UCLouvain

Institute of Condensed Matter and Nanosciences

MARIE CURIE ACTIONS

INITIAL TRAINING NETWORK

Synthesis and dynamics of double networks based on slide-ring materials

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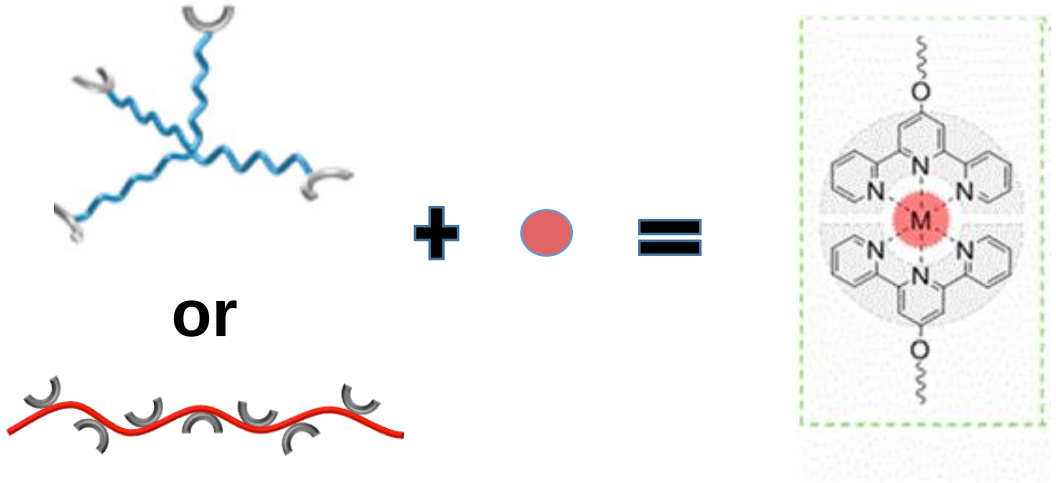
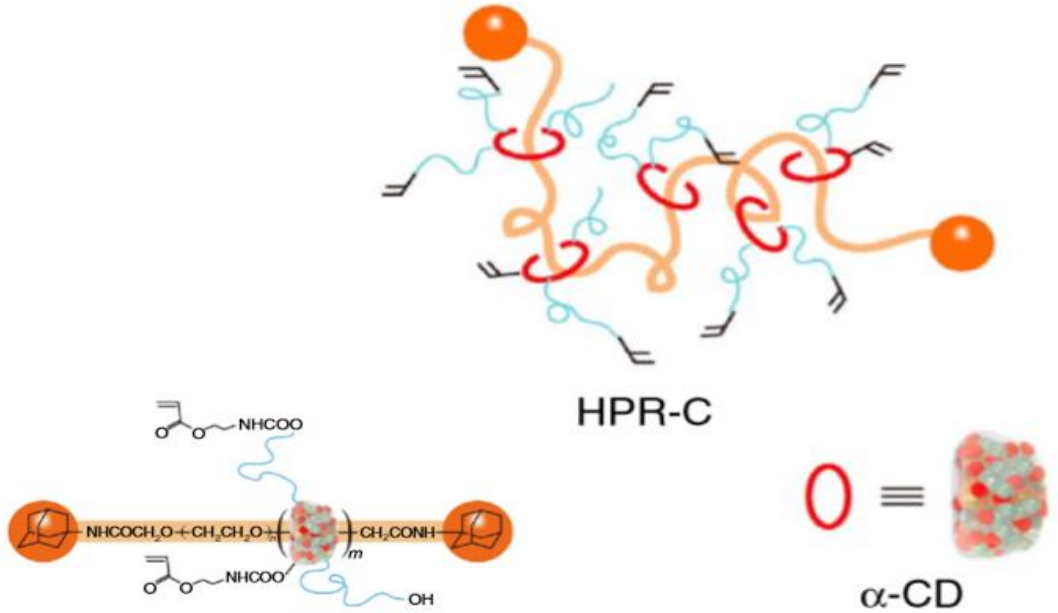
Synthesis of slide ring DDN



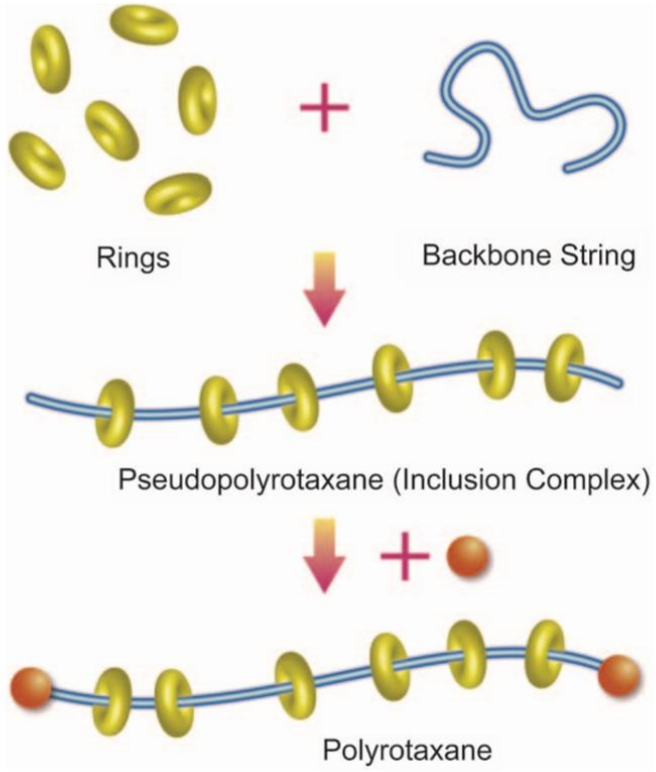
First network - Metal-terpyridine links



Second network - Slide ring crosslinks

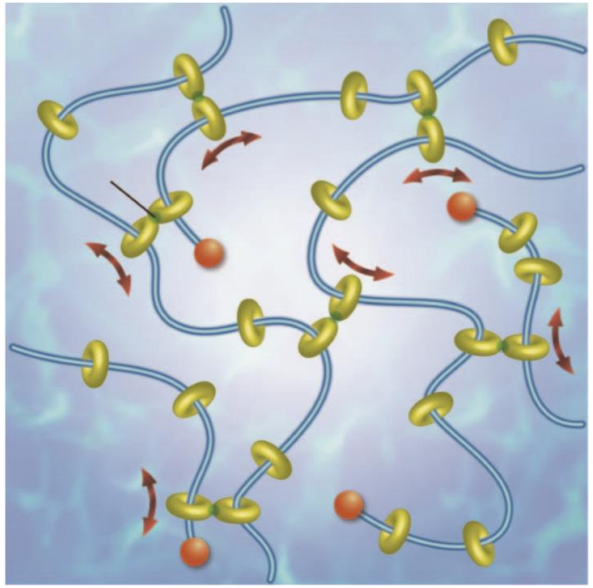
Macromolecules 2017, 50, 5165−5175
Nature Communications volume 5, Article number: 5124 (2014)

Slide Ring Gels



Crosslinker

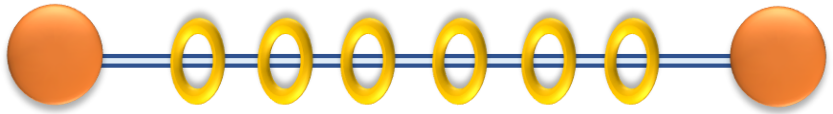
Mechanical interlocking of cyclodextrin to form movable “figure-of-eight” rings



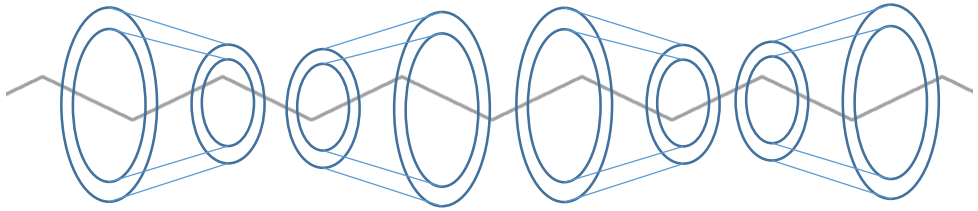
Coverage

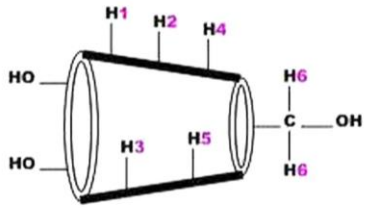
- Coverage = How densely packed the main polymer chain is

Low coverage



High coverage



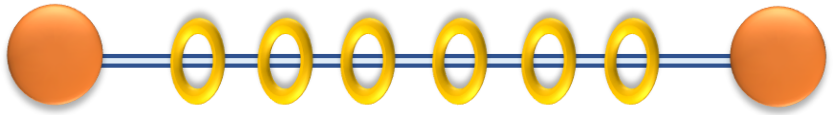


- Ratio of cyclodextrin to PEG monomer: 1:2 with 100% coverage
- Head to head arrangement stabilised by hydrogen bonds

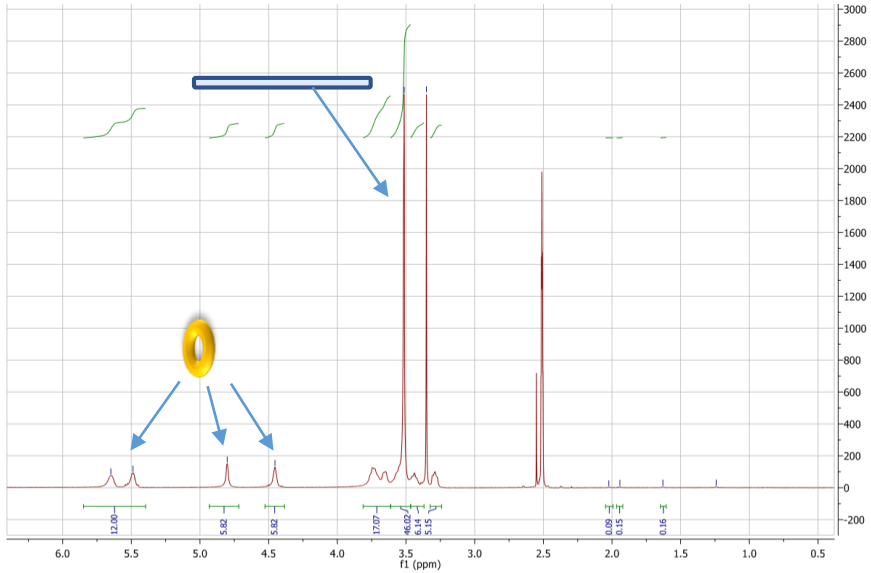
Coverage

- Coverage = How densely packed the main polymer chain is

Low coverage

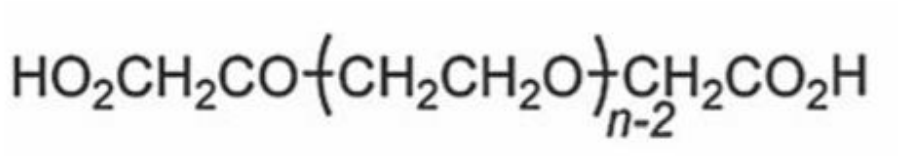


High coverage

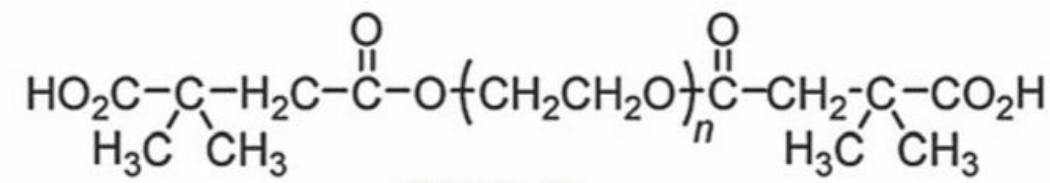


- Calculation: Compare characteristic NMR peaks of backbone to rings

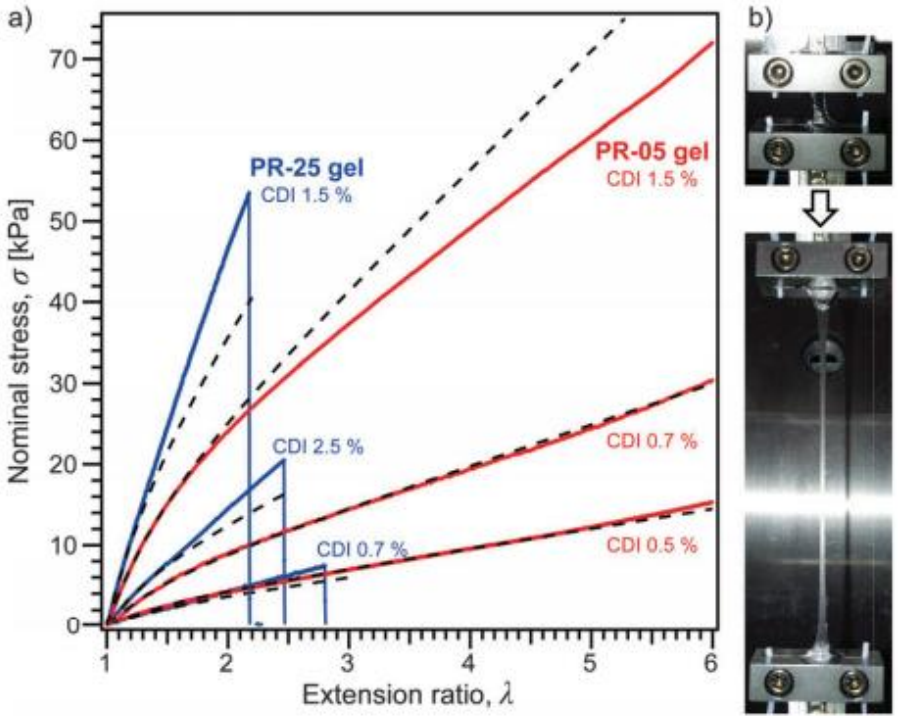
Coverage



25% coverage



5% coverage

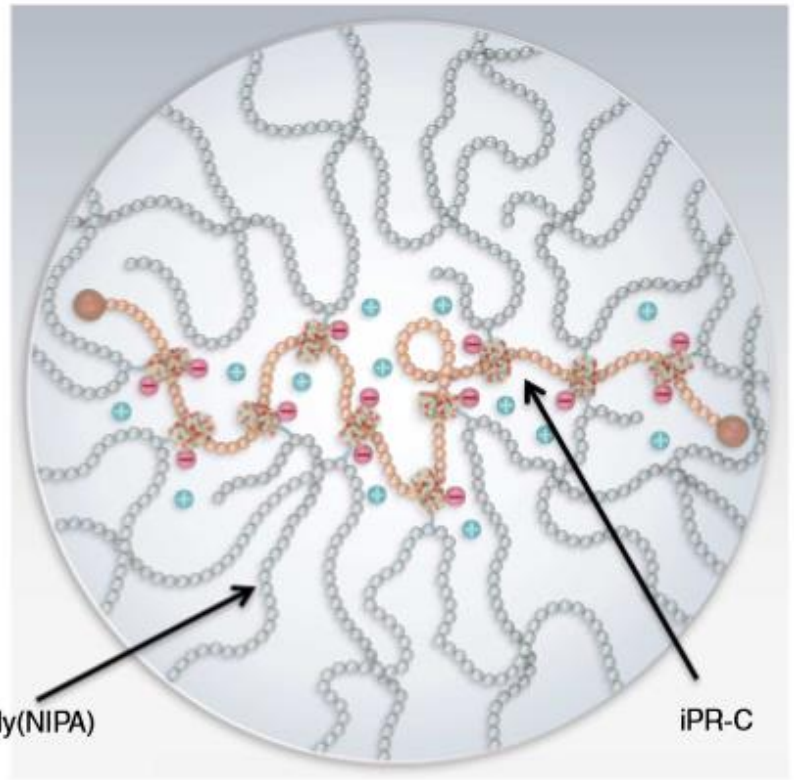


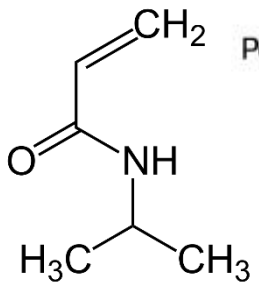
Kato, K., et al. (2015). Chem Commun **51**(90): 16180-16183.

Coverage controlled by the size of the stopper

Imran, A. et al (2014). Nature Communications **5:**5124

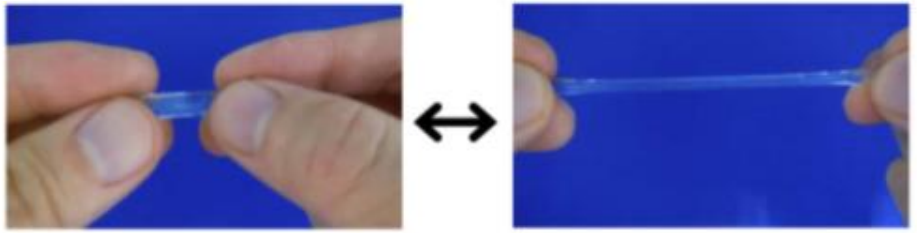
Charge

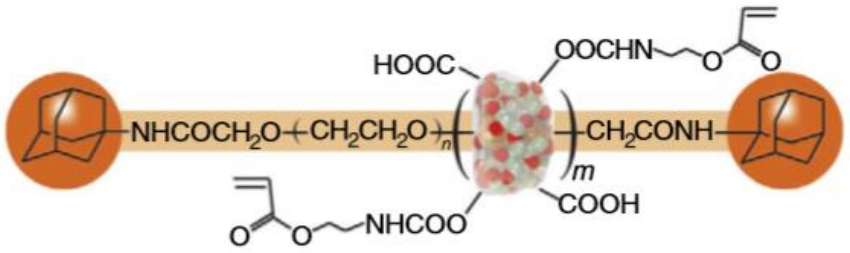




Ionic polyrotaxane:

- Well extended network with less aggregation
- Highly extensible





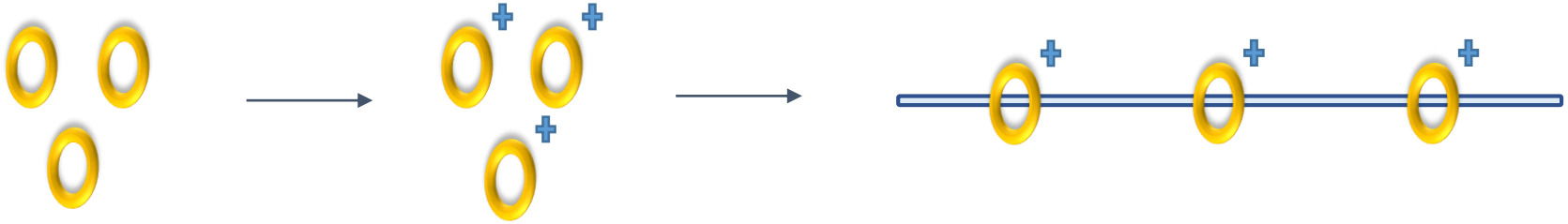
Control of Properties

Factors:

- Size of Chain-Ends
- Charge? Positive charge desired

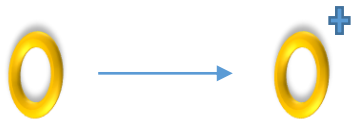
Objective

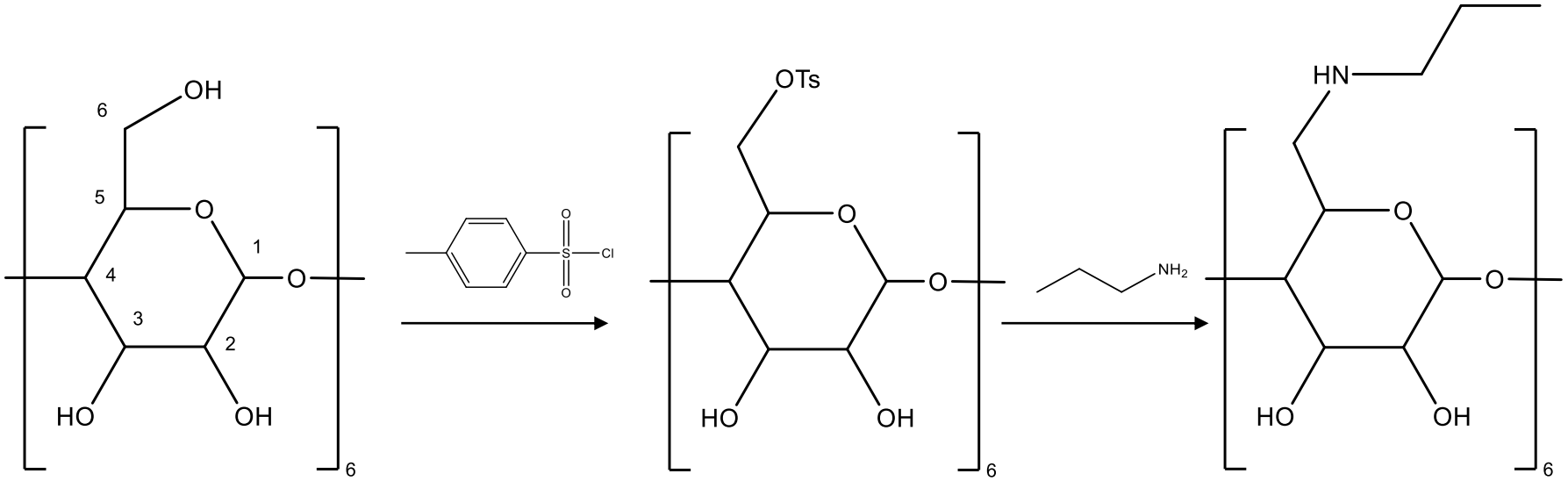
- Pre-functionalisation



- Post-functionalisation

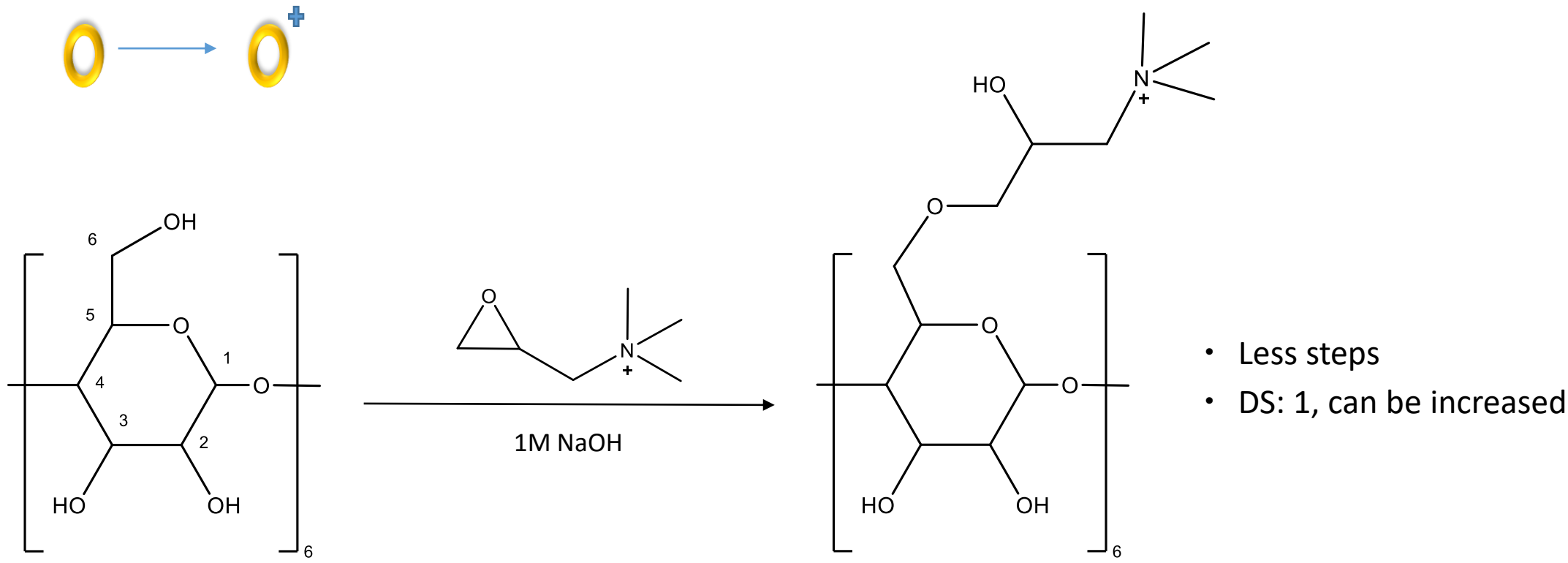
Synthesis - Cyclodextrins





- Low yield, difficult separation
- Degree of Substitution (DS): 1 or lower

Synthesis - Cyclodextrins



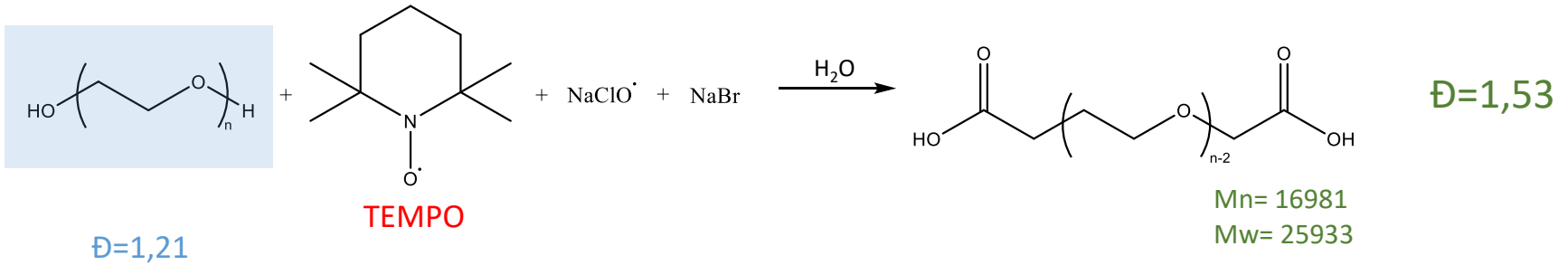
- Less steps
- DS: 1, can be increased

Synthesis - Polyrotaxanes

Araki, J., Changming; Ito, Kohzo (2005). Macromolecules **38**: 7524-7527.

Zalipsky, S. Gilon C.; Zilkha, A. (1983). European Polymer Journal **19**(12): 1177-1183.

PEG-OH (35000) + Oxidising agent = PEG-COOH



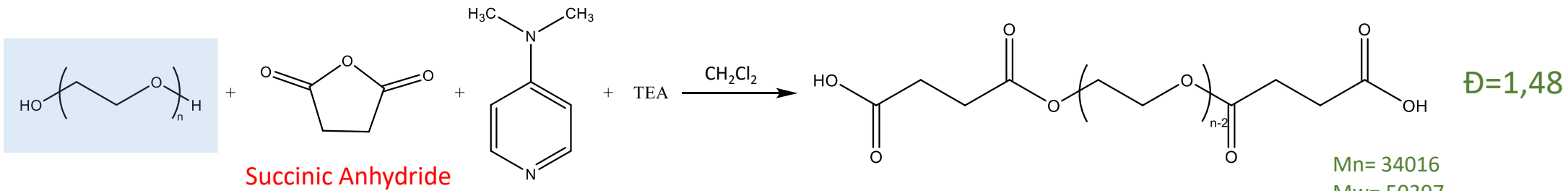
TEMPO

Đ=1,21

Mn= 28128
Mw= 33999

Đ=1,53

Mn= 16981
Mw= 25933



Succinic Anhydride

Đ=1,48

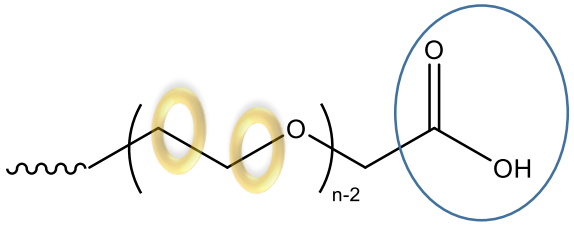
Mn= 34016
Mw= 50397

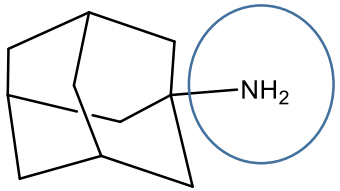
Synthesis - Polyrotaxanes

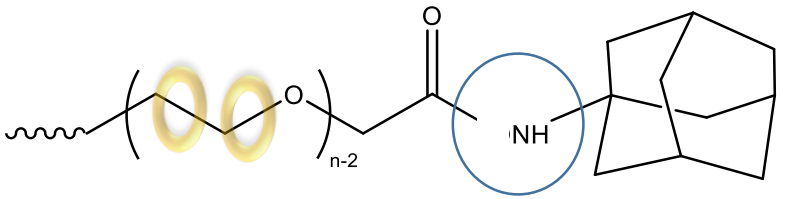
Araki, J., Changming; Ito, Kohzo (2005). Macromolecules **38**: 7524-7527.

1. PEG-COOH + α-CD = pseudo polyrotaxane (PPR)

2. PPR + adamantane = polyrotaxane







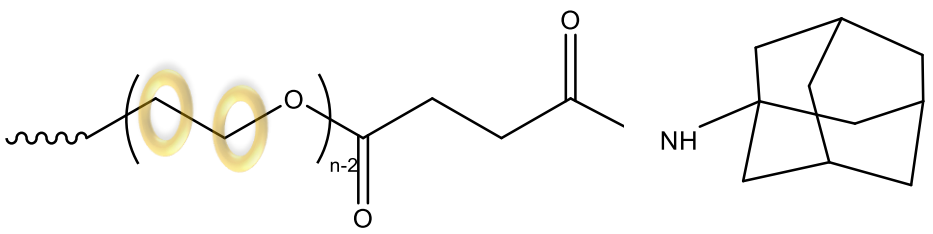
Only soluble in DMSO, 1M NaOH

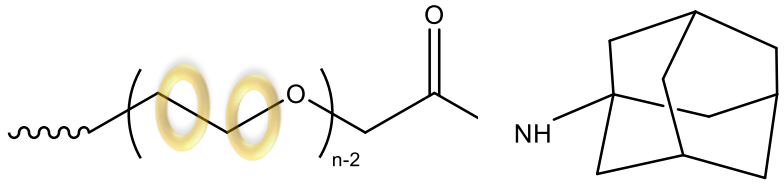
Synthesis - Polyrotaxanes

Chain-End

SA

TEMPO



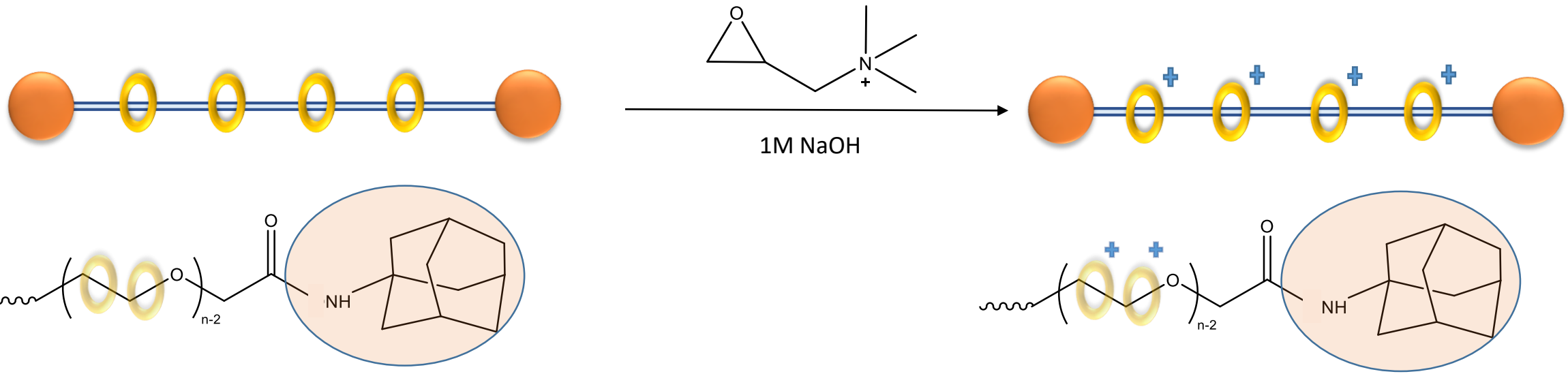


9% Coverage

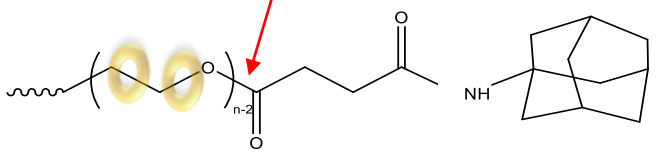
20% Coverage

Synthesis - Polyrotaxanes

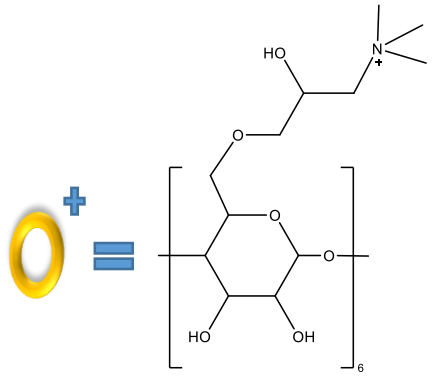
Araki, J. (2011). Journal of Polymer Science Part A: Polymer Chemistry **49**(10): 2199-2209.



- SA
  - Cleavage of ester linkage



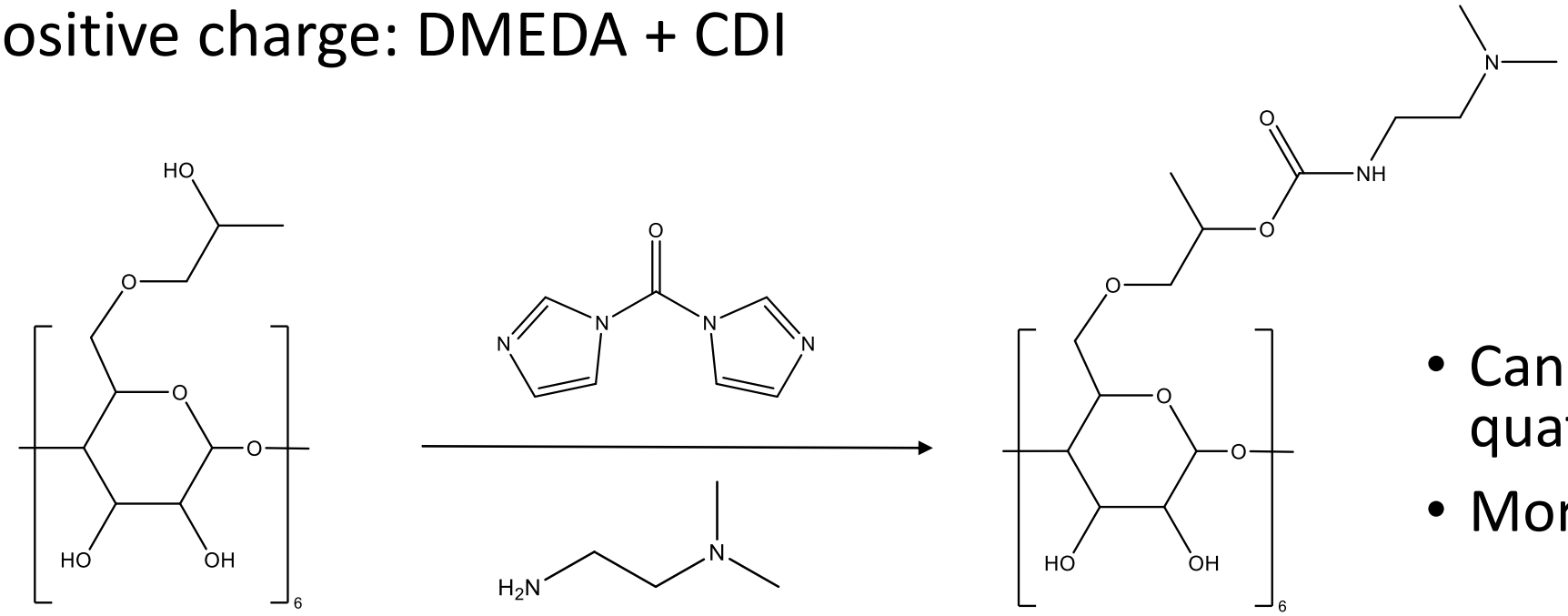
TEMPO
- 14% coverage
- DS: 2,8
- Water soluble



Badwaik, V., et al. (2016).
Macromol Biosci **16**(1): 63-73.

New Paths

- Neutral polyrotaxane: Hydroxypropyl α-CD
- Positive charge: DMEDA + CDI



- Can be quaternised
- More soluble

Summary

- Summary
  - Synthesis of functionalised cyclodextrin and polyrotaxane achieved via quaternary ammonium derivative

- Next Steps
  - Optimise PEG-COOH and PR synthesis
  - Synthesis of neutral PR
  - Formation of PR gels

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Thank you!
Questions?

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