UCLouvain
Institute of Condensed Matter and Nanosciences

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

Rowanne Lyons

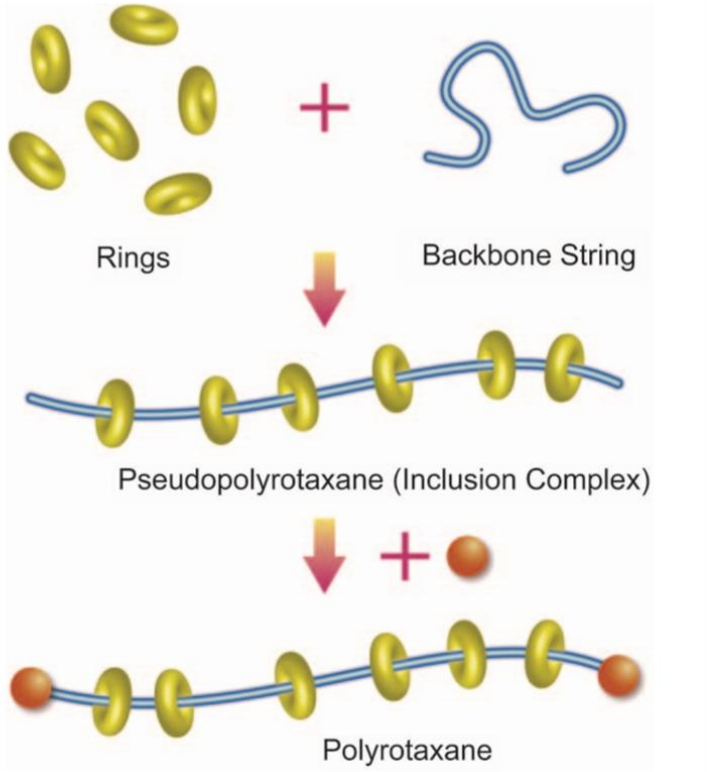
ESR 2, Université Catholique de Louvain

Supervisors: Charles-André Fustin, Evelyne van Ruymbeke

Outline

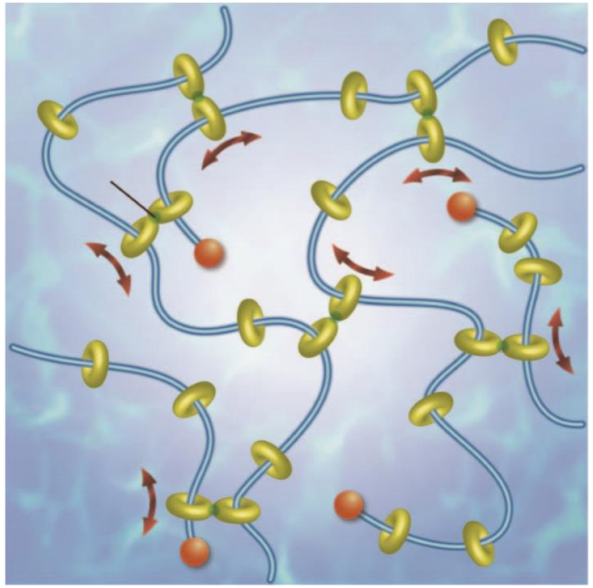
- Introduction
- Synthesis
- Gel Preparation/Rheology
- Conclusion

Slide Ring Gels

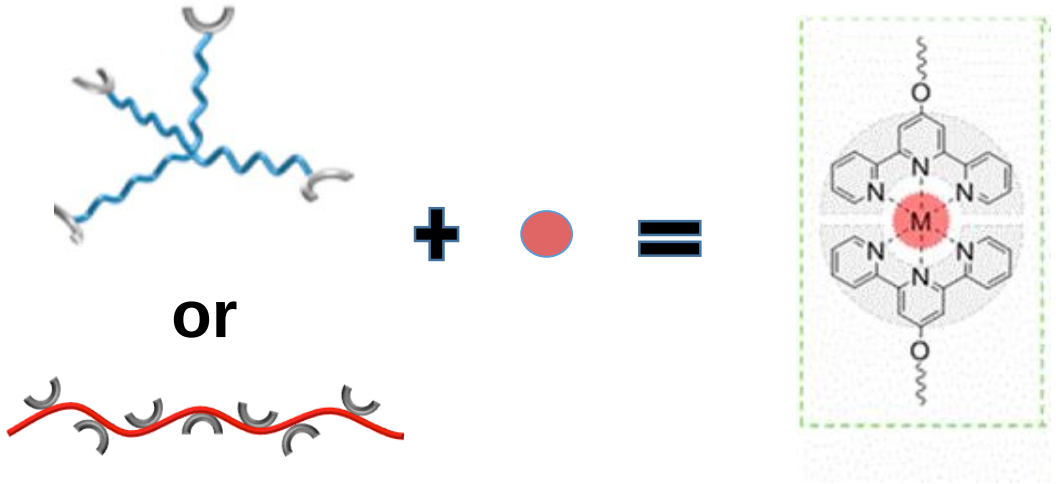


Crosslinker

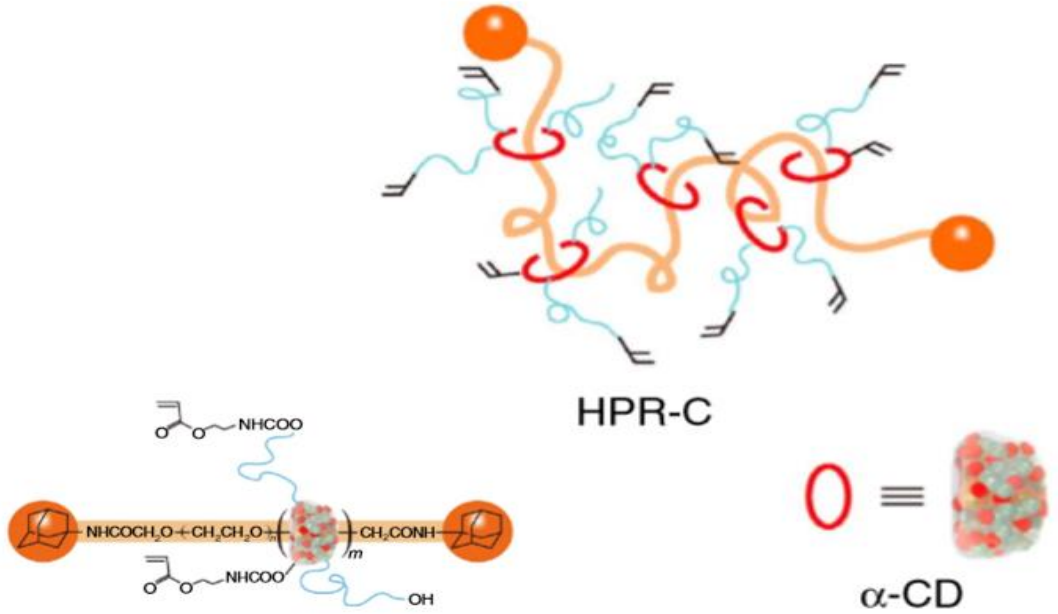
Mechanical interlocking of cyclodextrin to form movable “figure-of-eight” rings



Synthesis of slide ring DDN



First network - Metal-terpyridine links



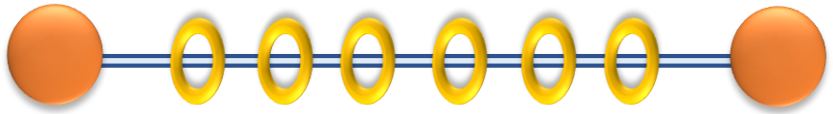
Second network - Slide ring crosslinks

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

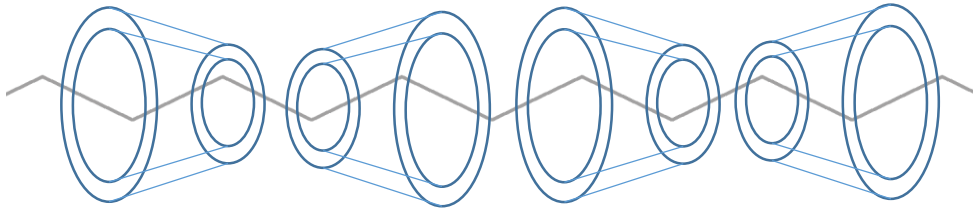
Coverage

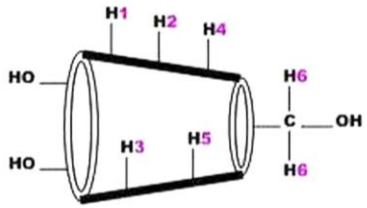
- Coverage = How densely packed the main polymer chain is

Low coverage



High coverage

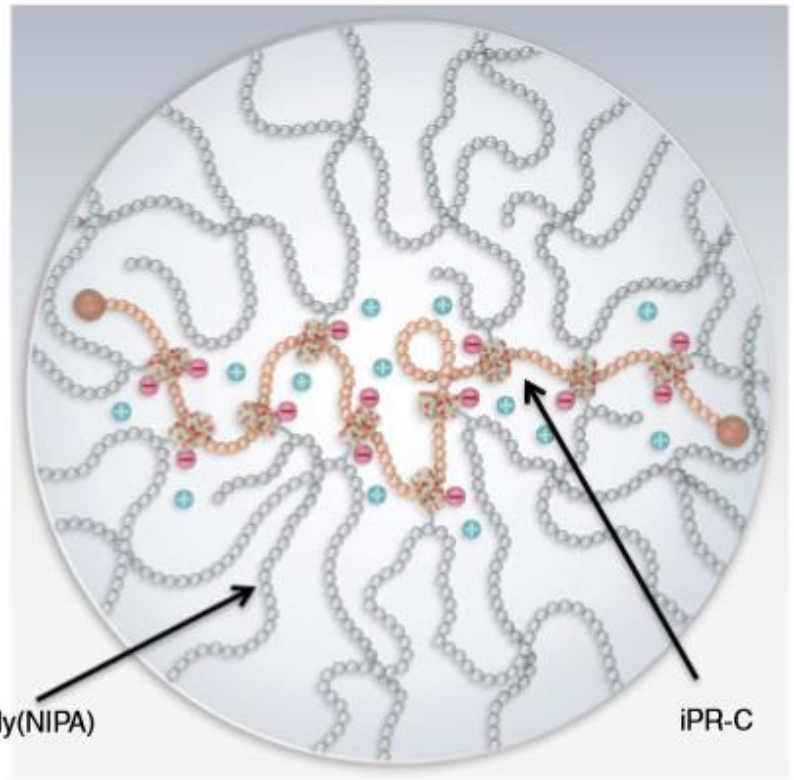


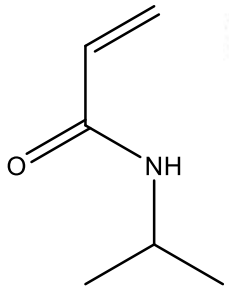


- Ratio of cyclodextrin to PEG monomer: 1:2 with 100% coverage
- Head to head arrangement stabilised by hydrogen bonds

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

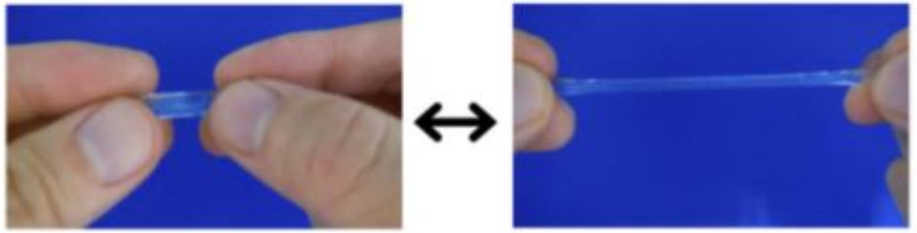
Charge

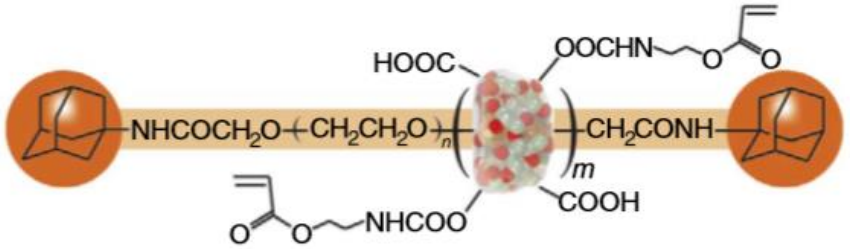




Ionic polyrotaxane:

- Well extended network with less aggregation
- Highly extensible





Synthesis of Polyrotaxane Crosslinker

Contributing Factors:

- Degree of Functionality
- Positive Charge

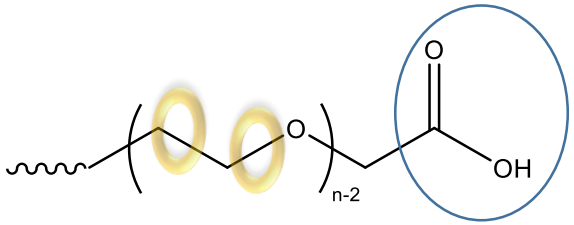
Synthesis - Polyrotaxanes

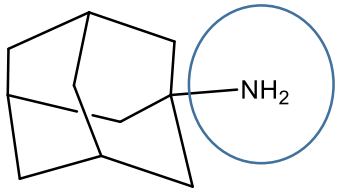
Araki, J., Changming; Ito, Kohzo (2005). Macromolecules **38**: 7524-7527.

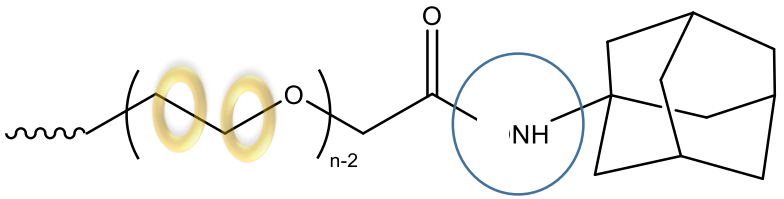
1. PEG-COOH + α-CD = pseudo polyrotaxane (PPR)

2. PPR + adamantane = polyrotaxane

20% coverage = ~80 CD/chain



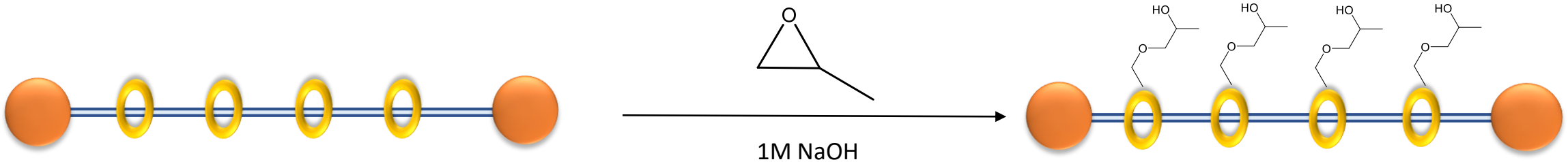




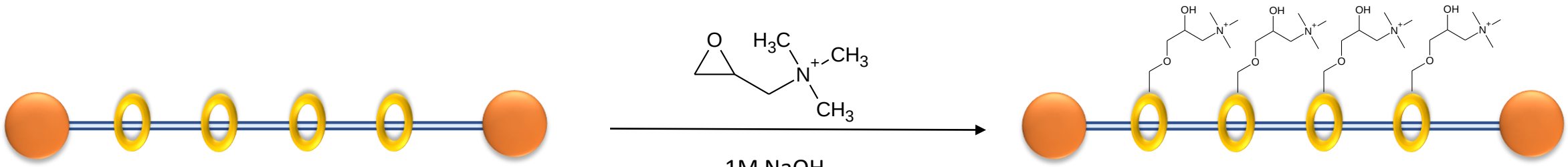
Only soluble in DMSO, 1M NaOH

Synthesis –Polyrotaxane Crosslinker

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



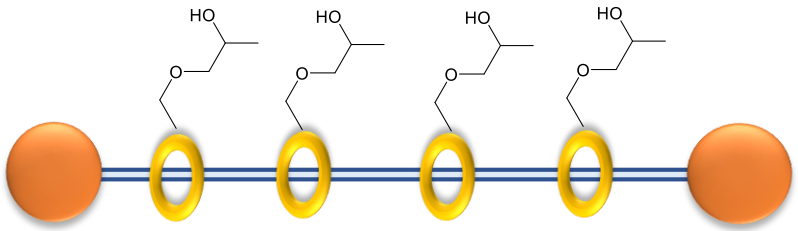
DS: ~2HP groups/CD

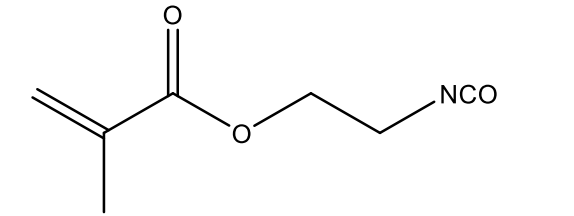


DS: ~3QA groups/CD

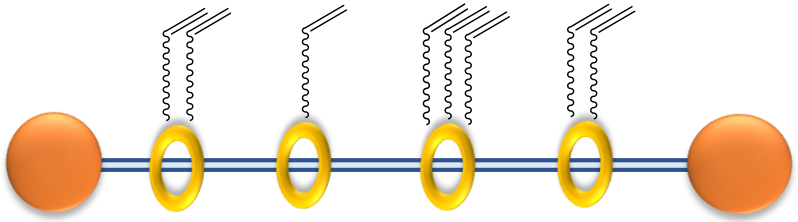
Synthesis –Polyrotaxane Crosslinker

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





BHT, DBTDL in DMSO

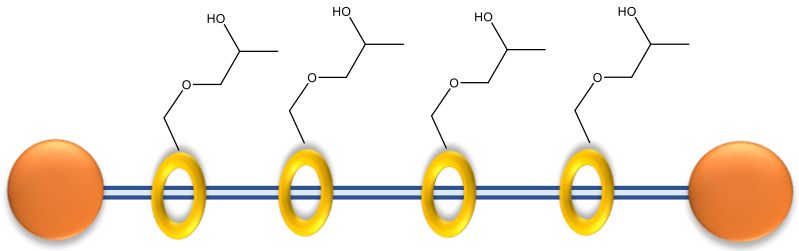


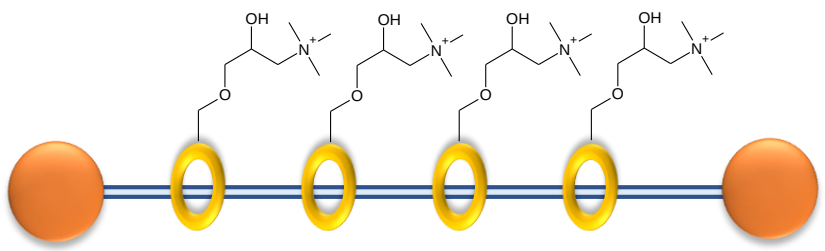
DS: ~2 vinyl groups/CD

= ~160 vinyl groups per chain
Highly functionalised!

Gel - Preparation

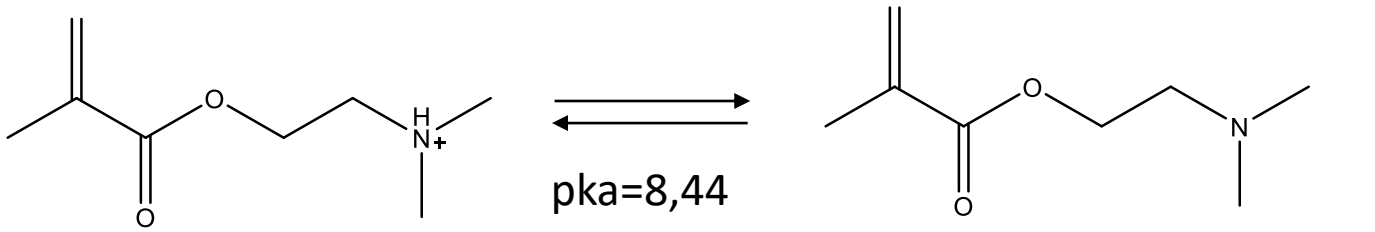
- Preparation of PDMA gels of different functionalities:
  - Quantity of crosslinker
  - Type of crosslinker – neutral and charged





Gel - Preparation

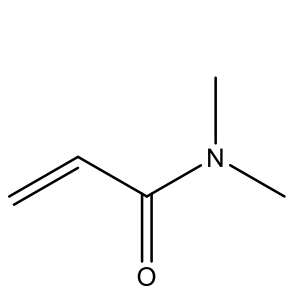
- PDMA gel with/without charged comonomer:
- Gel swollen in solution at pH 4 and 8



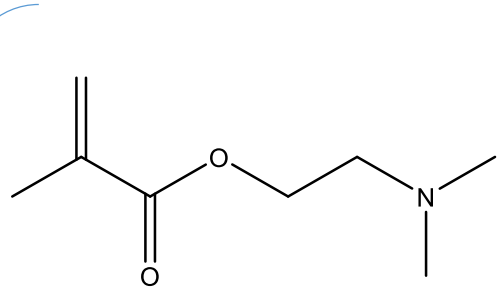
Di**M**ethyl**A**mino**E**thyl**A**crylate

Gel - Preparation

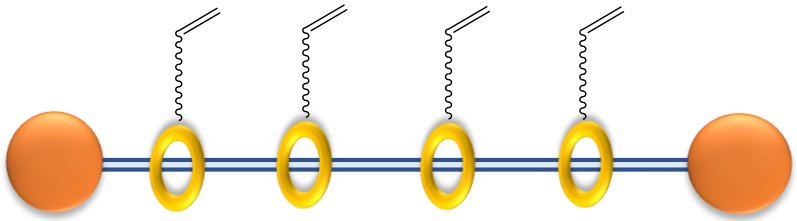
- Radical polymerisation in water with APS initiator and TEMED
- ~10-40mg polyrotaxane crosslinker to 1g monomer in 5g water
- Monomer:Initiator = 350:1
- DMA:DMAEA= 20:1



N,N - **Di**ethyl**A**crylamide



DMAEA



Polyrotaxane crosslinker

Pre-gel solution

Gel - Preparation

- Swelling to equilibrium in water (1 week)

Swollen and dry gel

$$\text{Swelling ratio} = \frac{W_{swollen\ gel}}{W_{dry\ gel}}$$

Gel - Preparation

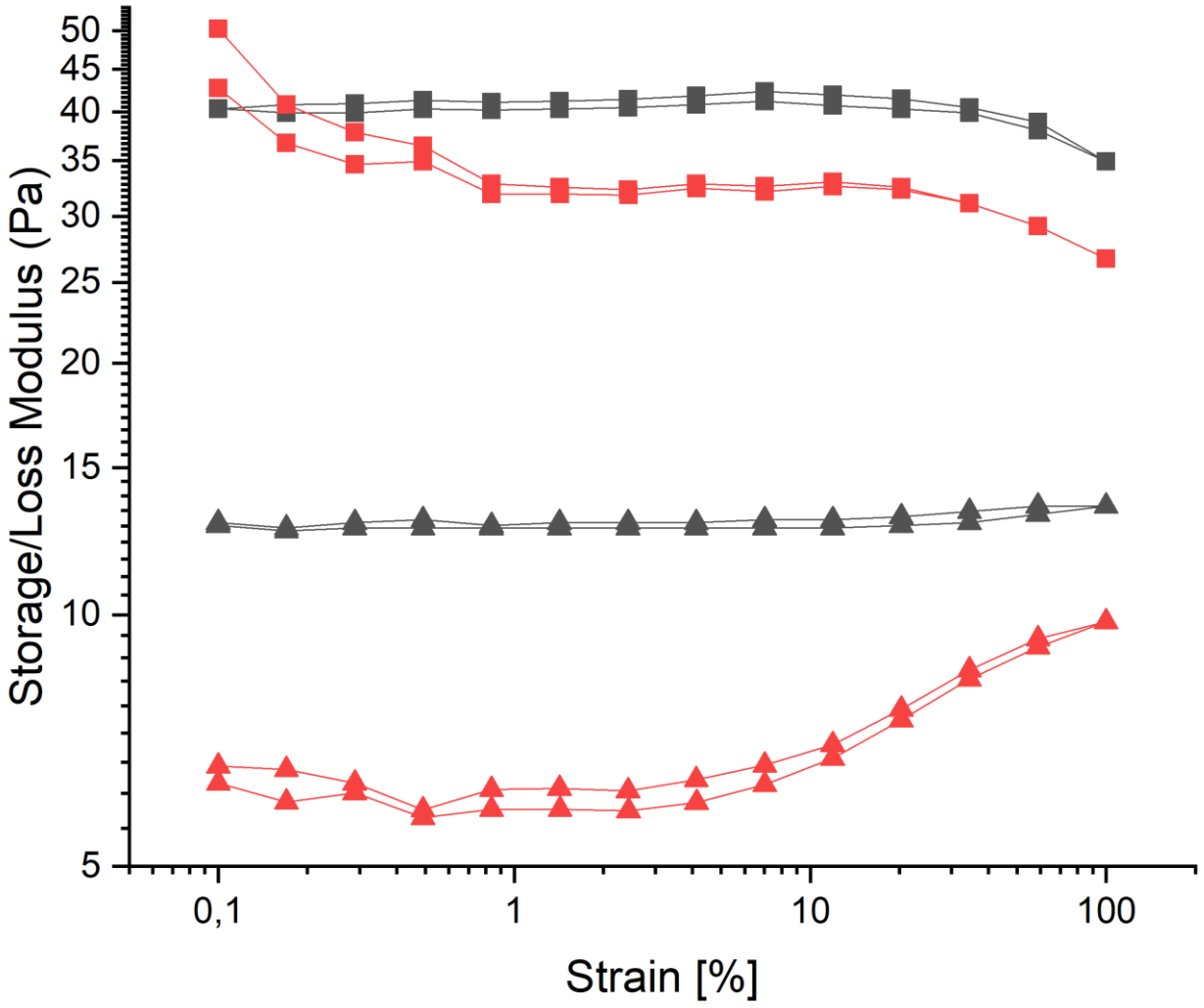
Hydrogel	Molar % vinyl groups	DMAEA(g)	Swelling Ratio	Comments
DMA-HPR-C-40	17,29		30,00	Tough
DMA-QAPR-C-60	35,23		-	No gel
DMA-DMAEA-HPR-C-40	17,26	0,072	75,00	Tough
DMA-HPR-C-10	4,73		66,50	Soft
DMA-DMAEA-HPR-C-10	4,72	0,072	78,50	Soft

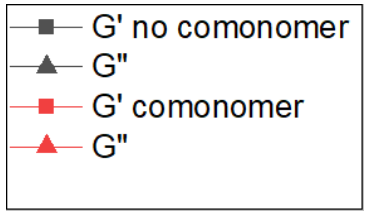
- **Charge has effect on swelling ratio**
- **Degree of functionality determines modulus**
- **Charged crosslinker insoluble in water**

Gel -Rheology

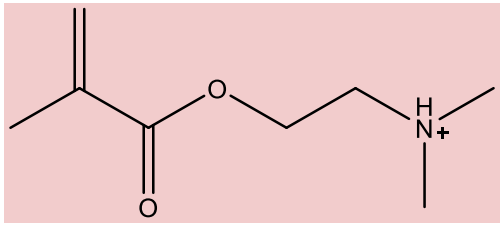
- Protocol
  - Gel swollen to equilibrium: polymer concentration = ~4%
  - Measurement on PP system at 25°C
  - Strain Sweep to determine linear range
  - Frequency Sweep in linear range

Gel – Rheology – Strain Sweep



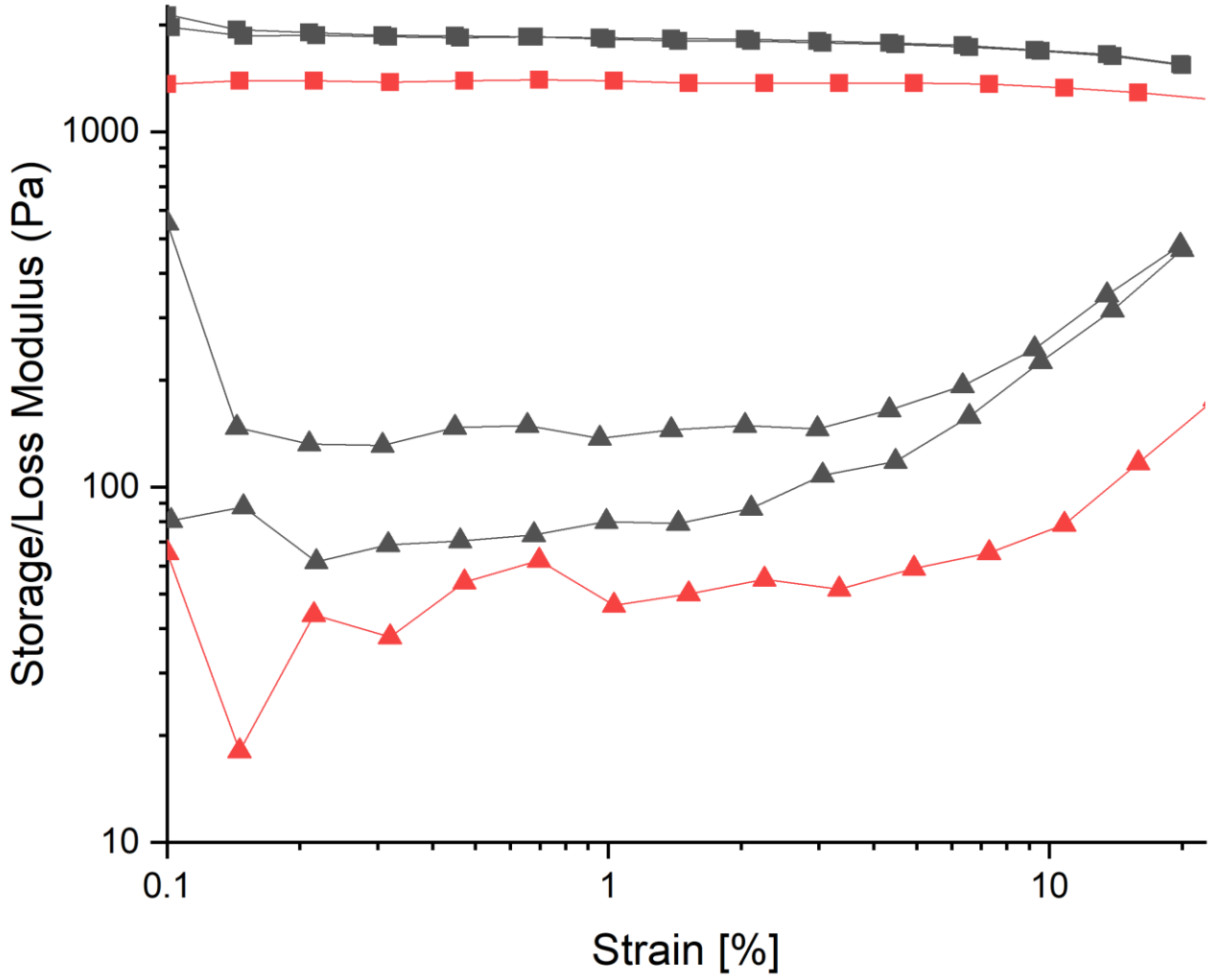


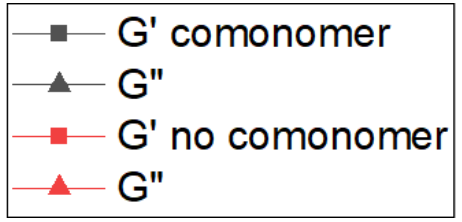
- Loosely crosslinked :
- mol. vinyl groups/mol. monomer = 2
- 10rd/s angular frequency



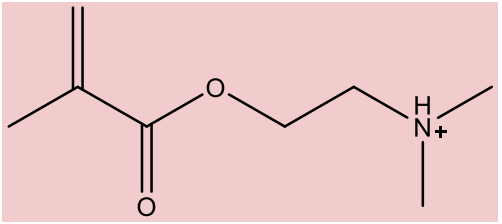
Charged comonomer

Gel – Rheology – Strain Sweep



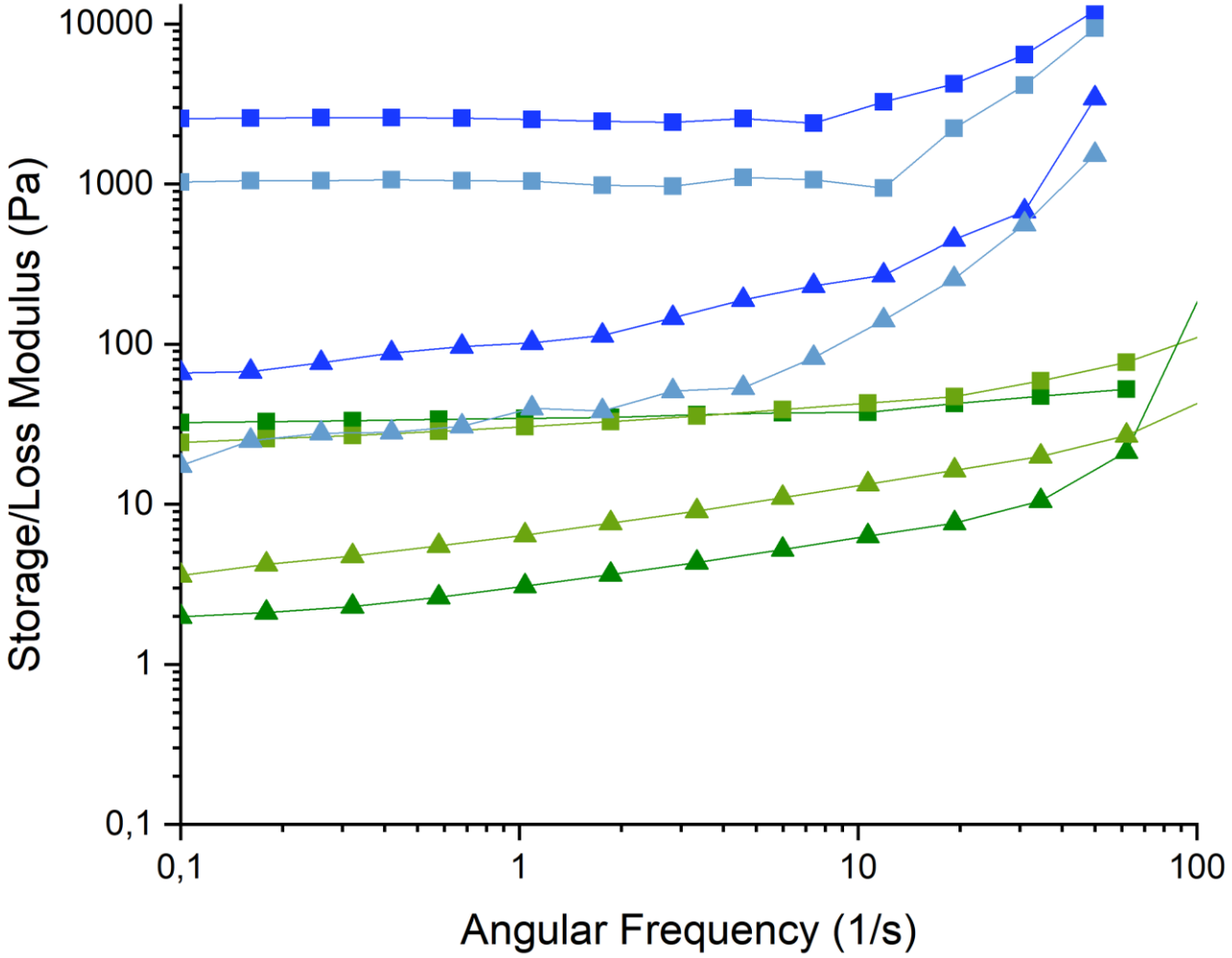


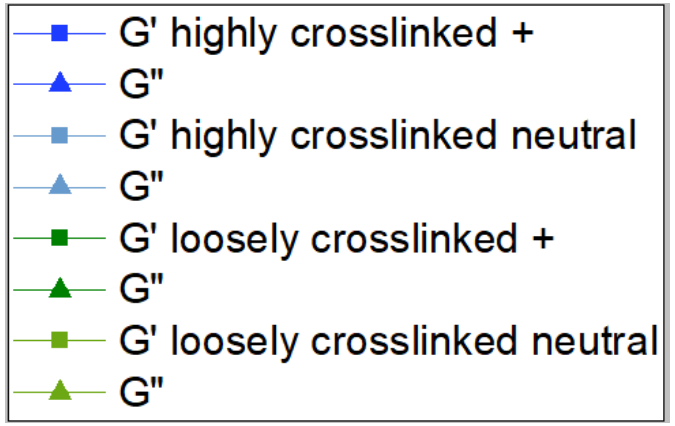
- Highly crosslinked :
- mol. vinyl groups/mol. monomer = 10
- 1rd/s frequency



Charged comonomer

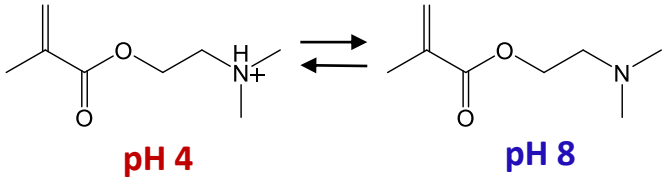
Gel – Rheology – Frequency Sweep

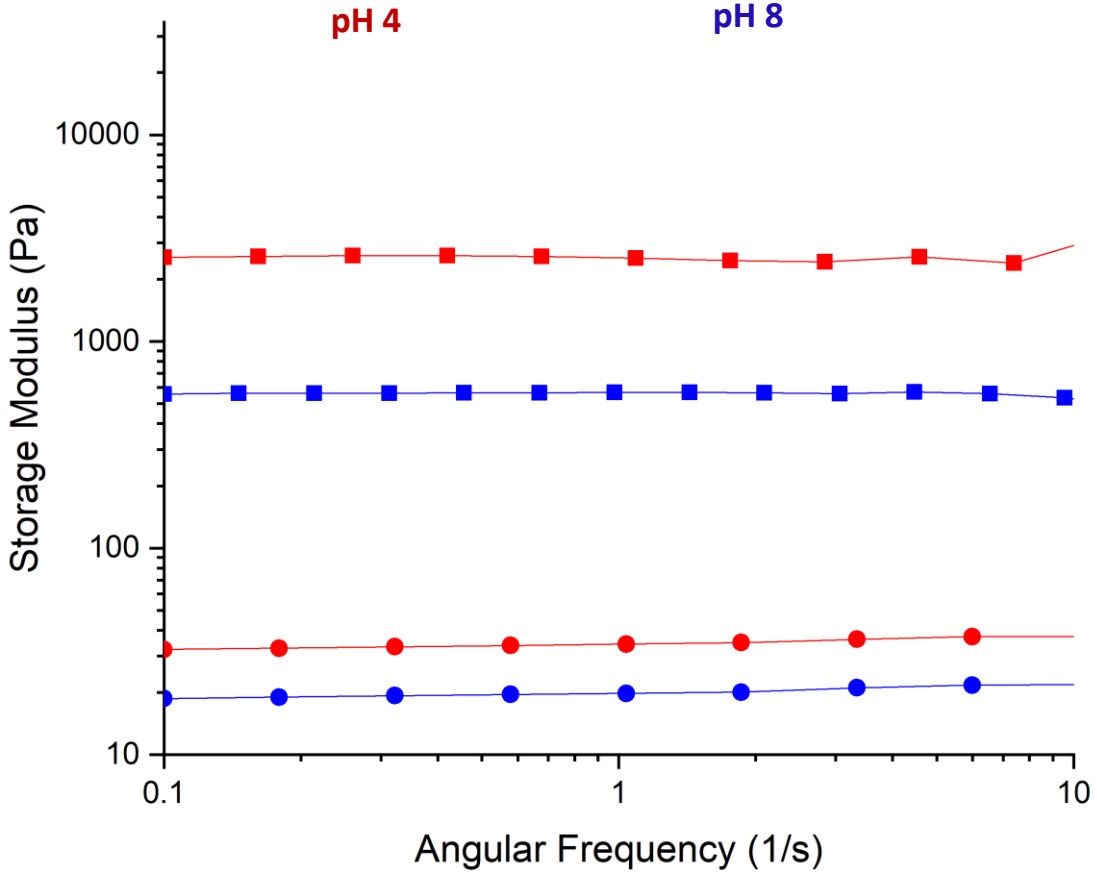


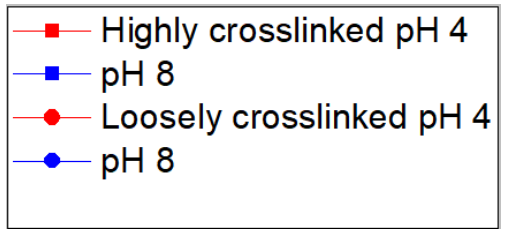


- Effect of charged comonomer and crosslinking density
- 1-5% strain rate

Gel – Rheology – Effect of pH







- Gels swollen in solutions of pH 4 and 8

Sample Stock – Approximate Scale

Name	Quantity
Polyrotaxane	5g
Polyrotaxane crosslinker	300mg
Gel	50-75cm^3

Conclusions

- Synthesis of slide ring gels of different compositions
- Gels with charged comonomer have higher swelling ratios
- Charge in polymer network can improve storage modulus

Next Steps

- Gels with lower coverage/more elasticity
- Different crosslinkers
- Mechanical characterisation of gels
- Study gels of mostly polyrotaxane (bulk)

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INITIAL TRAINING NETWORK
DODnet

Thank You