Double Dynamics for design of new responsive polymer networks and gels

Modelling the linear dynamics of Double Dynamics Polymer Networks

Blend two metal-ligand crosslinks with distinct relaxation modes in telechelic star polymer

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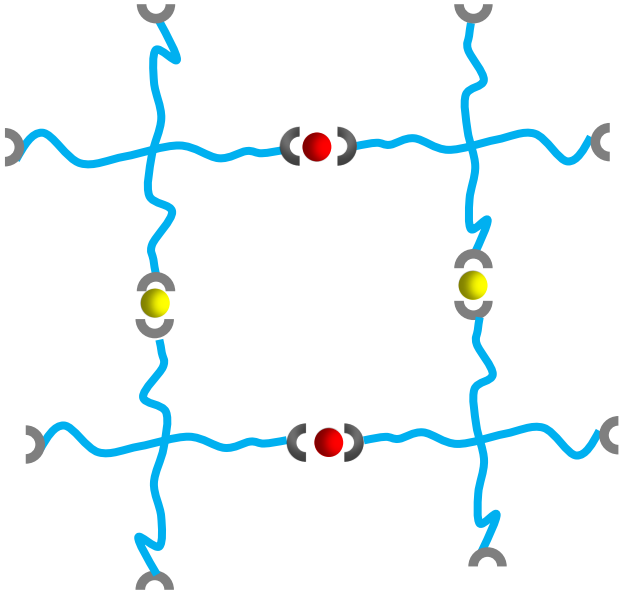
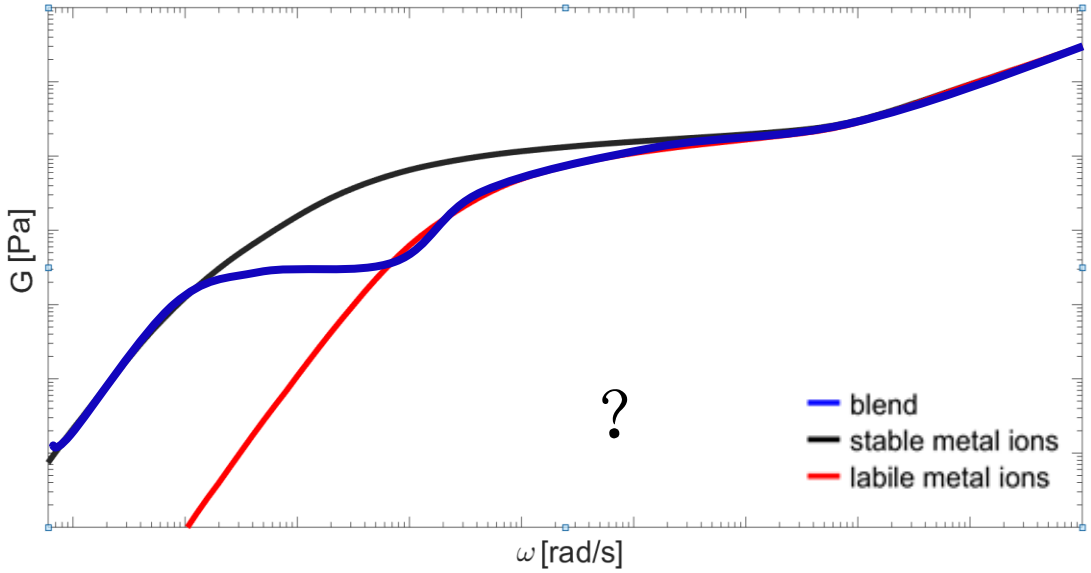
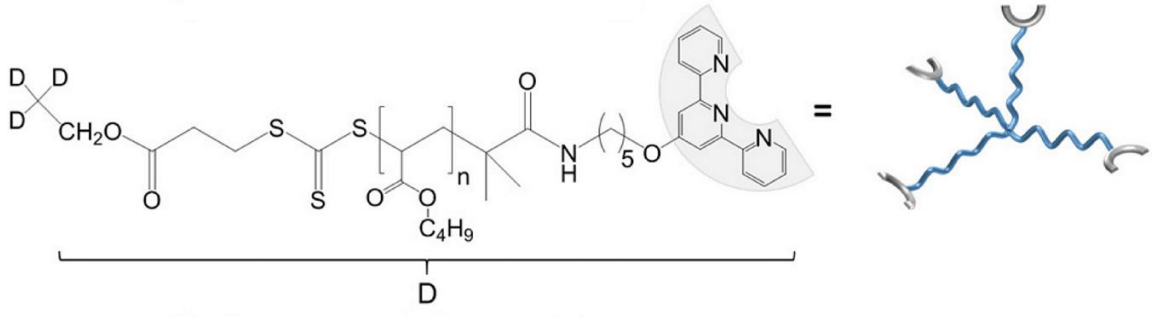
Objective

Understanding the dynamics of telechelic star polymer combined two metal-ligand crosslinks with distinct relaxation modes.





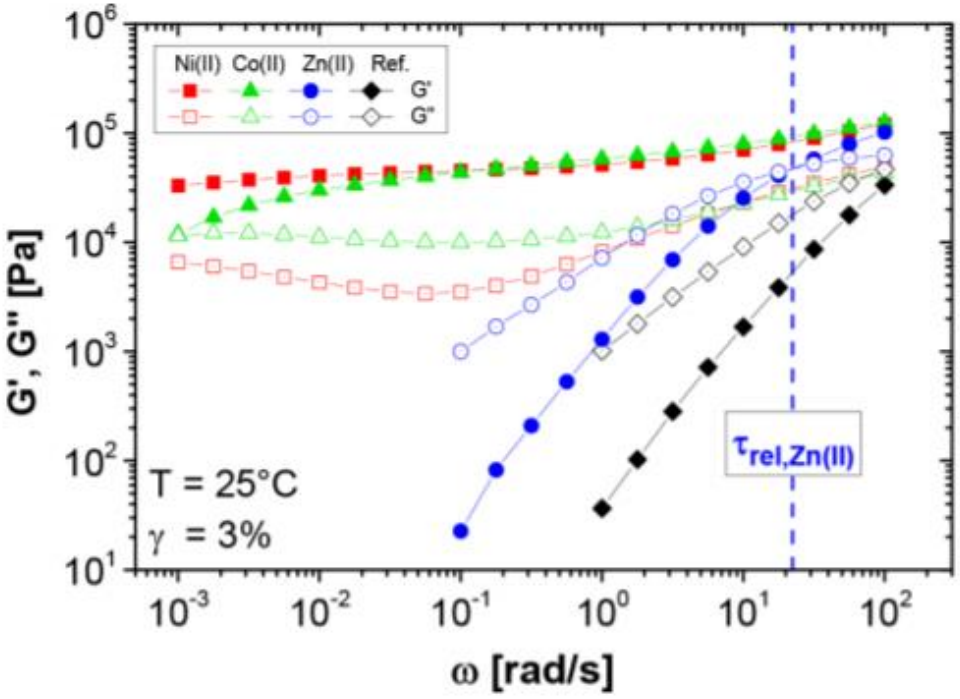
Zn^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+}



M_e = 18 kg/mol

M_n = 249kg/mol

Macromolecules, 2017, 50, 5165−5175.

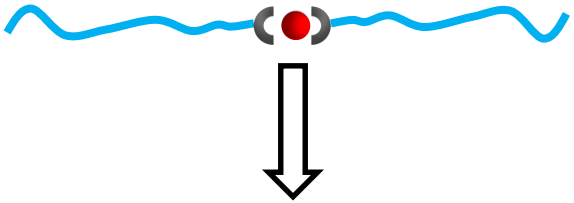


Labile **Stable**

Zn^{2+} Cu^{2+} (Co^{2+} or Ni^{2+})

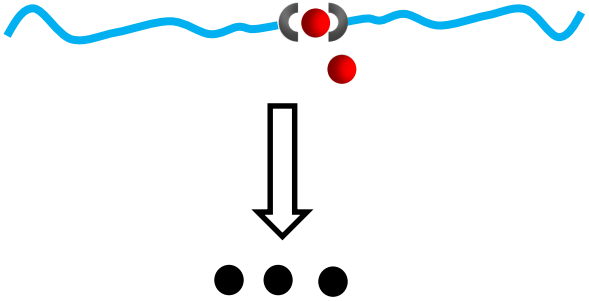
0.5eq. & 0.5eq.

(stoichiometric amount)



1.0eq. & 1.0eq.

(excess amount)



Interaction?

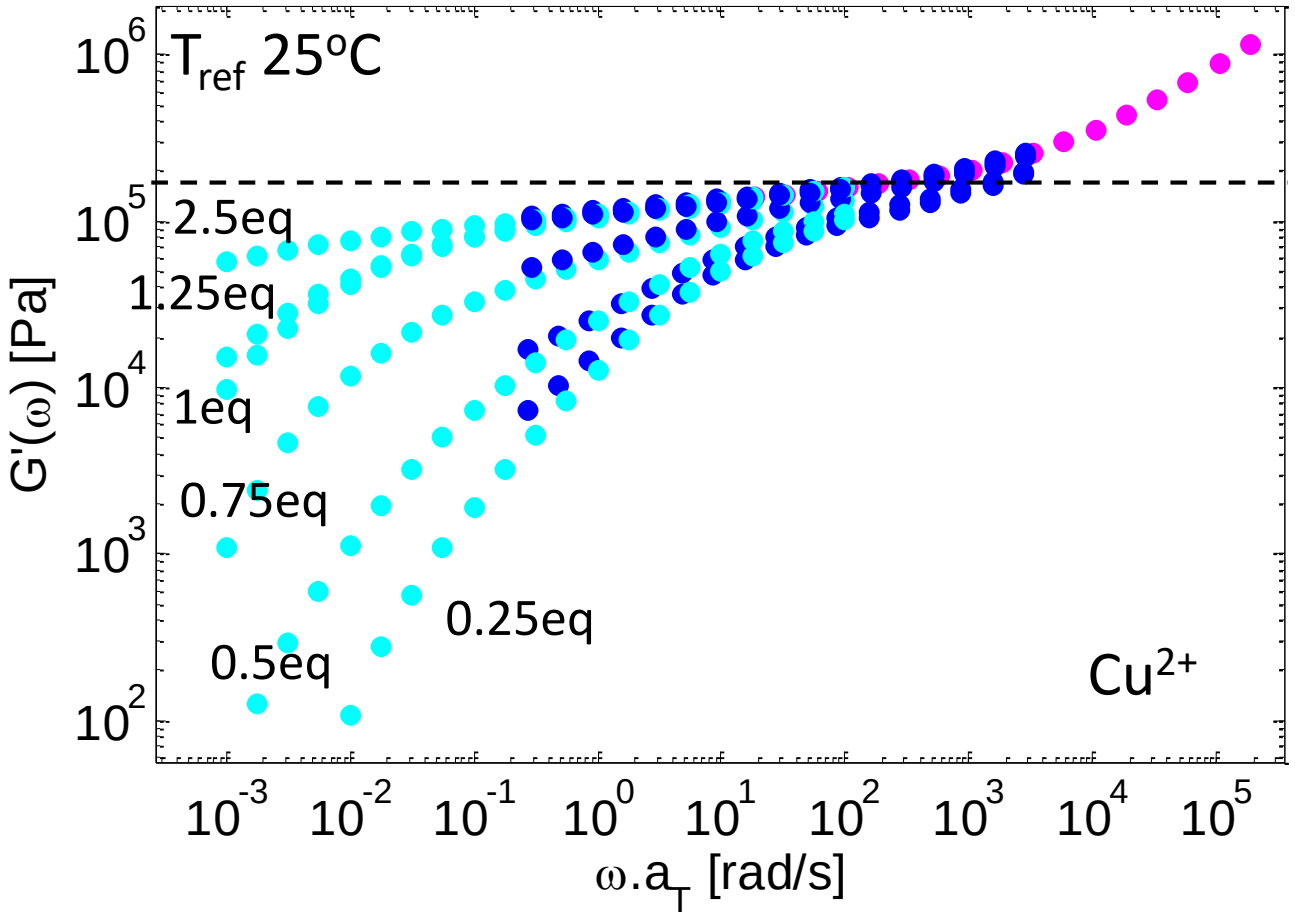
List of samples

Zn^{2+} and Cu^{2+}	0.5eq. 0.75eq. 1eq. 1.25eq. 2.5eq.
Cu^{2+} and Co^{2+}	0.5eq.
Co^{2+} and Zn^{2+}	0.5eq. 0.75eq.

At different temperature, from -20℃ to 100℃

Macromolecules, 2017, 50, 5165−5175.

Influence of the ions content

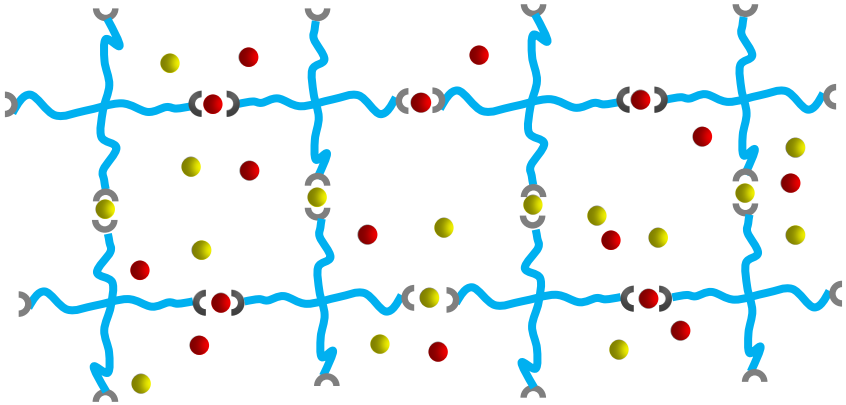


The network is fully saturated at 1eq.

J. Rheol., 2017, 61, 1245-1262

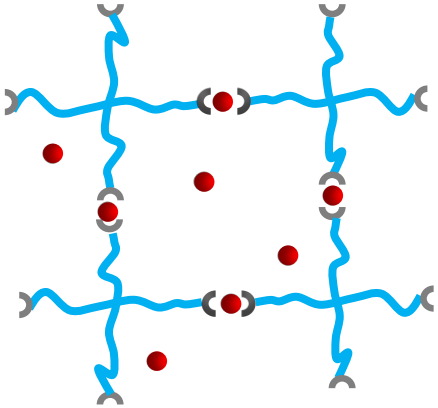
Blending Zn^{2+} and Cu^{2+}

blend (1eq. Zn^{2+} and 1eq. Cu^{2+})

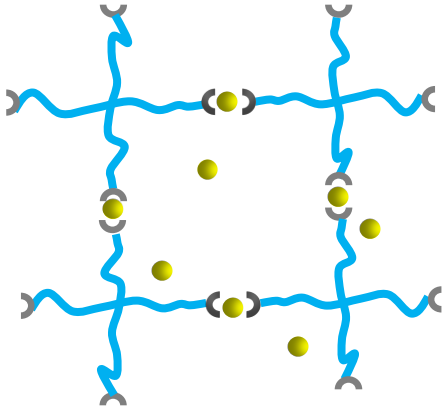


The total amount=1eq.

0.5eq. Zn^{2+} and 0.5eq. Cu^{2+}

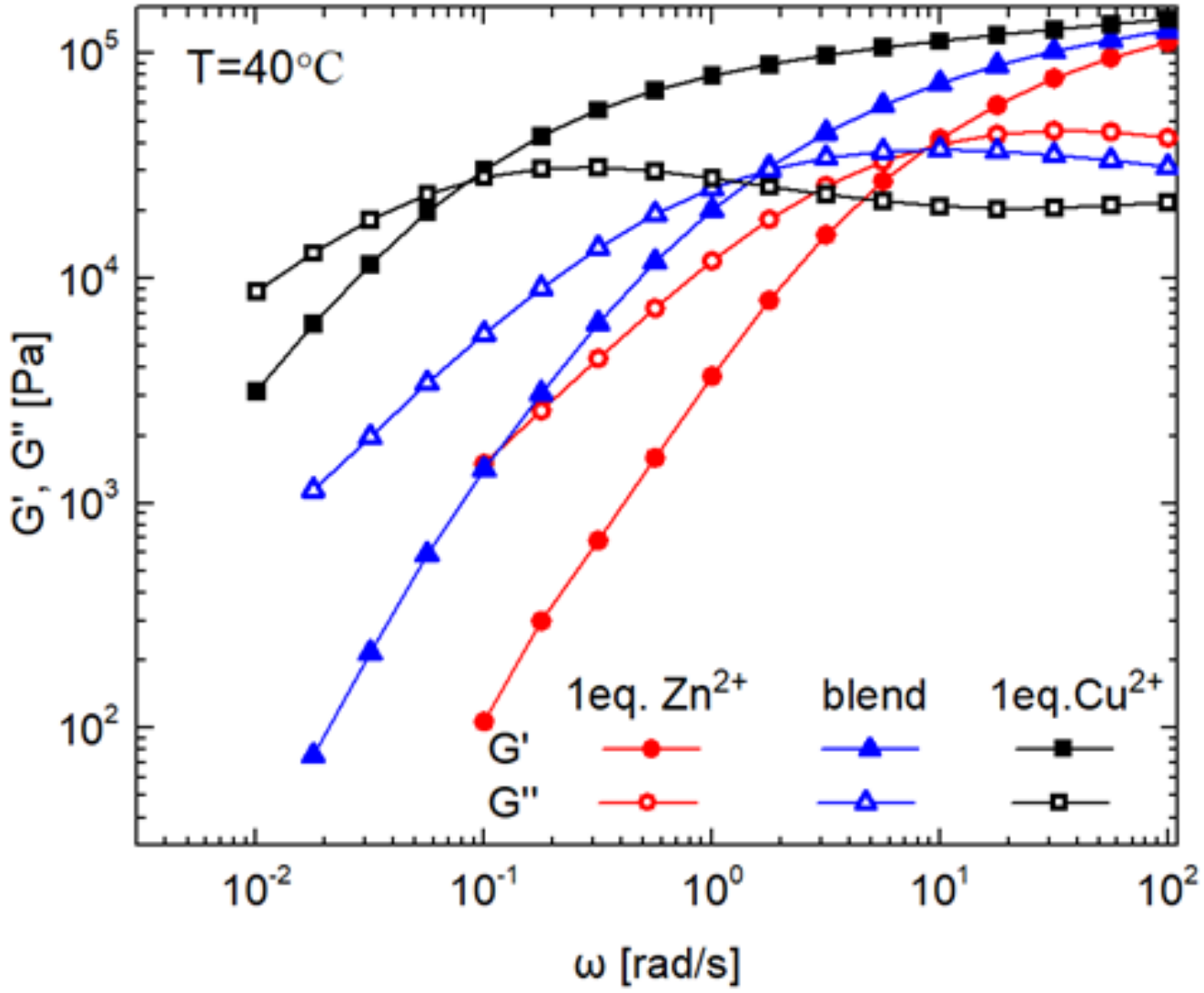


0.5eq. Zn^{2+}



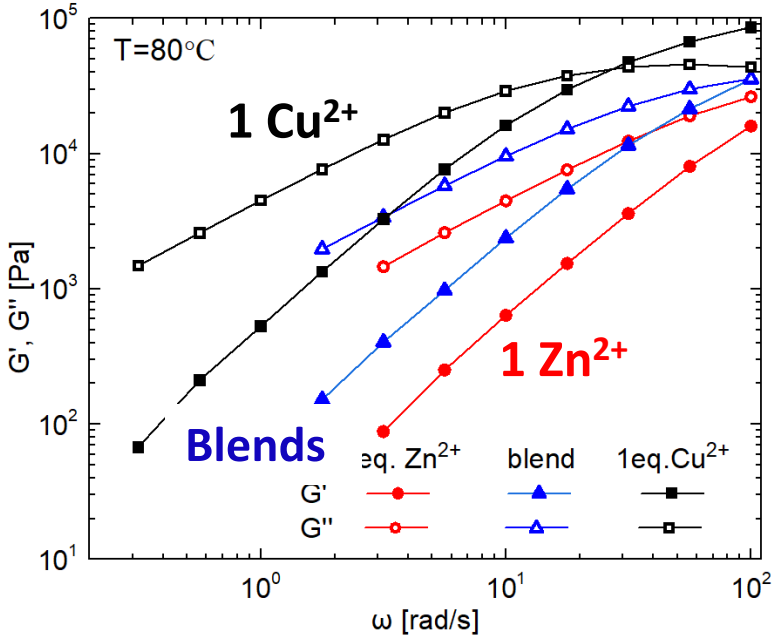
0.5eq. Cu^{2+}

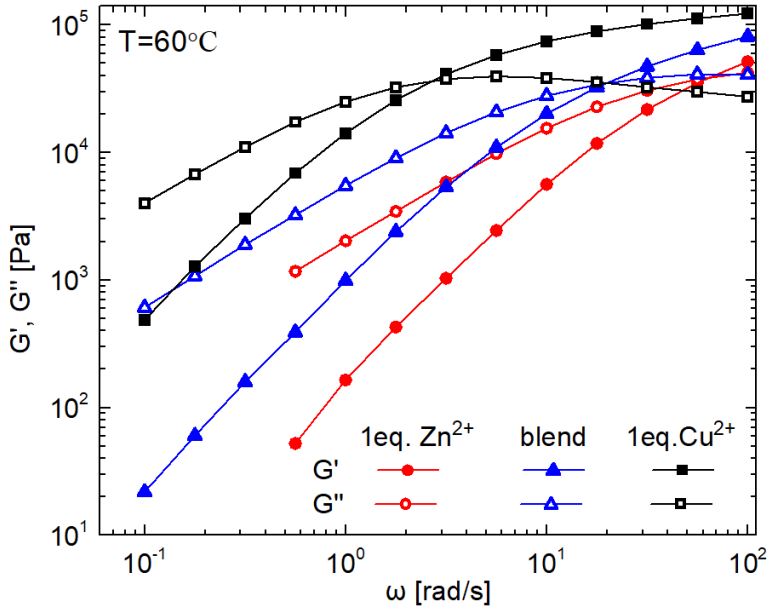
1eq. Zn^{2+} + 1eq. Cu^{2+}

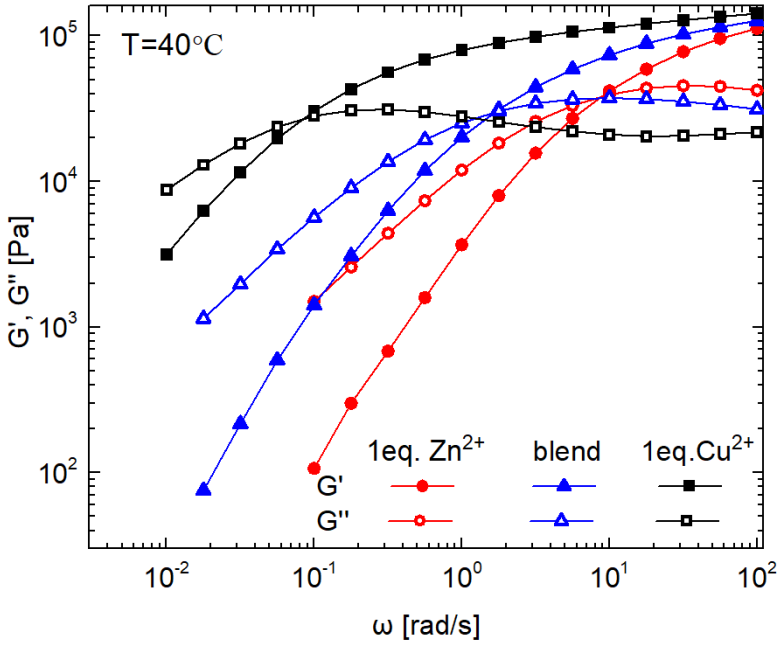


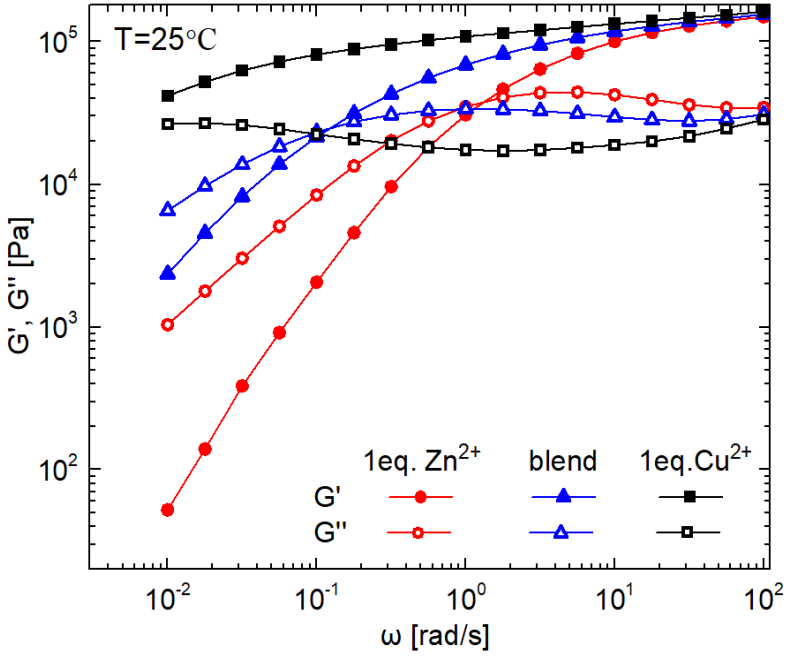
The blend shows relaxation behavior in between. No two relaxation peaks.

1eq. Zn^{2+} + 1eq. Cu^{2+}



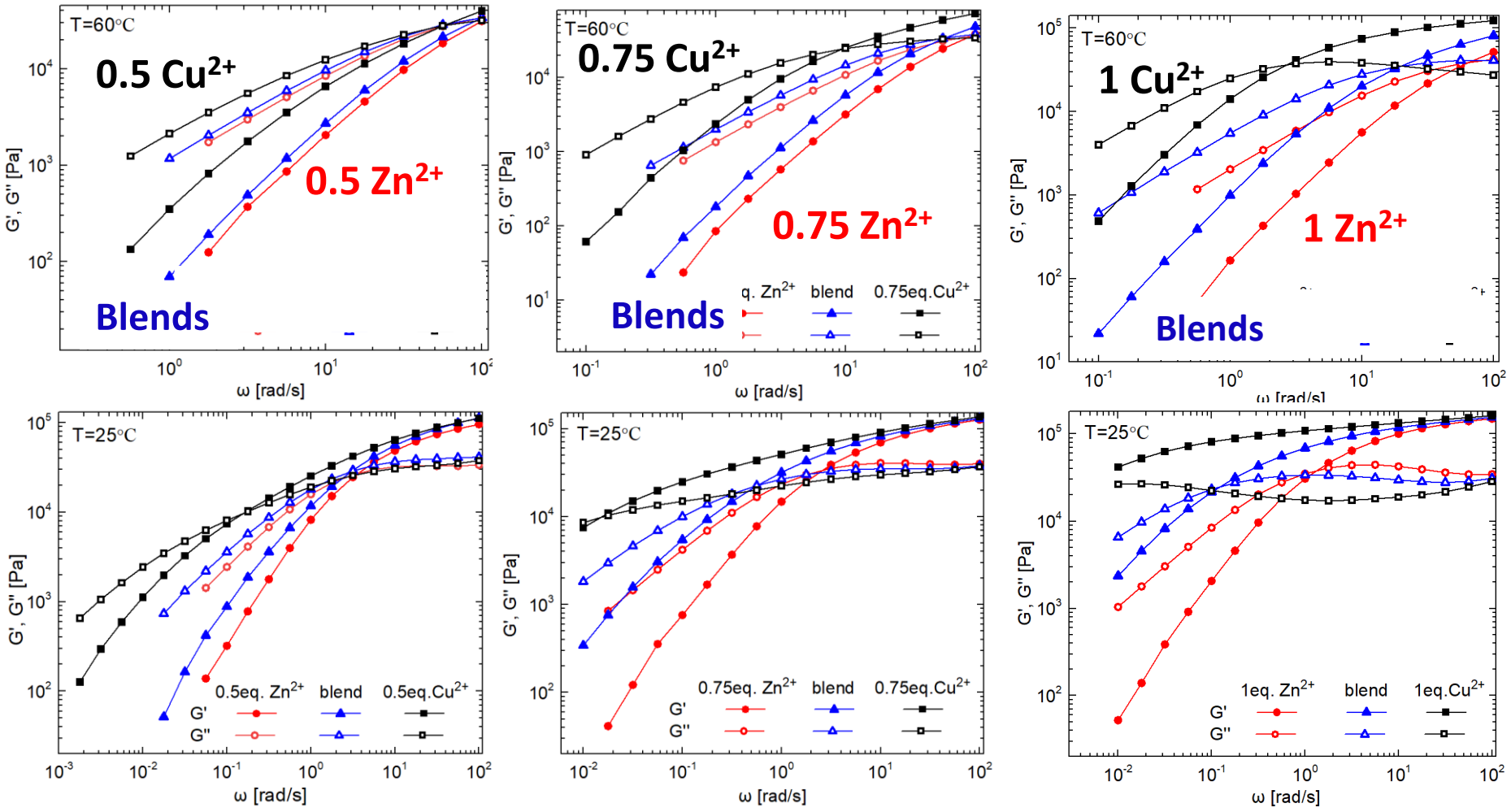






Influence of the amount of metal ions

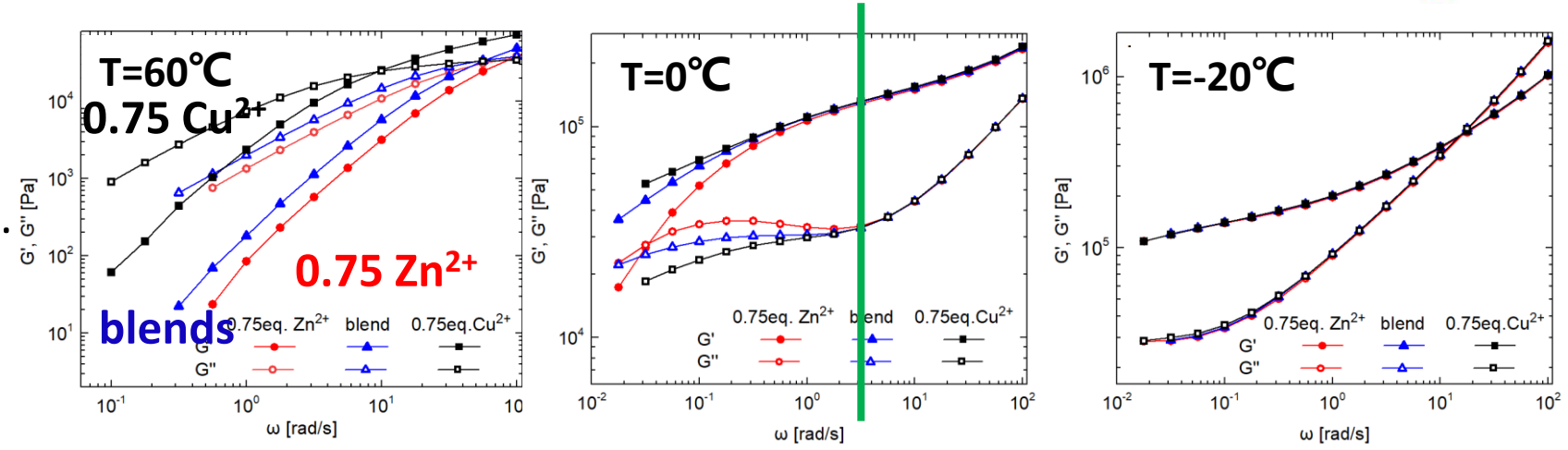
0.5eq. **0.75eq.** **1eq.**



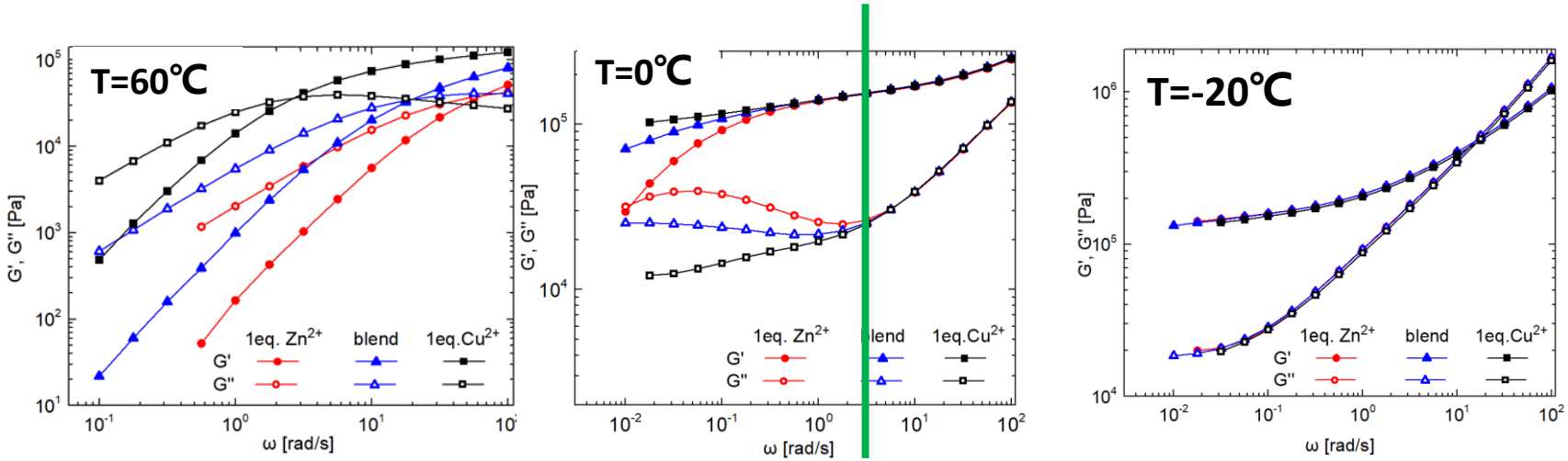
With the increasing amount of metal ions, the relaxation behavior of the blends shifts to Cu^{2+}, and close to the middle.

Influence of the temperature

0.75eq.

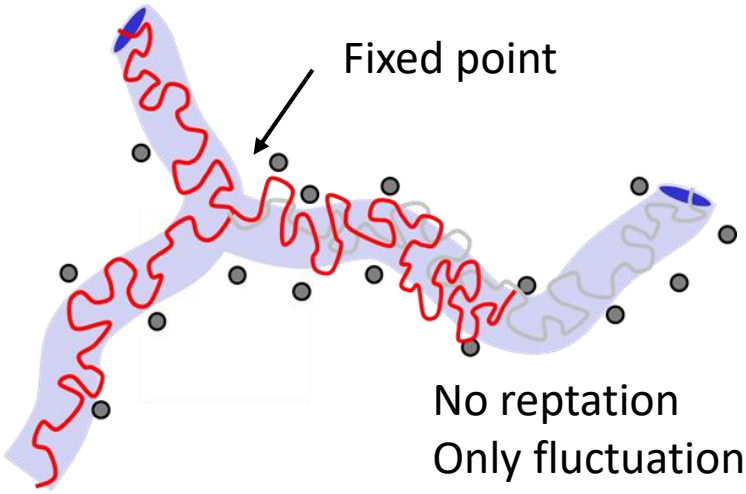


1eq.



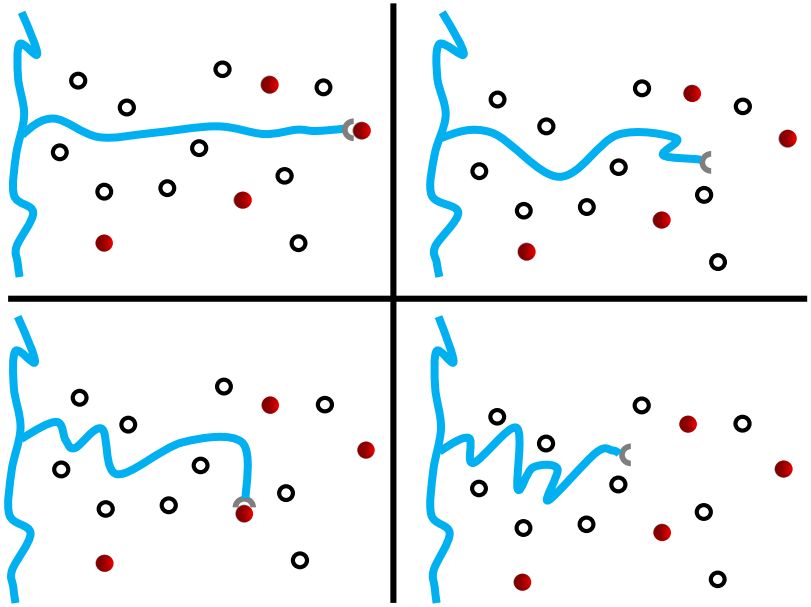
The sticker dynamics at 0℃ is visible, starting at a certain frequency(around 3rad/s)
At -20℃, the dynamics of stickers are frozen.

Modelling



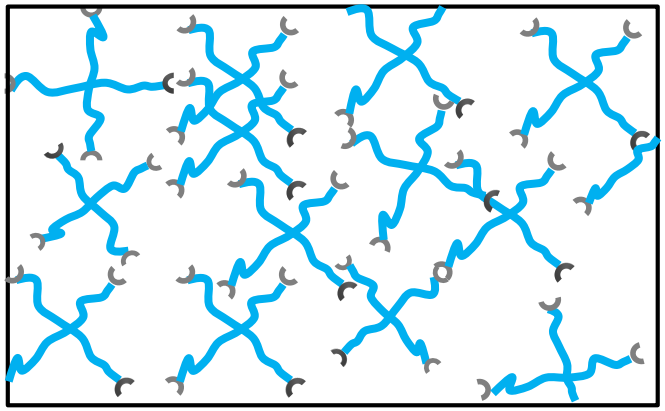
$$P(x,t) = \exp\left(\frac{-t}{\tau_{fluc}(x)}\right)$$

$$P(x,t) = \exp\left(\frac{-pfree\ t}{\tau_{fluc}(x)}\right)$$



- p_{free}, average probability for a sticker to be free
- $p_{dangling}$, the proportion of arms which do not participate at all to the network

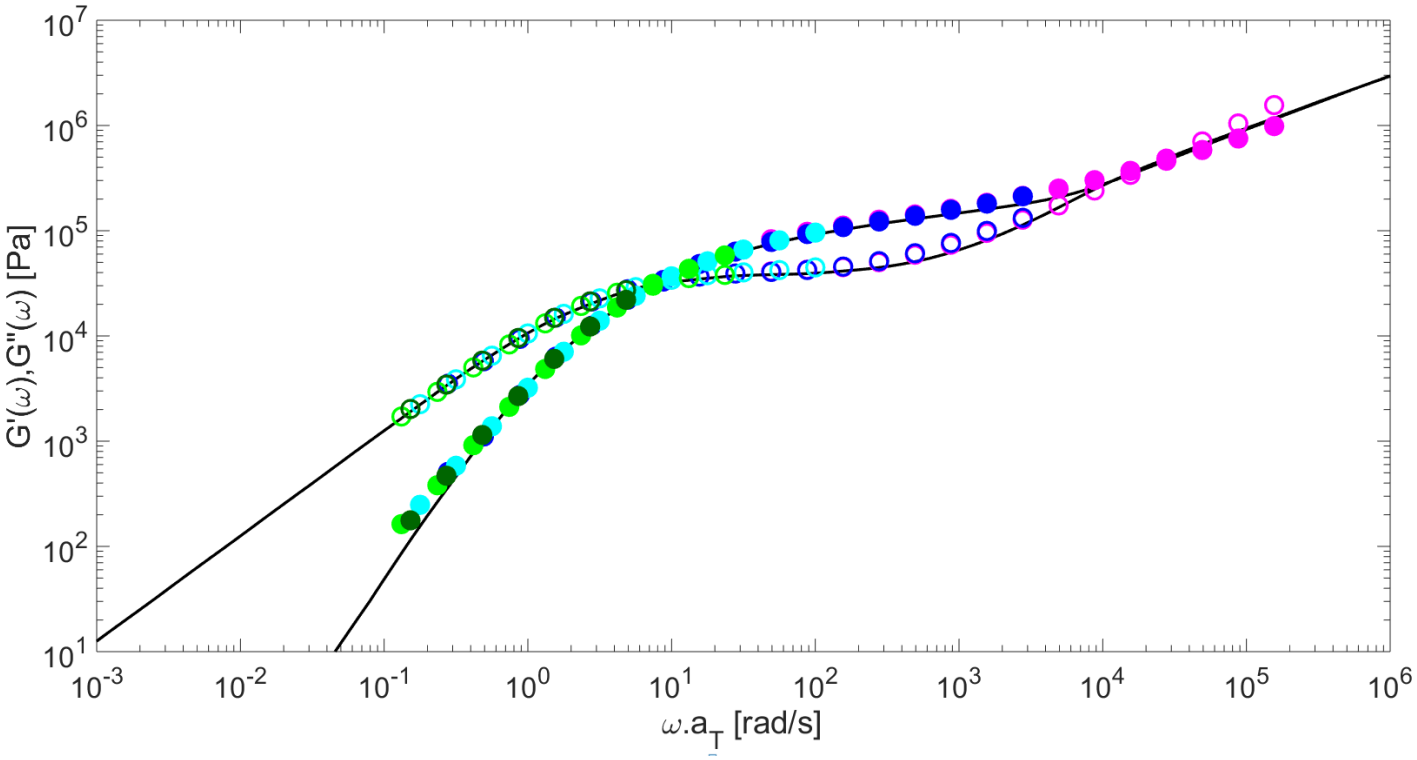
Reference sample



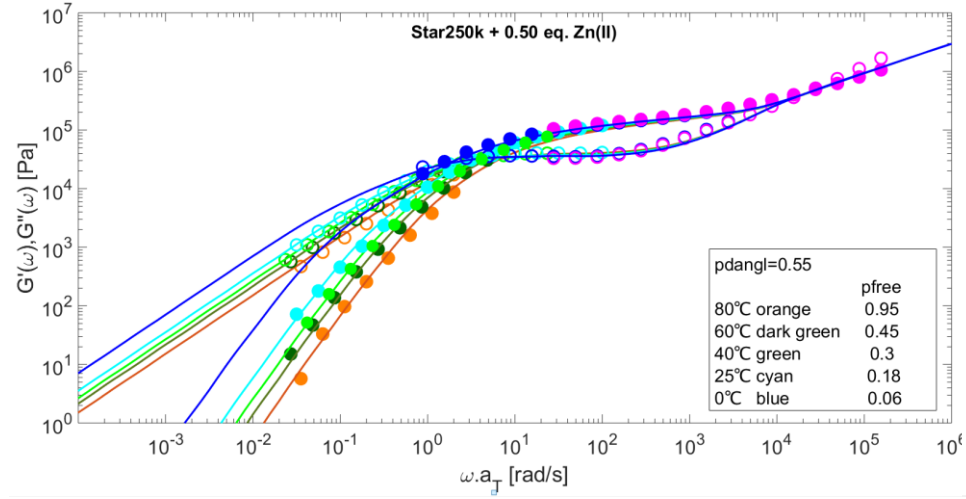
$$P(x,t)=\exp\left(\frac{-pfree\ t}{\tau_{fluc}(x)}\right)$$

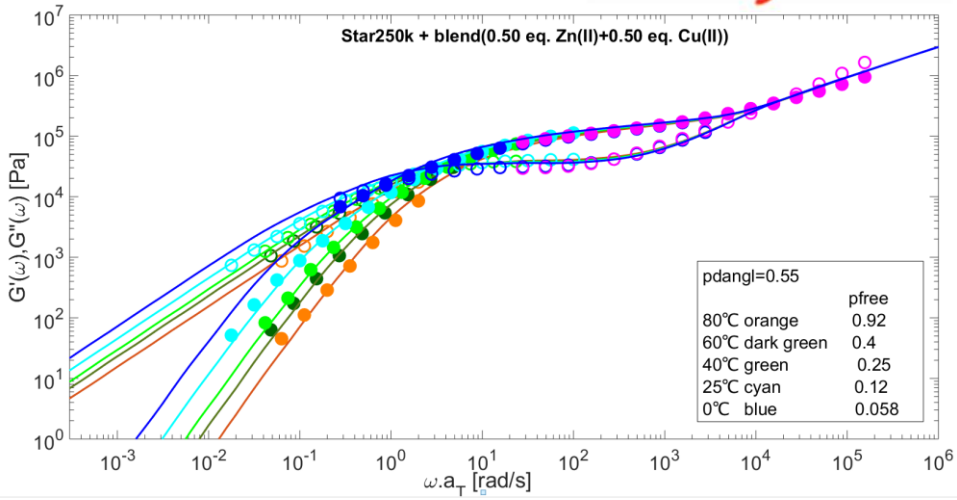
p_{free}=1

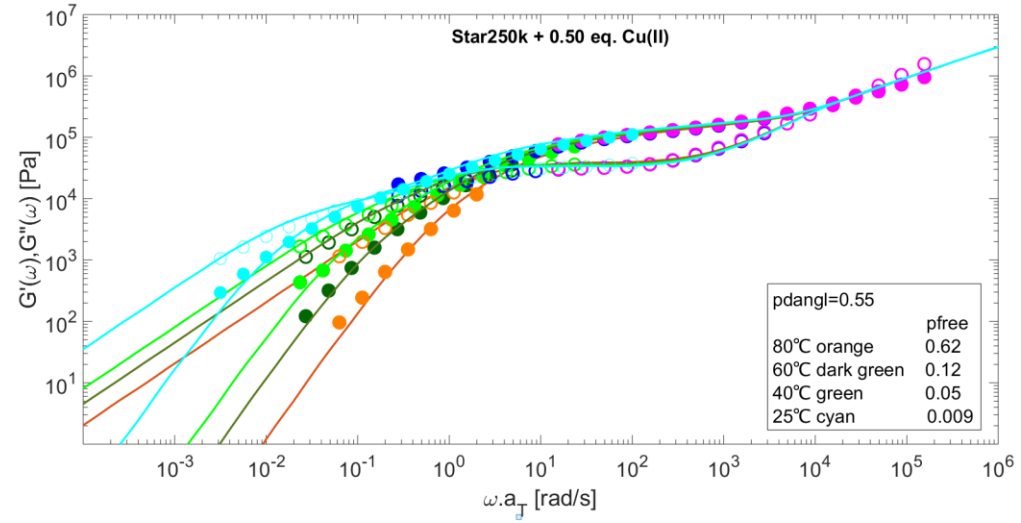
$p_{danging}$=1

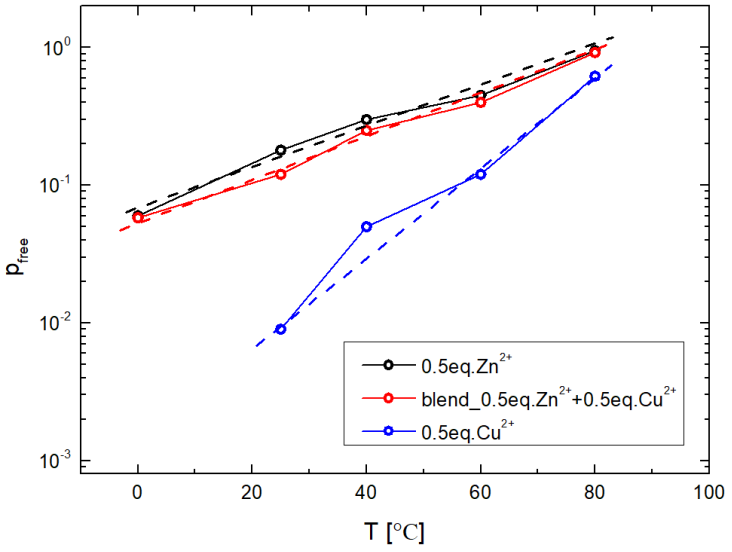


0.5eq. Zn^{2+} + 0.5eq. Cu^{2+}









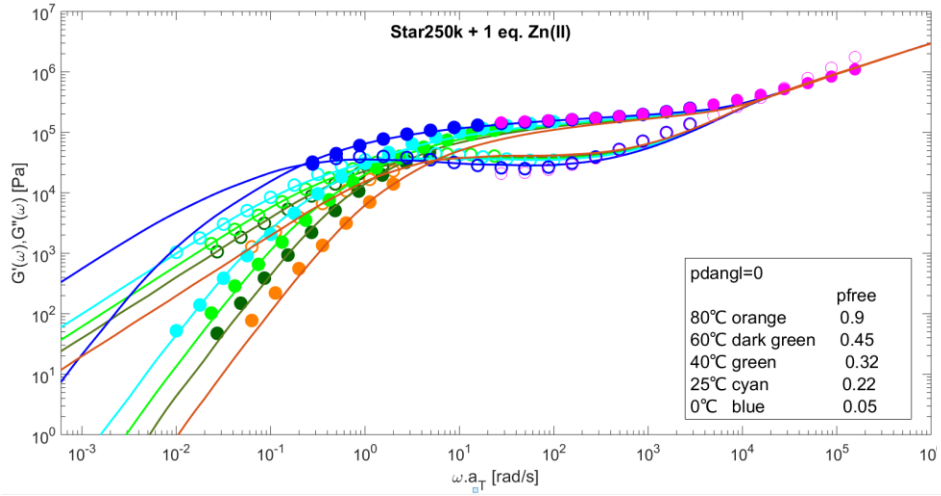
Shift factors: taken from the reference sample

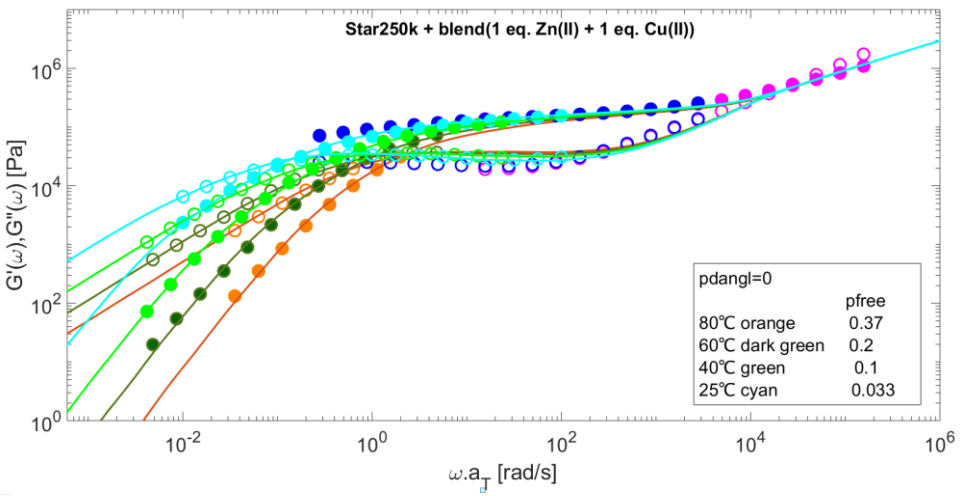
The Metal-ligand act as extra friction point

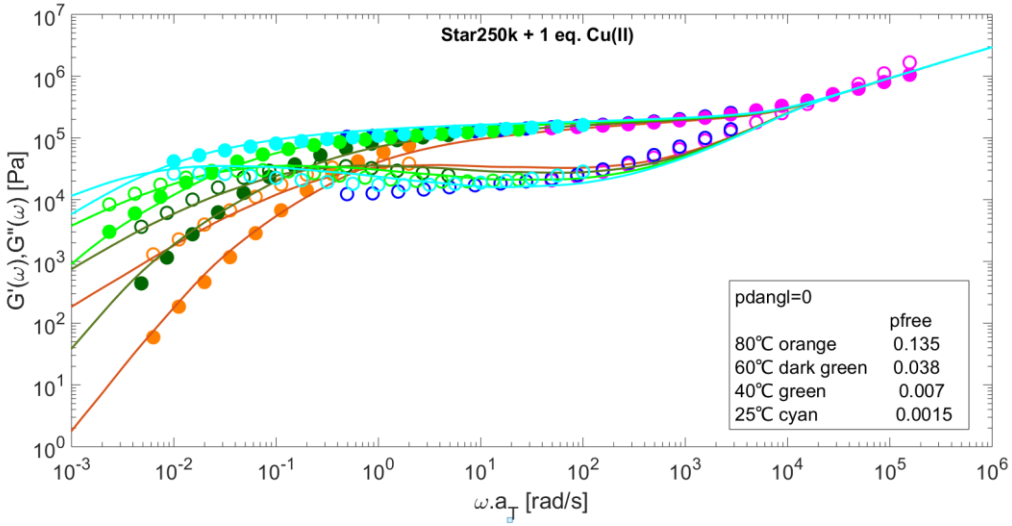
Overall delay of the star relaxation

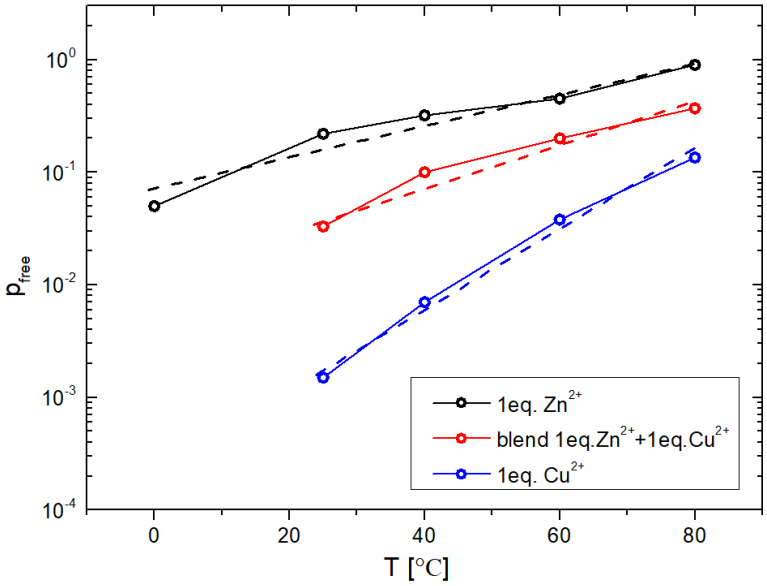
Arrhenius dependence of p_{free} on T

1eq. Zn^{2+} + 1eq. Cu^{2+}



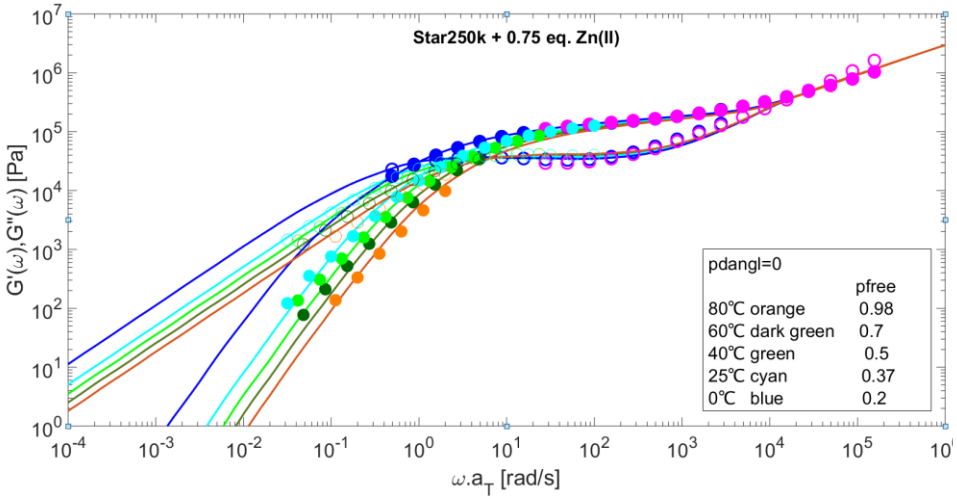


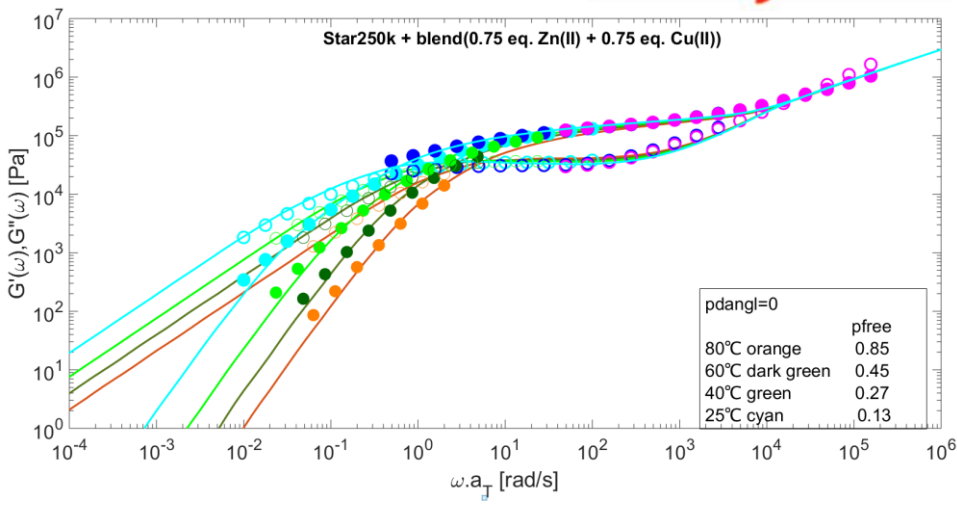


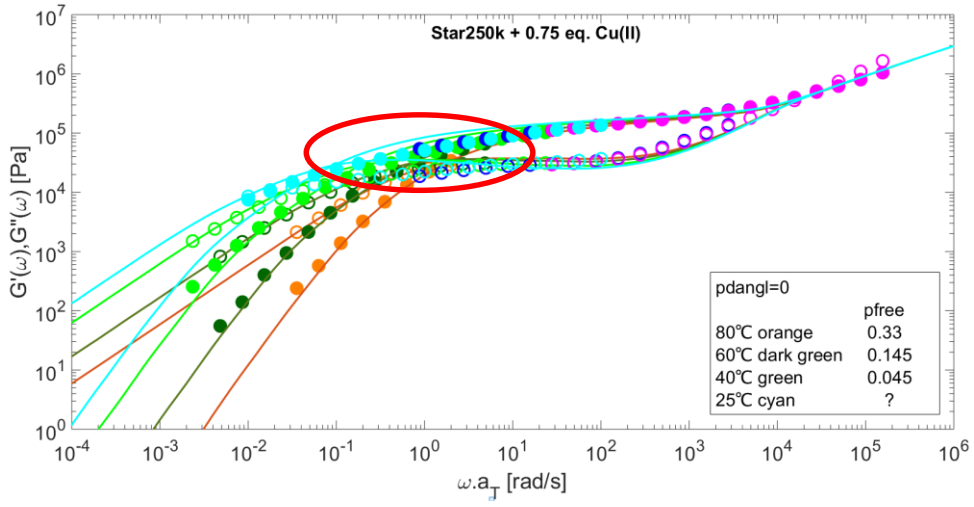


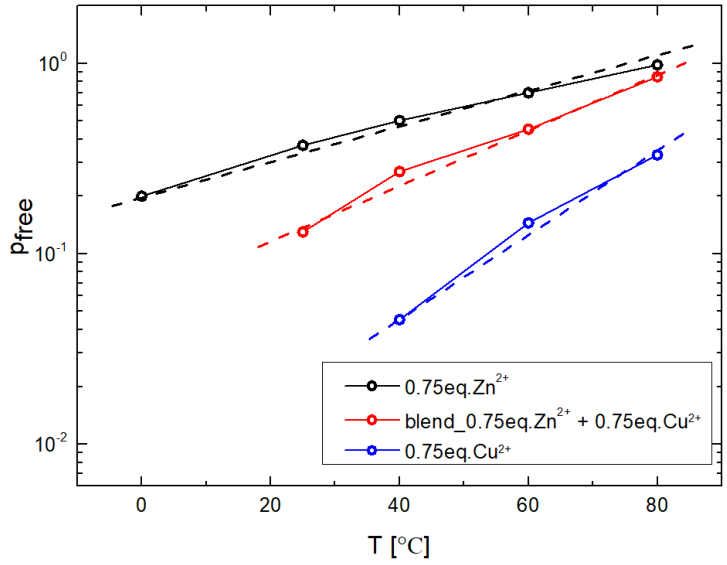
The network is completely connected. No dangling ends.

0.75eq. Zn^{2+} + 0.75eq. Cu^{2+}



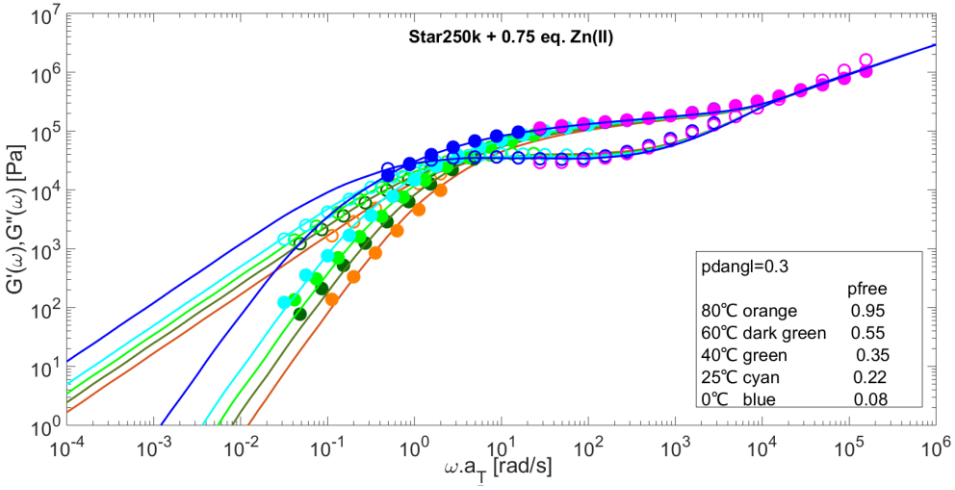


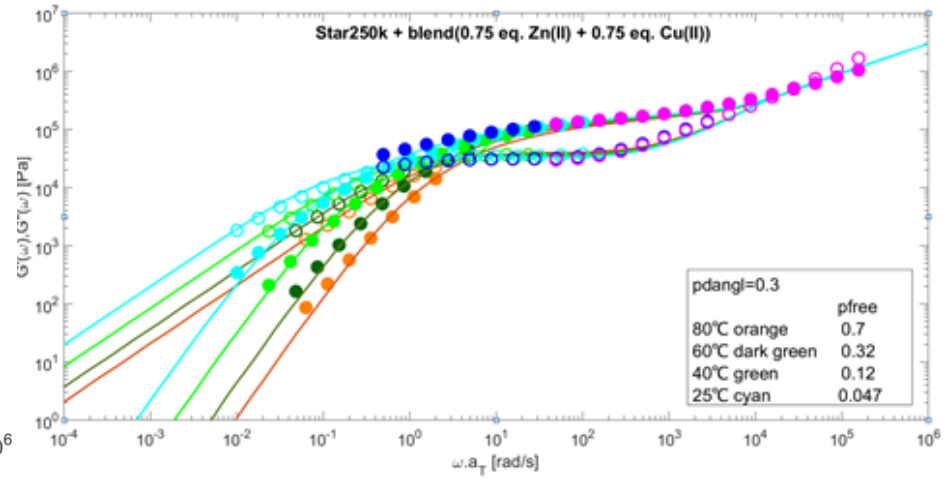


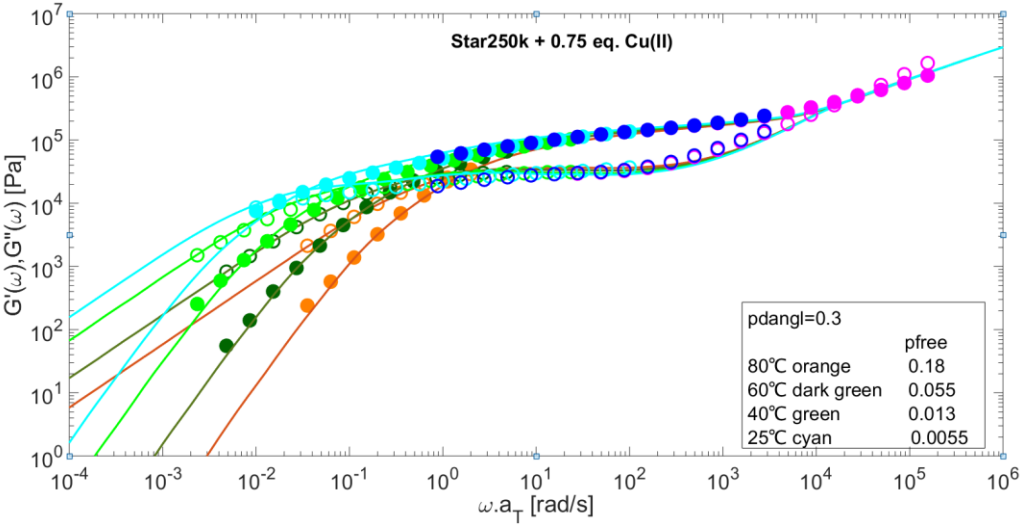


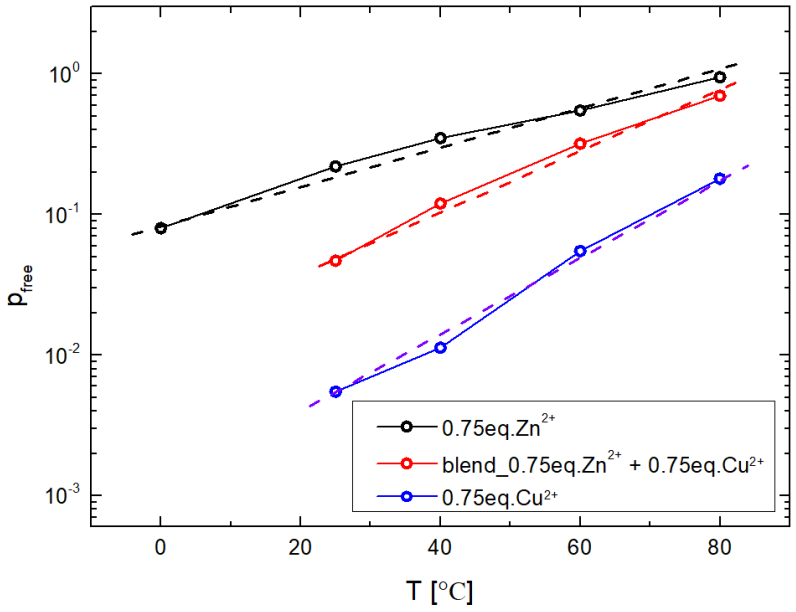
No dangling ends

0.75eq. Zn^{2+} + 0.75eq. Cu^{2+}









30% dangling ends

- Modelling predicts well with the experiment data, at 0.5eq., 0.75eq., and 1eq.

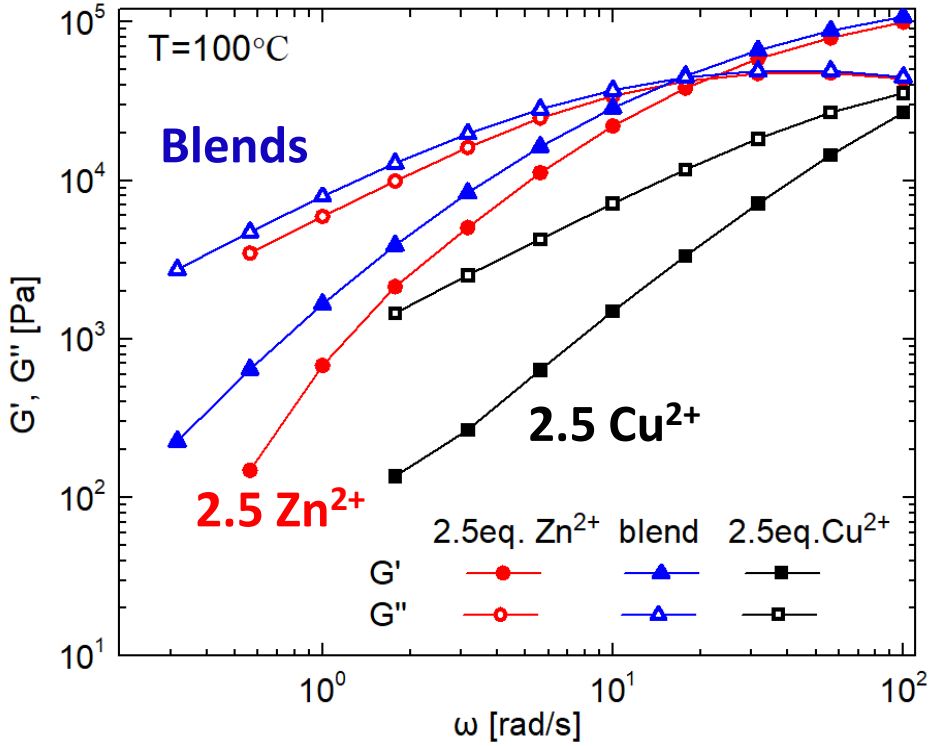
  Blends: an average lifetime for describing the stickers dynamics is found

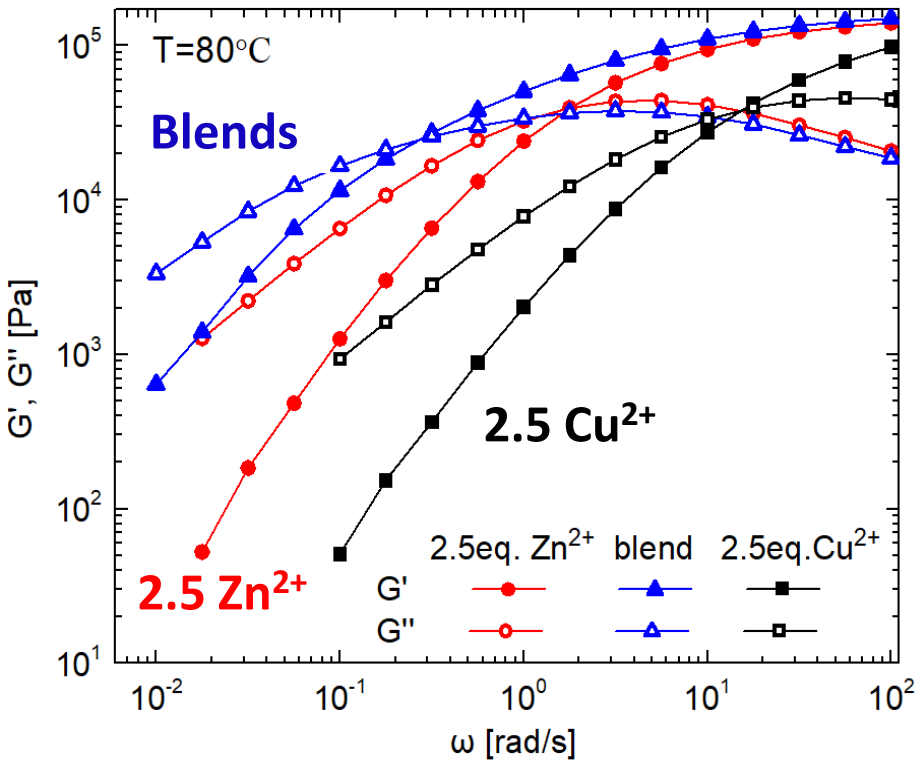
- Arrhenius dependence of p_{free} on T, the pfree(activation energy) of the blends is in between Zn^{2+} and Cu^{2+}, close to Zn^{2+} at 0.5eq., and shift close to the middle with increasing the amount of metal ions.

- At 0.5eq. and 0.75eq., for different metal ions(Zn^{2+}, Cu^{2+}, Co^{2+}), the proportion of the dangling ends?

What will happen on the relaxation dynamics with too much amount of excess metal ions?

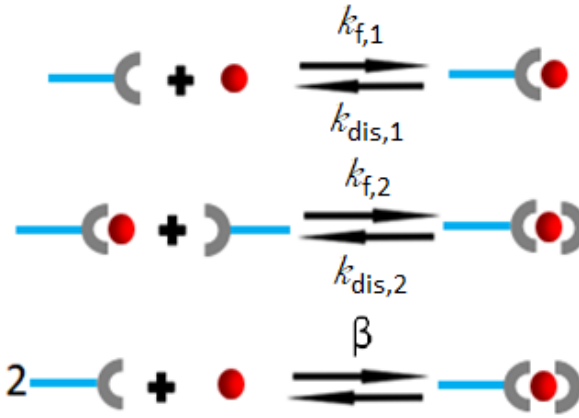
2.5eq. Zn^{2+} + 2.5eq. Cu^{2+}





The relaxation behavior of 2.5eq. Cu^{2+} becomes faster than 2.5eq. Zn^{2+}

The blend is slower than both single metal ions



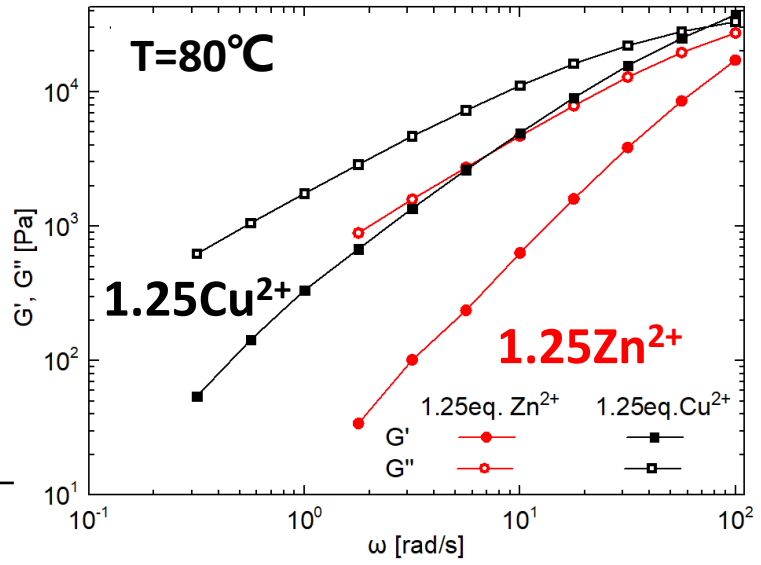
$K_1 = k_{f,1}/k_{dis,1}$

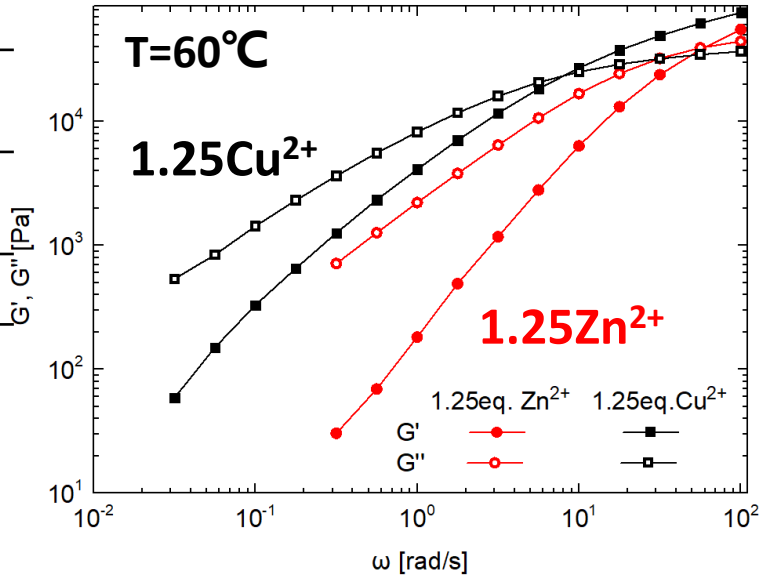
$K_2 = k_{f,2}/k_{dis,2}$

$\beta = K_1.K_2$

Ion	K_1 (M^{-1})	$k_{f,1}$ ($M^{-1}.s^{-1}$)	$k_{dis,1}$ (s^{-1})	K_2 (M^{-1})	$k_{f,2}$ ($M^{-1}.s^{-1}$)	$k_{dis,2}$ (s^{-1})	$\beta = K_1.K_2$ (M^{-2})
Co^{2+}	$10^{8.4}$	$10^{4.4}$	10^{-4}	$10^{9.9}$	$10^{6.7}$	$10^{-3.2}$	$10^{18.3}$
Cu^{2+}	10^{12}	$10^{7.3}$	-	$>10^{6}$	-	-	$>10^{18}$
Zn^{2+}	10^{6}	$10^{6.1}$	$10^{0.1}$	$10^{5.2}$	-	-	$10^{11.2}$

The formation and dissociation rate of terpyridine mono- and bis-complexes with different transition metal ions in water at 25℃

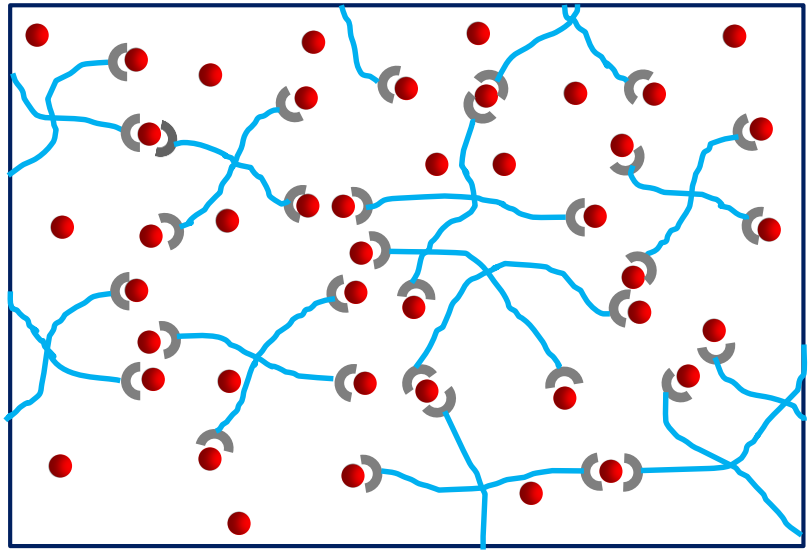




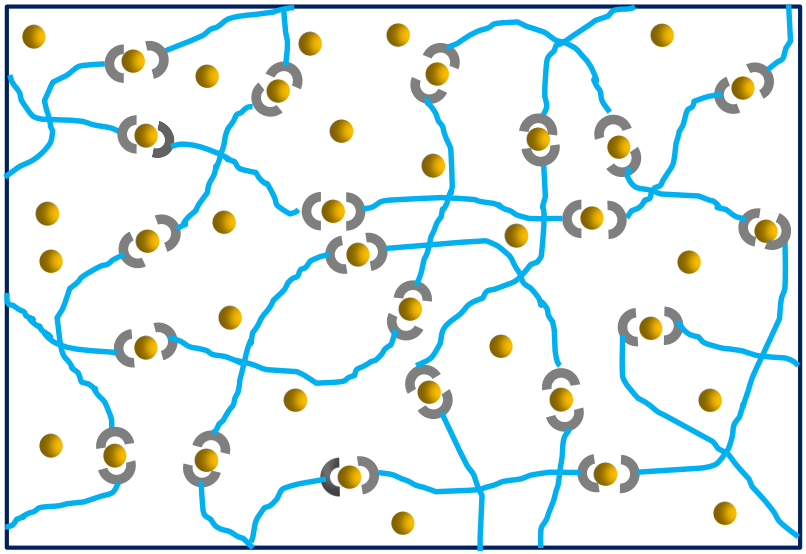
At a certain amount of metal ions, bis-complex transforms to mono-complex?

ACS Symp. Ser. 2006, 928, 43-62; Chem. 1966, 5, 622-625; Met. Chem. 1979, 4, 328-332

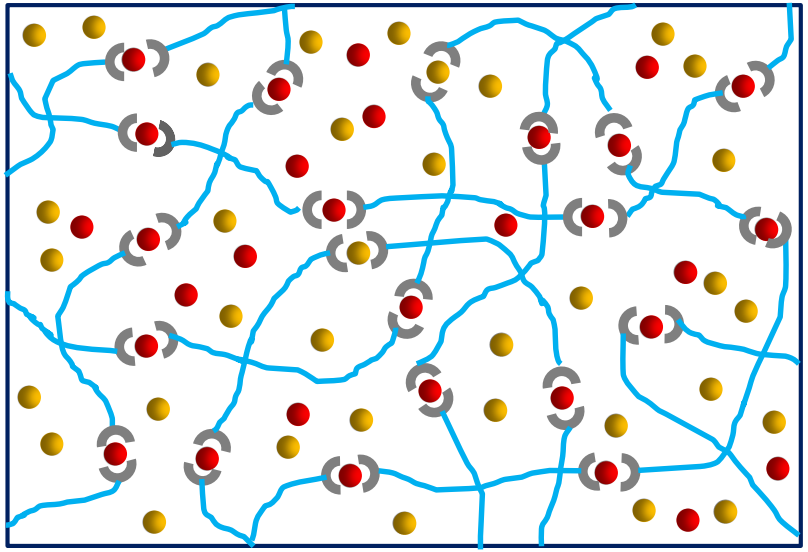
Mono-complex(2.5eq. Cu^{2+})



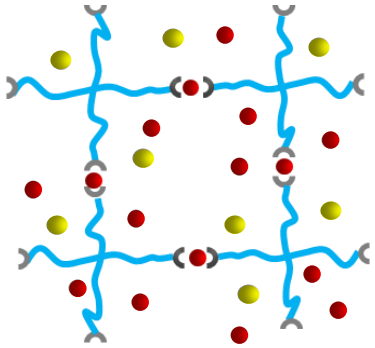
Bis-complex(2.5eq. Zn^{2+})



Blend(1.25eq. Cu^{2+} and 1.25eq. Zn^{2+})



Rebuild bis-complex



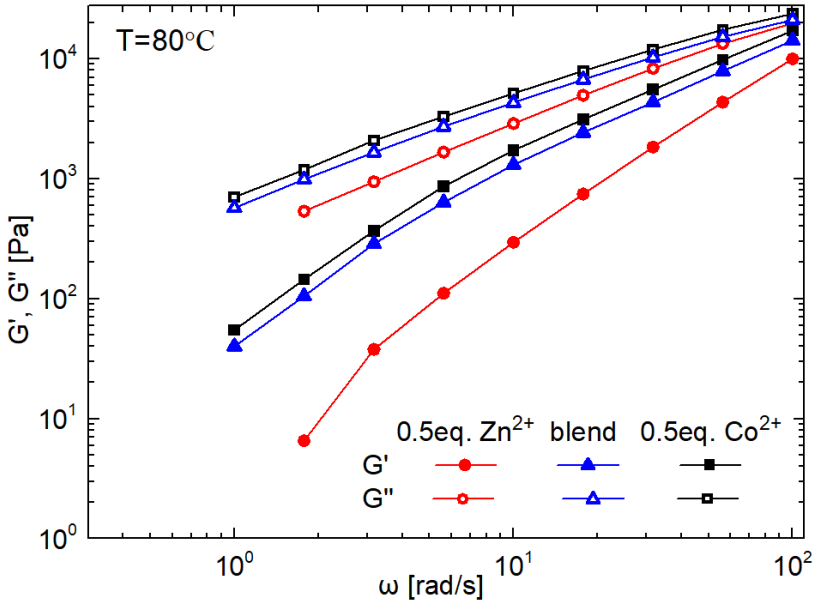
Stronger network

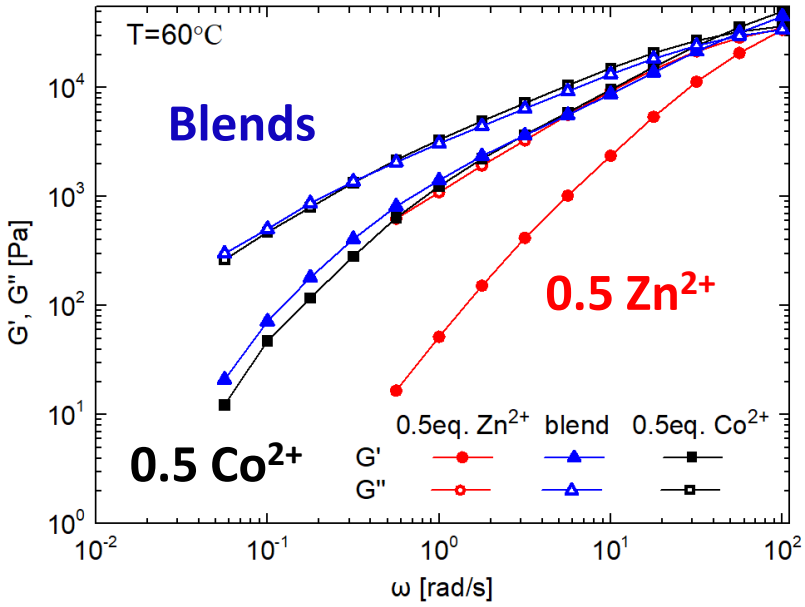
?

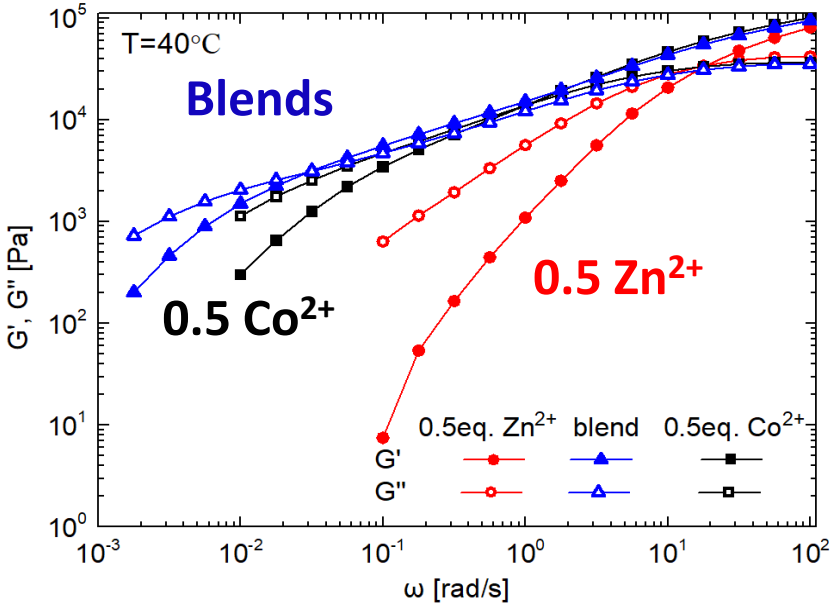
Influence of different nature of metal ions

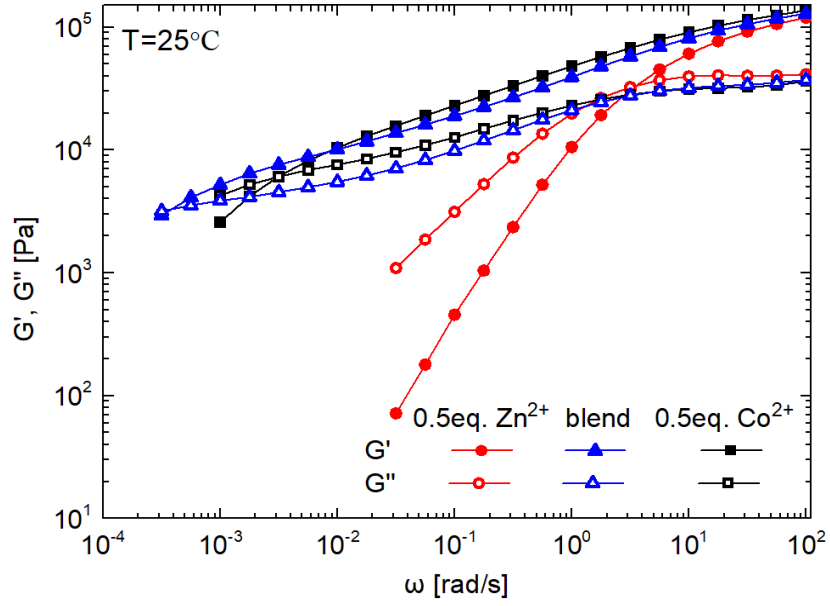
$Zn^{2+} + Co^{2+}$

0.5eq. Zn^{2+} + 0.5eq. Co^{2+}



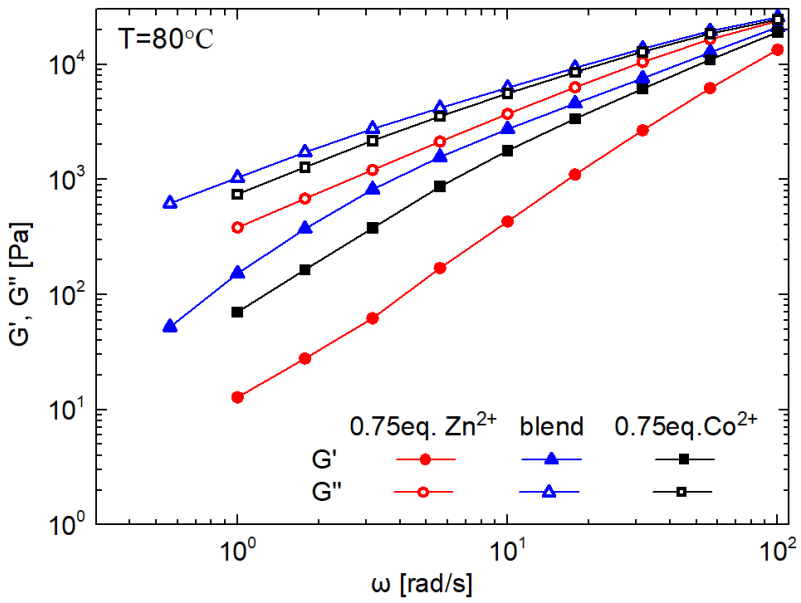


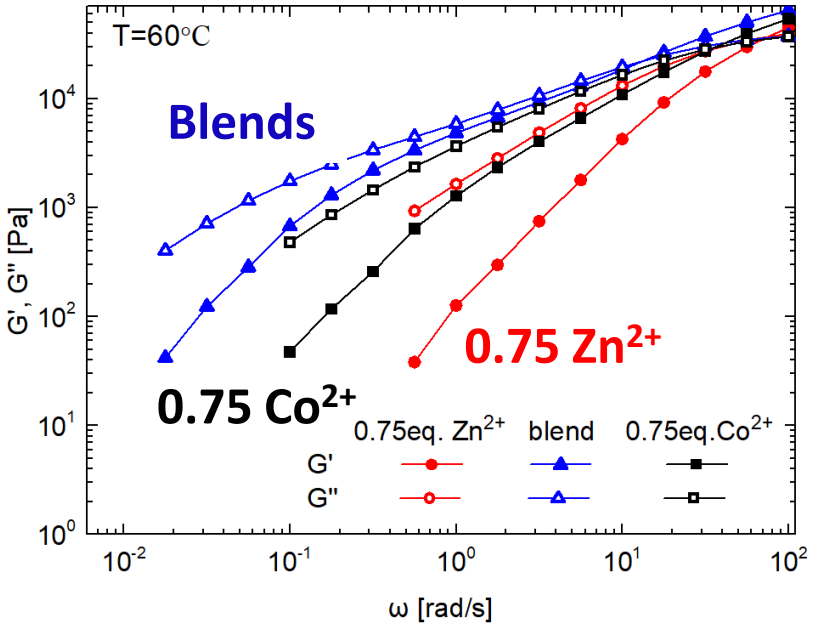


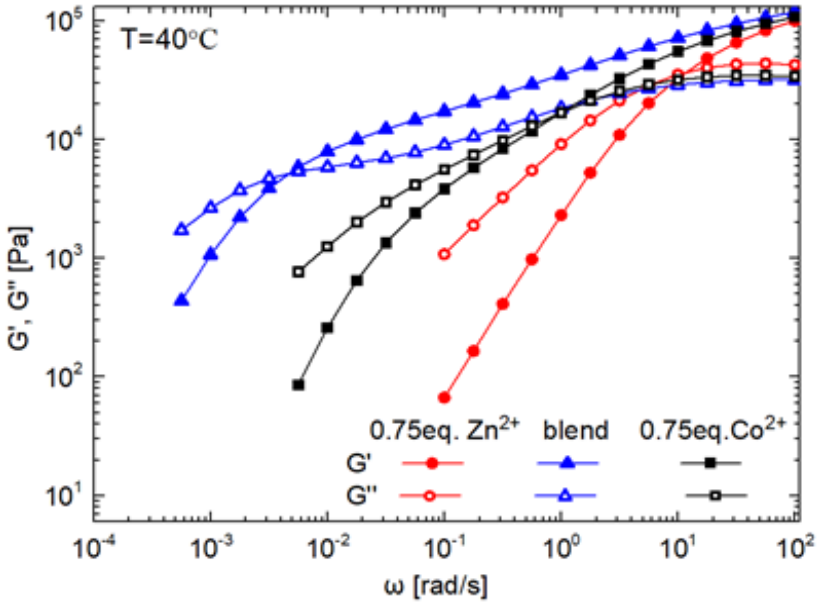


The blend shows relaxation behavior slower than both the single metal ions

0.75eq. Zn^{2+} + 0.75eq. Co^{2+}

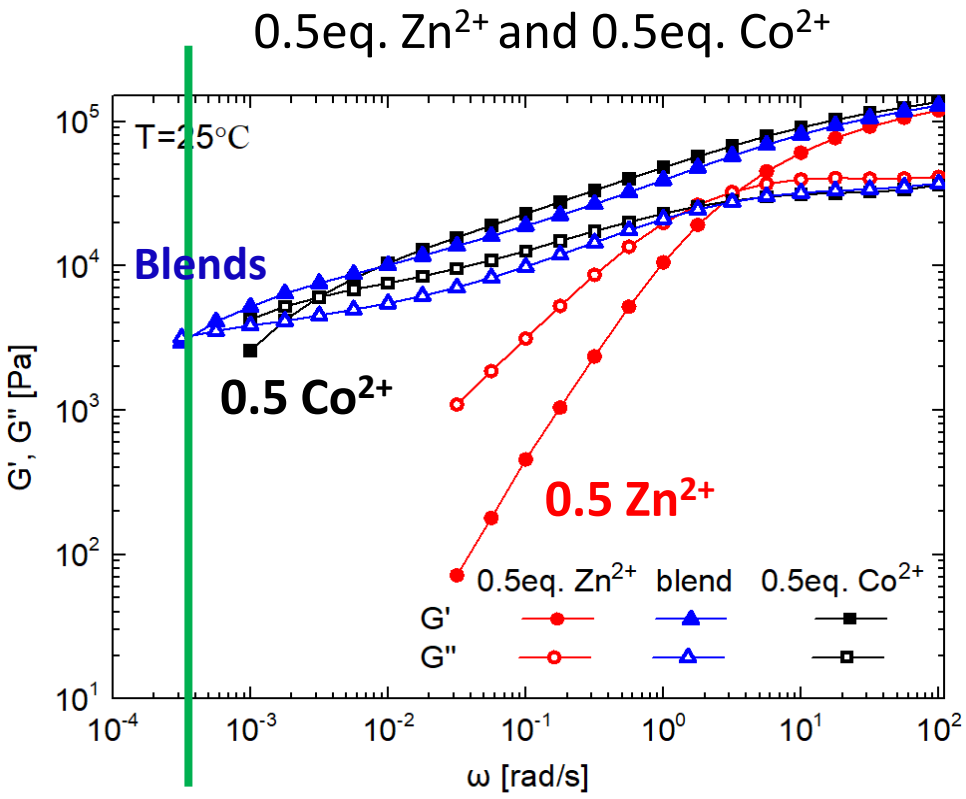


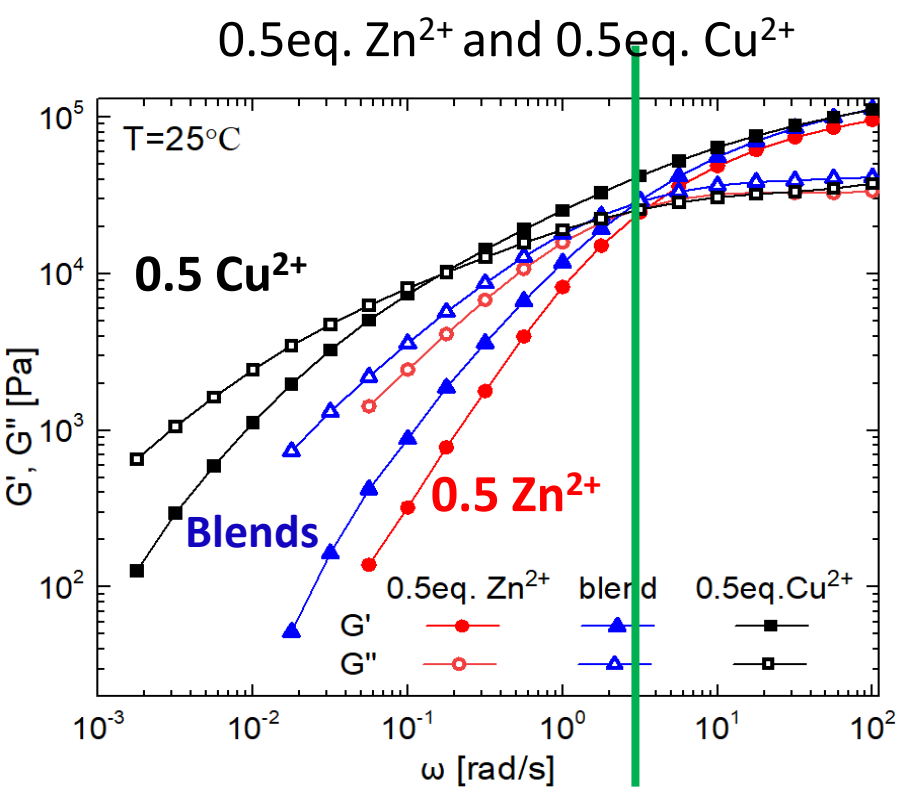




With increasing the amount of metal ions, at 80℃, the blend starts to relax slower than two single metal ions

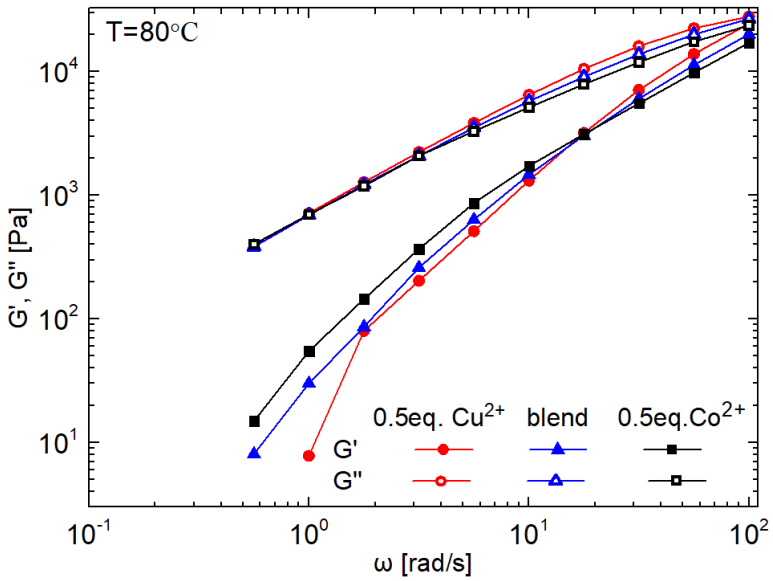
→ ?

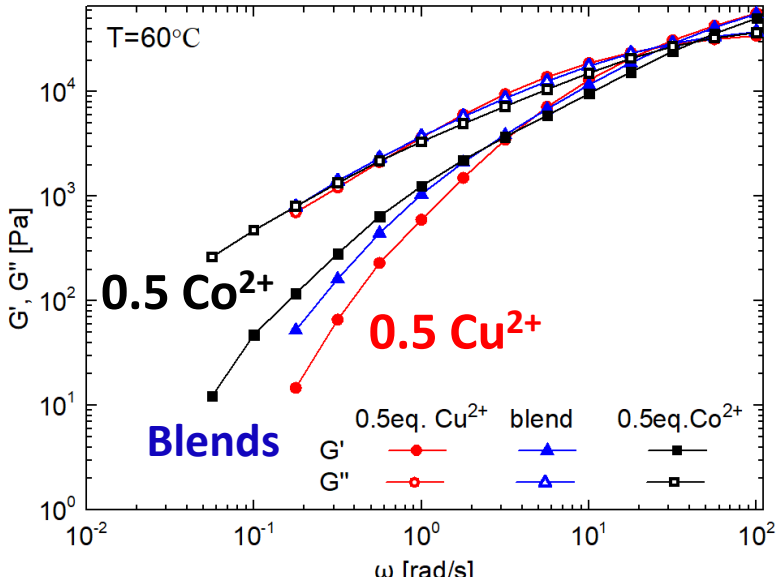


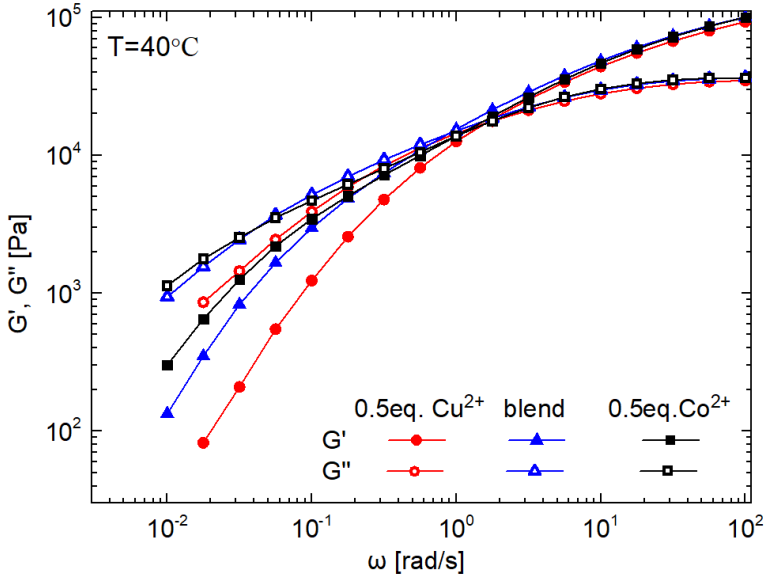


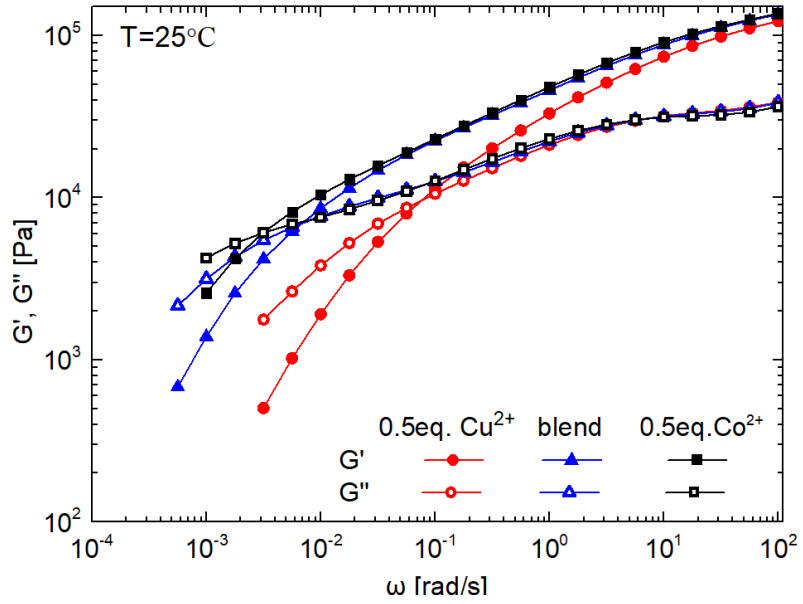
How about 0.5eq. Cu^{2+} + 0.5eq. Co^{2+} ?

0.5eq. Cu^{2+} + 0.5eq. Co^{2+}



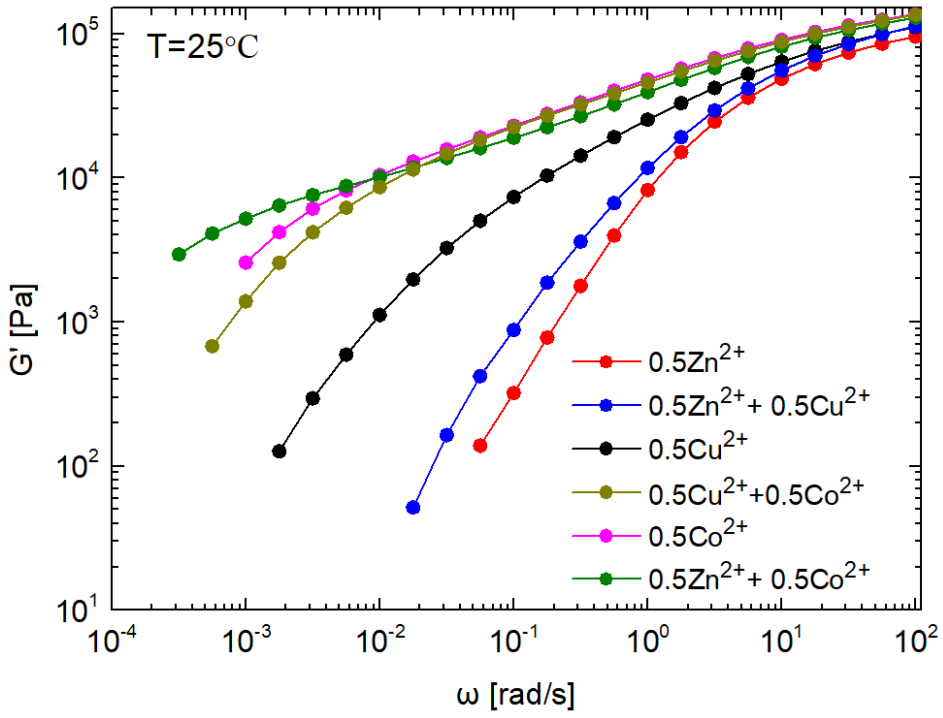


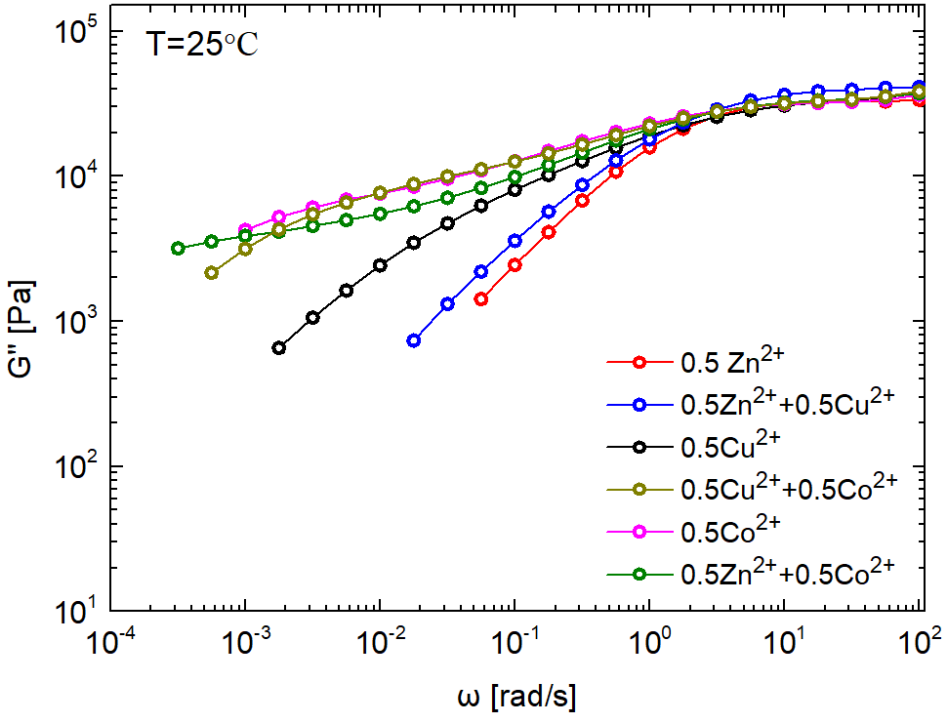




In between, close to the Co^{2+}, stronger one

0.5eq. Zn^{2+} , Cu^{2+} , Co^{2+} and blends



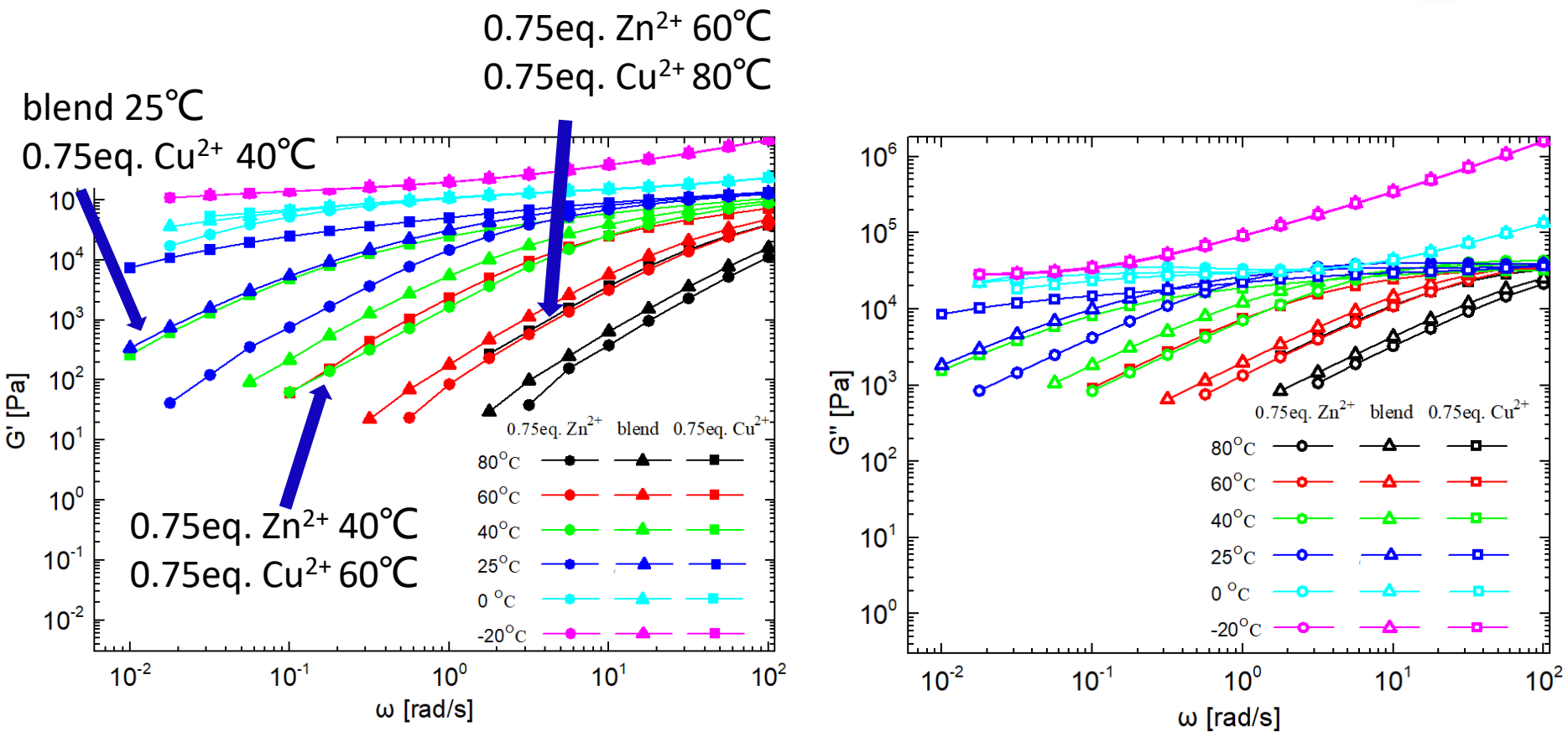


A large range of relaxation dynamics

The interaction of the nature of metal ions?

(the dangling ends, mono- and bis-complex as well as the bonding energy)

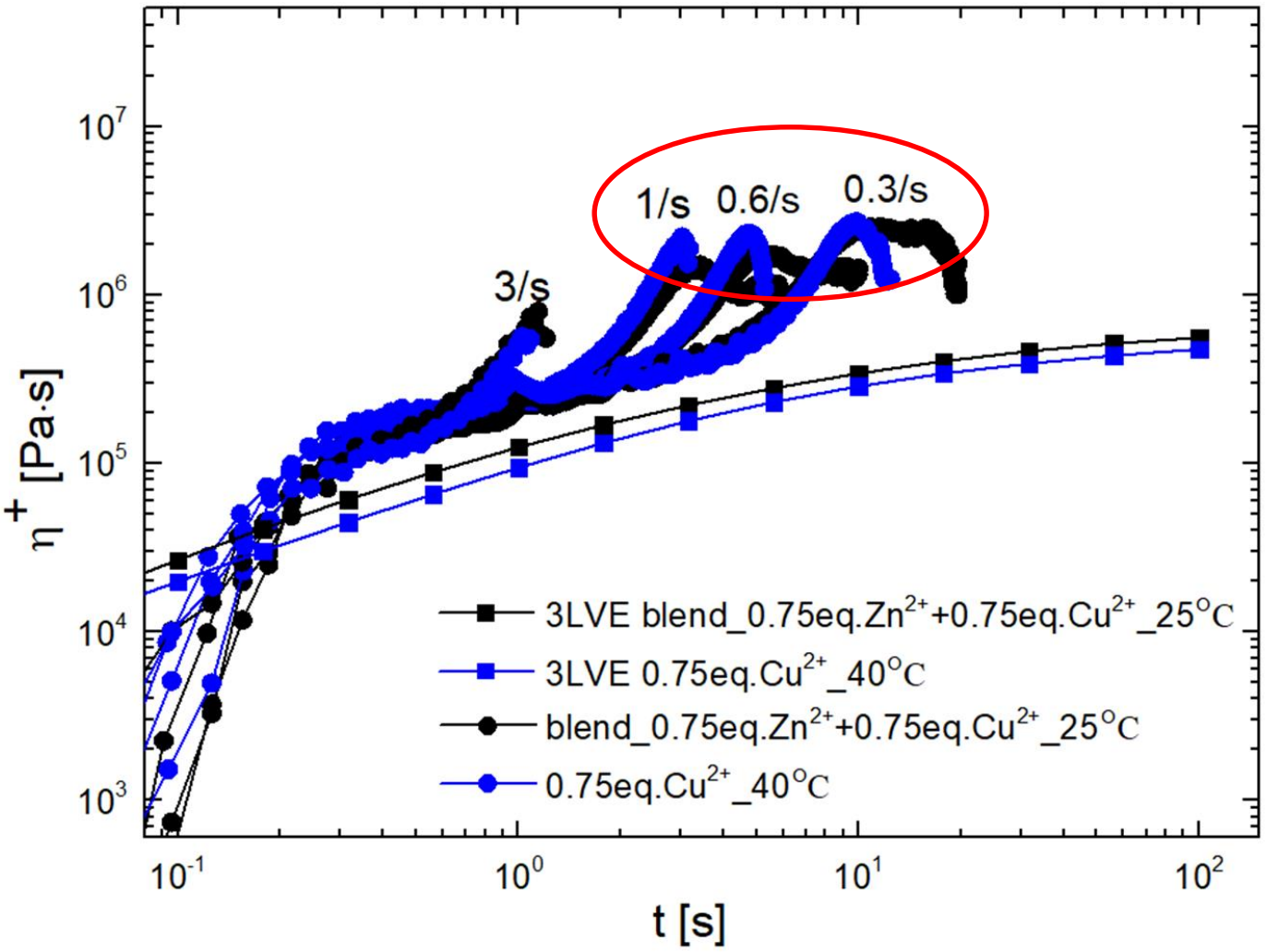
0.75eq. Zn^{2+} + 0.75eq. Cu^{2+}



The slowest one at temperature of 60℃ and 80℃ is more close to the fastest one at a lower contiguous temperature. At 40 ℃, the slowest one is close to the intermediate one at 25℃.

Elongation properties of these blends?

blend at 25℃ and 0.75eq. Cu^{2+} at 40℃



- The gap between the 3LVE and the elongation data?
- The different behavior after strain hardening?

Conclusions and Perspectives

- Blending two metal-ligand crosslinks with distinct relaxation mode in telechelic star polymers leads to a tunable and interesting associating system. Its relaxation dynamics depends on the nature of two metal ions, amount of metal ions and temperature, etc.
- The established model is based on two unknown parameters. Pfree of the blends based on Zn^{2+} and Cu^{2+} shows an Arrhenius dependence on T, in between of the two single metal ions.
- We should use other techniques to analyze the interaction of Zn^{2+}, Cu^{2+} and Co^{2+}, and try to elucidate relaxation dynamics of the blend of Zn^{2+} and Co^{2+}.
- The first elongation data on these samples seems interesting.

Double **Dy**namics for design of new responsive polymer **net**works and gels

Thank you for your attention.

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