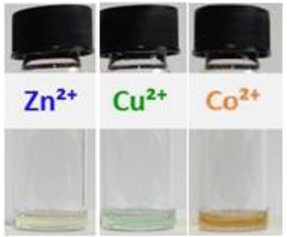
# Nonlinear Viscoelastic Response of Metallo-Supramolecular Polymeric Networks

ESR#5-Christina Pyromali

WP2, WP3: Structure & Dynamics

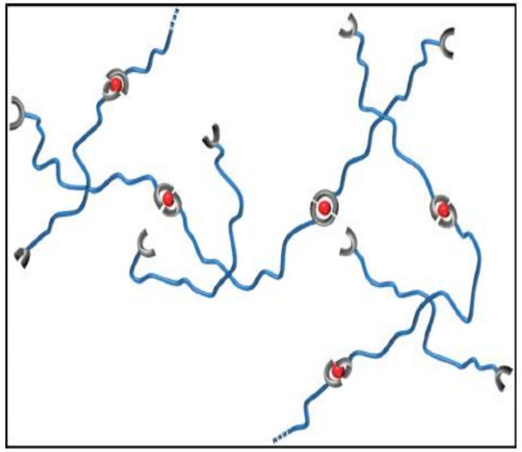
*Online Meeting III, 11-09-2020*

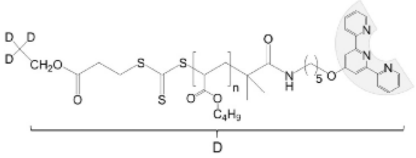

0.50

0.75

1.00



Terpyridine ligand



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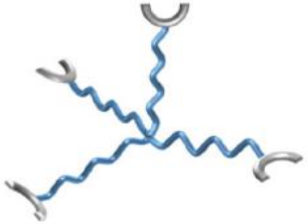


+

4 arm star poly(n-butyl acrylate)s

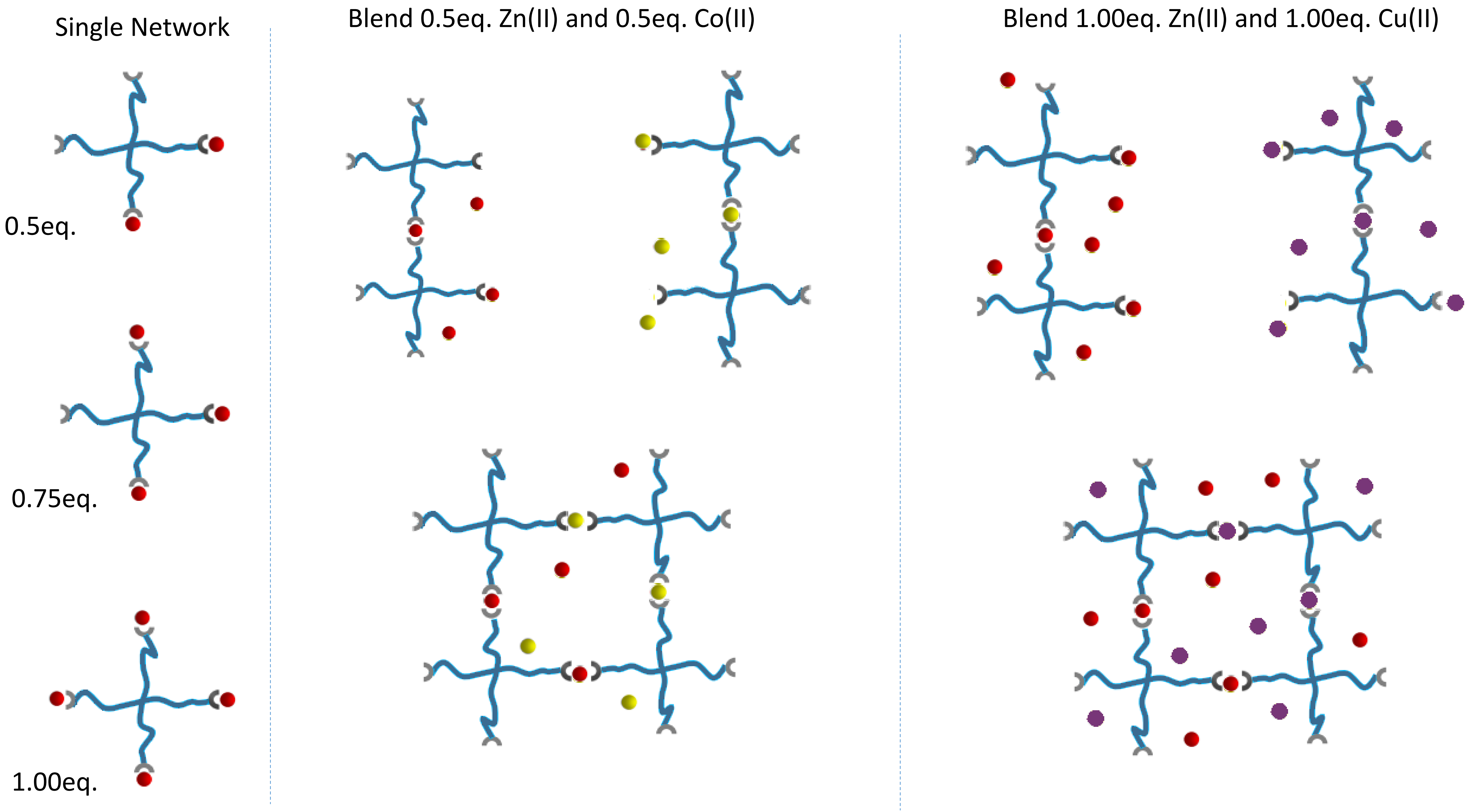
- ✓ Same Charge
  - ✓ Similar ionic radius
    - ✓ Thermodynamic stability

| | $K_1$ [$M^{-1}$] | $k_{a,1}$[$M^{-1}$ $s^{-1}$] | $k_{d,1}$ [$s^{-1}$] | $K_2$ [$M^{-1}$] | $k_{a,2}$[$M^{-1}$ $s^{-1}$] | $k_{d,2}$ [$s^{-1}$] | $\beta=K_1 \cdot K_2$ |
|---|---|---|---|---|---|---|---|
| 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.

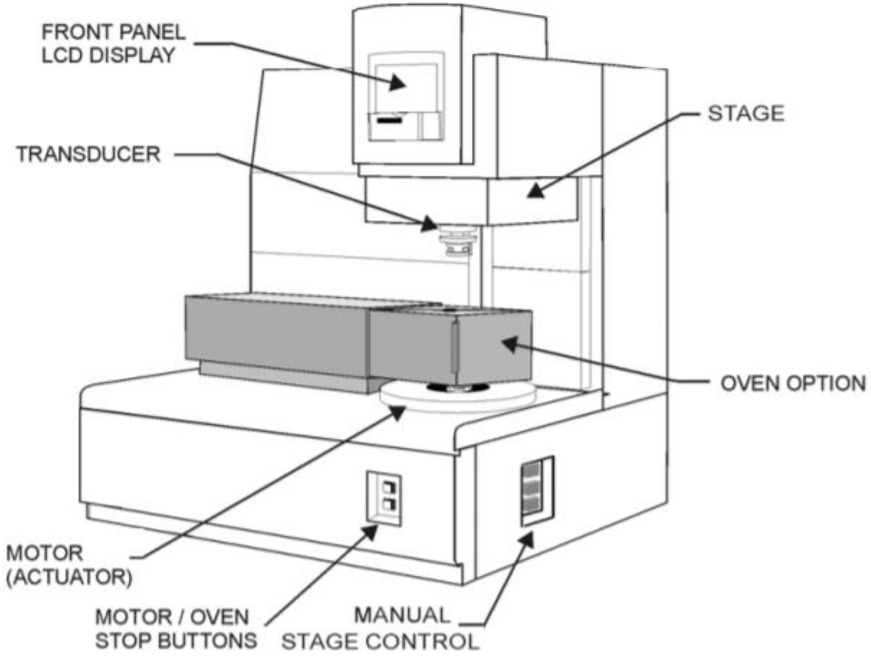
| $M_n$ [kg/mol] | $M_e$ [kg/mol] | $Z=M_n/M_e$ | Dispersity | Tg [°C] |
|---|---|---|---|---|
| 249 | 18 | 3.4 per arm | 1.2 | -52 |

INITIAL TRAINING NETWORK

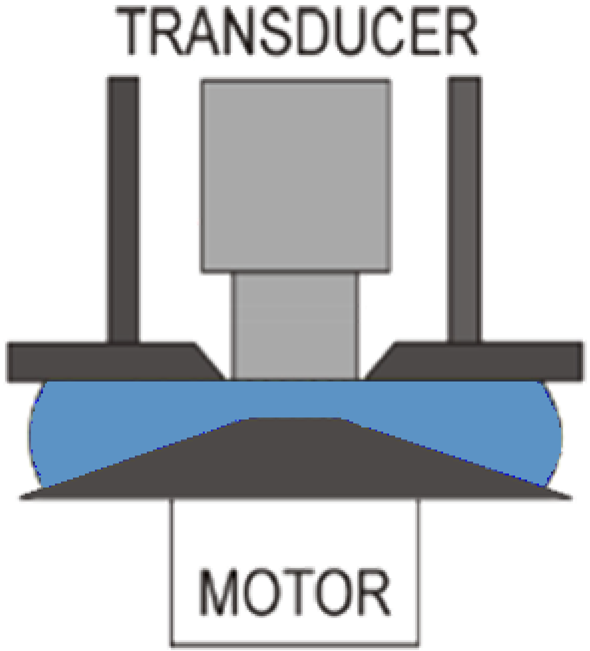


Single Network
Blend 0.5eq. Zn(II) and 0.5eq. Co(II)
Blend 1.00eq. Zn(II) and 1.00eq. Cu(II)
0.5eq.
0.75eq.
1.00eq.

# Methods




**Start-up shear and relaxation**

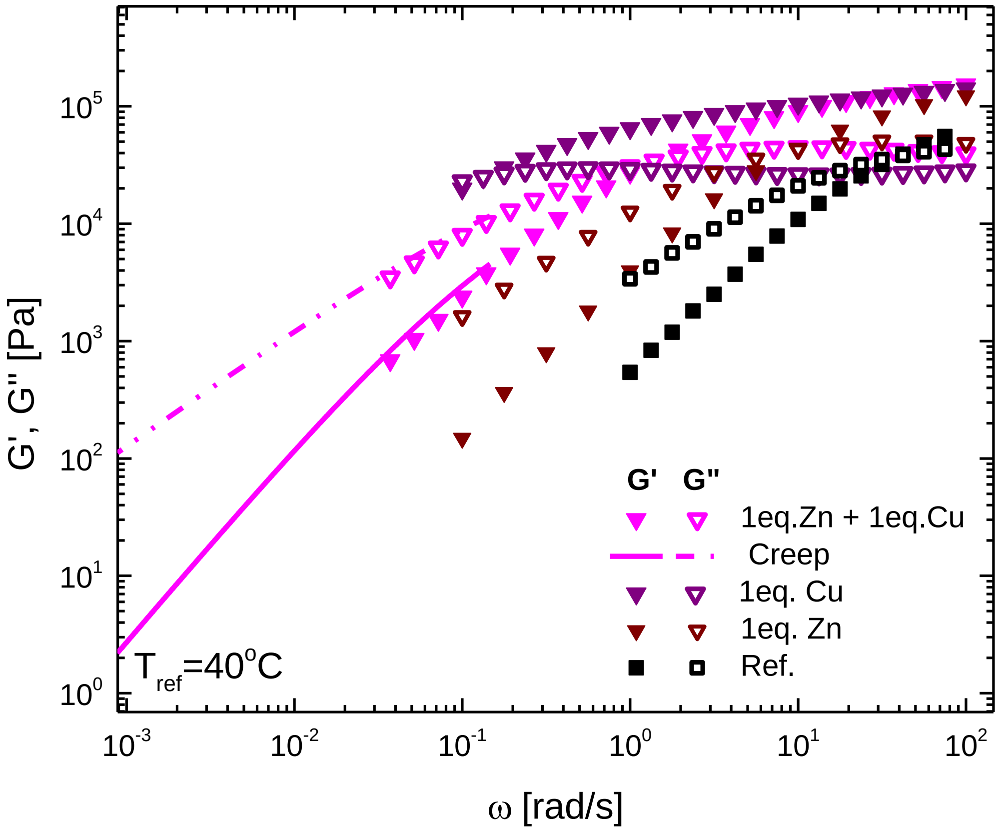


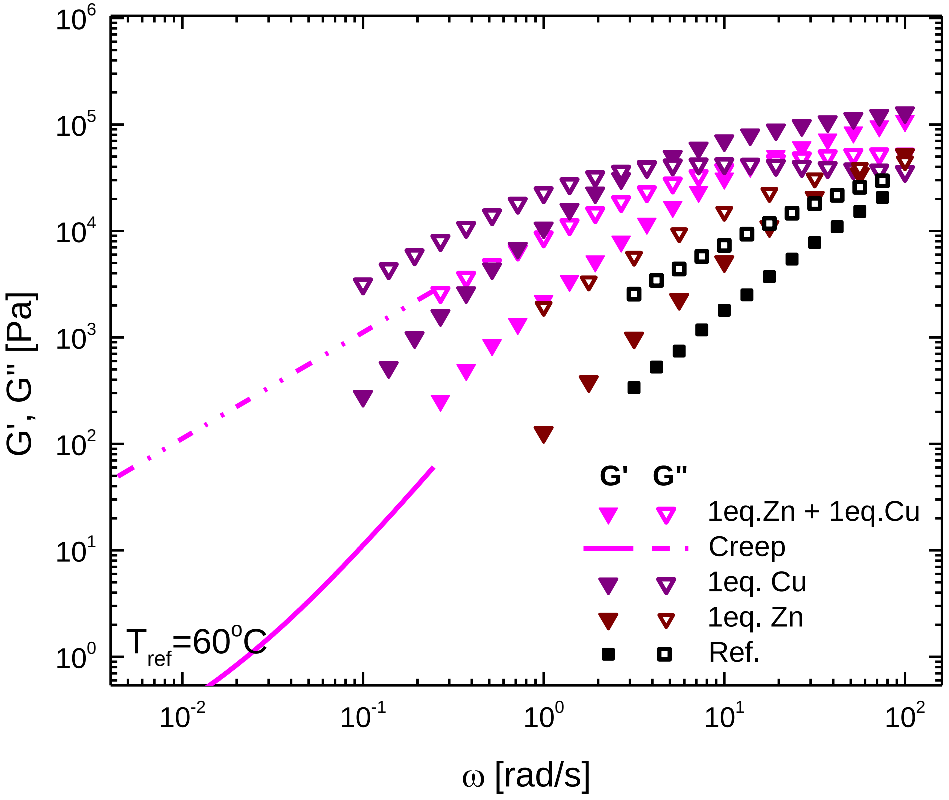

- ✓ 6.2 mm or 4.1 mm CPP
- ✓ 0.1 radians lower cone plate
- ✓ 0.051 μm fixed truncation
- ✓ Elimination of edge fracture
- ✓ Shear rates ranging from 0.1 to $1000 s^{-1}$

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

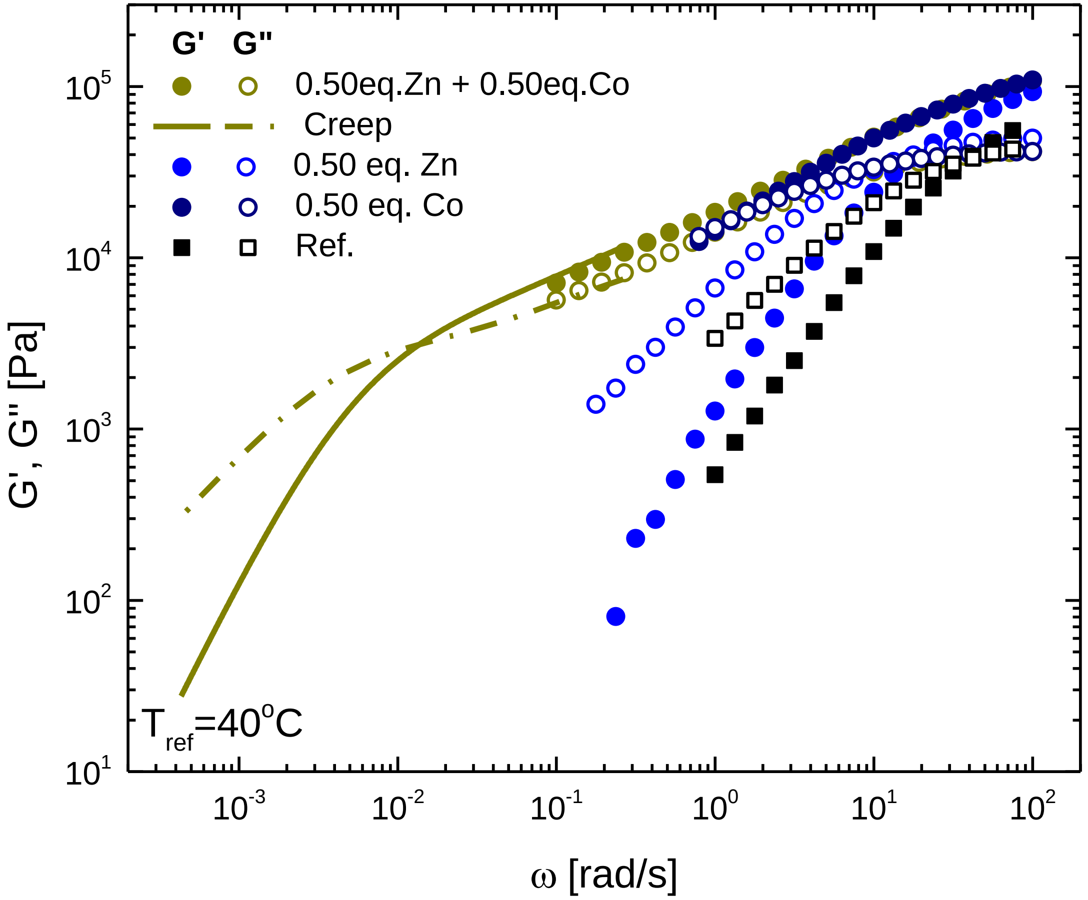
INITIAL TRAINING NETWORK

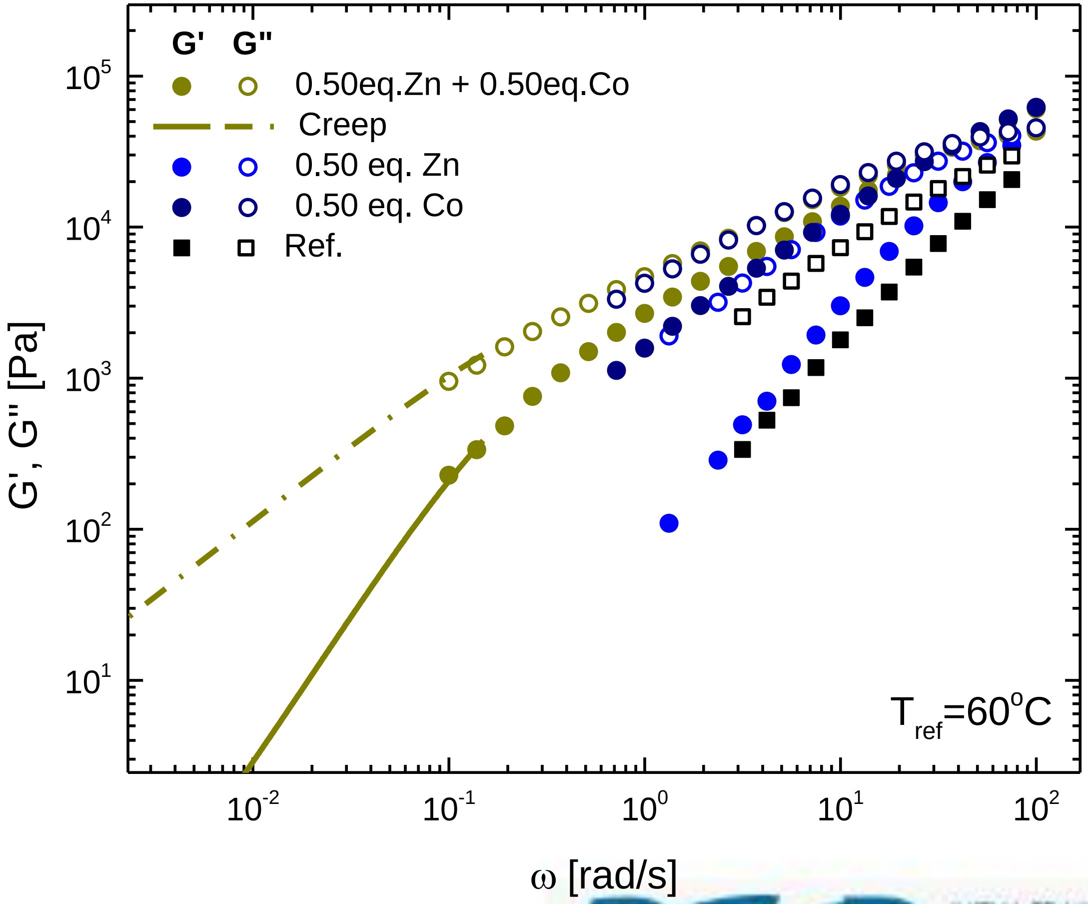
# LVE 1.00eq. Zn + 1.00eq. Cu



# LVE 0.50eq. Zn + 0.50eq. Co

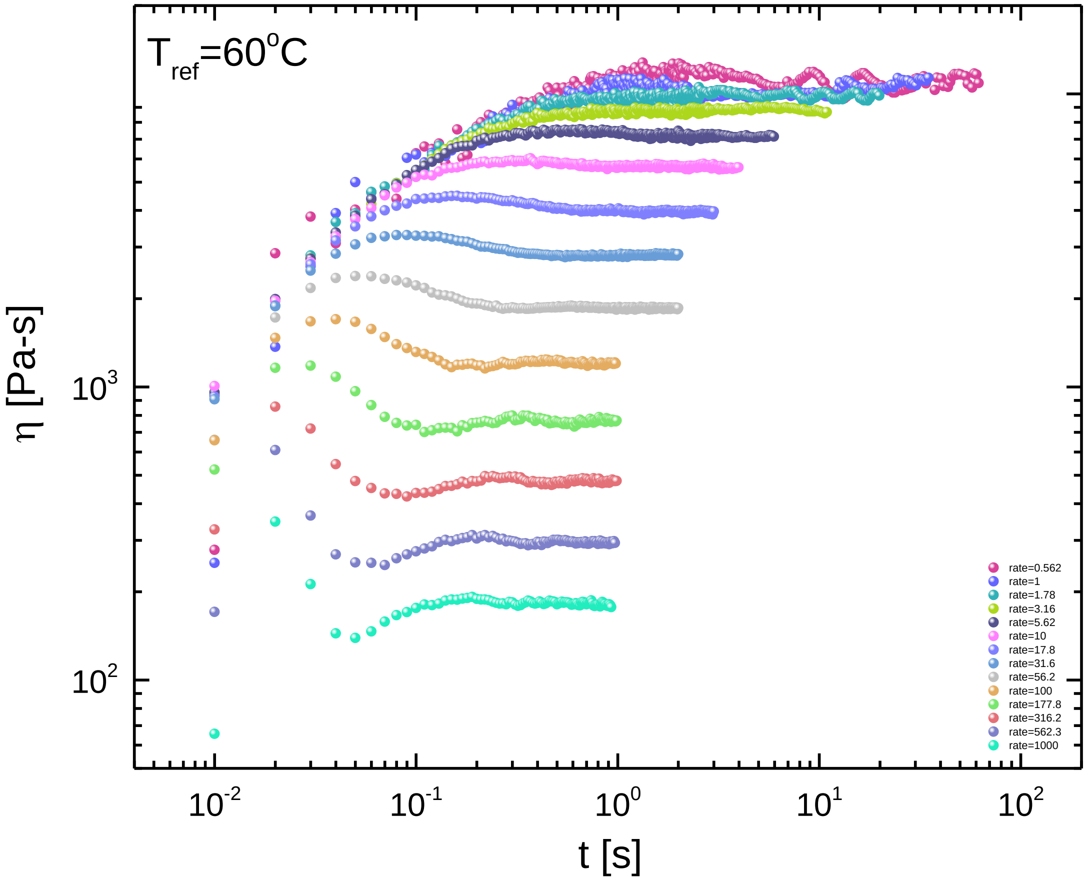


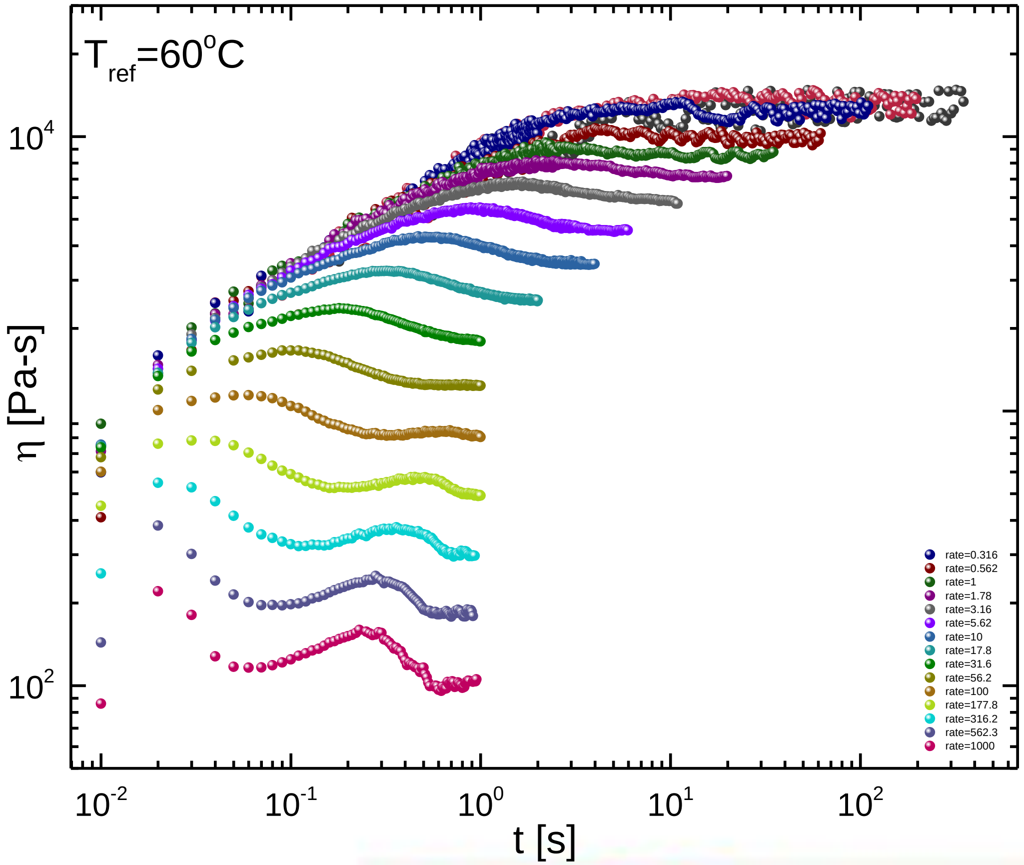

DDNs dynamics depends on the combination of the dynamics of the corresponding single networks at the specific **temperature**, **amount** and **nature** of the metal ions

# Start-up shear of DDNs

**$Star_{250k}$-$tpy_4$ + 1.00eq. Zn(II)+1.00eq. Cu(II)**

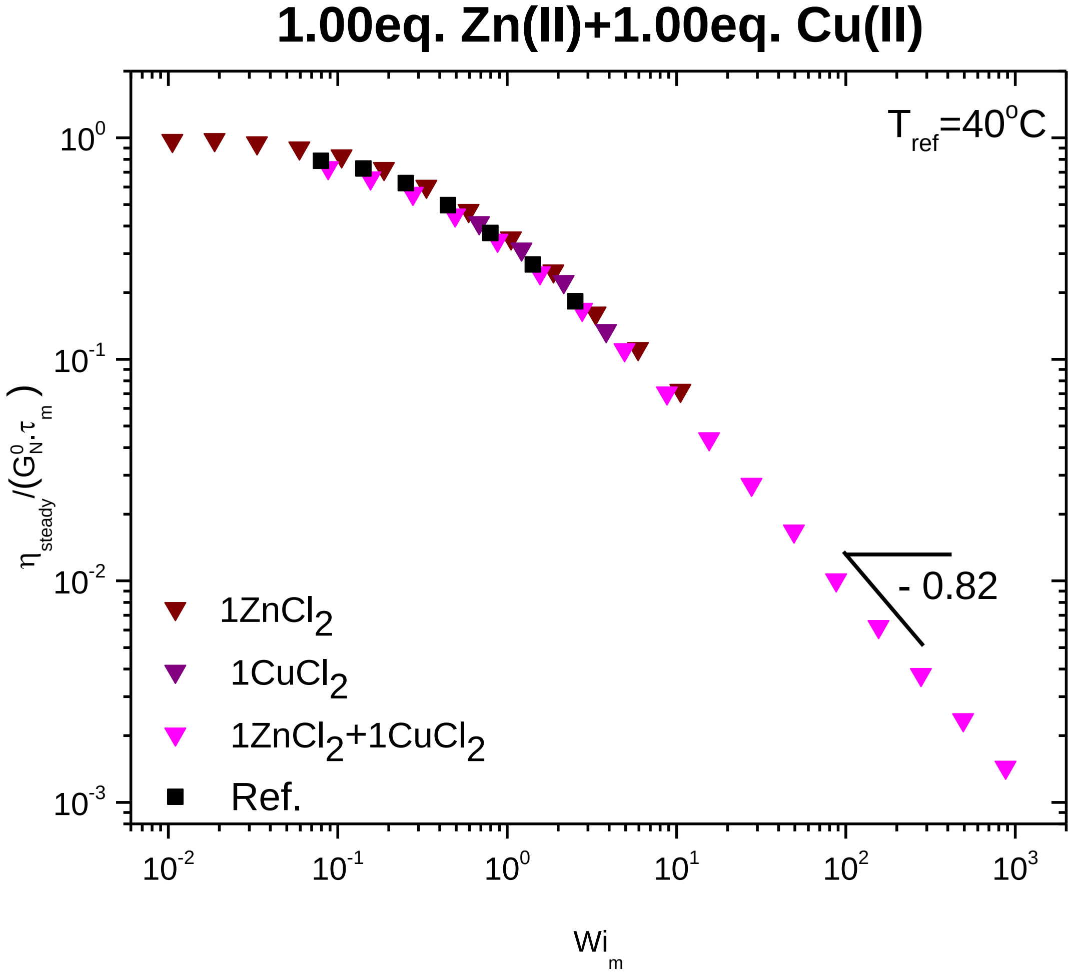


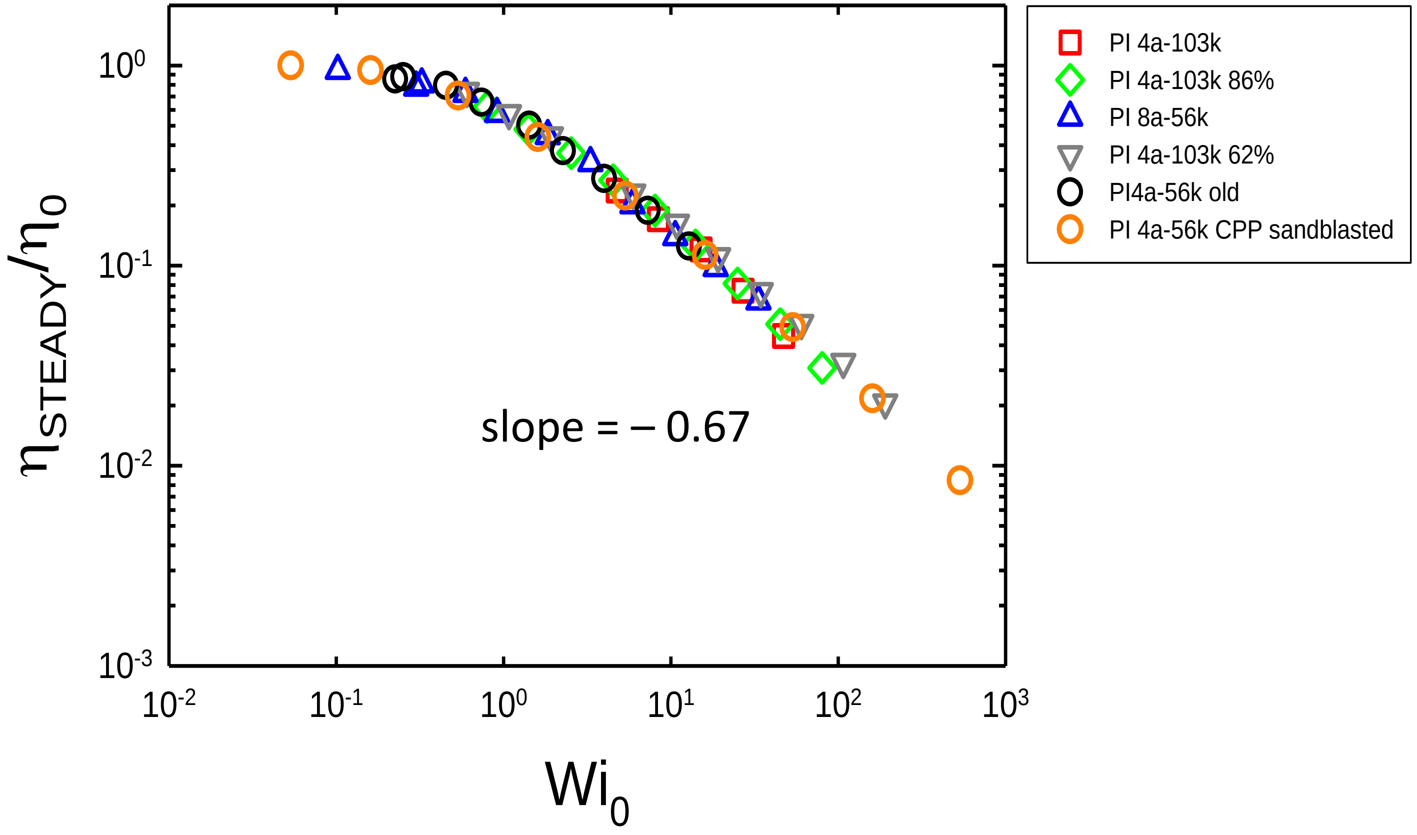

**$Star_{250k}$-$tpy_4$ + 0.5eq. Zn(II)+0.5eq. Co(II)**




One network might be more vulnerable to stretching and so M-L dissociate faster at high shear rates letting the second networks unaffected and by extend providing large deformability and coherence to the overall structure

# Shear Thinning I

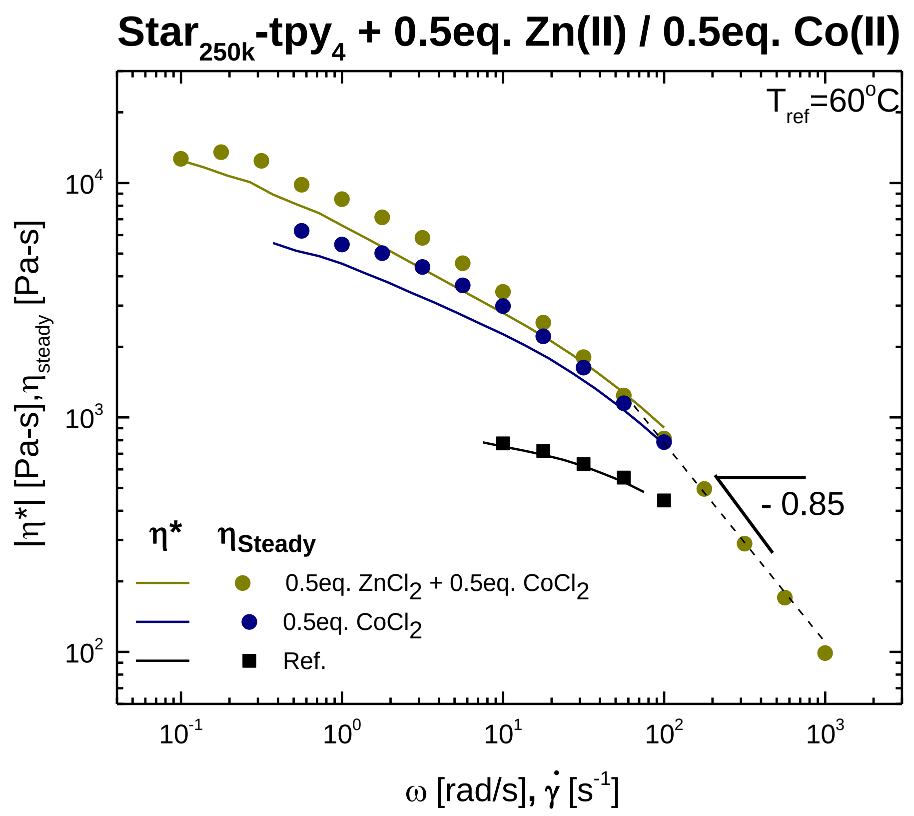


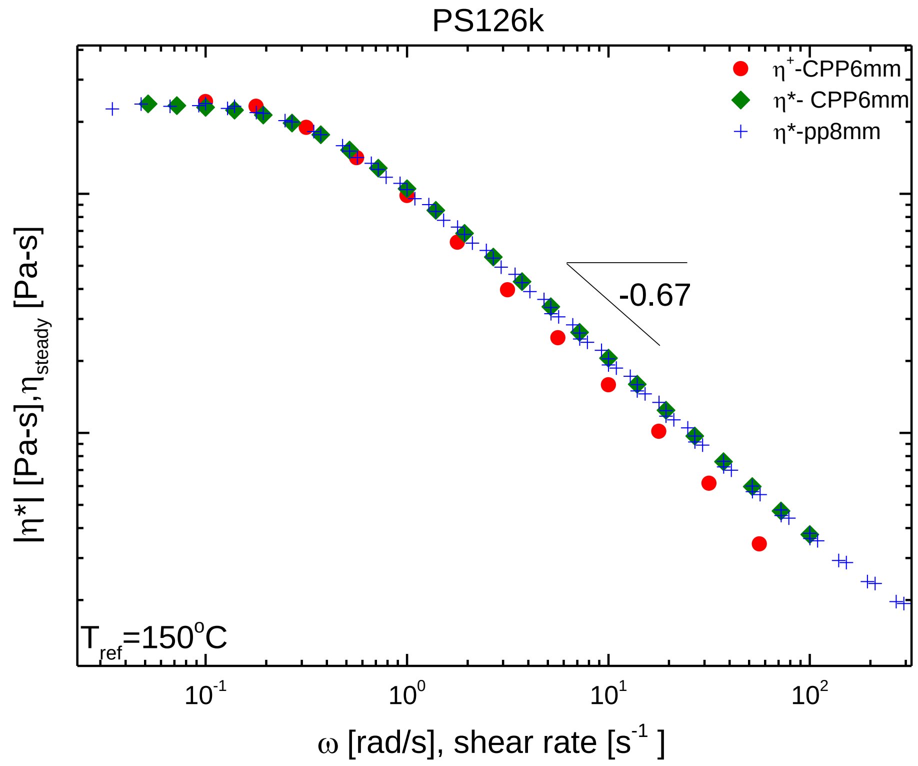




Snijkers et al. Macromolecules, 2014

Viscosity decay with shear strain or rate is more significant for DDN which is related to the cross-linked density and the stability of the network

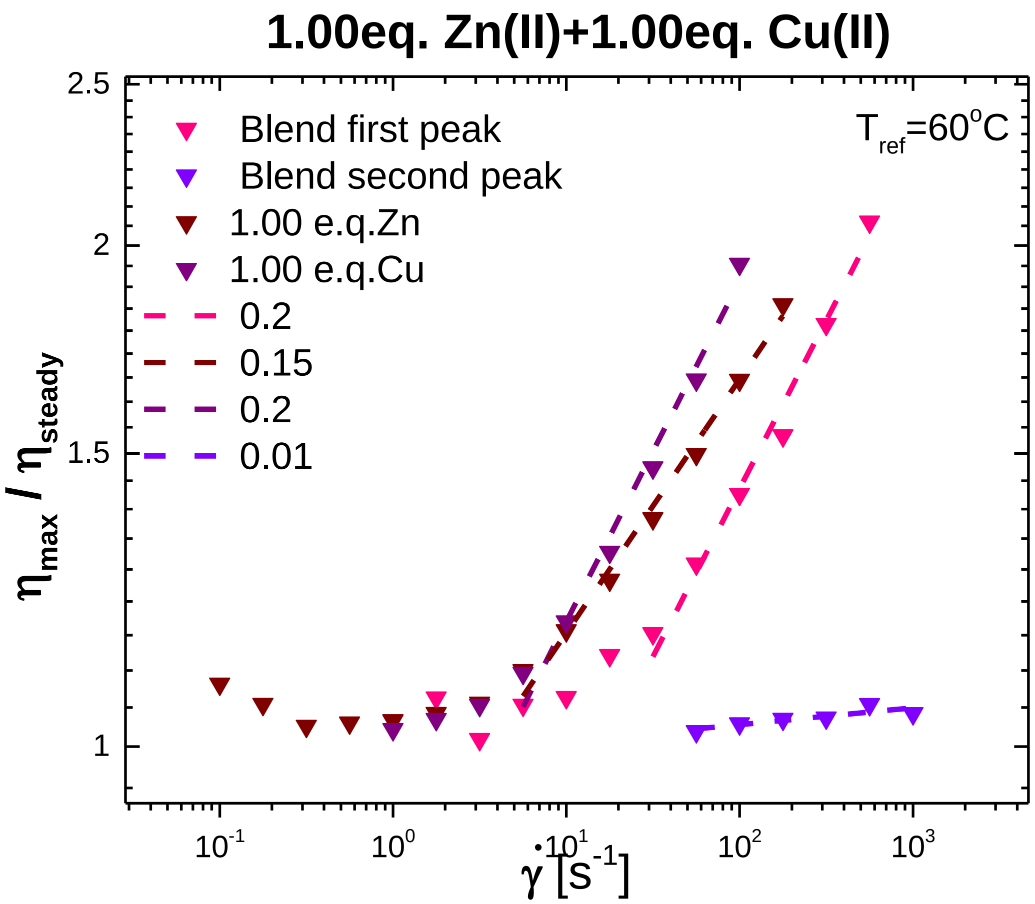
# Shear Thinning II

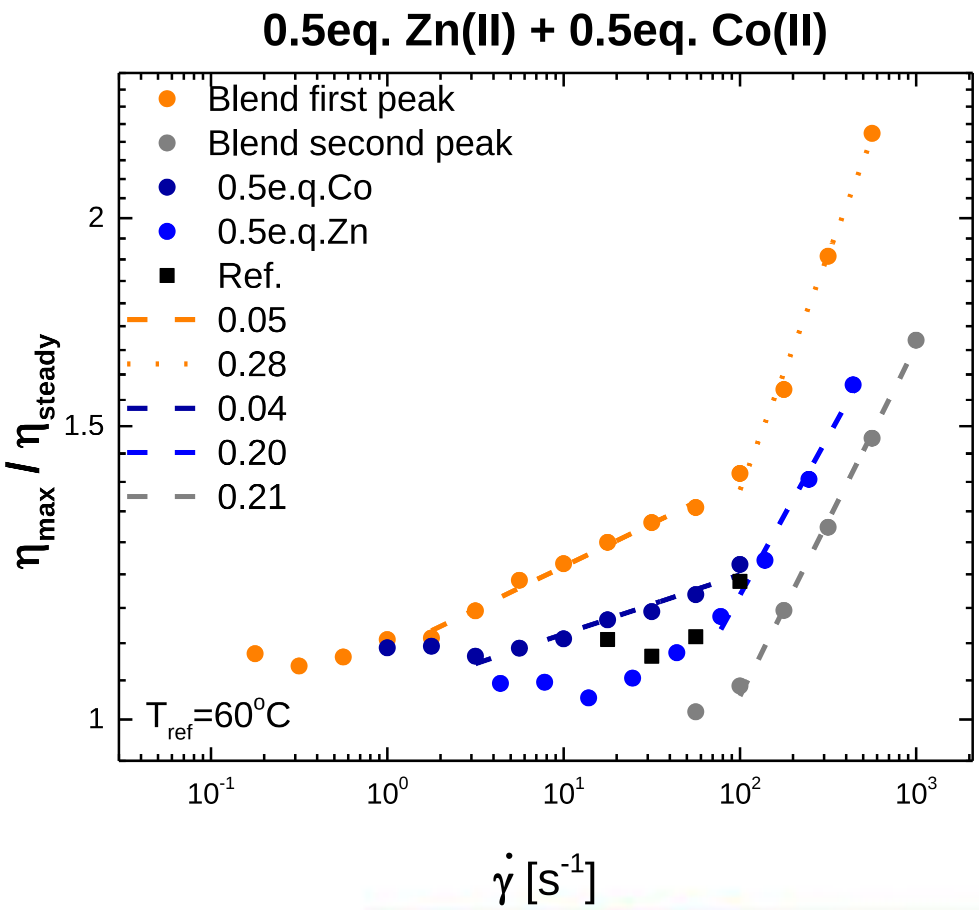



Viscosity decay with shear strain or rate is more significant for DDN which is related to the cross-linked density and the stability of the network

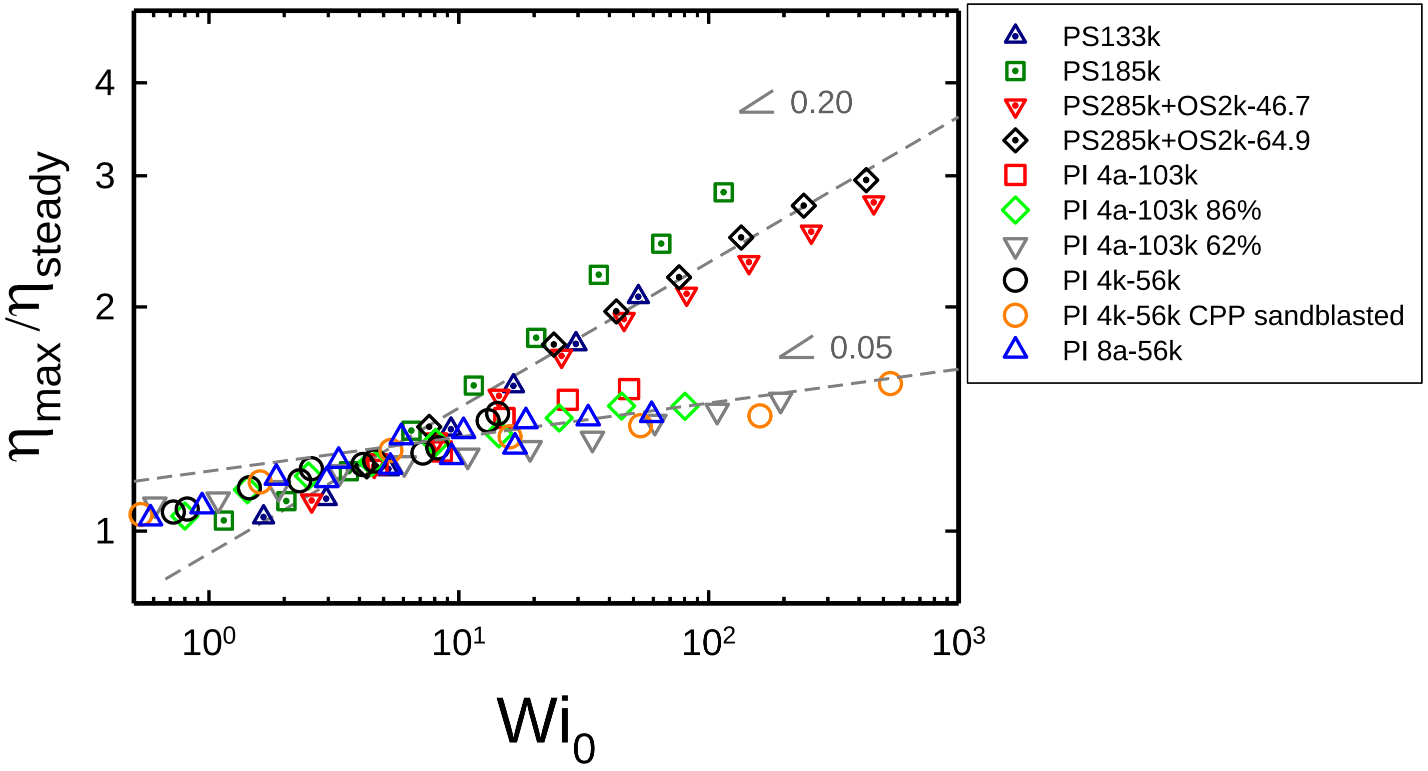
# Fractional Viscosity Overshoot

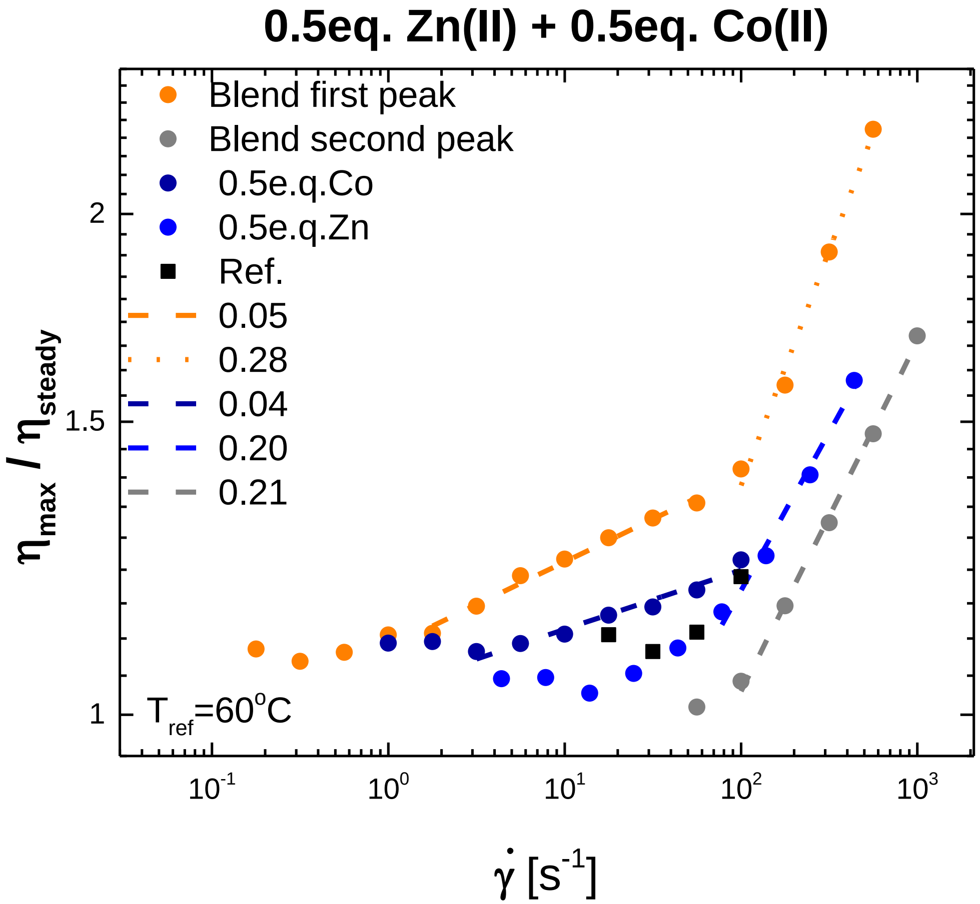



The ability to insist deformation is higher for the DDN with 0.5eq.Zn+0.5eq.Co

# Fractional Viscosity Overshoot

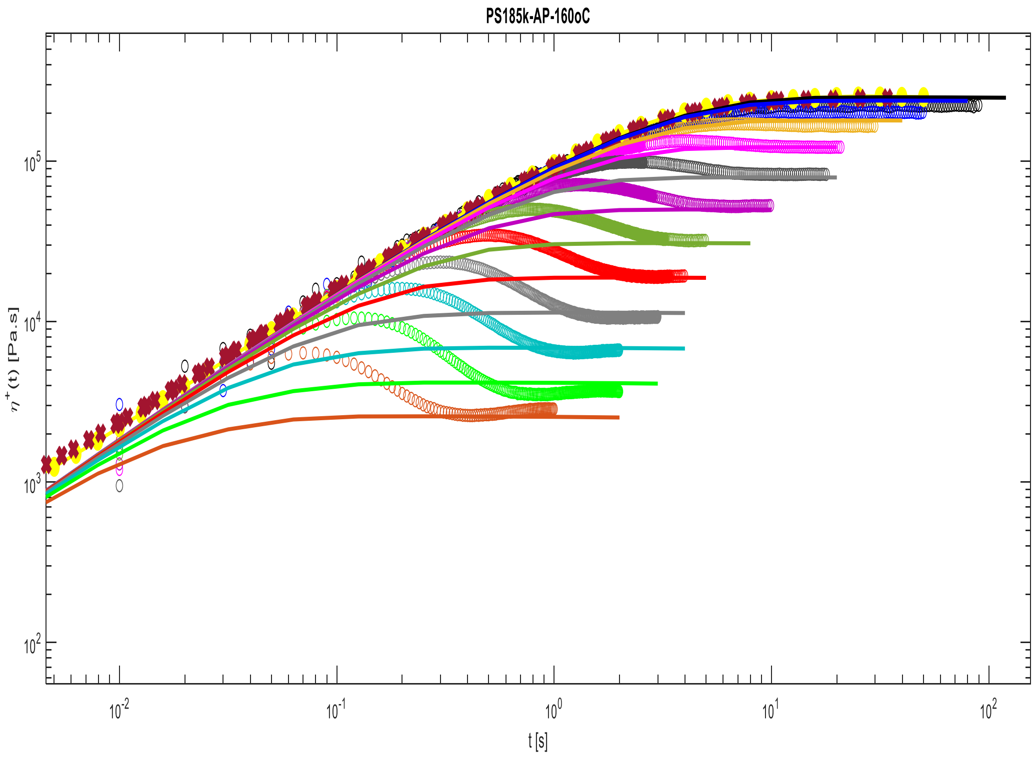


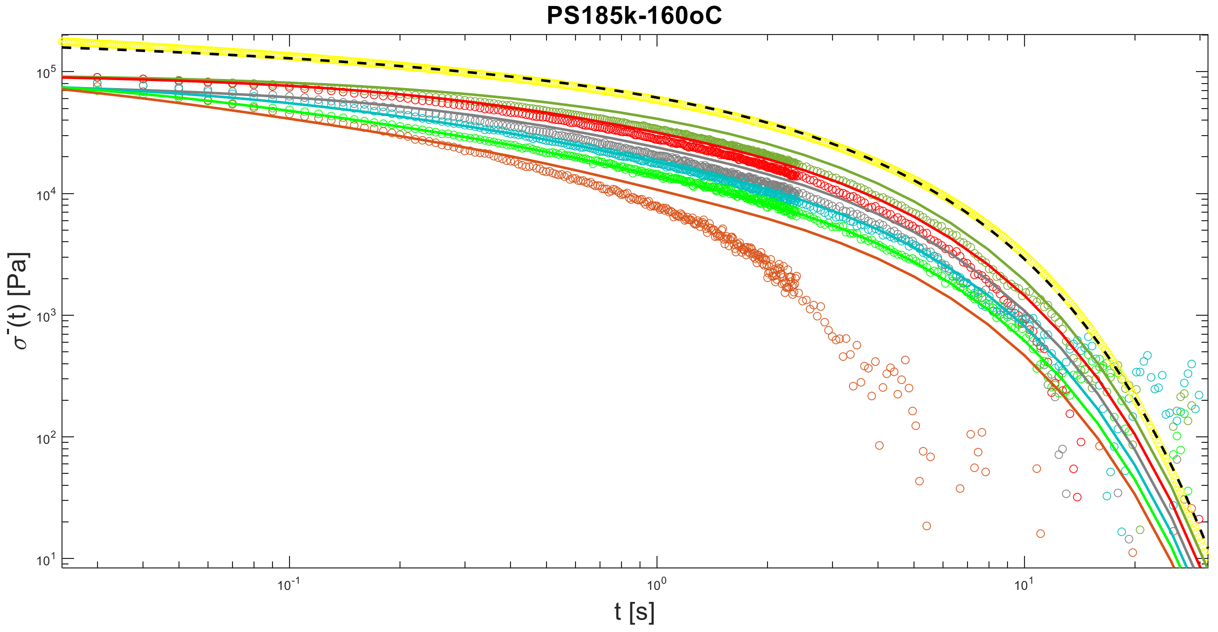




PI stars exhibit weaker fractional overshoot and dependence on Wi

# Future work

- Develop a tube based model that predicts the stress growth and relaxation upon cessation of shear flow for DDNs



# Thank you for your attention!

Questions?