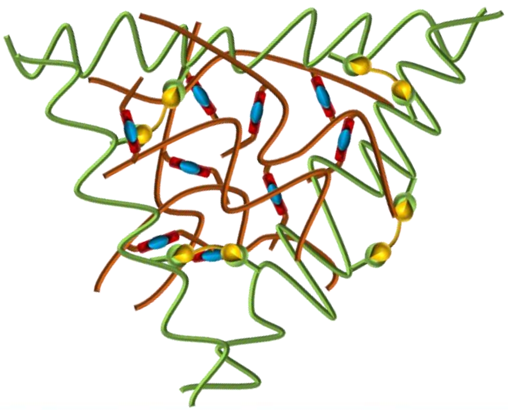
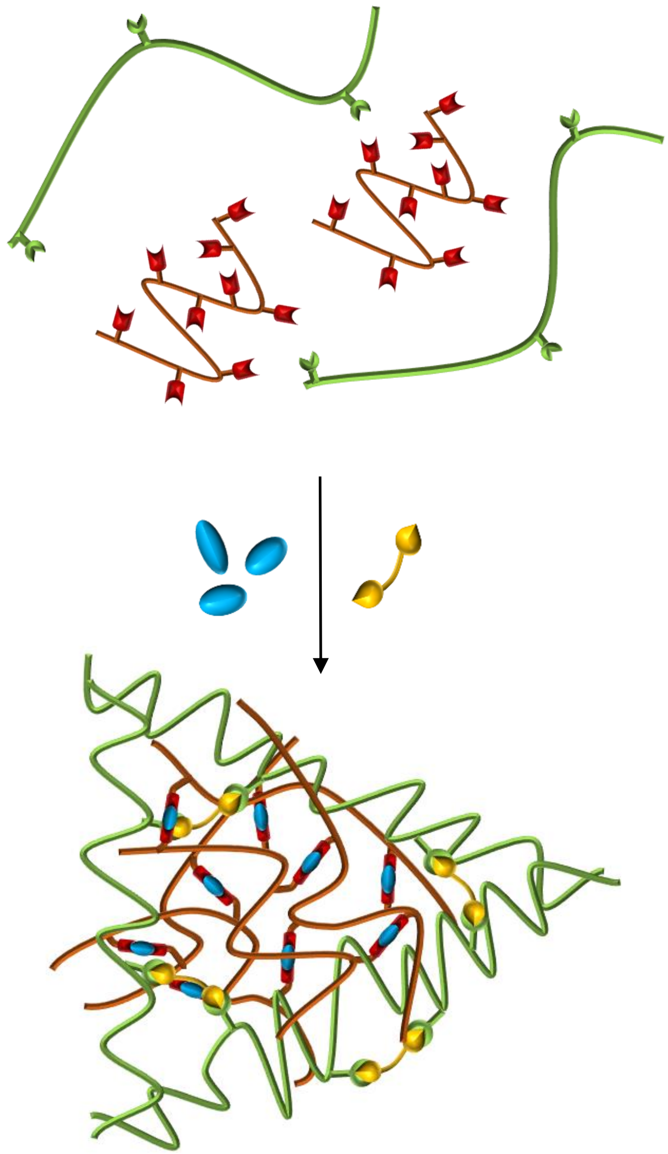


UPDATE DSM

Larissa Hammer, ESPCI Paris

My Part of the Project

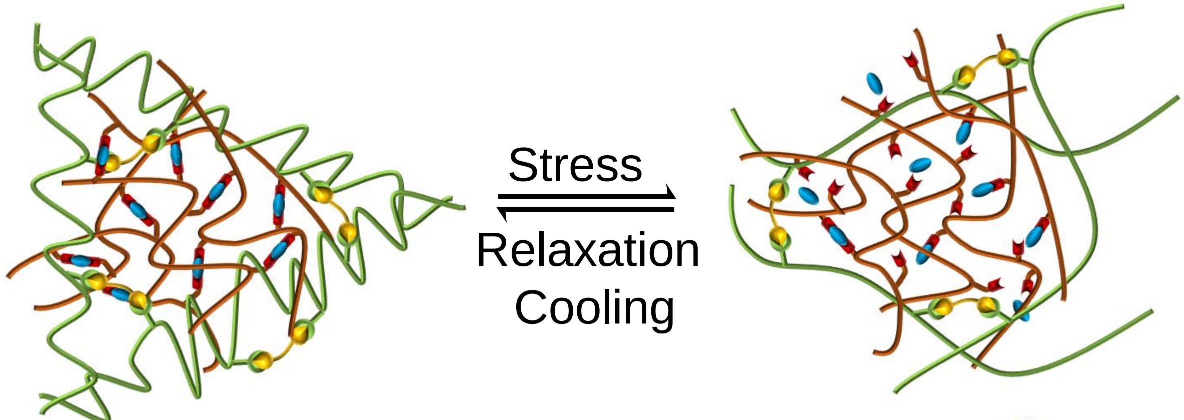
- Design and synthesize DDNs based on reversible covalent bonds
- Creating two interpenetrating network structures
- Creating thermoplastics with functional groups
- Orthogonal cross-linking



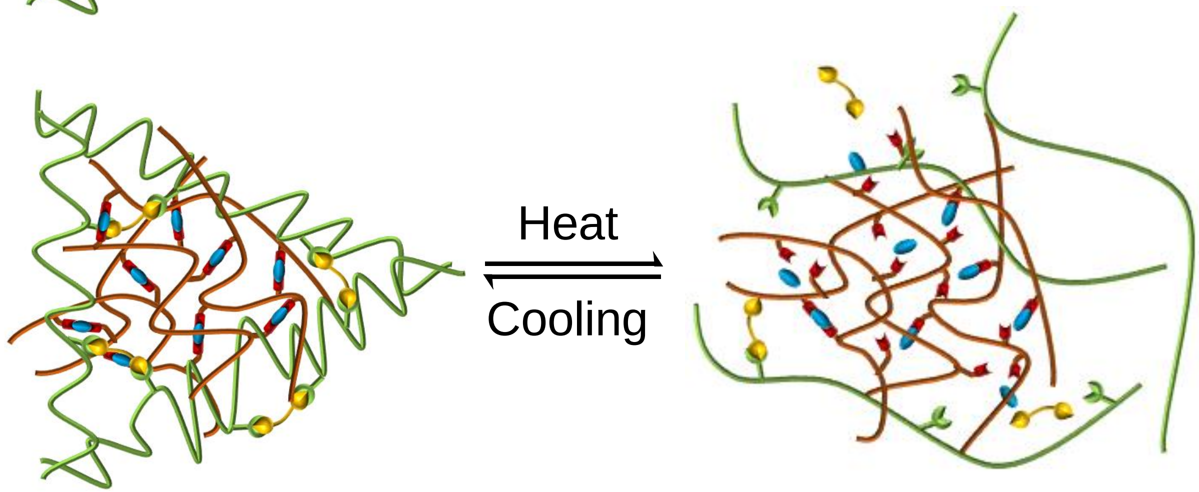
DDN Concept

- Network 1: Brittle, sacrificial bonds, very dynamic
- Network 2: Soft, dynamic at high T

- Network 1 dissipates energy
- Heals itself



- Network 2 only gives up form at high T
- Recyclability

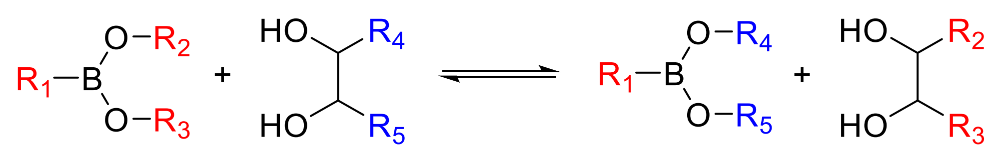


System Network 1

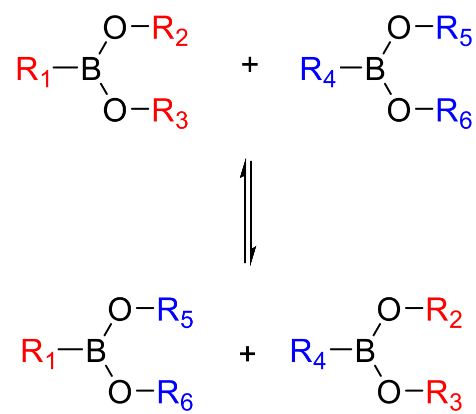
- Dynamic, brittle network
- Sacrificial
- Self-healing through dynamic covalent bonds

- Boronic ester exchange
- Works at rt/ in bulk
- ‘Vitrimer Network’
- Maintains same number of crosslinks
- Self-healing, processable

Boronic ester / diol exchange:



Boronic ester exchange:

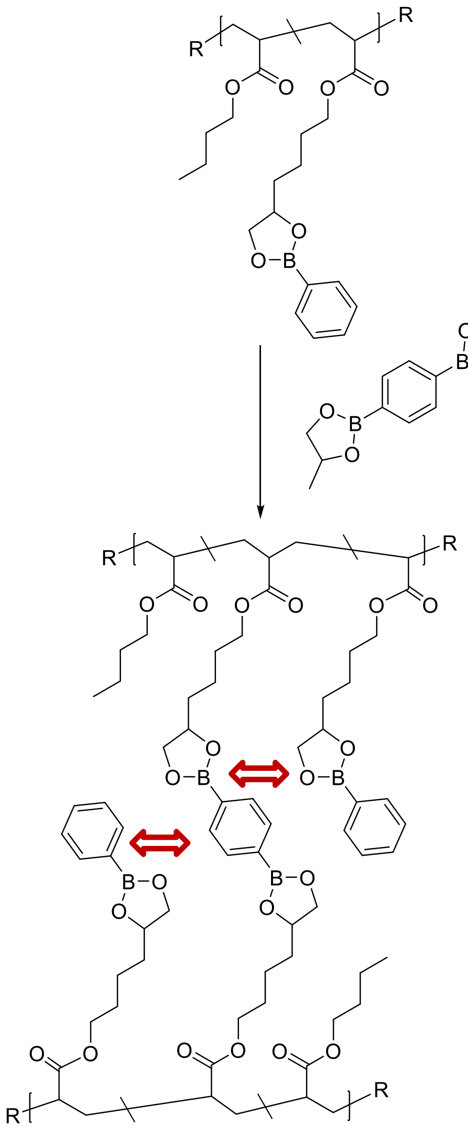


Exchange accelerates in presence of diols

System Network 1

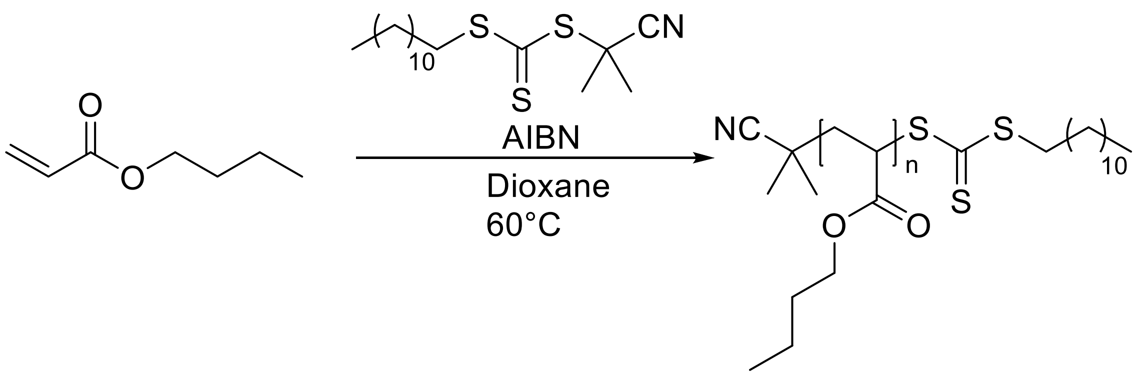
- Butyl acrylate system (low T_g)
- High density of cross links
  - DP 1000 (~100 000 Da)
  - ~100 links/chain (10% functionality)

- Diol-based polymer protected with boronic acid
- Cross-linking via di-boronic ester



Test Polymerization

- Free radical polymerization $\rightarrow$ $Đ \sim 3$
- Reversible addition−fragmentation chain-transfer (RAFT) polymerization
- Looking for right conditions (Agent, T, solvent…)
- RAFT agent: CPDT[1)]



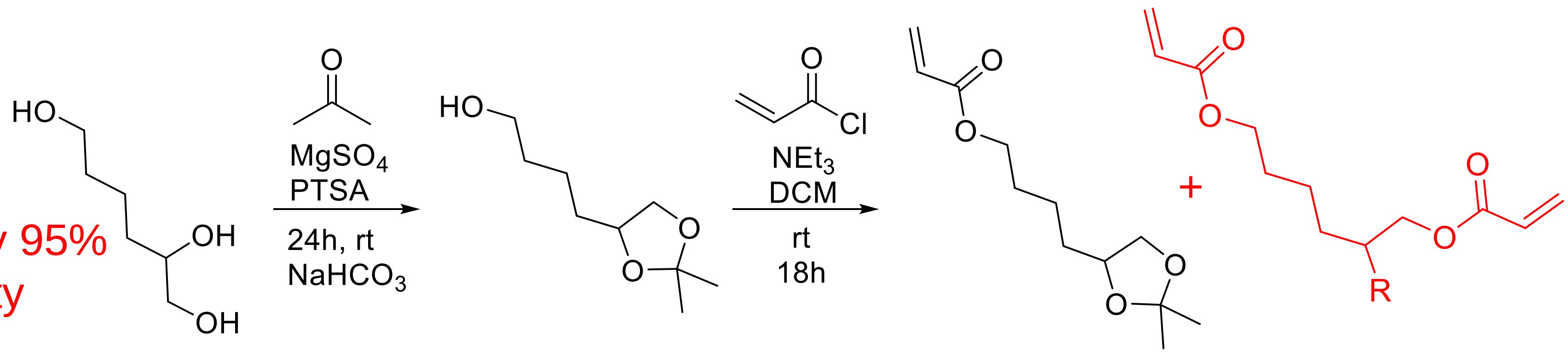
- M_n = 84,000 Da, $Đ$ = 1.20

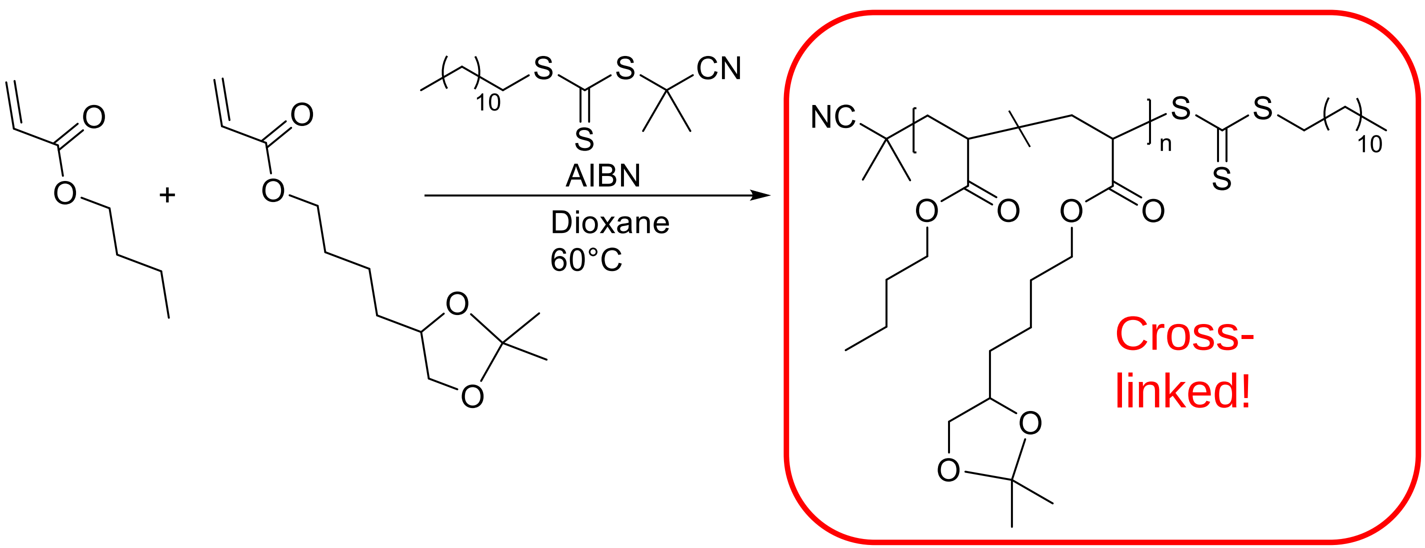
1) 2-Cyano-2-propyl dodecyl trithiocarbonate

Monomer Synthesis

- Monomer synthesis for diol monomer

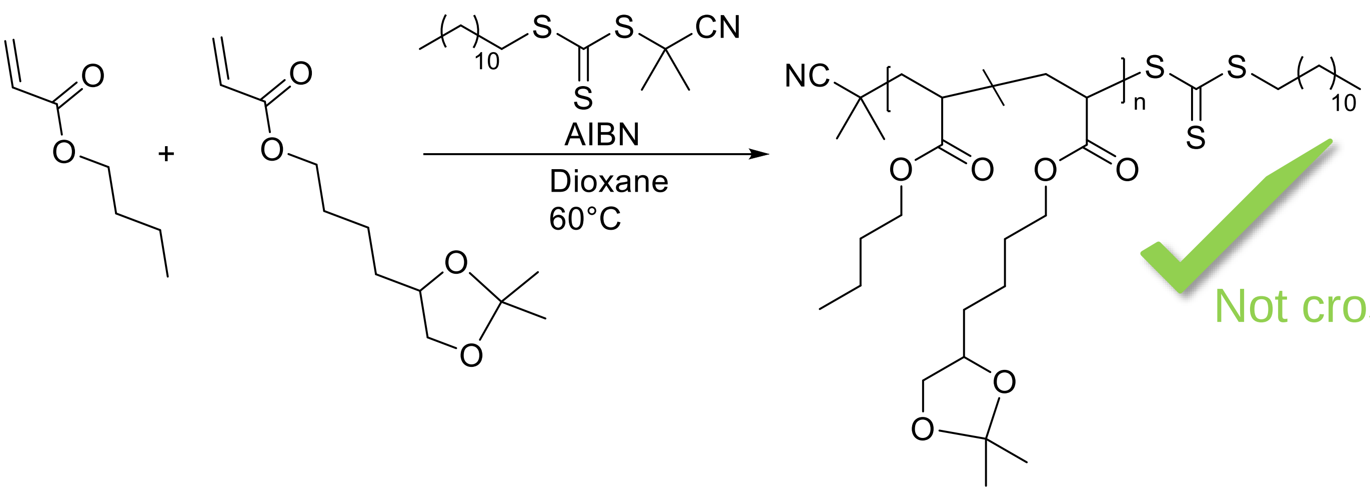
Only 95% purity





Monomer Synthesis

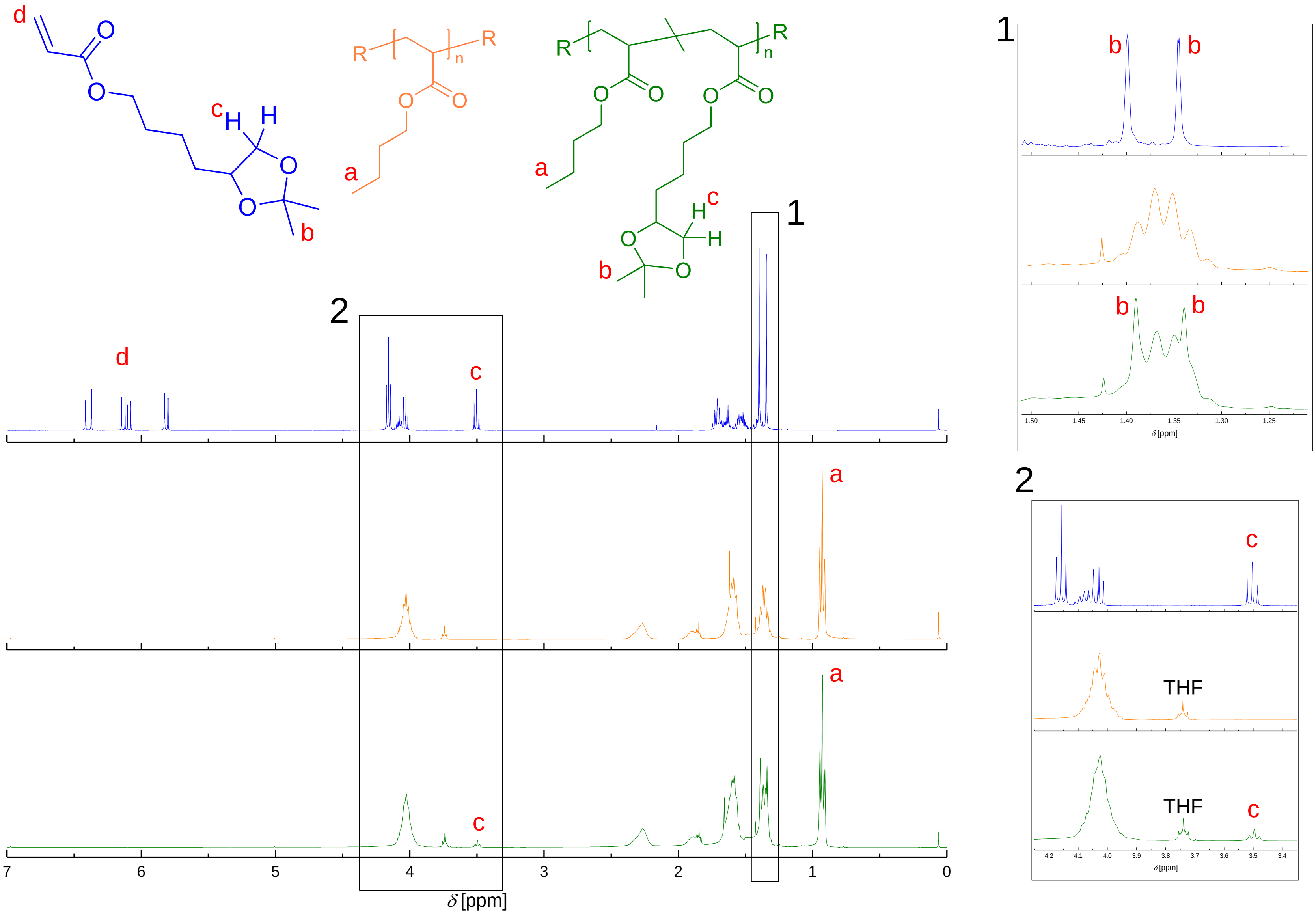
- Purify starting materials
- Fractionated Distillation… Column Chromatography…



Not cross-linked anymore

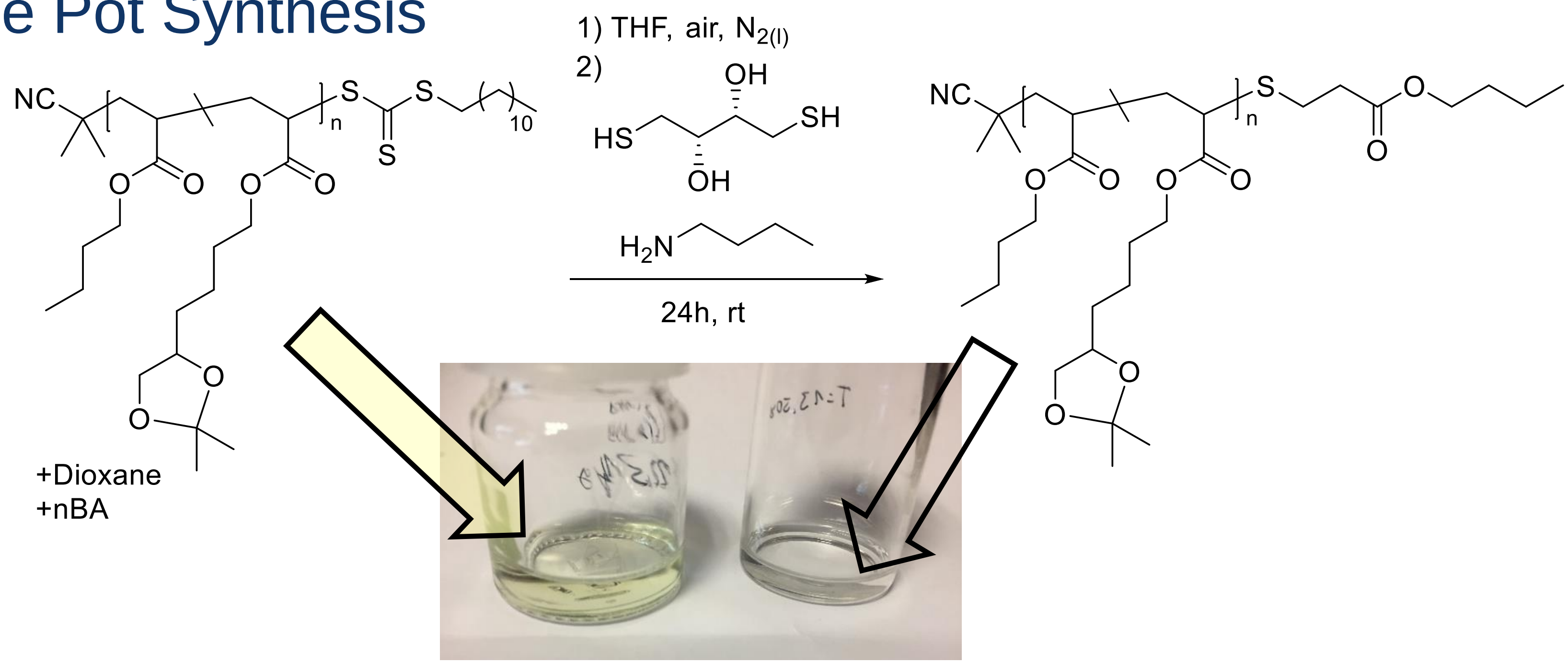
- M_n = 88 000; $Đ$ = 1.90, 10% functionality, >95% monomer conv.

Diol Copolymer NMR



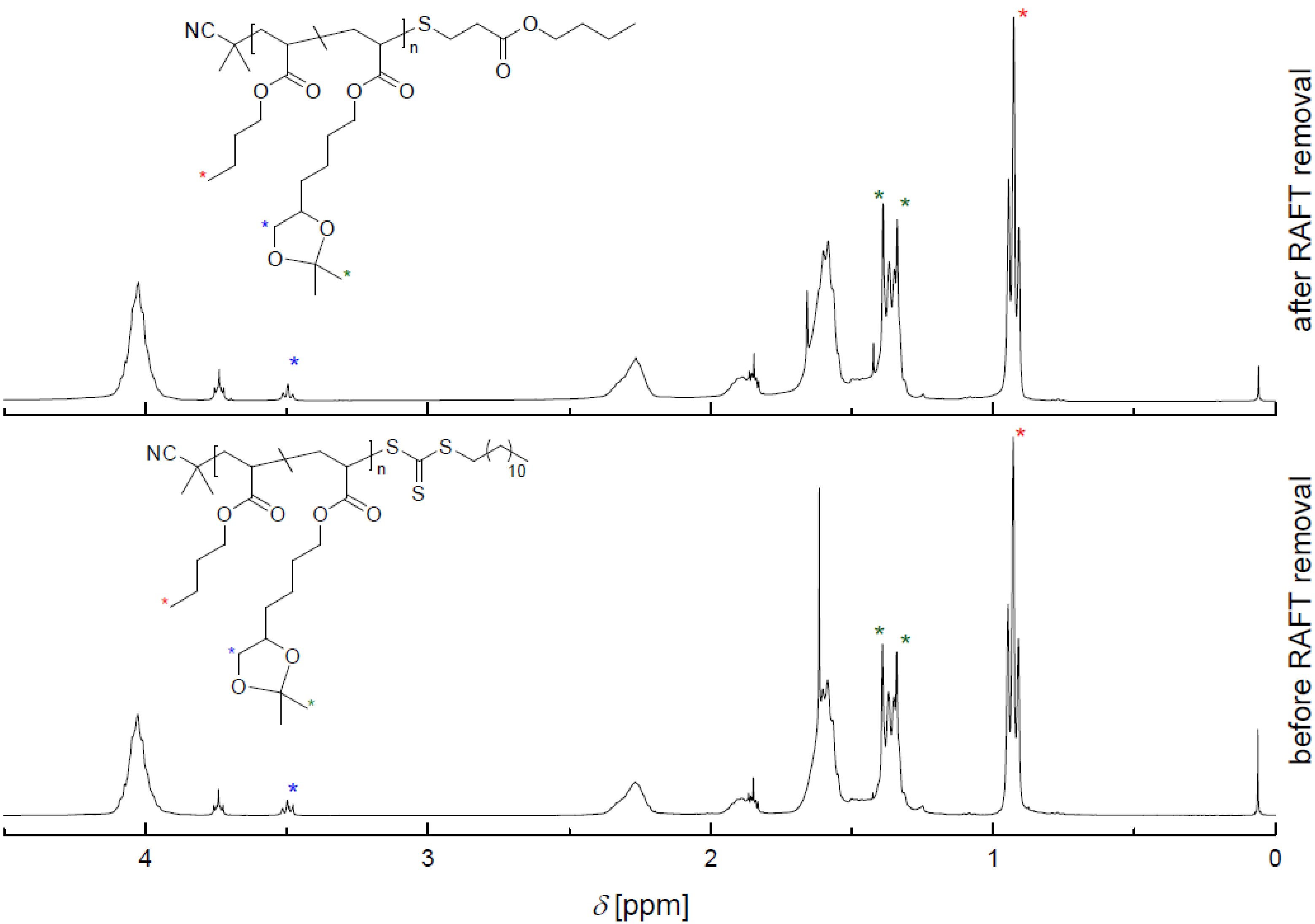
RAFT Group Removal

- RAFT group removal: aminolysis/Michael addition
- One Pot Synthesis

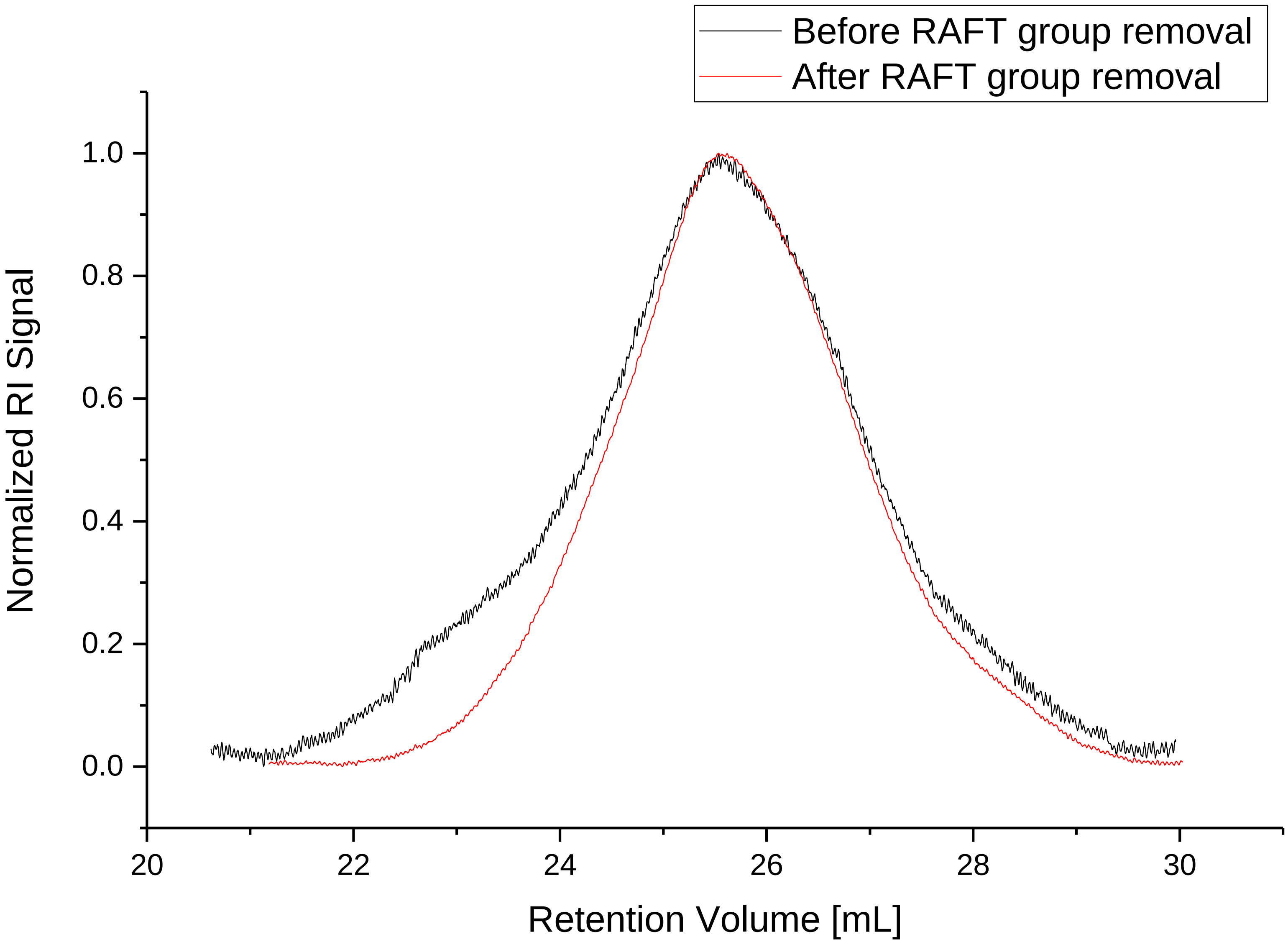


- NMR and SEC: no cross-linking or chemical changes in the polymer
- To do: verify/quantify via UV-Vis

RAFT Group Removal NMR

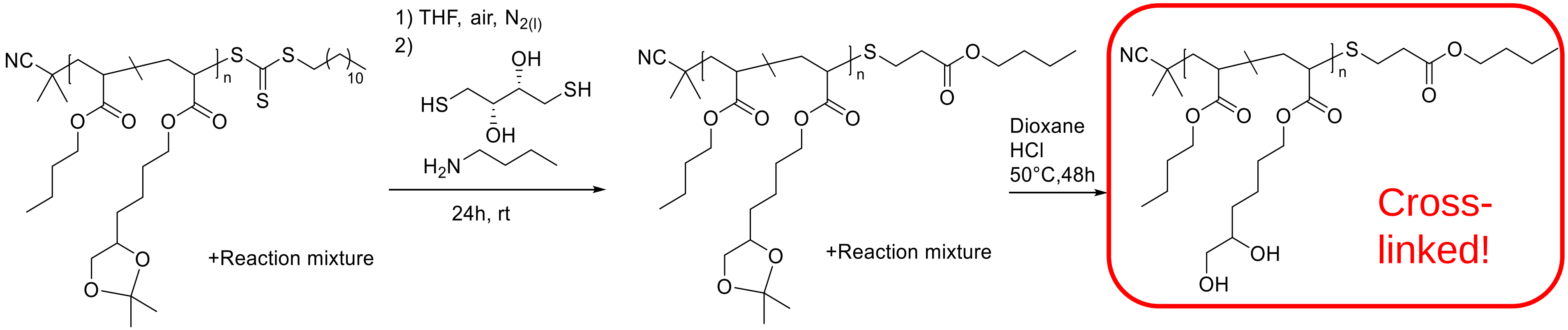


RAFT Group Removal SEC



Deprotection

- Deprotection: One-Pot

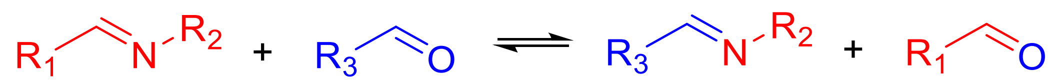


- Try to clean intermediate polymer first
- Try different acid, milder conditions

System Network 2

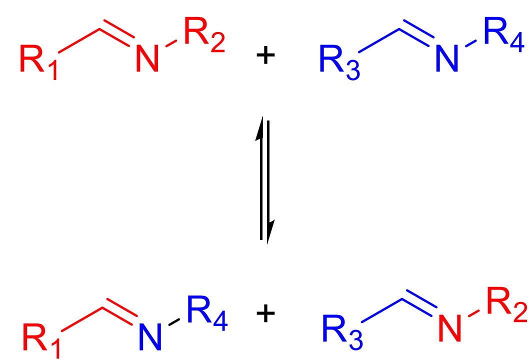
- Extendable network
- Employ dynamic bonds

Imine / aldehyde exchange:



- Imine exchange
- Imine: Aldehyde + Amine
- Works at elevated T
- ‘Vitrimer Network’
- Maintains same number of crosslinks

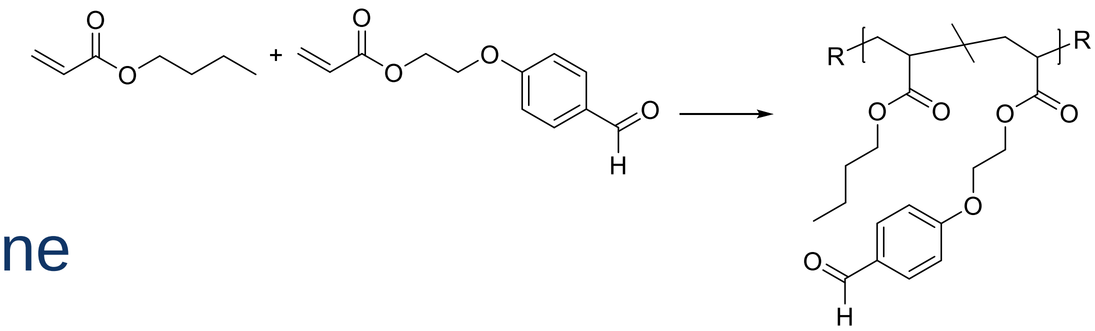
Imine exchange:



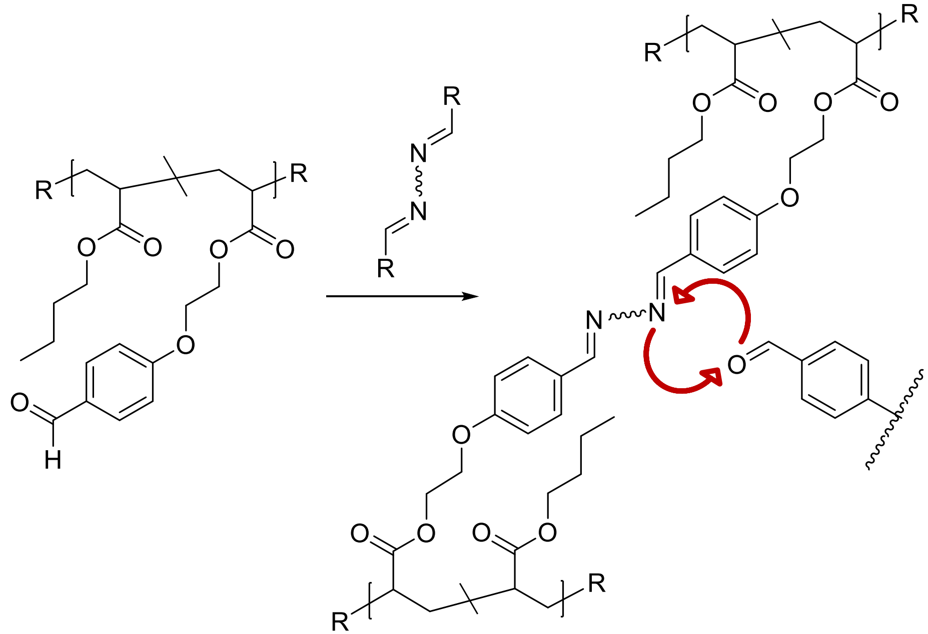
Exchange accelerates in presence of aldehydes

System Network 2

- Aldehyde functional polymer
- Cross-linking with diimine

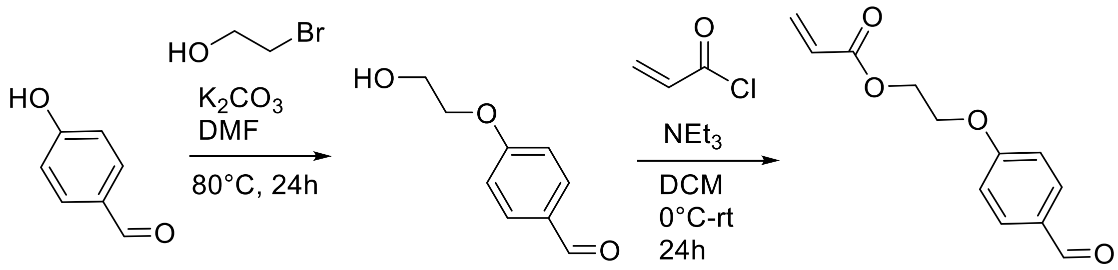


- Low density of cross-links
  - DP 5000 (~500 000 Da)
  - ~10 links/chain (0.2% functionality)

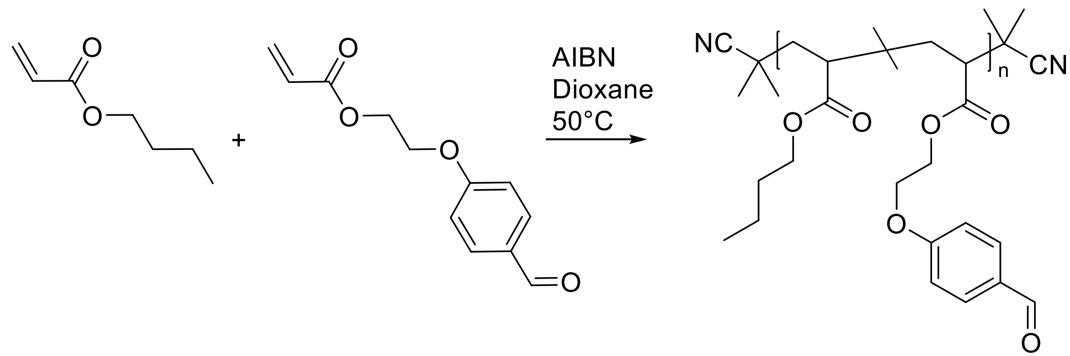


Monomer Synthesis

- Two step synthesis

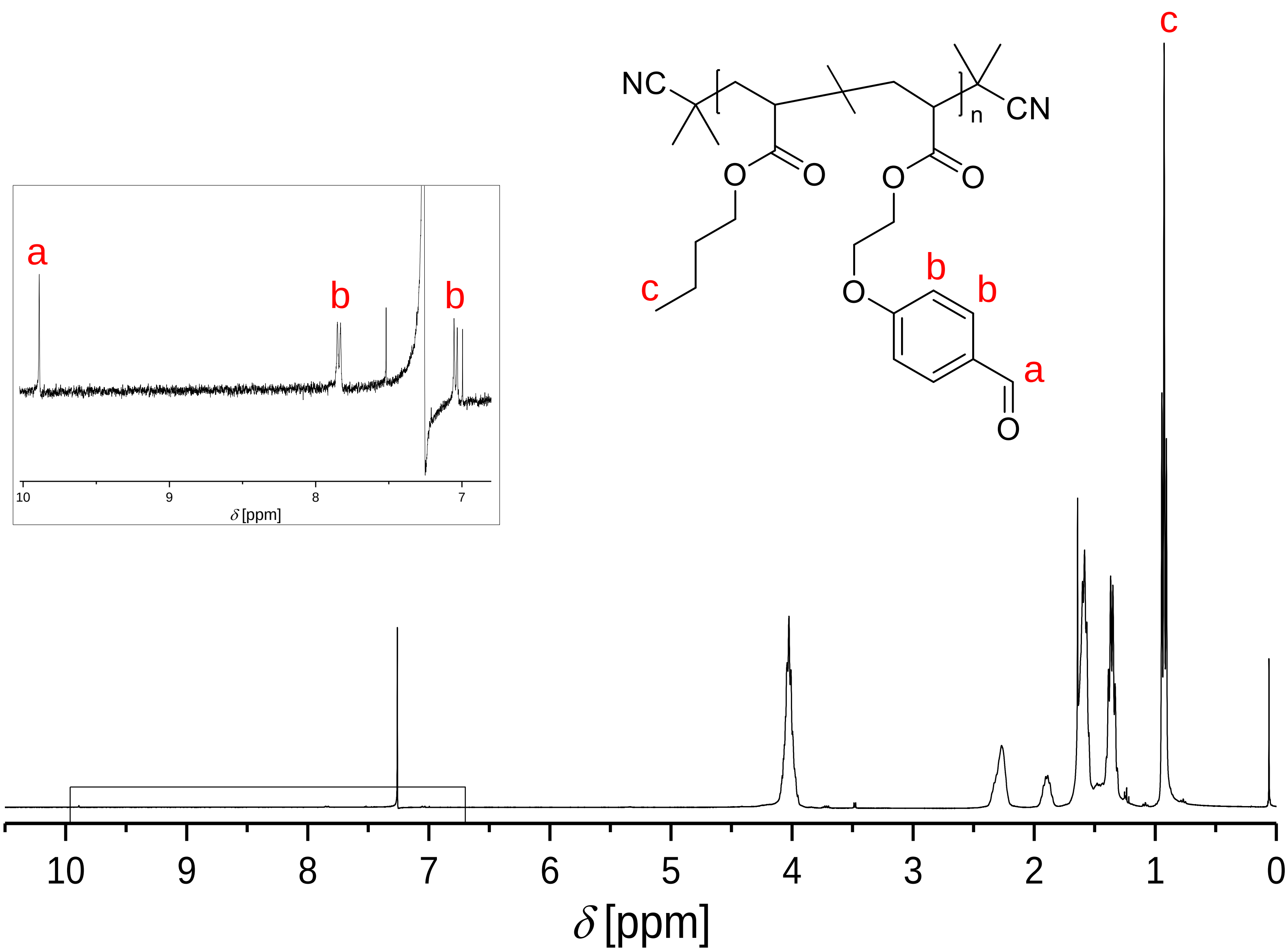


- Employment in free radical polymerization (FRP)



- M_n = 300 000 Da; $Đ$ = 2.16, ~0.2% functionality

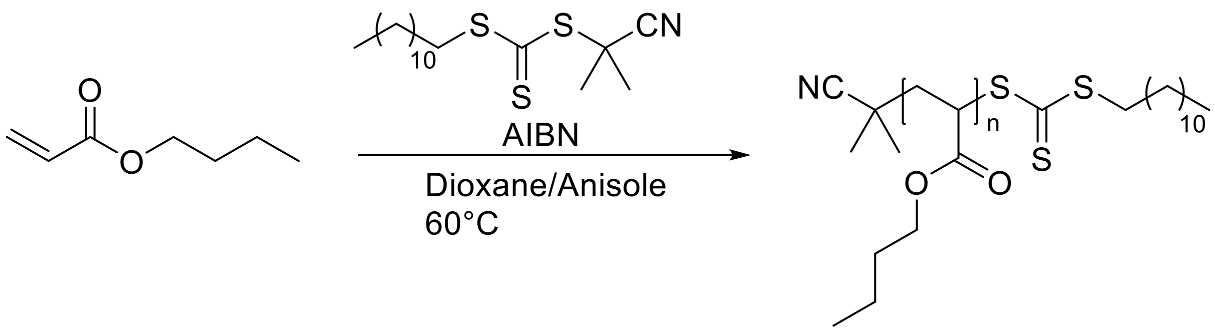
Aldehyde Copolymer NMR



Polymer Size

- Experiments with FRP
- Best case: M_n ~ 400 000 Da; $Đ$ = 2.00

- RAFT Polymerization



- Dioxane: M_n ~ 200 000 Da; $Đ$ ~ 2.00
- Anisole: M_n ~ 500 000 Da; $Đ$ ~ 1.50; but no clean SEC
- Work with FRP results
- ATRP? Color? Orthogonality to aldehyde?

Future Plan

- Make deprotection work
- Test cross-linking reactions
- Synthesize single and double networks
- Explore more systems (dynamic/ non-dynamic)
- Try to accomplish larger polymer sizes
- Mechanical testing