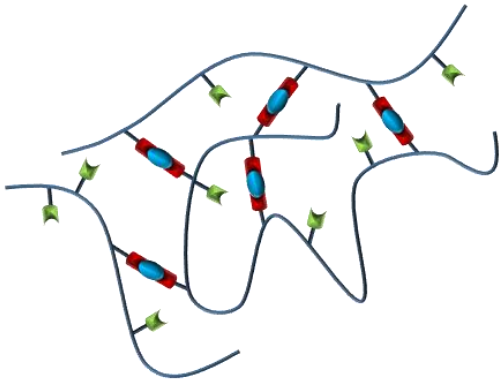
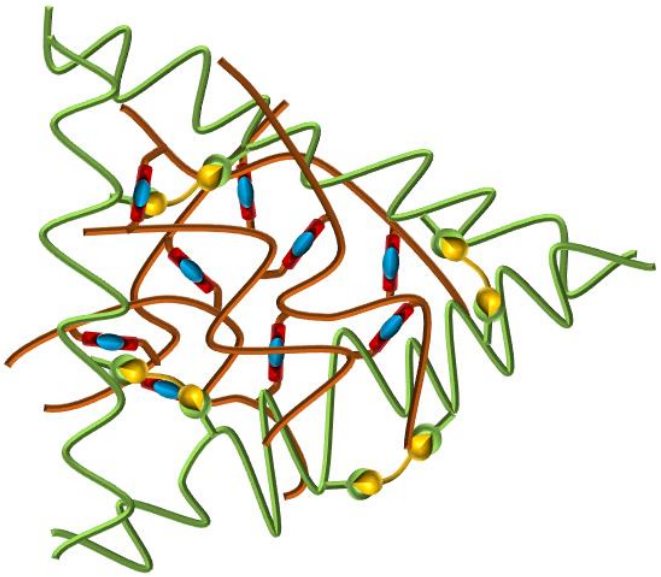


Update Copenhagen

Larissa Hammer

Projects

Double Networks



Thermoplastic Elastomers

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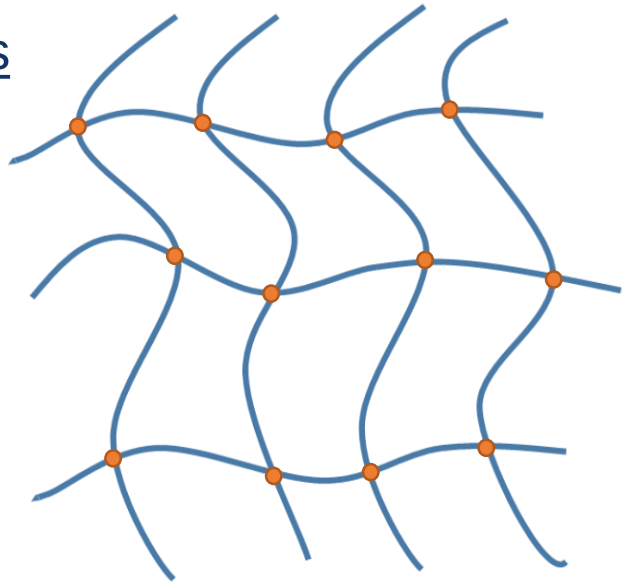
Double Dynamic Networks

- Network/gel: cross-linked polymer chains

<u>Permanent cross-links</u>

- creep resistance
- enhanced mechanical strength
- no coherence loss

- no processing
- no recycling



<u>Non-permanent cross-links</u>

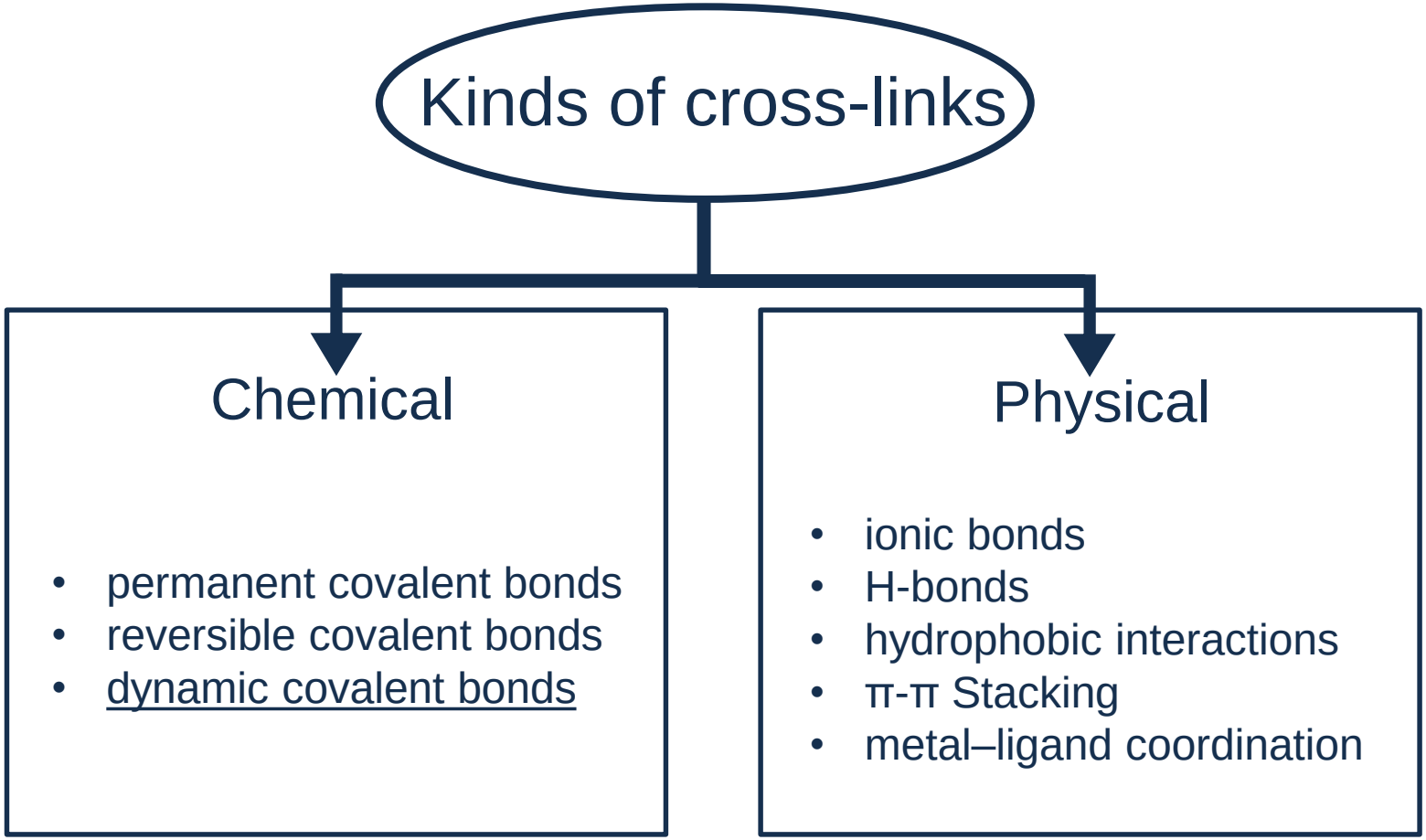
- easily processable
- recyclable

- creep
- limited mechanical properties

→ Combine the best of both

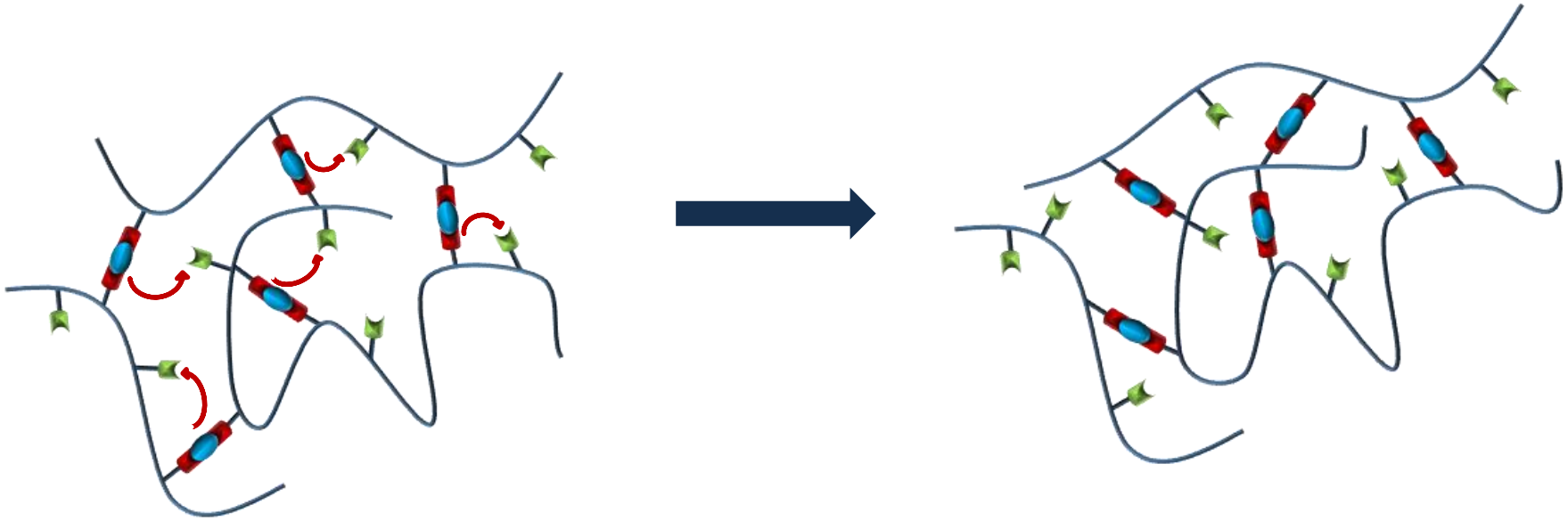
Double Dynamic Networks

- Combination of at least two distinct dynamic modes
- ‘Double’ mechanical behaviour



Double Dynamic Networks

- Employ dynamic ‘vitrimeric’ bonds in network



Vitrimeric bonds:

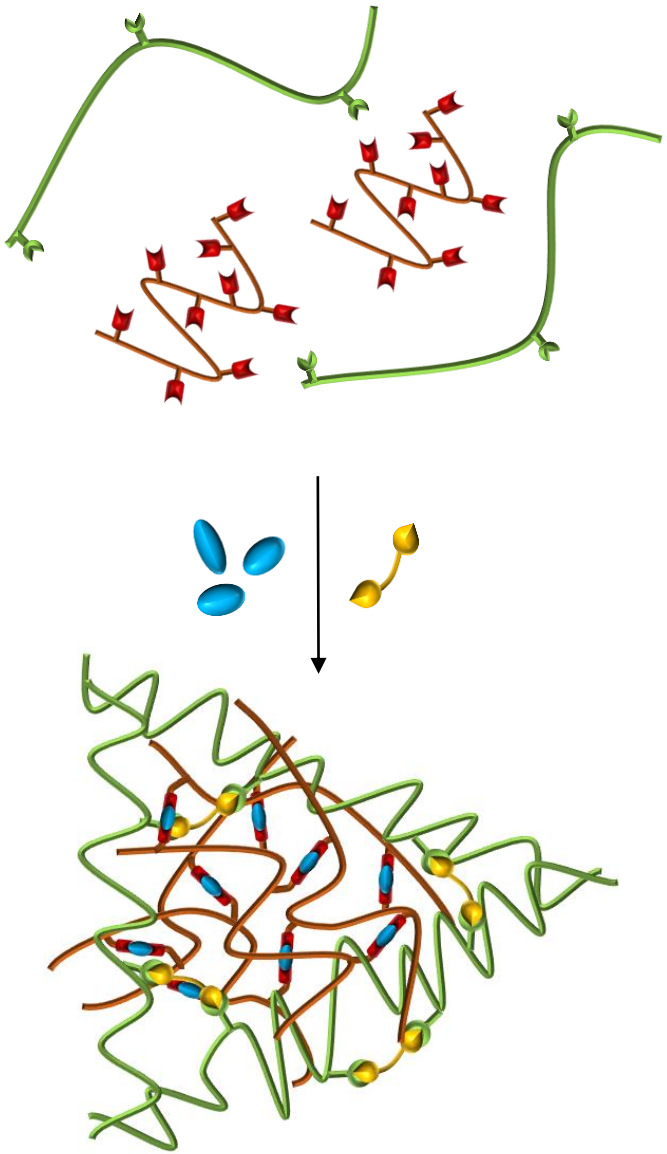
- Associative mechanism
- New linking point involved in reaction
- No bond breaking
- Same amount of cross-links

Material:

- Self-healing
- Malleable
- Reprocessable
- Maintains network integrity
- Tough

Project Goal

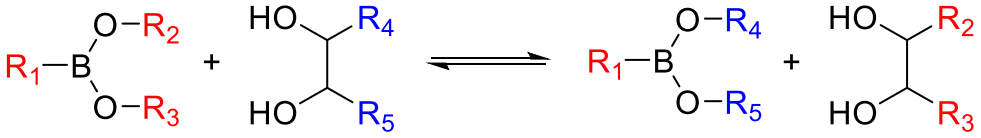
- Goal: create a elastomer Double Network based on dynamic covalent bonds
- Creating two interpenetrating network structures
  - Creating thermoplastics with functional groups
  - Orthogonal cross-linking
- Two independent modes



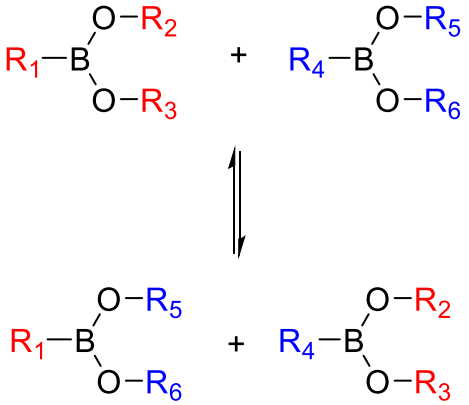
System Network 1

- ‘Vitrimer Network’
- Boronic ester exchange
- Works at rt/ in bulk

Boronic ester / diol exchange:



Boronic ester exchange:

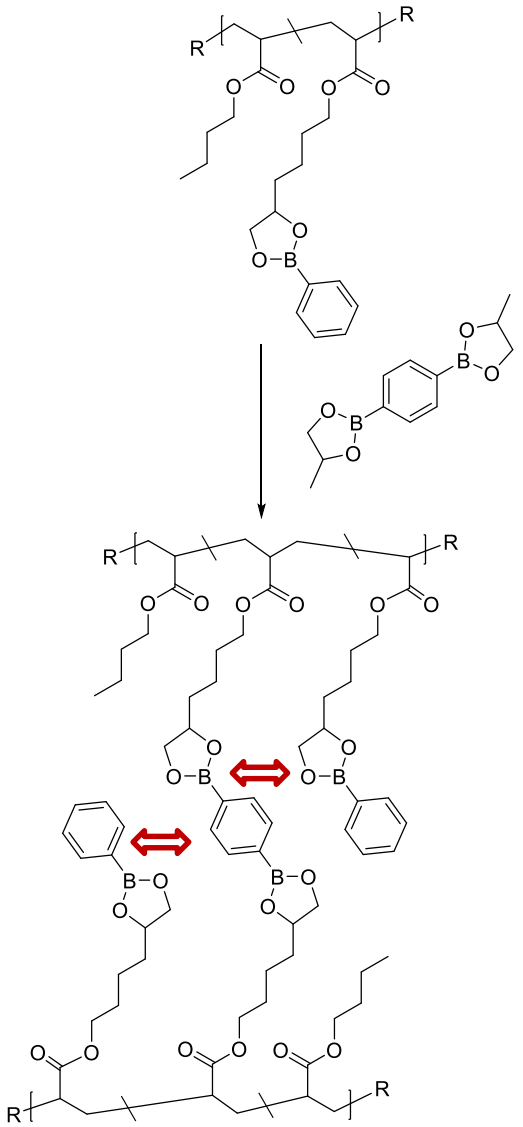


Exchange accelerates in presence of diols or moisture

System Network 1

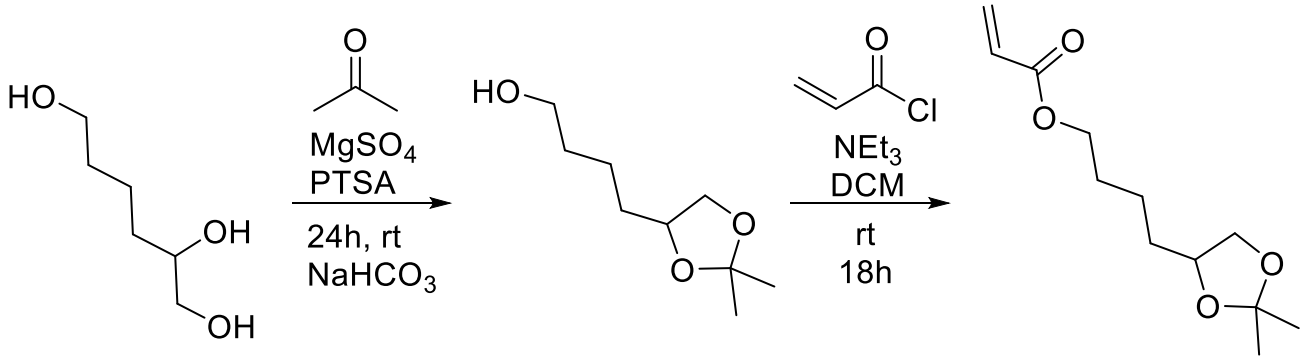
- Butyl acrylate system (low T_g)
- High density of cross links
  - DP 1000 (~100 000 Da) or lower
  - 10% functionality
- Diol-based polymer protected with boronic acid
- Cross-linking via di-boronic ester

- Rapid exchange
- Active at RT

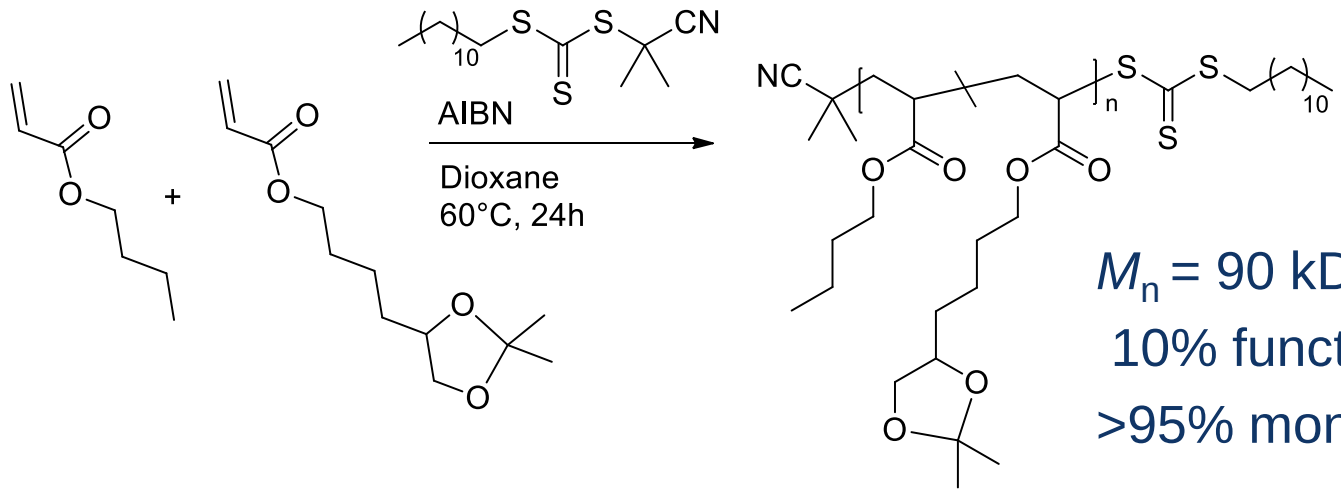


Copolymer Synthesis

- Monomer synthesis for diol monomer



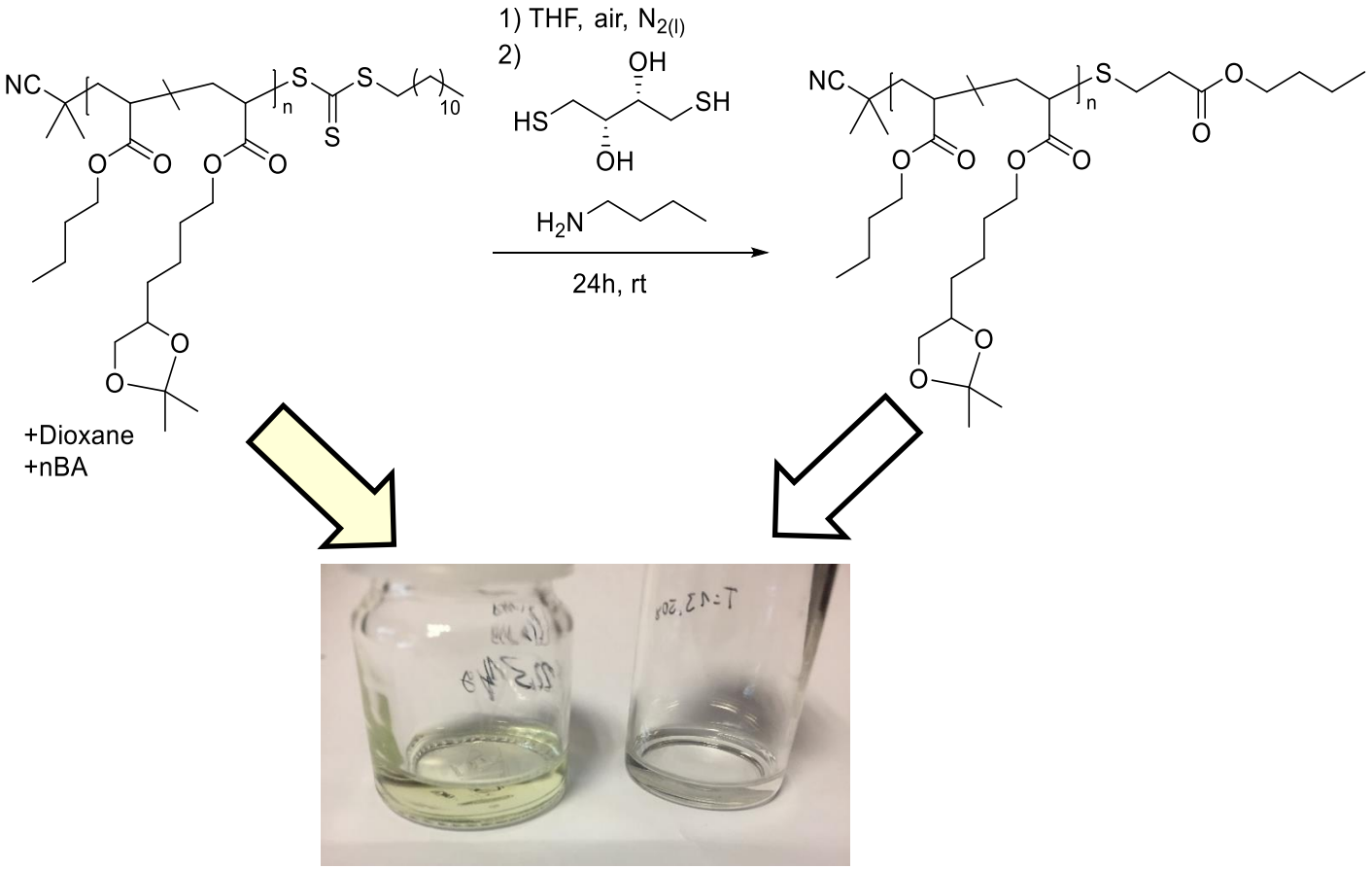
- Employment in RAFT polymerization



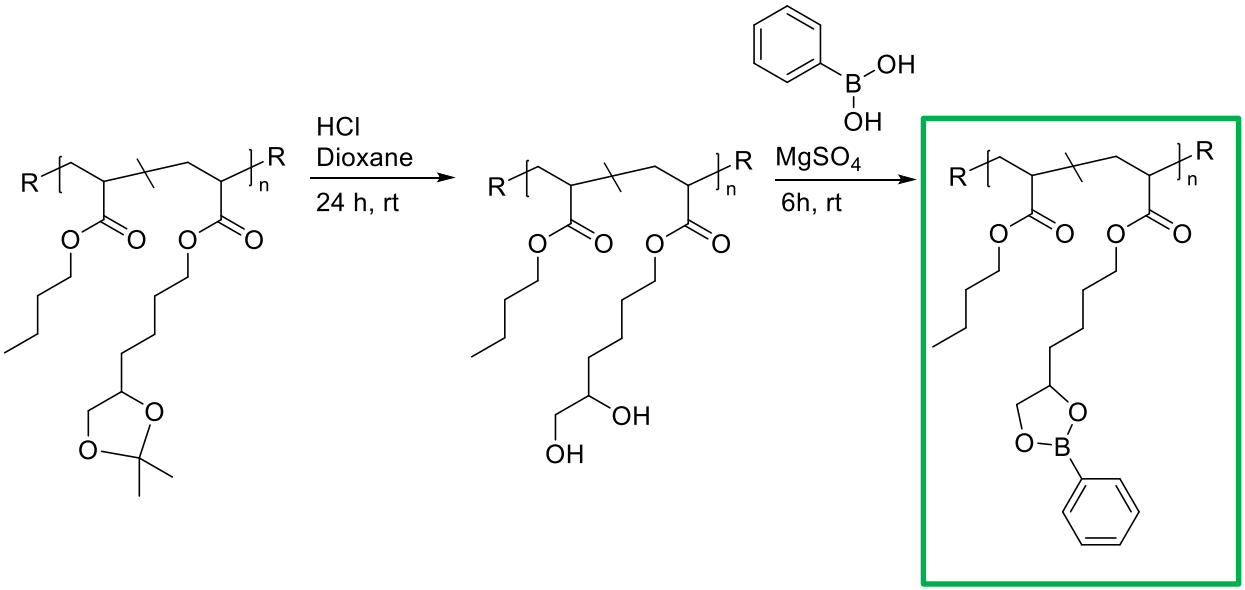
M_n = 90 kDa; $Đ$ = 1.25,
10% functionality,
>95% monomer conv.

RAFT Group Removal

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



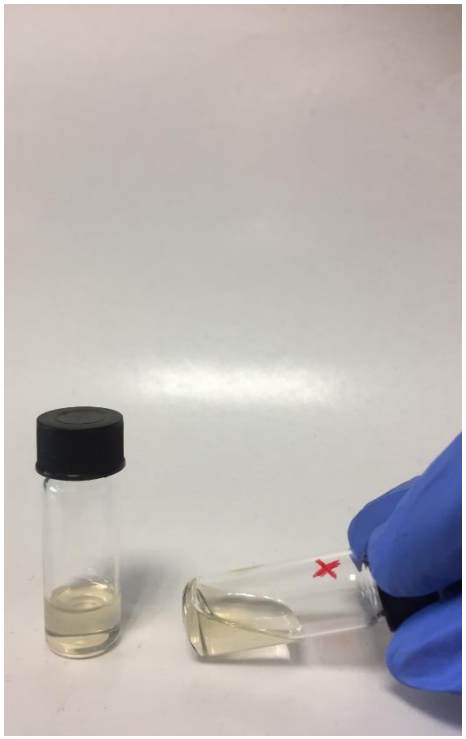
Deprotection and Reprotection

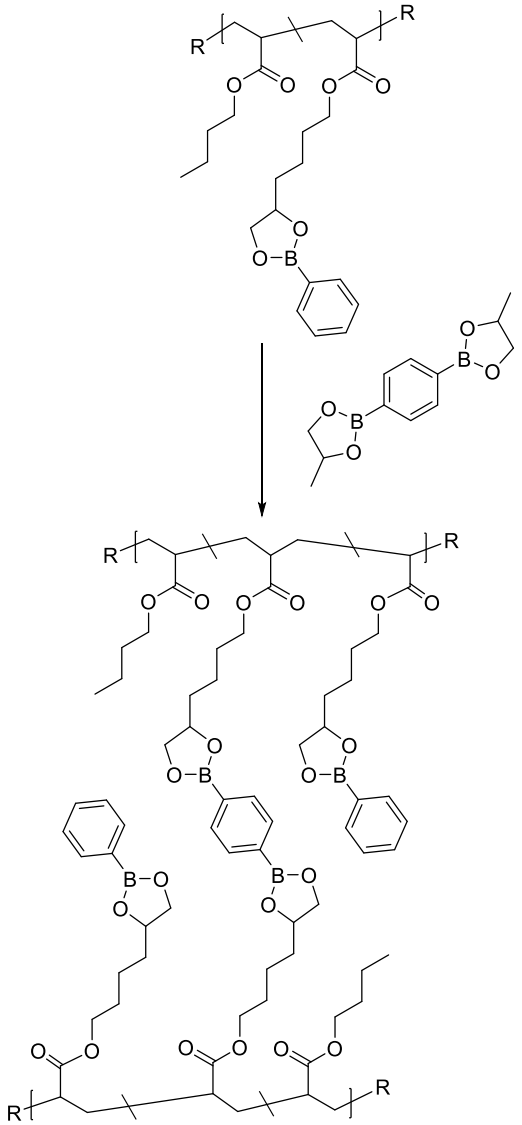


- Thermoplastic precursor for Network 1

Cross-linking Test

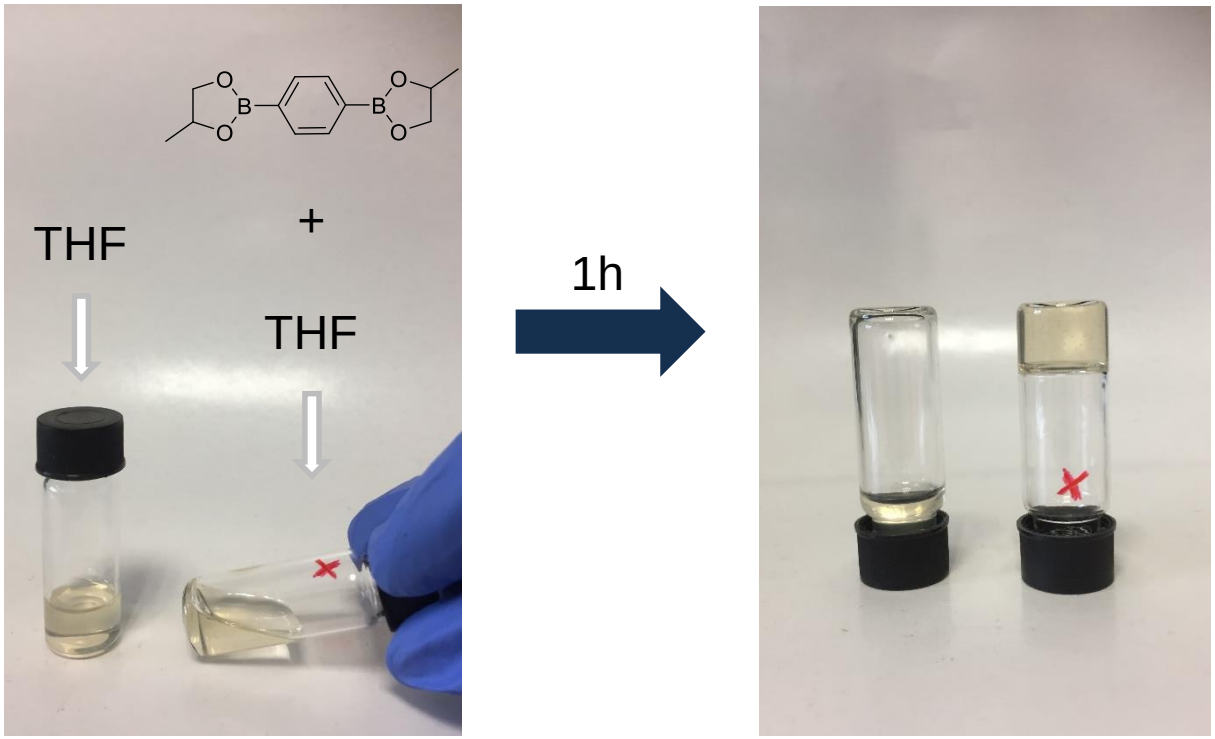
- Solution of precursor in THF

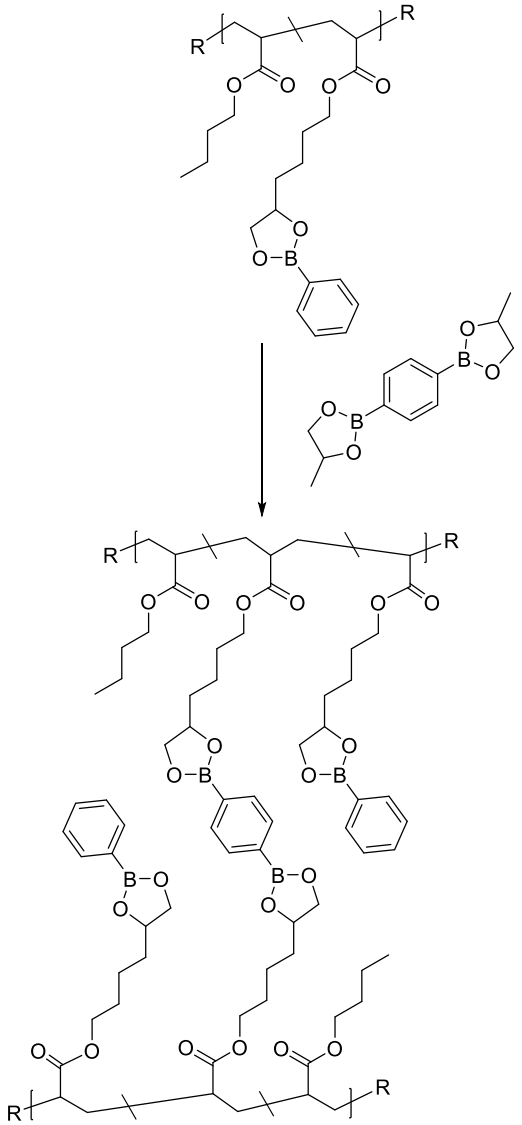




Cross-linking Test

- Solution of precursor in THF





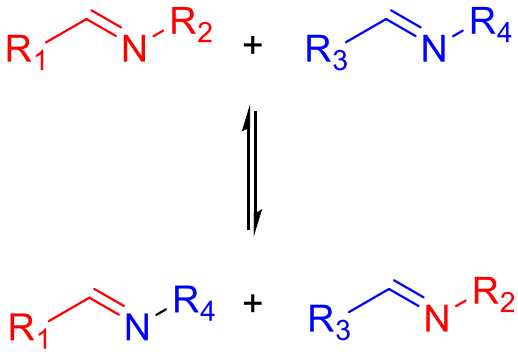
System Network 2

- Second dynamic mode

Imine / aldehyde exchange:

- ‘Vitrimer Network’
- Imine exchange
- Imine = Amine + Aldehyde
- Slower than boronic ester exchange

Imine exchange:

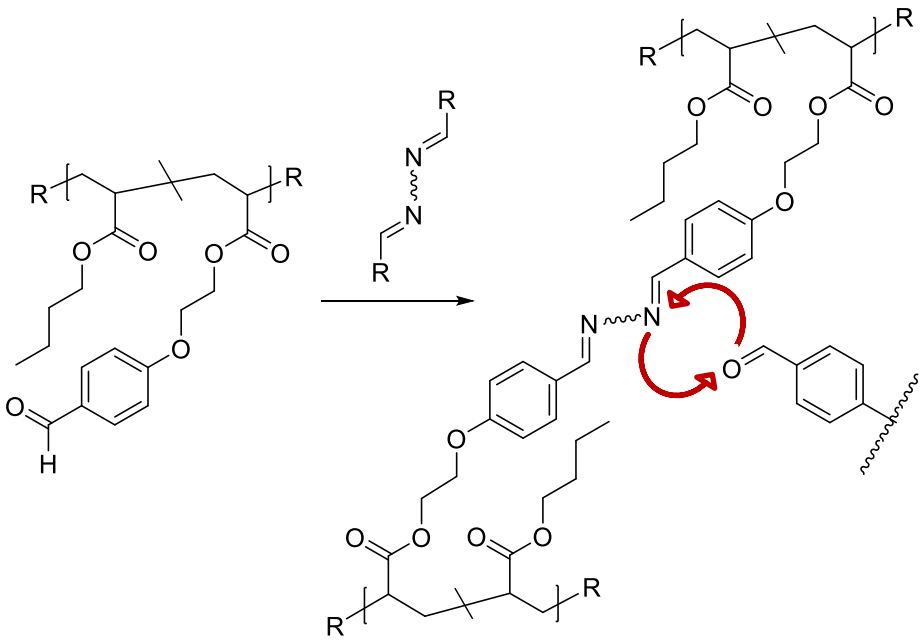


Exchange accelerates in presence of aldehydes

System Network 2

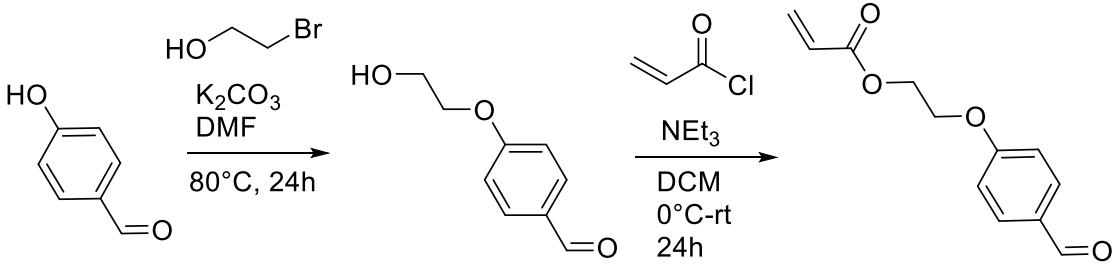
- Aldehyde functional polymer
- Cross-linking with diimine

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

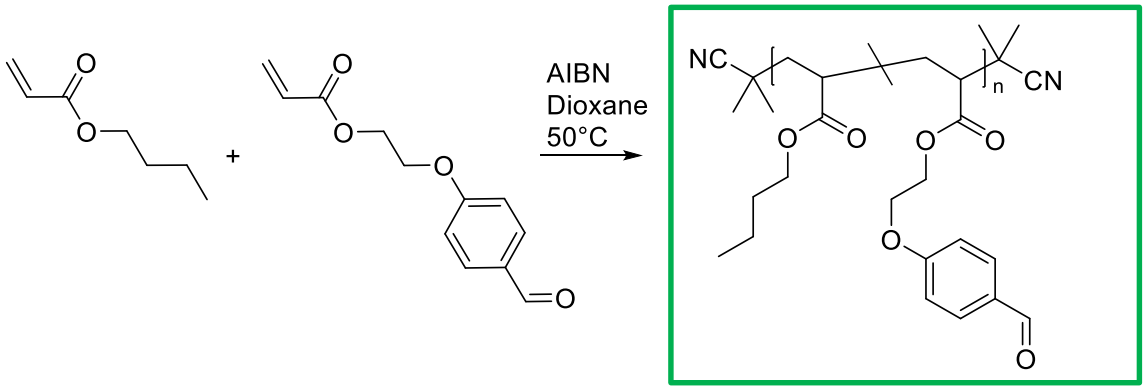


Copolymer Synthesis

- Two step synthesis



- Employment in free radical polymerization (FRP)



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

- Thermoplastic precursor for Network 2

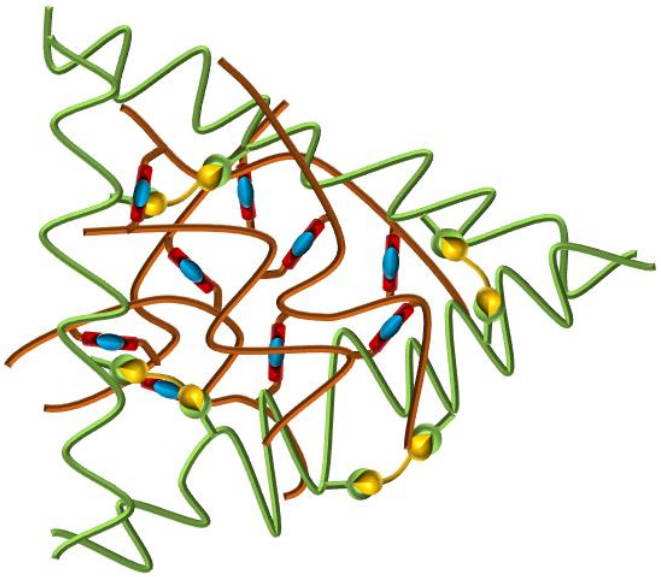
Outlook

- Verify cross-linking reactions by
  - IR spectroscopy
  - Swelling tests
  - Rheometry
- Combine both precursors
- Create Double Network
- Testing

- Use know-how to create new Double Networks
- Single Networks
- Connected Double Networks
- Integrate permanent bonds

Projects

Double Networks



Thermoplastic Elastomers

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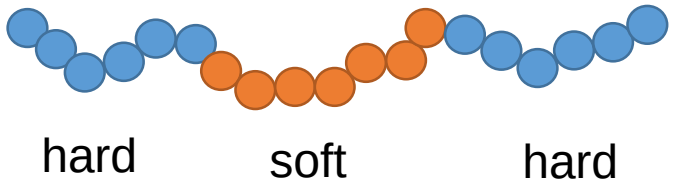
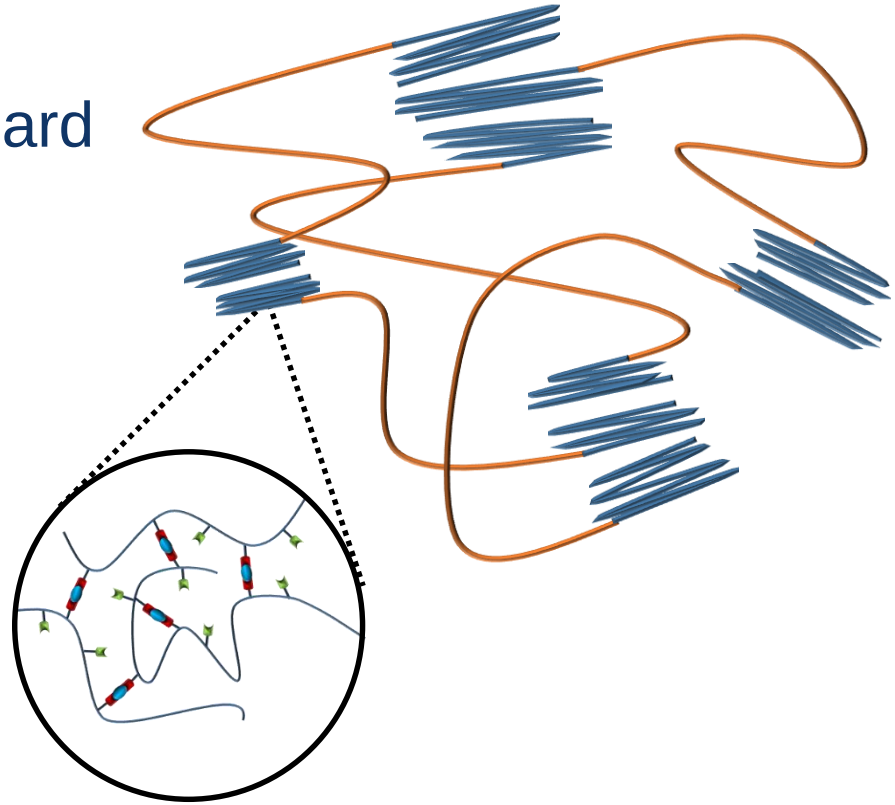
Project Goals

- Thermoplastic Elastomer
- A-B-A triblock co-polymer
- Hard-soft-hard phase
- Microphase separation
  - ➢ One dynamic below T_g of hard phase

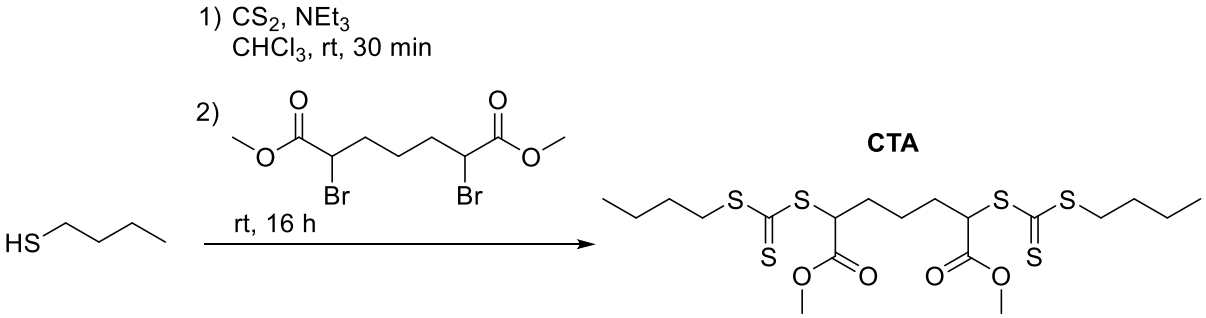




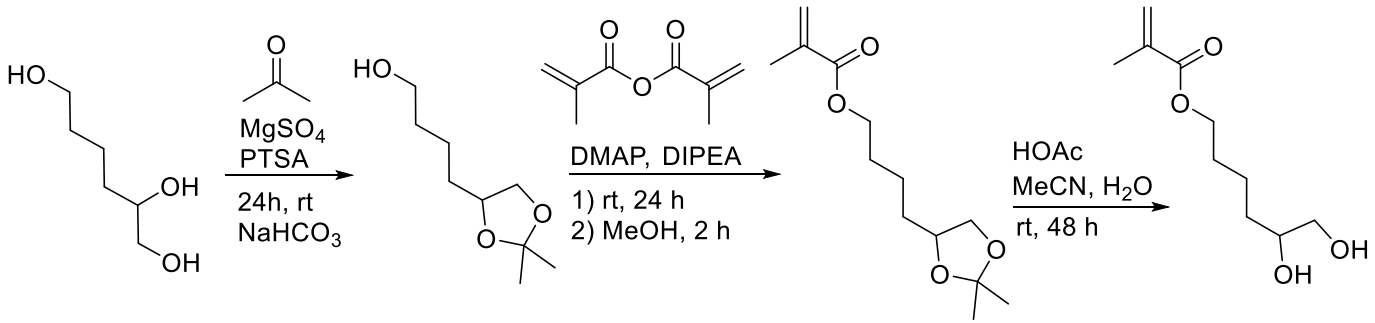
- Decorate hard phase with dynamic covalent bonds
  - ➢ Second dynamic mode
  - ➢ Retain structure above T_g

Synthesis of A-B-A Block Co-polymers

- Requires double functional symmetric CTA for RAFT polymerization

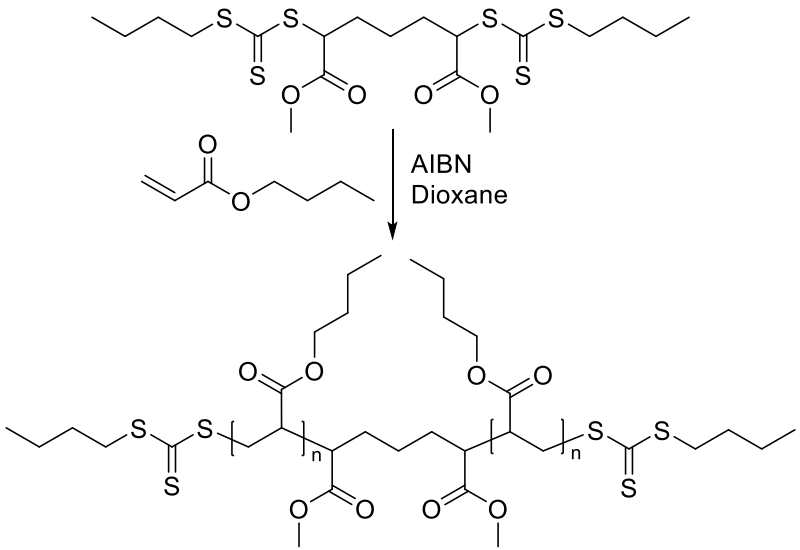


- Diol functional monomer for hard phase (MMA)



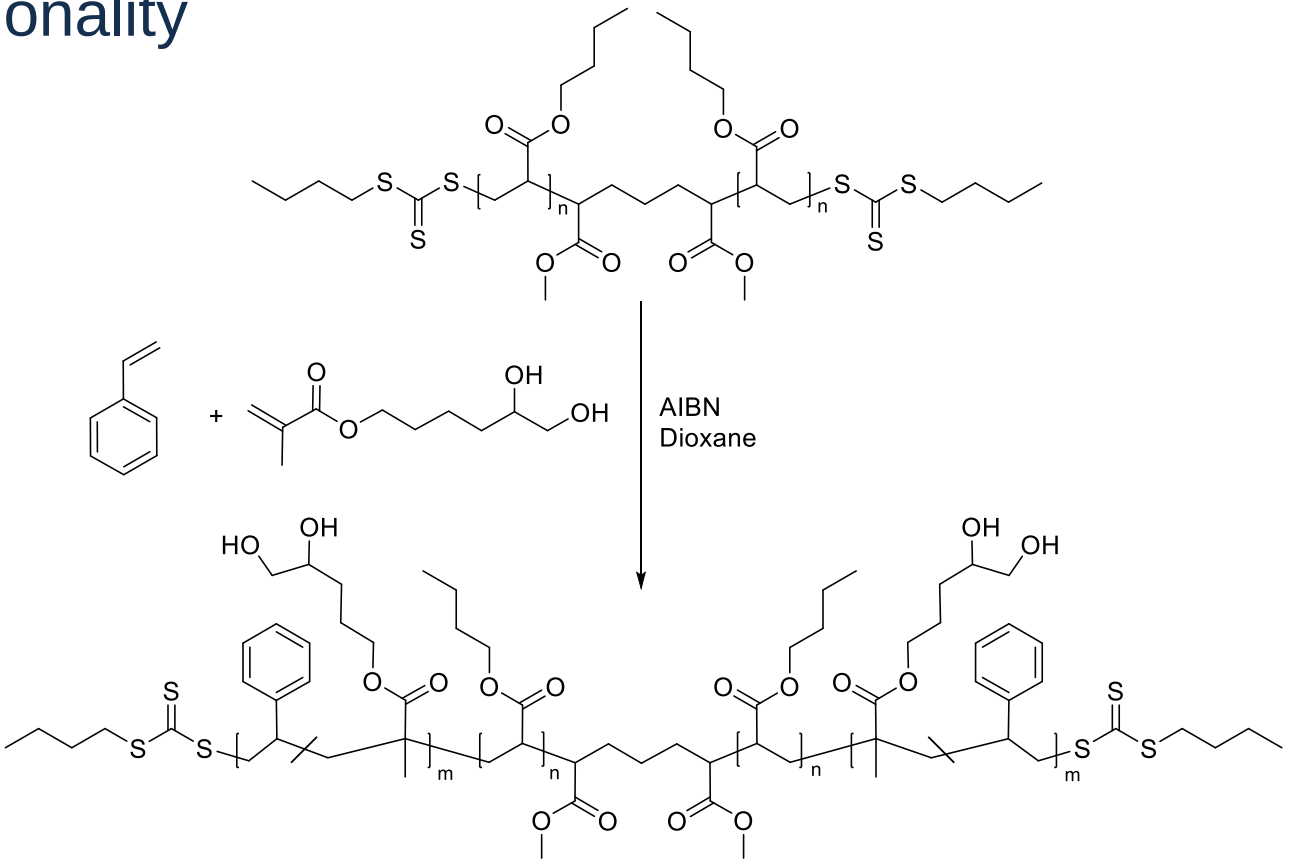
Synthesis of A-B-A Block Co-Polymer

- Polymerization soft block
- Approx. 100 kDa, narrow PDI
- Kinetic studies



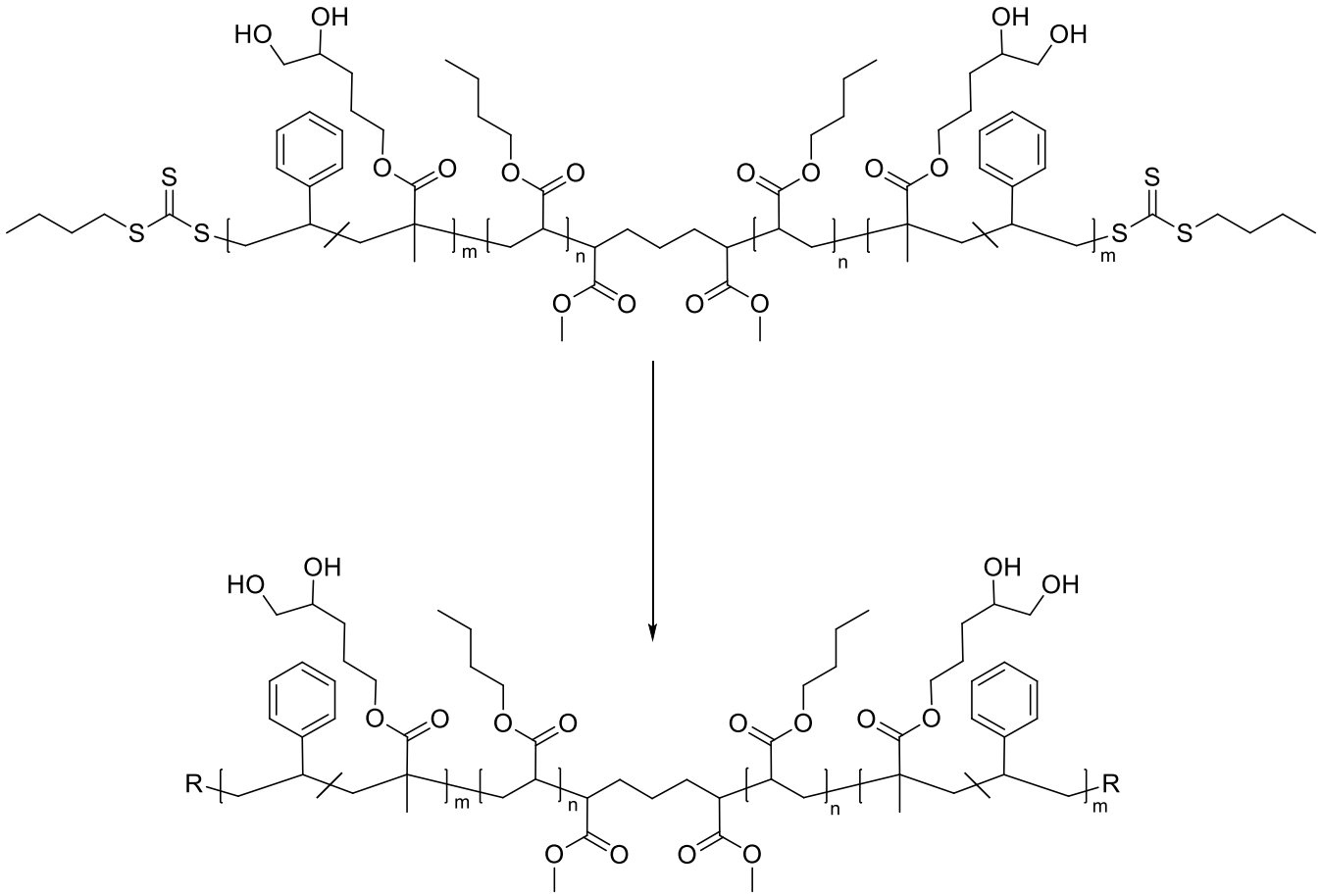
Synthesis of A-B-A Block Co-Polymer

- Polymerization hard block
- 10% functionality



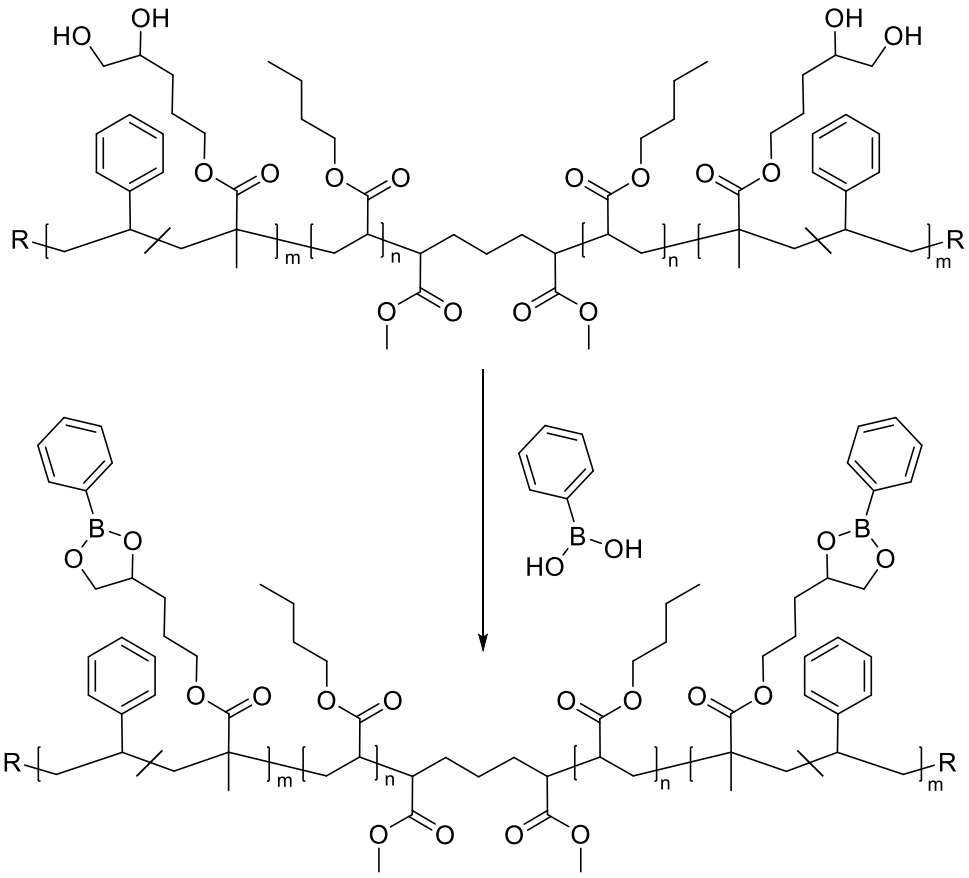
Synthesis of A-B-A Block Co-Polymer

- RAFT group removal



Synthesis of A-B-A Block Co-Polymer

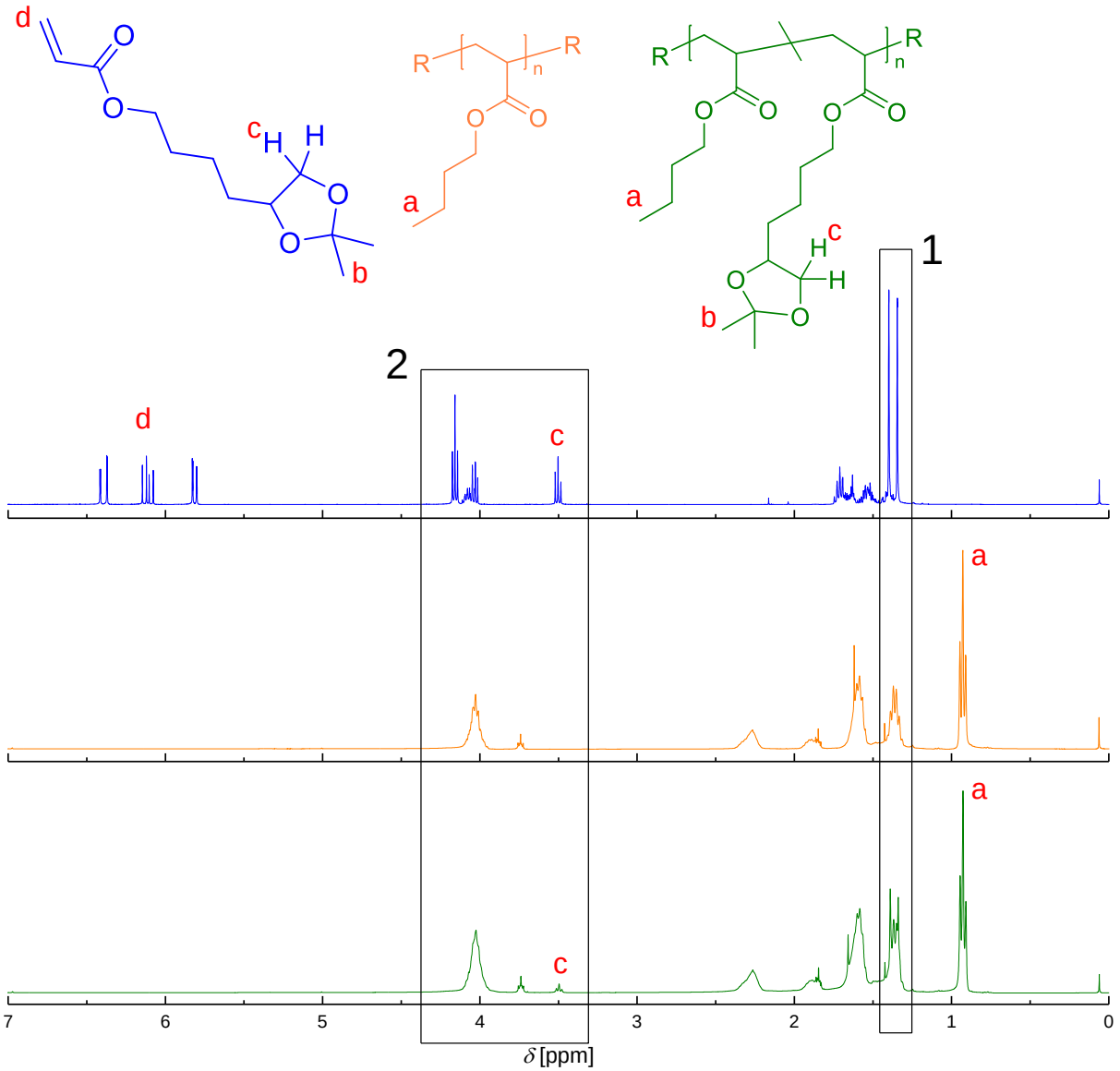
- Protection with phenylboronic acid



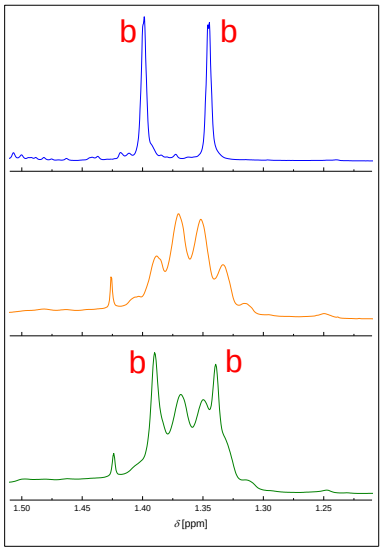
Thank you for your attention!

This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 765811.

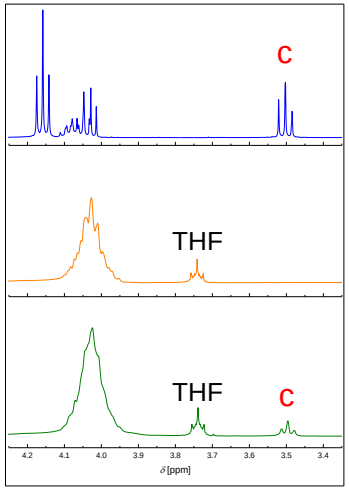
Appendix

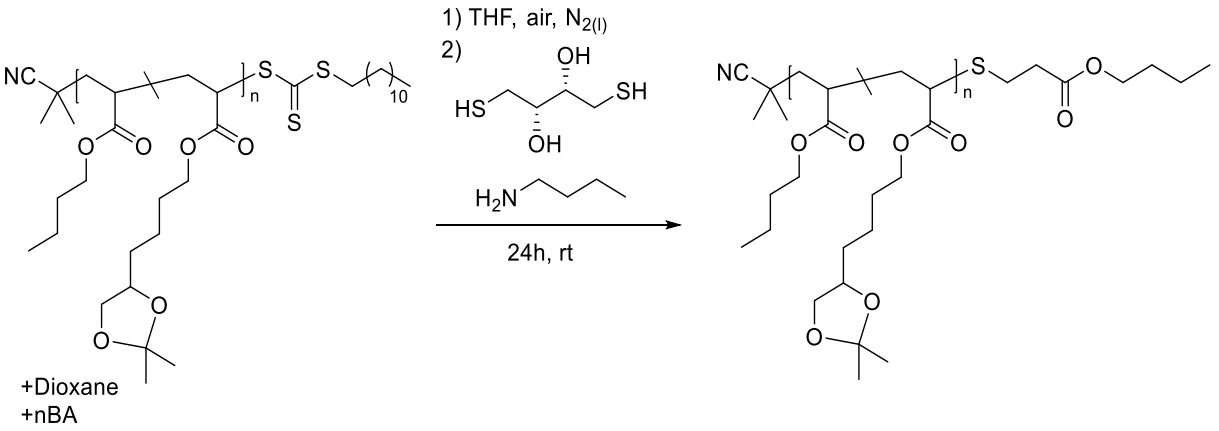

d
c
H
H
O
O
O
b
R
n
R
O
O
a
R
n
R
O
O
O
O
a
H
c
H
O
O
b
1
2
d
c
a
a
c
7
6
5
4
3
2
1
0
δ [ppm]

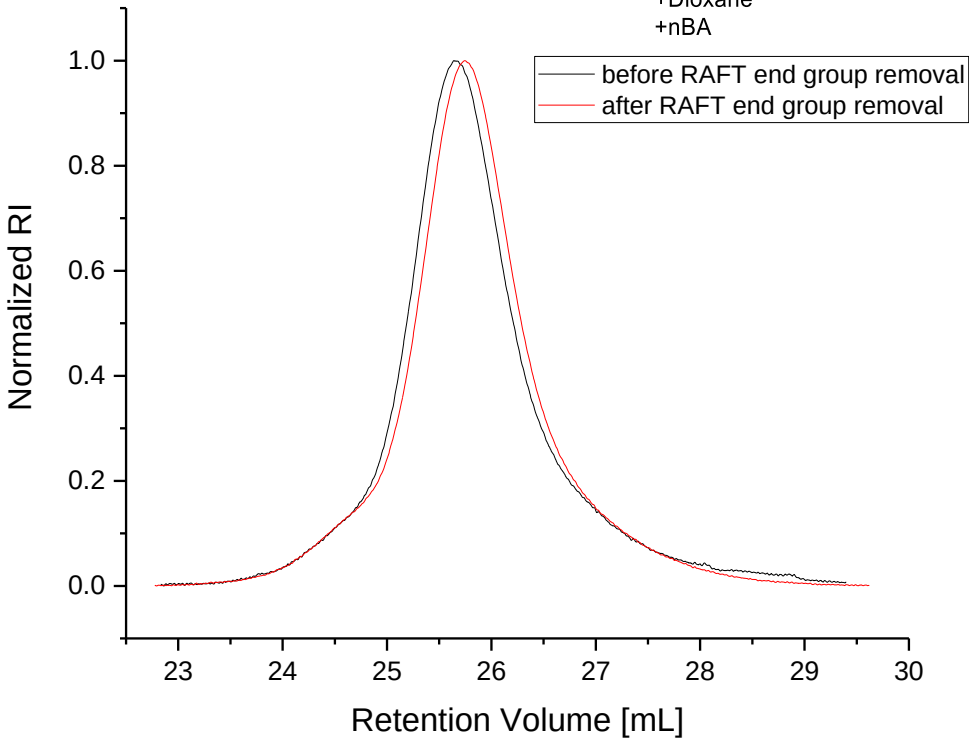
1

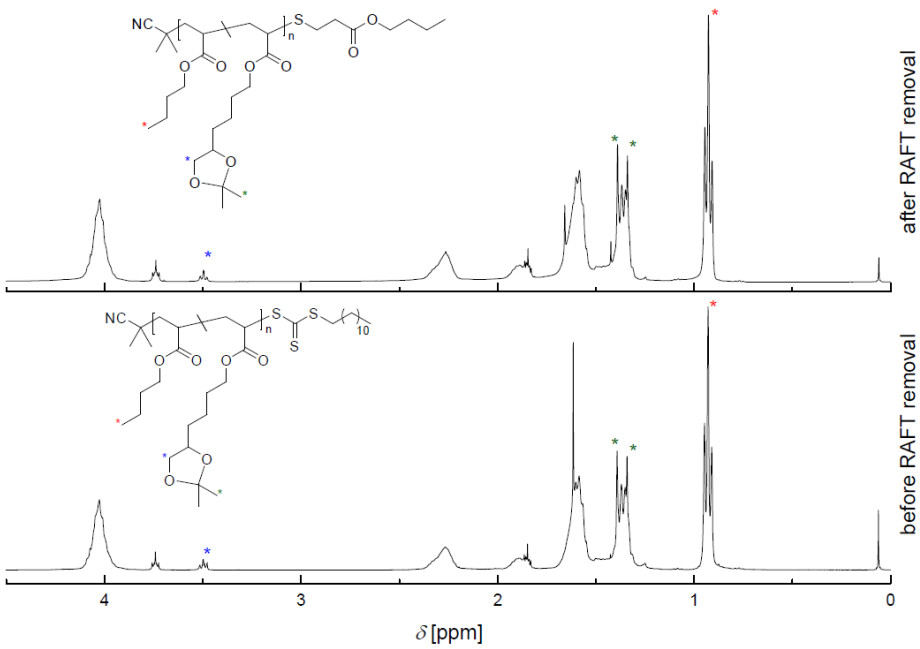

b
b
b
b
1.50
1.45
1.40
1.35
1.30
1.25
δ [ppm]

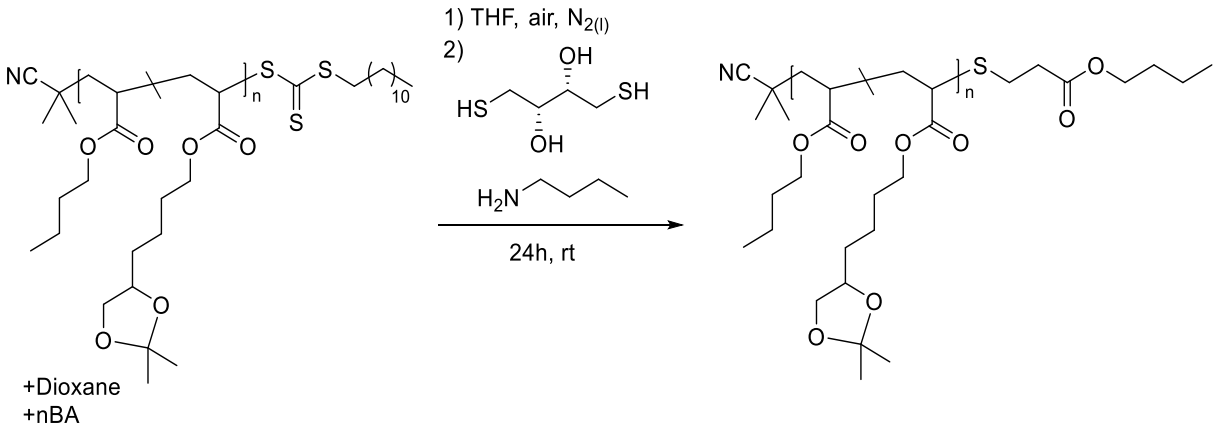
2

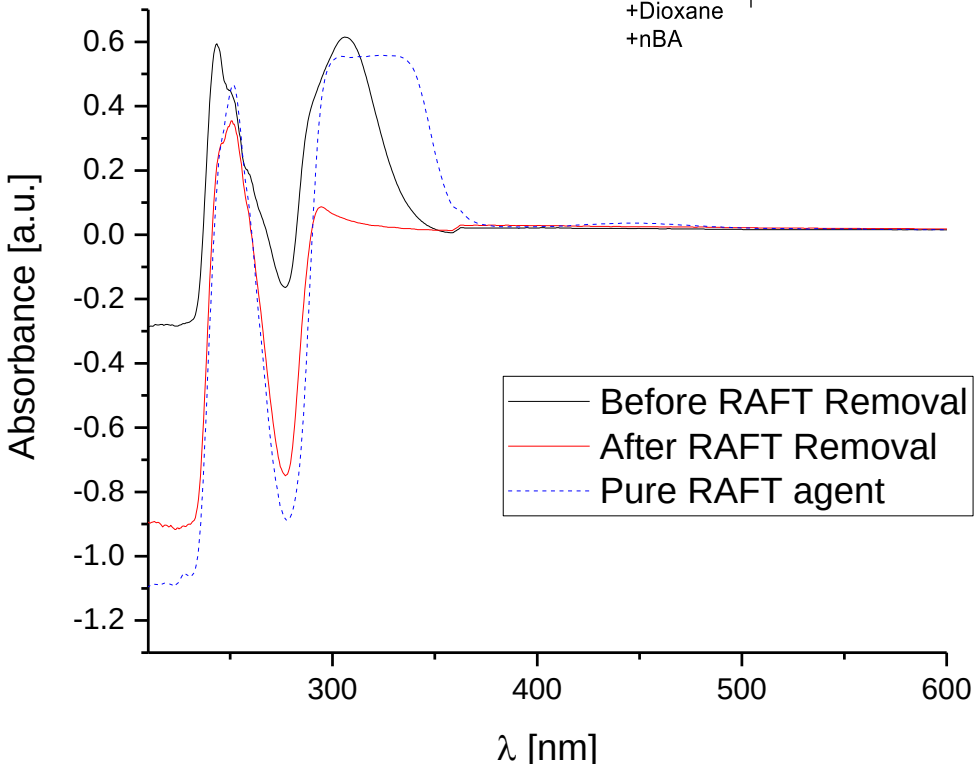

c
THF
THF
c
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
δ [ppm]

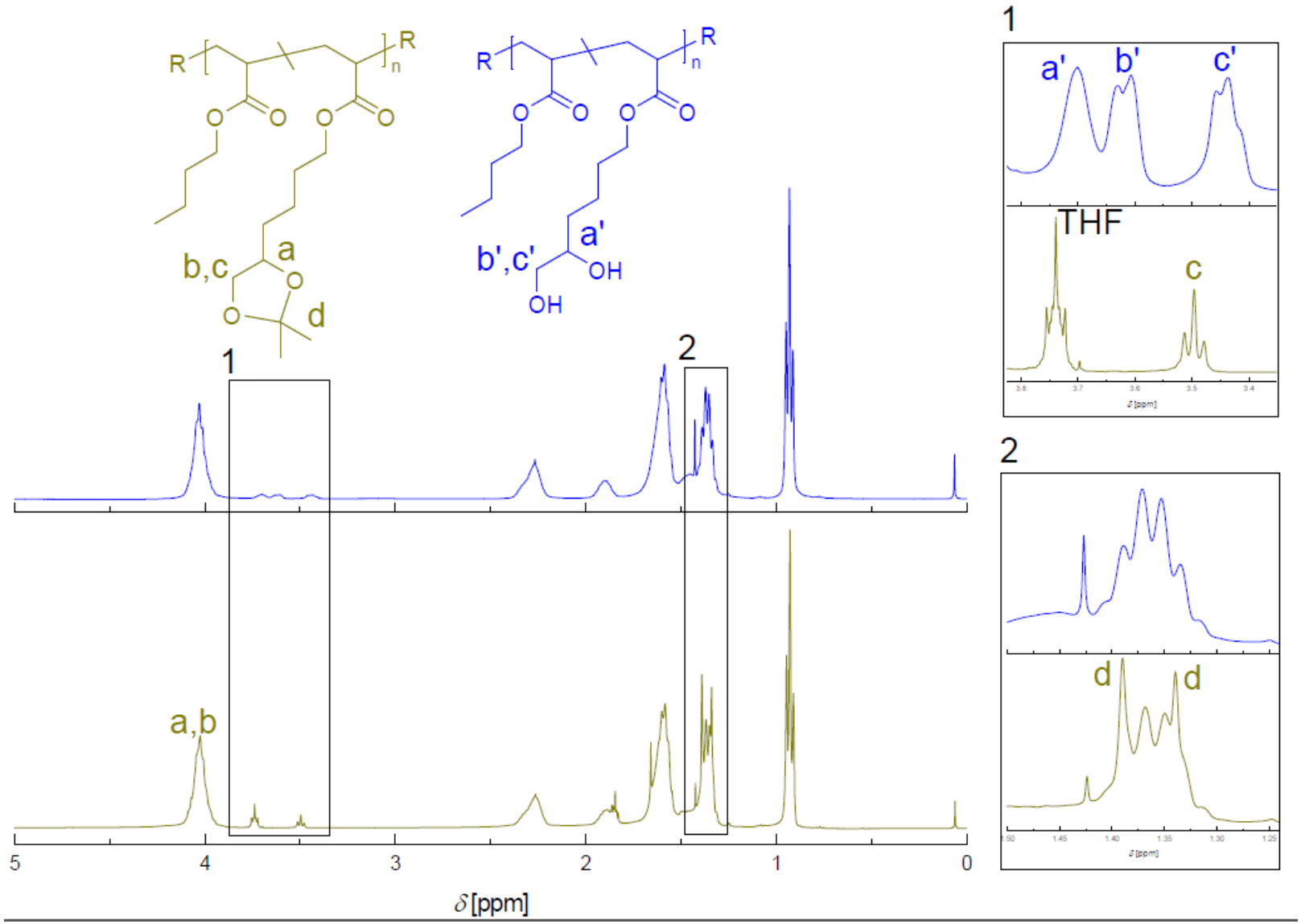

1) THF, air, $N_{2(l)}$
2)
OH
HS
SH
OH
H_2N
24h, rt
NC
S
n
S
S
10
O
O
O
O
O
O
+Dioxane
+nBA

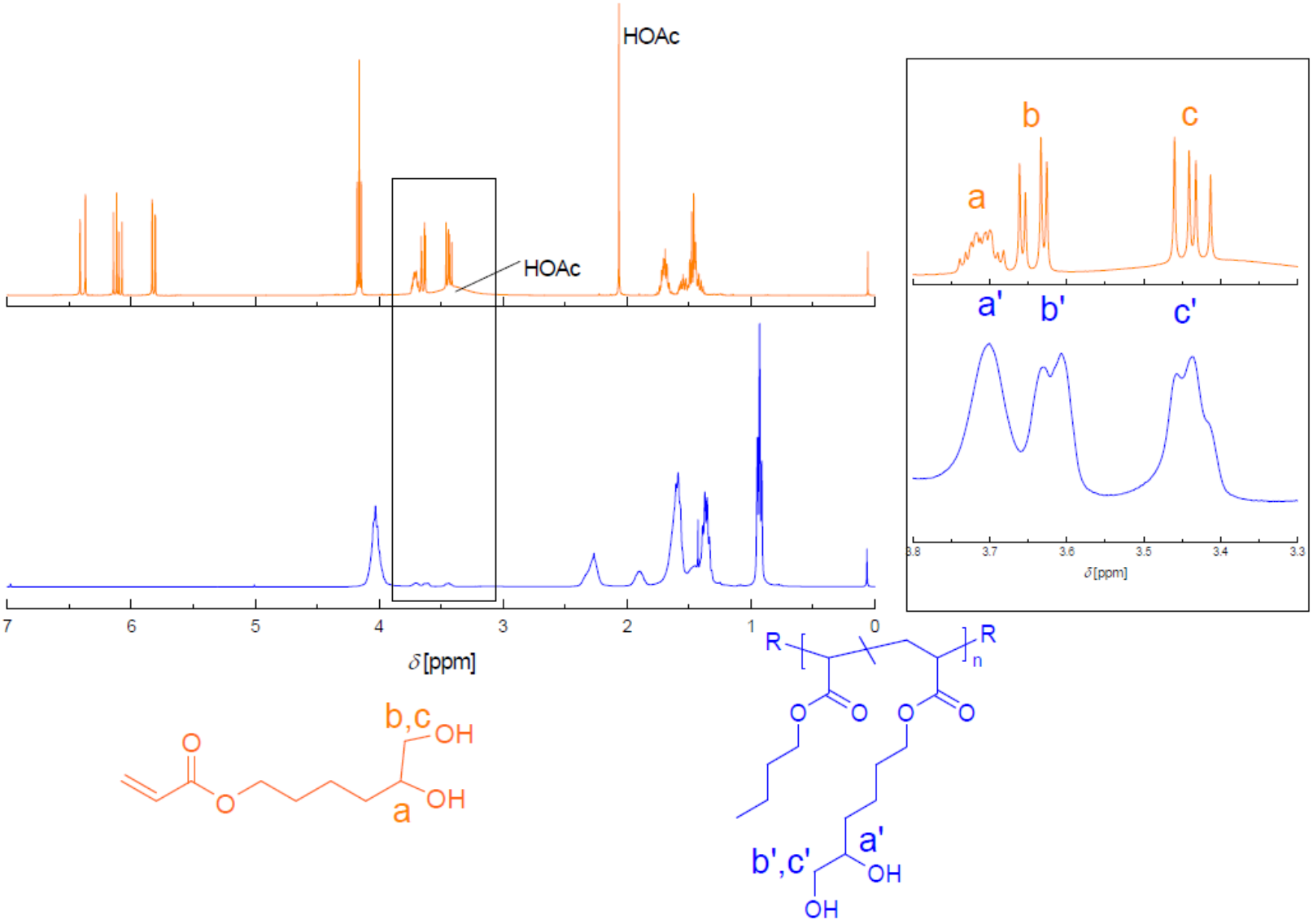

before RAFT end group removal
after RAFT end group removal
Normalized RI
1.0
0.8
0.6
0.4
0.2
0.0
23
24
25
26
27
28
29
30
Retention Volume [mL]

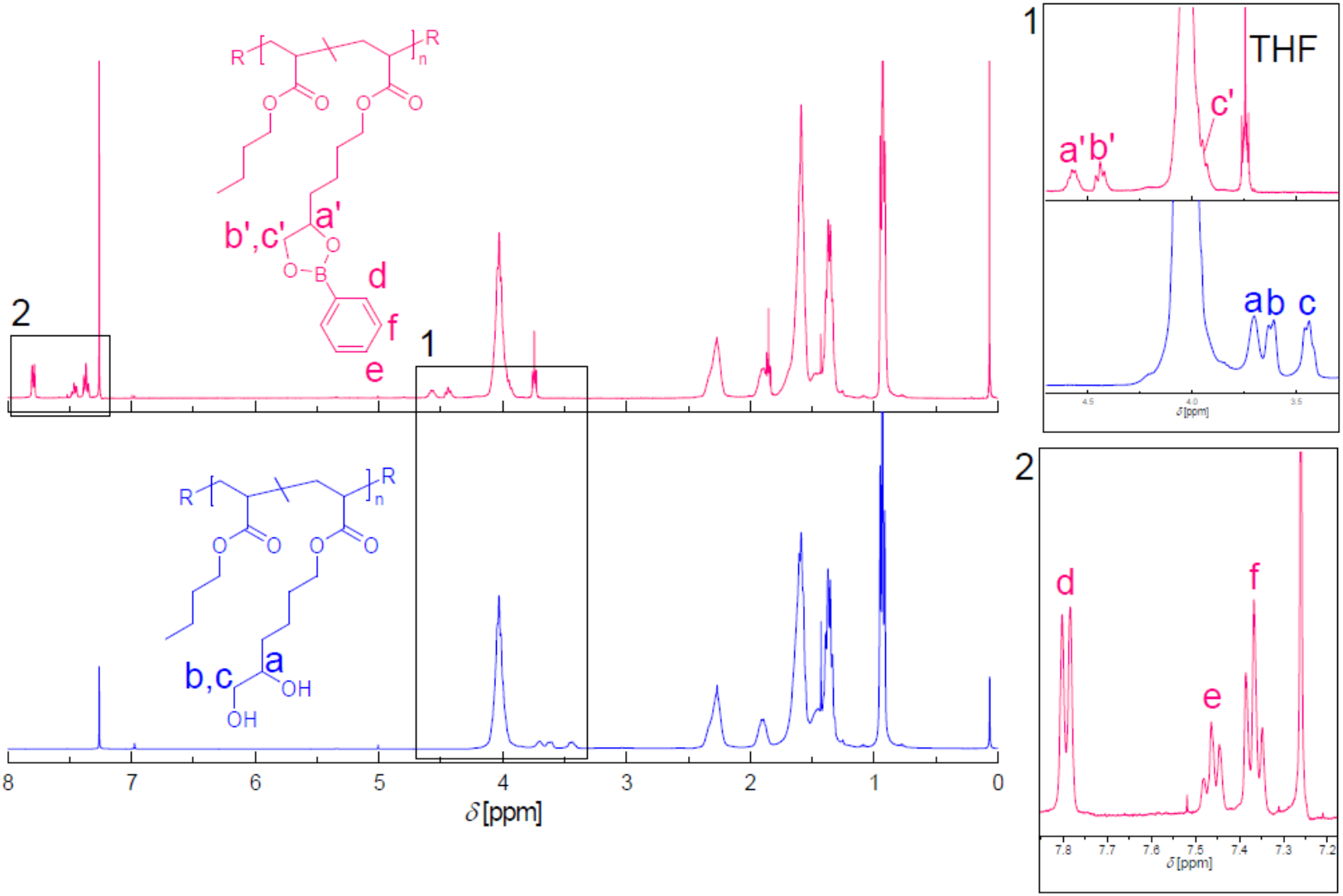

after RAFT removal
before RAFT removal
4
3
2
1
0
δ [ppm]

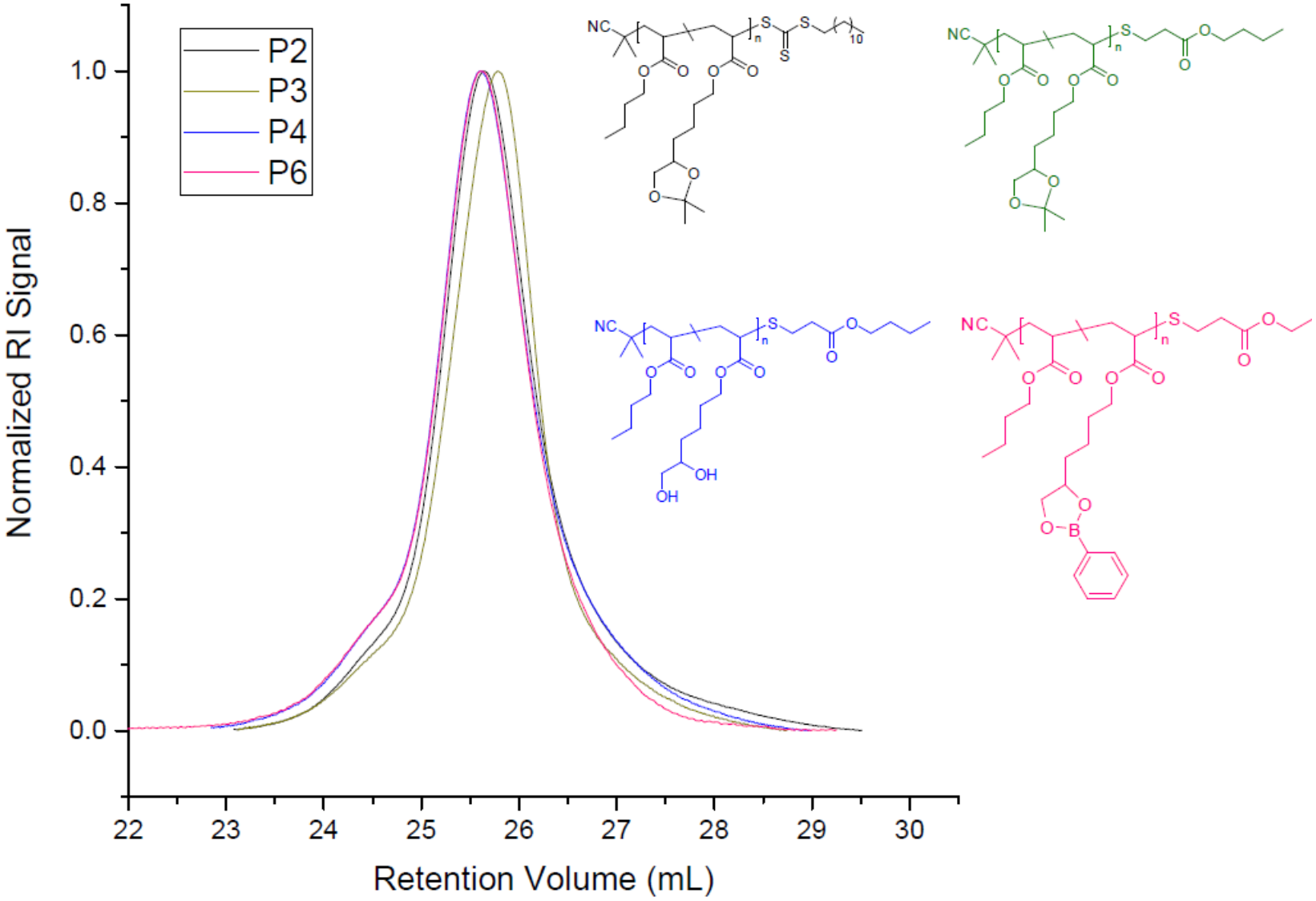

1) THF, air, $N_{2(l)}$
2)
NC
S
S
S
n
10
O
O
O
O
HS
SH
OH
OH
H_2N
24h, rt
+Dioxane
+nBA

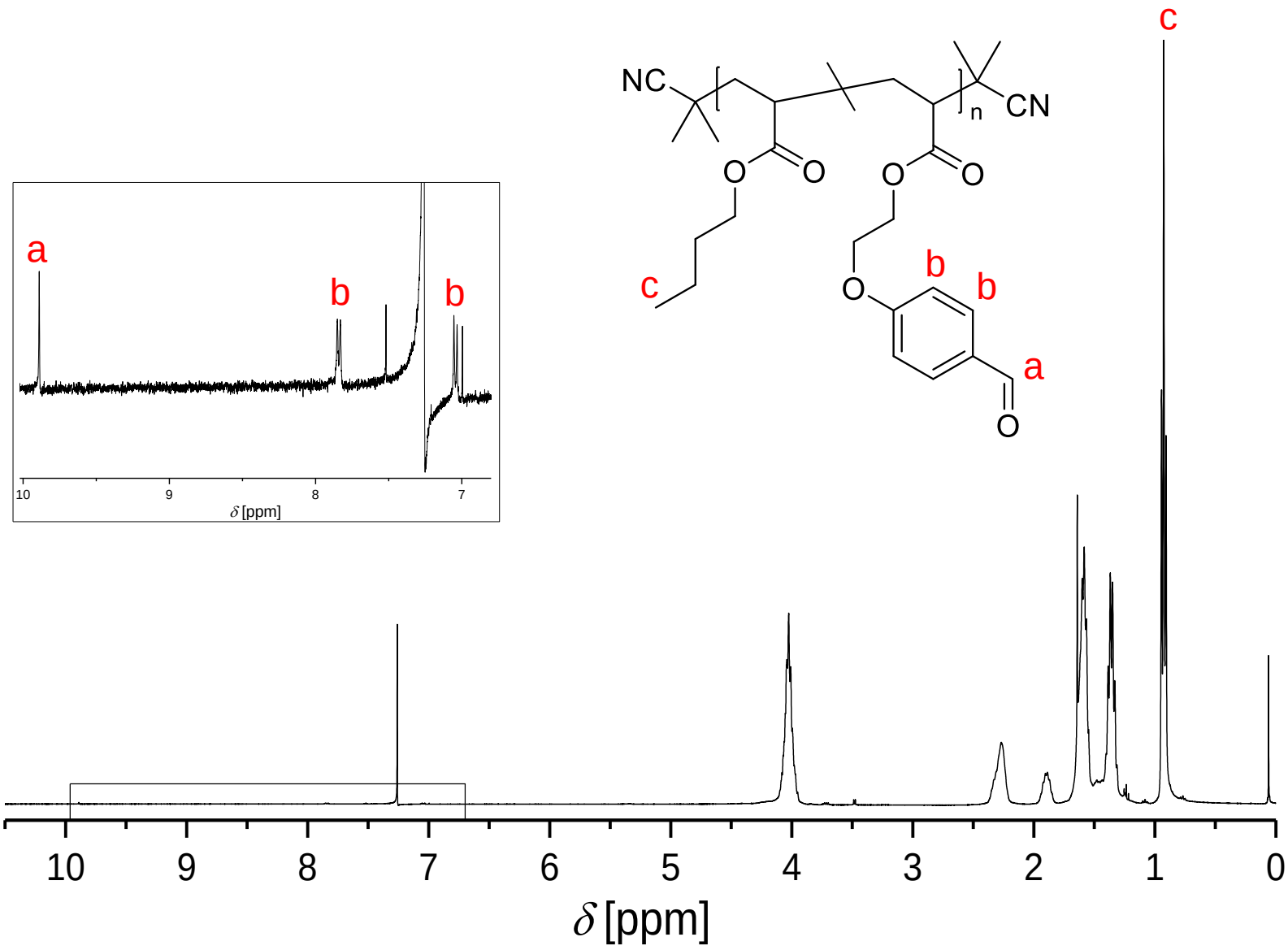

Absorbance [a.u.]
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
300
400
500
600
λ [nm]
Before RAFT Removal
After RAFT Removal
Pure RAFT agent


R
n
b,c
a
d
b',c'
a'
OH
OH
1
2
a,b
5
4
3
2
1
0
δ [ppm]
1
a'
b'
c'
THF
c
2
d
d


HOAc
HOAc
7
6
5
4
3
2
1
0
δ[ppm]
a
b
c
a'
b'
c'
3.8
3.7
3.6
3.5
3.4
3.3
δ[ppm]
b,c
OH
O
O
OH
a
R
R
n
O
O
O
O
b',c'
a'
OH
OH


2
1
b',c'
a'
d
f
e
b,c
a
OH
OH
8
7
6
5
4
3
2
1
0
δ[ppm]
1
THF
a'b'
c'
ab c
δ[ppm]
2
d
e
f
δ[ppm]


P2
P3
P4
P6
Normalized RI Signal
1.0
0.8
0.6
0.4
0.2
0.0
22
23
24
25
26
27
28
29
30
Retention Volume (mL)
NC
S
S
10
O
OH
B


c
NC
n
CN
O
O
O
O
c
b
b
O
a
O
a
b
b
10
9
8
7
δ [ppm]
10
9
8
7
6
5
4
3
2
1
0
δ [ppm]