Nonlinear shear rheology of metallo-supramolecular polymer networks

Christina Pyromali[1,2*], Yanzhao Li[3], Flanco Zhuge[3], Charles-André Fustin[3], Evelyne van Ruymbeke[3] and Dimitris Vlassopoulos[1,2]

DoDyNet Montpellier Meeting

21-10-2021

Motivation

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

Structure

Entanglements

M-L coordination

Dangling ends

Properties

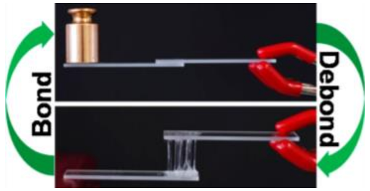
Tunability (Temperature, Ion content and Metal type)

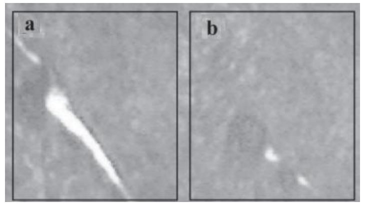
Deformability

Coherence

Function

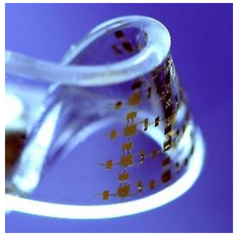
Light induced adhesives





Self-healing coatings

Stretchable electronics



✓ Industrial Exploitation

Processability and rheological behaviour under large shear deformation

Heinzmann et al., *ACS Appl. Mater. Interfaces* **6**, 4713–4719 (2014).

Bode, S. *et al*. *Advanced Materials* **25**, 1634–1638 (2013).

Rao, Y.-L. *et al. J. Am. Chem. Soc.* **138**, 6020–6027 (2016).

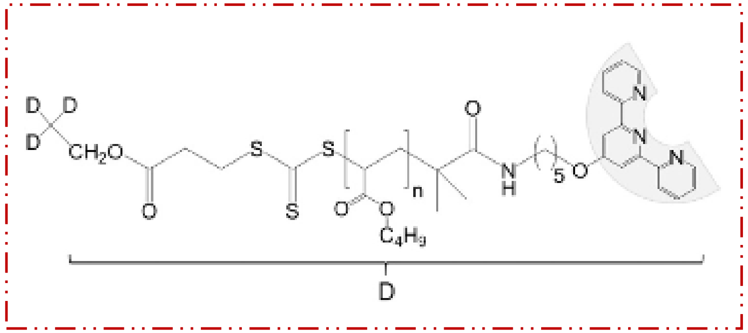
Materials

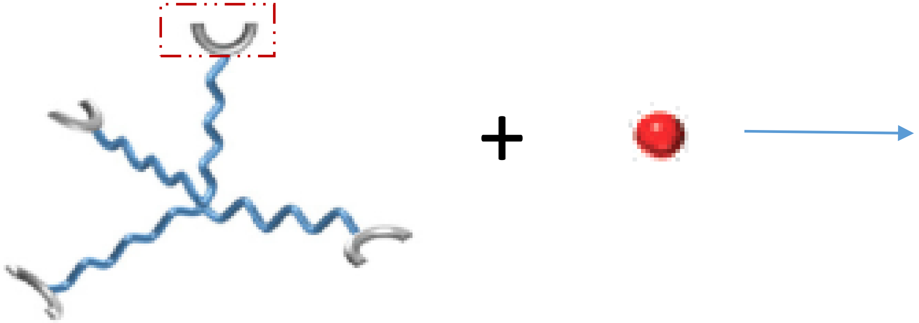
Same Charge

Similar ionic radius

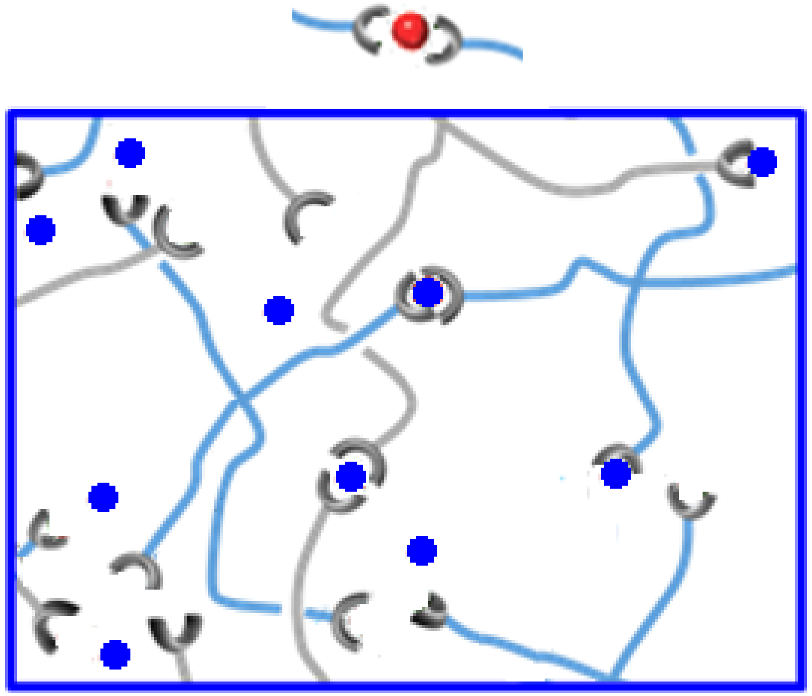
Thermodynamic stability

Terpyridine ligand





Zn^{2+}



M-L cross-linking stability

4 arm star poly(n-butyl acrylate)s

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

	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}	$10^{9.9}$	$10^{6.7}$	$10^{-3.2}$	$10^{18.3}$

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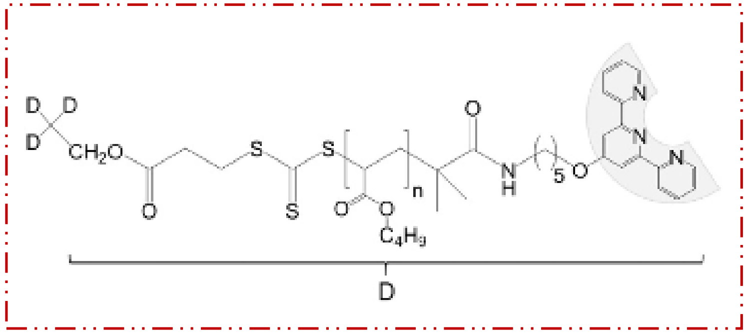

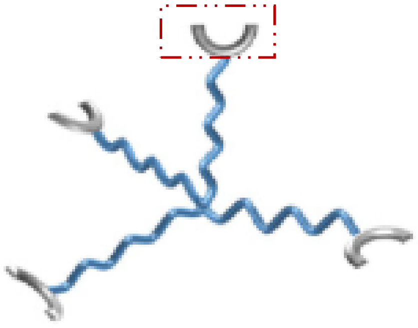

+

→

Cu^{2+}

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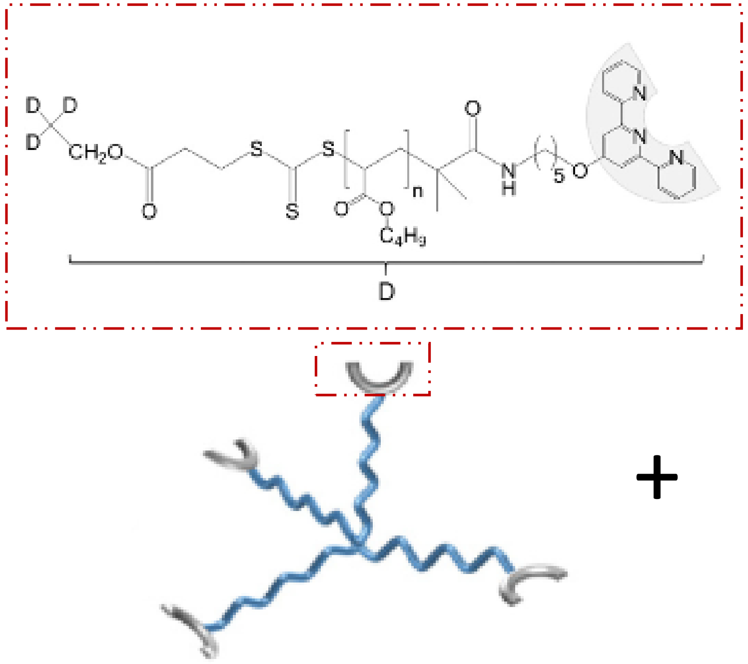
Terpyridine ligand



+

→ Co^{2+}

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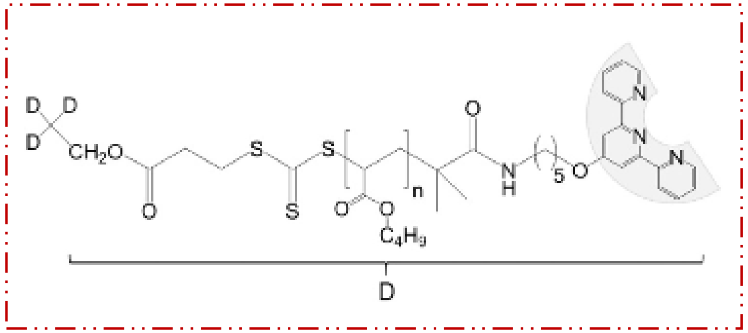
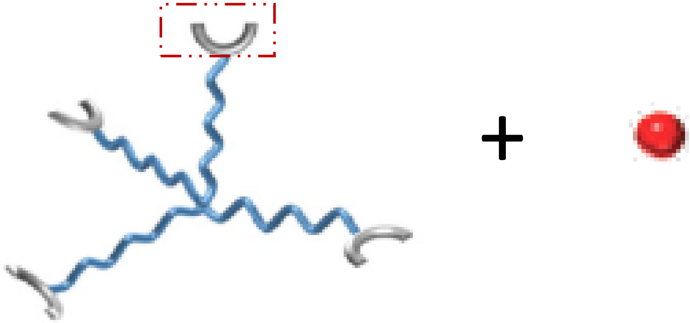
Materials

Terpyridine ligand





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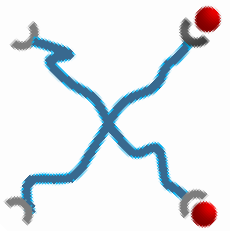
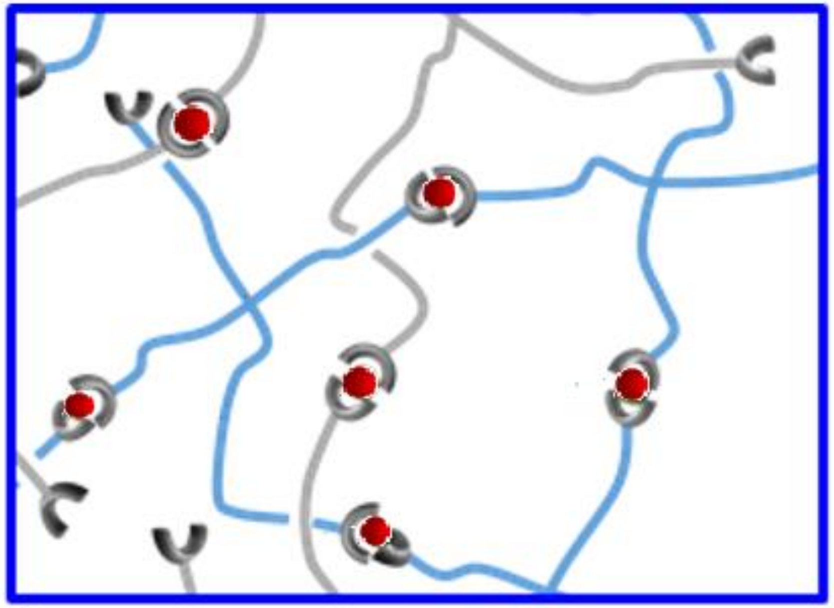
Single Network



0.5eq.

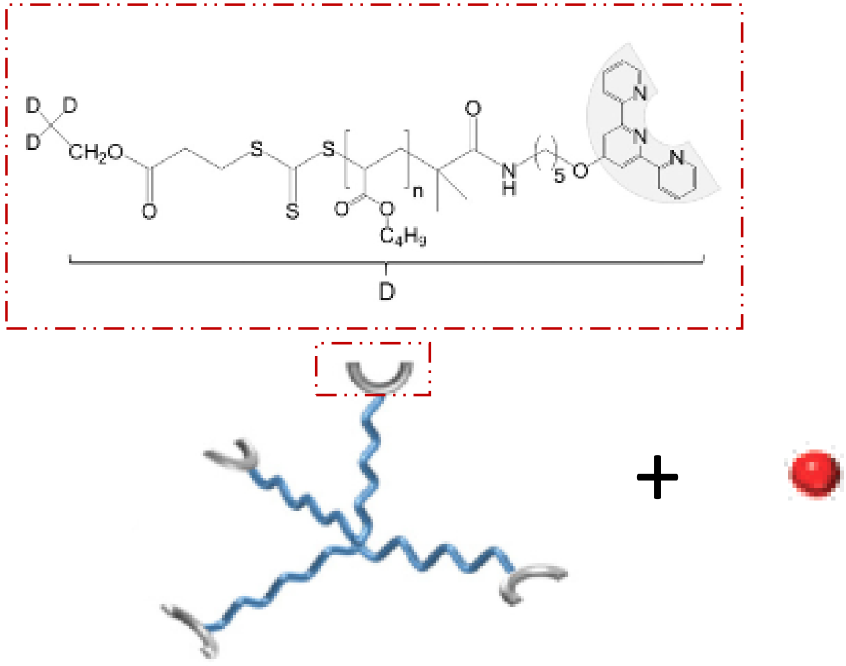
Stoichiometric amount



M-L cross-linking density

Materials

Terpyridine ligand



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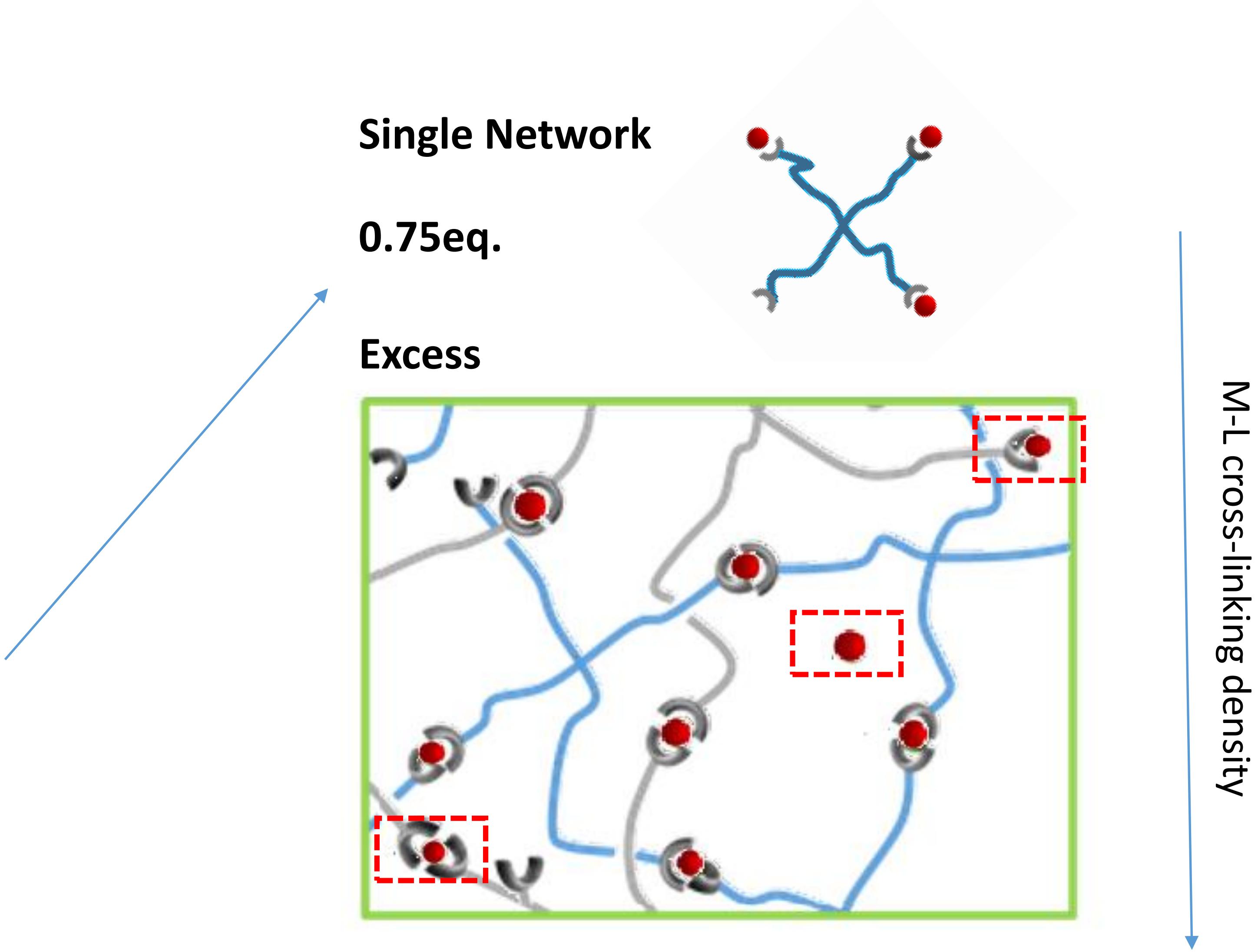
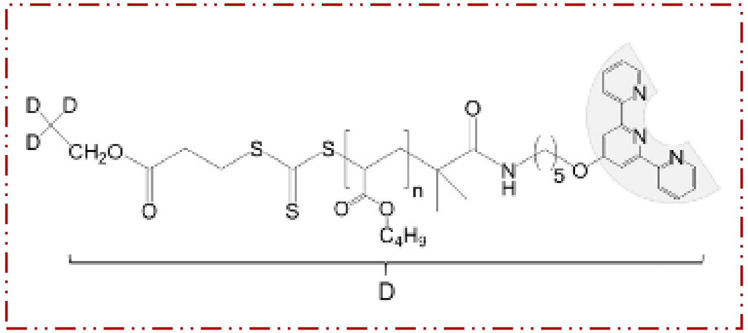
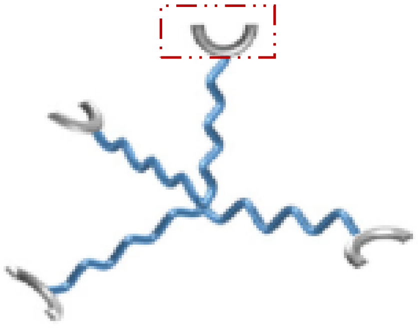


Materials

Terpyridine ligand





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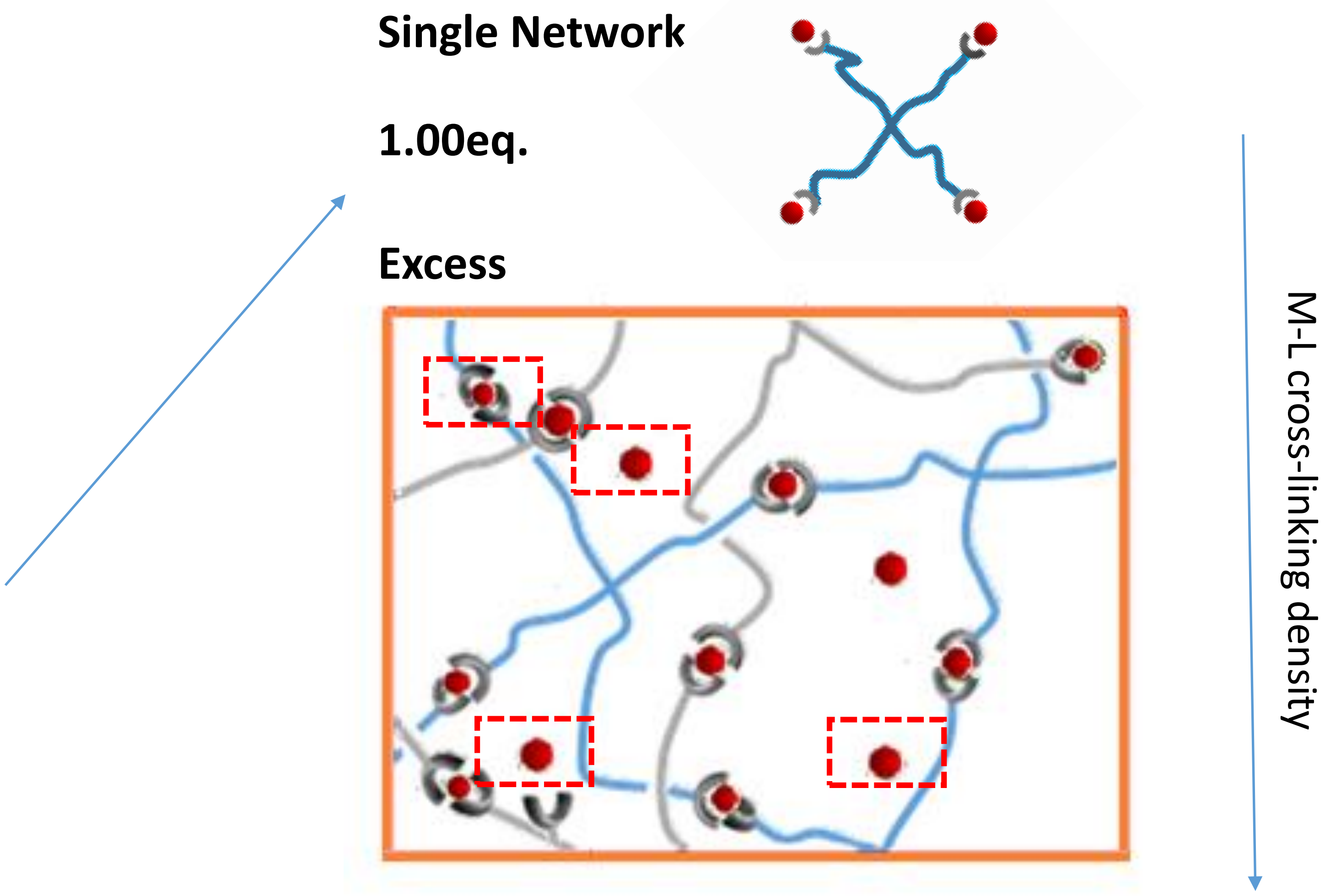
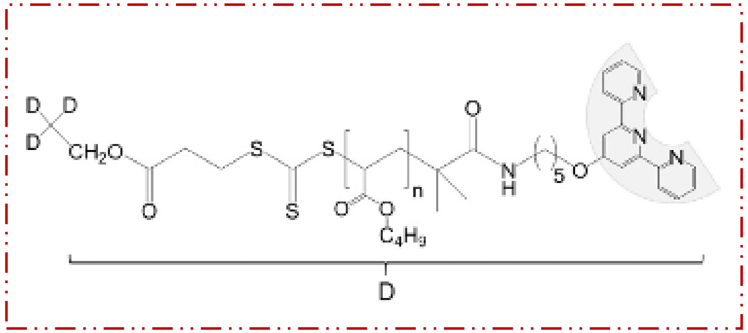
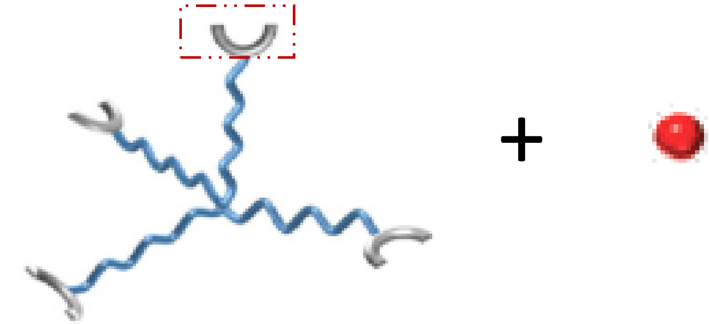


Materials

Terpyridine ligand





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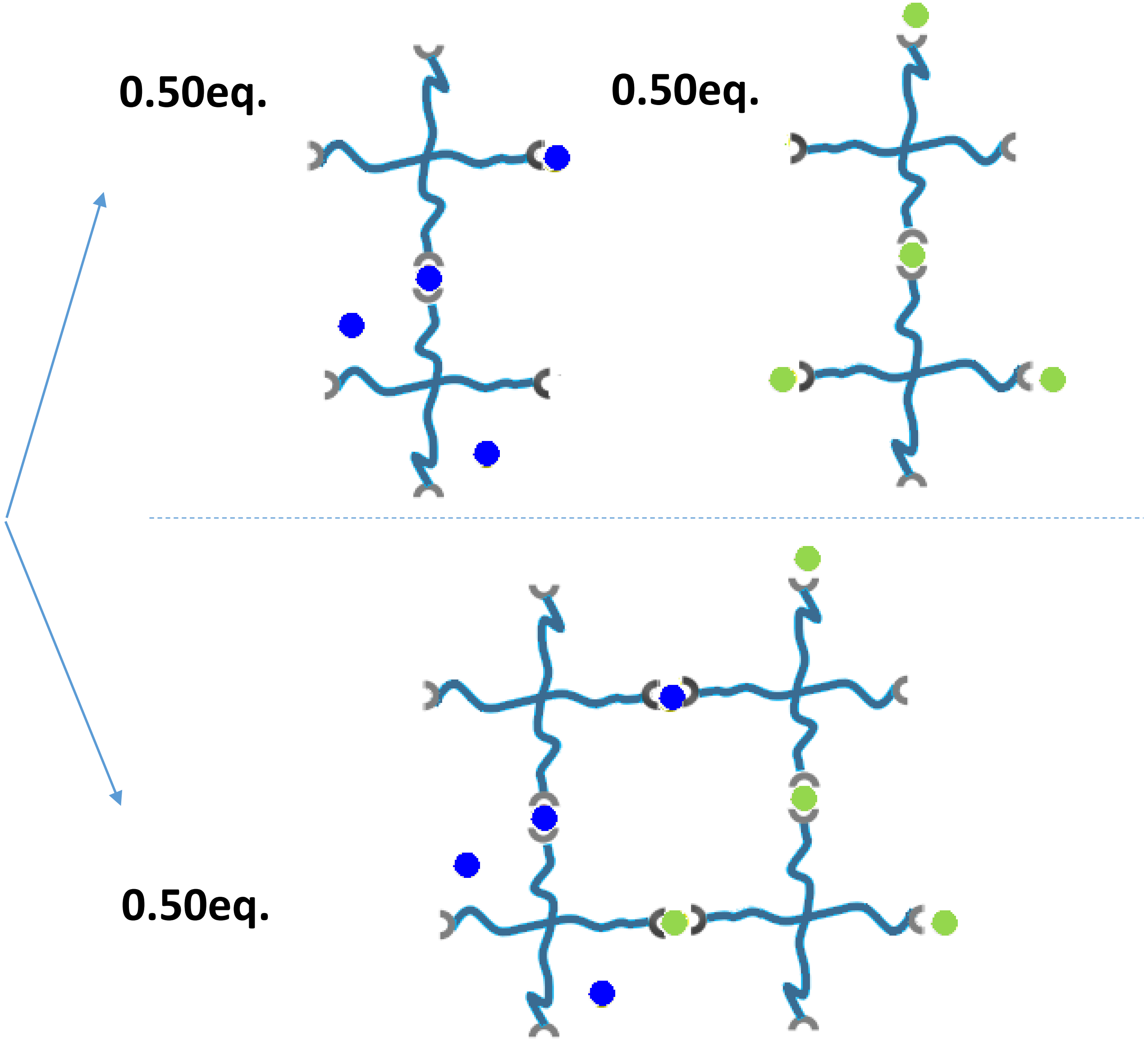
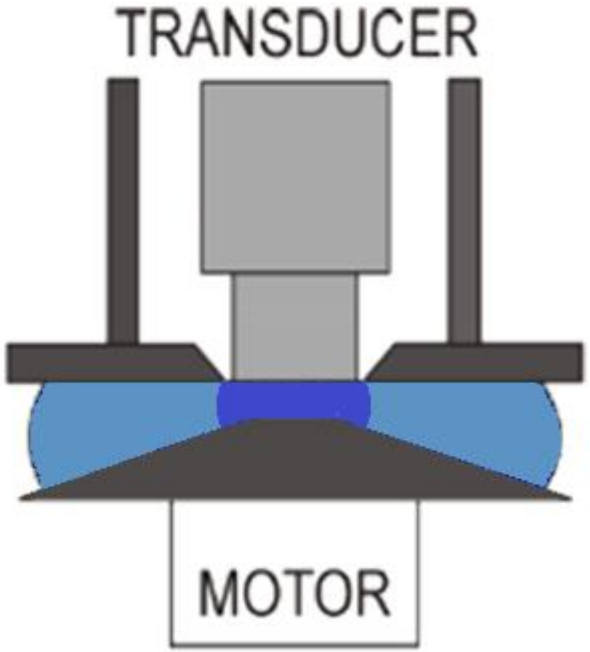
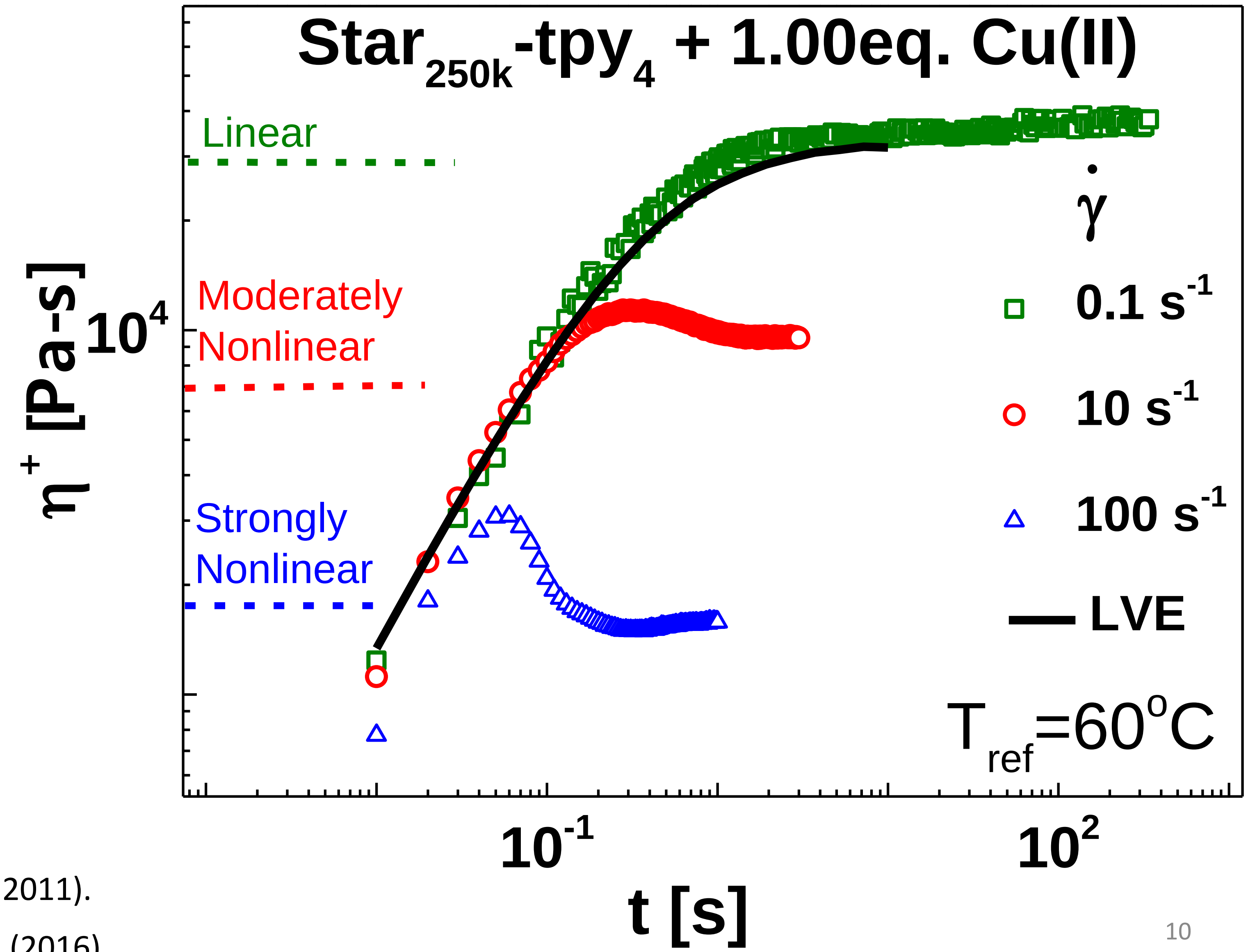
Blends



Methods



Edge fracture mitigation delay



Snijkers, F. & Vlassopoulos, D., *JoR* **55**, 1167–1186 (2011).

Costanzo, S. *et al.*, *Macromolecules* **49**, 3925–3935 (2016).

Methods

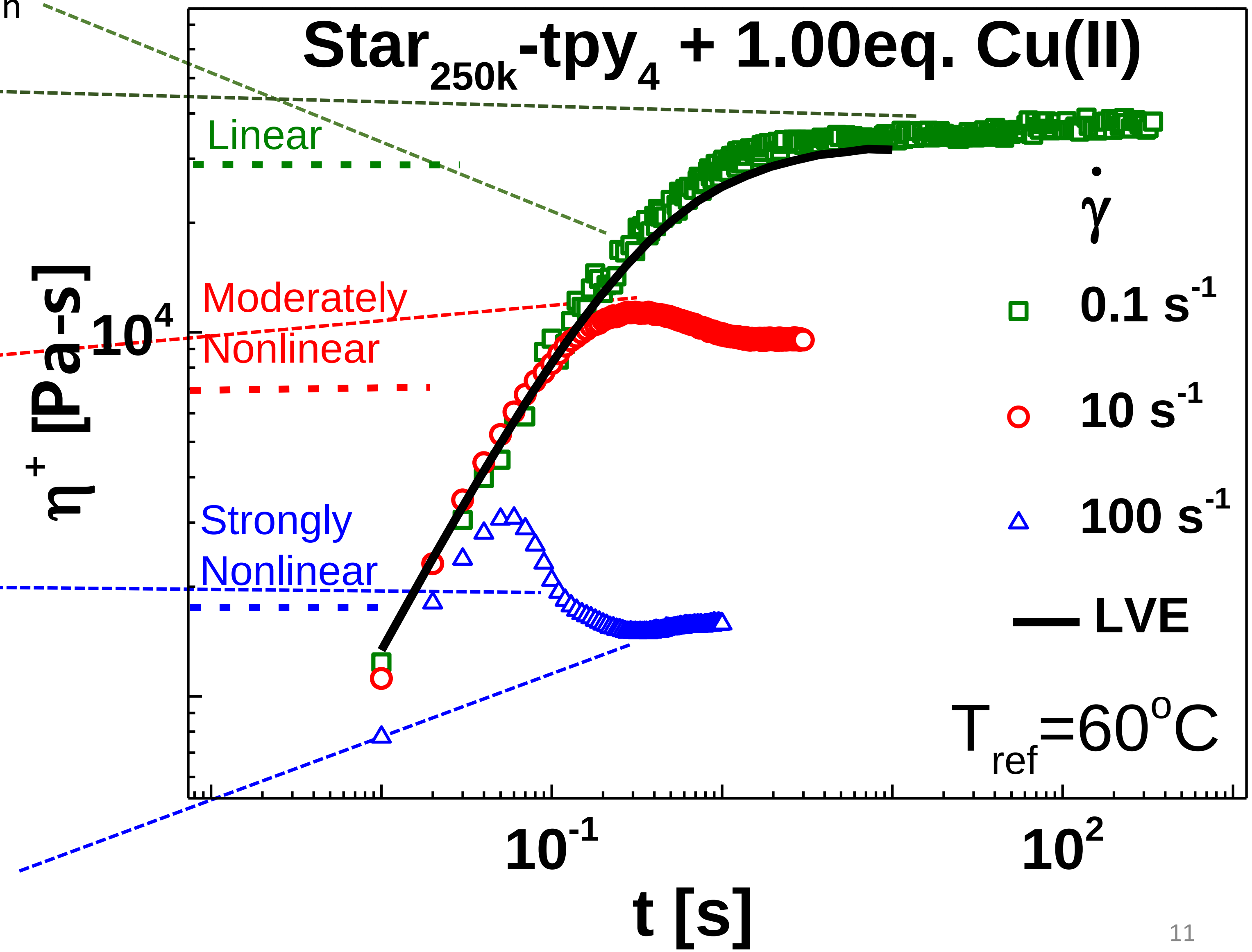
Linear response: elastic deformation region

Structure has time to rearrange and the deformation is dissipative

Overshoot: collective orientation and stretching/ dynamic bond breakage

Flow-induced disentanglement
Bond rearrangement

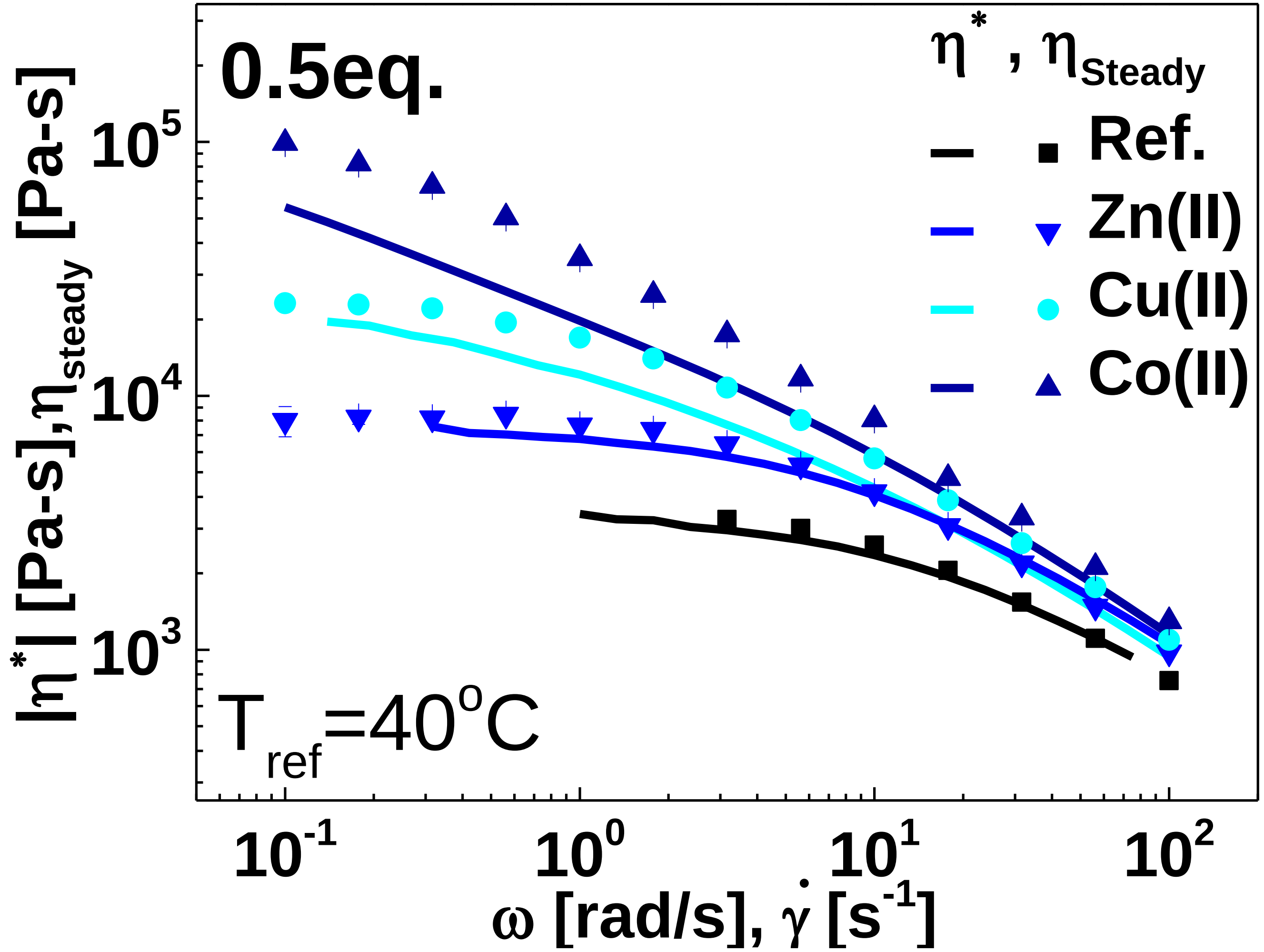
Steady state region: macroscopic flow/ dissipative deformation

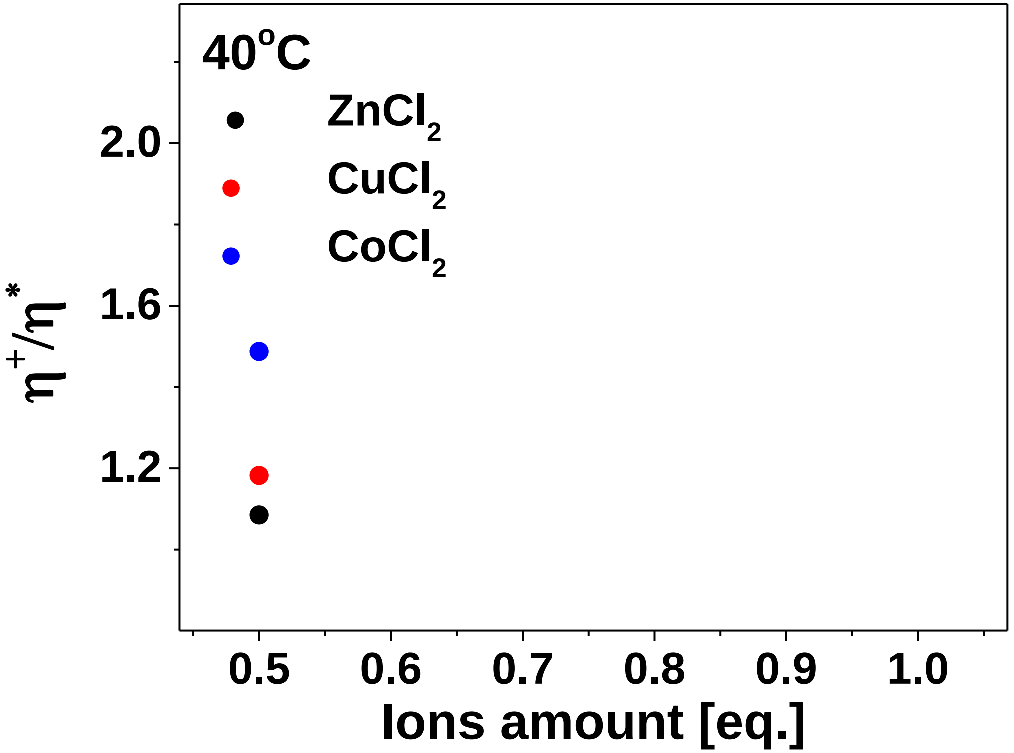


Cox-Merz Rule Fails

Ion Strength
Ion Content
Temperature

$\dot{\gamma} = 10s^{-1}$, ω=10rad/s





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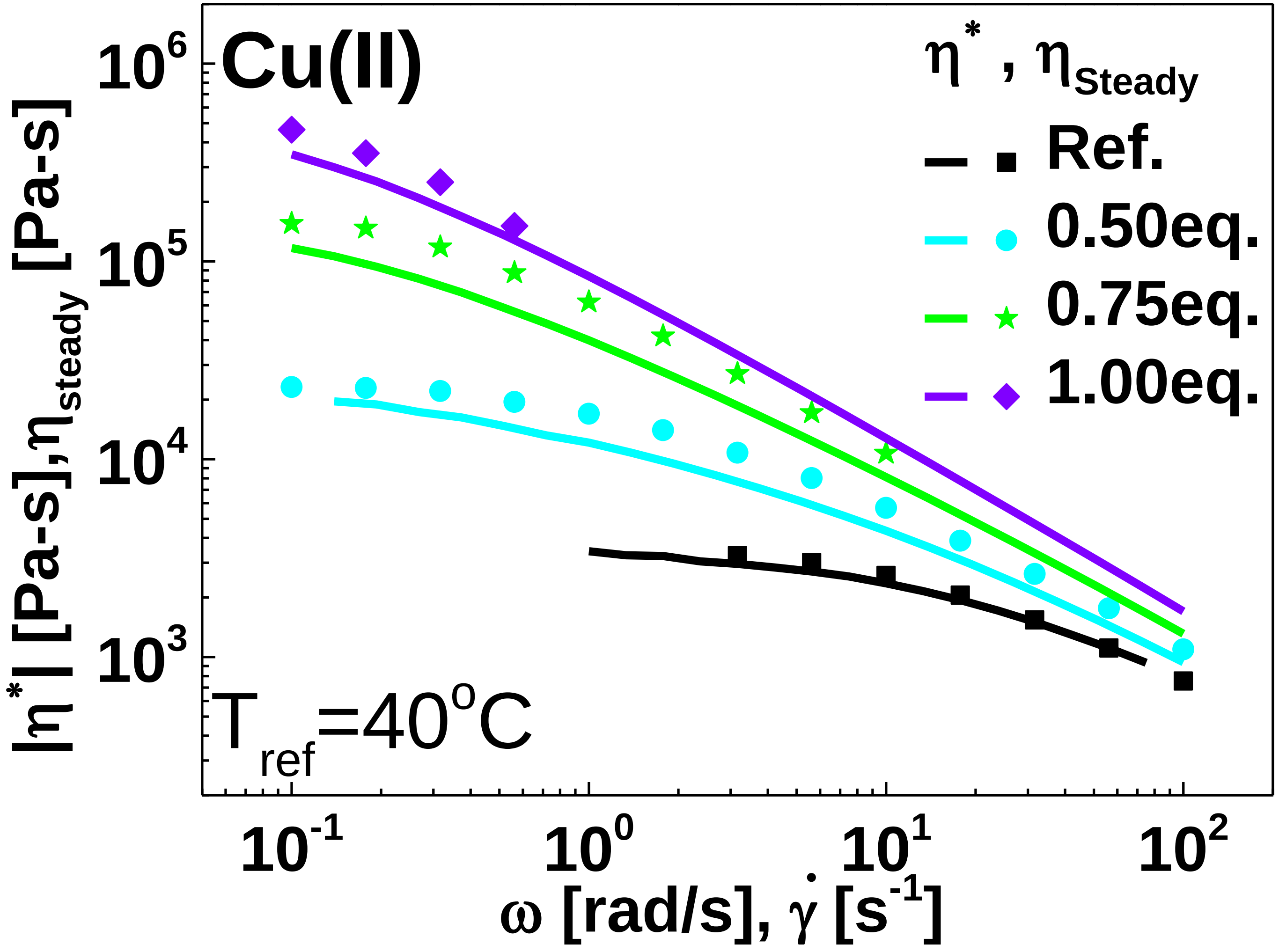
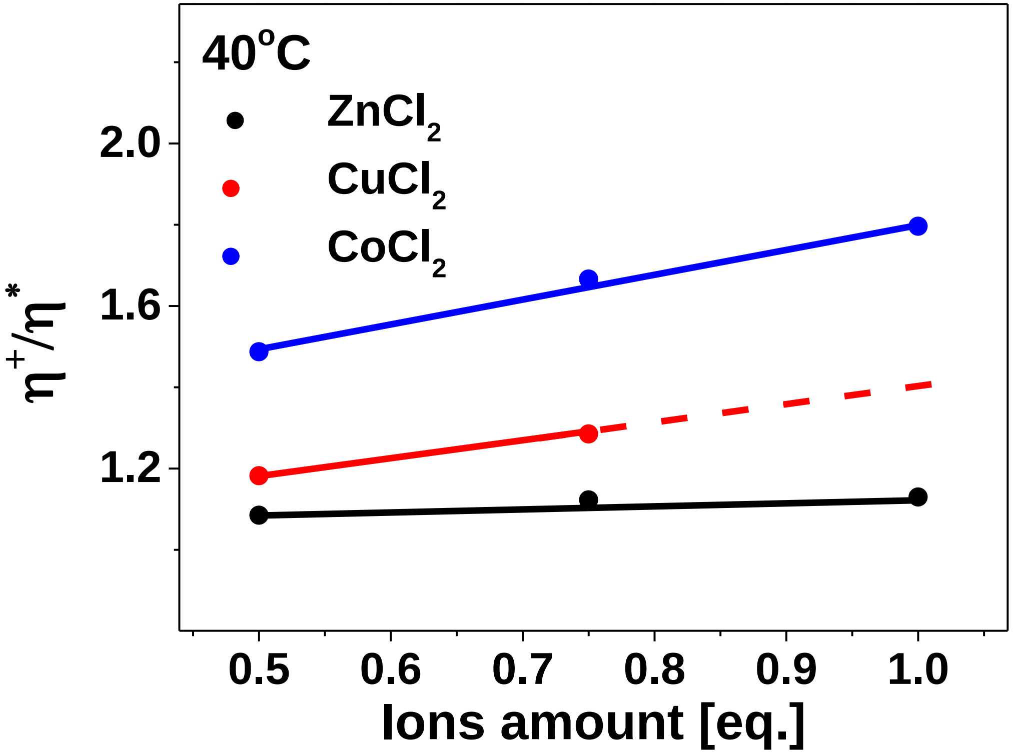
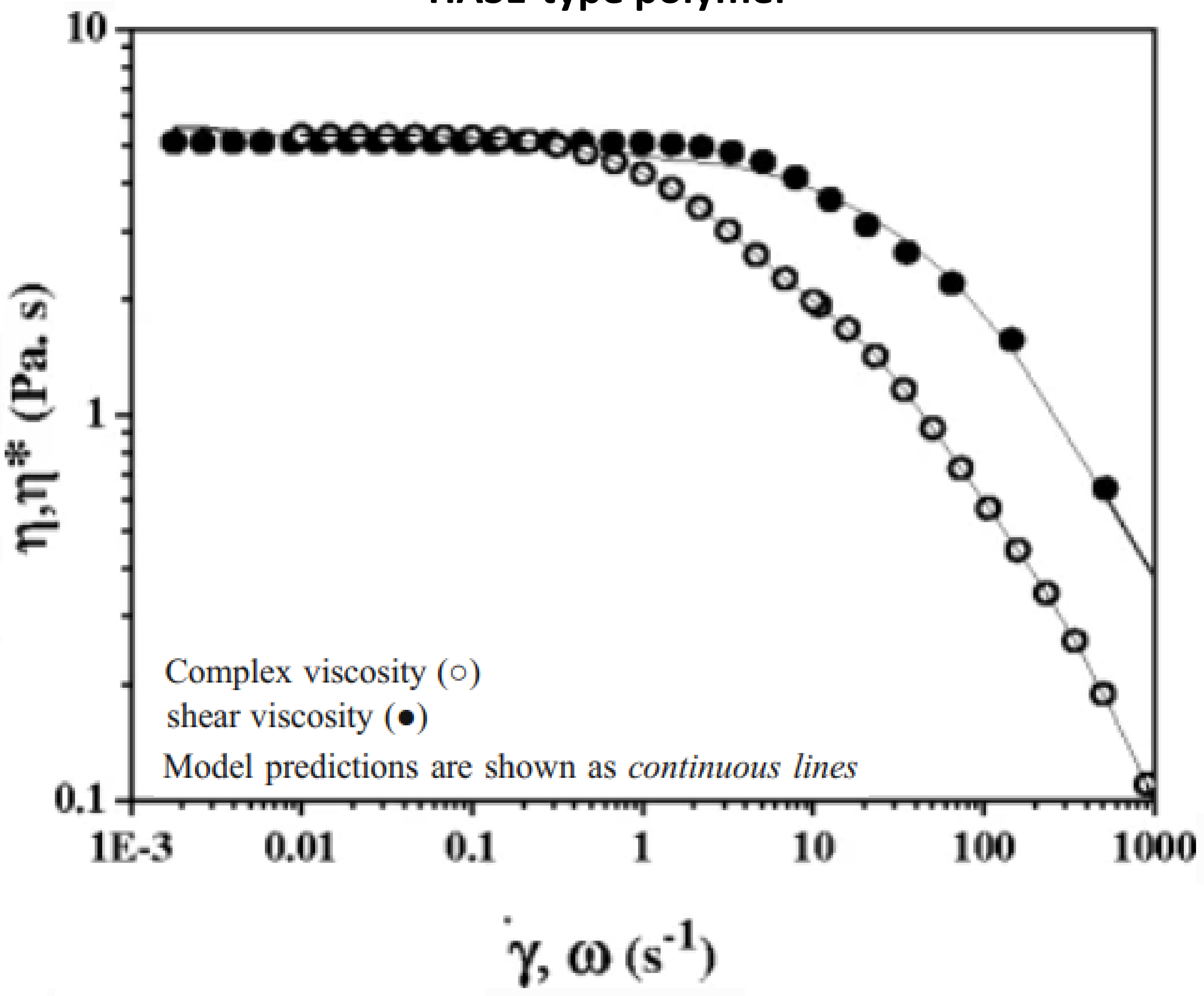




Origin of Cox-Merz Rule Failure

HASE-type polymer



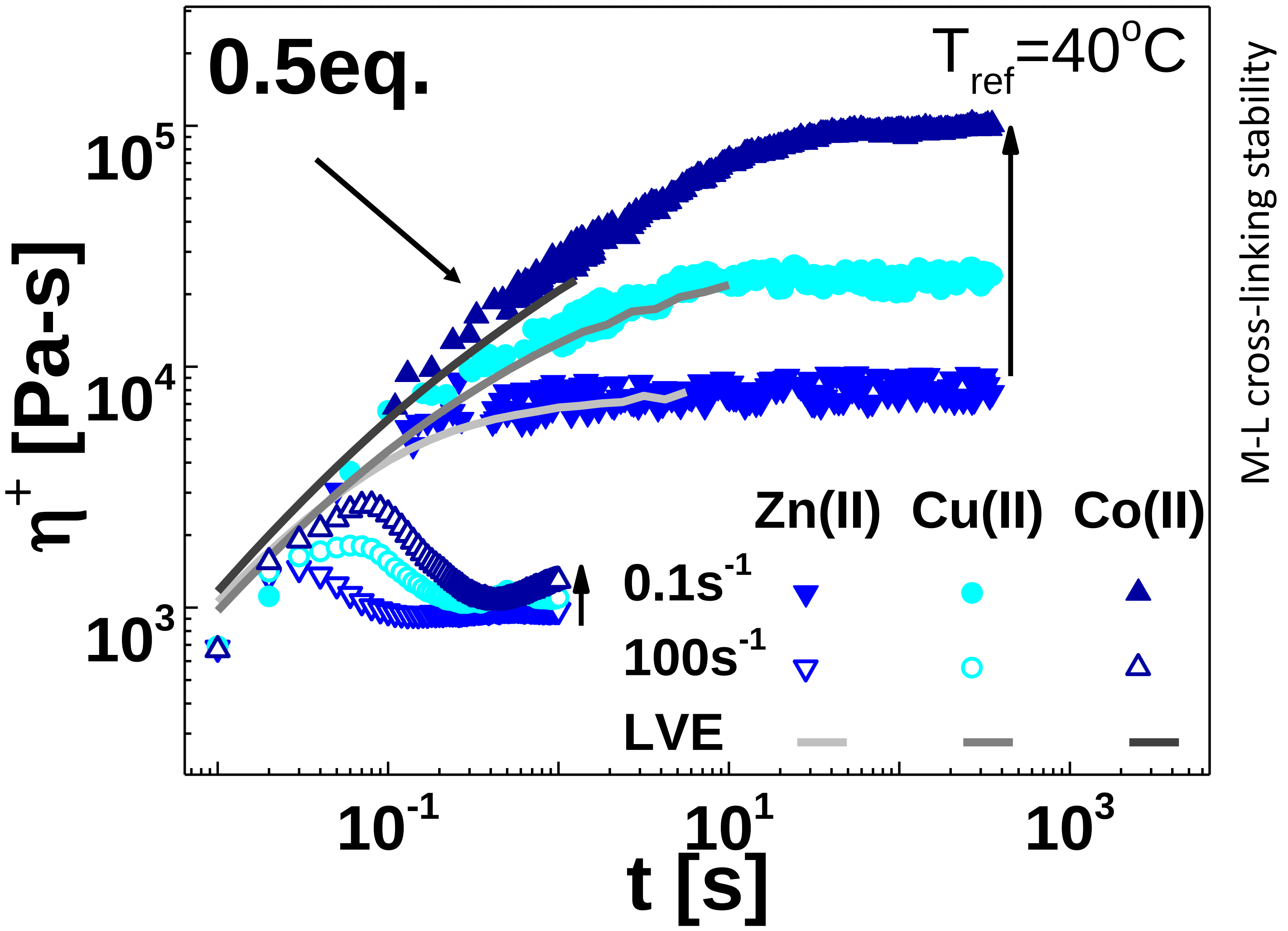
- Associative polymers do not obey Cox-Merz rule
- Viscosity ratio is typically higher than unity
- Multi-mode model with a kinetic balance that destruction (convective) of long-range associations prevails over formation (diffusive) of short-range associations.

Caram, Y., et al., *Rheol Acta* **46**, 45–57 (2006)

Pellens, L., et al., *JoR* **48**, 379–393 (2004)

Shear stress growth coefficient

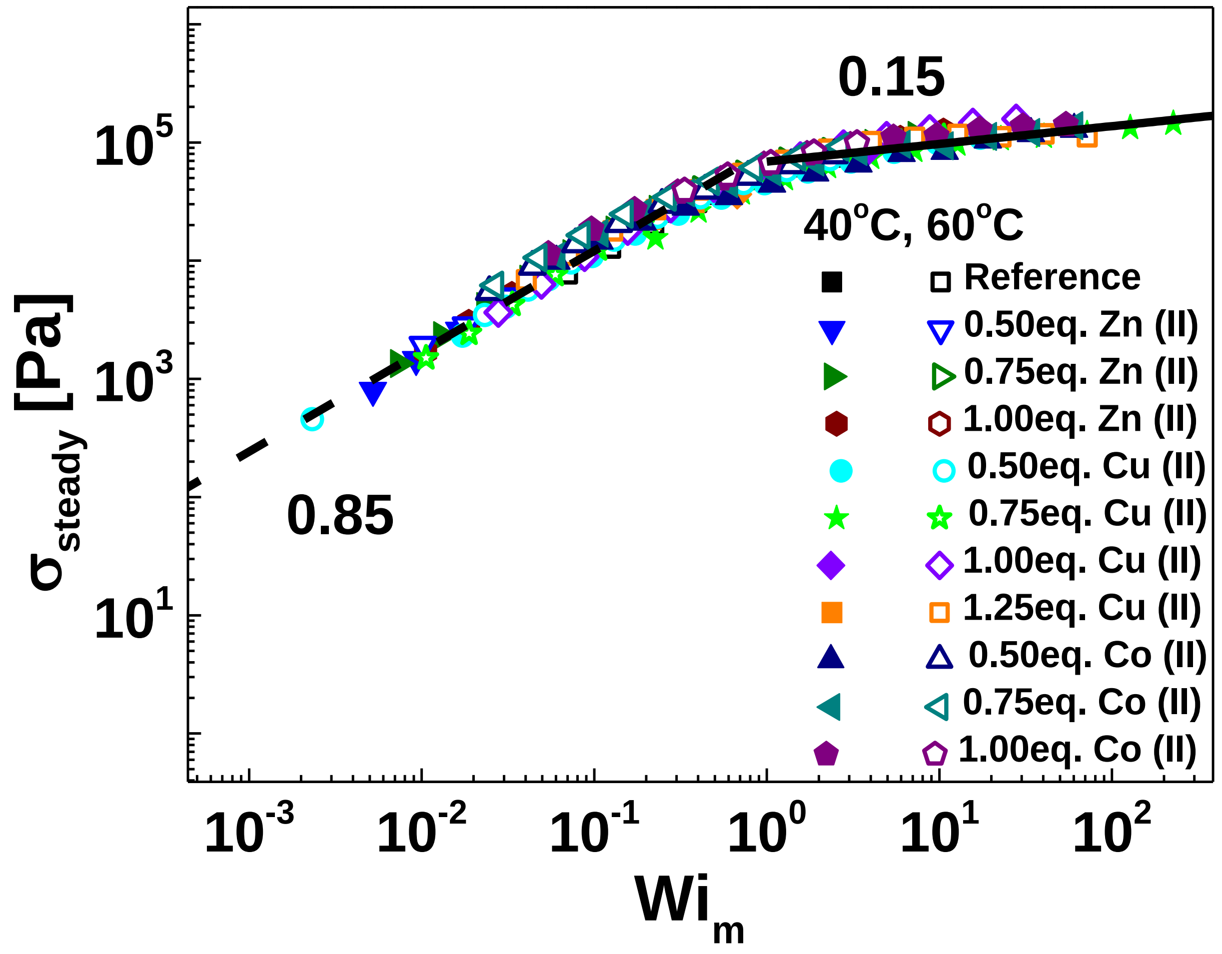
Ion Strength
Ion Content
Temperature



- Steady-state viscosity increase with M-L crosslinking stability
- Pronounced overshoot for stable ion
- Shear strain hardening region is related to slow disassociation kinetics that result strong resistance to deformation
- Supramolecular dynamics dominate the response lower deformation rates (or longer times)

Steady-state stresses

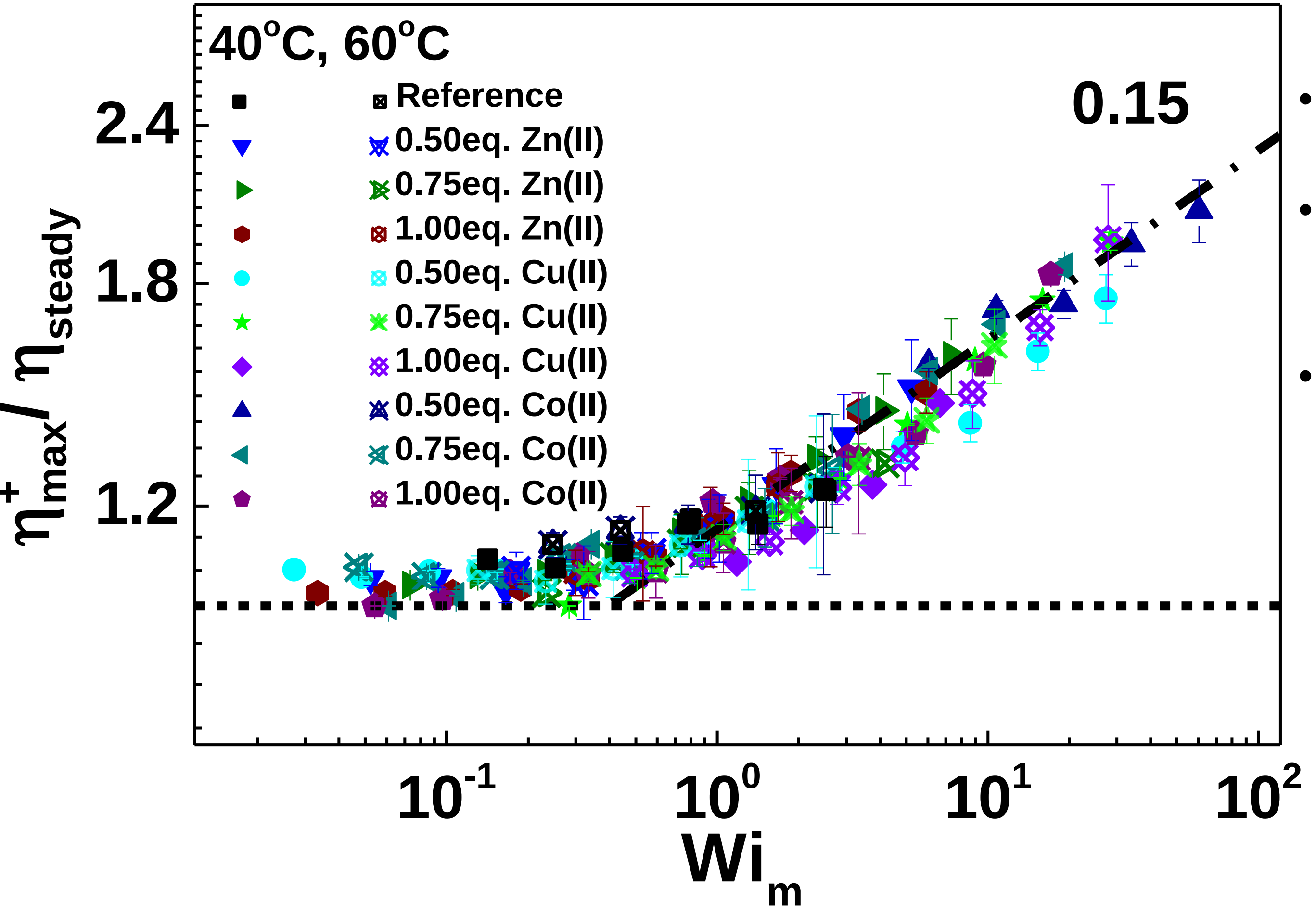
Ion Strength
Ion Content
Temperature



- Steady state stresses of all systems collapse into a universal trend
- Coupling of star-arm and sticker dynamics
- Universal 0.85 slope indicates dynamic bond predominance for Wi<1
- becomes weaker indicating the control of the star-arm dynamics at Wi>1

Fractional viscosity overshoot

Ion Strength
Ion Content
Temperature

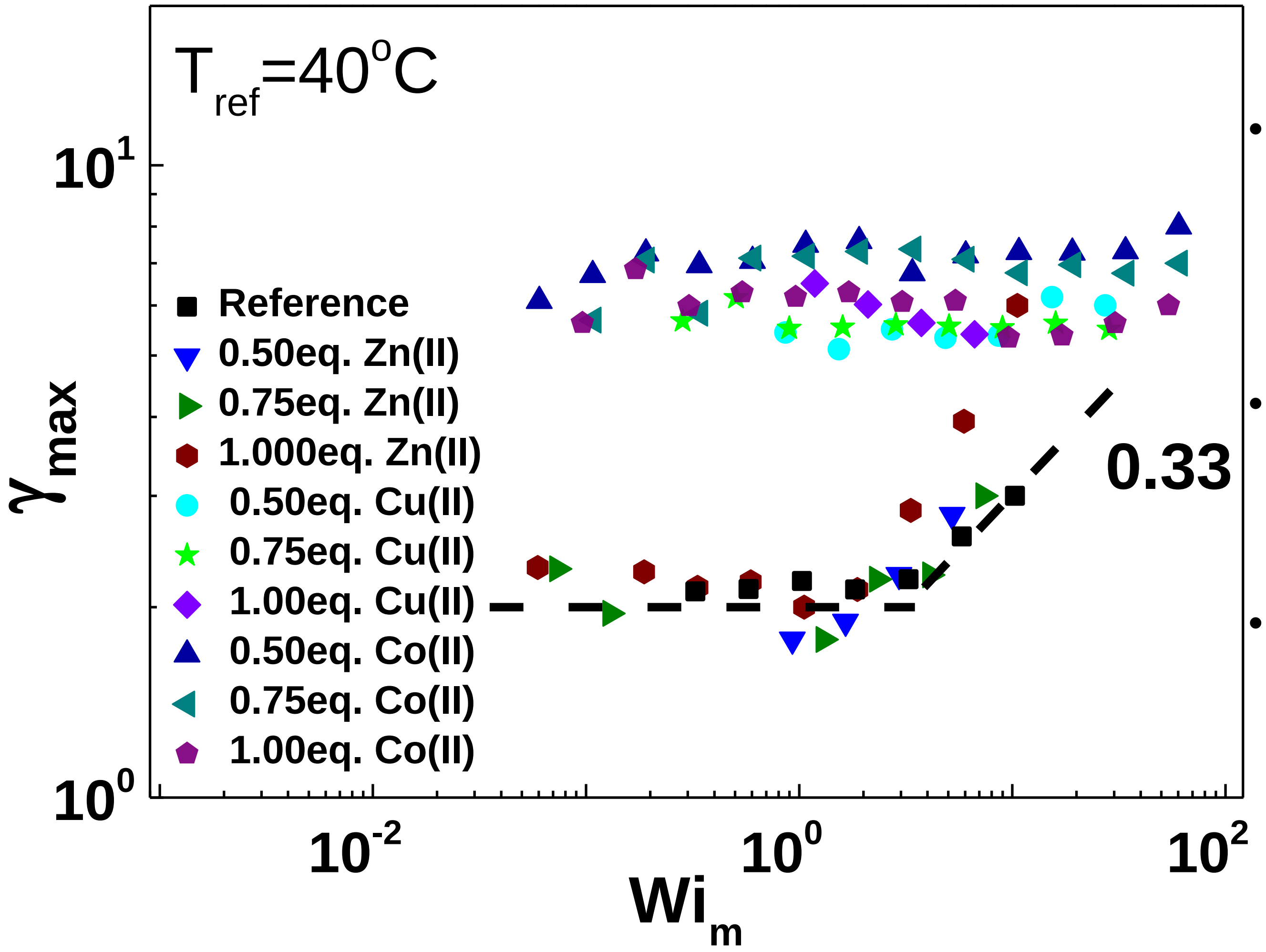


- Data of all systems collapse in a universal trend
- Fractional overshoot is a measure of mechanical coherence.
- The associated networks exhibit an improved coherence compared to the reference sample without metal ions, reaching larger yield stress and having enhanced topological/bond rearrangement until steady state

Polgar, L. M. *et al., Macromolecules* **48**, 6662–6671 (2015).

Costanzo, S. *et al.*, *Macromolecules* **49**, 3925–3935 (2016).

Maximum (yield) strain



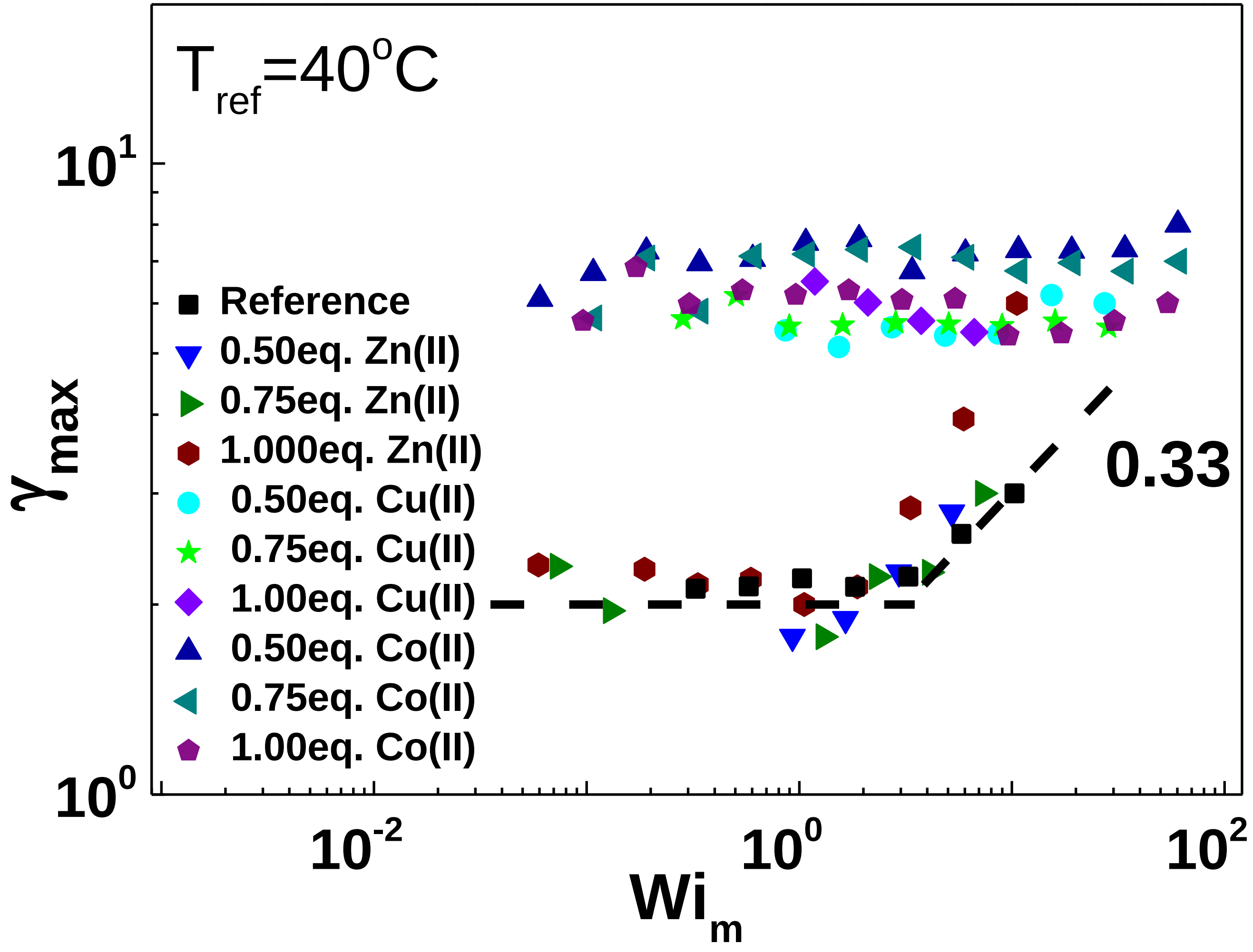
- Weakly associated networks are dominated by polymeric response. First orientation and then stretching at Wi >1 with the 0.33 slope of entangled polymers

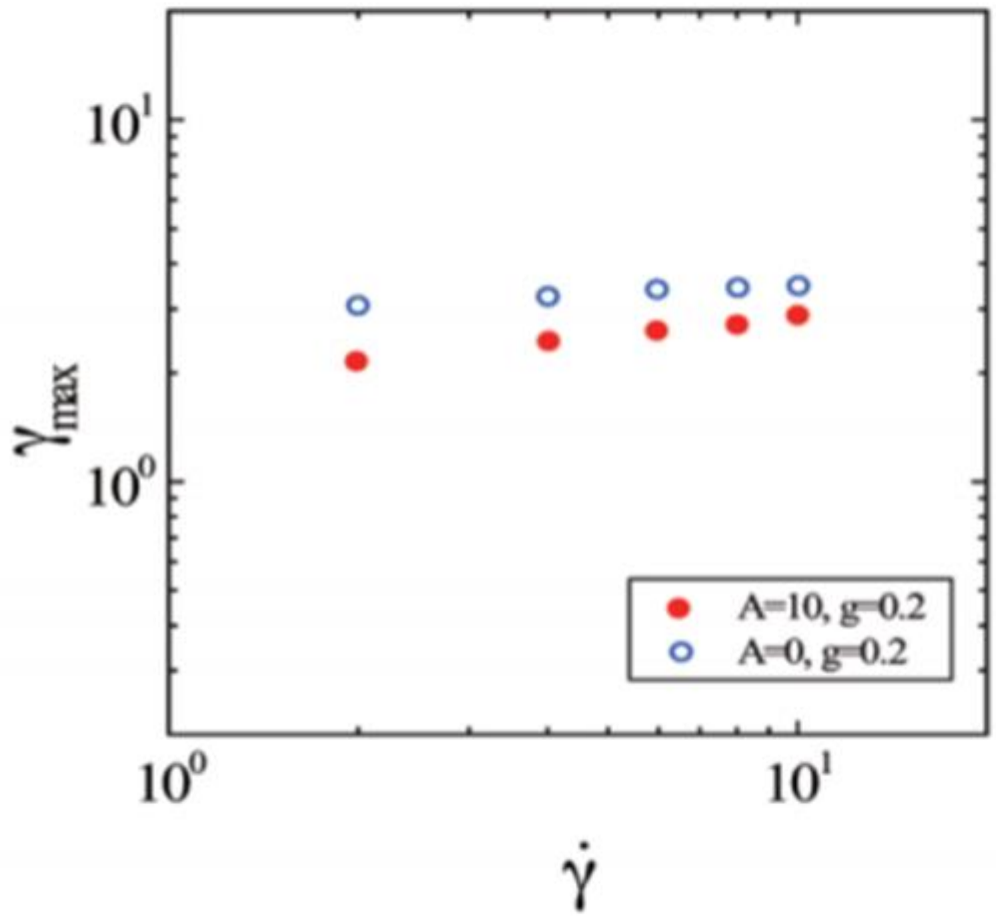
- Yielding in strongly associated networks is independent to Wi, the network strands seem fully deformed- strain saturation.

- Accumulation of strain indicates that the lifetime of the dynamic bonds remains unchanged during deformation

Maximum (yield) strain

Fixed coupling constant, g

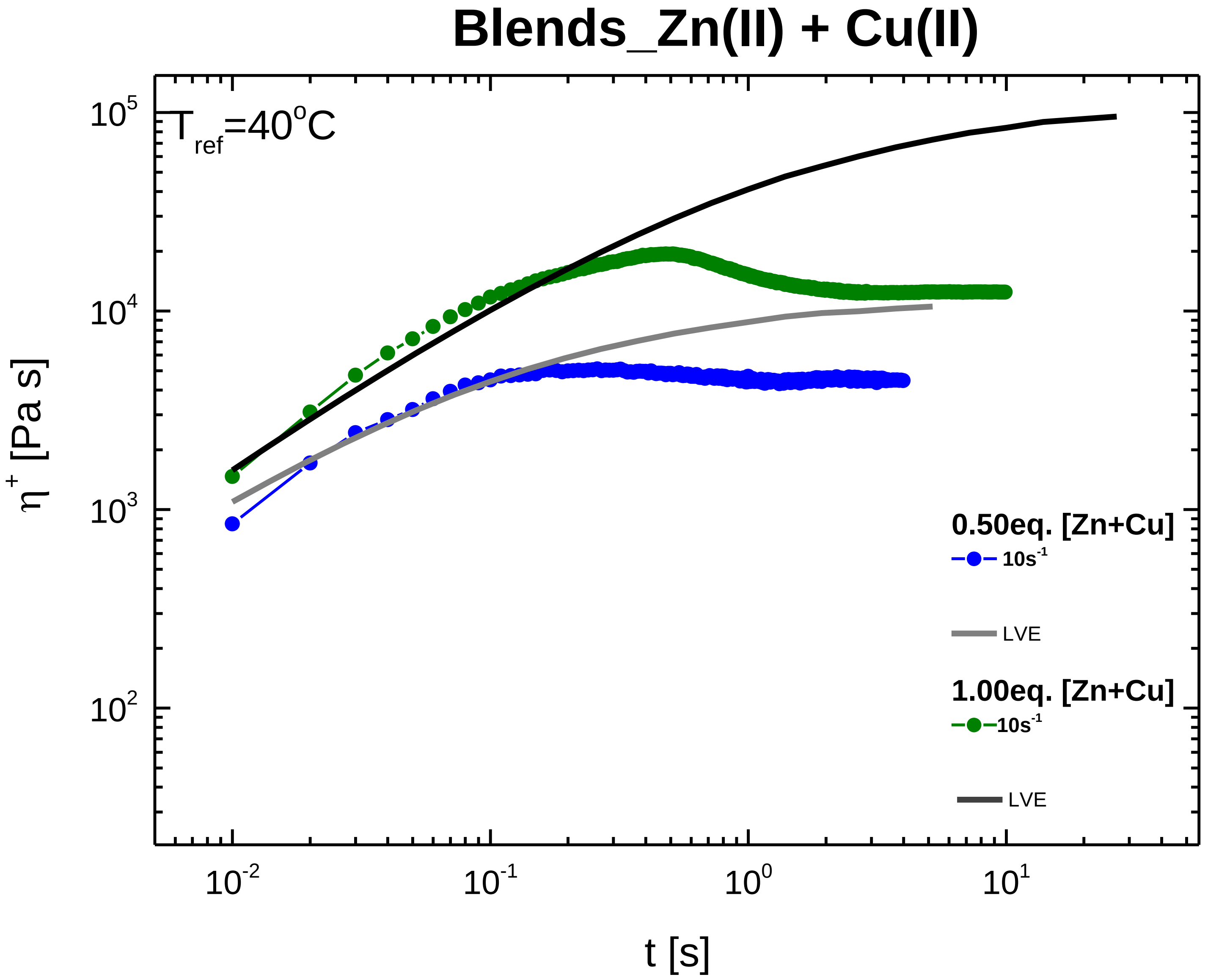


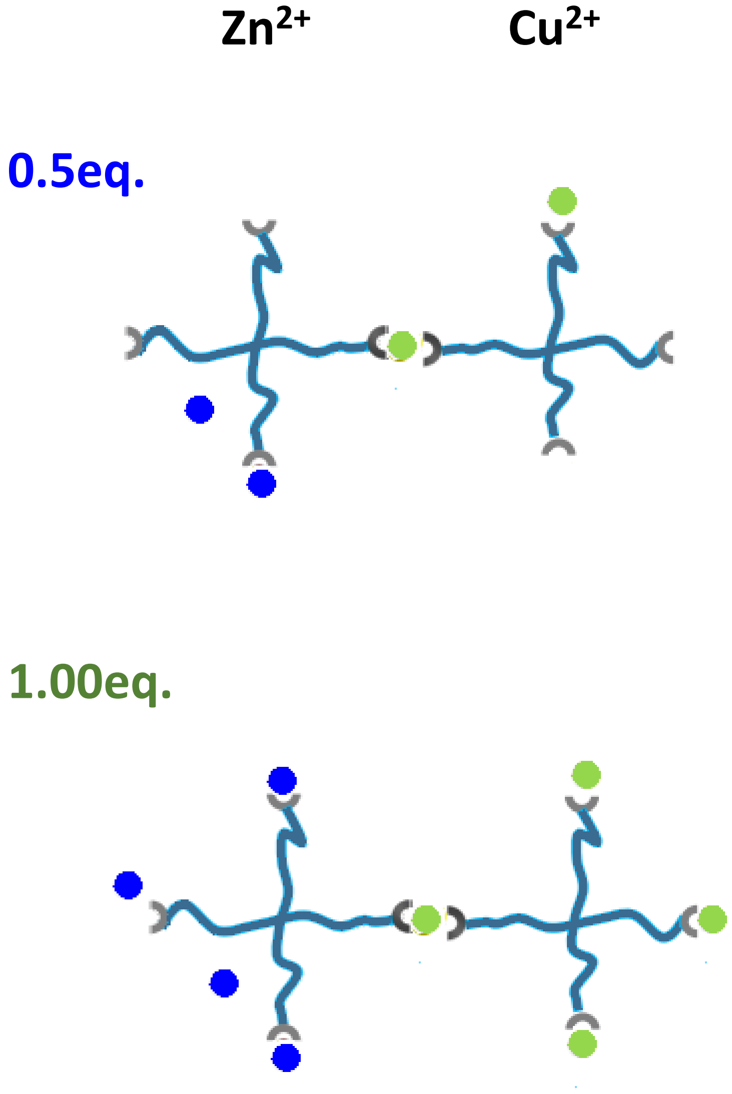


Koga, T., et al,. *Langmuir* **25**, 8626–8638 (2009)

Zhang, Q. *et al.*, *Macromolecules* **52**, 660–668 (2019)

Double sticker dynamic networks





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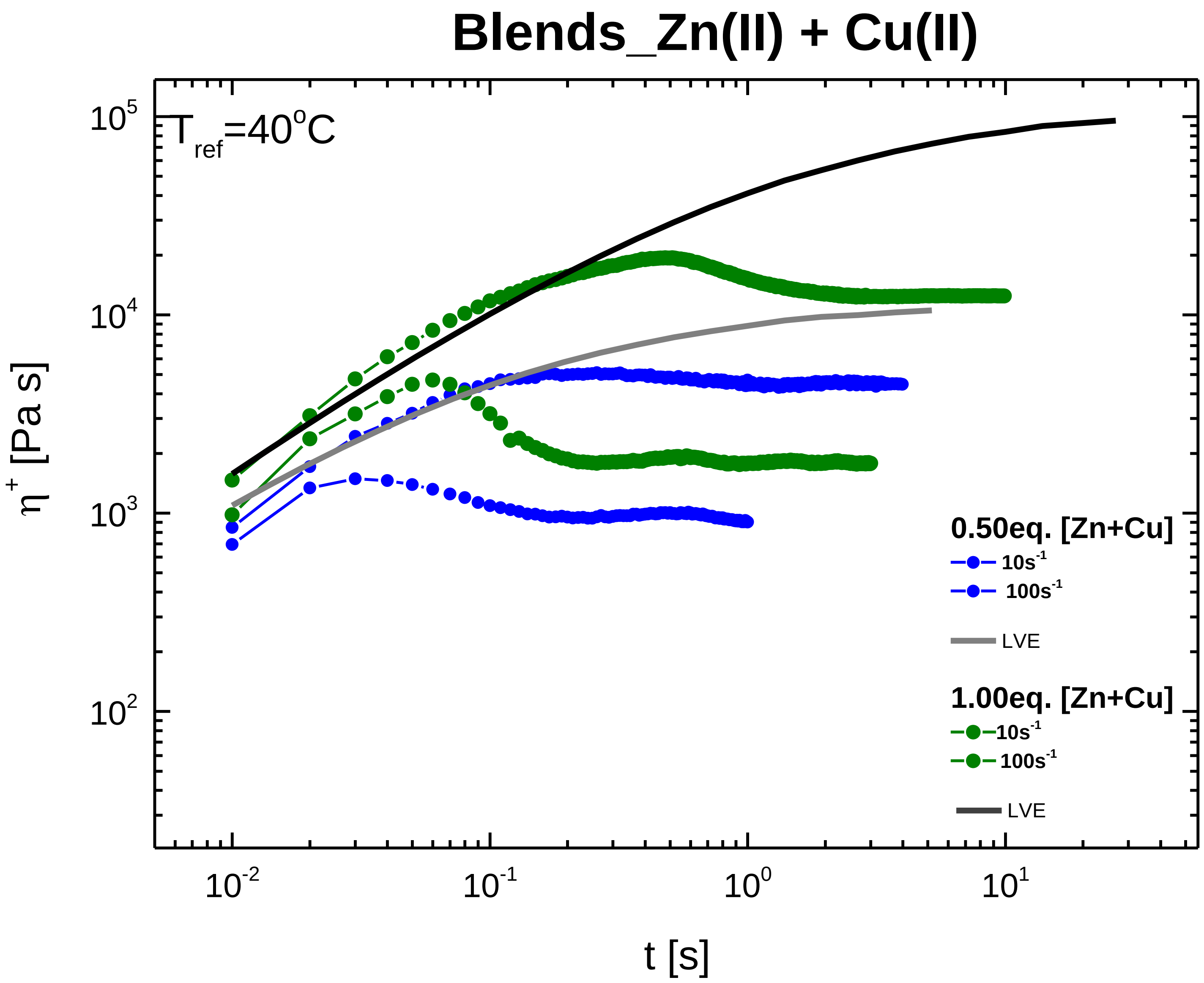

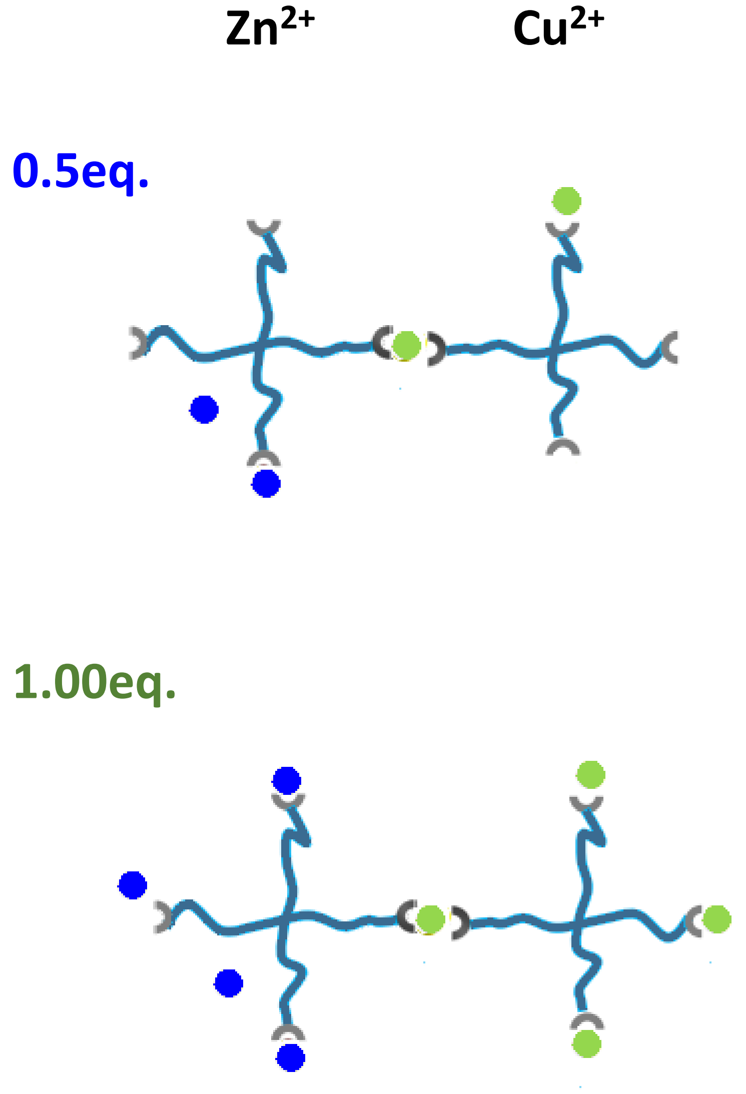

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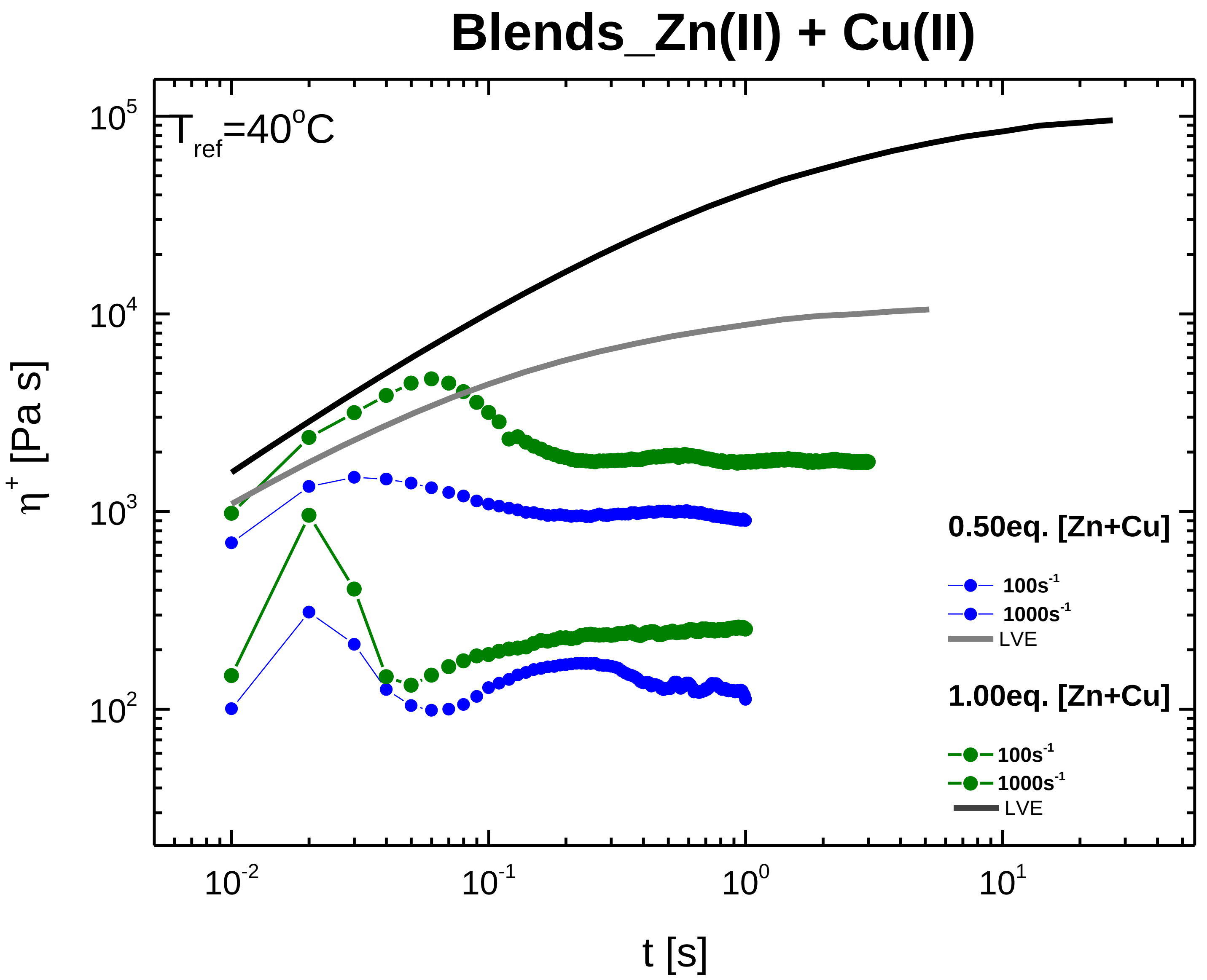
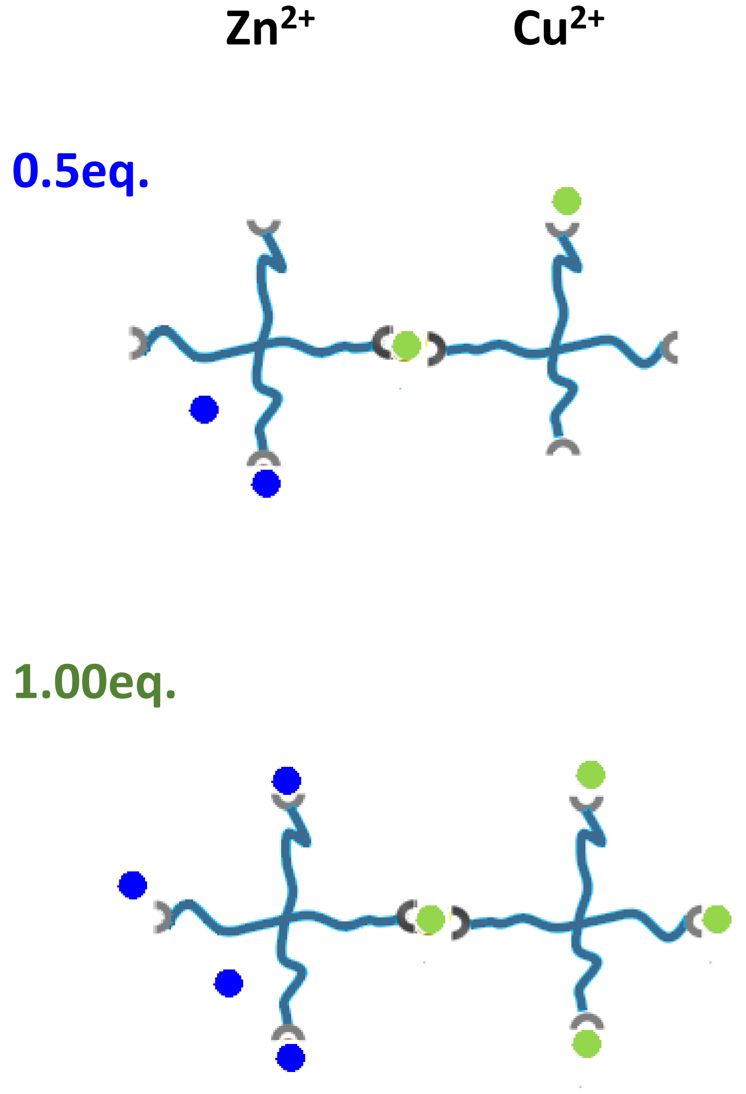
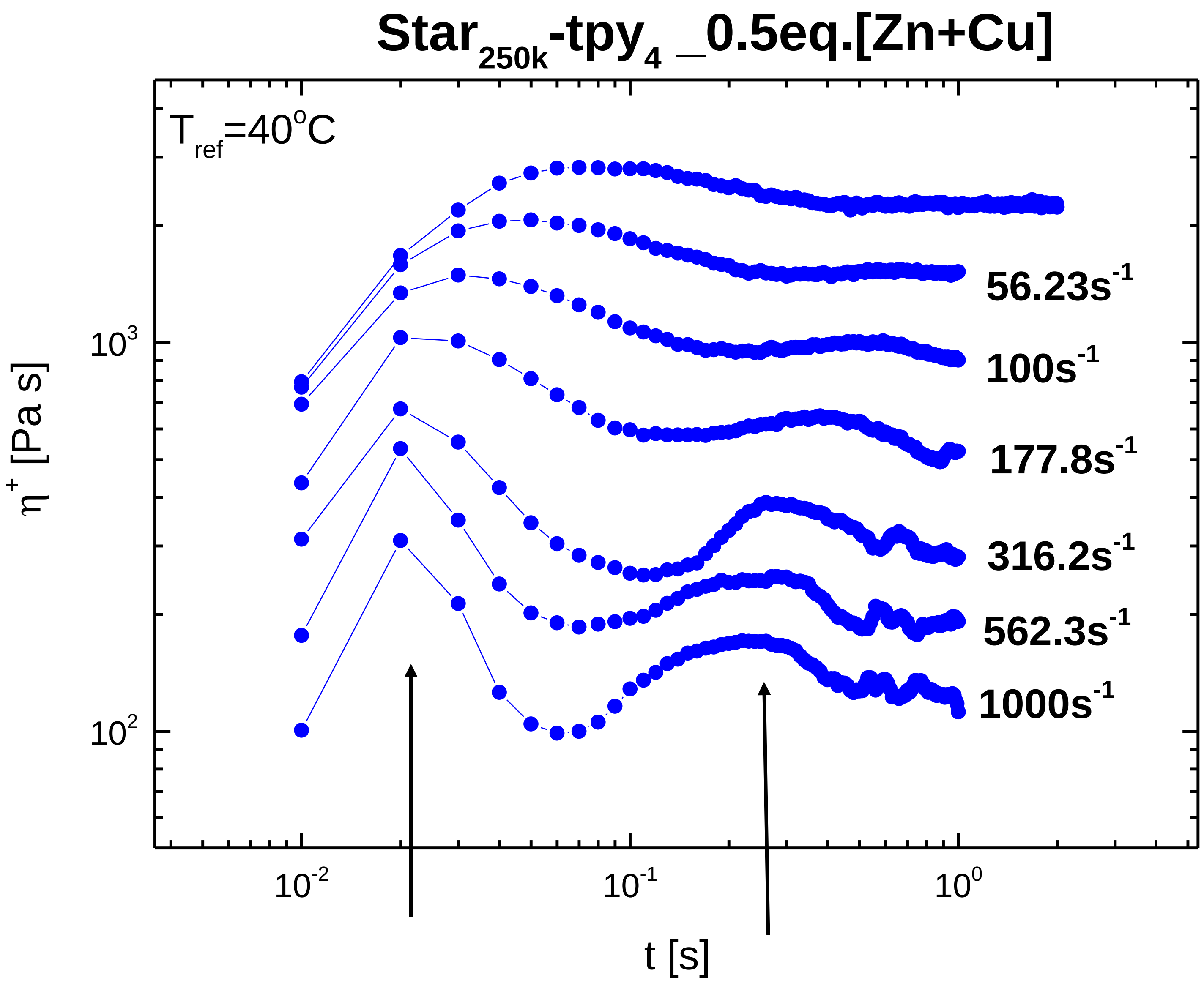
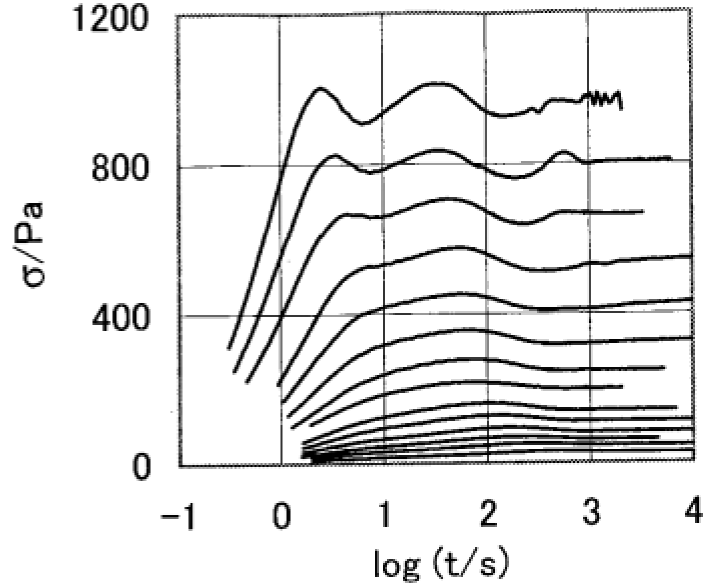




Double peak in transient response



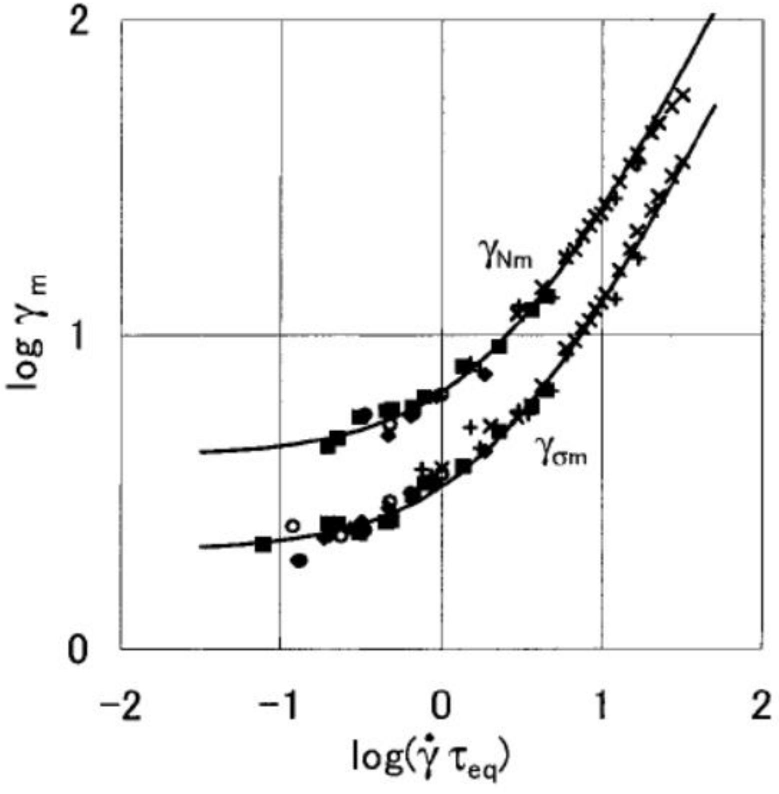
PS solutions with bimodal molecular weight distributions



Osaki, K., et al., *Journal of Polymer Science: Polymer Physics* **38**, 2043–2050 (2000).

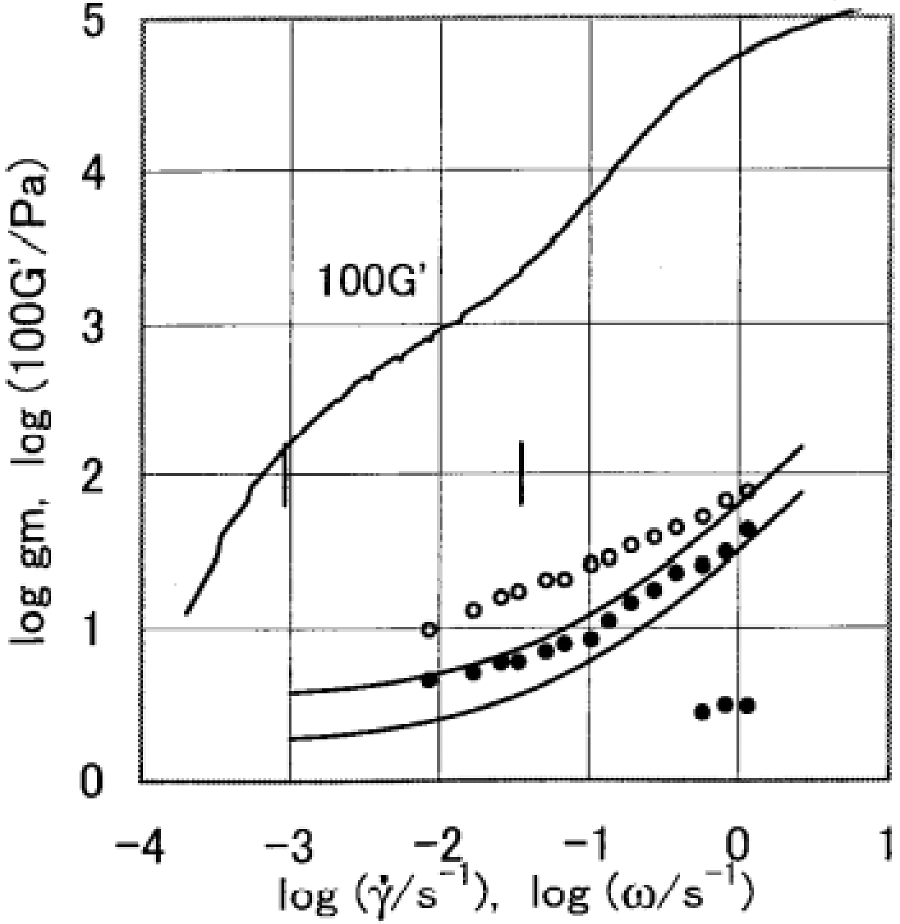
Snijkers, F. *et al.*, *ACS Macro Lett.* **2**, 601–604 (2013).

Evidence if double peak: interplay of relaxation times of blend components



$$\gamma_{max} = 0.87[1.59 + (\dot{\gamma}\tau_R)^{2/3}]^{3/2}$$

Osaki, K., et al., *Journal of Polymer Science: Polymer Physics* **38**, 1917–1925 (2000).



Osaki, K., et al., *Journal of Polymer Science: Polymer Physics* **38**, 2043–2050 (2000).

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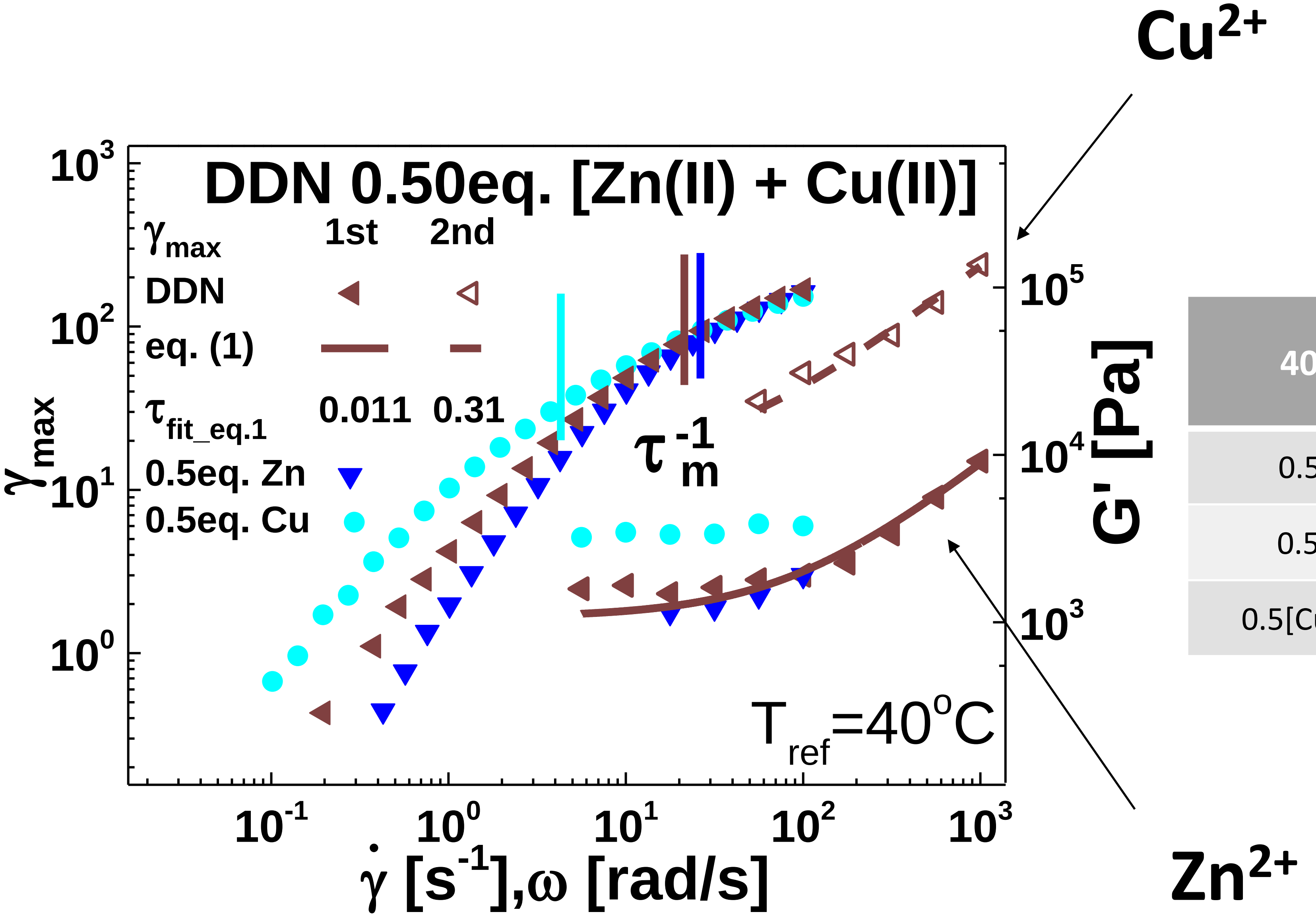
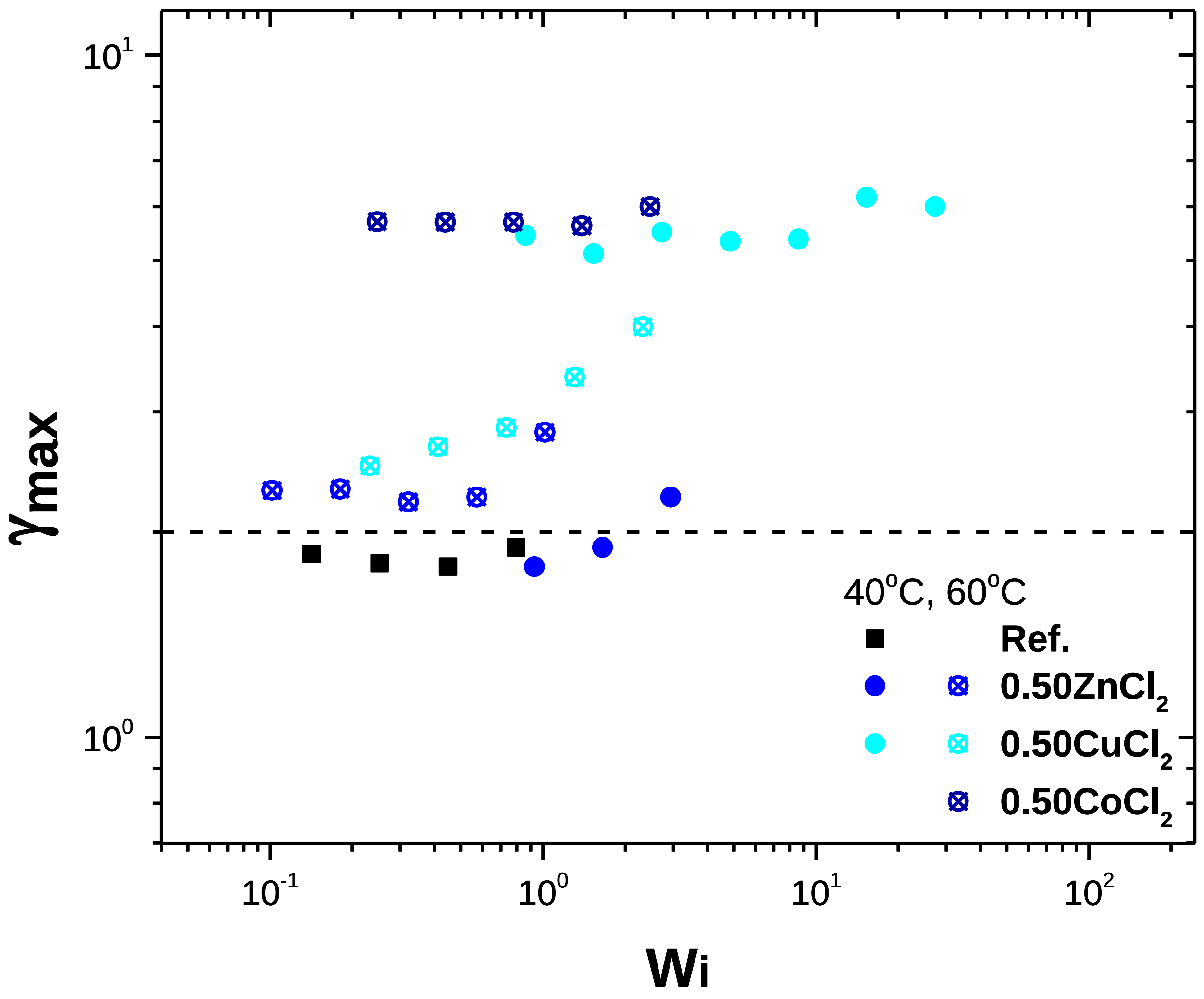
Peak allocation



$$\gamma_{max} = A[1 + (\dot{\gamma}\tau)]^{B}$$

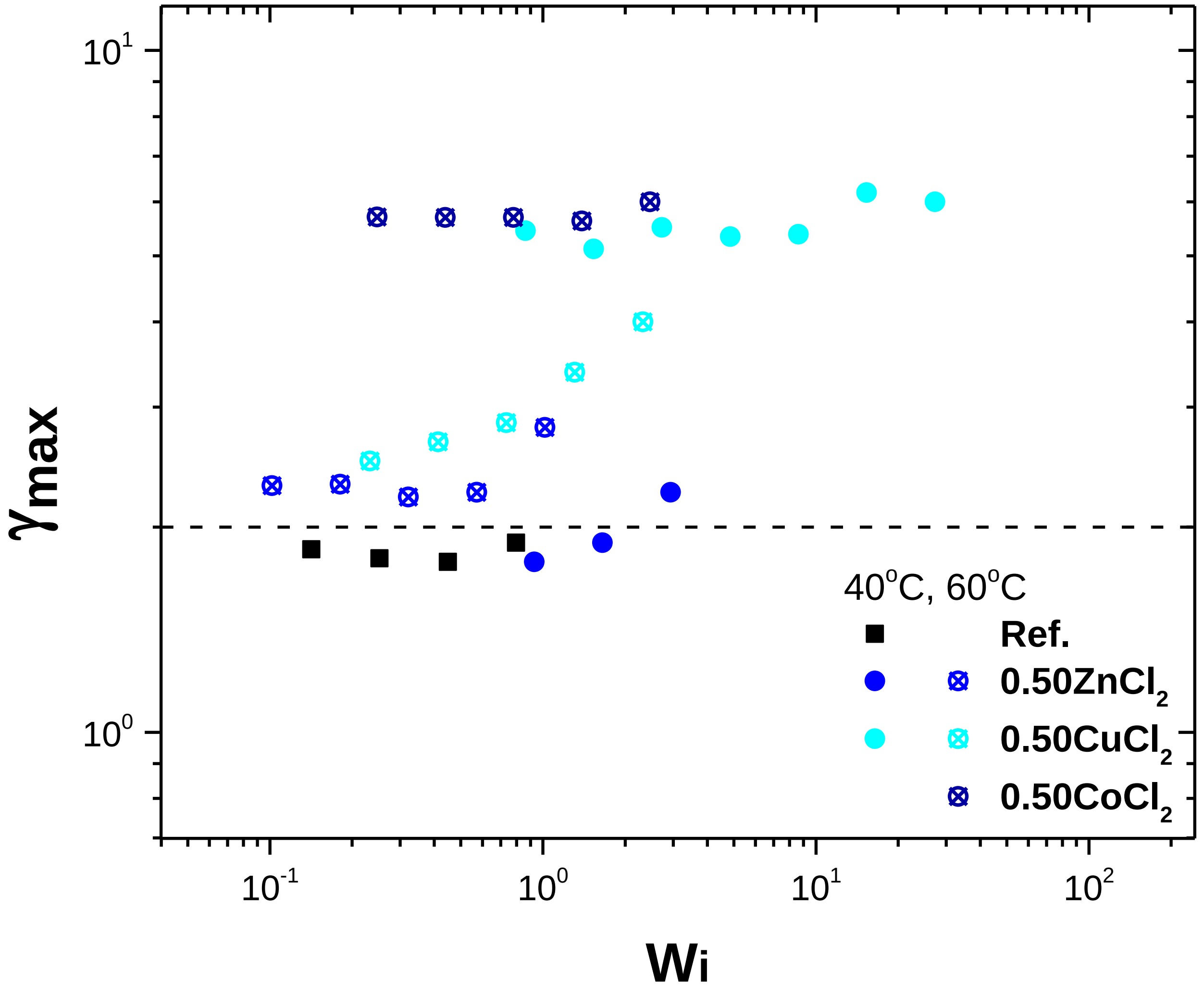
40ºC	τ_{cross} [sec] Experimental	τ_{cross} [sec] TMA
0.5Zn	0.052	**0.047**
0.5Cu	0.27	**0.31**
0.5[Cu+Zn]	0.068	**0.071**

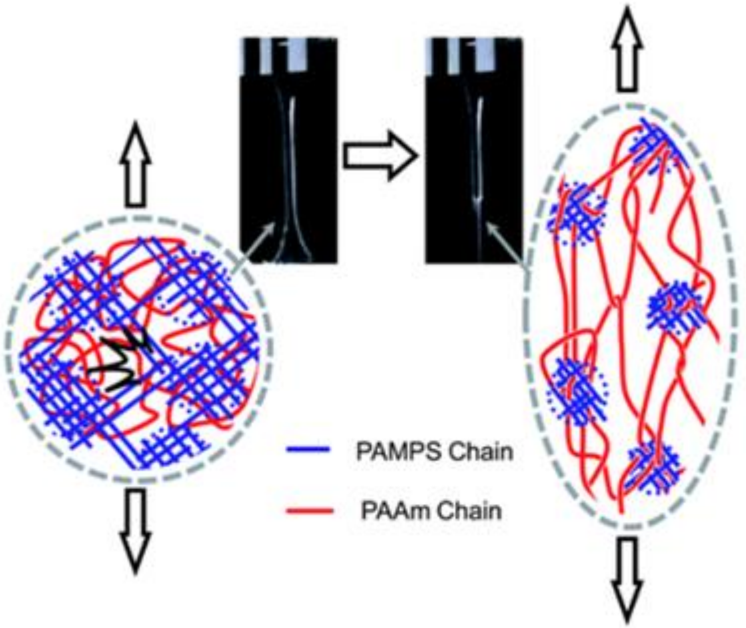
Proposed criterion for double overshoot



- Double peak is attributed to the coupled response of the two single network components
- The proposed criterion for double dynamics: one relatively weak single network with disassociation rate that depends shear rate (sacrificial bond) while the disassociation rate of the other is independent of the applied rate (deformability & coherence)

Proposed criterion for double overshoot





Gong, J. P. *Soft Matter* **6**, 2583–2590 (2010)

Sun, T. L. *et al. Nat Mater* **12**, 932–937 (2013)

Filippidi, E. *et al.*, *Science* **358**, 502–505 (2017)

Li, Y. *et al.*, *Chemistry of Materials* (2019)

Li, S. *et al.*, *Advanced Functional Materials* **30**, 2000130 (2020).

Conclusions

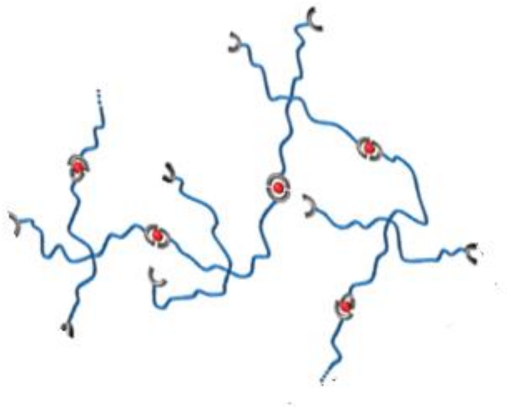
- Systematic nonlinear rheological study unravels the role of molecular parameters on properties
- Enhanced mechanical properties, coherence and deformability
- Role of associations strength is important in ultimate tunability- from polymer to bond dominated response

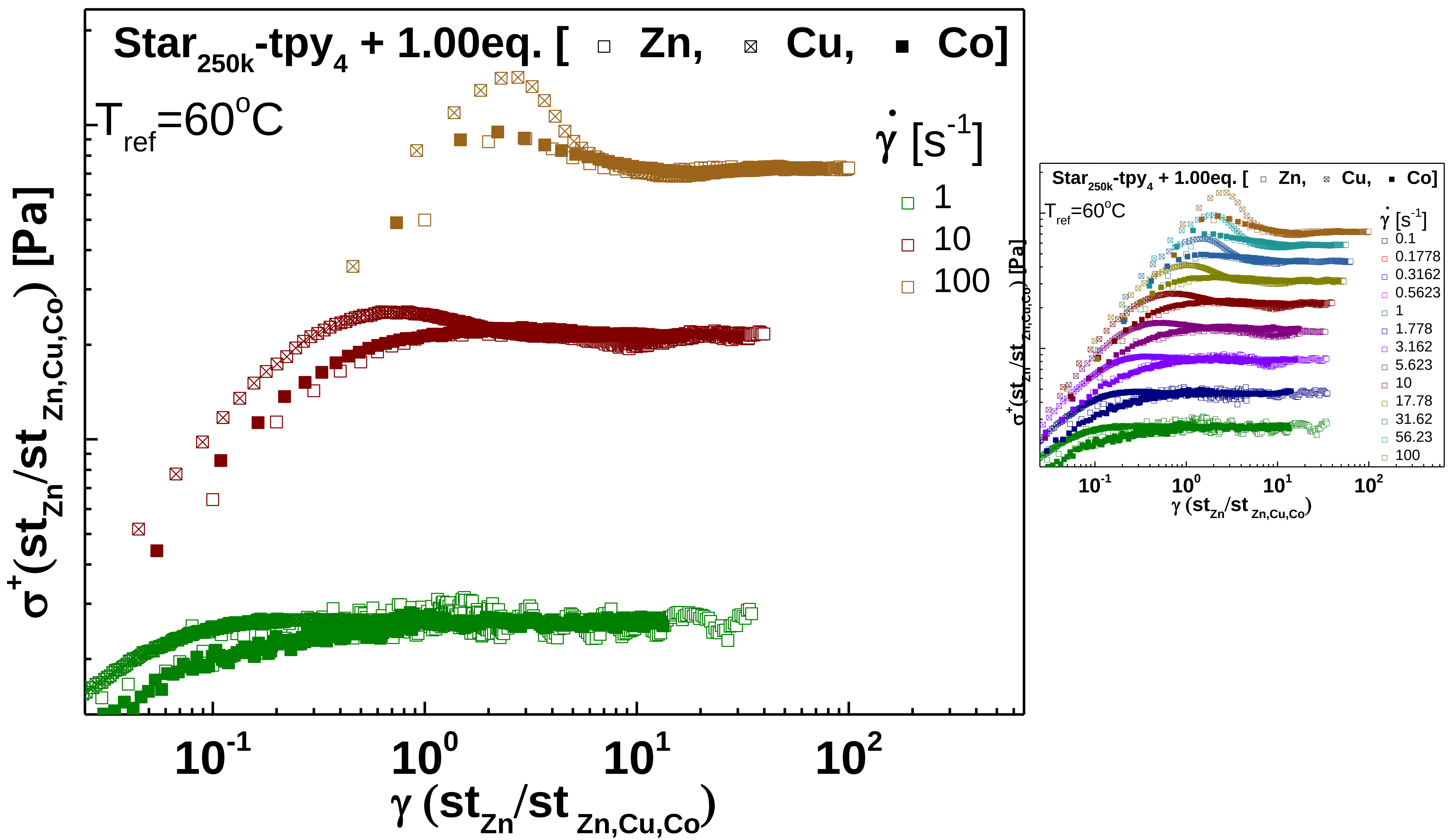
Perspectives

- Further double peak study, including extensional deformation
- Understanding the relaxation mechanism of transient networks
- Rationalization of experimental observations using TMA

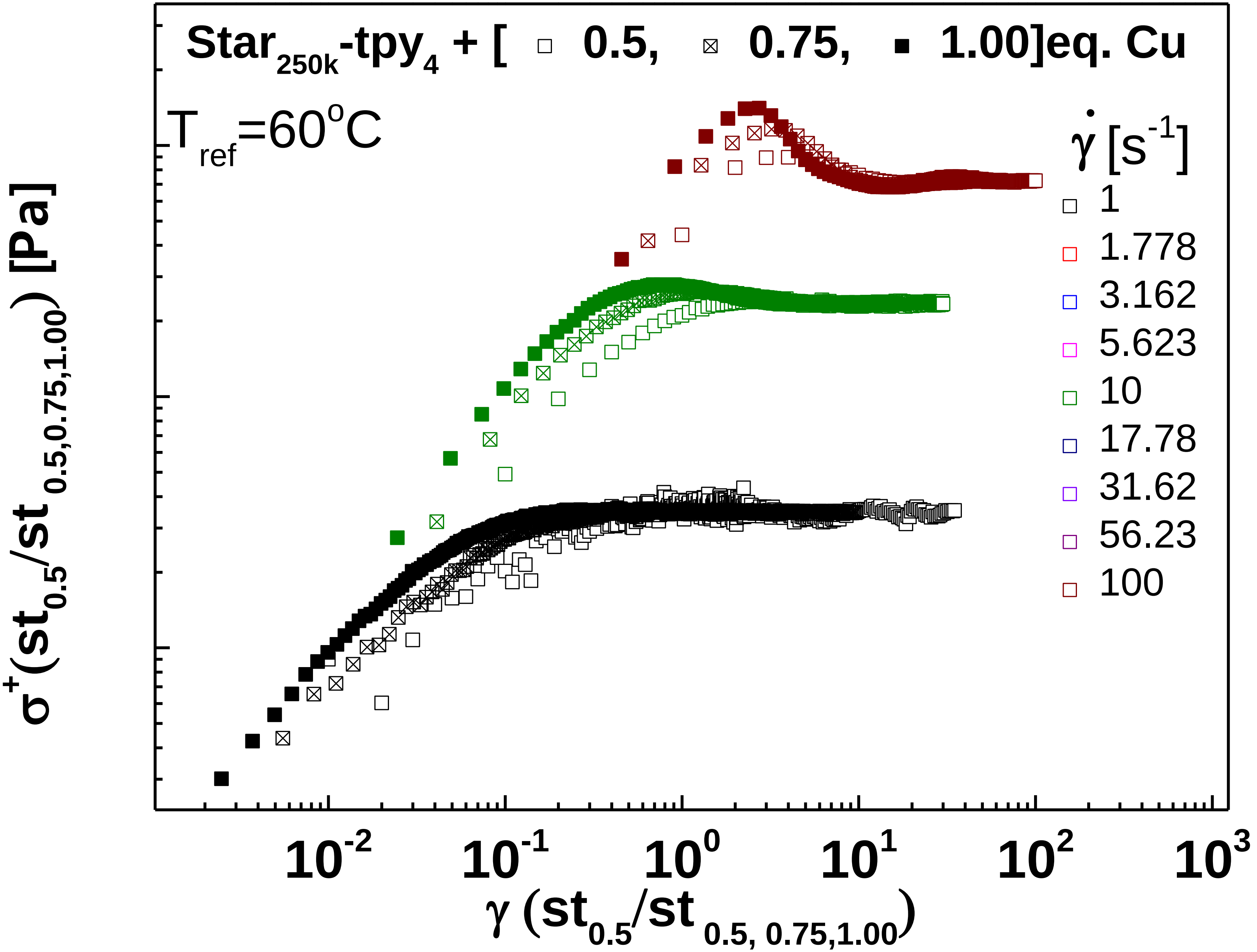
Thank you for your attention!

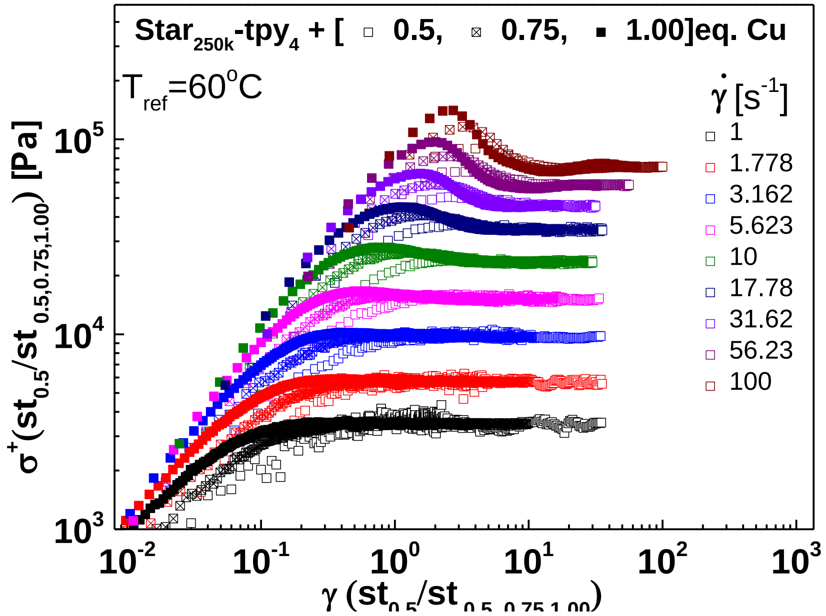
Questions?

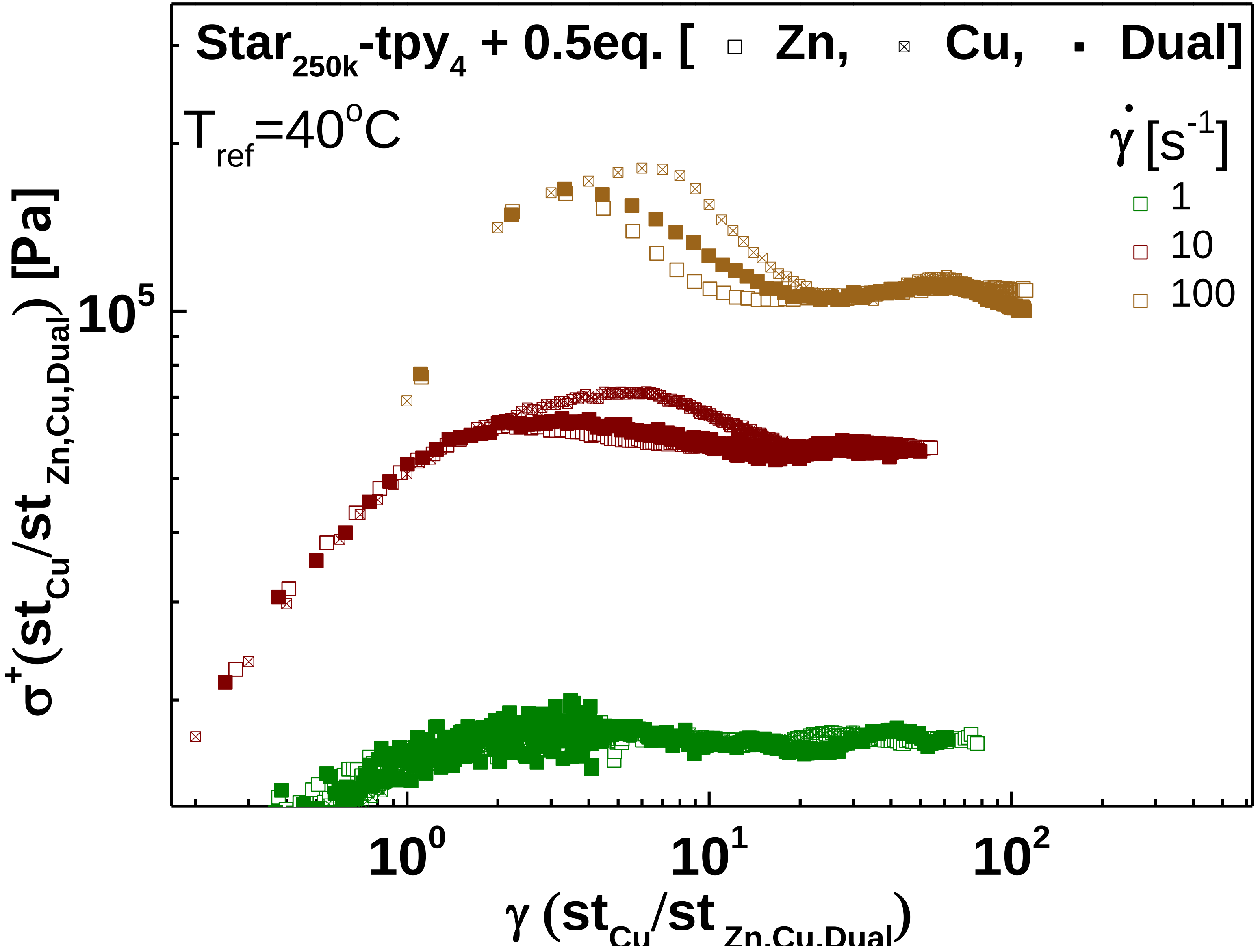




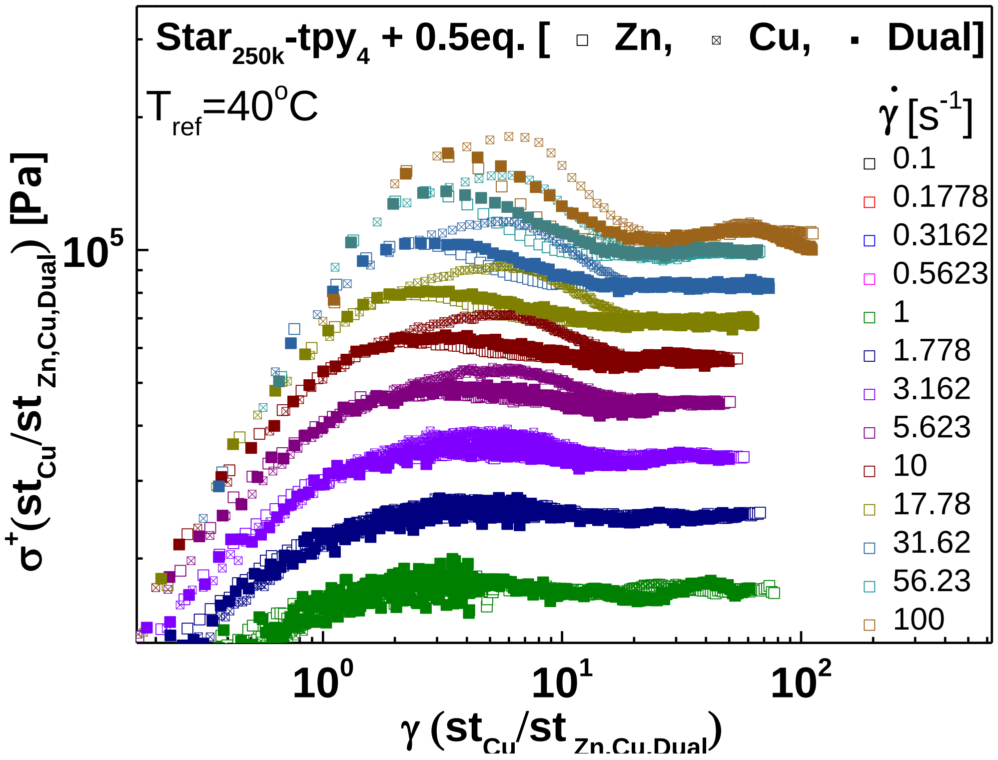
Star$_{250k}$-tpy$_4$ + 1.00eq. [□ Zn, ⊠ Cu, ■ Co]
T$_{ref}$=60^{o}C
$\dot{\gamma}$ [s^{-1}]
1
10
100
σ^+(st$_{Zn}$/st$_{Zn,Cu,Co}$) [Pa]
γ (st$_{Zn}$/st$_{Zn,Cu,Co}$)
10^{-1}
10^0
10^1
10^2
0.1
0.1778
0.3162
0.5623
1
1.778
3.162
5.623
10
17.78
31.62
56.23
100


Star250k-tpy4 + [0.5, 0.75, 1.00]eq. Cu
Tref=60oC
γ̇ [s-1]
1
1.778
3.162
5.623
10
17.78
31.62
56.23
100
σ+(st0.5/st0.5,0.75,1.00) [Pa]
10-2
10-1
100
101
102
103
γ (st0.5/st 0.5, 0.75,1.00)

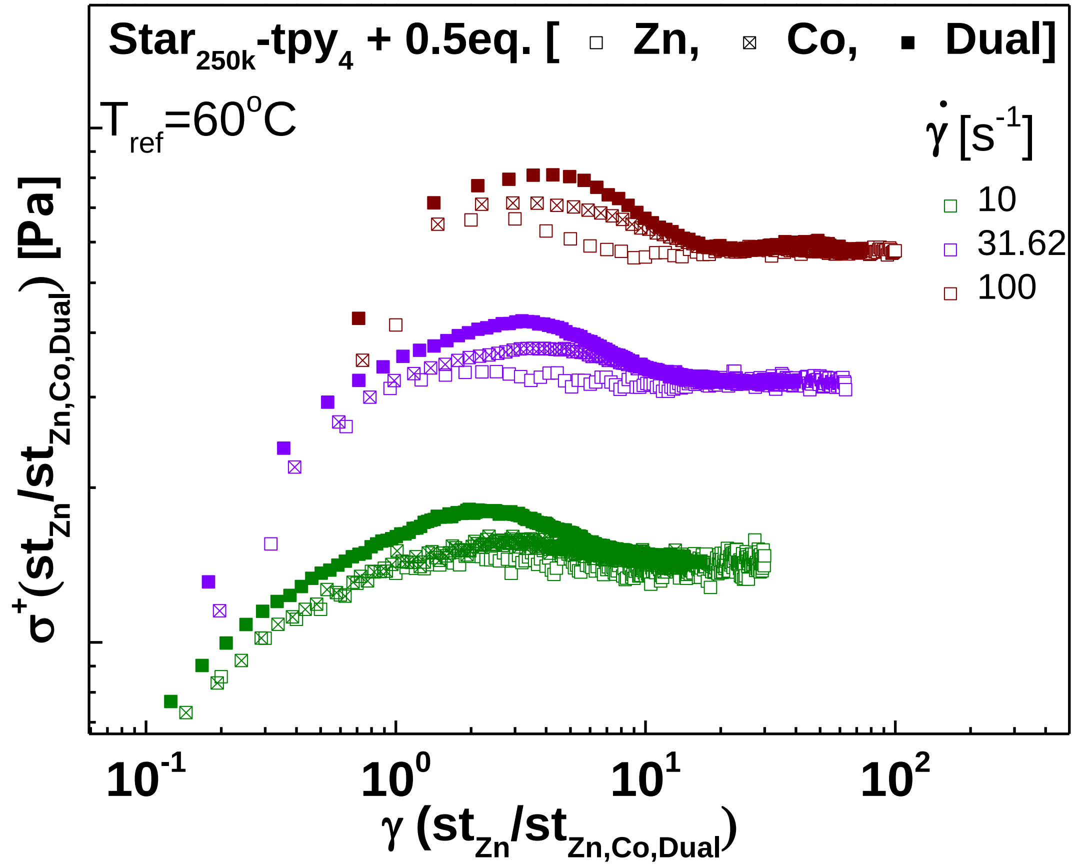

Star250k-tpy4 + [0.5, 0.75, 1.00]eq. Cu
Tref=60oC
γ̇ [s-1]
1
1.778
3.162
5.623
10
17.78
31.62
56.23
100
σ+(st0.5/st0.5,0.75,1.00) [Pa]
105
104
103
10-2
10-1
100
101
102
103



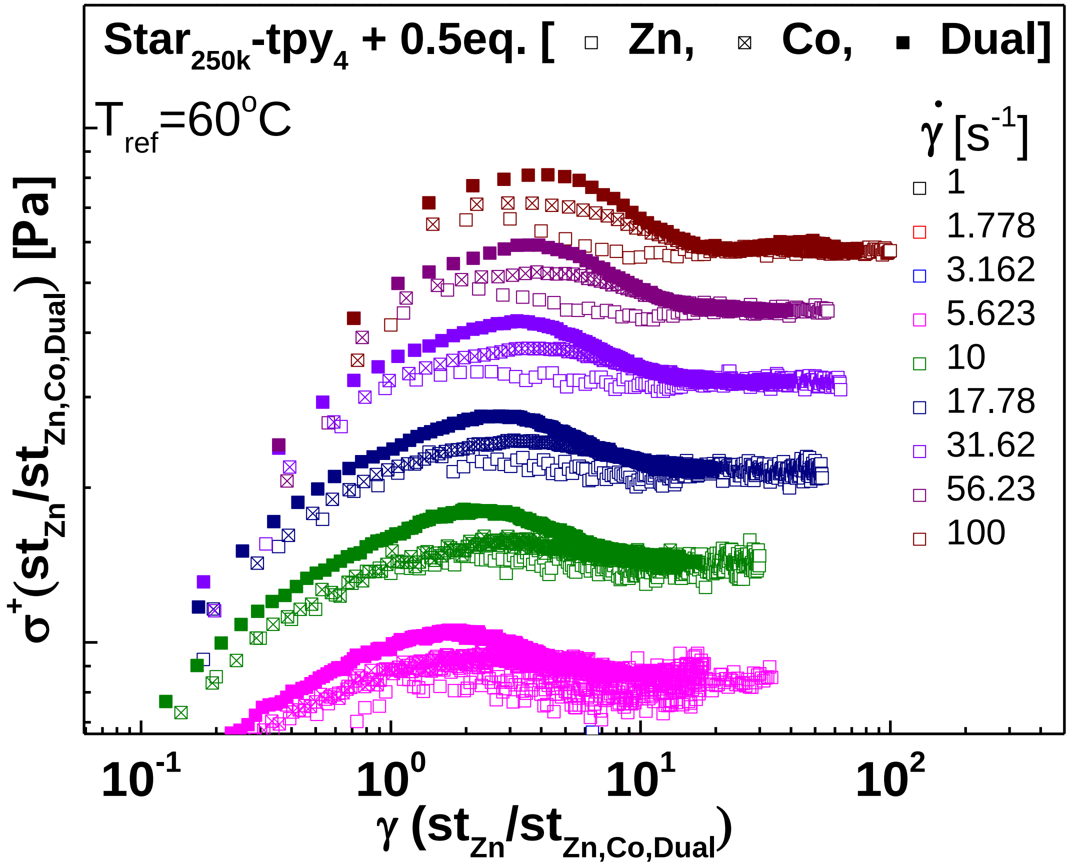
Star250k-tpy4 + 0.5eq. [Zn, Cu, Dual]
Tref=40°C
γ̇ [s-1]
1
10
100
σ+(stCu/stZn,Cu,Dual) [Pa]
10^5
10^0
10^1
10^2
γ (stCu/st Zn,Cu,Dual)



Star250k-tpy4 + 0.5eq. [Zn, Cu, Dual]
Tref=40°C
γ̇ [s-1]
0.1
0.1778
0.3162
0.5623
1
1.778
3.162
5.623
10
17.78
31.62
56.23
100
σ+(stCu/stZn,Cu,Dual) [Pa]
10^5
10^0
10^1
10^2
γ (stCu/st Zn,Cu,Dual)

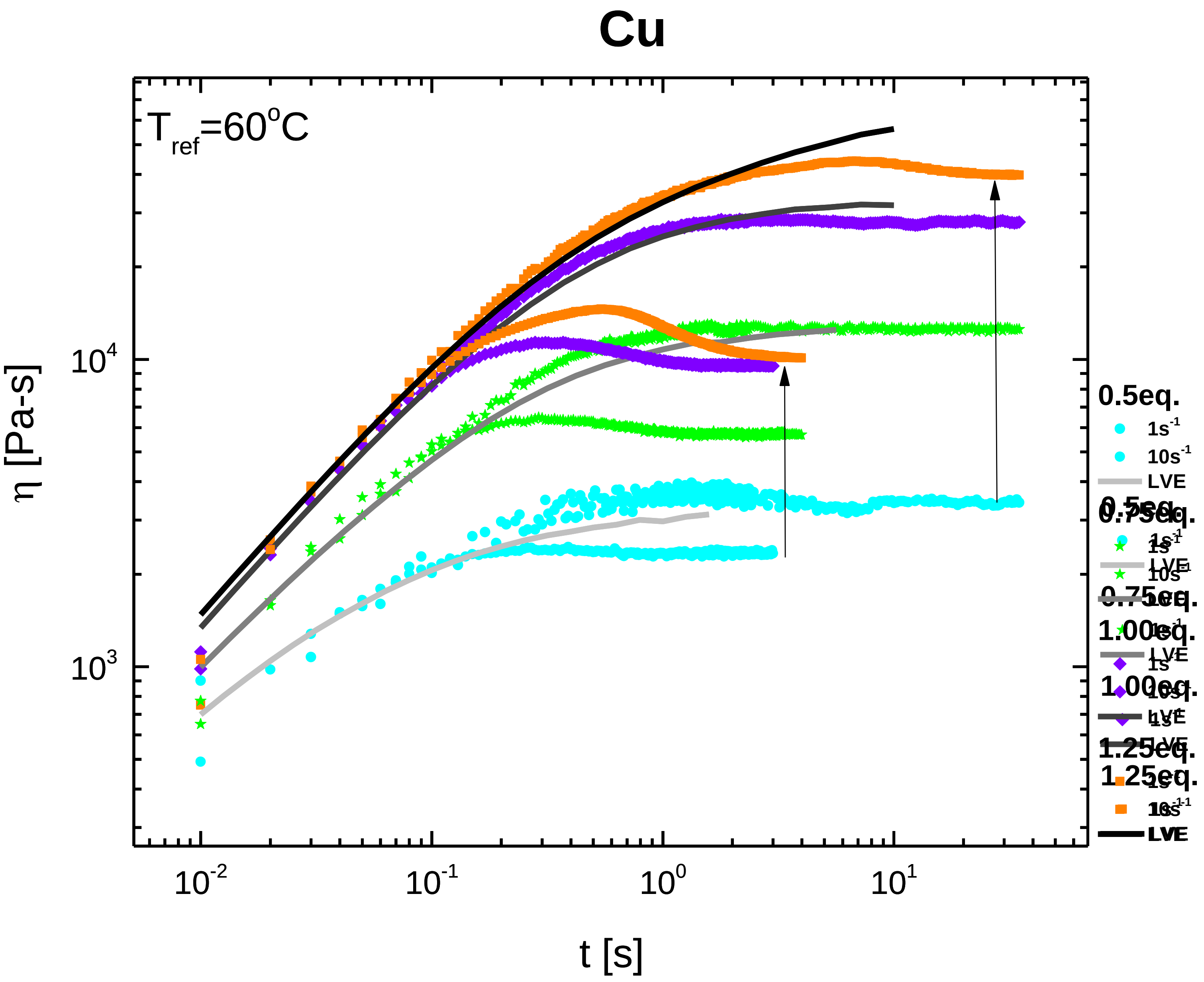


Star250k-tpy4 + 0.5eq. [Zn, Co, Dual]
Tref=60°C
γ̇ [s-1]
10
31.62
100
σ+(stZn/stZn,Co,Dual) [Pa]
γ (stZn/stZn,Co,Dual)



Star250k-tpy4 + 0.5eq. [Zn, Co, Dual]
Tref=60°C
γ̇ [s-1]
1
1.778
3.162
5.623
10
17.78
31.62
56.23
100
σ+(stZn/stZn,Co,Dual) [Pa]
γ (stZn/stZn,Co,Dual)

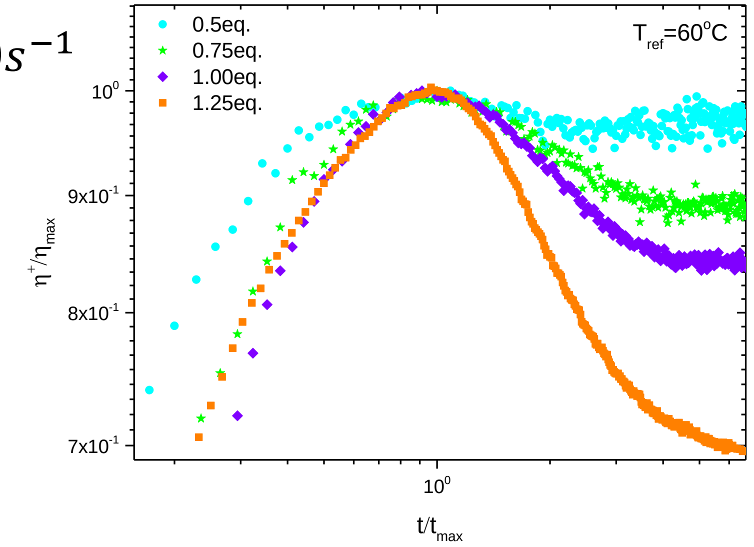
Single Networks_Ion Content



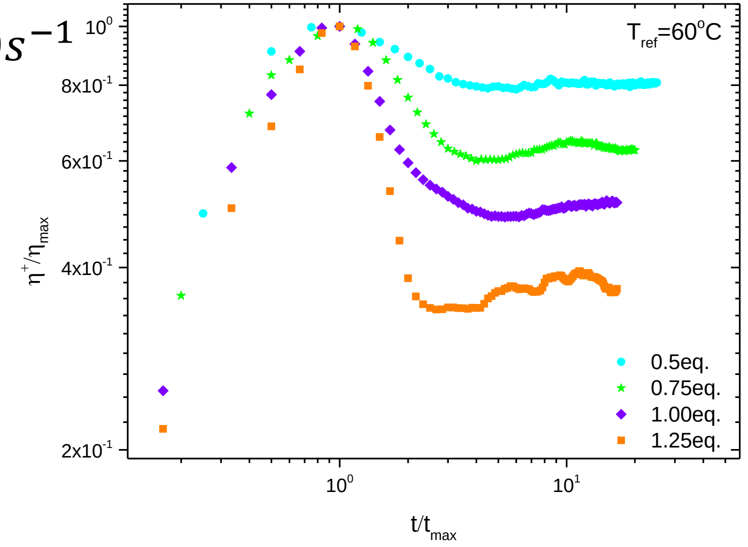
Half Height Width

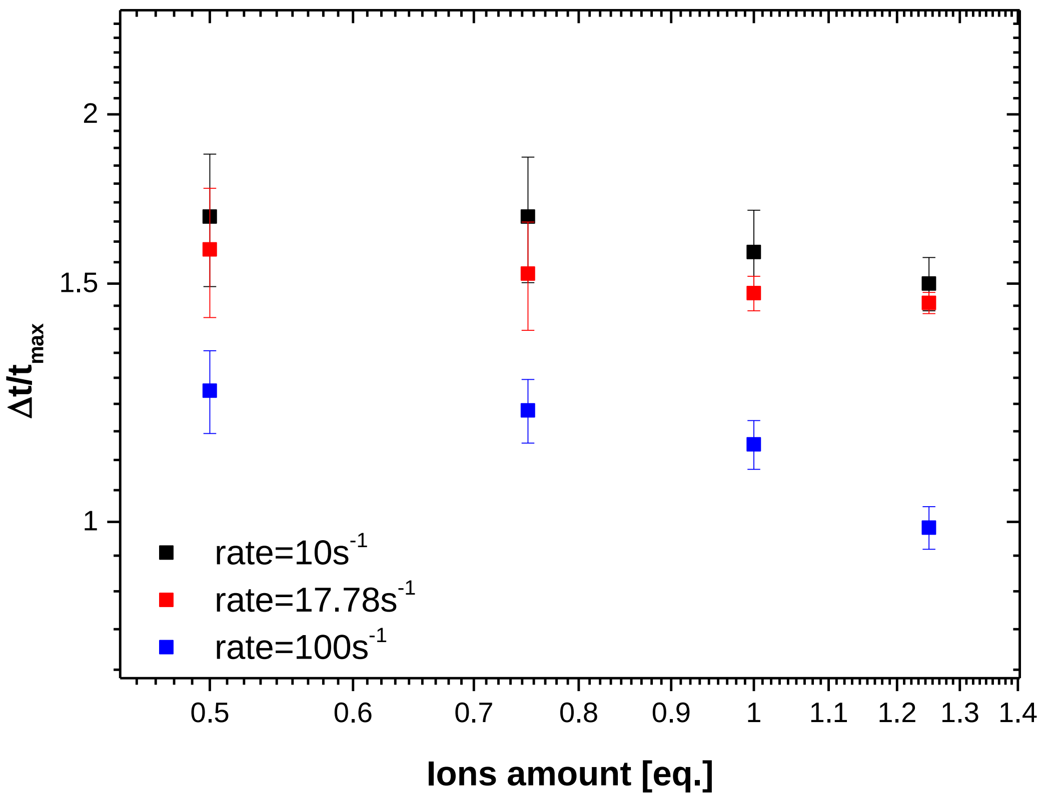
Ion Nature
Ion Content
Temperature

$\dot{\gamma} = 10s^{-1}$



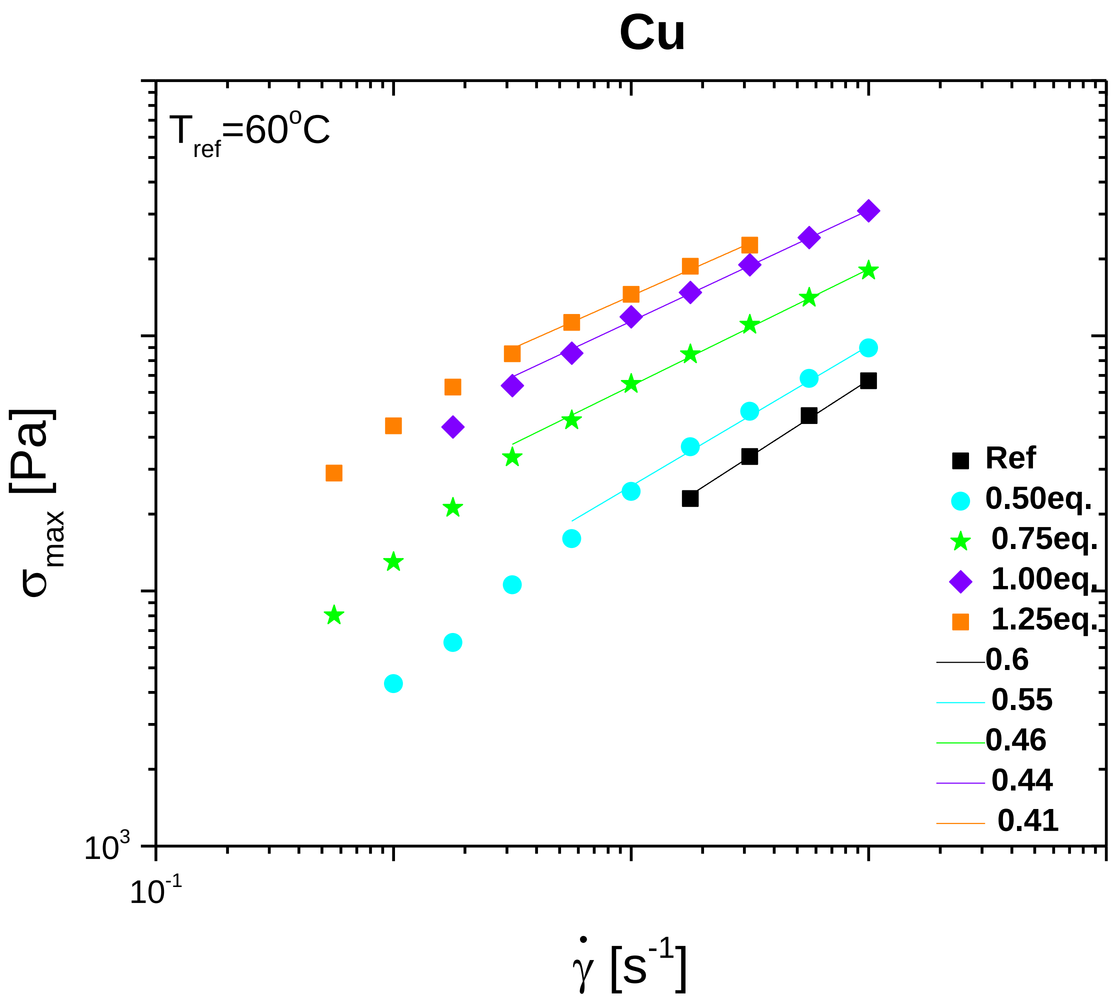
$\dot{\gamma} = 100s^{-1}$

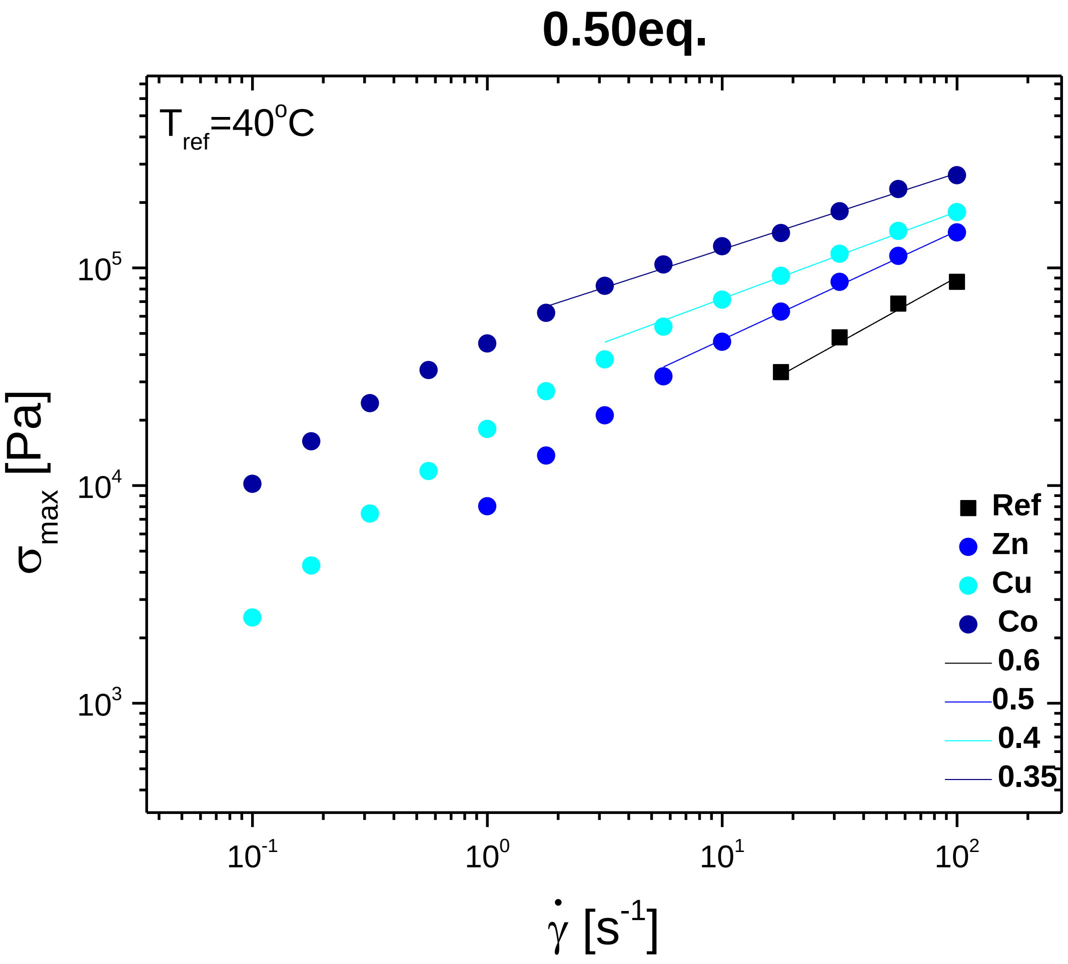




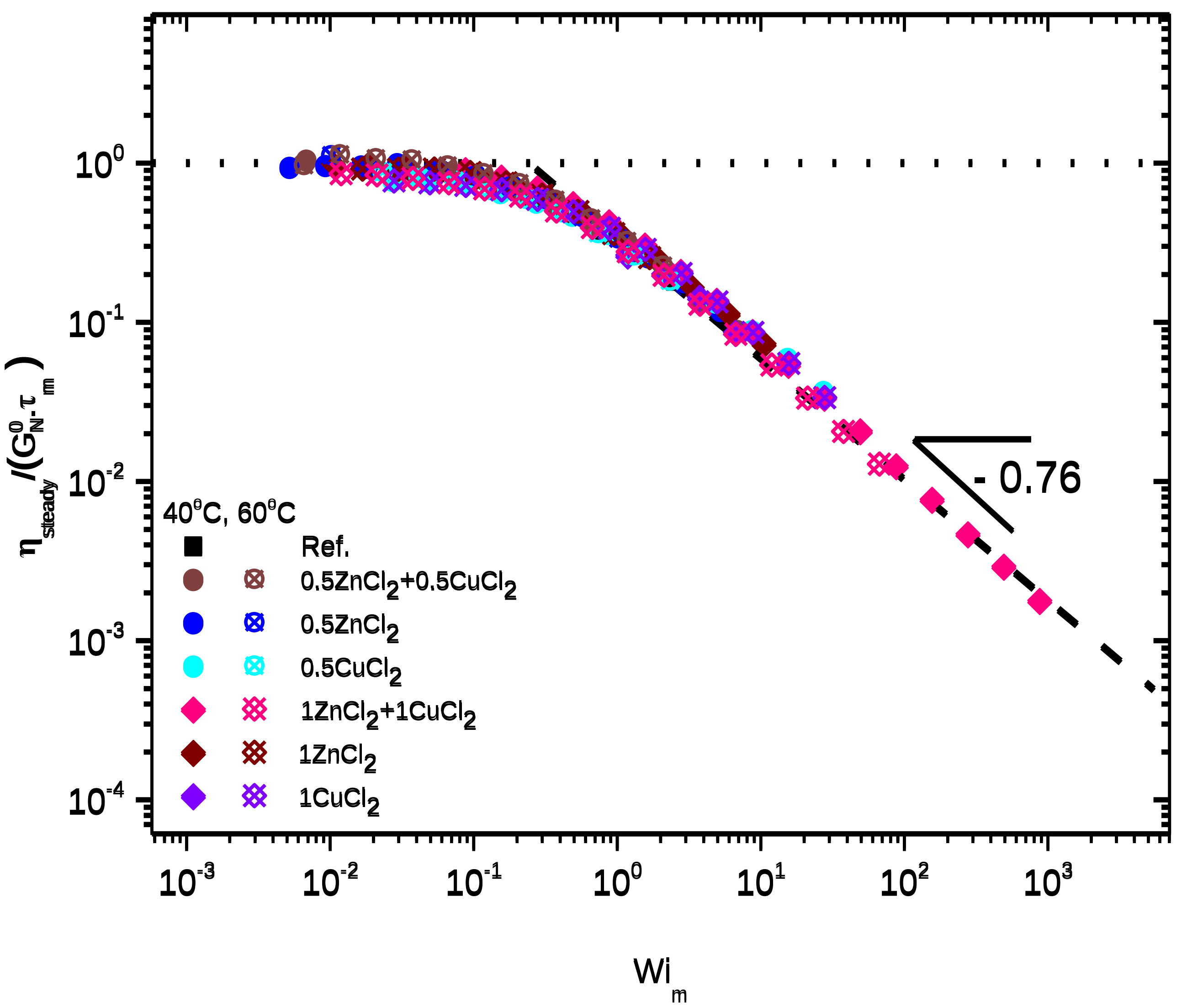
Half height width of peak transient viscosity decrease as the ions content increase i.e. elastic recoil to the initial structure is enhanced in abundant of metal ions

Yield Stress

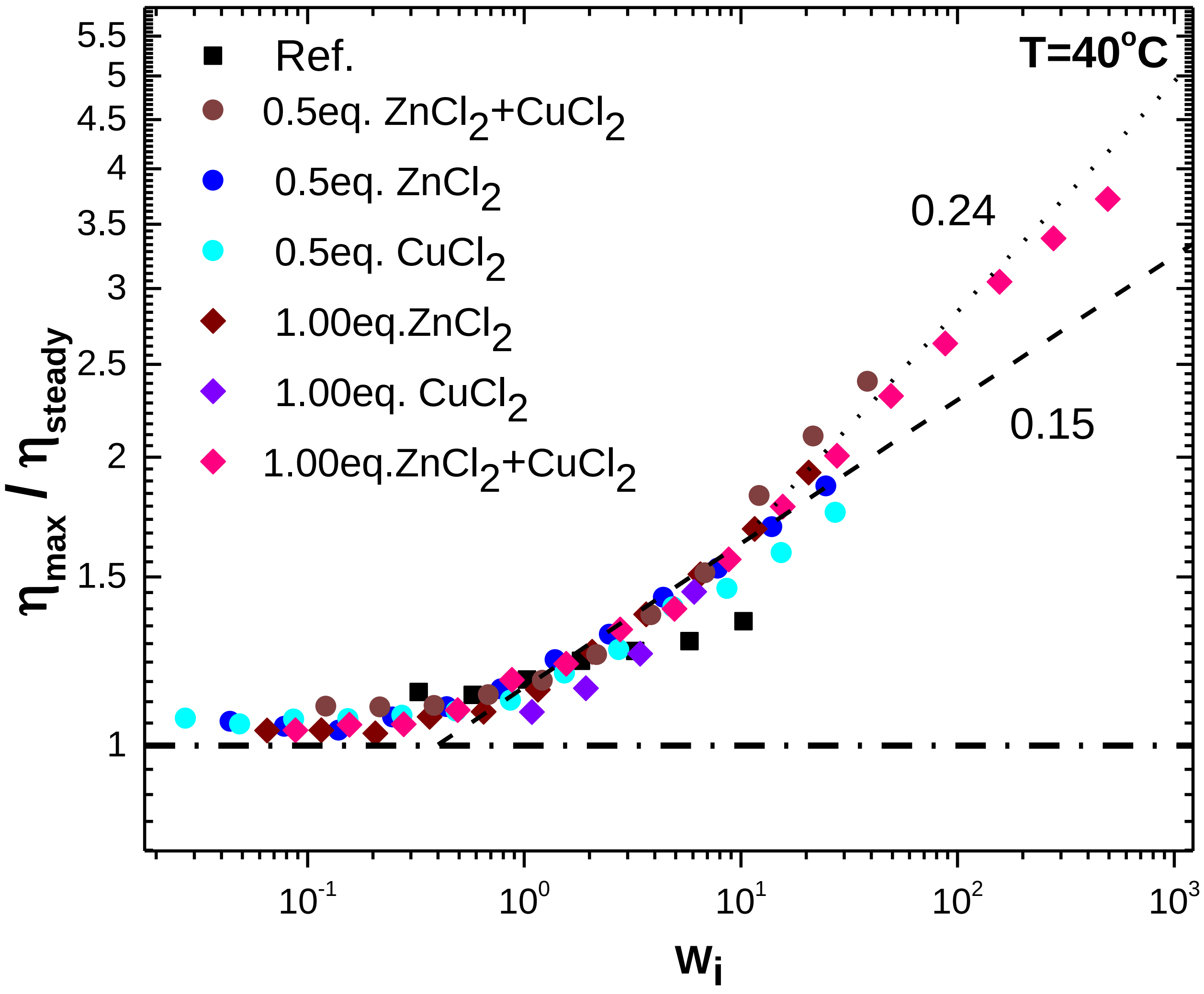




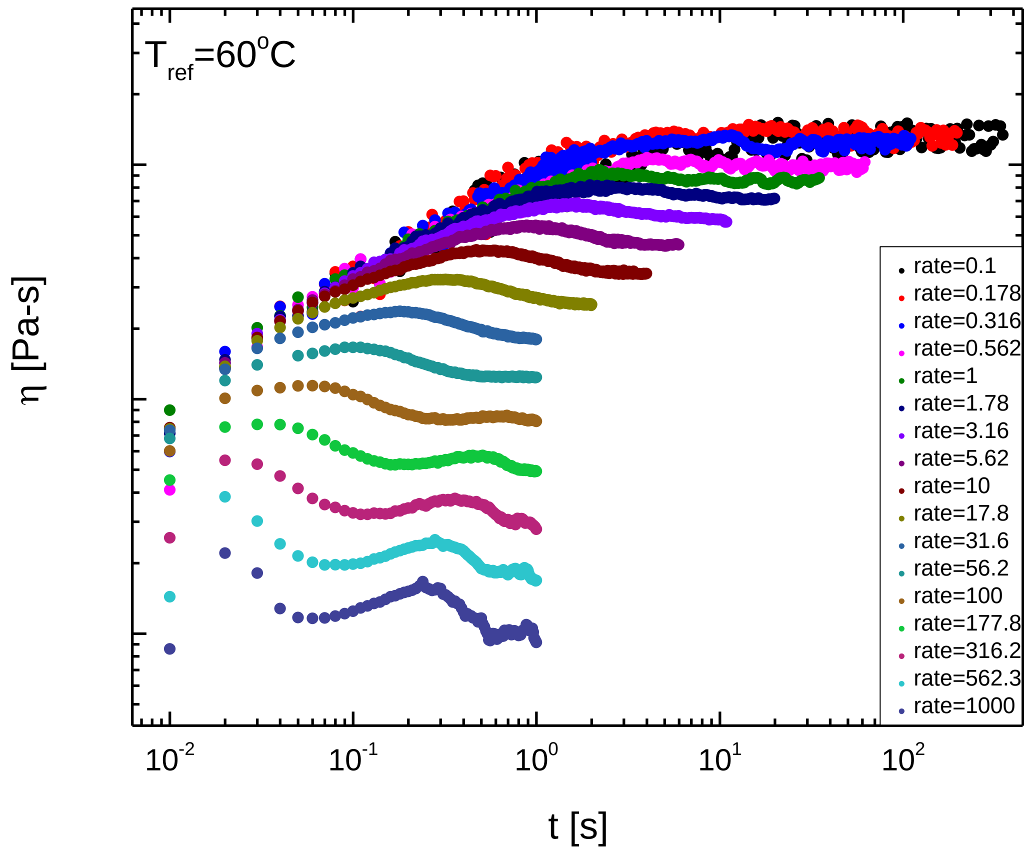
Shear Thinning_Single & Double Sticker Lifetime



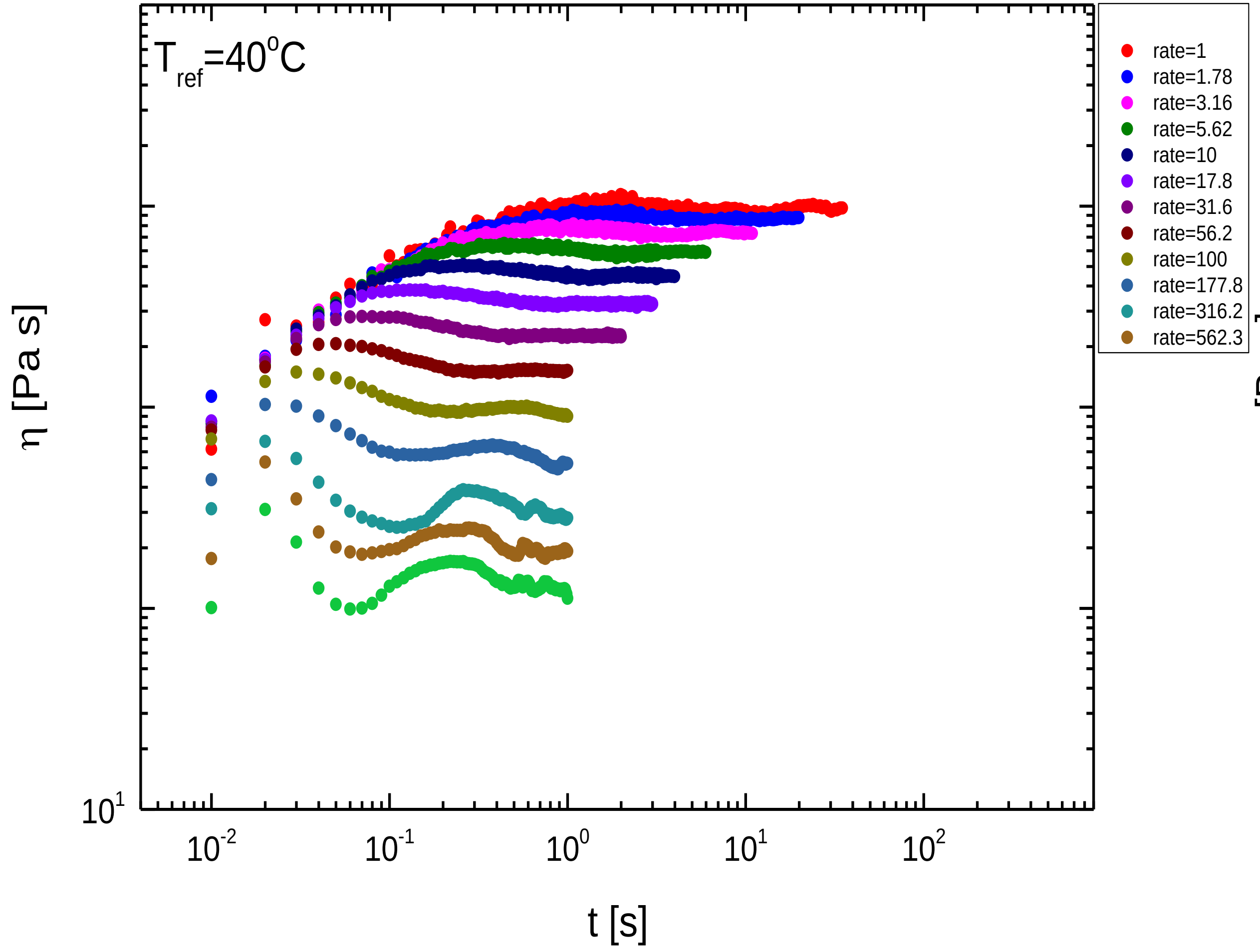
Fractional viscosity overshoot_Single & Double Sticker Lifetime



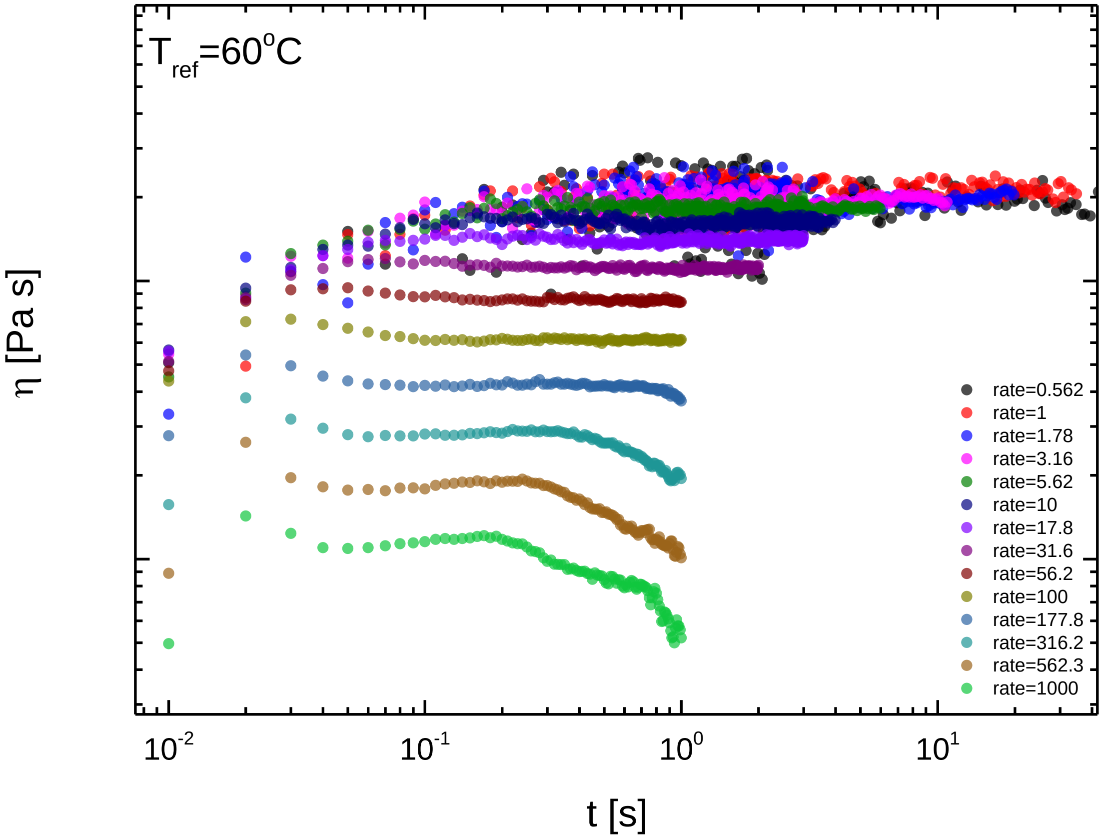
$Star_{250k}$-tpy_4 + 0.5eq. Zn(II) + 0.5eq. Co(II)



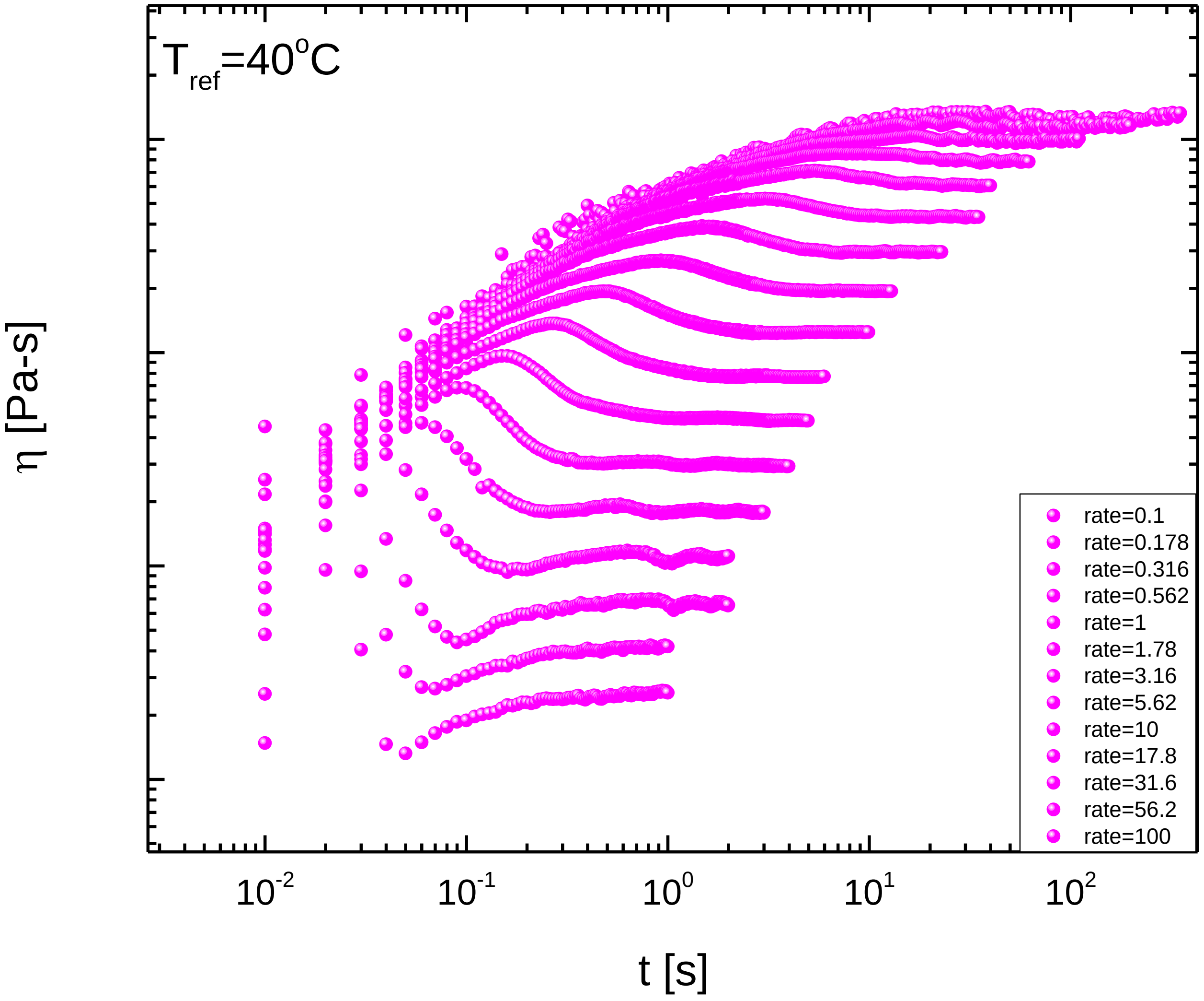
$Star_{250k}$-tpy_4 _0.5eq.Zn(II) + 0.5eq. Cu(II)



$Star_{250k}$-tpy_4 _0.5eq.Zn(II) + 0.5eq. Cu(II)



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



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