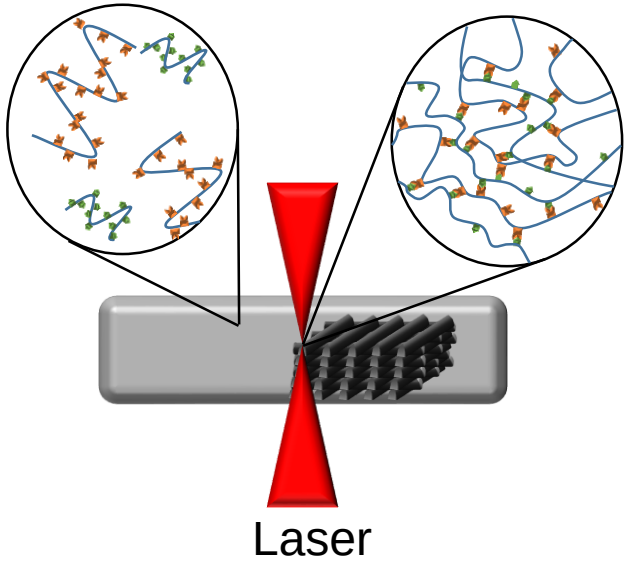



➢ **Direct Laser Writing 2D**

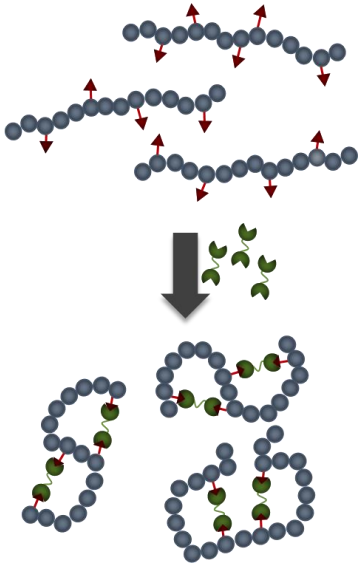




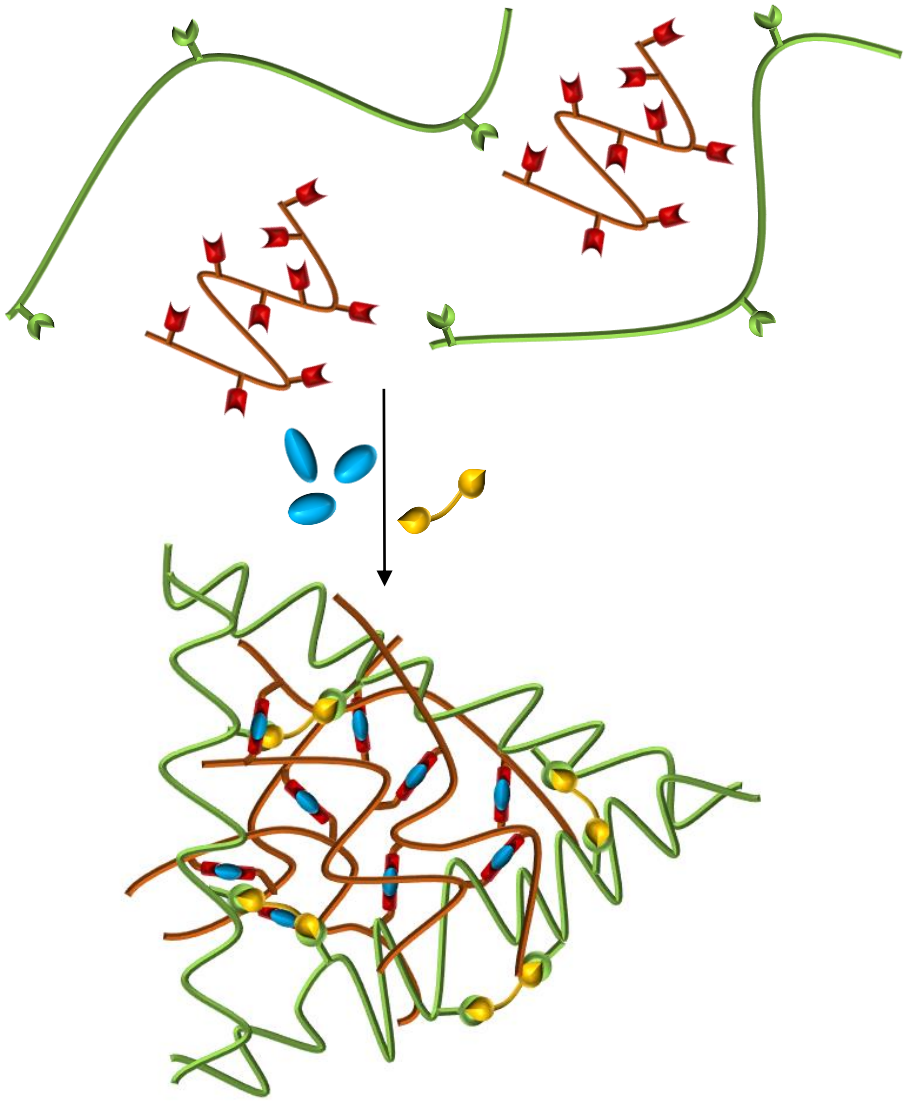
➢ **DLW 3D**




➢ **SCNP**



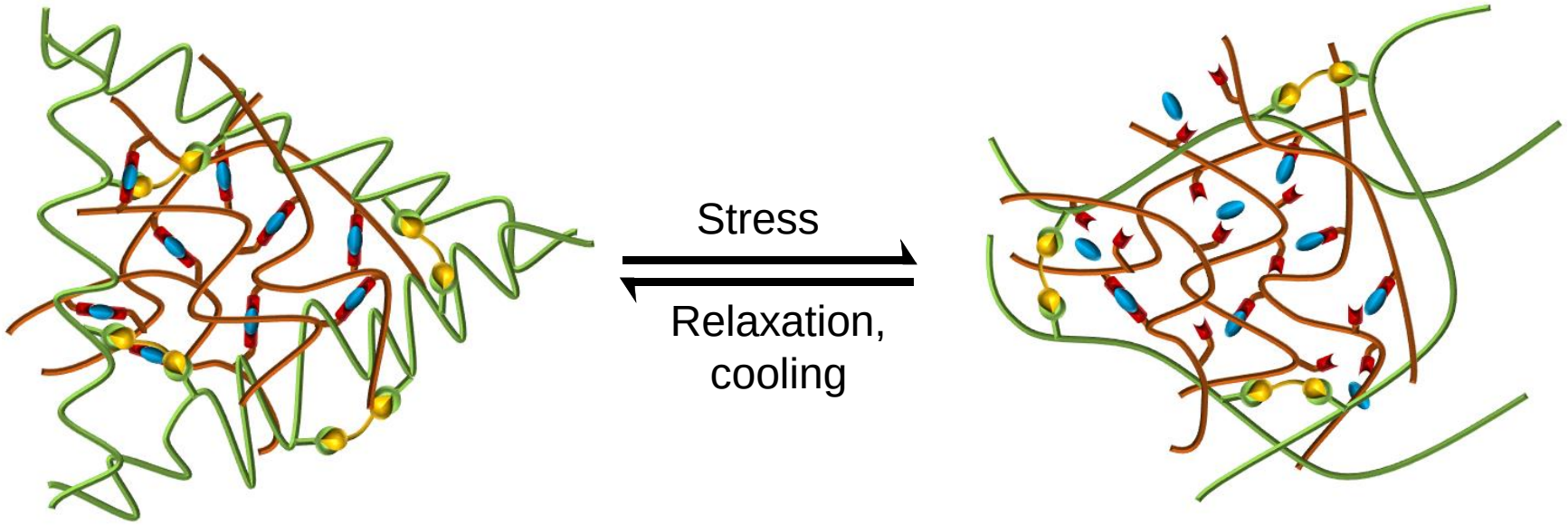
# Concept



- Reversible crosslinked Double Dynamic Networks
- Two interpenetrating networks employing two different (reversible) crosslinkers
- Crosslinking occurs orthogonally from functionalized thermoplasts

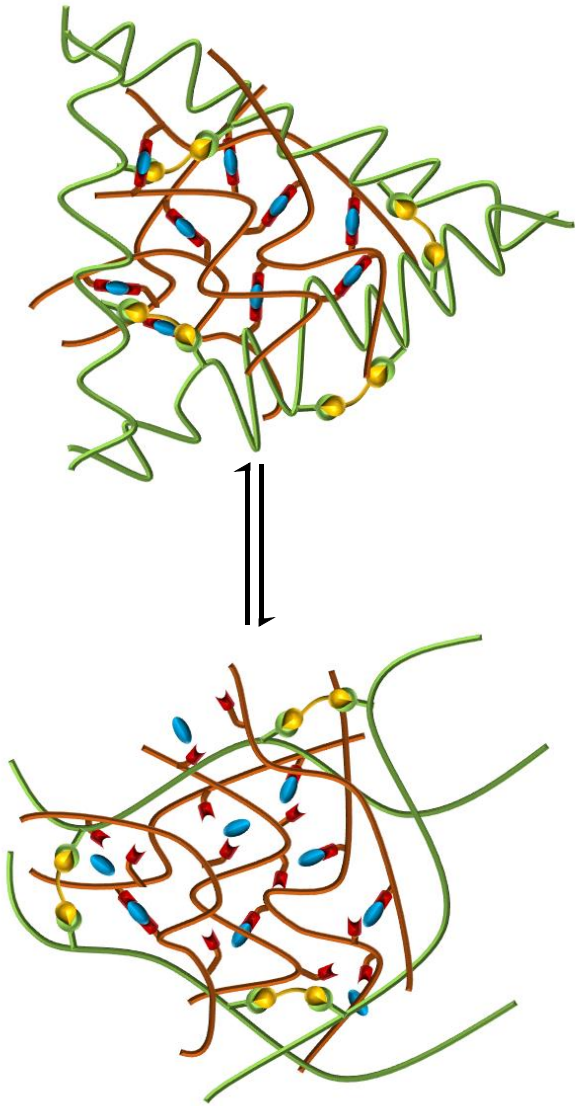
# Concept

- First Network (red)
  - Brittle: thightly crosslinked
  - Sacrificial
  - Reversibly crosslinked
- Second Network (green)
  - Soft: loosely crosslinked
  - Deformable
  - Permanently crosslinked at rt
  - Can be reversible at elevated T



# Aimed Properties

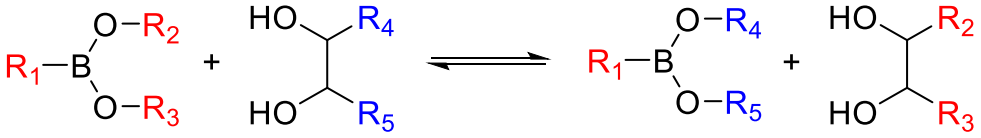
- Self-healing
- Fatigue resistance
- High toughness
- High fracture energy
- Enhanced stress at break
- Shape memory
- Creep resistance
- Reversible elasticity



# System Network 1

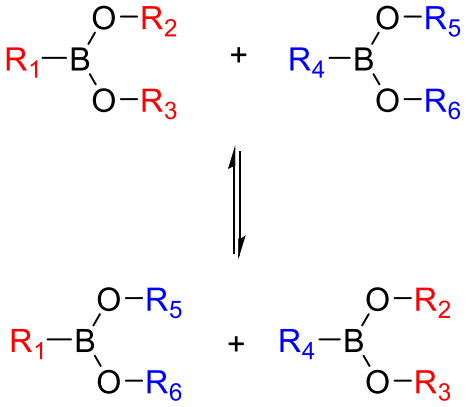
- Dynamic, ‘brittle’ network
- Sacrificial
- Self-healing through reversible covalent bonds

Boronic ester / diol exchange:



- Boronic ester exchange
- Could even work at rt
- Tuneable reactivity
- ‘Vitrimer Network’
- Maintains same number of crosslinks
- Still self-healing, processable

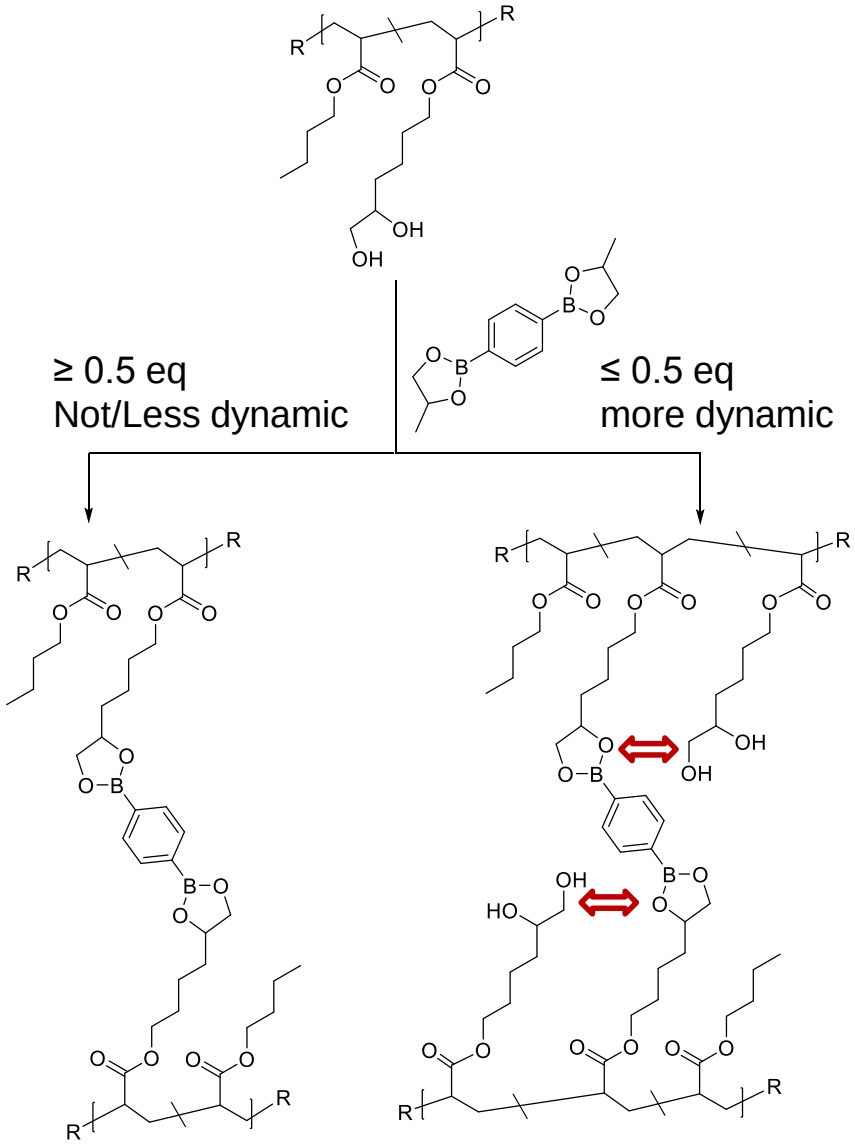
Boronic ester exchange:



Exchange accelerates in presence of diols

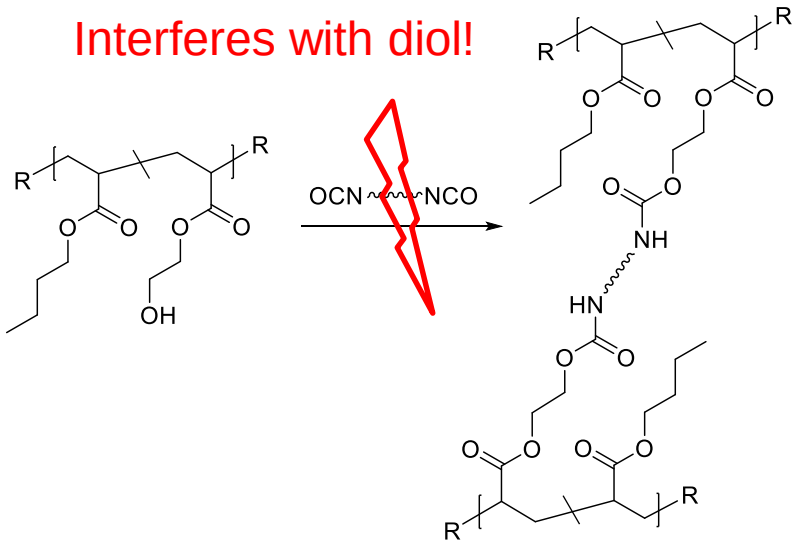
# System Network 1

- High density of cross links
  - DP 1000 (~100 000 Da)
  - ~100 links/chain (10% functionality)
- Butyl acrylate system (low $T_g$)
- Cross-linking via di-boronic ester
- Reactivity tuneable via equivalents



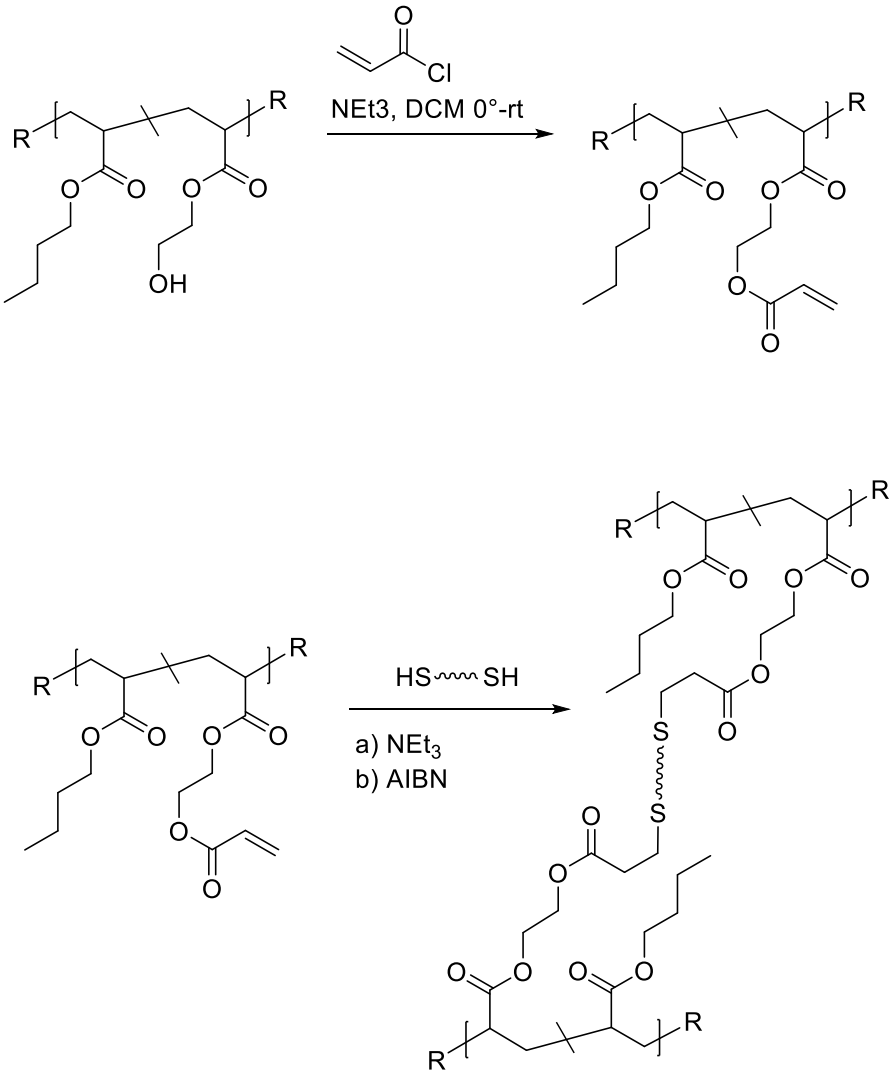
# System Network 2

- Network 2 (N2)
- Low density of crosslinks
  - DP 5000 (~500 000 Da)
  - ~10 links/chain (0.2% functionality)
- Permanent or reversible crosslinks (at elevated T)
- Effective ‘click’ reaction
- Orthogonality to N1 !



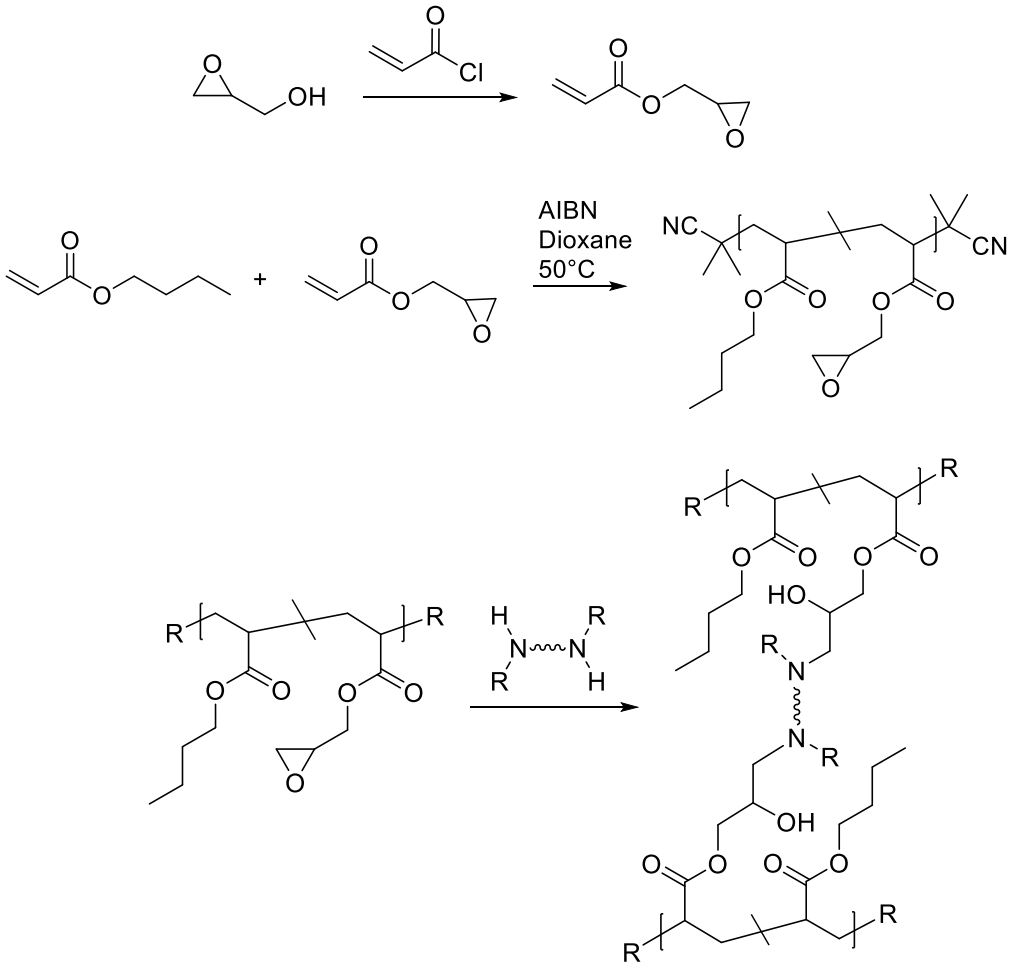
# System N2: Thiol-ene

- Thiol-ene reaction
- Incorporate alkene groups in polymer
- **Permanent crosslinking** via dithiol either via:
  - a) Michael addition
  - b) Free radical addition
  - Kat. necessary
  - Possible in bulk?
- **Orthogonal** to diol/boronic ester system



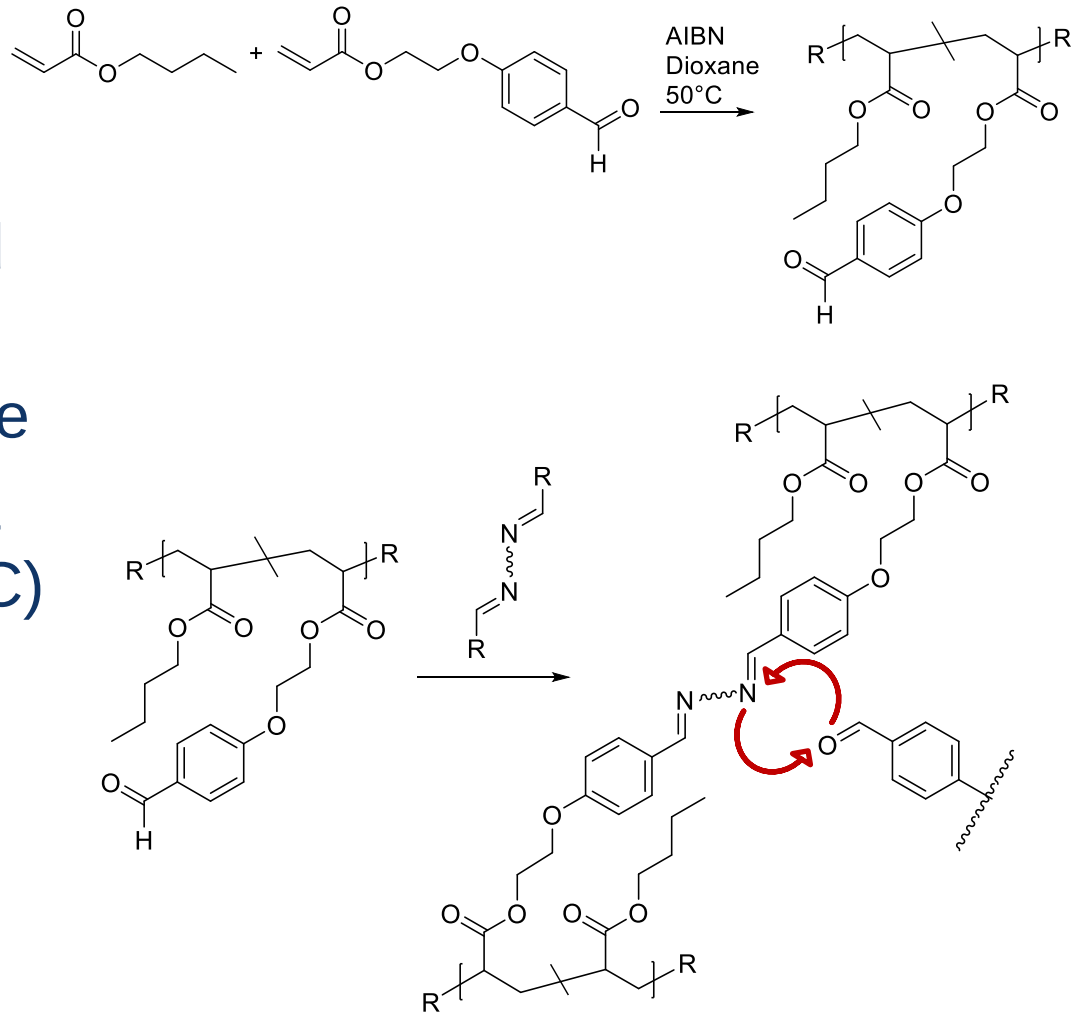
# System N2: Epoxy Opening

- Epoxide ring-opening reaction
- Synthesis of epoxy monomer
- **Permanent crosslinking** via diamine
- Kat. needed?
- Reaction at low T
- Orthogonal to diol/boronic ester system



# System N2: Imine Formation

- Aldehyde and imine exchange reaction
- Aldehyde functionalized polymer
- Crosslinking with diimine
- **Dynamic crosslinks** at slightly elevated T (60°C)
- Exchange reaction between imines/aldehydes or imines/imines (Vitrimer)



# Plan

- Test polymerizations to determine best conditions (size of polymer, T, solvent, [I], [M])

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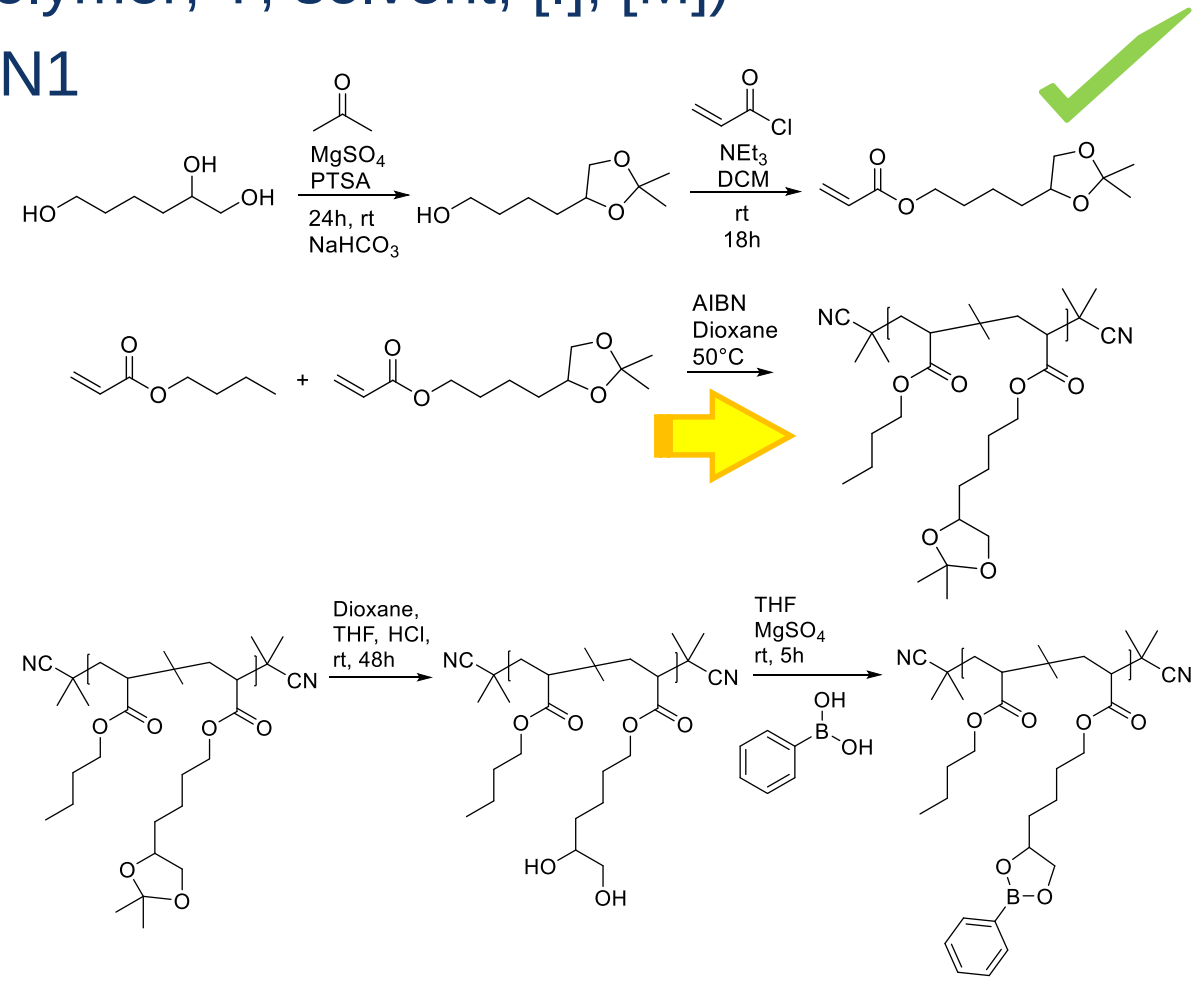
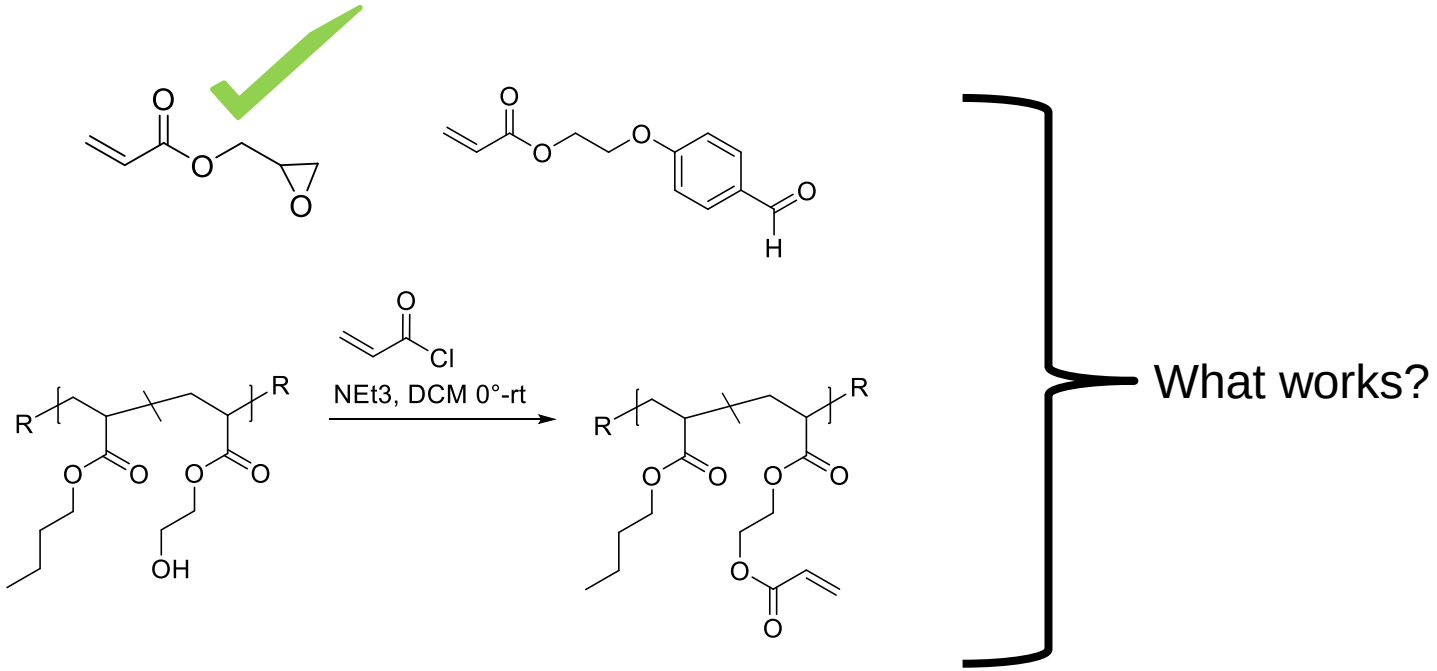
- Monomer synthesis N1



# Plan

- Test polymerizations to determine best conditions (size of polymer, T, solvent, [I], [M])
- Monomer synthesis N1
- Synthesis of building blocks for N2



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- Test polymerizations to determine best conditions (size of polymer, T, solvent, [I], [M])
- Monomer synthesis N1
- Synthesis of building blocks for N2
- Copolymerization of thermoplasts
- Separate/ simultaneous cross-linking of N1/N2
- Property Testing