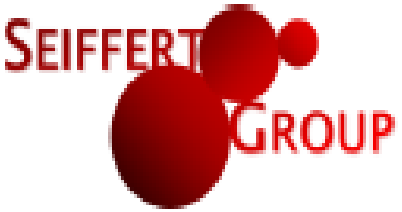
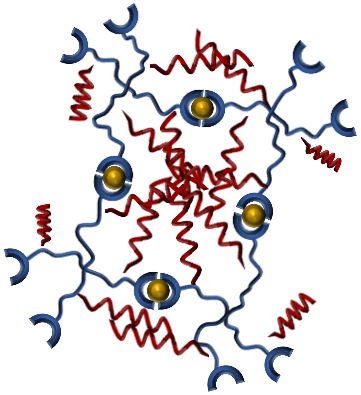
Connectivity-tailored properties in dual dynamic networks

Paola Nicolella

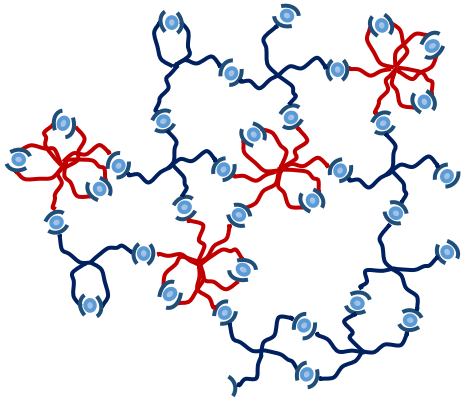
Montpellier, 22th October 2021



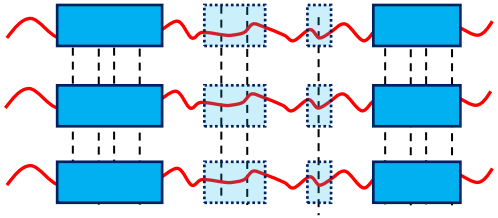
Connectivity



How to control connectivity in our sample through application of external stimuli

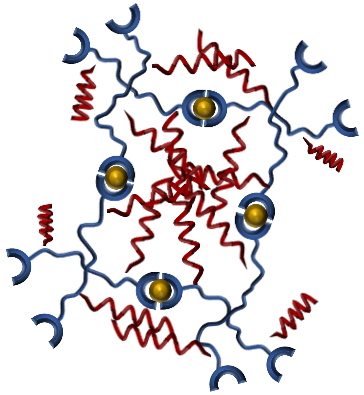


How connectivity changes when we introduce known defects in our sample



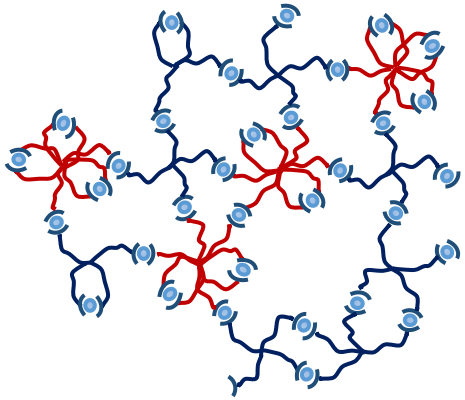
How crystallinity changes with temperature and how we can follow changes in the sample

Connectivity



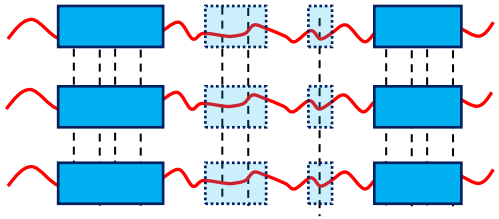
Mechanical switching of a comb-like dual-dynamic polymer network

Nicolella P., Lauxen D., Ahmadi M., Seiffert S.
[to be submitted in the special issue]



Defect-controlled softness, diffusive permeability, and mesh-topology of metallo-supramolecular hydrogels

Nicolella P., Koziol M. F. , Löser L., Saalwächter K., Ahmadi M., Seiffert S.
[recently submitted in Soft Matter]



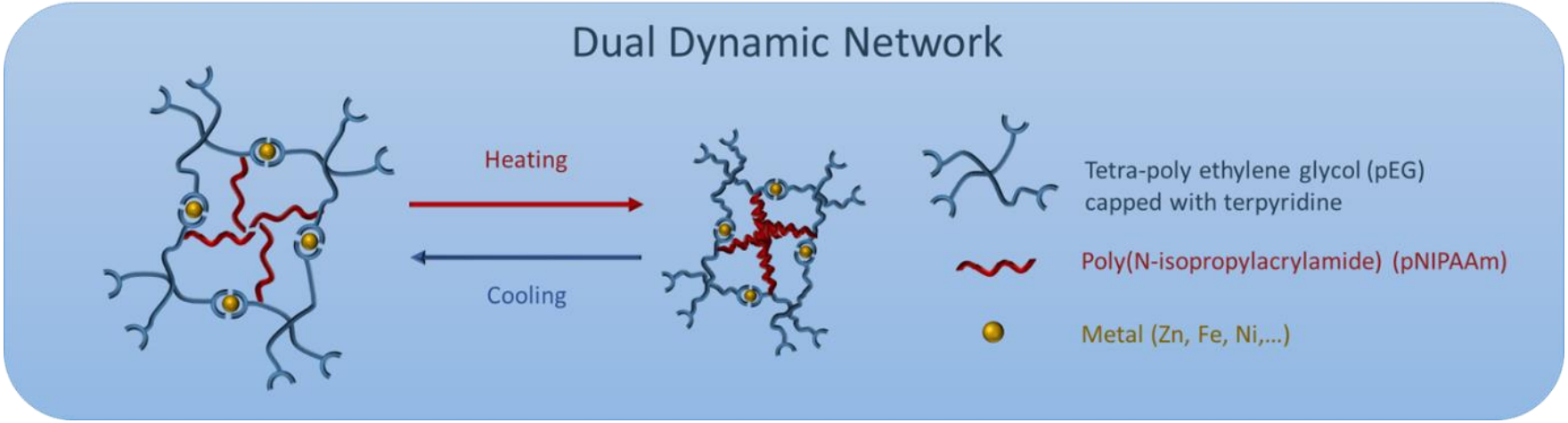
Effect of block length and polydispersity on the network connectivity and temperature resistance of model soft TPE

Sbrescia S., Nicolella P., Engels T., Seitz M., [submitted for the special issue]

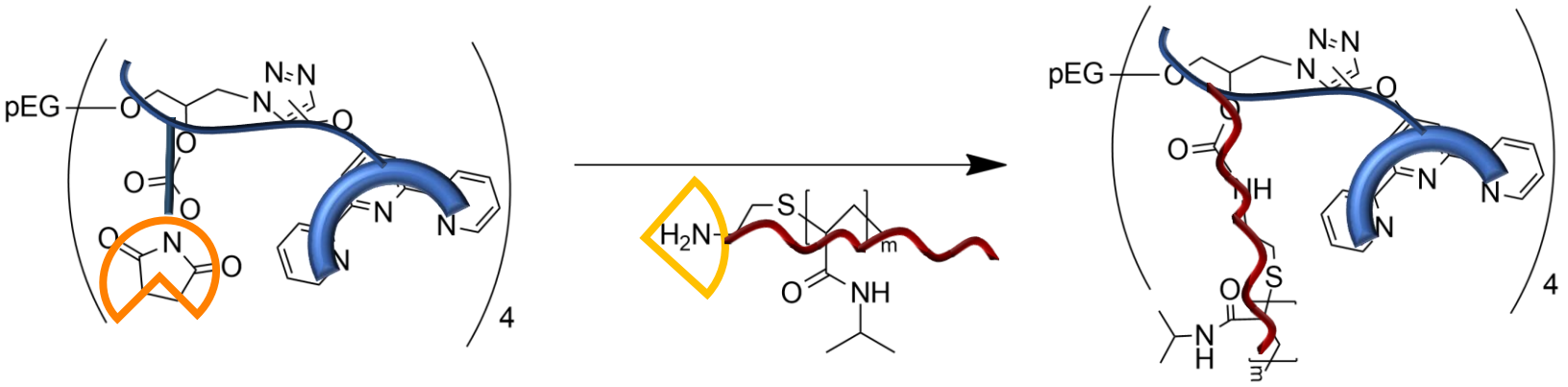
DSM
BRIGHT SCIENCE. BRIGHTER LIVING.

Saved for later

How to control connectivity in our sample through application of external stimuli



Synthesis



tetra-pEG-terpyridine-NHS

10 kg mol^{-1}

20 kg mol^{-1}

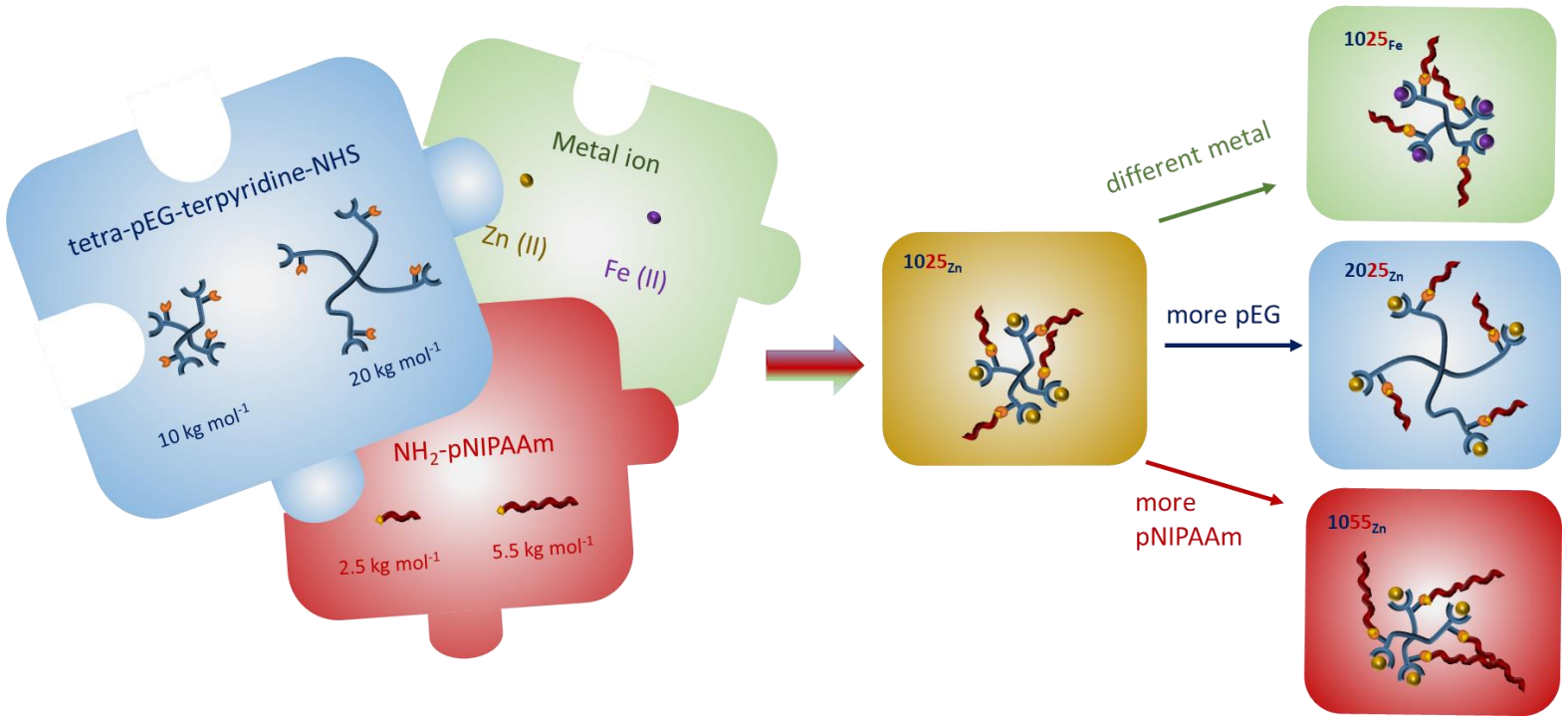
NH_2-pNIPAAm

2.5 kg mol^{-1}

5.5 kg mol^{-1}

P. Nicolella, D. Lauxen, M. Ahmadi, and S. Seiffert, “Reversible Hydrogels with Switchable Diffusive Permeability,” Macromol. Chem. Phys., vol. 222, no. 16, p. 2100076, 2021

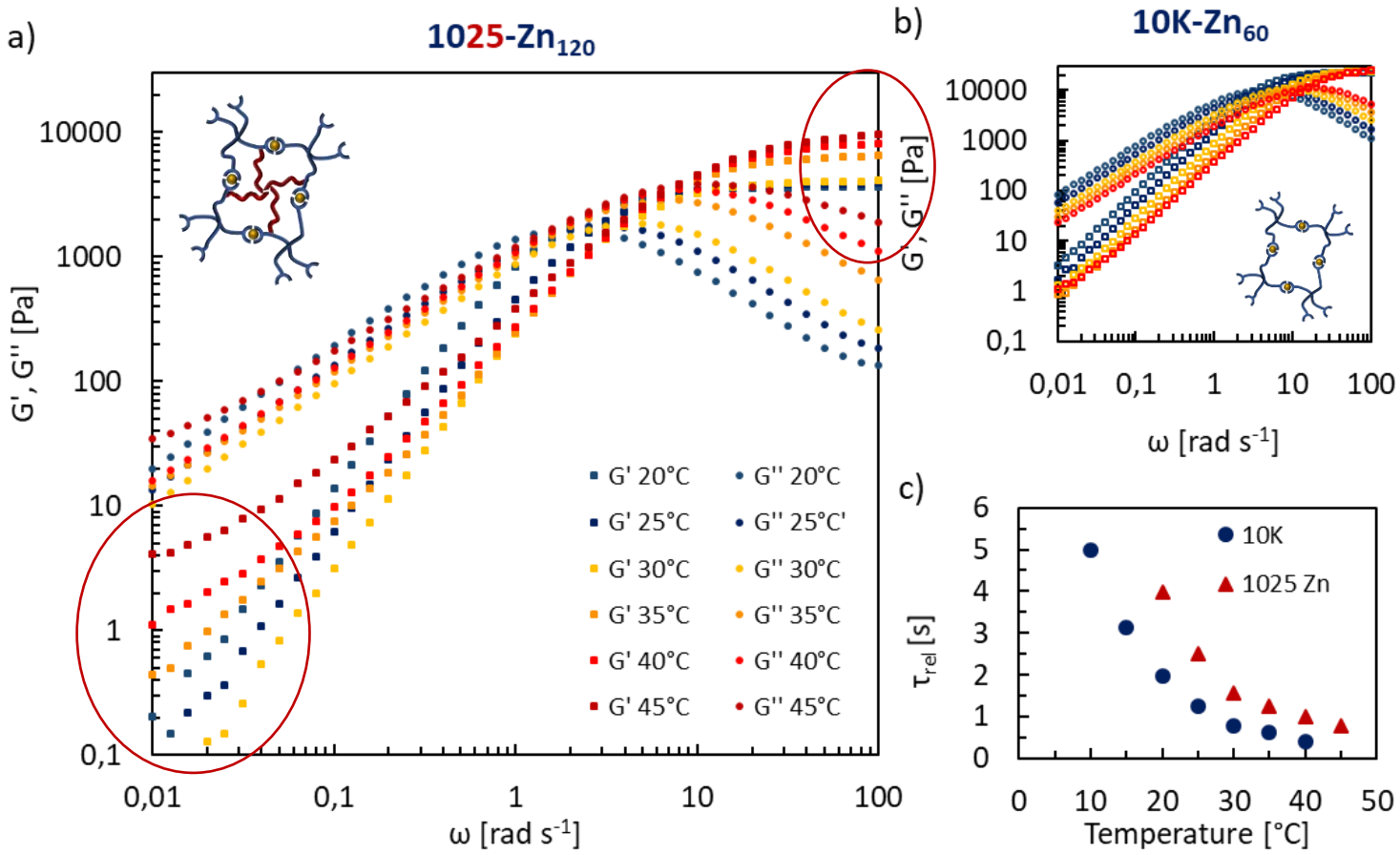
Tool-kit for dual dynamic networks



Sample	*pEG*	*pNIPAAm*	*Metal*	*Concentration*
10K-Zn$_{60}$	10 kg mol^{-1}	-	Zn	**60 g L^{-1}**
1025-Zn$_{120}$	10 kg mol^{-1}	2500 g mol^{-1}	Zn	**120 g L^{-1}**
1025-Fe$_{120}$	10 kg mol^{-1}	2500 g mol^{-1}	Fe	**120 g L^{-1}**
1025-Zn$_{85}$	10 kg mol^{-1}	2500 g mol^{-1}	Zn	**85 g L^{-1}**
1055-Zn$_{192}$	10 kg mol^{-1}	5500 g mol^{-1}	Zn	**192 g L^{-1}**
2025-Zn$_{70}$	20 kg mol^{-1}	2500 g mol^{-1}	Zn	**70 g L^{-1}**

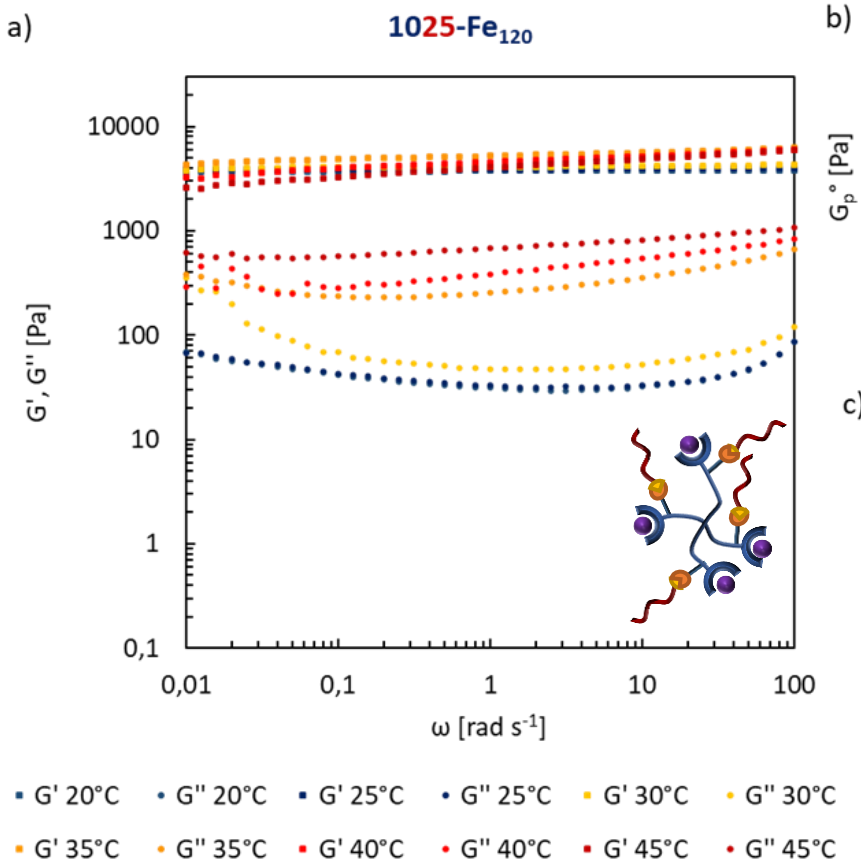
Constant metal-complex concentration

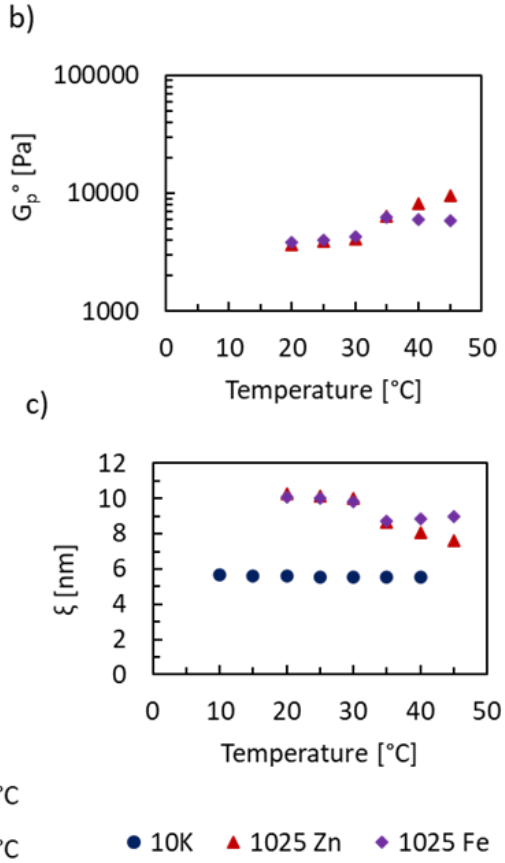
Dual vs Single network



- The dual network shows constant plateau modulus (like the single network) up to the LCST
- Above the LCST the plateau modulus increases
- Above the LCST a second plateau occurs
- The relaxation time shifts with temperature

Dual network with different metal





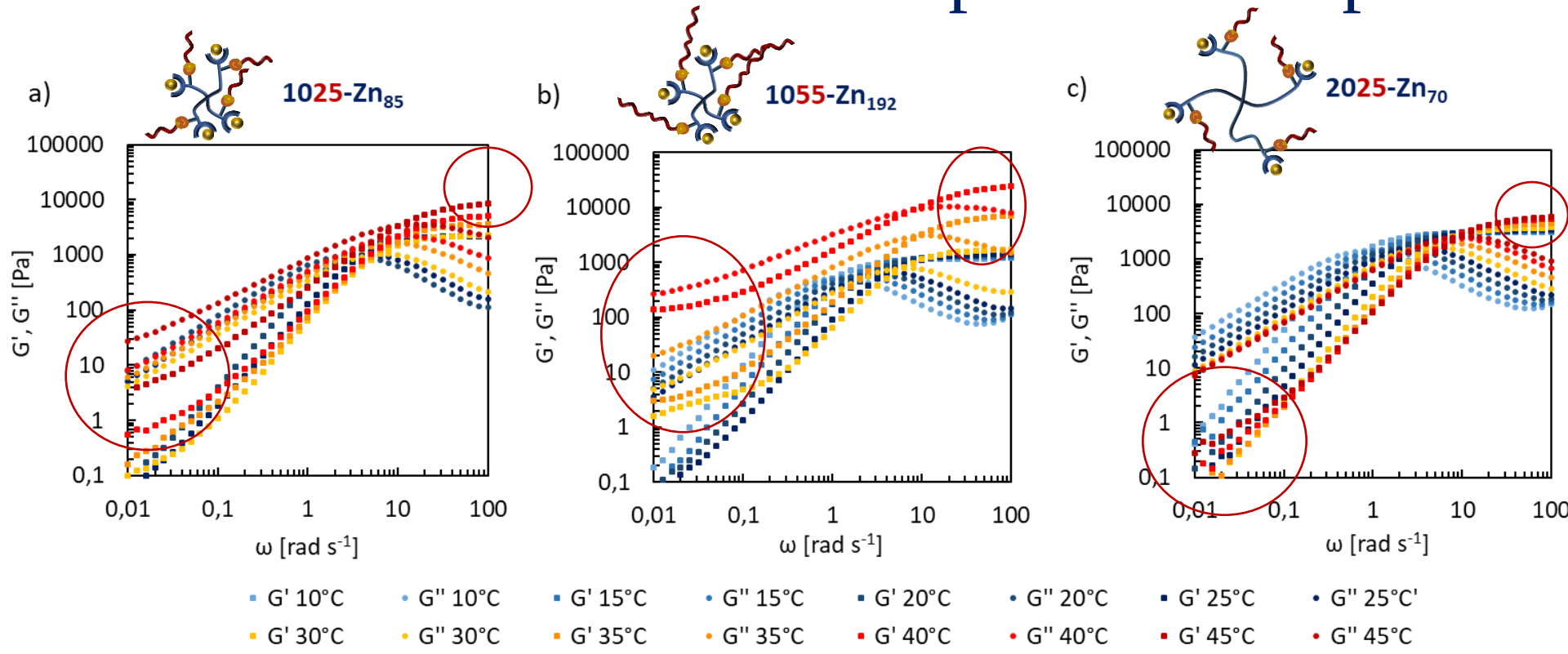
- The dual network with iron shows constant plateau up to the LCST, then it increases and stays constant
- The plateau modulus of the dual network with zinc is constant below LCST and then continues to increase

- The mesh-size of the single network stays constant
- The one of the dual network with iron decreases above LCST and then stays constant
- The mesh-size of the dual network with zinc is constant below LCST and then linearly decreases

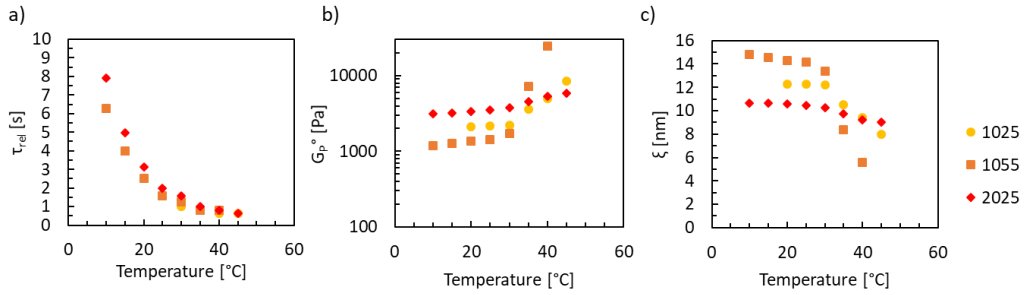
- The dual network with iron shows constant plateau up to the LCST
- Above the LCST, the elastic modulus show linear increase with frequencies

Is there for iron a configuration ‘before’ and a configuration ‘after’ the LCST?
While the network with zinc continues to adjust?

Dual network with different pNIPAAm / pEG



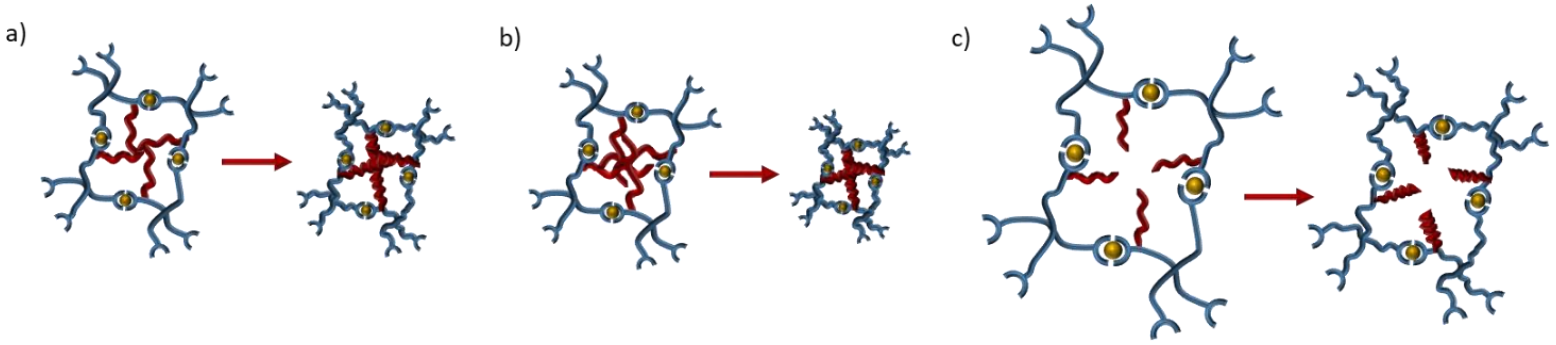
- The plateau modulus increase above LCST is higher with higher amount of pNIPAAm
- The same trend is valid for the second plateau at low frequencies



- The relaxation time is the same for all (small deviations for 2025)
- The plateau modulus and the mesh-size change with temperature is different

Summary and Conclusions

By playing with different pEG / pNIPAAm and metal ions we can build a toolkit that allows us to change the elastic properties on demand

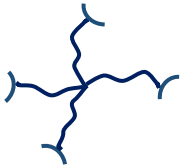


- With increasing pNIPAAm chains the plateau modulus increases more -> pNIPAAm chains are longer and can find themselves more (and collapse together)
- The sample with more pEG than pNIPAAm has a behavior similar to the single network -> the pNIPAAm chains collapse on themselves rather than together

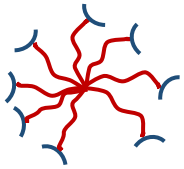
Questions or suggestions?

Part 1

How connectivity changes when we introduce known defects in our sample



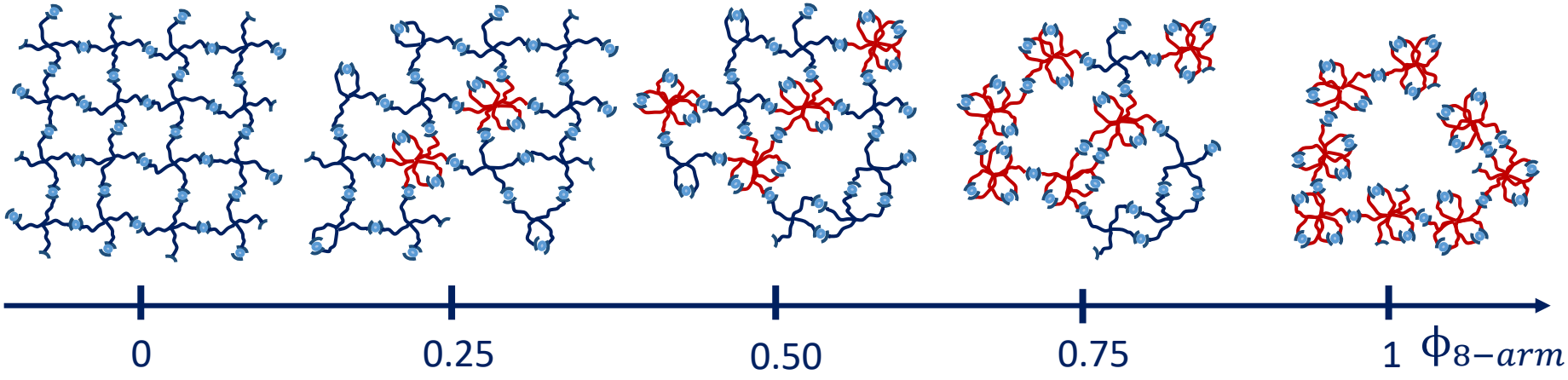
4-arm pEG-terpyridine 20 000 g mol^{-1}



8-arm pEG-terpyridine 40 000 g mol^{-1}

<u>4-arm / 8-arm</u>

- Same arm length
- Same mesh-size
- Same n° terpyridine stickers
- Same potential n° of connections



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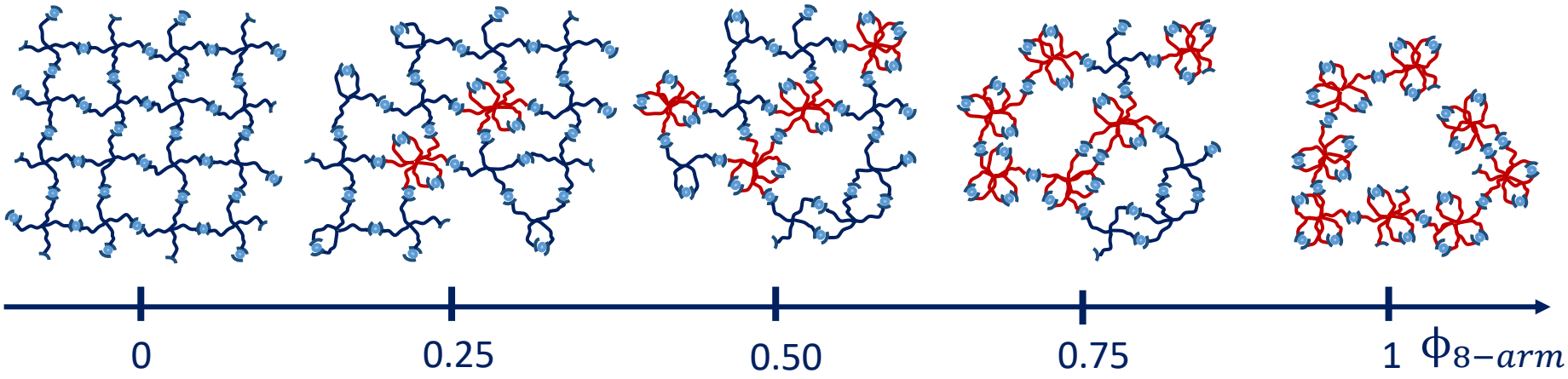
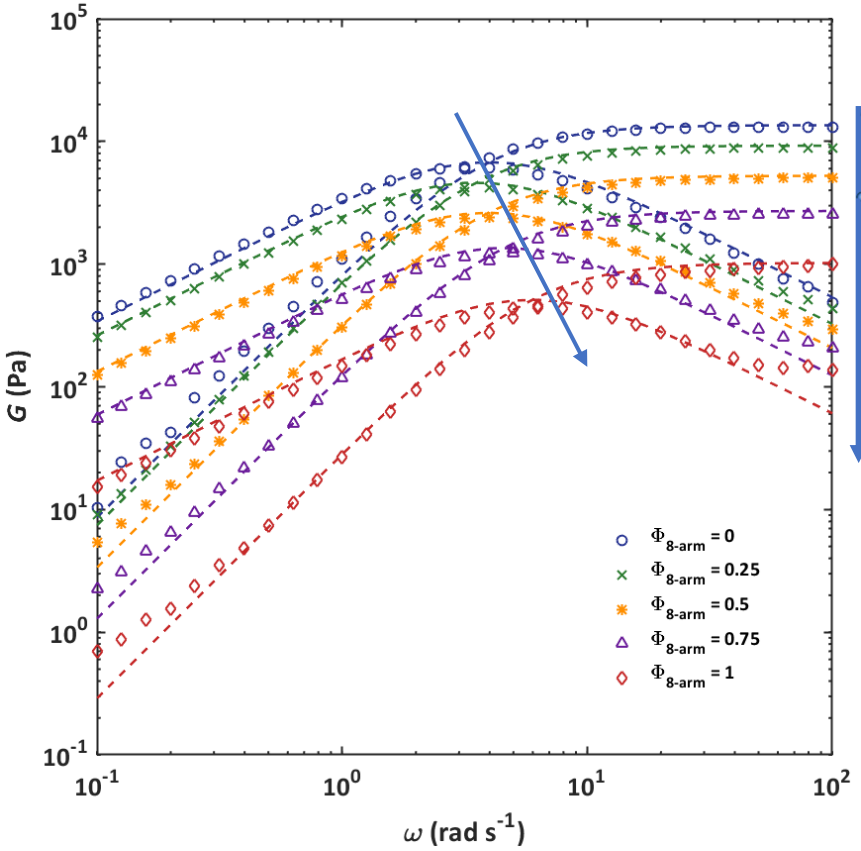


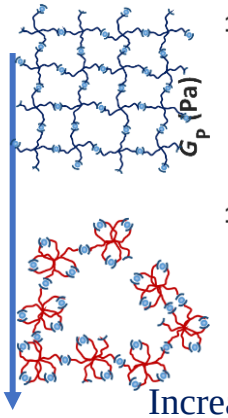
Macro-elastic properties -> oscillatory shear rheology

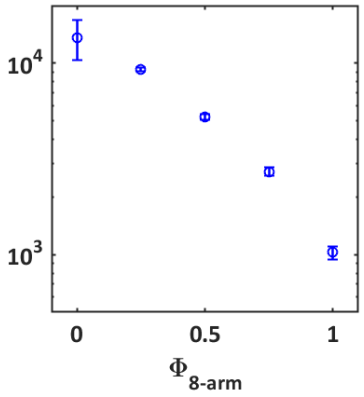
Micro-structure -> fluorescence recovery after photobleaching (FRAP)

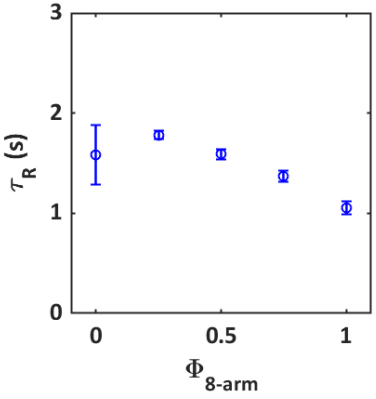
Defects on the nano-scale-> DQ-NMR

Oscillatory shear Rheology



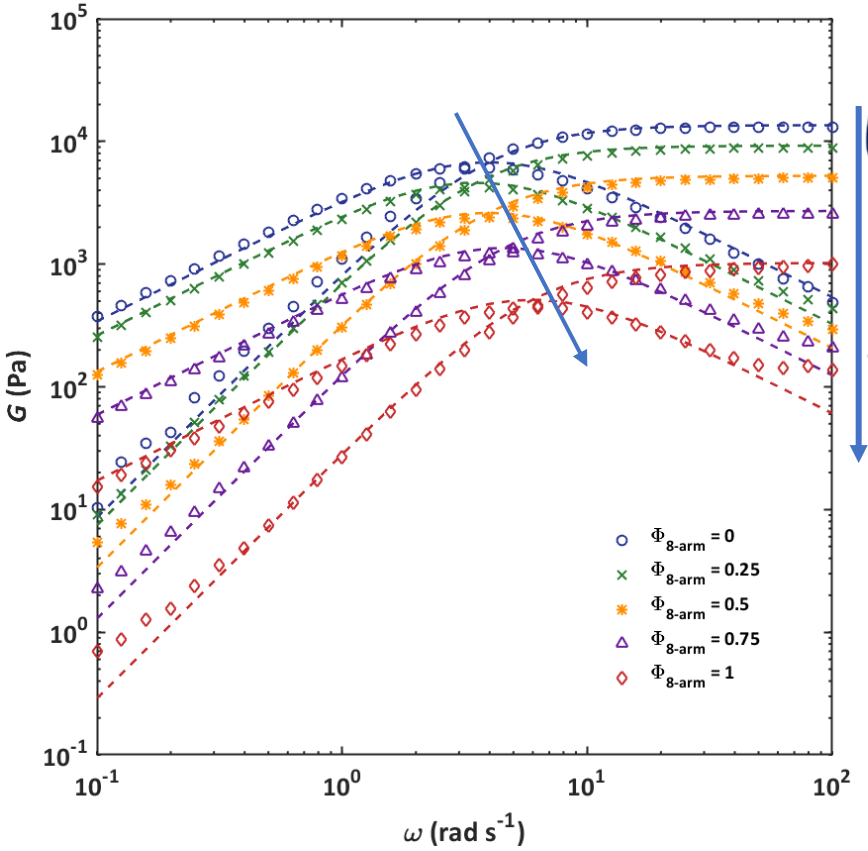






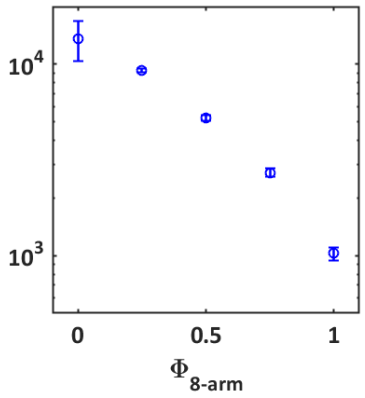
Increasing 8-arm pEG in the network **the plateau modulus and the relaxation time decrease systematically**

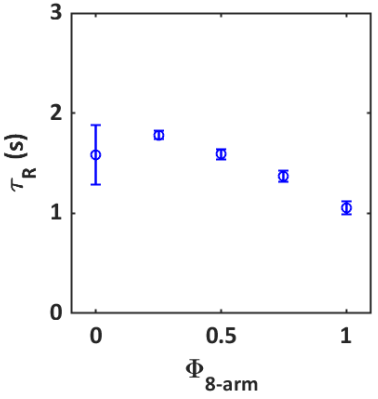
Oscillatory shear Rheology



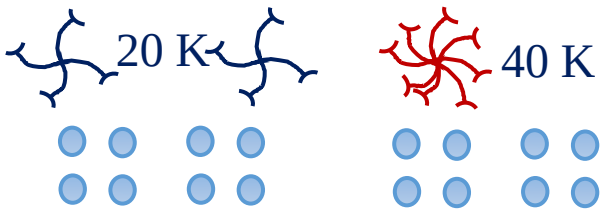
$$G^{\circ}_{N_{Affine}} = \nu RT$$

$$\nu = \frac{\mu * f}{2}$$





Increasing 8-arm pEG in the network **the plateau modulus and the relaxation time decrease systematically**

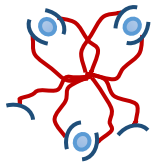


$C_{4\text{-arm}} = C_{8\text{-arm}} = [70\ g/L]$

M : Tpy = 1 : 2

N° 20 K = 2 x N° 40 K

Same n° of bonds



LOOPS ?!

$$G^{\circ}_{N_{Affine}} = \nu RT$$

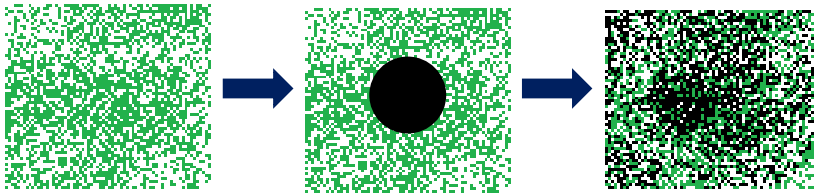
$$\nu = \frac{\mu * f}{2}$$

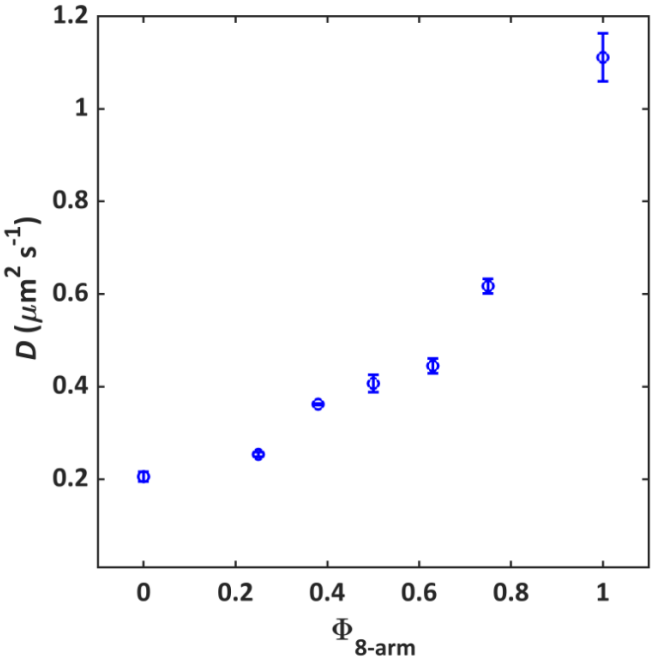
$$\mu = mol\ L^{-1}$$

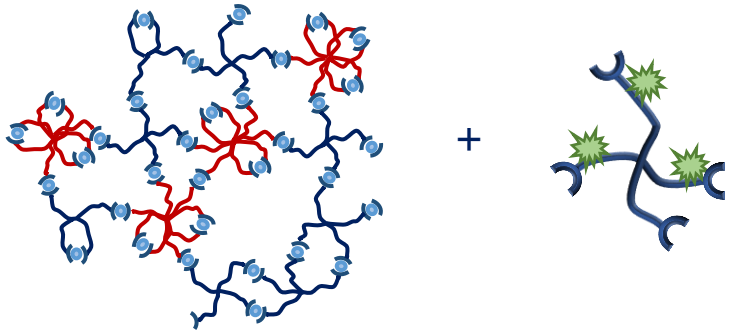
$\Phi_{8\text{-arm}}$	Affine [kPa]	G_p° [kPa]
0	17	13
0.25	17	8.8
0.50	17	5
0.75	17	2.5
1	17	1

FRAP

(self-diffusion)





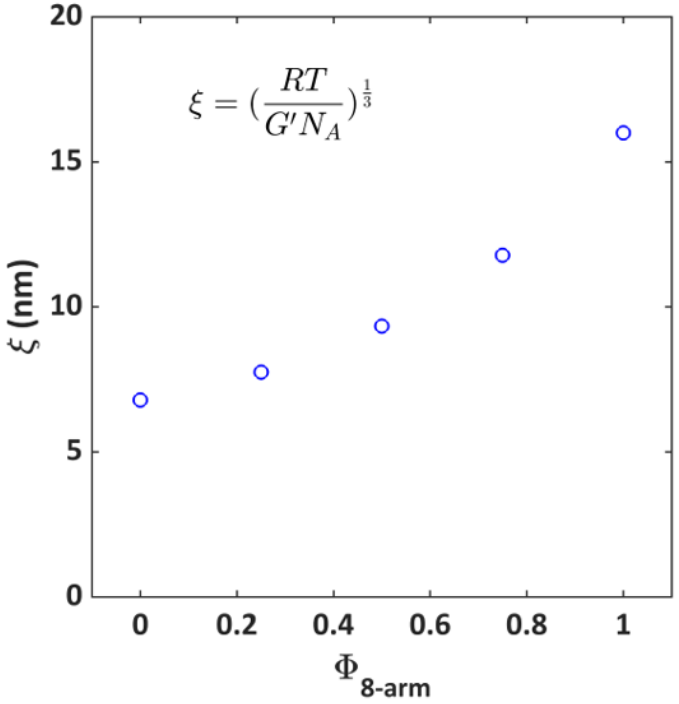


The self-diffusion coefficient increases with increasing 8-arm pEG

With connectivity defects, the diffusant travels faster without actually forming transient bonds, because the next available terpyridine is farther away.

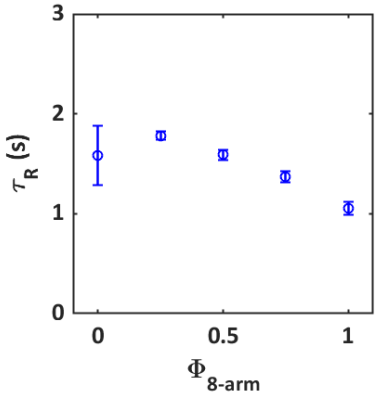
Mesh-size
(through rheology)

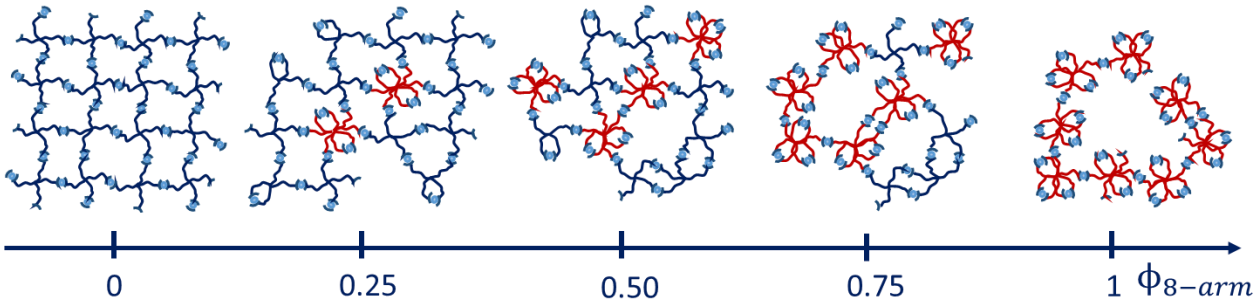
This vision is coherent also with the increasing mesh-sizes calculated through rheology.



The mesh-size increases with increasing 8-arm content

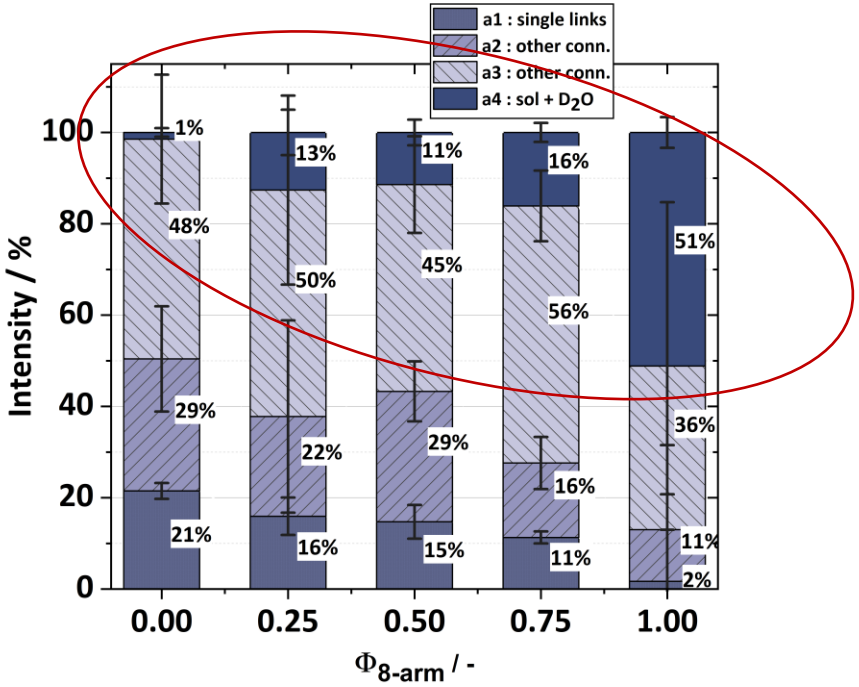
The trend of the diffusion coefficient follows also the trend of the relaxation time calculated through rheology.
As, a faster exchange is strictly connected to a faster diffusion.





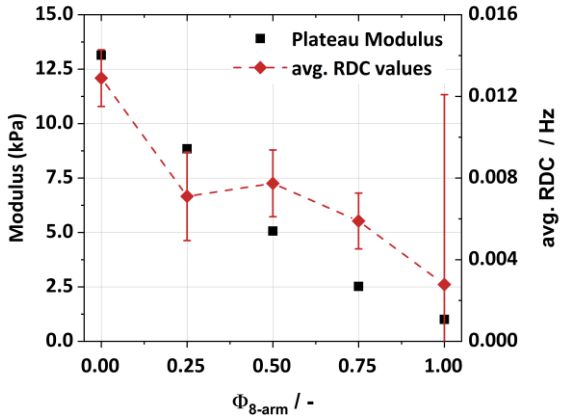
With increasing ϕ_{8-arm}, more connectivity defects form and the mesh-sizes increases.
The type of defects can be quantified with DQ-NMR

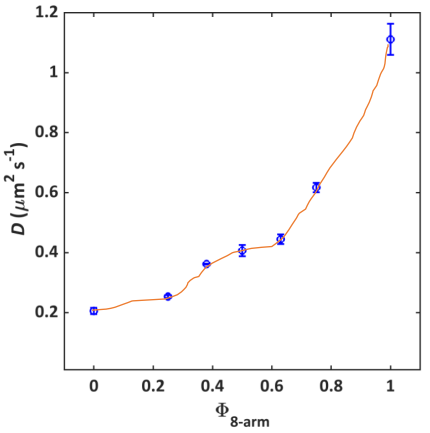
DQ-NMR



The amount of defects increases with increasing 8-arm content that is forming intra-molecular instead of inter-molecular associations

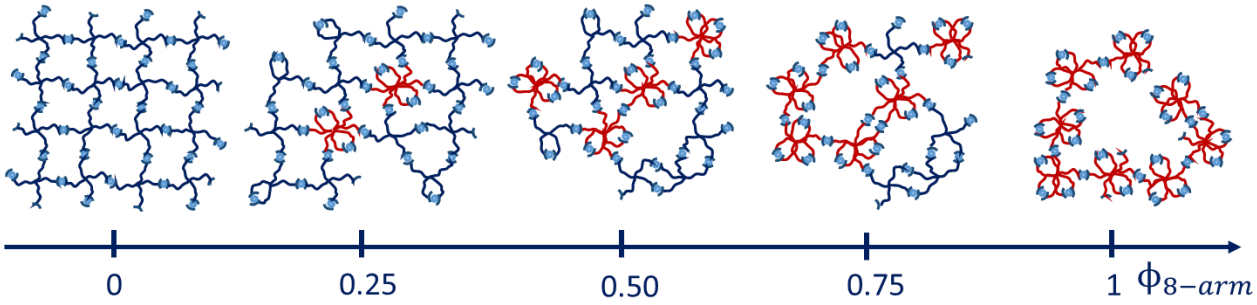
The trend is consistent with Rheology and FRAP

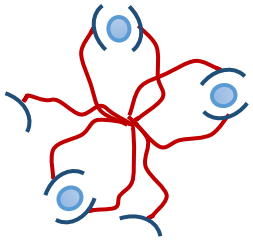




Summary & Conclusions

We investigated connectivity defects systematically by introducing twofold molar mass 8-arm pEG-terpyridine in 4-arm pEG-terpyridine system





With increasing $\Phi_{8\text{-arm}}$ the amount of intra-molecular loops increases

- There are less active chains -> the plateau modulus decreases
- There are more intra-molecular connections -> the mesh-size increases
- The 8-arm pEG forms more connections with itself -> the next available sticker is further away -> the self-diffusion coefficient increases

Thank you for your attention!

JOHANNES GUTENBERG UNIVERSITÄT MAINZ

INITIAL TRAINING NETWORK

SEIFFERT GROUP