Viscoelastic Response Of Metal-Ligand Associated Polymer Network Under Large Shear Deformation

Christina Pyromali

WP2, WP3: Structure & Dynamics

DSM Meting, 31-01-2019

Motivation

Structure ⟷ **Properties** ⟷ **Function**

Entanglements

M-L coordination

Dangling ends

Tunability

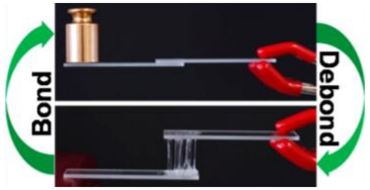
Self-healing
Shape memory

Magnetic

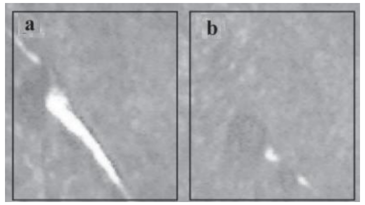
Optical

Electro chromic properties

Light induced adhesives



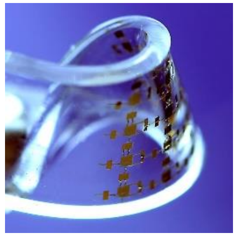
(Heinzmann et al., 2014)



(Bode et al., 2013)

Self-healing coatings

Stretchable electronics



(Rao et al., 2016)

!!! Industrial Exploitation

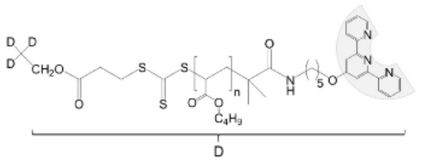
Processability and rheological behaviour under large shear deformation

Outline

- ✓ Materials
- ✓ Methods
- ✓ Protocols
- ✓ Results
- ✓ Discussion
- ✓ Further Research

Materials

Terpyridine ligand



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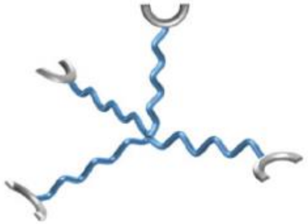


+

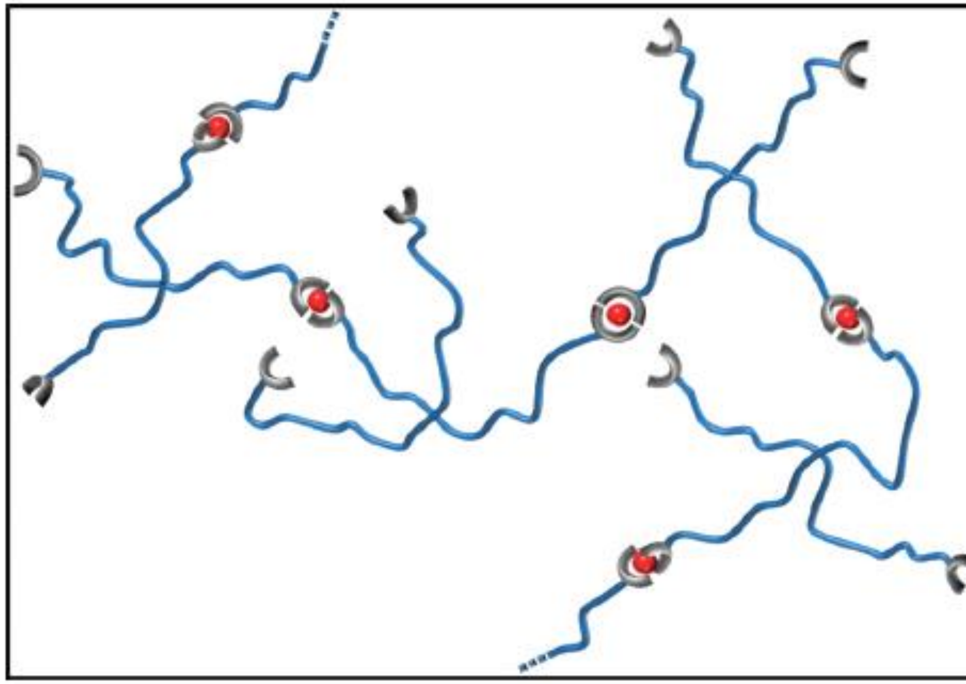
Metal Ions:

$ZnCl_2$
$CuCl_2$

star poly(n-butyl acrylate)s

0.50 0.75 1.00

- ✓ Thermodynamic stability
- ✓ Same Charge
- ✓ Similar ionic radius



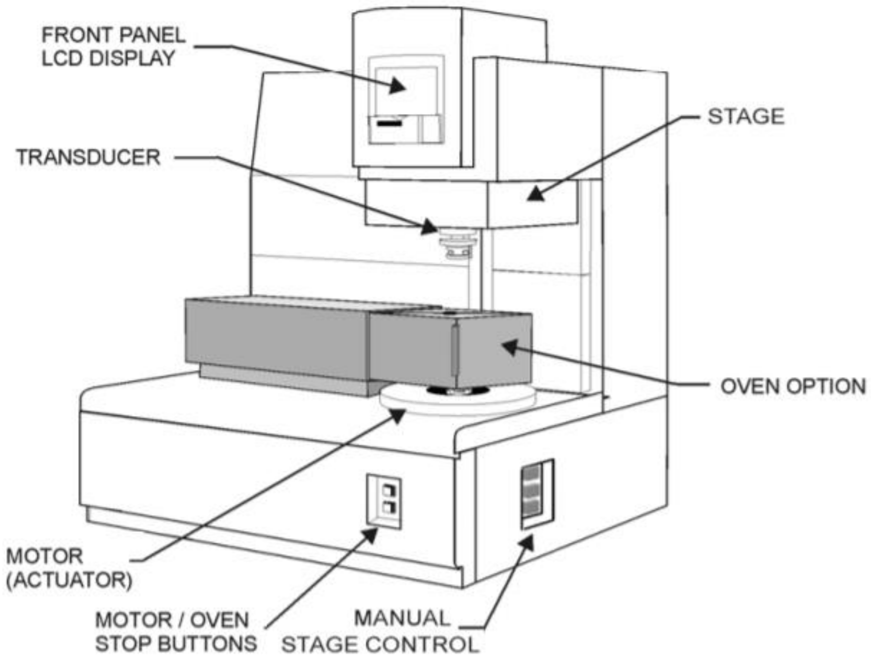
(Zhuge et al., 2017)

	K_1 [M^{-1}]	K_2 [M^{-1}]
Zn(II)	10^6	$10^{5.2}$
Cu (II)	10^{12}	10^6

M_n [kg/mol]	M_e [kg/mol]	$Z=M_n/M_e$	Dispersity	Tg [ºC]
249	18	3.4 per arm	1.2	-52

INITIAL TRAINING NETWORK

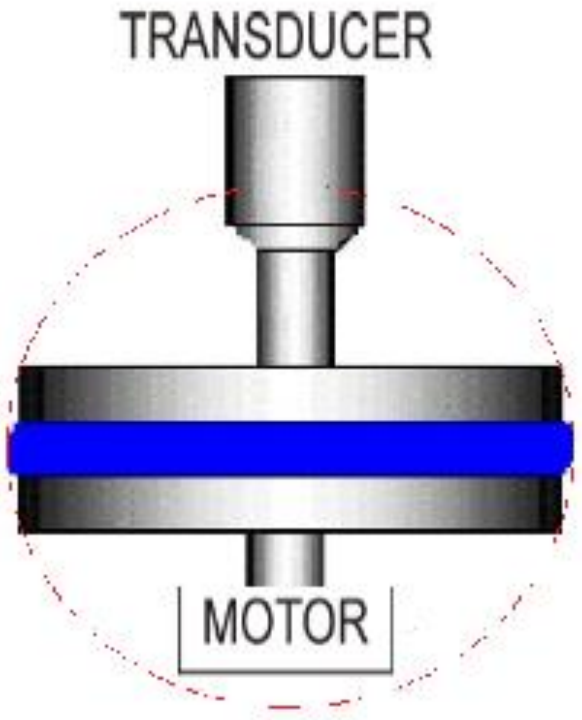
Methods



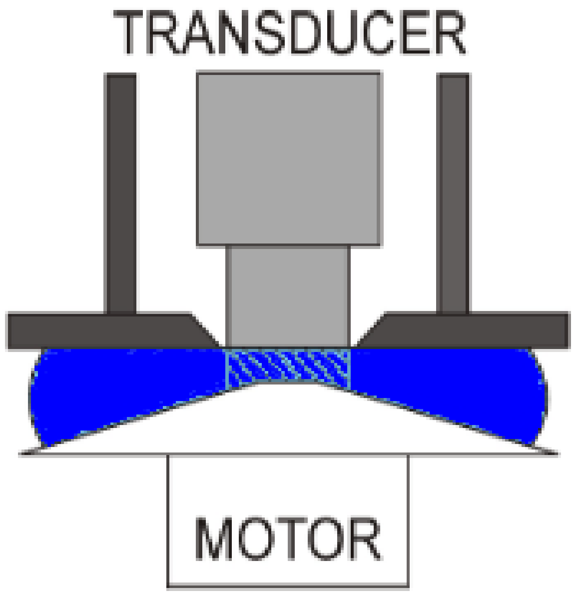
- ✓ Strain Control
- ✓ Force rebalance transducer
- ✓ Convection Oven
- ✓ Nitrogen/ Air flow for accurate temperature control

SAOS

- ✓ 4mm Plate-Plate Geometry
- ✓ 600-700 µm gap
- ✓ Imaginary spherical segment

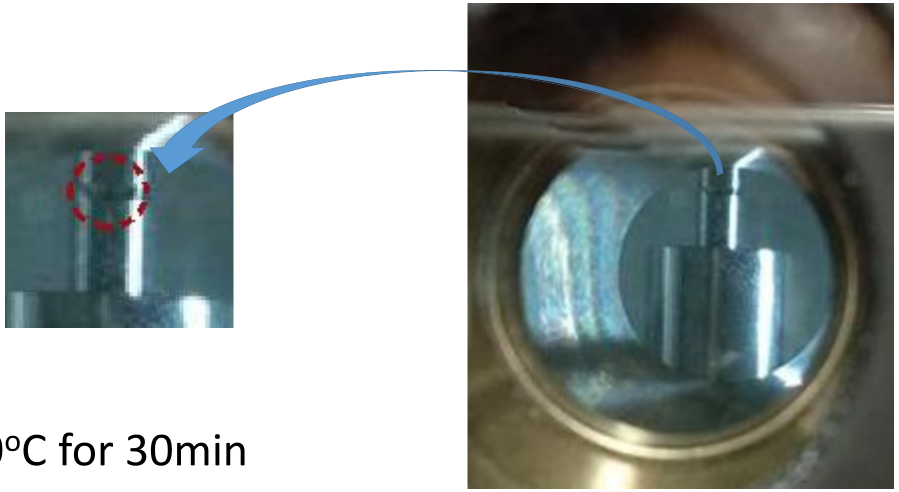


Startup Shear

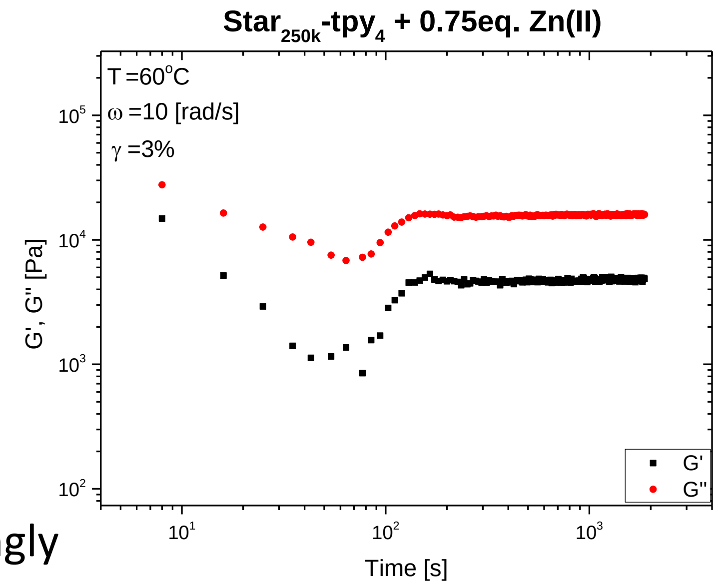


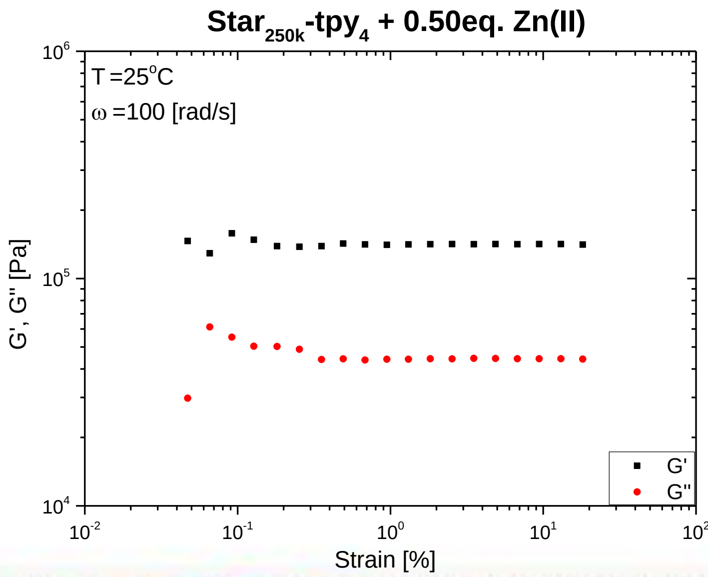
- ✓ 6.2 mm CPP
- ✓ 0.1 radians lower cone plate
- ✓ 0.051 µm fixed gap
- ✓ Elimination of edge fracture

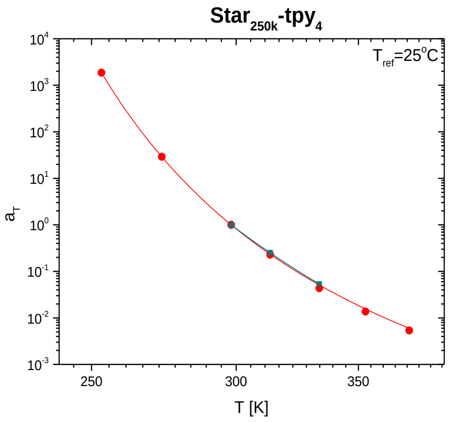
Protocols

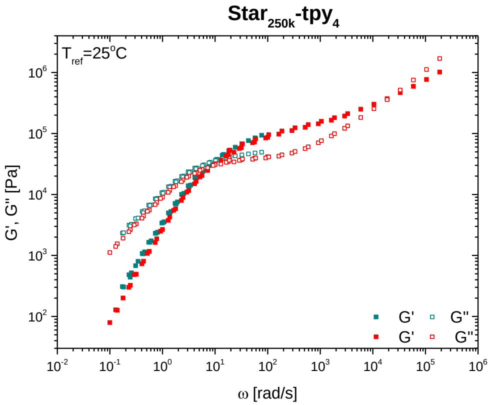


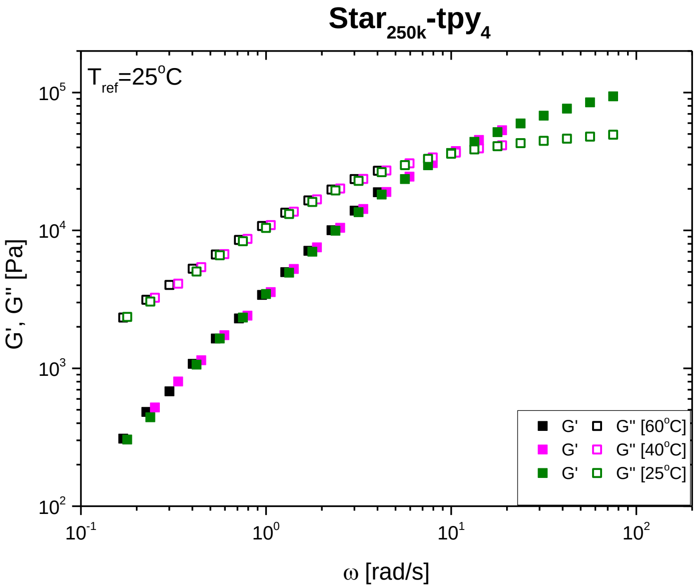
- ✓ Loading
- ✓ Sample equilibration at 130ºC for 30min
- ✓ DTS at each temperature for thermal equilibration-gap adjustment accordingly
- ✓ DSS to determine a deformation in the linear regime
- ✓ DFS at different temperatures with strain in the linear regime



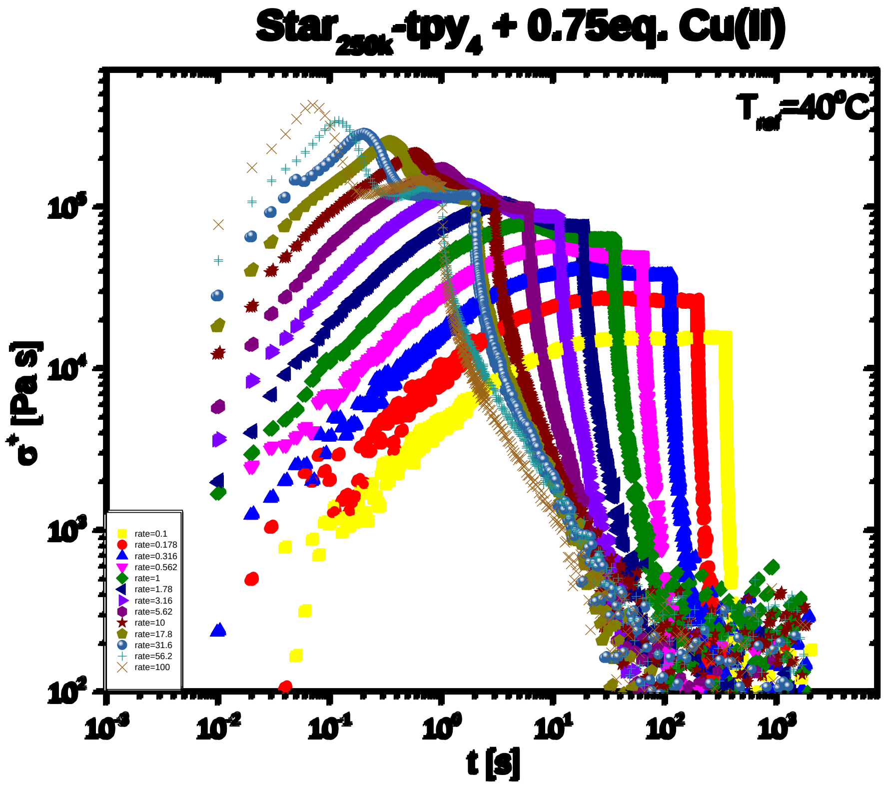


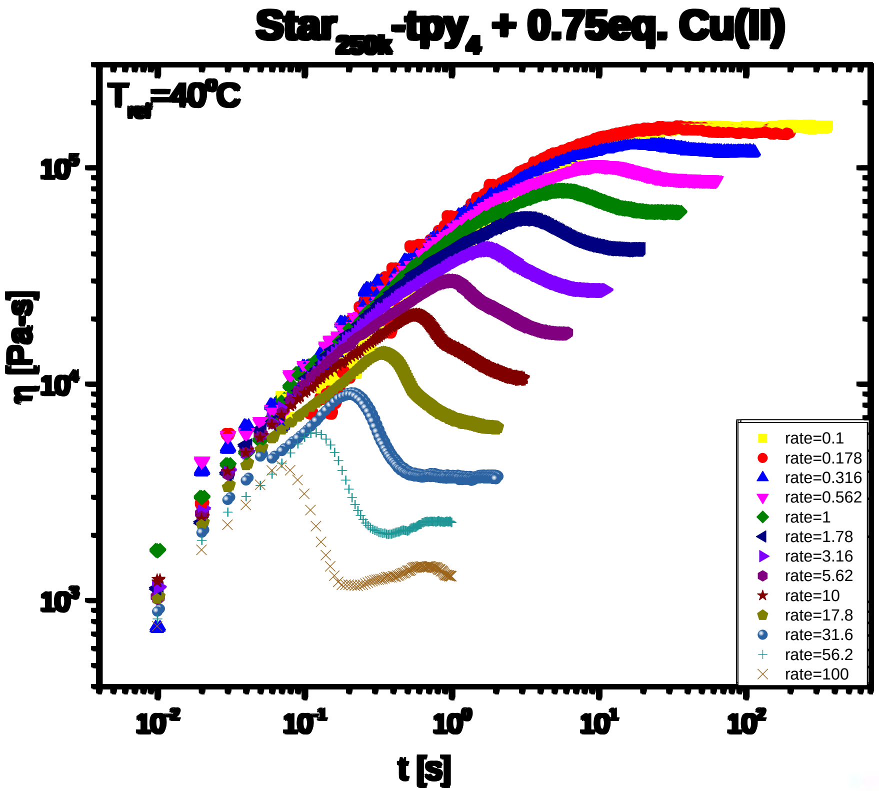




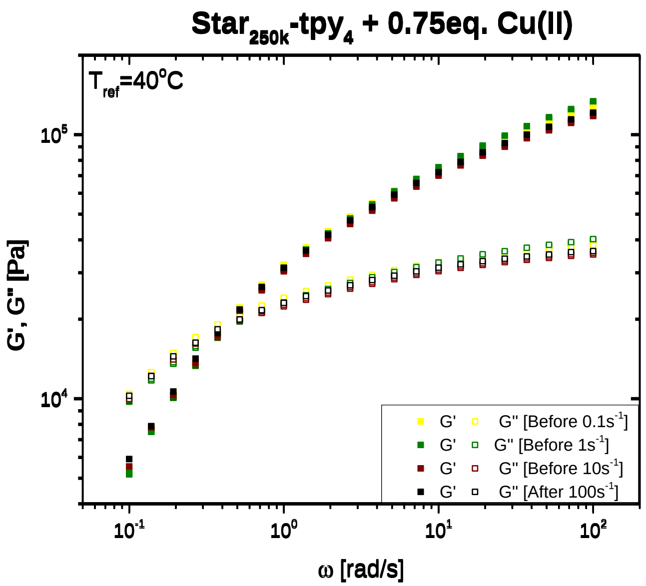


Protocols





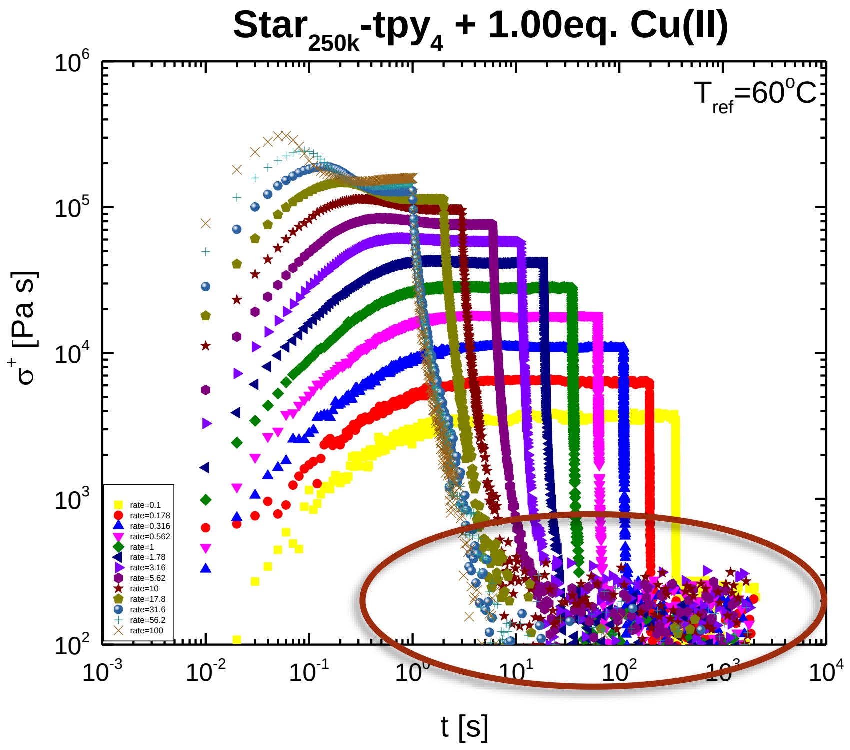
rubbery plateau

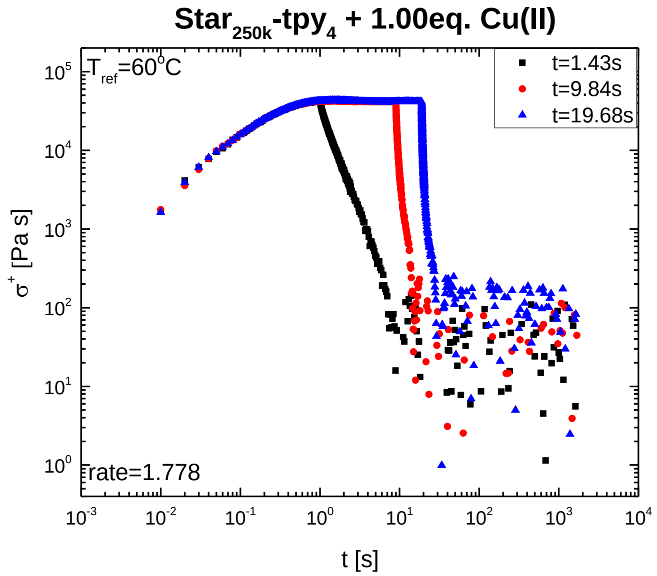


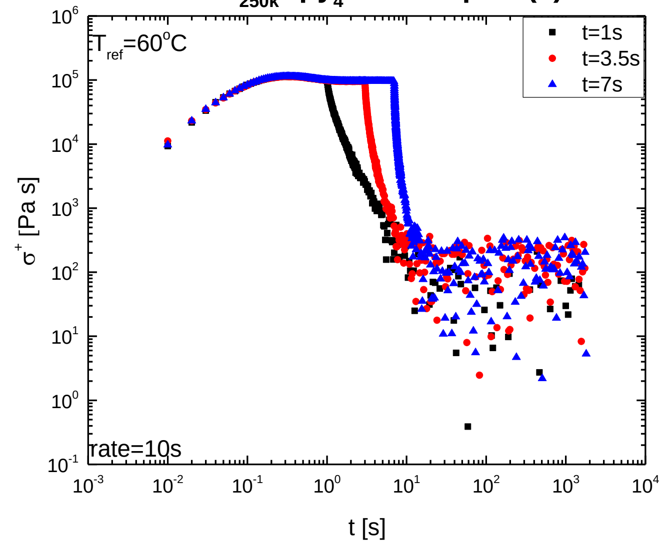
terminal flow

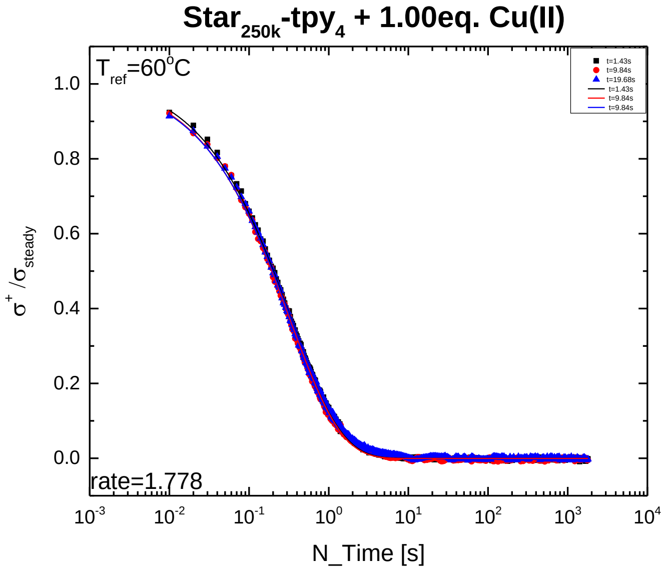
INITIAL TRAINING NETWORK

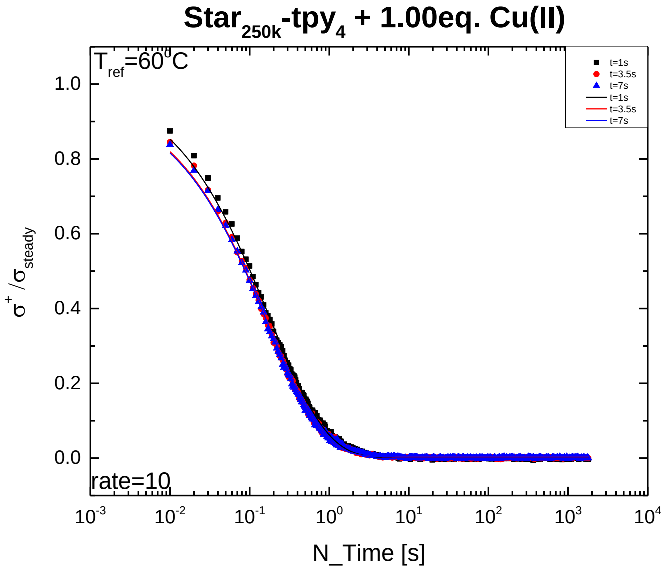
Protocols


Star250k-tpy4 + 1.00eq. Cu(II)
Tref=60°C
σ+ [Pa s]
t [s]
rate=0.1
rate=0.178
rate=0.316
rate=0.562
rate=1
rate=1.78
rate=3.16
rate=5.62
rate=10
rate=17.8
rate=31.6
rate=56.2
rate=100


Star250k-tpy4 + 1.00eq. Cu(II)
Tref=60°C
t=1.43s
t=9.84s
t=19.68s
σ+ [Pa s]
rate=1.778
t [s]

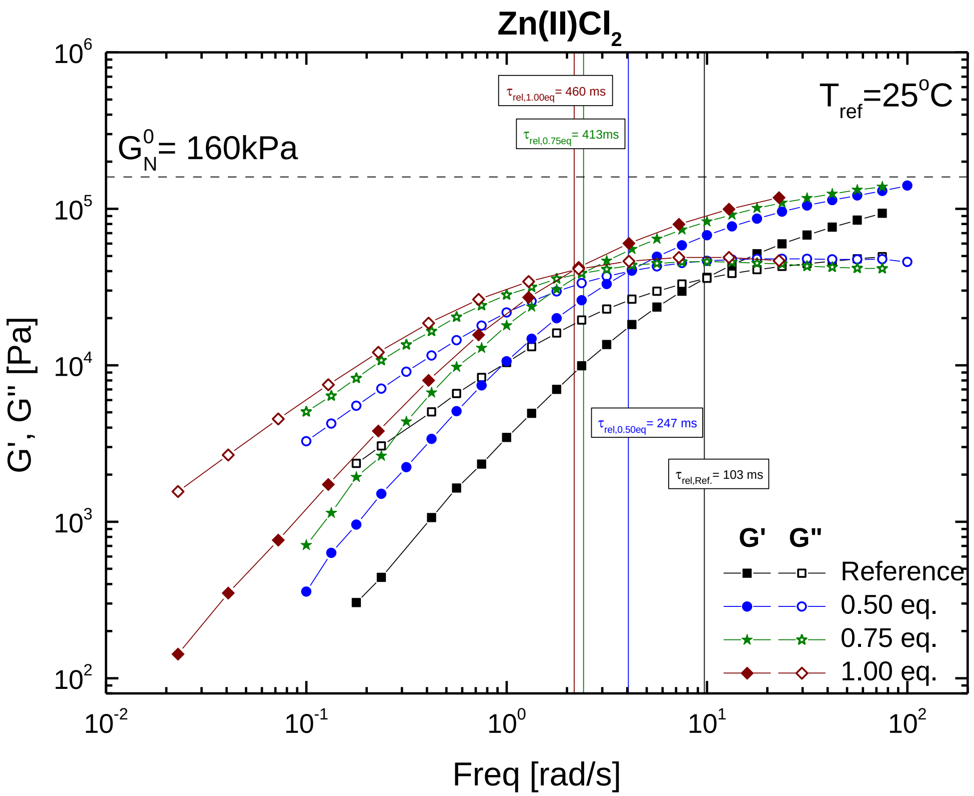

Star250k-tpy4 + 1.00eq. Cu(II)
Tref=60°C
t=1s
t=3.5s
t=7s
σ+ [Pa s]
rate=10s
t [s]

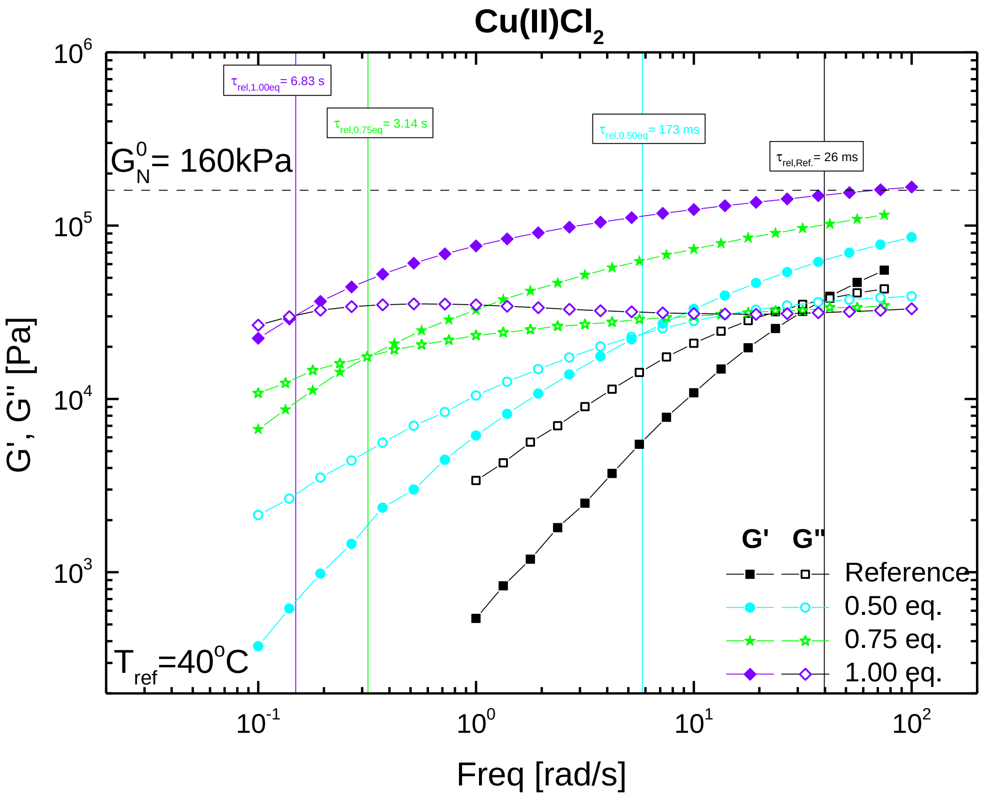

Star250k-tpy4 + 1.00eq. Cu(II)
Tref=60°C
σ+/σsteady
rate=1.778
N_Time [s]


Star250k-tpy4 + 1.00eq. Cu(II)
Tref=60°C
t=1s
t=3.5s
t=7s
σ+/σsteady
rate=10
N_Time [s]

Results-LVE

- ✓ More stable reversible network
- ✓ Higher cross-linked system





× Plenty of ions unable to coordinate with ligands

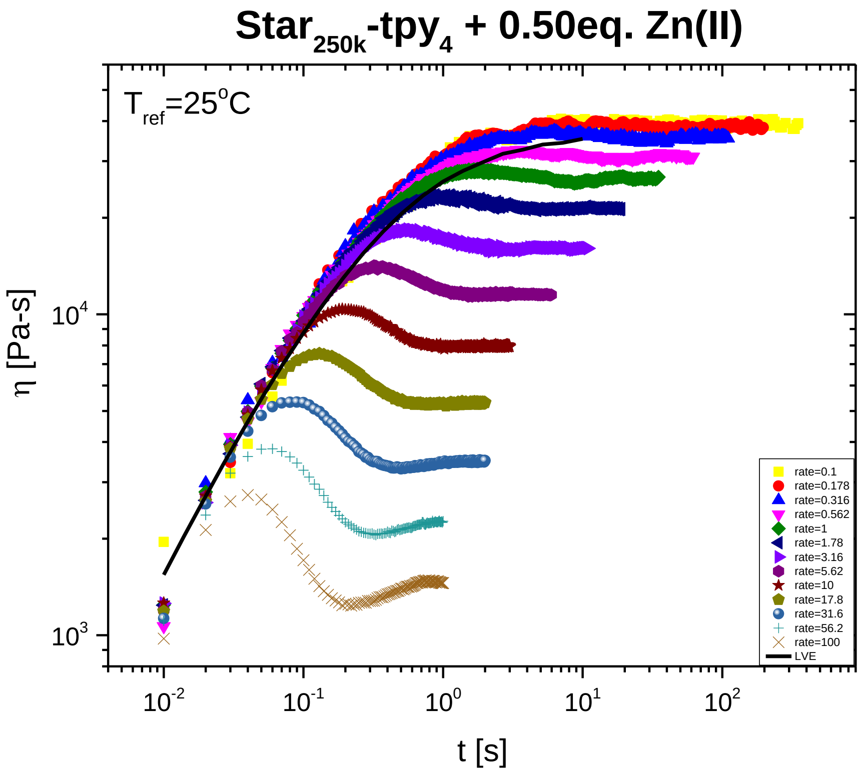
Results

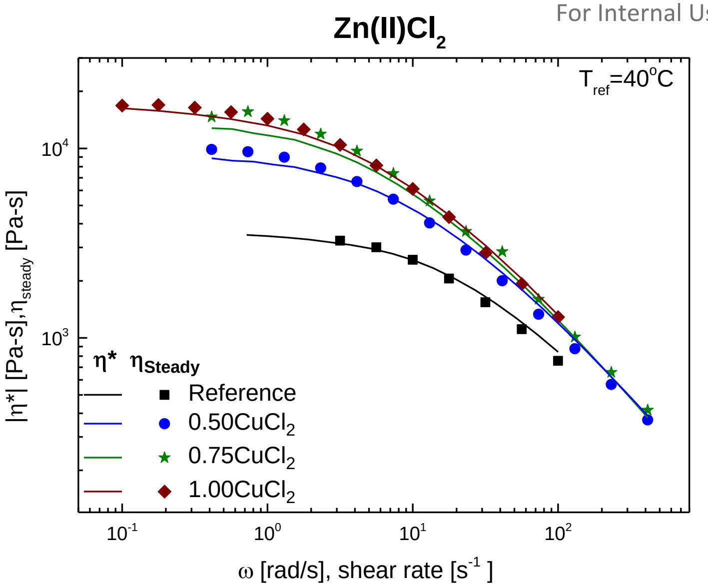
- Thermo rheological complexity

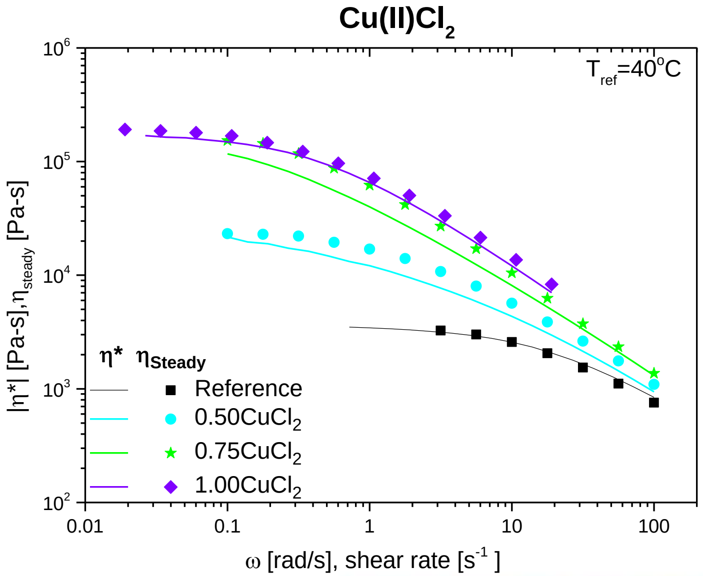
  Entanglement / disentaglement

  Association/ Disassociation

  Dangling chains

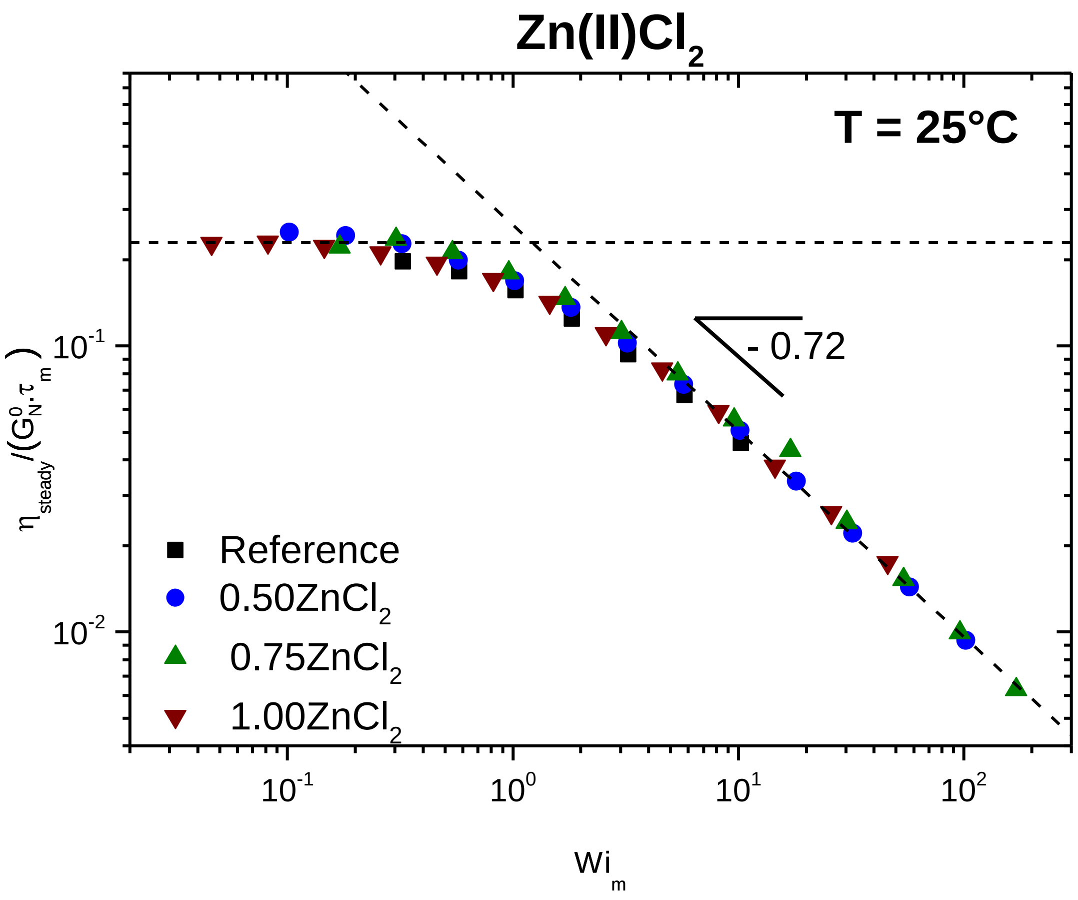


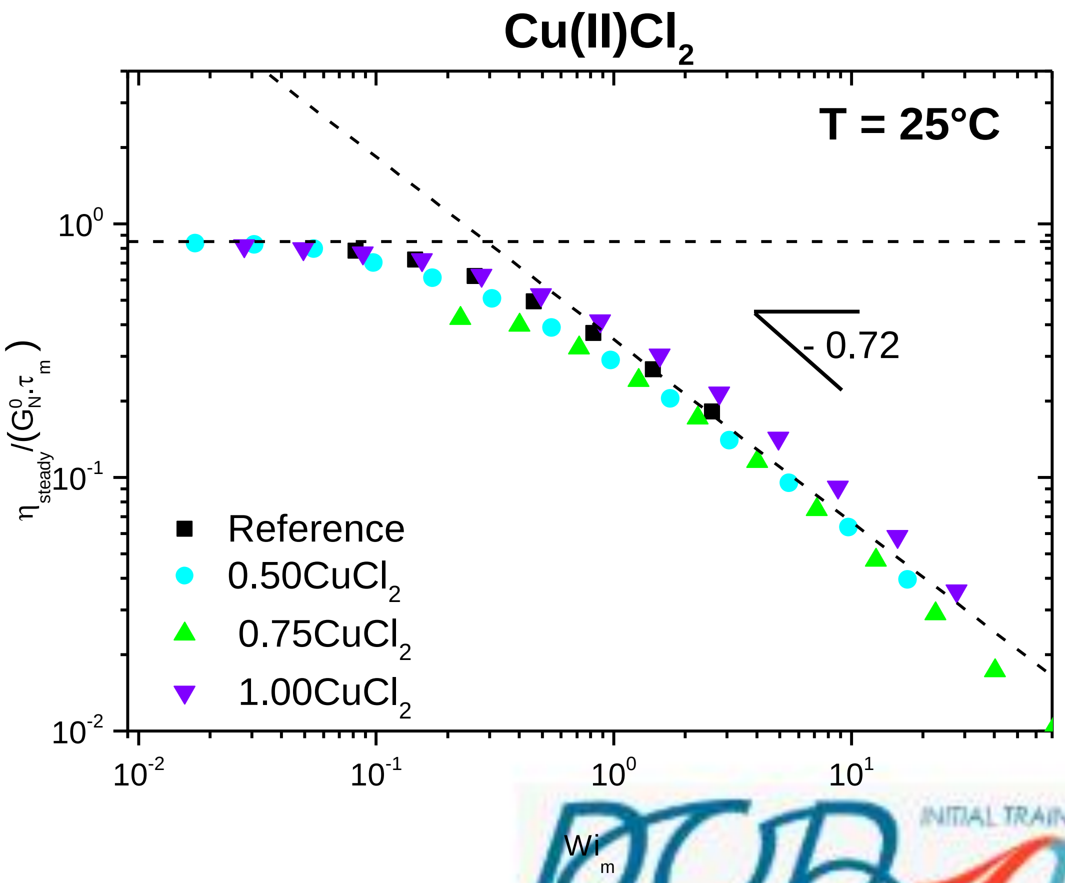




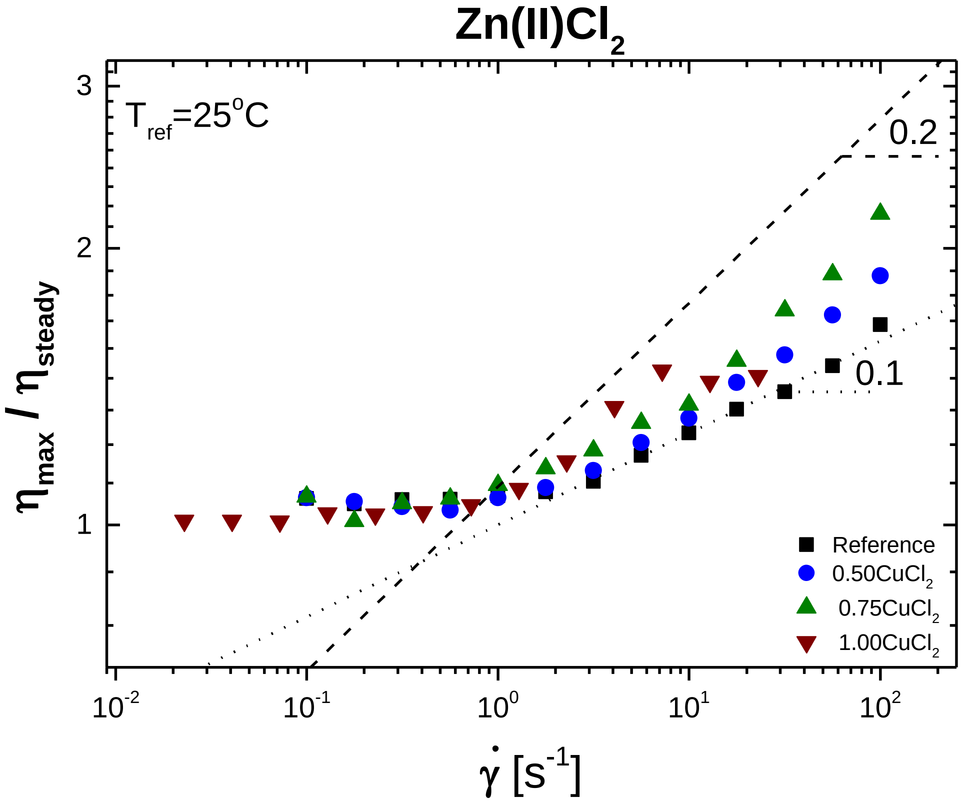
Results

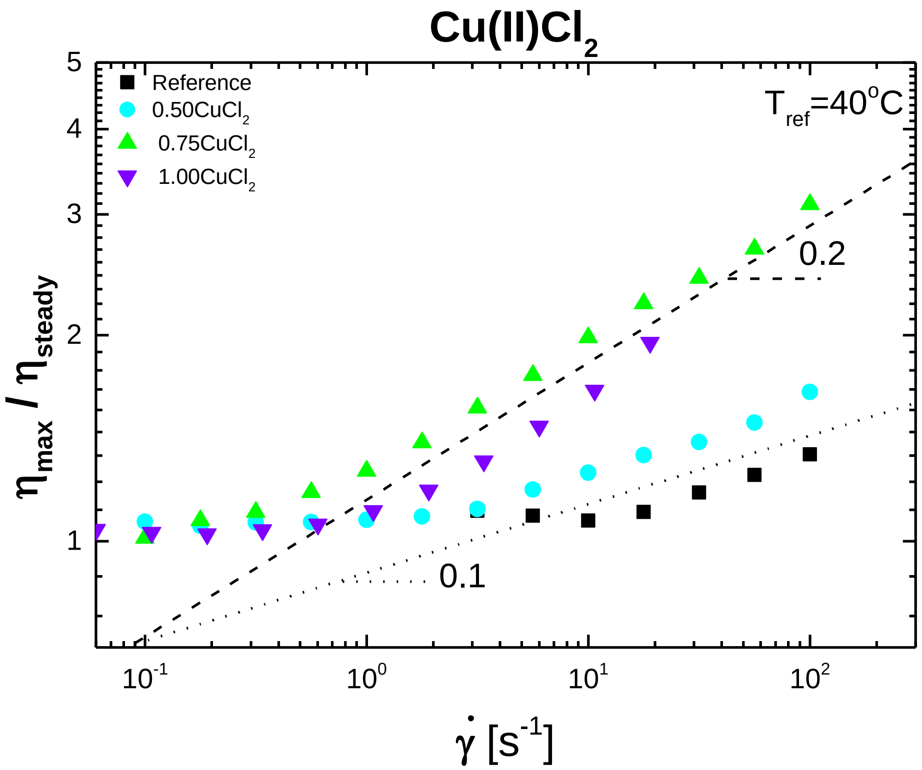
Shear Thinning Behavior



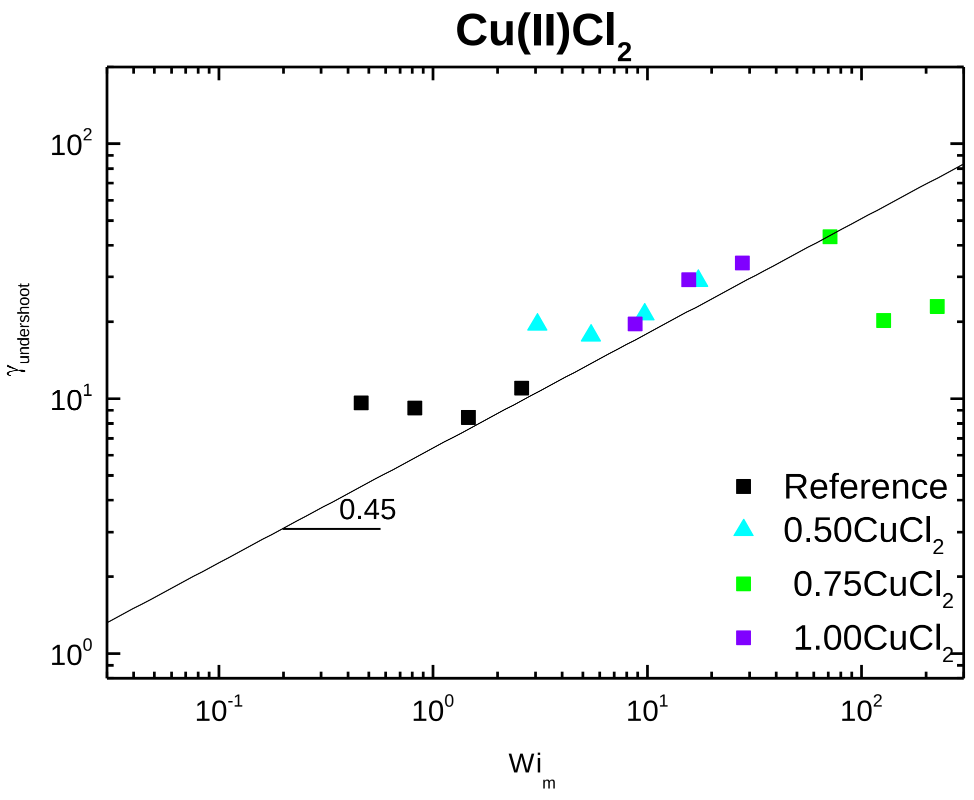


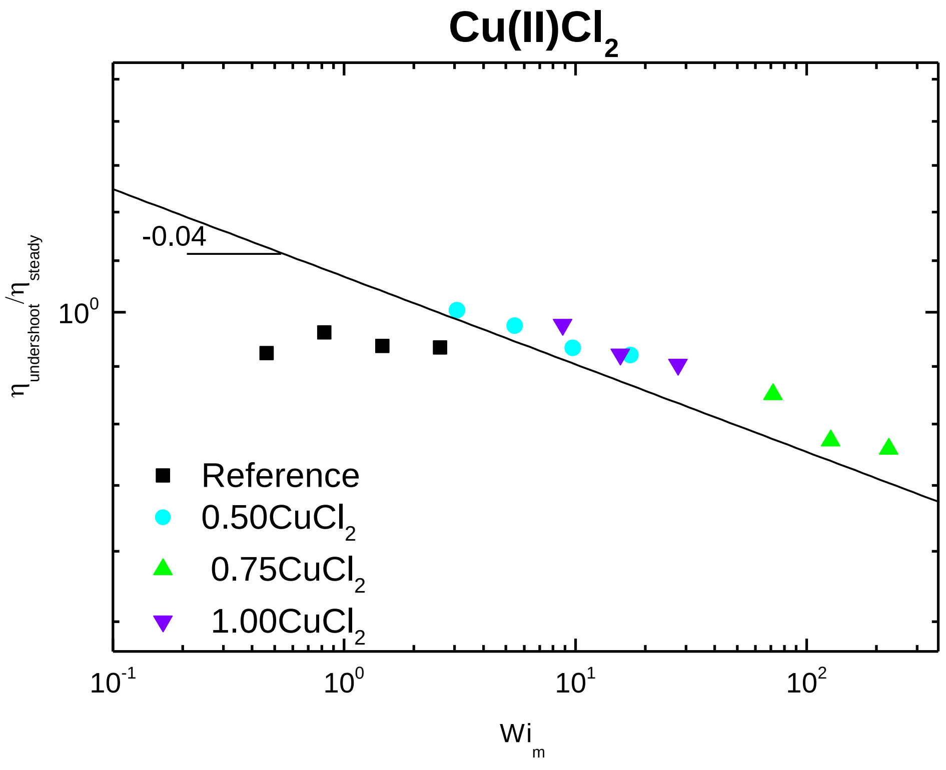
Results


Zn(II)Cl2
Tref=25°C
0.2
0.1
Reference
0.50CuCl2
0.75CuCl2
1.00CuCl2
ηmax / ηsteady
γ̇ [s-1]
10-2
10-1
100
101
102
1
2
3

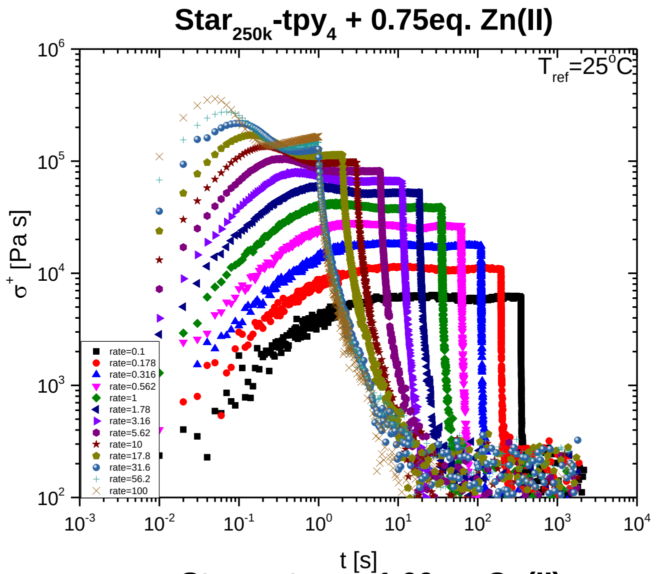

Cu(II)Cl2
Tref=40°C
Reference
0.50CuCl2
0.75CuCl2
1.00CuCl2
0.2
0.1
ηmax / ηsteady
γ̇ [s-1]
10-1
100
101
102
1
2
3
4
5

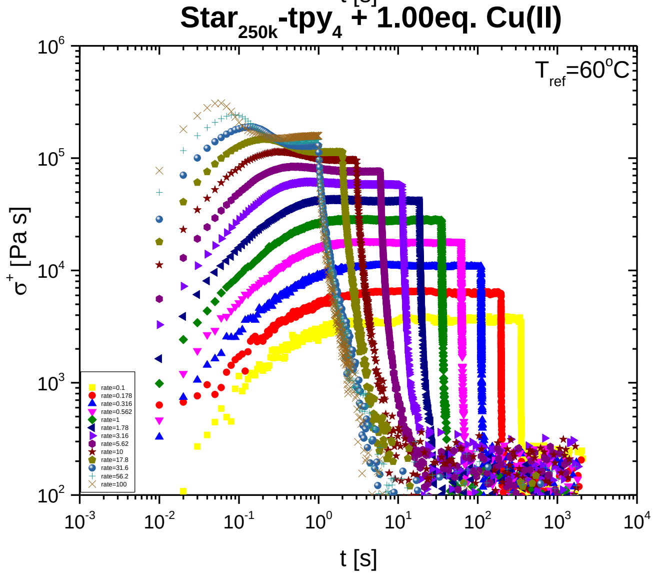
Results-Undershoot

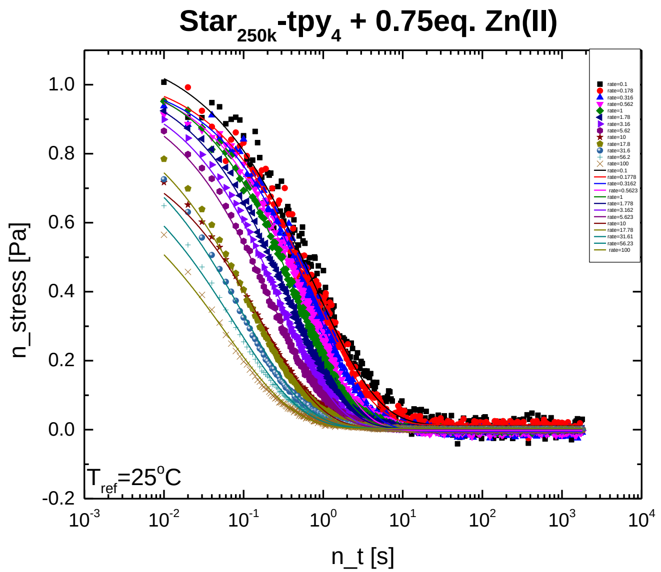


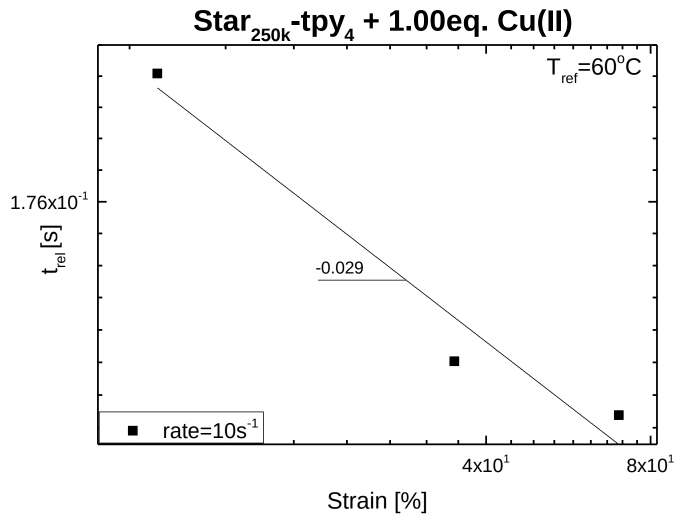


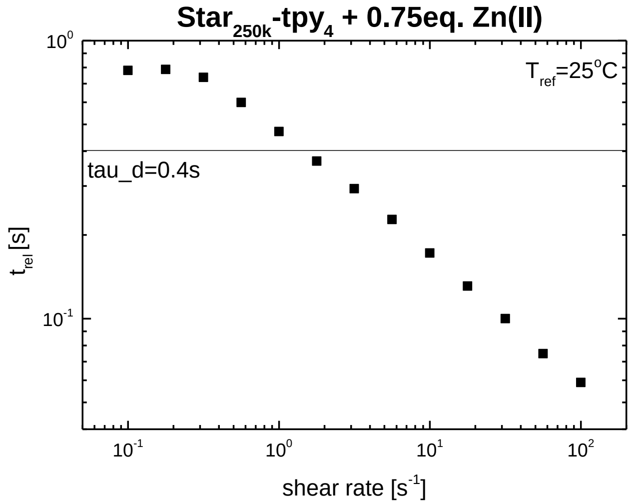
Results

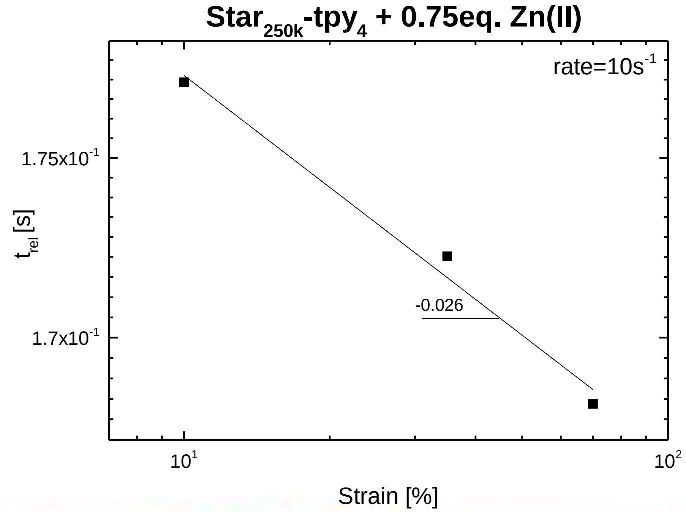

Star$_{250k}$-tpy$_4$ + 0.75eq. Zn(II)
T_{ref}=25°C
σ^+ [Pa s]
t [s]
rate=0.1
rate=0.178
rate=0.316
rate=0.562
rate=1
rate=1.78
rate=3.16
rate=5.62
rate=10
rate=17.8
rate=31.6
rate=56.2
rate=100


Star$_{250k}$-tpy$_4$ + 1.00eq. Cu(II)
T_{ref}=60°C
σ^+ [Pa s]
t [s]

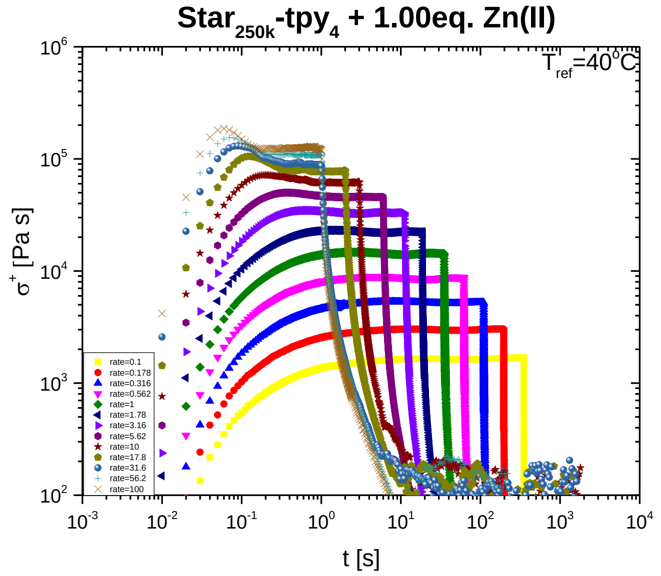

Star$_{250k}$-tpy$_4$ + 0.75eq. Zn(II)
n_stress [Pa]
n_t [s]
T_{ref}=25°C

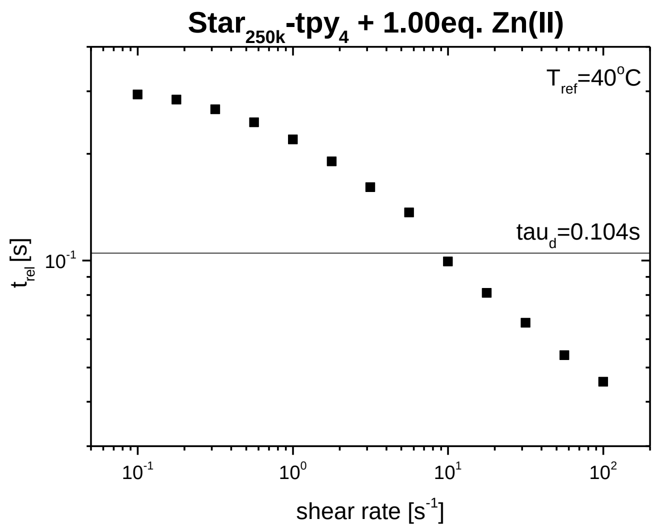

Star$_{250k}$-tpy$_4$ + 1.00eq. Cu(II)
T_{ref}=60°C
t_{rel} [s]
Strain [%]
-0.029
rate=10s^{-1}

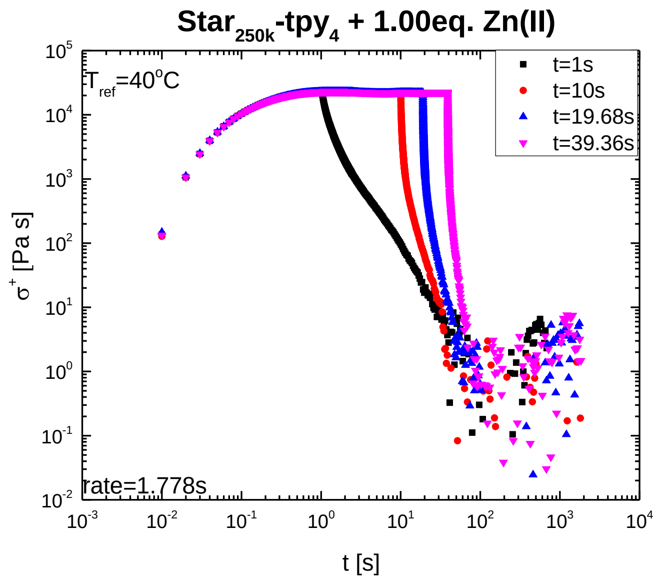

Star$_{250k}$-tpy$_4$ + 0.75eq. Zn(II)
T_{ref}=25°C
tau_d=0.4s
t_{rel} [s]
shear rate [s^{-1}]

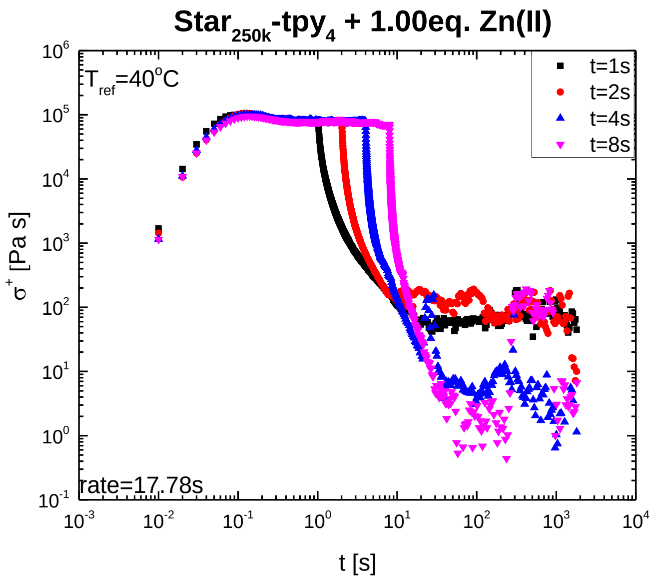

Star$_{250k}$-tpy$_4$ + 0.75eq. Zn(II)
rate=10s^{-1}
t_{rel} [s]
Strain [%]
-0.026

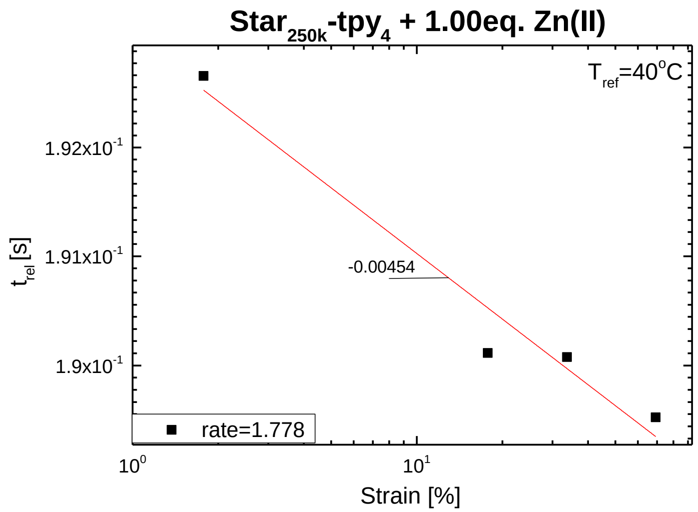
Discussion

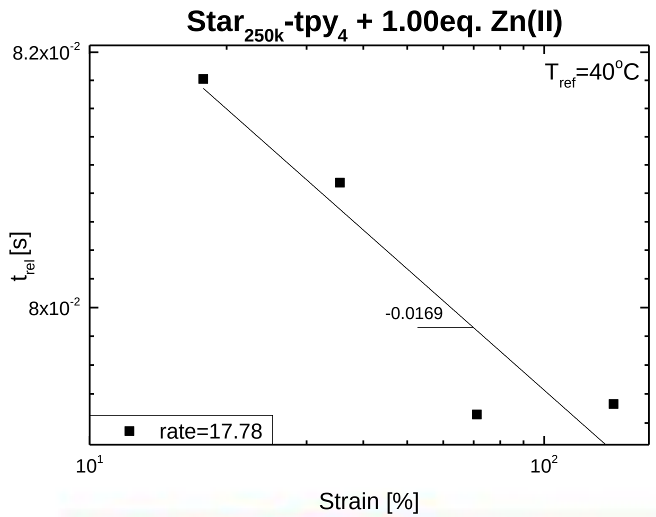












Critical strain > yield strain?

Future work

- Repeat experiments of samples that indicate residual stresses
- Systematic study of single networks with higher binding constant
- Further investigation of slow dynamic with techniques such as light scattering
- Solutions
- Double dynamic networks consisting of two different metal ions characterization.

Thank you for your attention!

Questions?

References

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