“Structure-property relationships in double dynamic networks at the nano- to micro- scale”

“Structure and diffusion in DDNs at the nano- to micro- scale”

Marie Sklodowska Curie ITN-DoDyNet
Double dynamics for design of new responsive polymer networks and gels

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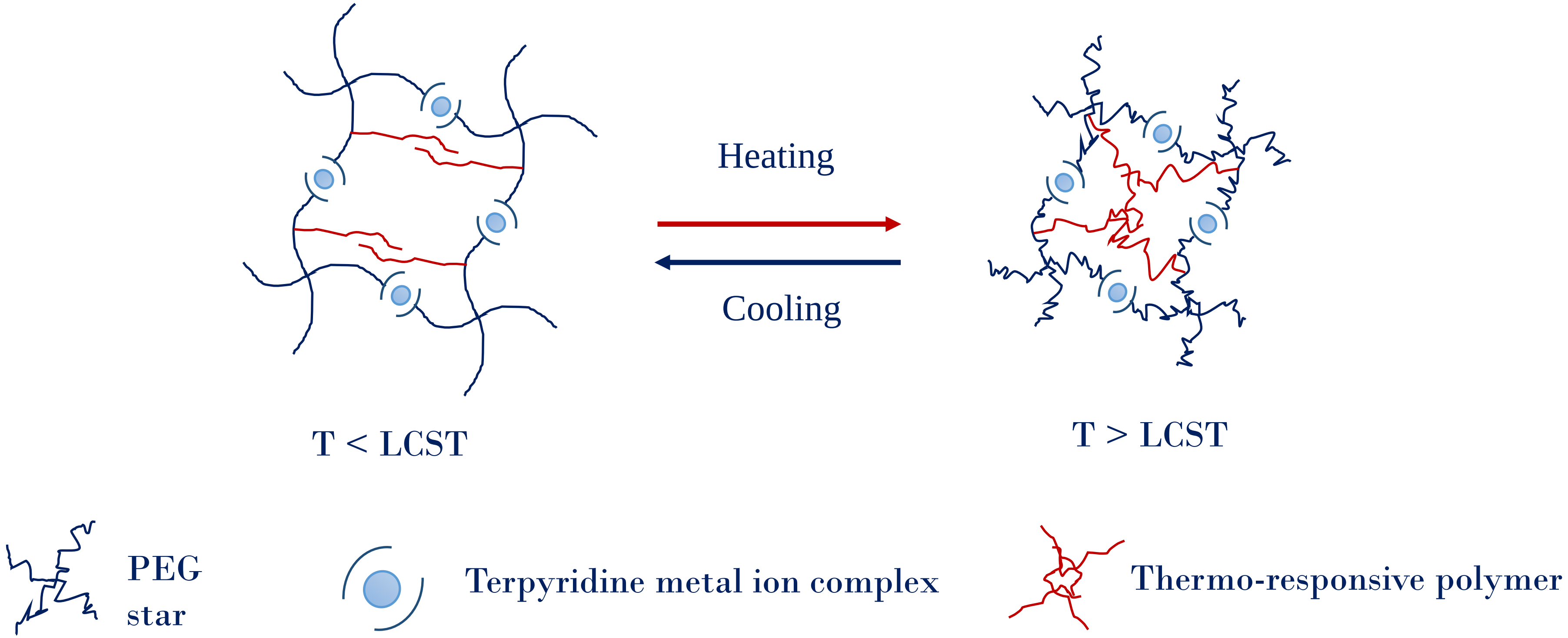
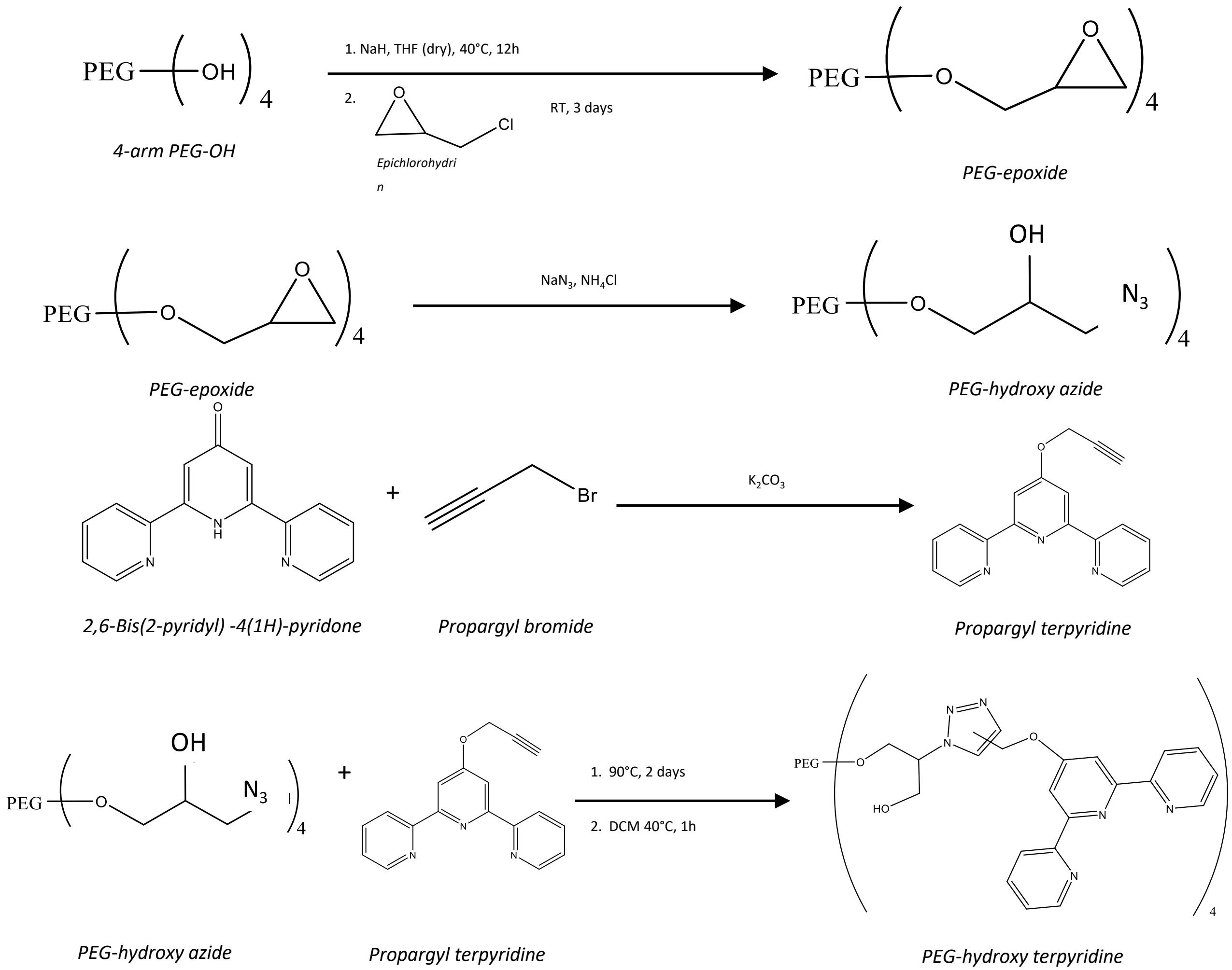
- **The role of network density and connectivity on the structure and dynamics of metallo-supramolecular hydrogels**
- **Covalent Dynamic Double Network**

Synthesis of double dynamic thermo-responsive hydrogel



Synthesis of Peg-hydroxy terpyridine



Functionalization of Terpyridine

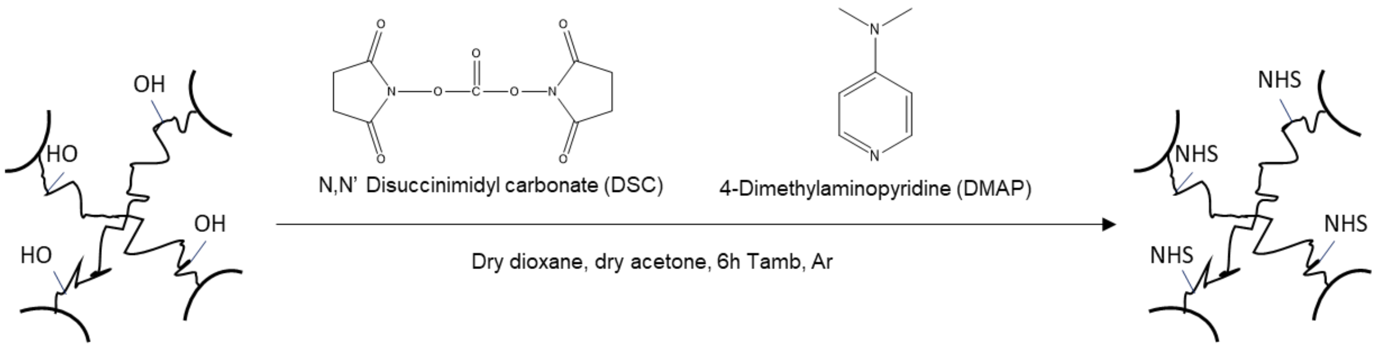
Achieved functionalization: 38 - 62%

New functionalization: 98 %

New procedure:

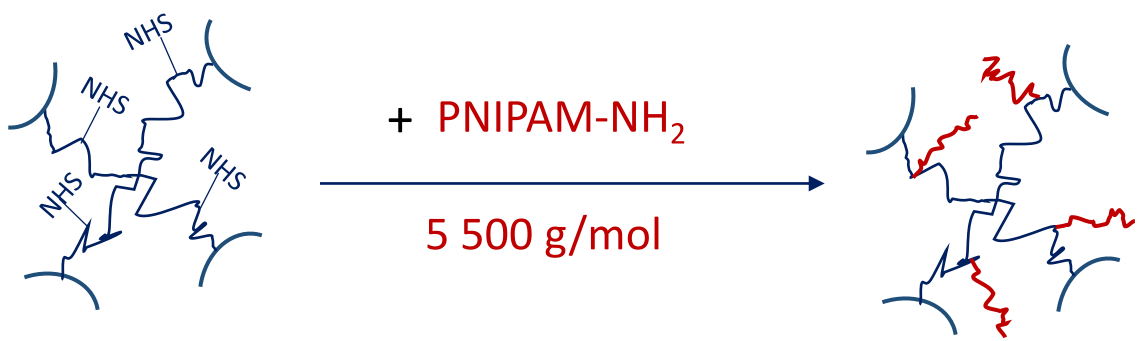
- Increased equivalents of propargyl terpyridine to 8
- Add reagents in powder and then melt them
- Increase reaction time under vacuum

Attachment of Pnipam



Peg-hydroxy terpyridine

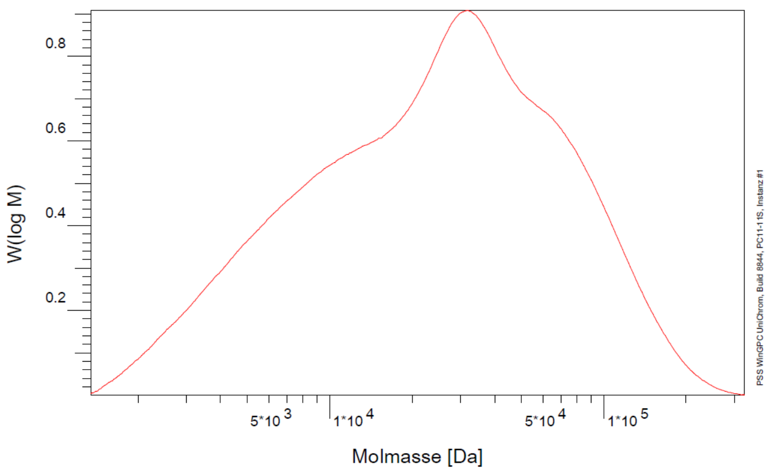
Peg-succinimidyl terpyridine

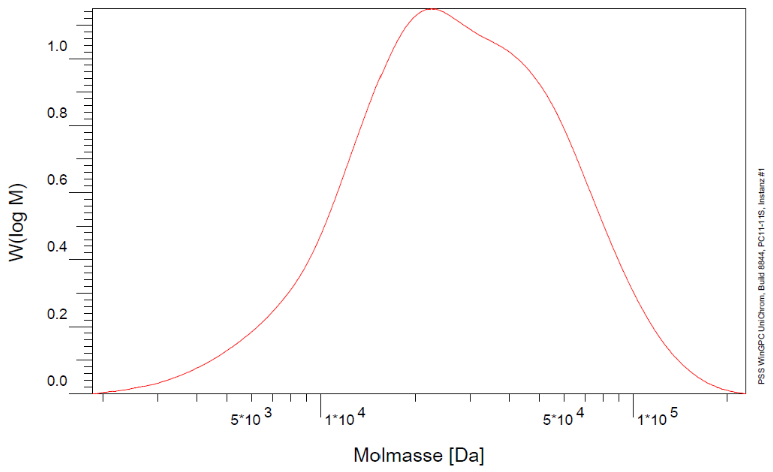


20 000 g/mol

Removal of Pnipam

GPC Peg-Pnipam-Tpy before and after dyalisis

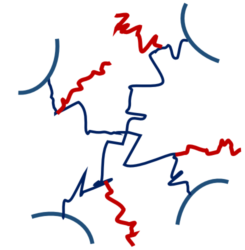




Before dyalisis there were 3 peaks given from the Pnipam (at 5500 Da), from the Peg (at 20 000 Da) and from the Peg-Pnipam (at 42 000 Da)

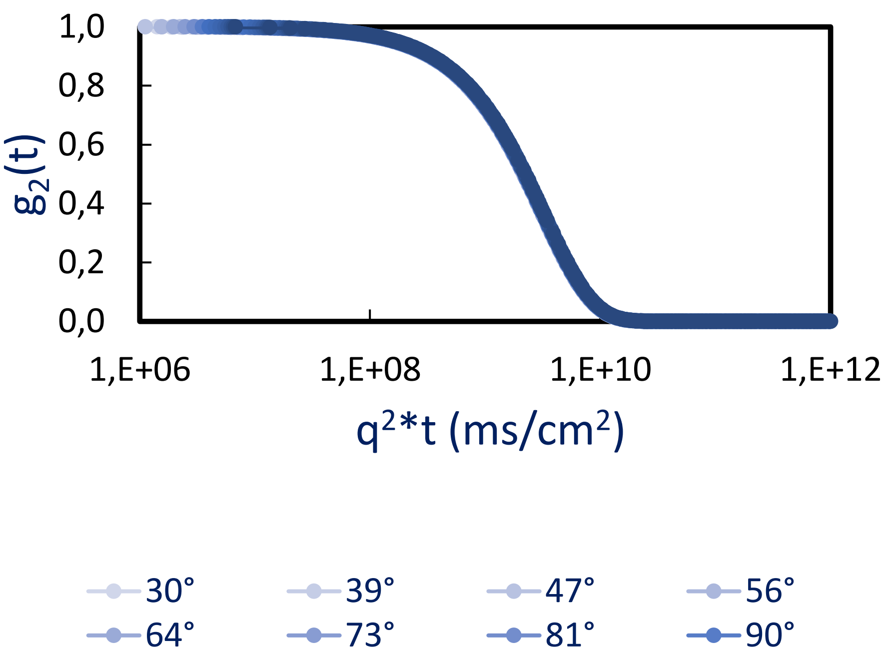
After dyalisis there are only 2 peaks given from the Peg (at 20 000 Da) and from the Peg-Pnipam (at 42 000 Da)

Dynamic Light Scattering

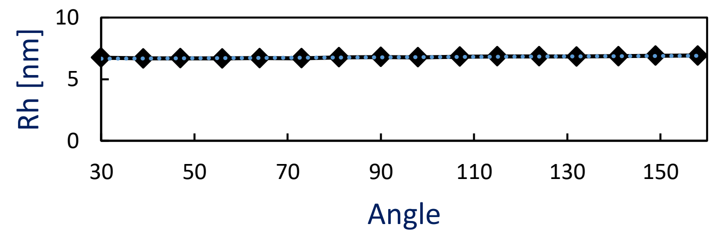


Solution in water 5 g/L

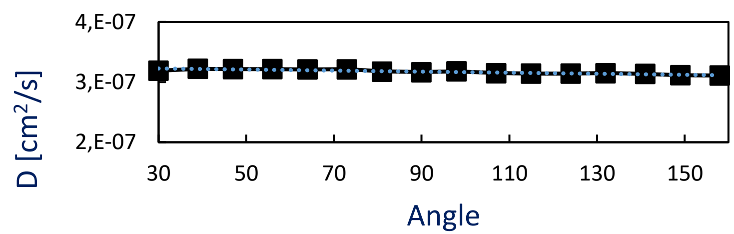
Fit function



$R_h = 6.79\ nm\ \pm 0.12$



$D_a = 3.17 * 10^{-7}\ cm^2/s\ \pm\ 5.56 * 10^{-9}$

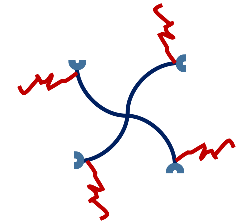


The autocorrelation function could be fitted monoexponentially and the hydrodynamic radius and diffusion coefficient are independent of the angle. This brings to the conclusion that the Pnipam has been efficiently removed and that the Peg-Pnipam is uniform in size.

Gel formation

20 000 g/mol

5 500 g/mol



C= [70 g/L]

Solvent: water

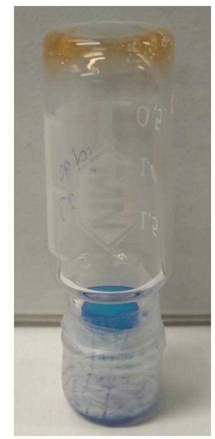
Fe < LCST

Fe > LCST

Ni < LCST

Ni > LCST

Co < LCST



Co > LCST

Zinc below LCST

With Zinc it does not form a gel

(but with the precursor

without Pnipam yes)

Zinc above LCST

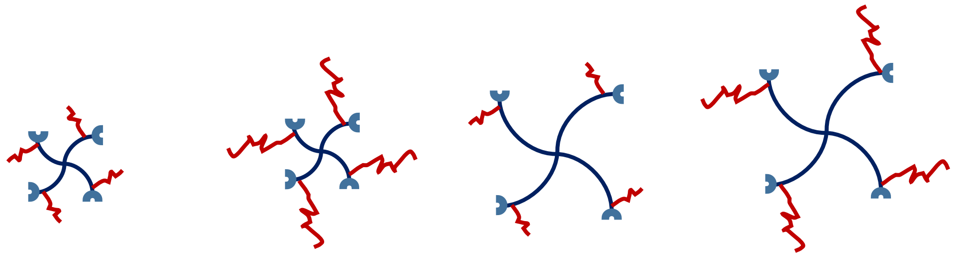
Conclusions and future plans (1)

- The higher functionalization of terpyridine could be achieved
- Pnipam has been successfully attached
- The system can form hydrogels (except Zn)

- The Zn system has to be further investigated
- The hydrogels can be now characterized

Characterization

➢ Different lenghts of Pnipam



Peg	10 000 g/mol	10 000 g/mol	20 000 g/mol	20 000 g/mol
Pnipam	2 500 g/mol	5 500 g/mol	2 500 g/mol	5 500 g/mol

➢ Different metal ions

Fe

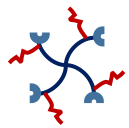
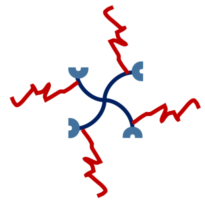
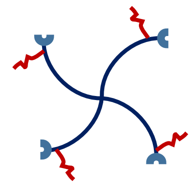
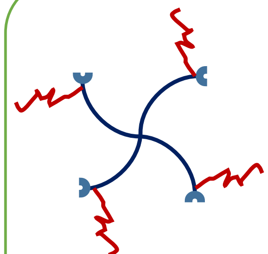
Ni

Co

Zn

Characterization

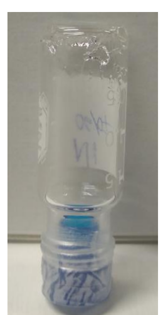
- Different lenghts of Pnipam

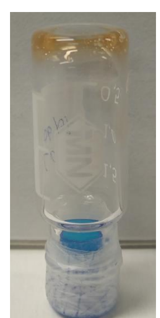
Peg	10 000 g/mol	10 000 g/mol	20 000 g/mol	20 000 g/mol
Pnipam	2 500 g/mol	5 500 g/mol	2 500 g/mol	5 500 g/mol

- Different metal ions

Fe



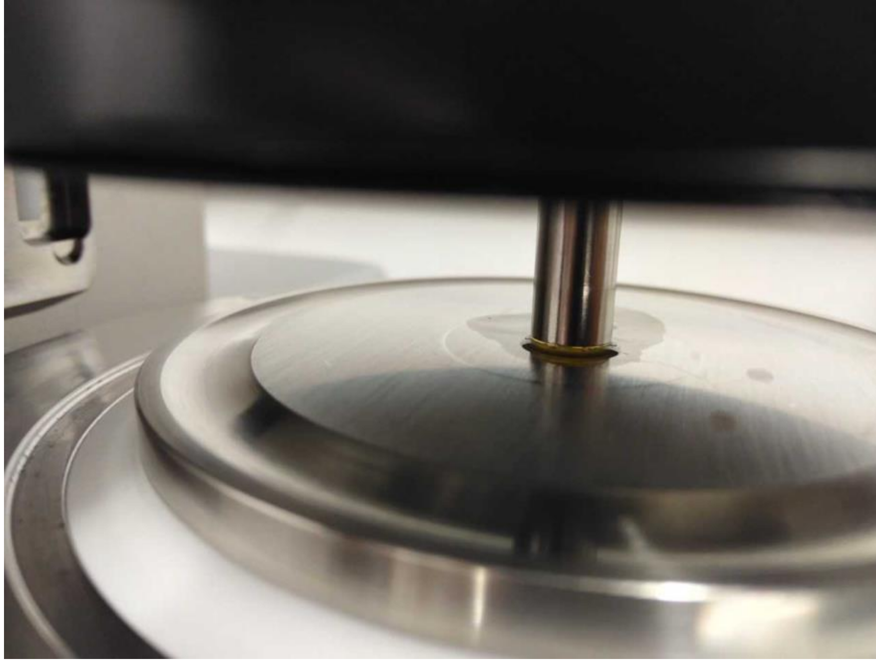
Ni



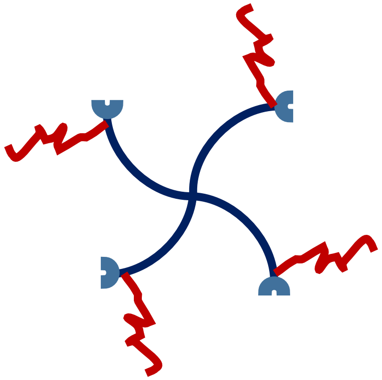
Co

Zn

Linear Rheology



- FORTH
- These are preliminary results
- Measuring protocol has to be changed



20 000 g/mol

5 500 g/mol

C= [70 g/L]

Different metal ions

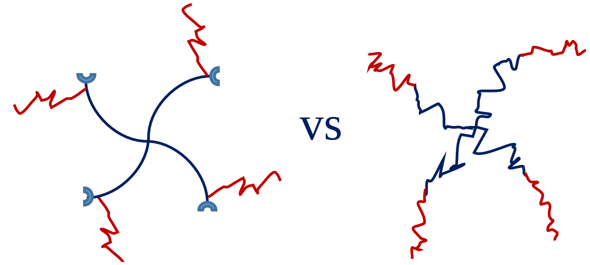
Fe

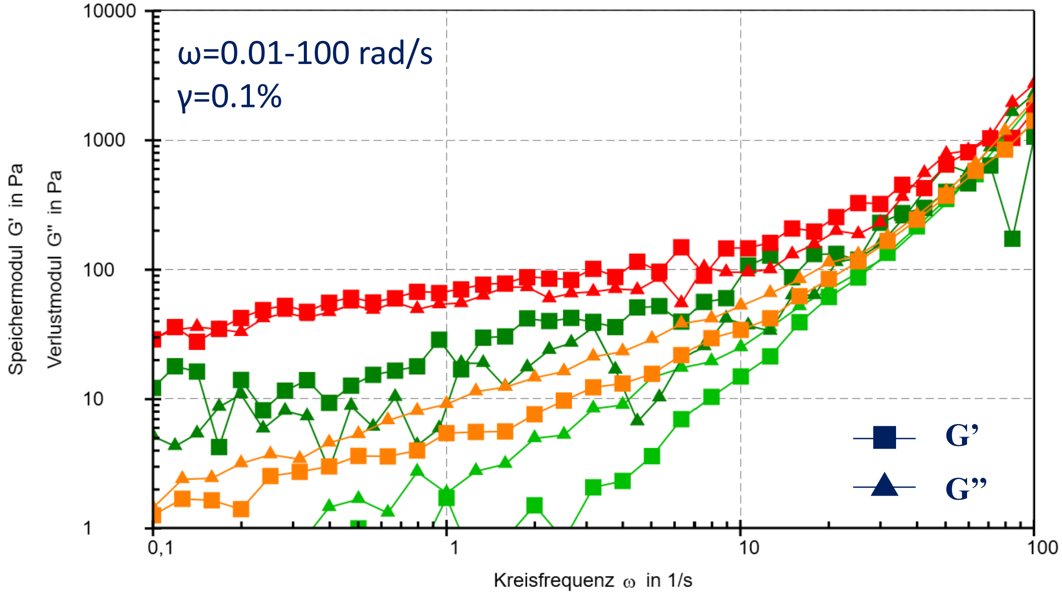
Ni

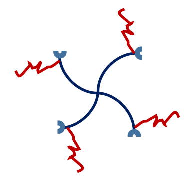
Co

Zn

Zinc

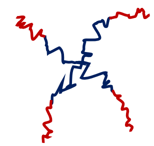






T = 35 °C

T = 25 °C



T = 35 °C

T = 25 °C

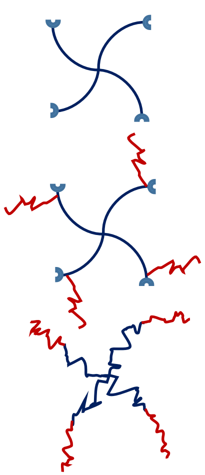
By increasing the Temperature above the LCST G' increases

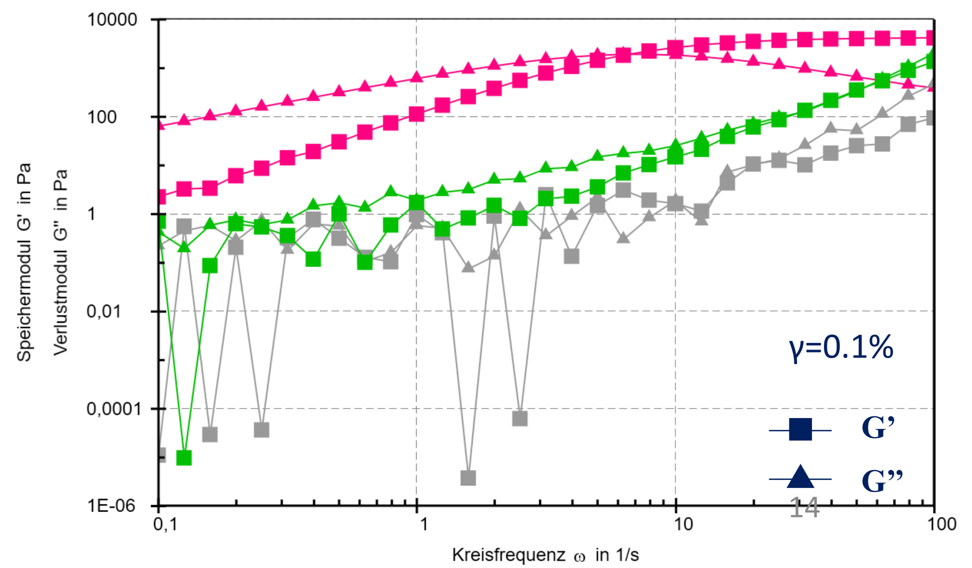
With the introduction of Pnipam chains, the network loses elasticity

T = 25 °C

T = 25 °C

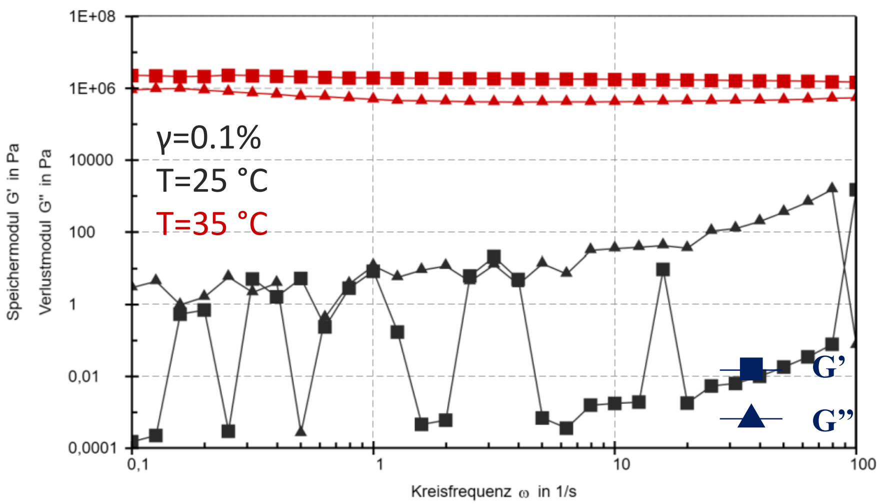
T = 25 °C



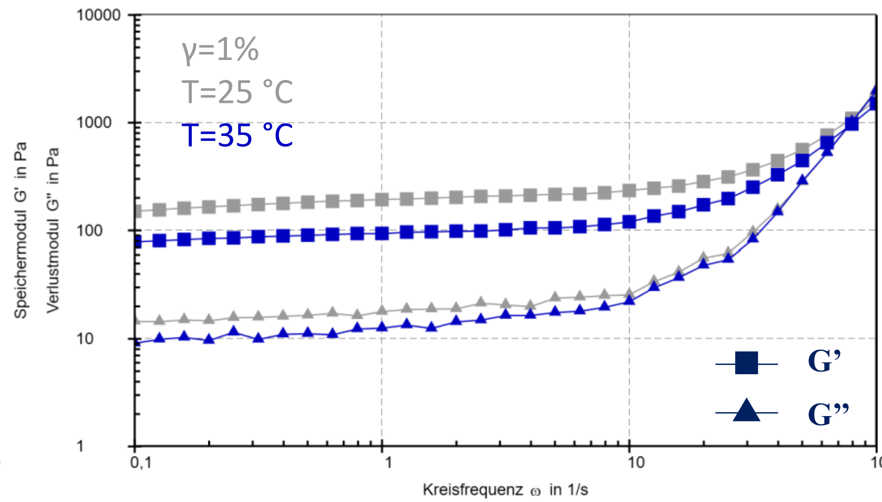


- # Nikel

M : Tpy = 1 : 1



M : Tpy = 1 : 2

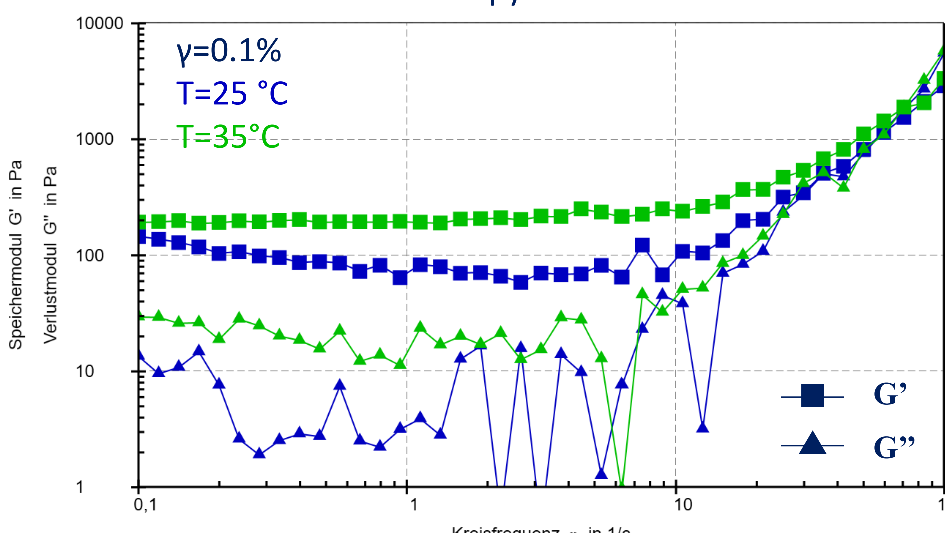


G' increases with the Temperature

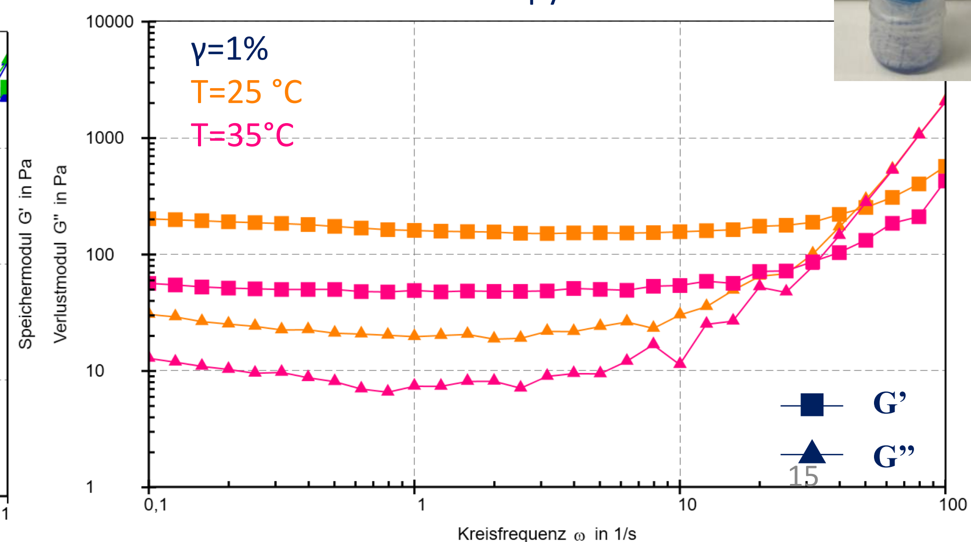
G' decreases with the Temperature

- # Cobalt

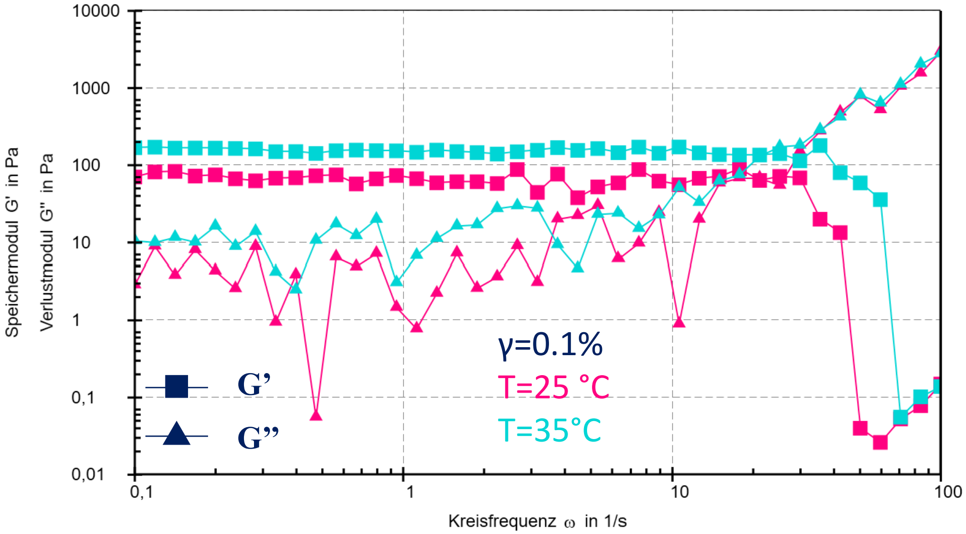
M : Tpy = 1 : 1



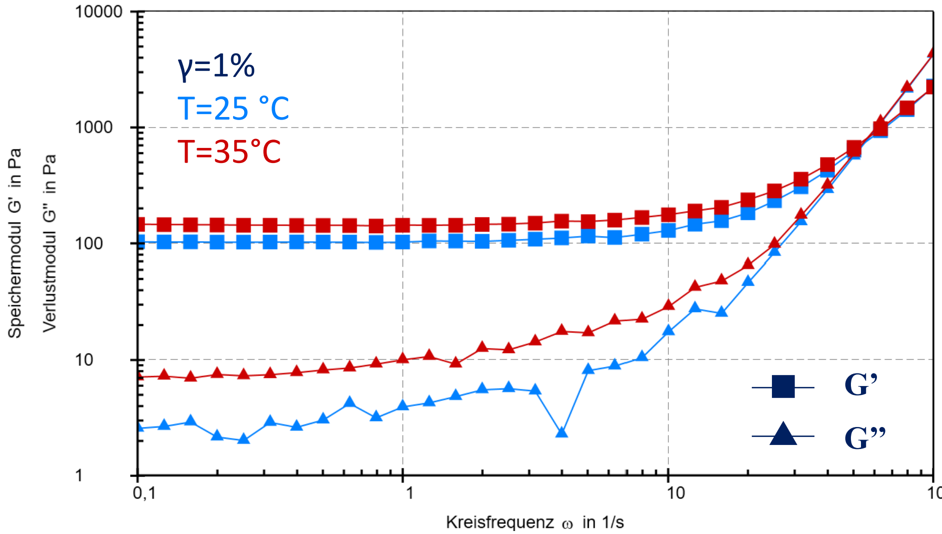
M : Tpy = 1 : 2



Iron



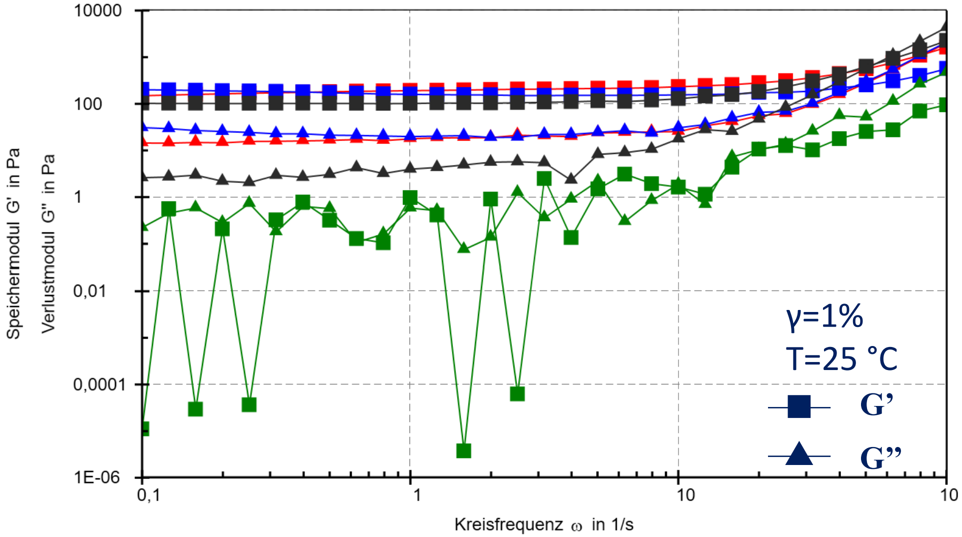
M : Tpy = 1 : 1

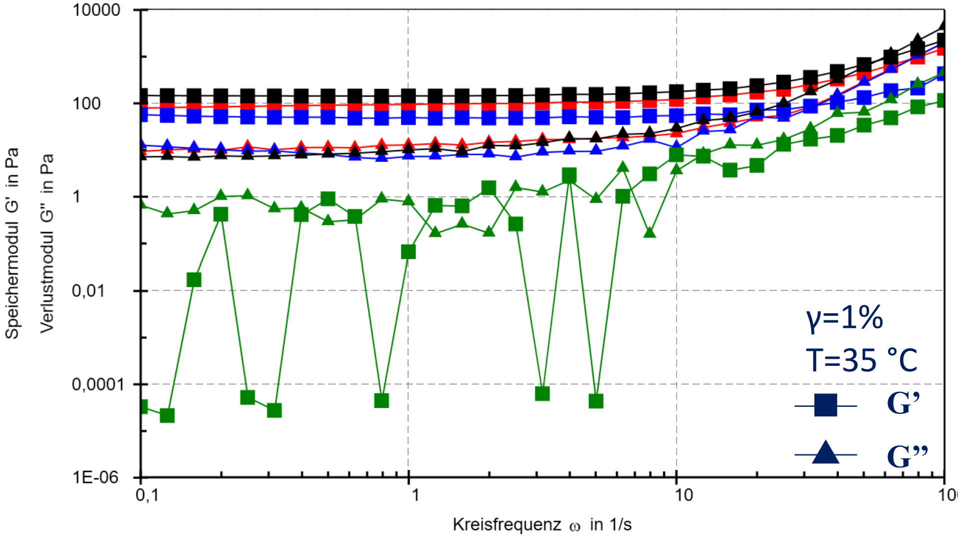


M : Tpy = 1 : 2

Iron is the only one that improves the modulus in both cases

Ni Co Zn Fe



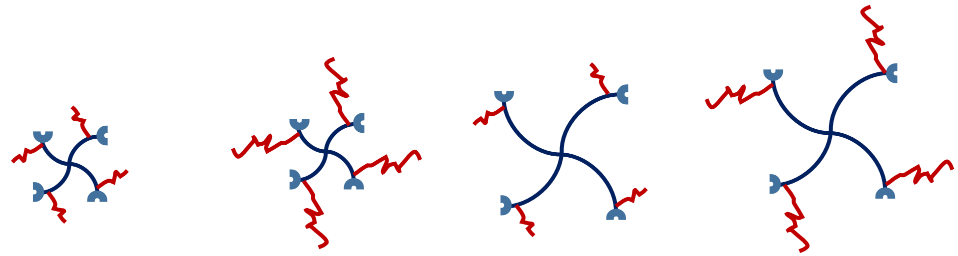


- Overall Ni, Co and Fe show very similar moduli
- Focus on Zn + one strong ion (Ni)
- And maybe a combination of the two?

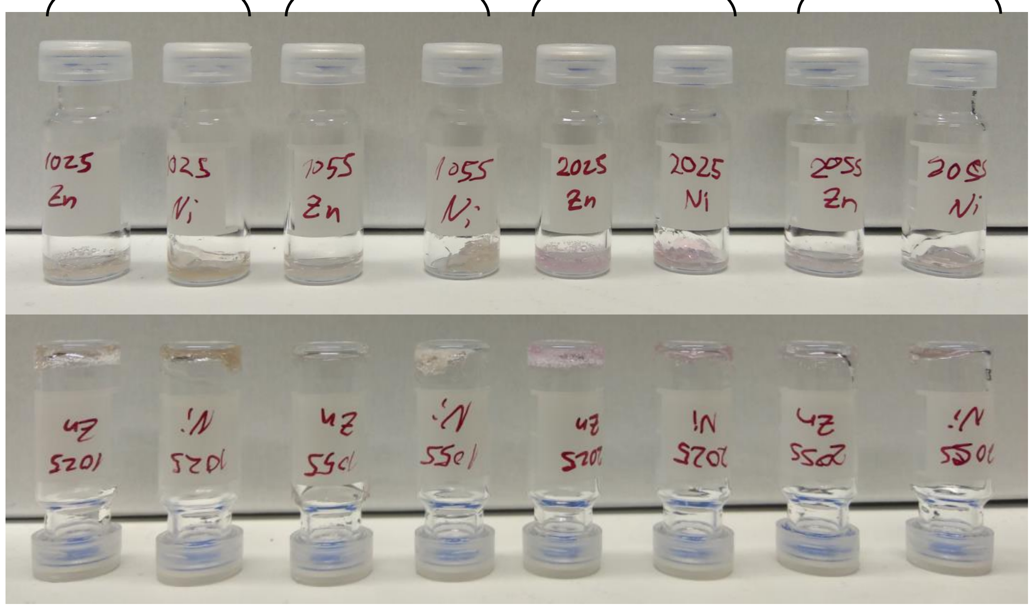
Zn

Zinc does not form a gel in the case of

20K Peg + 5.5 K Pnipam and 10K Peg + 5.5 K Pnipam



Peg	10 000 g/mol	10 000 g/mol	20 000 g/mol	20 000 g/mol
Pnipam	2 500 g/mol	5 500 g/mol	2 500 g/mol	5 500 g/mol

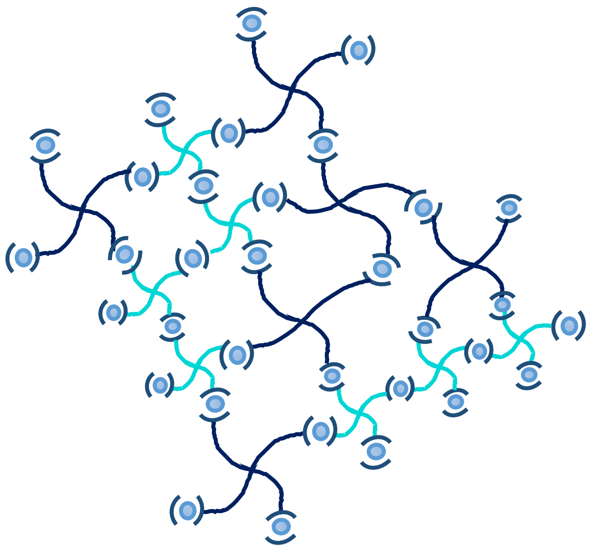


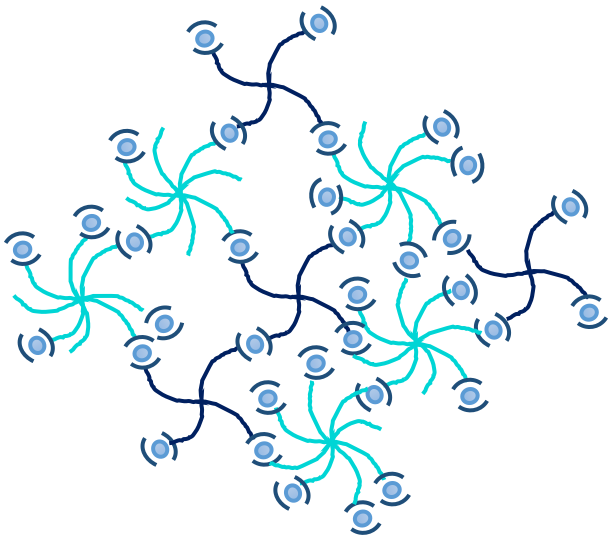
Conclusions and future plans (2)

- The non formation of a hydrogel with Zinc has to be further investigated
- Rheology curves have to be repeated with new measurement protocol

- Linear vs non linear rheology (FORTH)
- Extensional rheology at different Temperatures?

The role of network density and connectivity on the structure and dynamics of metallo-supramolecular hydrogels

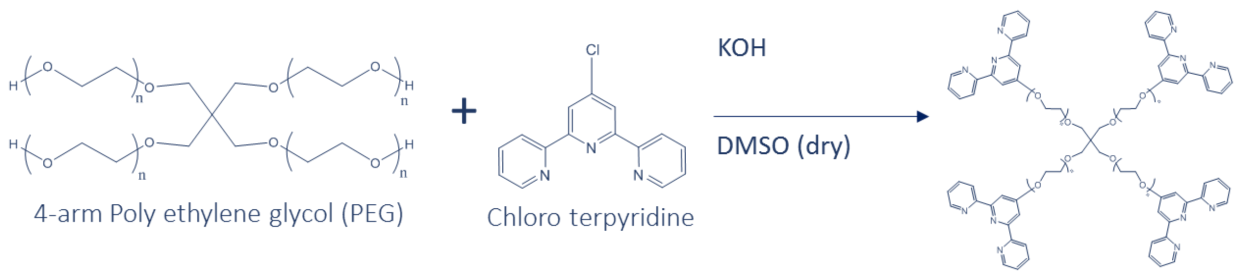




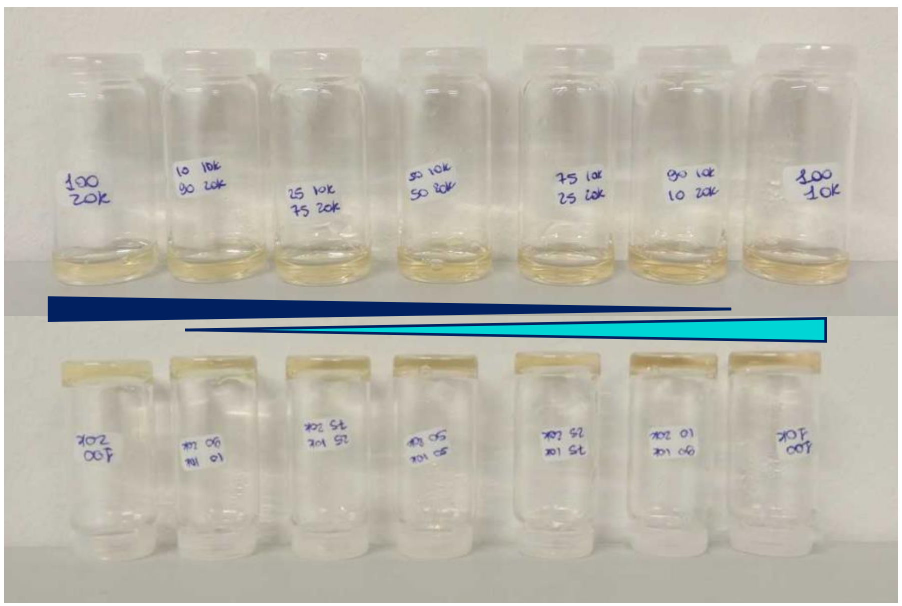
- ➢Same network connectivity
- ➢Different network density

- ➢ Different network connectivity
- ➢ Same network density

Synthesis and preparation of the Gels



100%



100%

The percentages for the gel were taken in Volume.

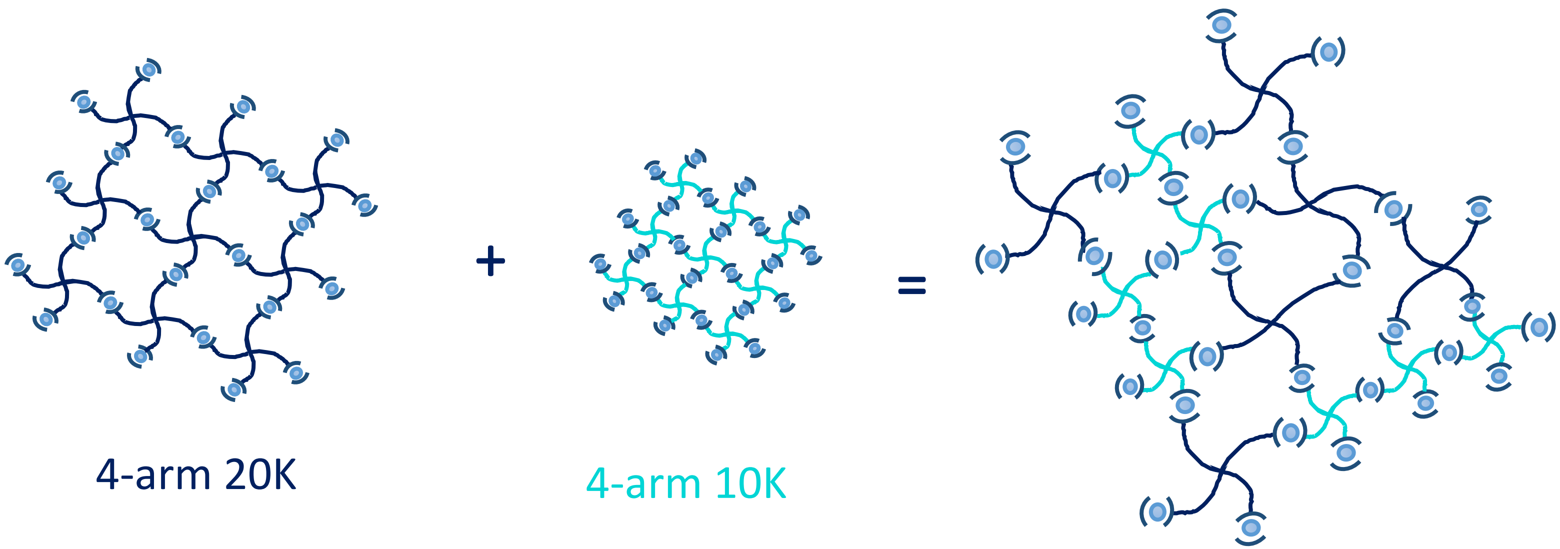
First the 2 solutions of Polymers were mixed and then the metal ion solutions were added.

The gel was centrifugated and equilibrated overnight.

Metal ion: Zinc (stoichiometric amount)

Solvent: water

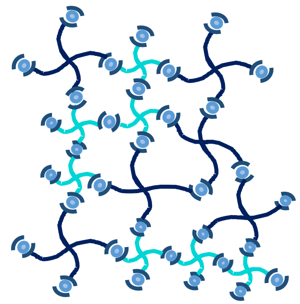
Different molar mass



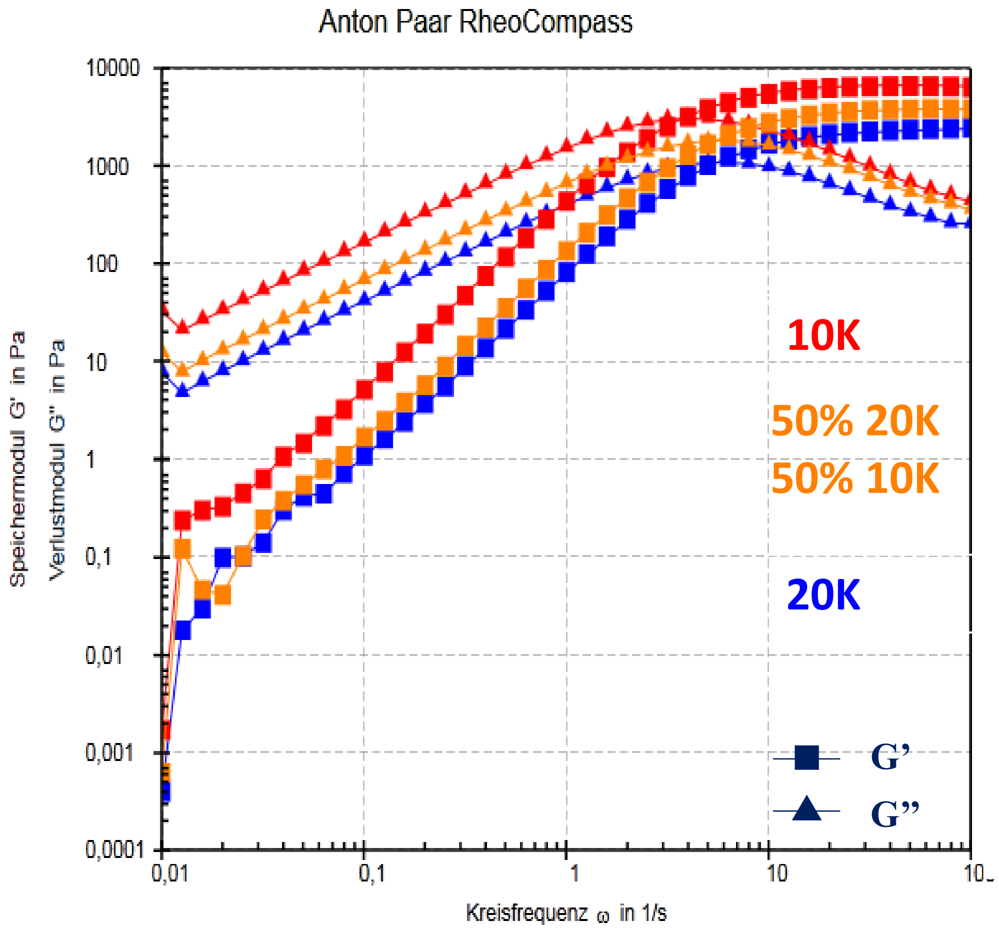
- Same branching
- Different molar mass

- Same network connectivity
- Different network density

4-arm 10K + 4-arm 20K, 2 x C*



10K A1 – 100%
20K A1 – 100%



ω=0.01-100 rad/s
γ=0.1%
T=25 °C

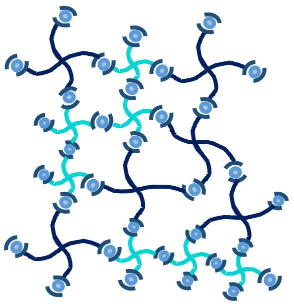
10 K = [112 g/L] = 2 x C*
20 K = [70 g/L] = 2 x C*

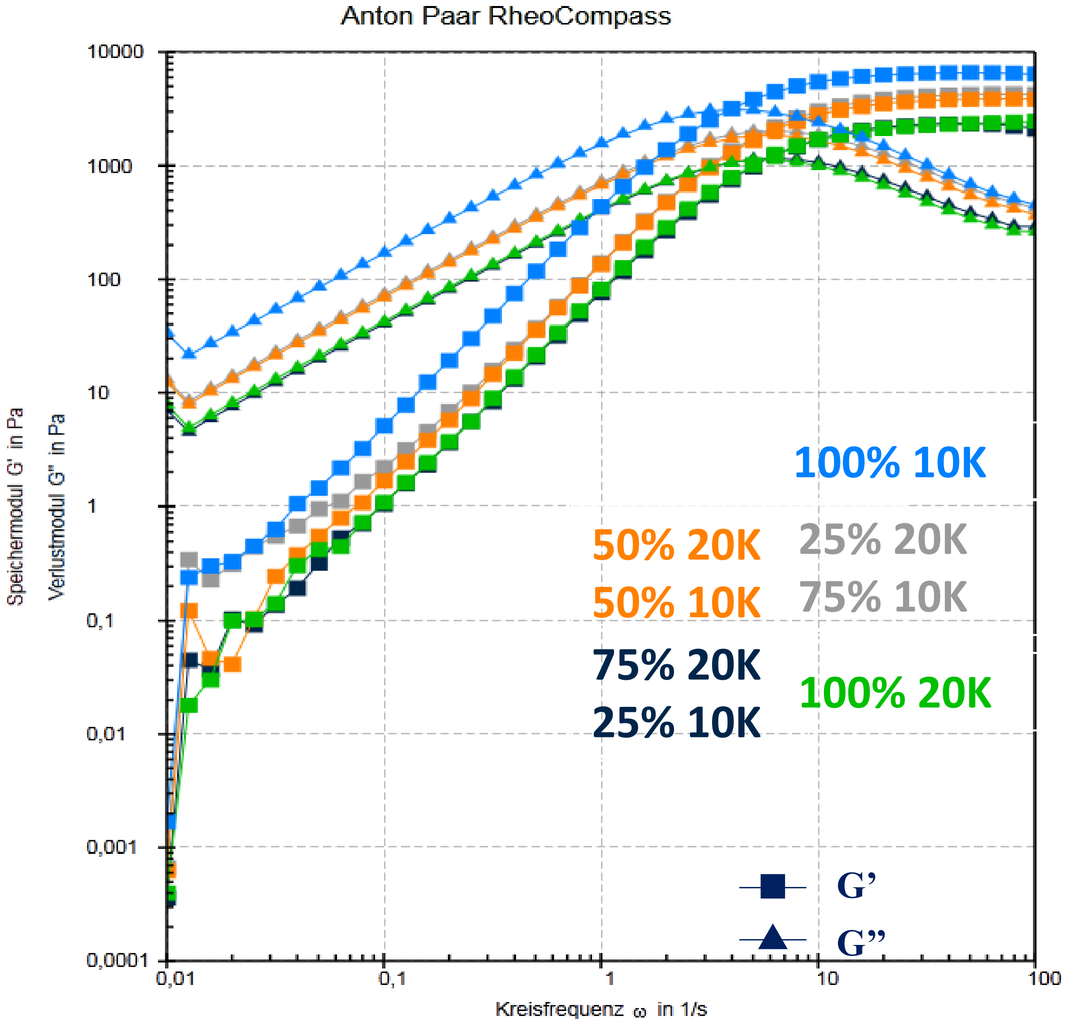
M : Tpy = 1 : 2

The 50% is in the middle.

It seems that the precursors contribute equally to the modulus

4-arm 10K + 4-arm 20K, 2 x C*





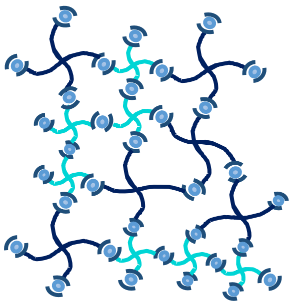
ω=0.01-100 rad/s
γ=0.1%
T=25 °C

10 K = [112 g/L] = 2 x C*
20 K = [70 g/L] = 2 x C*

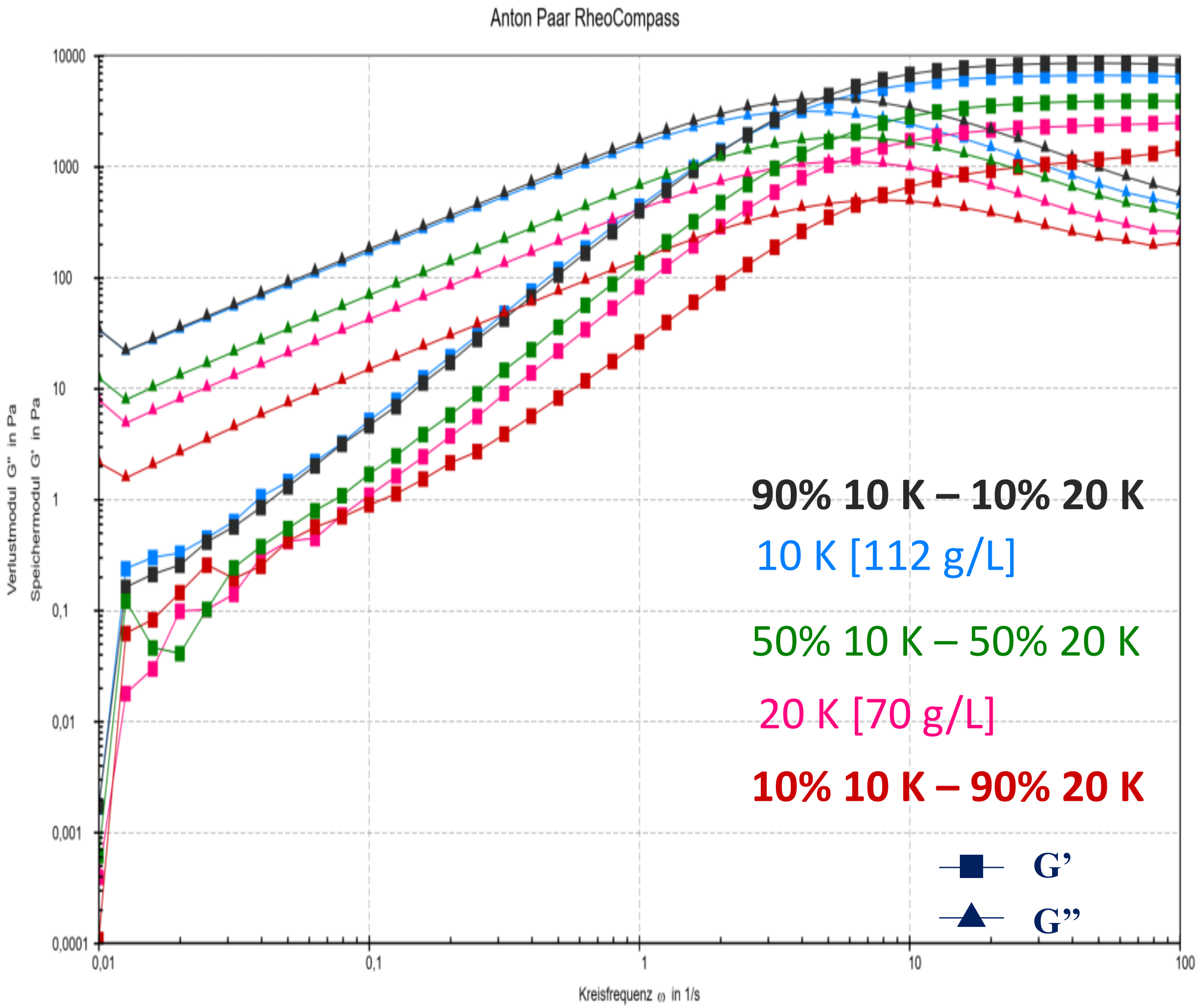
M : Tpy = 1 : 2

The one with the highest molar mass has more influence on the properties of the gel.

4-arm 10K + 4-arm 20K, 2 x C*



10K A1 – 100%
20K A1 – 100%



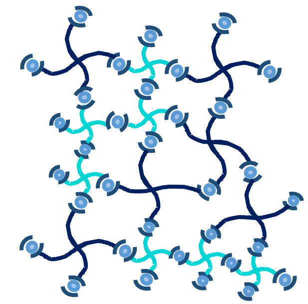
ω=0.01-100 rad/s
γ=0.1%
T=25 °C

10 K = [112 g/L] = 2 x C*
20 K = [70 g/L] = 2 x C*
M : Tpy = 1 : 2

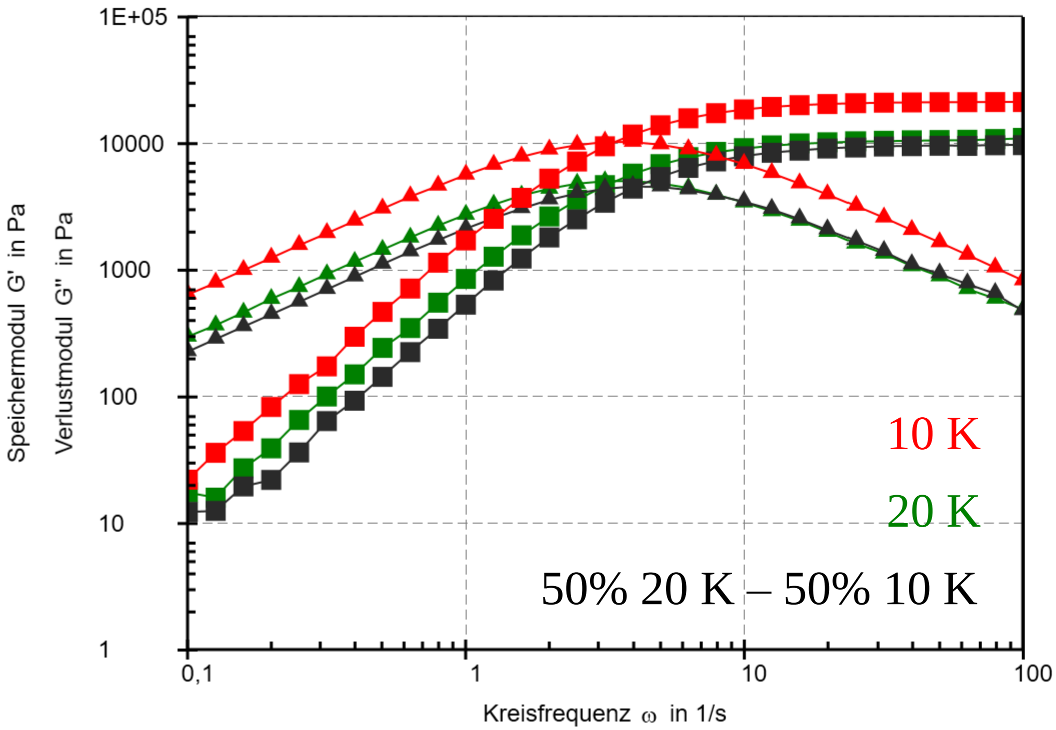
Introducing 10% of 20K, the modulus of 10K increases

Introducing 10% of 10K, the modulus of 20K decreases

4-arm 10K + 4-arm 20K, same C



10K A1 – 100%
20K A1 – 93%

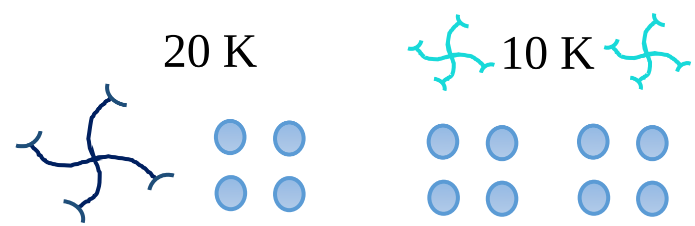


ω=0.01-100 rad/s
γ=0.1%
T=25 °C

■ G'
▲ G''

10 K = 20 K = [112 g/L]

N° 10 K = 2 x N° 20 K



The gel with 10K precursor has double modulus as the one with 20K precursor.

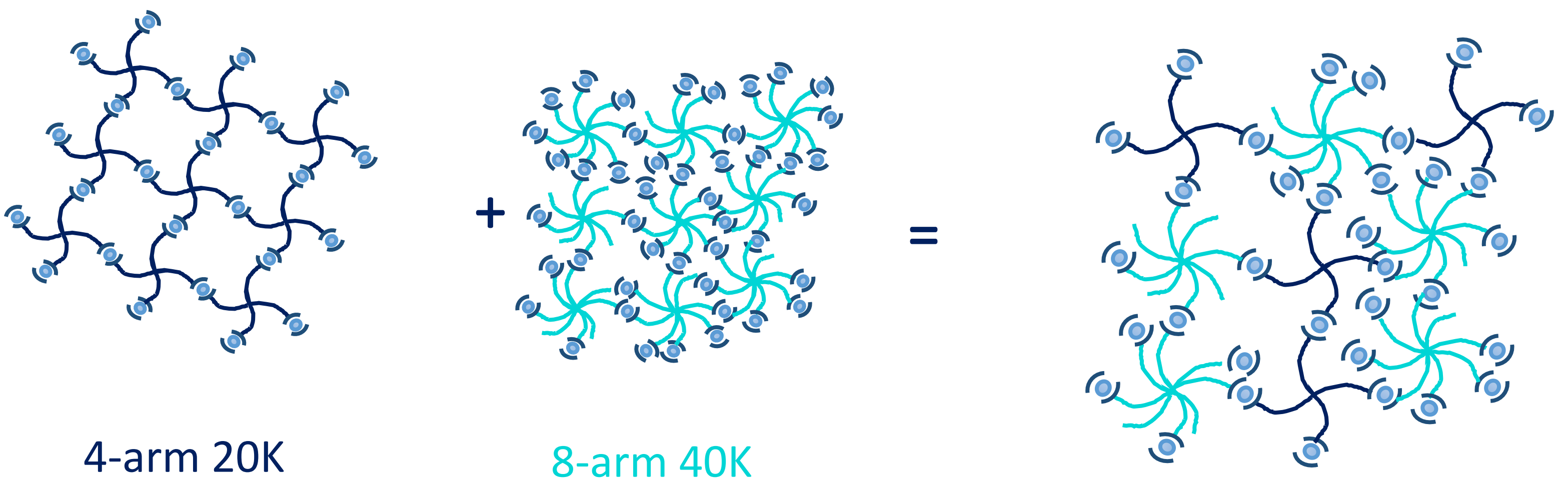
The bimodal gel has lower modulus.

10 K G° = 21183 Pa

20 K G° = 11022 Pa

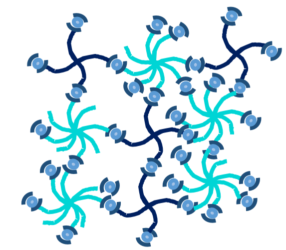
50% 20 K – 50% 10 K G° = 9660 Pa

Different number of arms

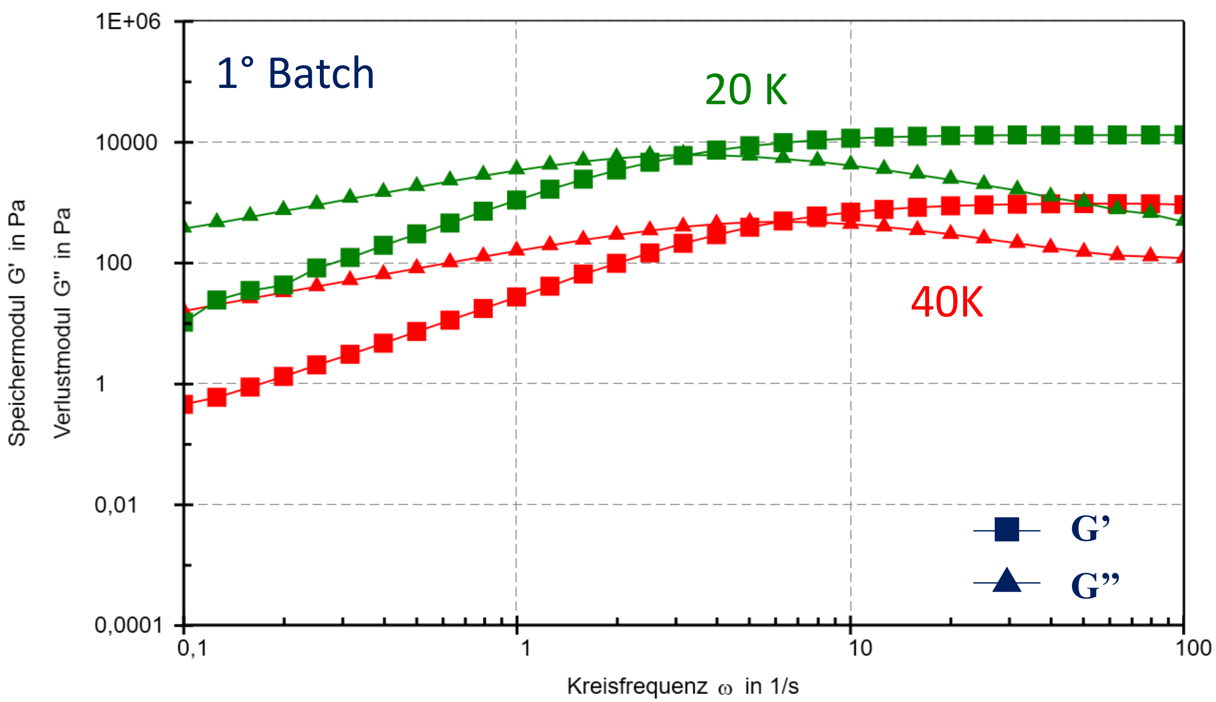


- Double molar mass (same arm length)
- Different branching
- Same network density
- Different network connectivity

8-arm 40K + 4-arm 20K, same C



40K A2 – 90%
20K A2 – 100%



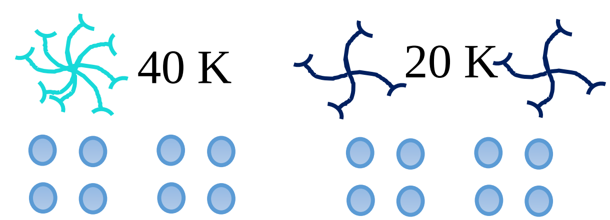
ω=0.01-100 rad/s
γ=0.1%
T=25 °C

M : Tpy = 1 : 2

20 K = 40 K = [70 g/L]

N° 20 K = 2 x N° 40 K

Same n° of bonds

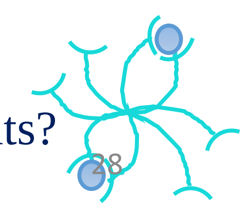


In the octa-Peg there is a higher density of arms at the core.

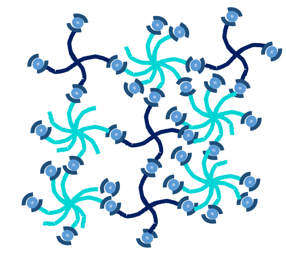
Therefore, it is more likely that two neighbour arms find each other creating shortcuts, than two adjacent stars.

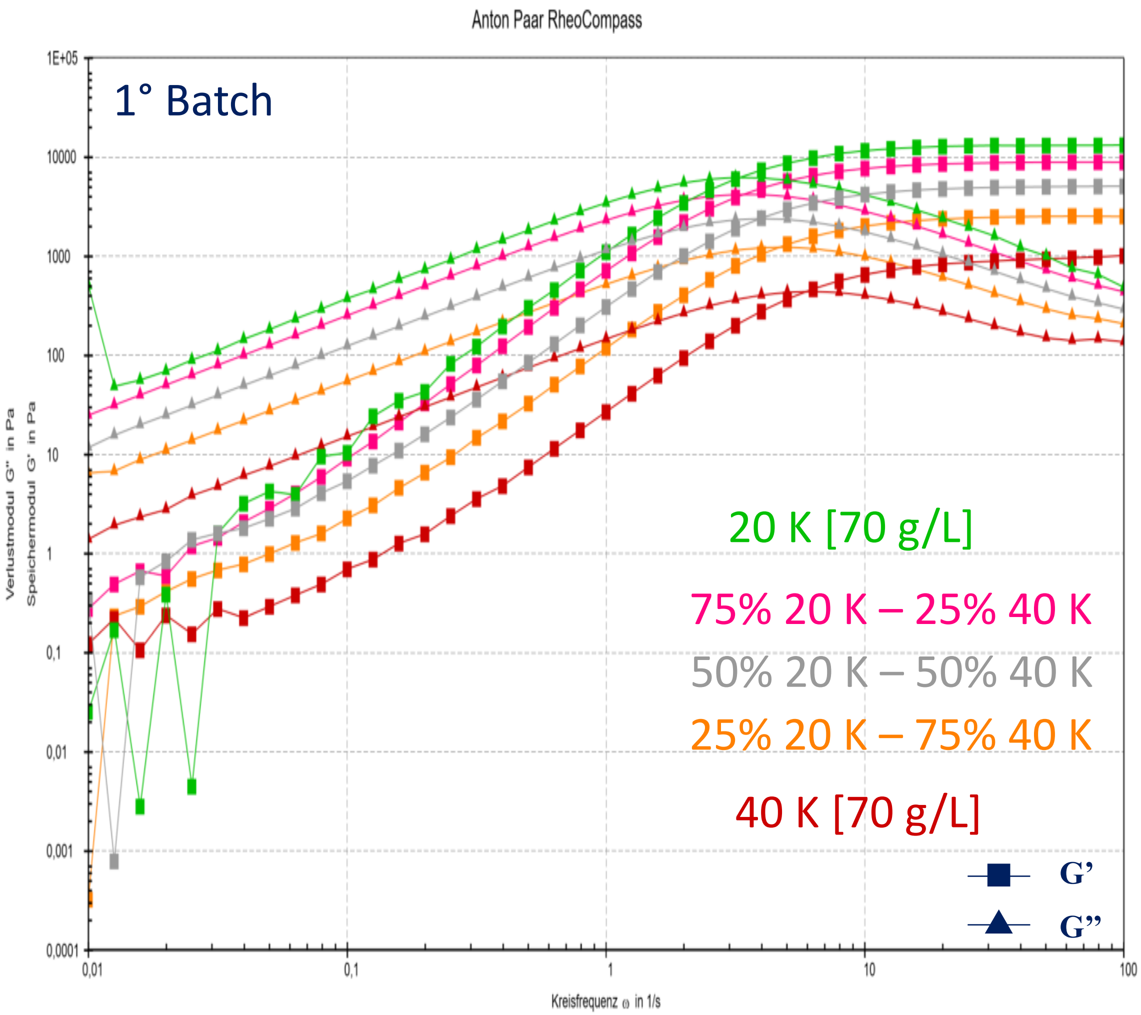
These shortcuts might explain the lower modulus.

Is the 40K creating short-cuts?



8-arm 40K + 4-arm 20K, same C





ω=0.01-100 rad/s

γ=0.1%

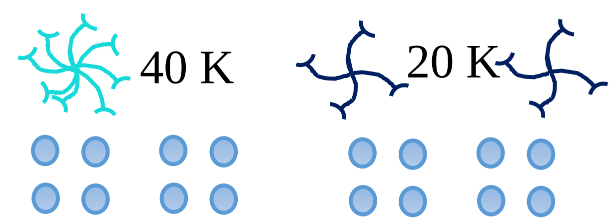
T=25 °C

M : Tpy = 1 : 2

20 K = 40 K = [70 g/L]

N° 20 K = 2 x N° 40 K

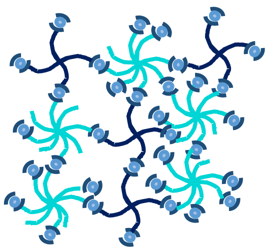
Same n° of bonds

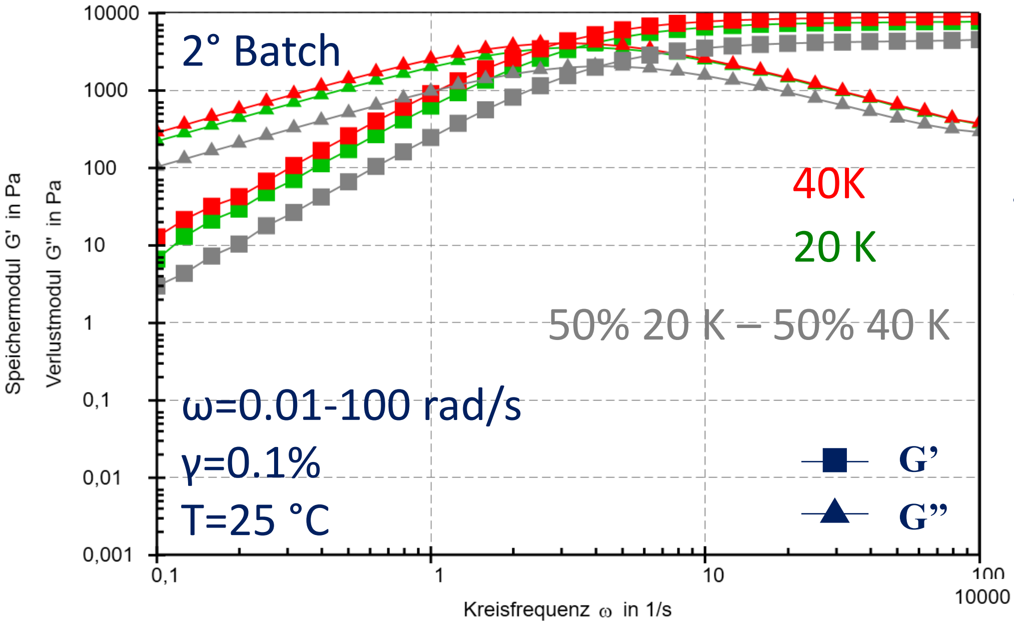


All the percentages are in the middle

8-arm 40K + 4-arm 20K, same C

40K A3_J2 – 88%
20K A3_J2 – 93%

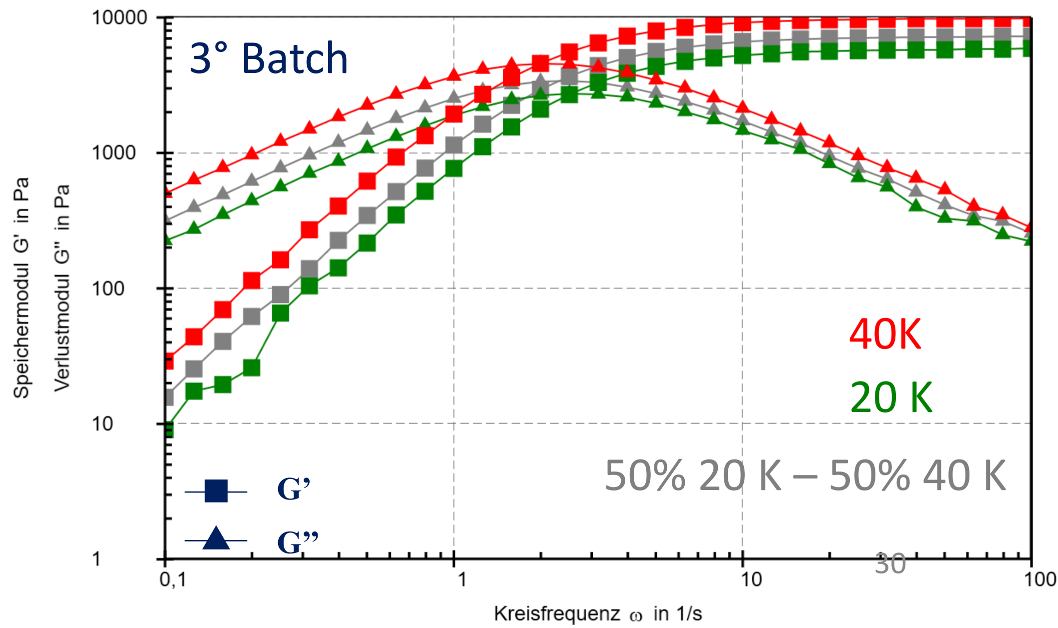




In this case, 40K has slightly higher modulus.

The functionalization is still lower, but closer to the 20K.

Why has the 50% sample lower modulus?

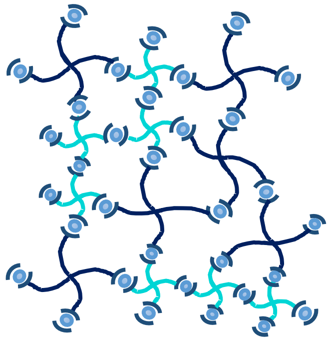


In this case, 40K has higher modulus and the 50% is in the middle.

Why it is not consistent?

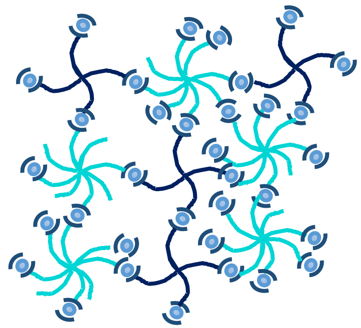
In progress:

4-arm 20K + 4-arm 40K



- Same network connectivity
- Different network density

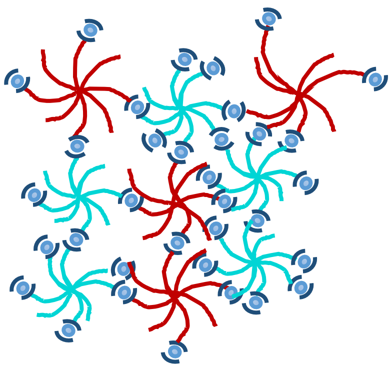
4-arm 20K + 8-arm 40K



- Different network connectivity
- Same network density

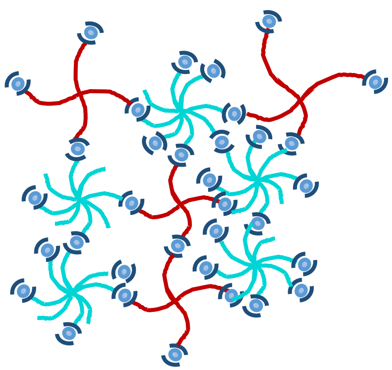
Do?

8-arm 20K + 8-arm 40K



- Same network connectivity
- Different network density

4-arm 40K + 8-arm 40K

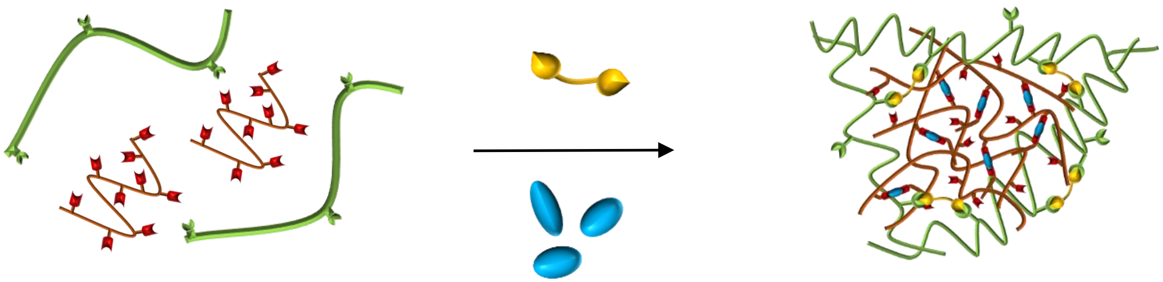


- Different network connectivity
- Different network density

Conclusions and future plans (3)

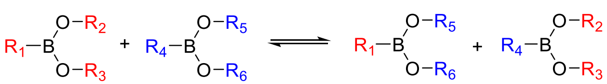
- It is possible to tune the properties by changing the network density or network connectivity
- However, to fully control it, further studies are required
- The bimodal gel with tetra- and octa-Peg needs reproducibility
- Modelling would be beneficial
- Double quantum NMR can give more insights about heterogeneities (is planned)
- Extensional rheology would be interesting

Double Network elastomer based on dynamic covalent bonds

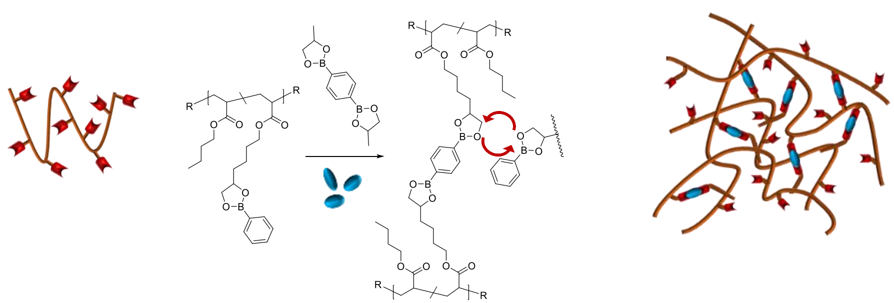


Larissa Hammer

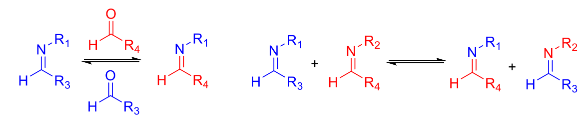
Boronic ester exchange:



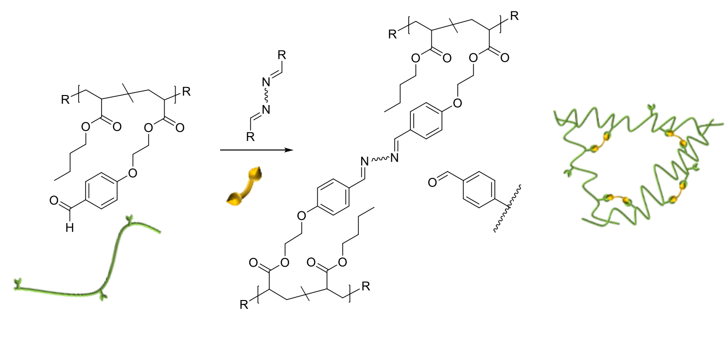
$Mw_{polymer}$ = 78 000 g/mol
$Mw_{crosslinker}$ = 245.88 g/mol



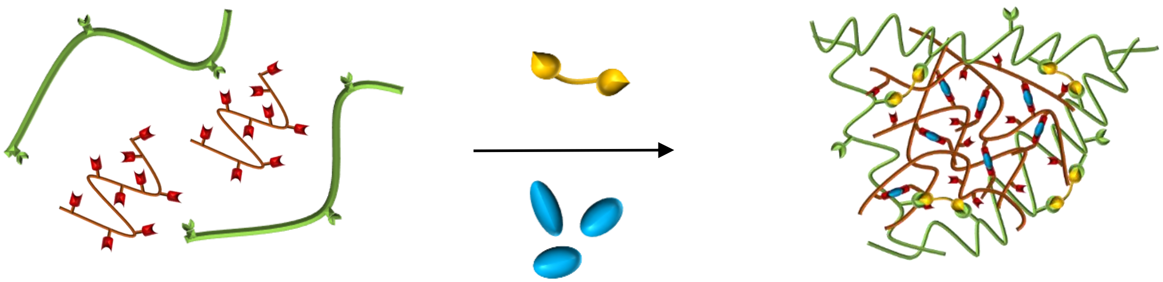
Imine/Aldehyde and Imine/Imine exchange:



$Mw_{polymer}$ = 438 000 g/mol
$Mw_{crosslinker}$ = 292.43 g/mol

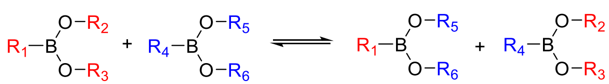


Double Network elastomer based on dynamic covalent bonds



Larissa Hammer

Boronic ester exchange:



$Mw_{polymer}$ = 78 000 g/mol
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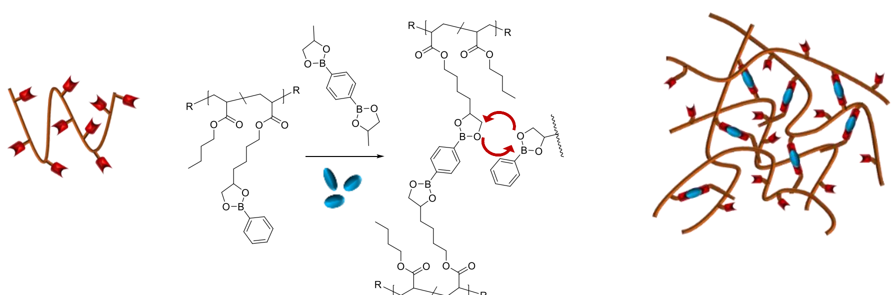
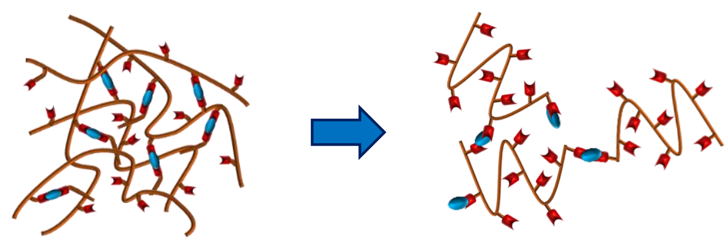
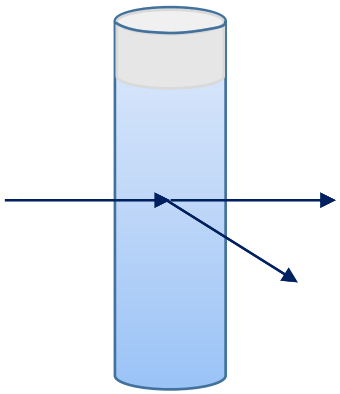


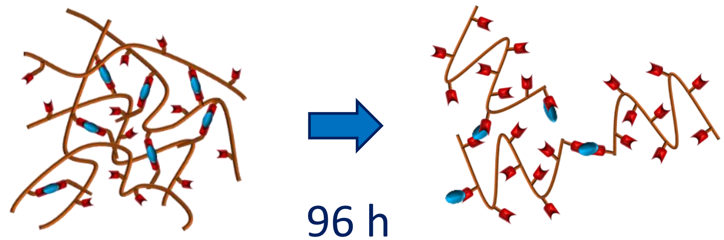
Degradation over time



Degradation over time

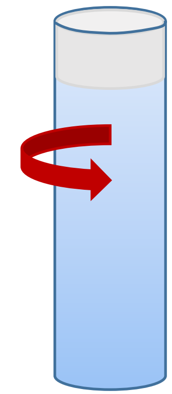
- Light scattering





Non ergodic

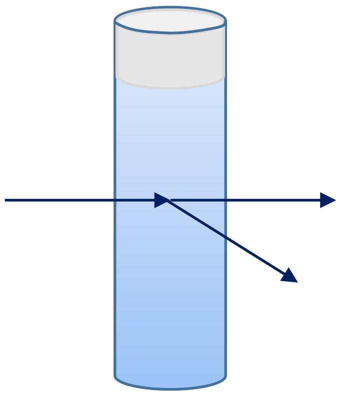
500 positions

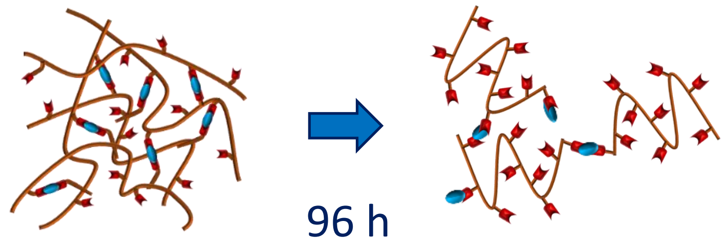


5 measurements days!

Degradation over time

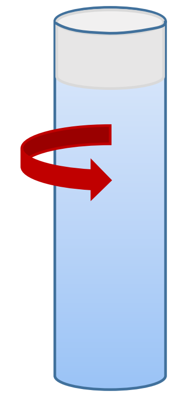
- Light scattering





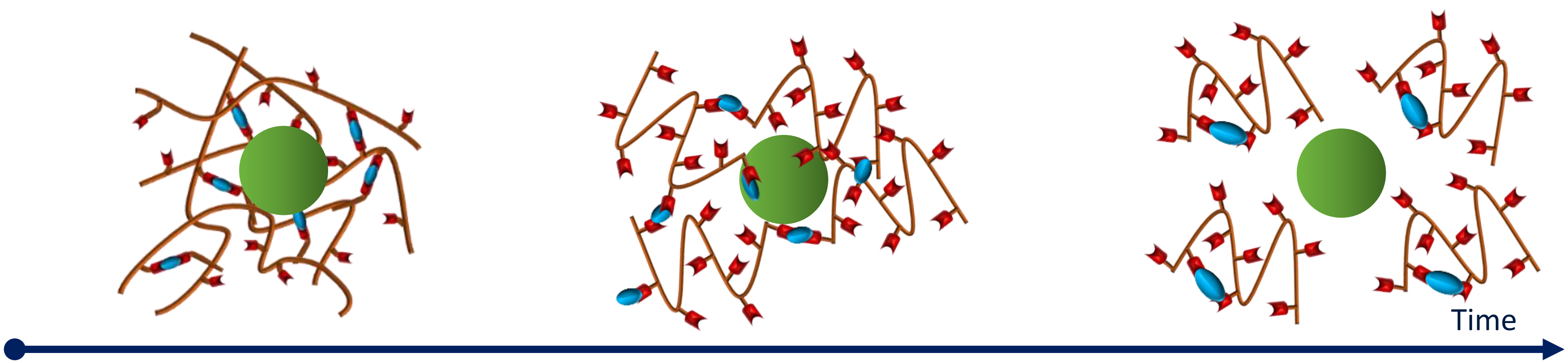
Non ergodic

500 positions



5 measurements days!

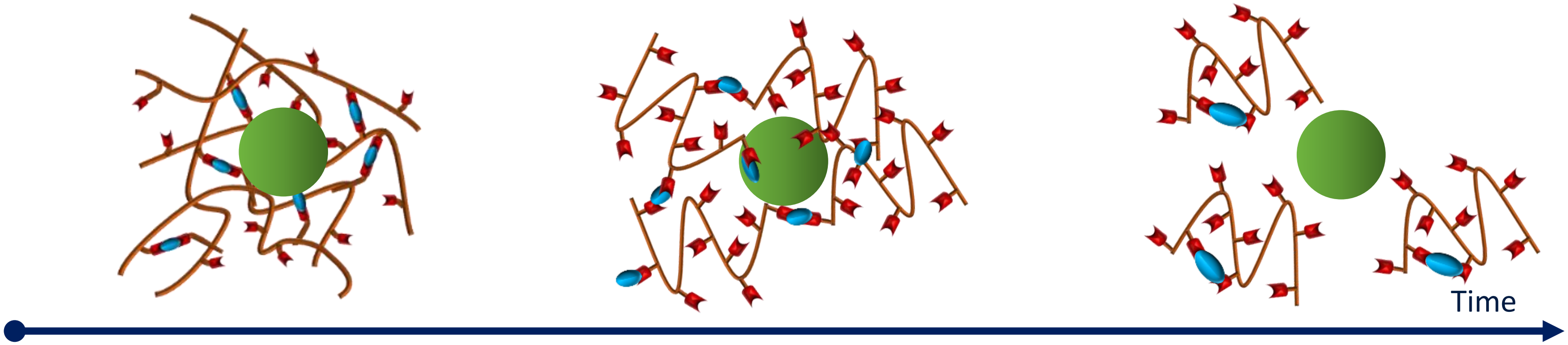
- Fluorescence Correlation Spectroscopy (probe diffusion)



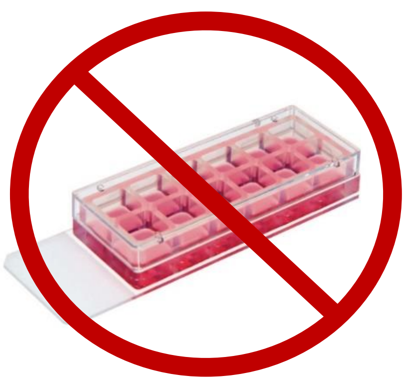
Variations on the diffusion coefficient over time

Degradation over time

- Fluorescence Correlation Spectroscopy

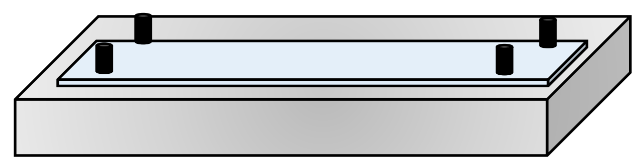


Variations on the diffusion coefficient over time



THF

Evaporation!



Custom made
Solvent chamber

Future Plans (Global)

- Continue the characterization of the samples of Larissa
- DQ-NMR for better understanding the role of connectivity and network density in supramolecular hydrogels
- Repeat measurements on thermo-responsive double networks with new protocol
- Investigate further the non-gelation of Zinc
- Influence on rheological properties of different lenghts of Pnipam (Forth)
- Diffusion in the double dynamic thermo-responsive network with the variation of the Temperature (FCS/Frap)
- Extensional rheology

➢ Exchange of samples

Thank you for your attention