Nonlinear Viscoelastic Response of Metallo-Supramolecular Polymeric Networks

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WP2, WP3: Structure & Dynamics

DTU Intermediate Meeting II, 07-05-2019

Motivation

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

Entanglements

M-L coordination

Dangling ends

Tunability

Self-healing

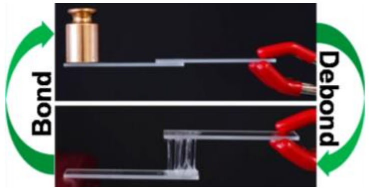
Shape memory

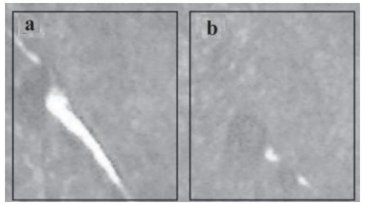
Magnetic

Optical

Electro chromic properties

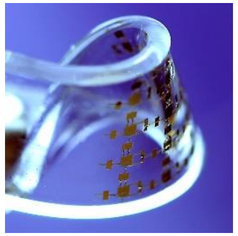
Light induced adhesives





Self-healing coatings

Stretchable electronics



!!! Industrial Exploitation

Processability and rheological behaviour under large shear deformation

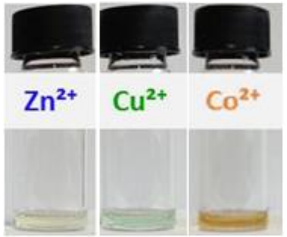
Heinzmann et al., *Light-Induced Bonding and Debonding with Supramolecular Adhesives. ACS Applied Materials & Interfaces* , 2014

Bode et al., *Self-Healing Polymer Coatings Based on Crosslinked Metallosupramolecular Copolymers. Advanced Materials*, 2013

Rao et al., *Stretchable Self-Healing Polymeric Dielectrics Cross-Linked Through Metal–Ligand Coordination. Journal of the American Chemical Society*, 2016

Outline

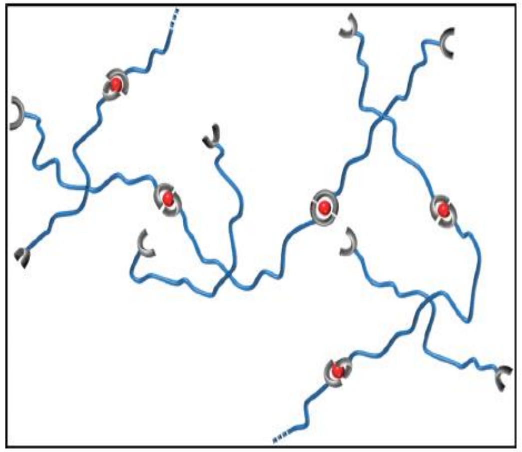
- ✓ Materials
- ✓ Methods
- ✓ Protocols
- ✓ Results
- ✓ Conclusions
- ✓ Further Research



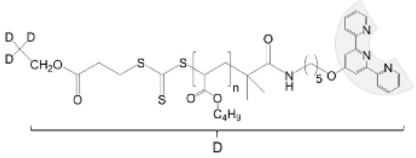
0.50

0.75

1.00



Terpyridine ligand



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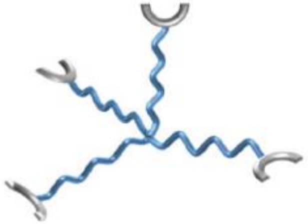


+

4 arm star poly(n-butyl acrylate)s

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

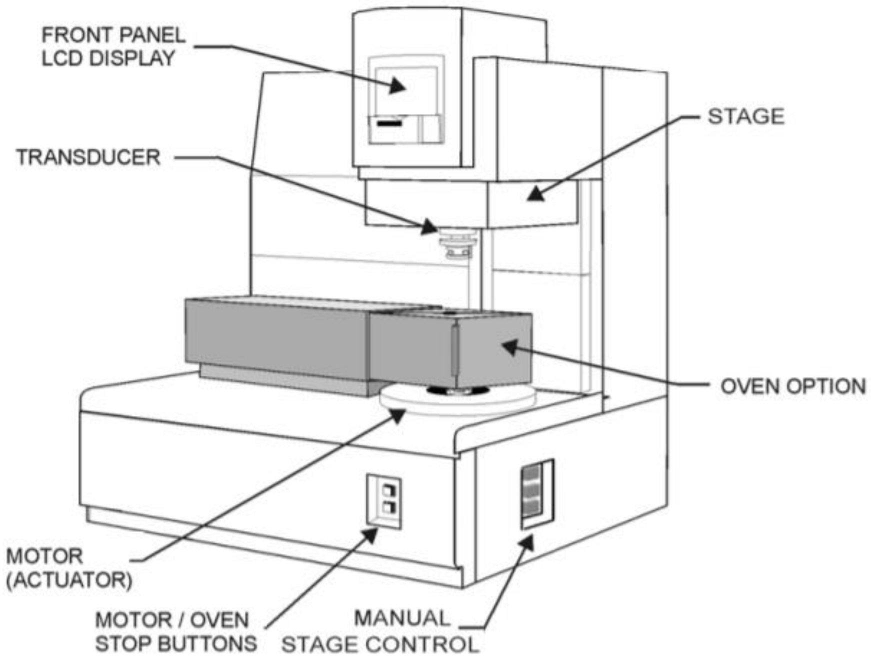
	K_1 [M^{-1}]	$k_{a,1}$[$M^{-1}s^{-1}$]	$k_{d,1}$ [s^{-1}]	K_2 [M^{-1}]	$k_{a,2}$[$M^{-1}s^{-1}$]	$k_{d,2}$ [s^{-1}]	$\beta=K_1 \cdot K_2$
Zn(II)	10^{6}	$10^{6.1}$	$10^{0.1}$	$10^{5.2}$	-	-	$10^{11.2}$
Cu (II)	10^{12}	$10^{7.3}$	-	10^{6}	-	-	10^{18}
Co (II)	$10^{8.4}$	$10^{4.4}$	10^{-4}	$10^{9.9}$	$10^{6.7}$	$10^{-3.2}$	$10^{18.3}$

Zhuge, F., *Synthesis and dynamics of metallo-supramolecular polymeric assemblies*. Université catholique de Louvain, 2018.

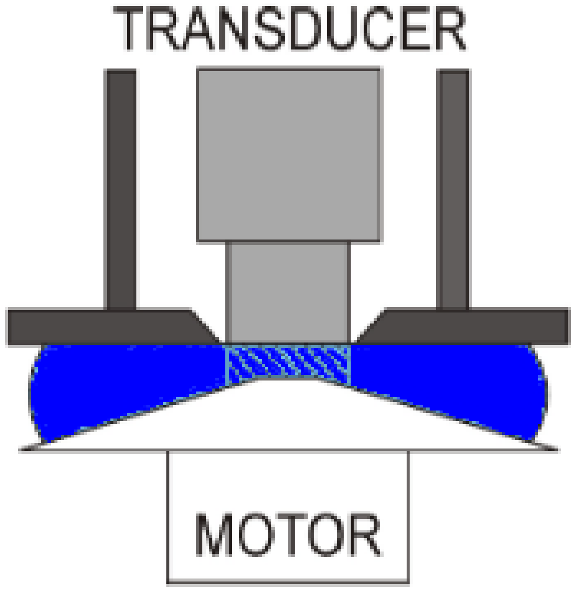
M_n [kg/mol]	M_e [kg/mol]	$Z=M_n/M_e$	Dispersity	Tg [°C]
249	18	3.4 per arm	1.2	-52

DODYnet INITIAL TRAINING NETWORK

Methods



Start-up shear and relaxation

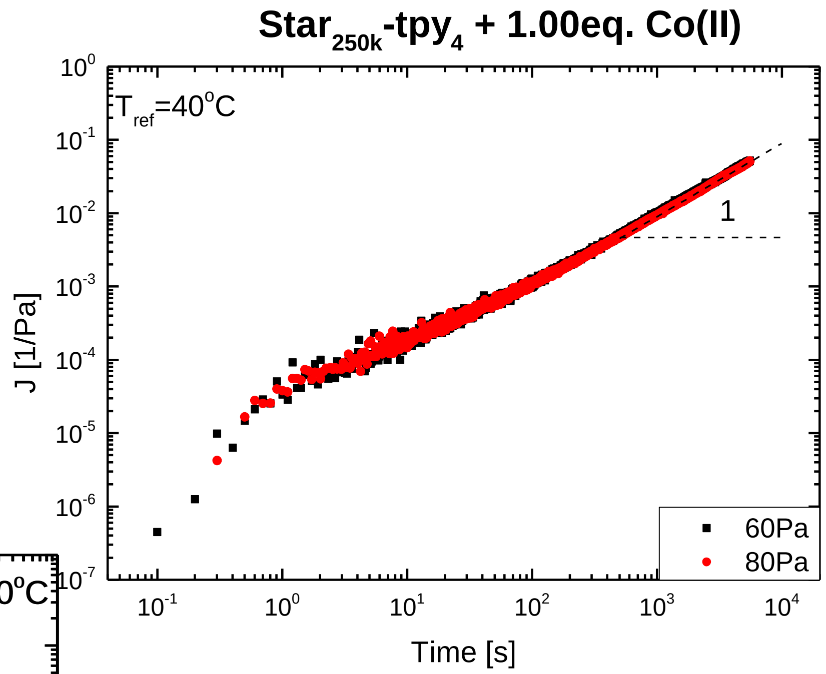


- ✓ 6.2 mm or 4.1 mm CPP
- ✓ 0.1 radians lower cone plate
- ✓ 0.051 µm fixed truncation
- ✓ Elimination of edge fracture

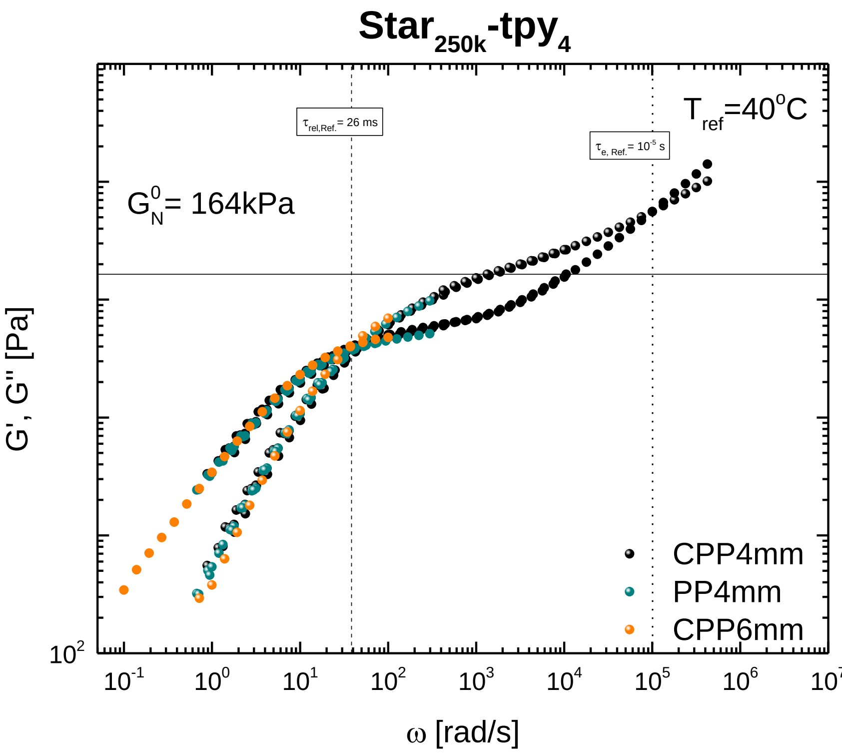
- ✓ Strain Control
- ✓ Force rebalance transducer
- ✓ Convection Oven
- ✓ Nitrogen/ Air flow for accurate temperature control

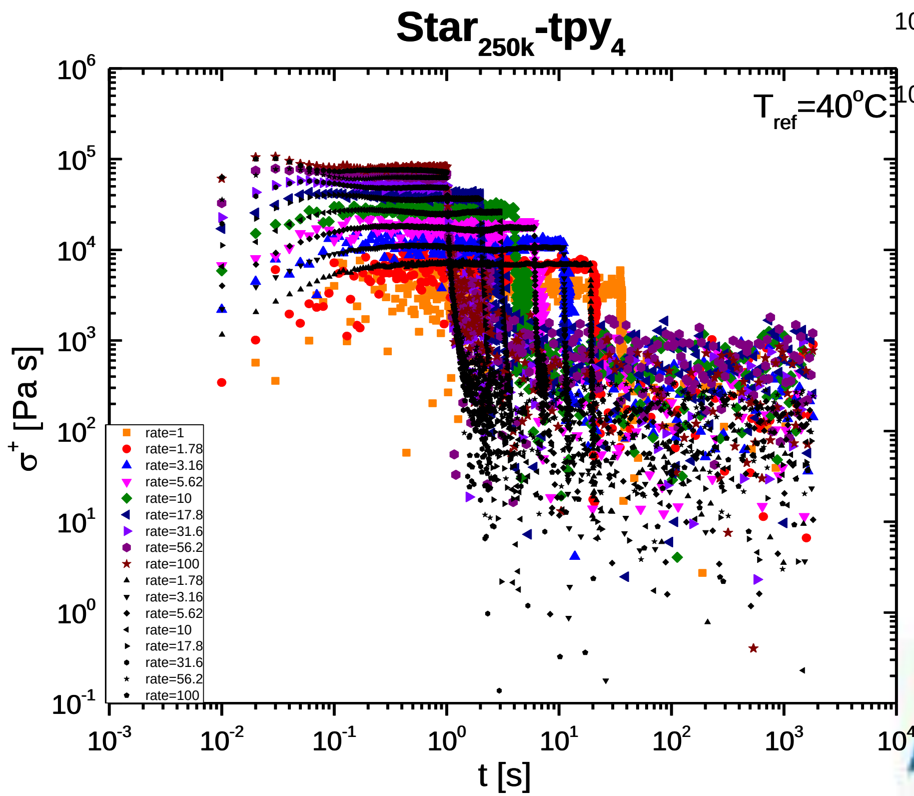
Protocols

- ✓ Sample equilibration at 130ºC for 30min
- ✓ Linear and nonlinear shear measurements
- ✓ Creep test

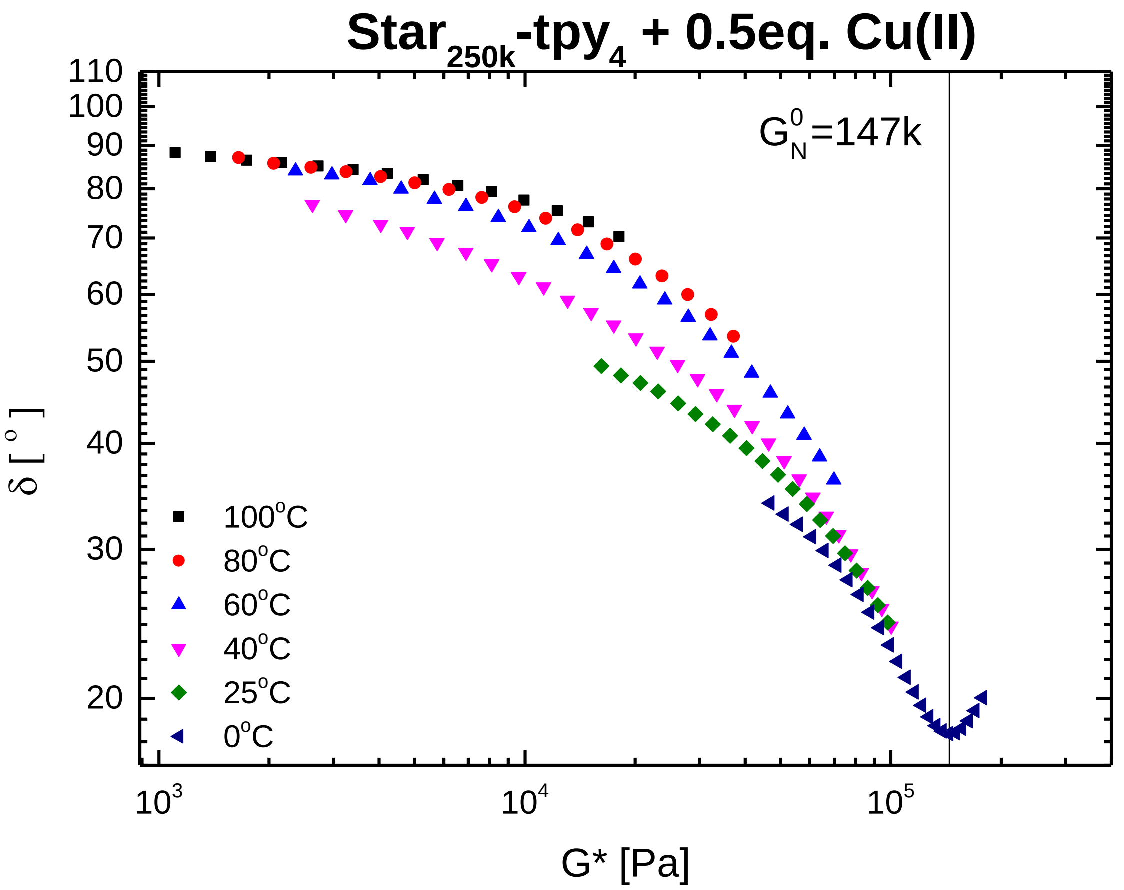


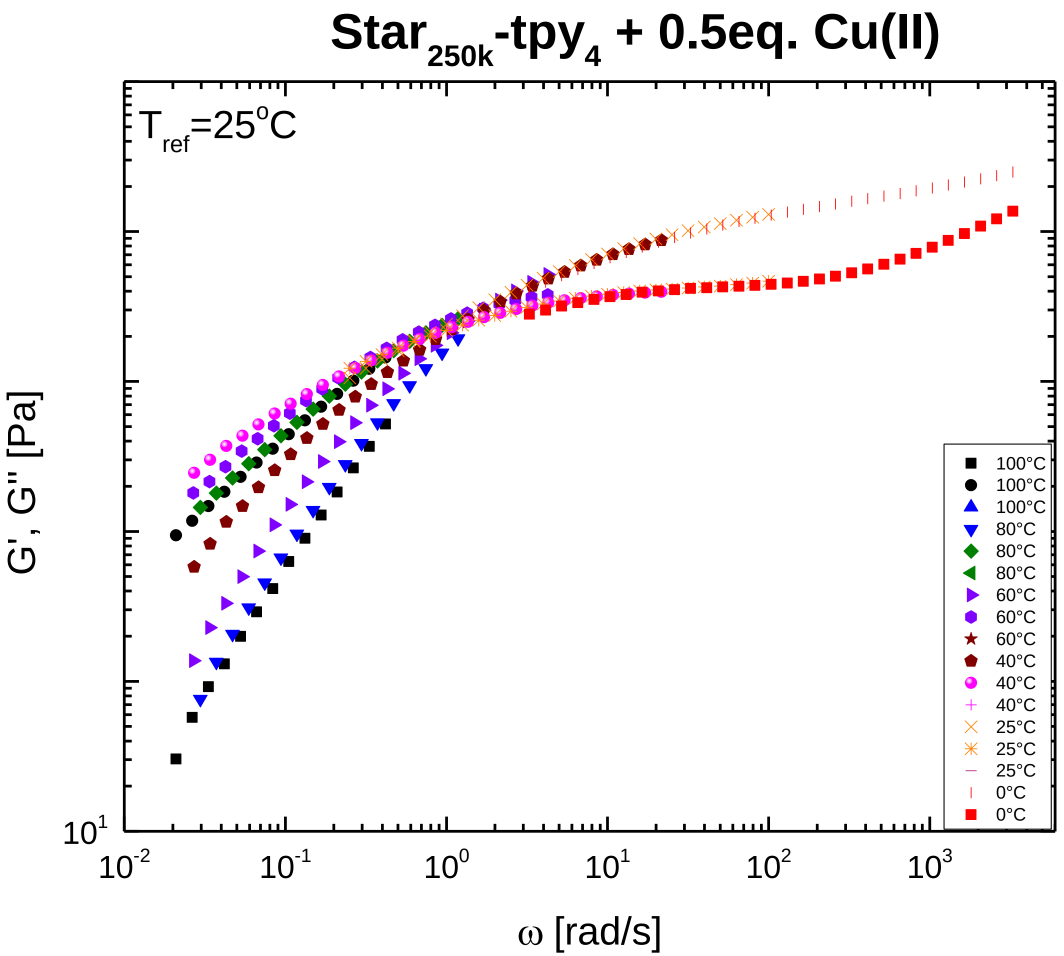
- ✓ Reproducibility at different conditions and geometries





TTS Failure





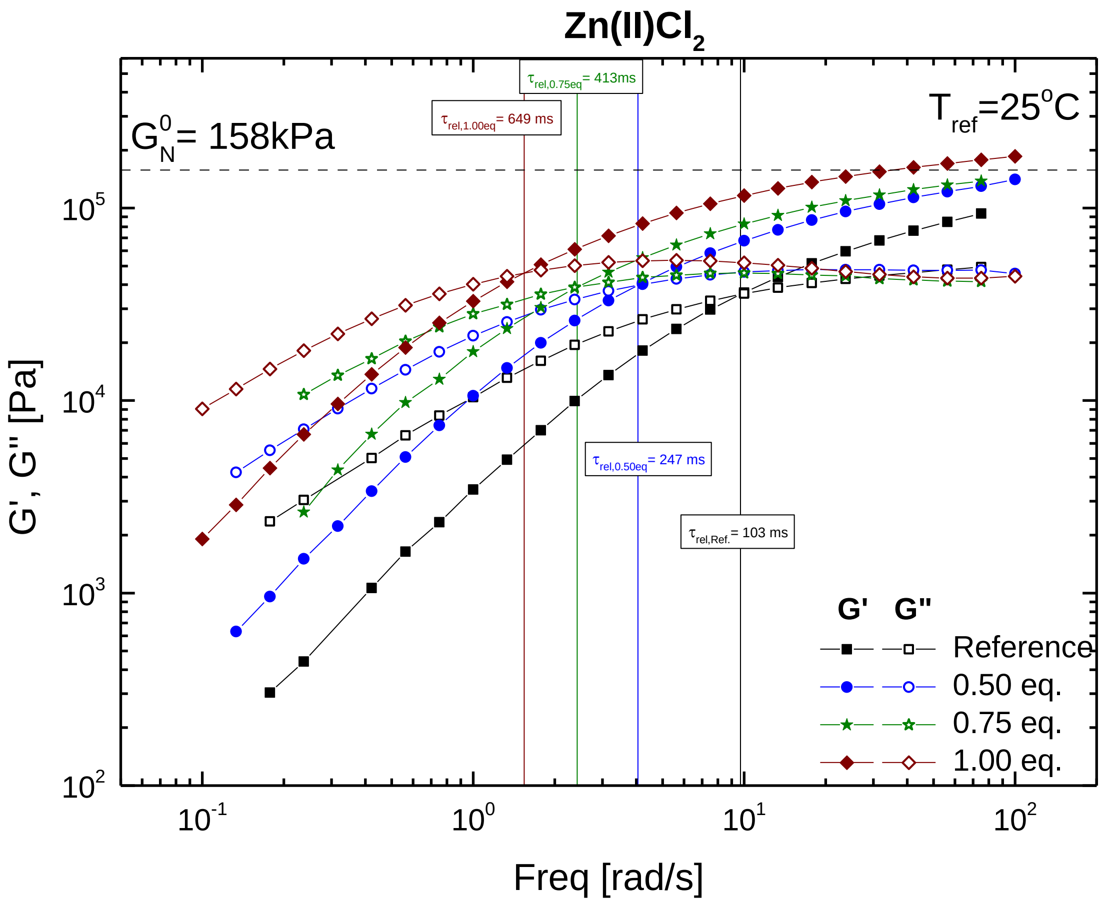
× Thermo rheological complexity

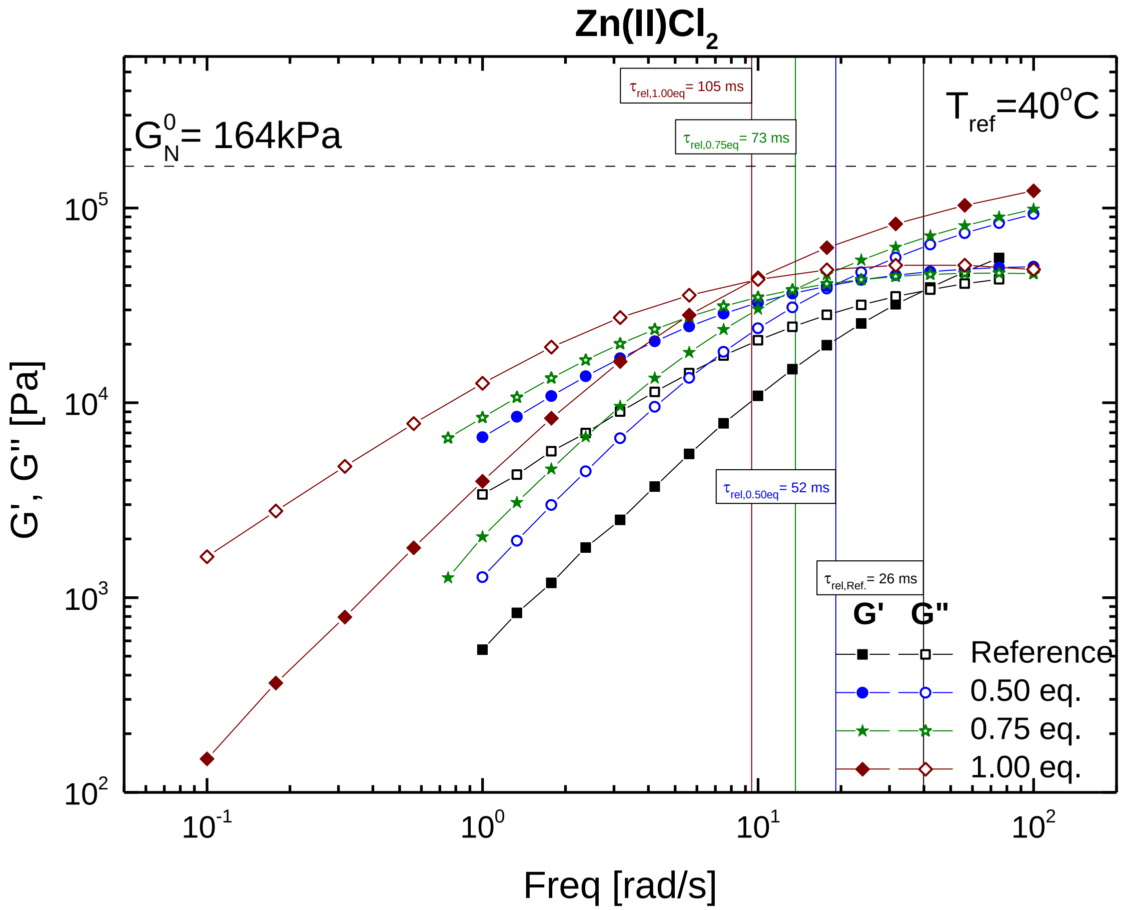
Entanglement / Disentanglement

Association/ Disassociation

Dangling chains

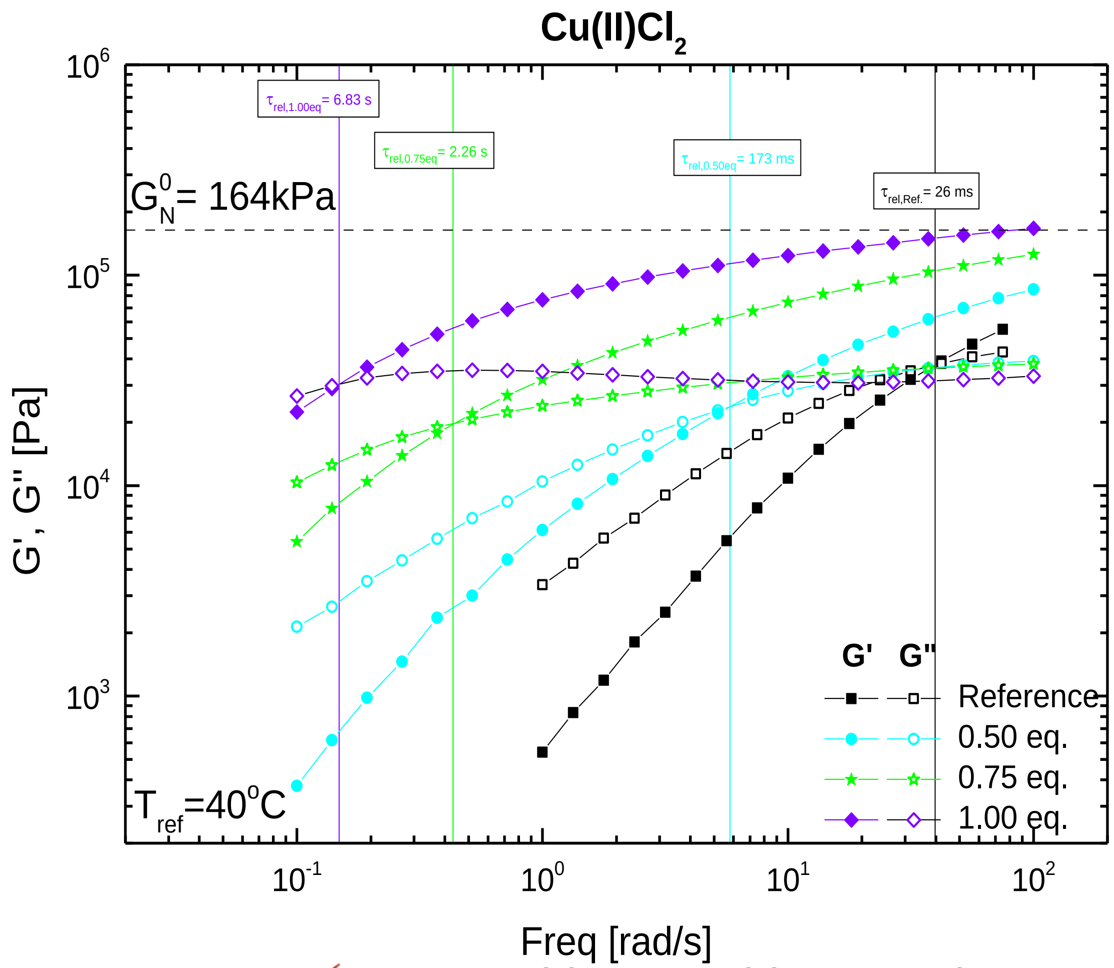
Results-LVE

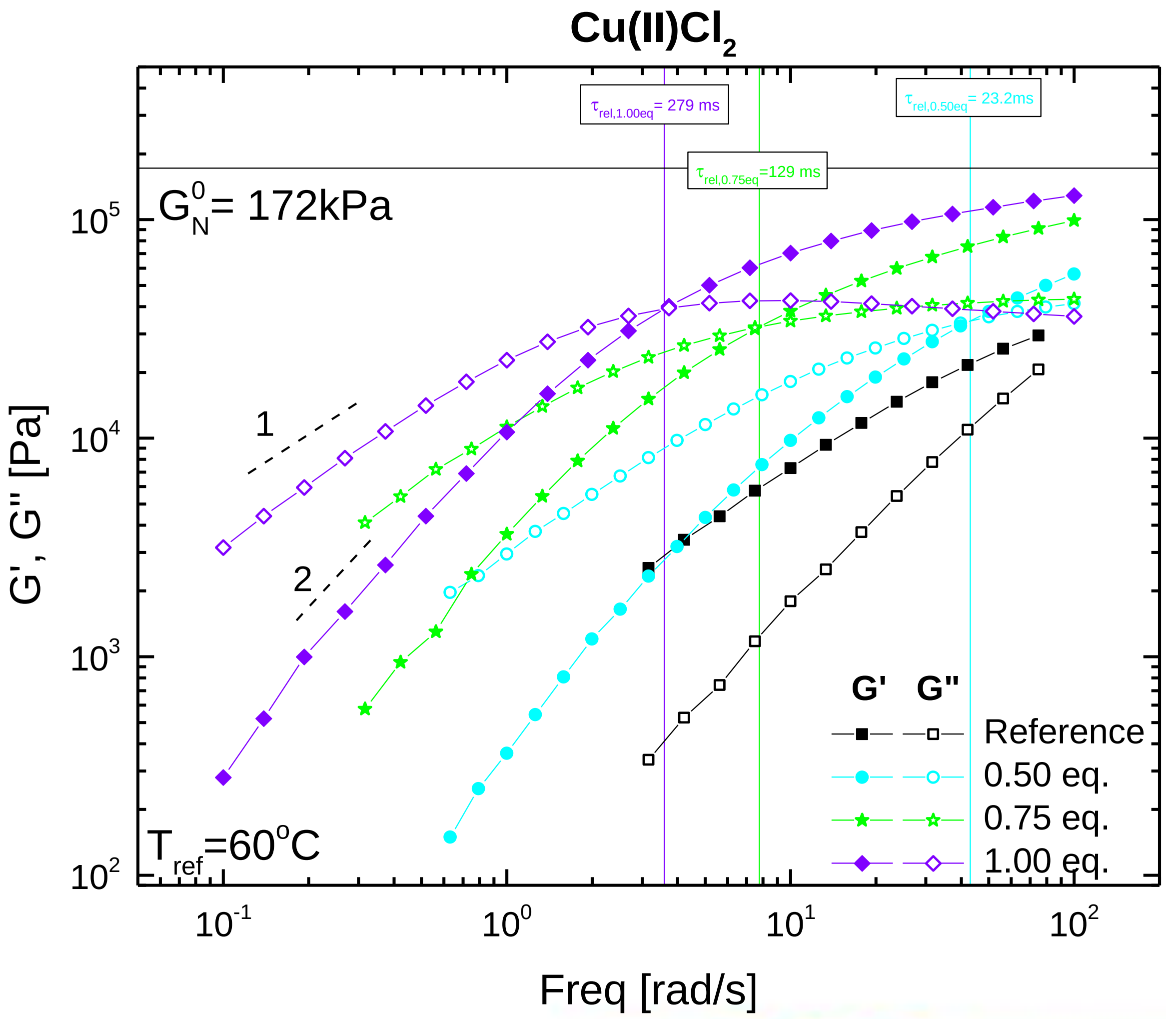




- Plenty of ions unable to coordinate with ligands when 0.5eq is added

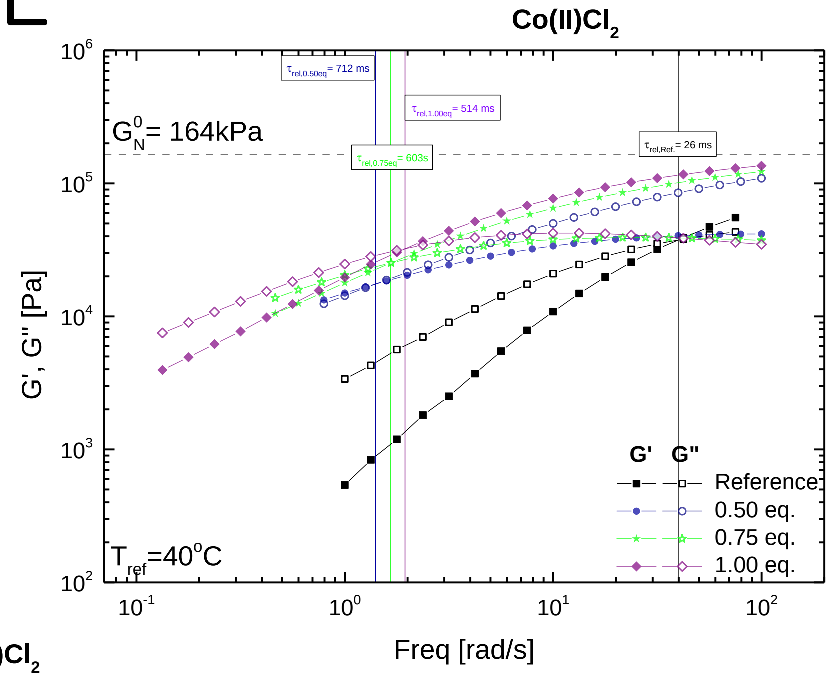
Results-LVE



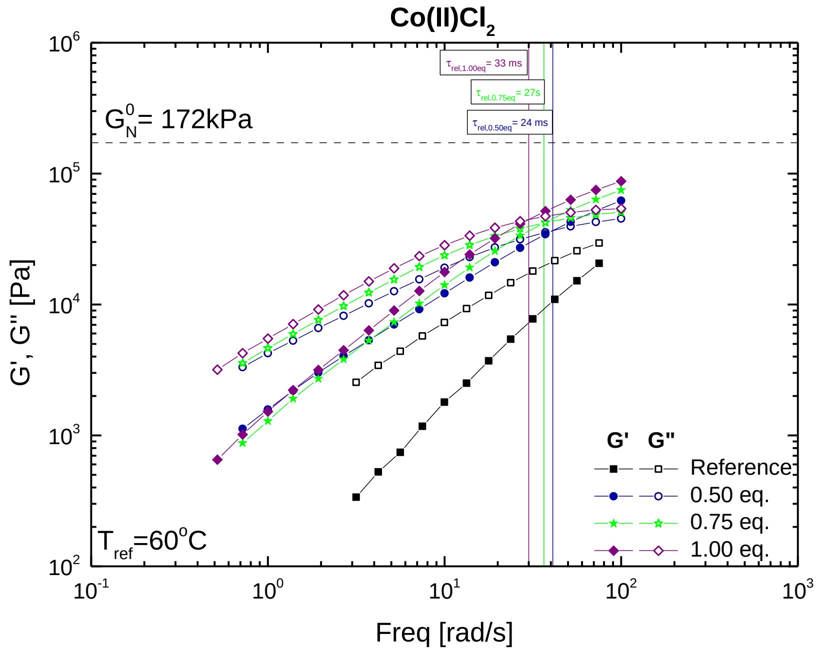


- ✓ More stable reversible network
- ✓ Higher cross-linked system

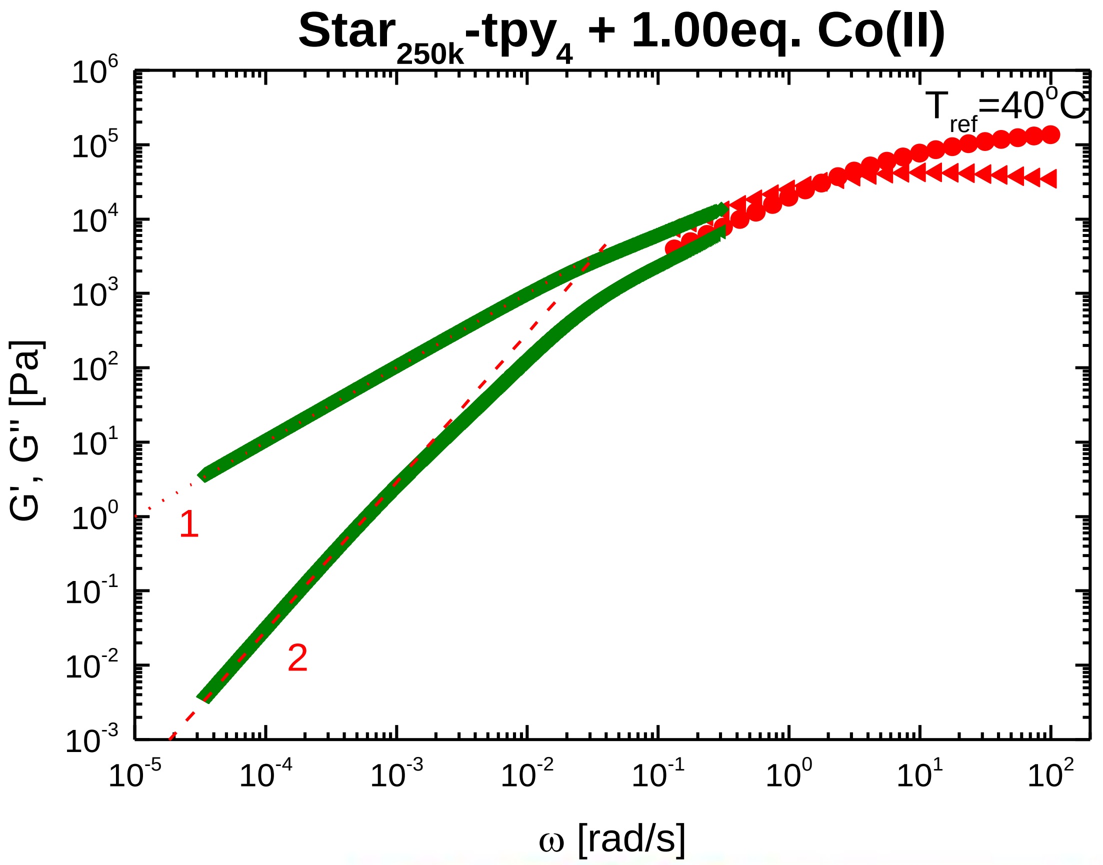
Results-LVE



Co(II)Cl2
G_N^0= 164kPa
τrel,0.50eq= 712 ms
τrel,1.00eq= 514 ms
τrel,0.75eq= 603s
τrel,Ref.= 26 ms
G', G'' [Pa]
Freq [rad/s]
G' G''
Reference
0.50 eq.
0.75 eq.
1.00 eq.
T_{ref}=40°C

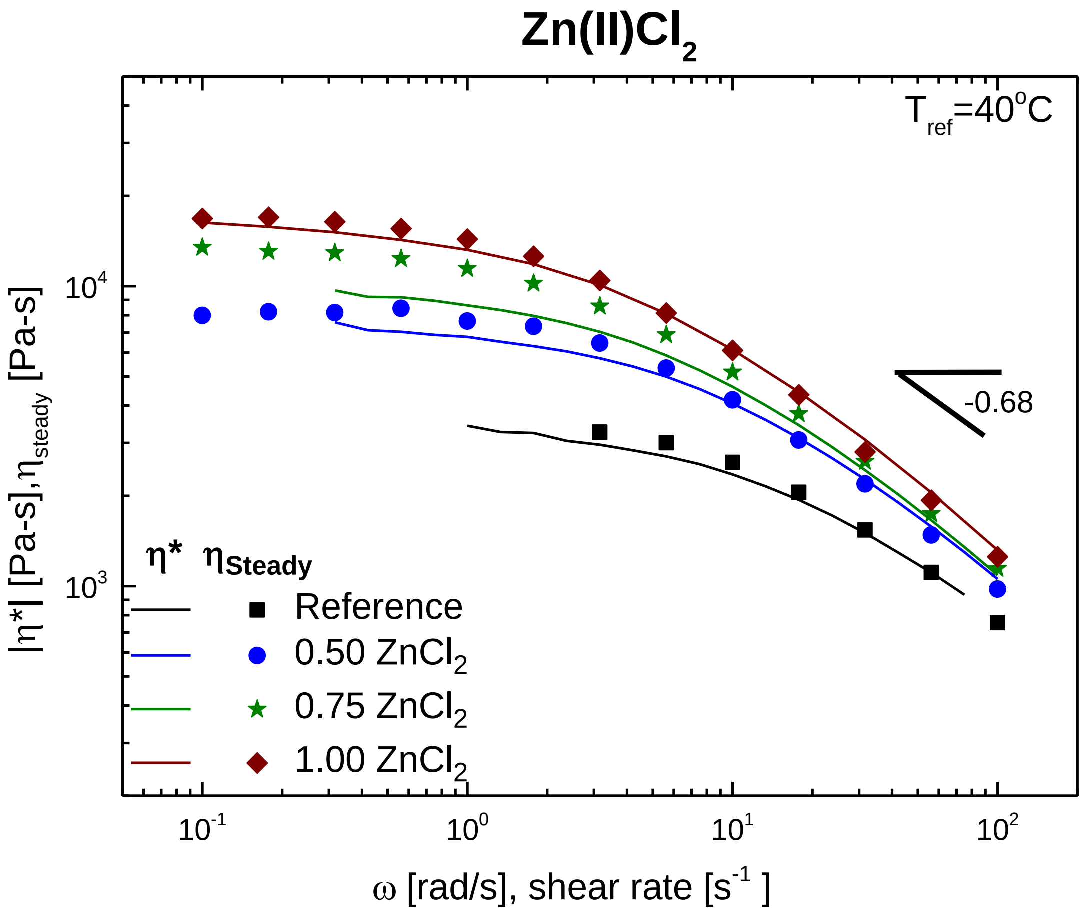


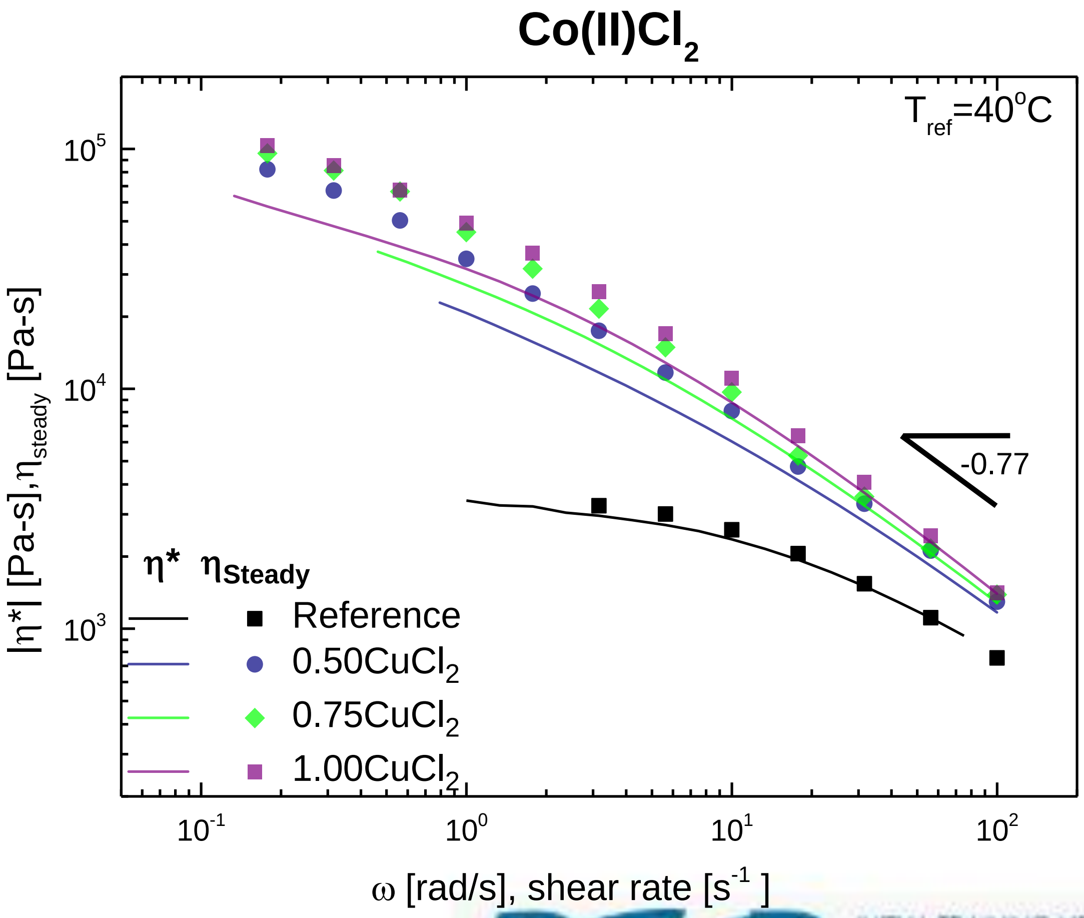
Co(II)Cl2
G_N^0= 172kPa
τrel,1.00eq= 33 ms
τrel,0.75eq= 27s
τrel,0.50eq= 24 ms
G', G'' [Pa]
Freq [rad/s]
G' G''
Reference
0.50 eq.
0.75 eq.
1.00 eq.
T_{ref}=60°C



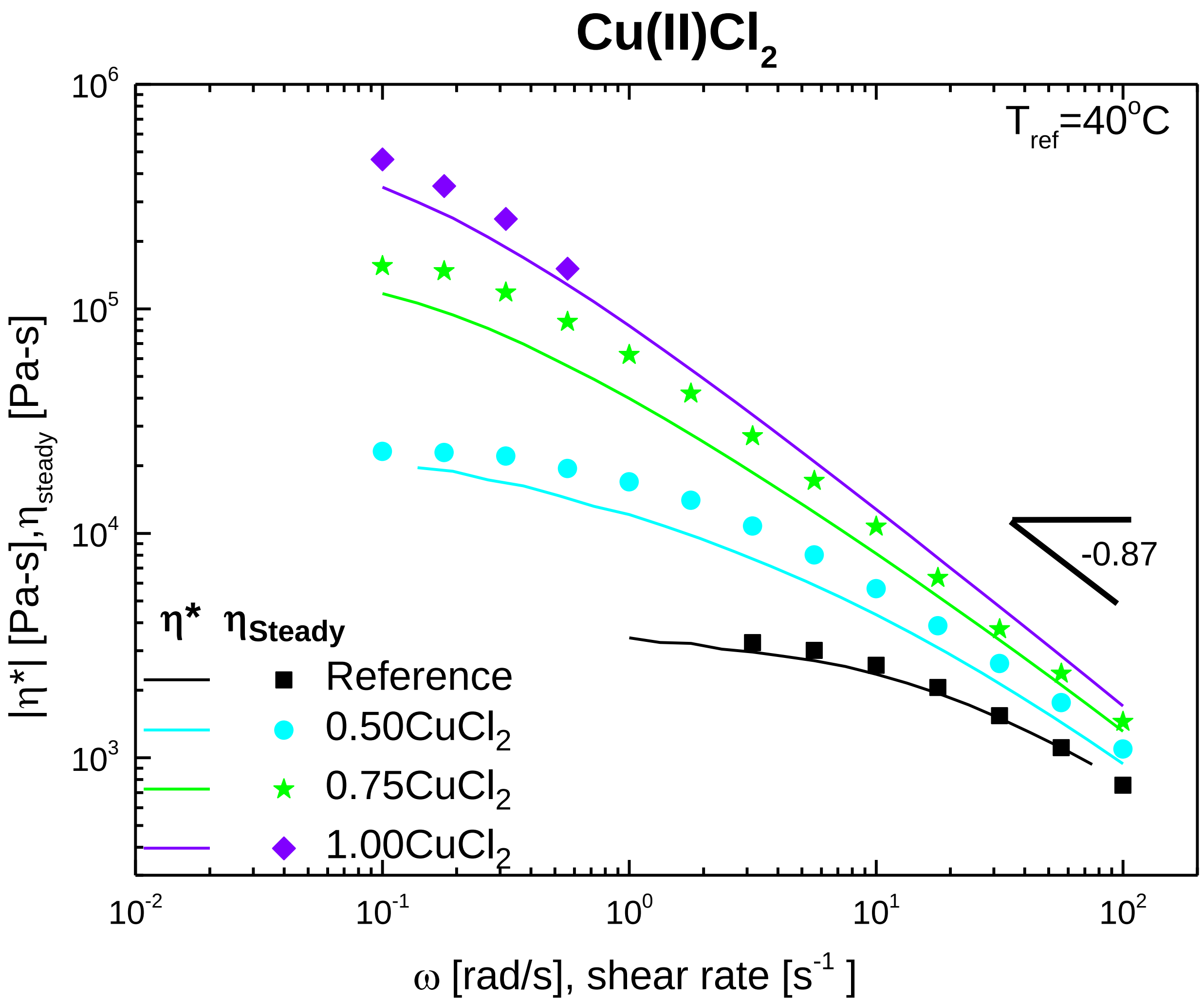
Star250k-tpy4 + 1.00eq. Co(II)
T_{ref}=40°C
G', G'' [Pa]
ω [rad/s]
1
2

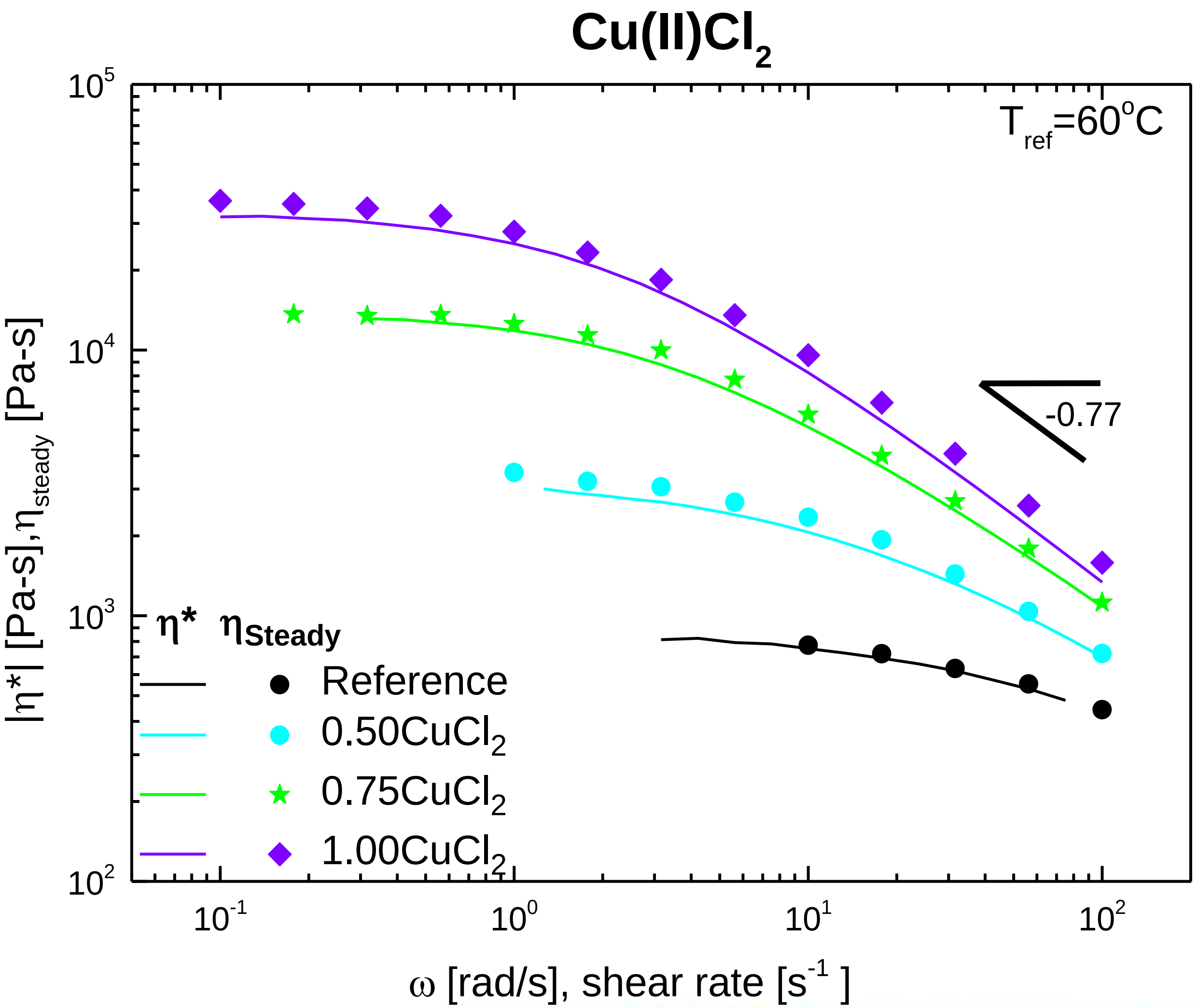
Cox-Merz rule





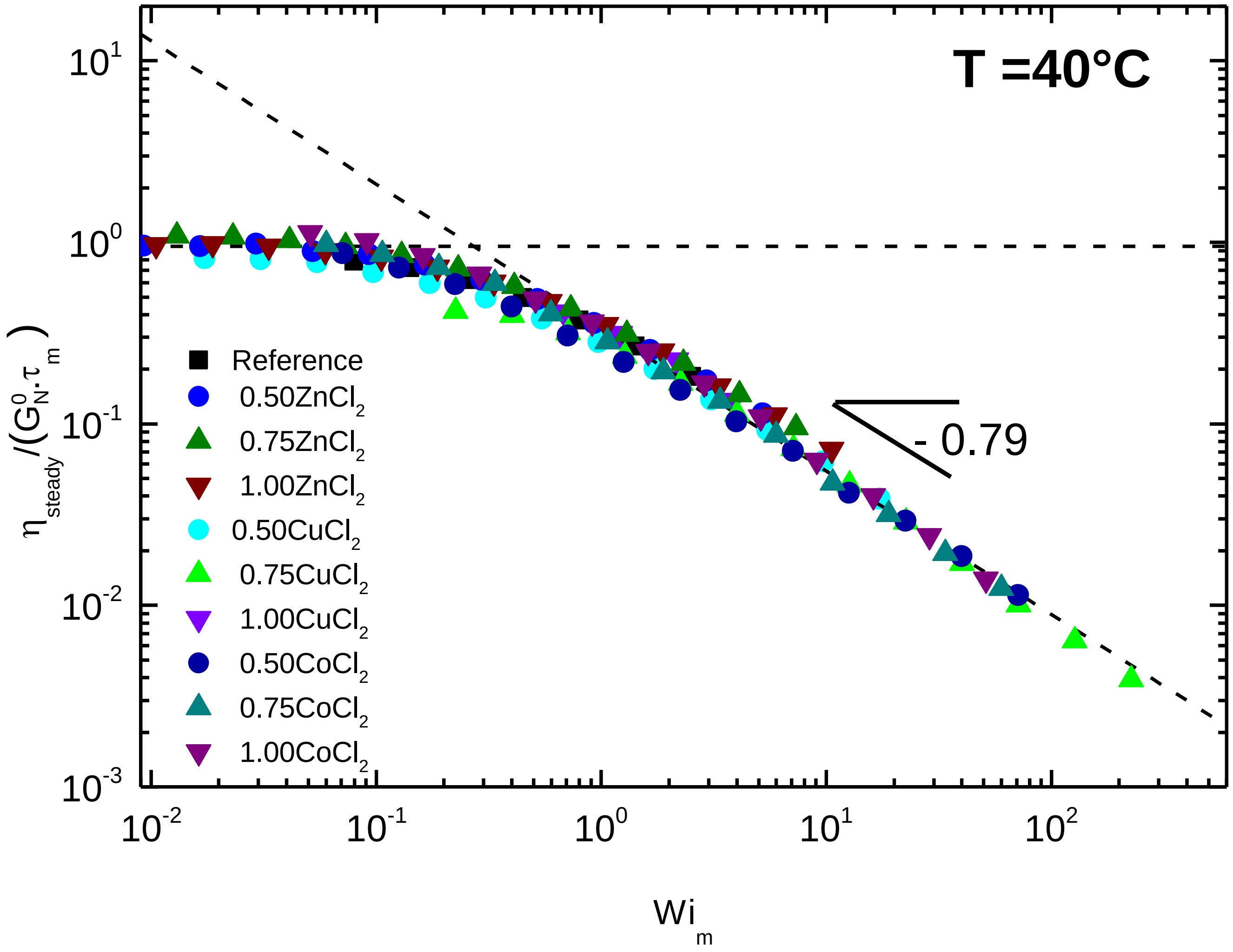
Cox-Merz rule



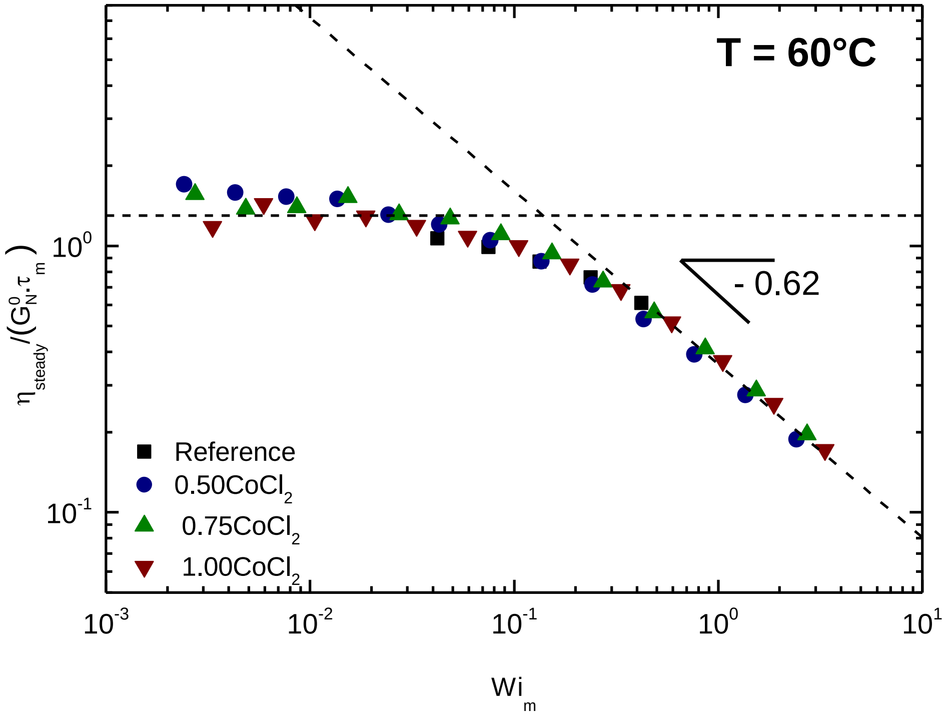


Shear Thinning

- ✓ Steady state viscosities of all systems collapse in a universal trend



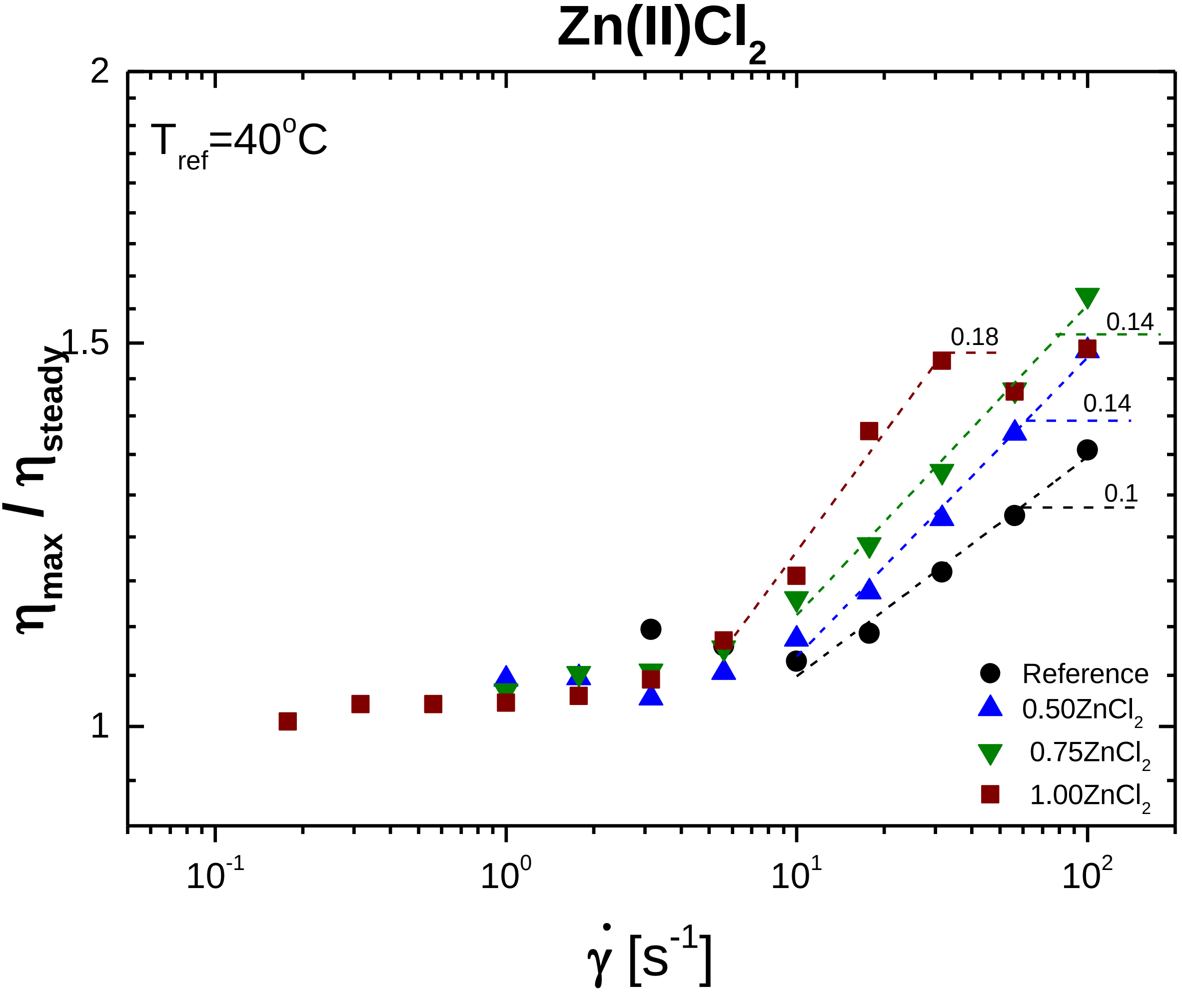
Co(II)Cl$_2$

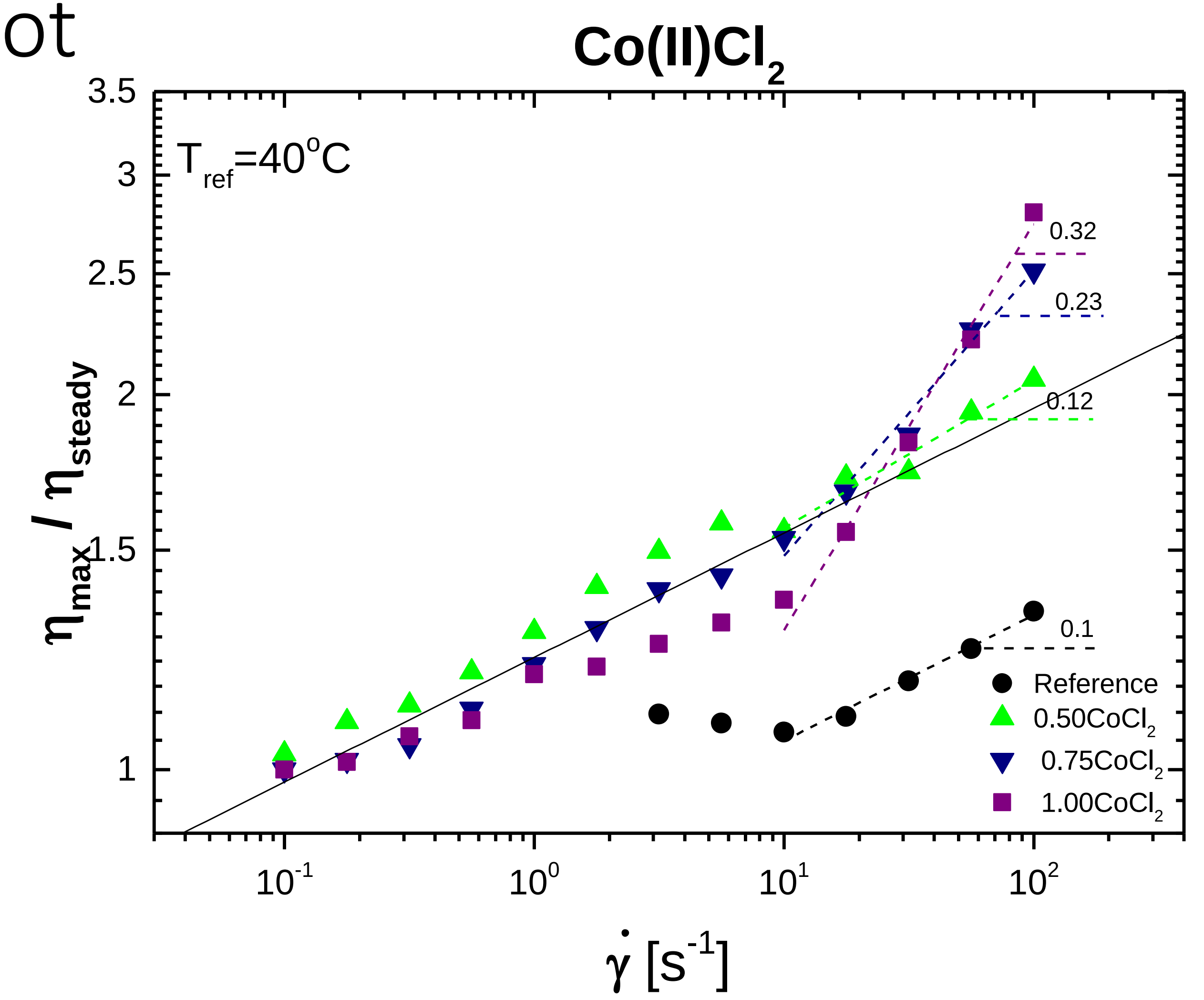


- ✓ Viscosity decay with strain is more significant at lower temperatures

- ✓ Highly cross-linked network are more vulnerable to stretching

Fractional Viscosity Overshoot





The ability of the network to insist deformation is higher:

- ✓ At higher concentrations of metal ions
- ✓ For stronger associations

Conclusions

Nature of ions

- ✓ The stronger metal ions associations, the more stable network and greater cross-linking density.

Ions amount

- ✓ More metal ions result in a dynamic network with higher resistance to deformation

Temperature

- ✓ Influence of metal-ligand coordination on dynamics is promoted at higher temperature

Future work

- Describe the linear and nonlinear viscoelastic properties with models in collaboration with UCL
- Further investigation of slow dynamics with techniques such as Dynamic Light Scattering and stress relaxation upon shear flow cessation
- Extensional Rheology in collaboration with DTU
- Double dynamics networks consisting of two different metal ions structure and dynamics exploration.
- Different architectures influence in dynamics

Thank you for your attention!

Questions?