# Synthesis and dynamics of double networks based on metal-ligand crosslinks and imine-aldehyde exchange

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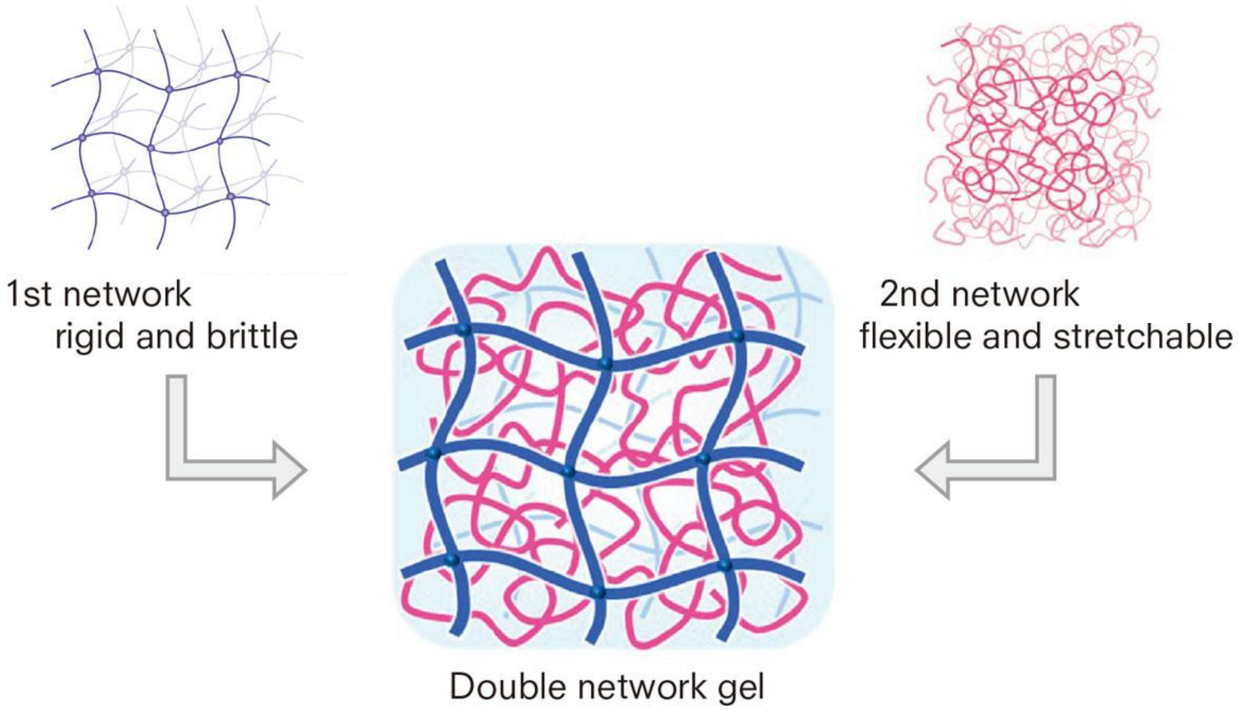
# Introduction – Double Networks

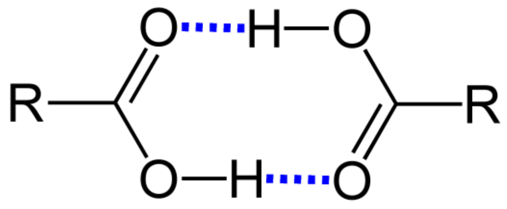
- Made of two interpenetrating networks with different physical properties
- When combined, they create a material with the advantages of both networks



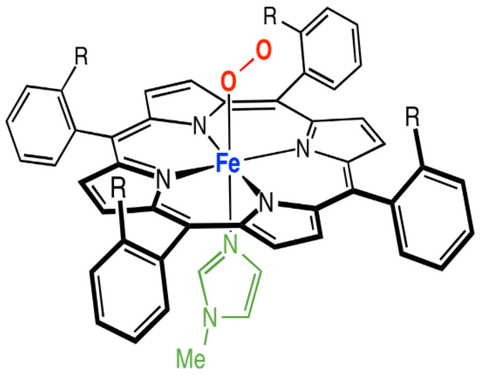
# Introduction – Dynamic Networks

Reversible bonds give materials properties which are tunable by external stimuli

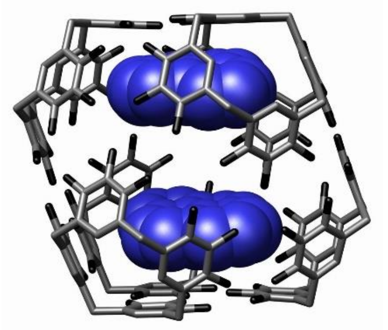
Hydrogen bonding




Metal Ligand Coordination

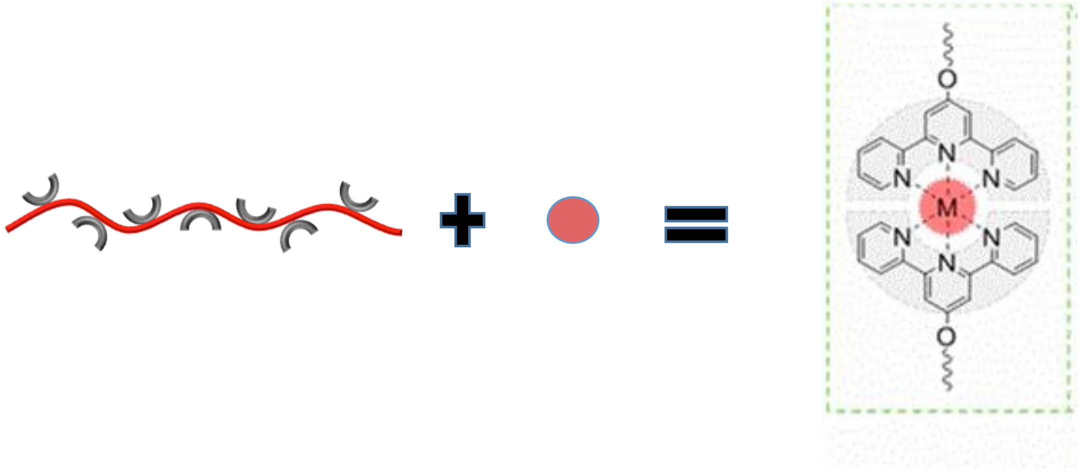


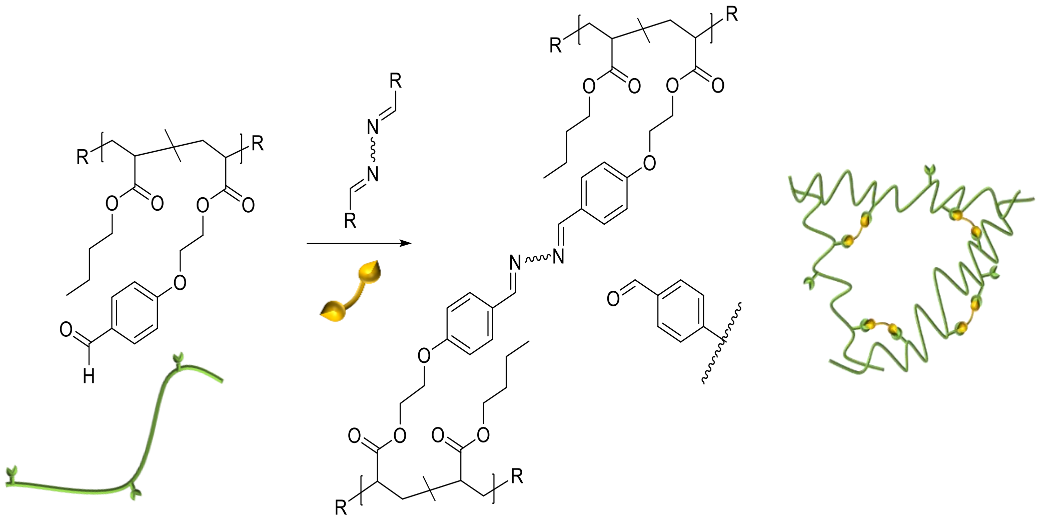

Host-Guest Chemistry



# Synthesis of double dynamic network

**In the melt state**




First network – Reversible metal-terpyridine links

Unentangled PnBA

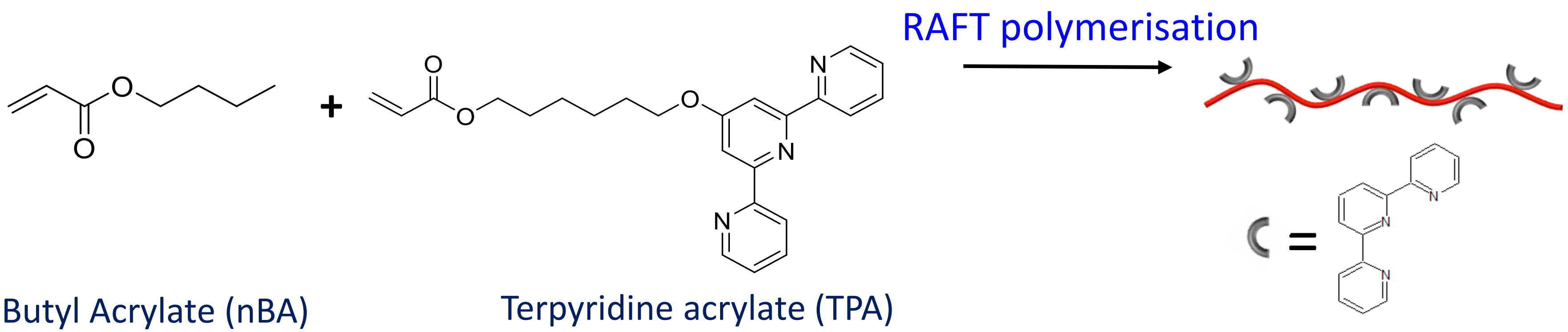
Mxx = 5 000g/mol

Second network – Imine-Aldehyde reversible covalent bonds

Entangled PnBA

Mxx = 50 000g/mol

# Network 1 – Unentangled Metallo-supramolecular Network

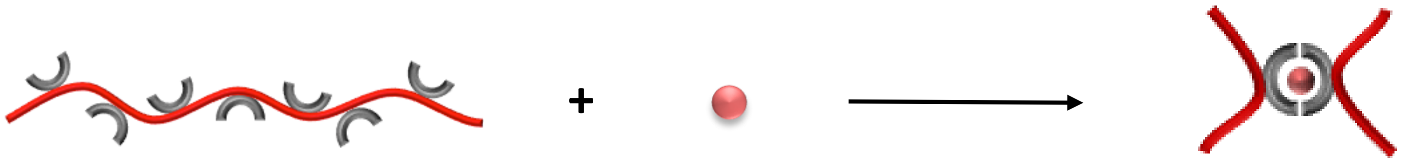



n-Butyl Acrylate (nBA)

Terpyridine acrylate (TPA)

pNBA-co-TPA

Mn = 27kg/mol
7 terpyridine/chain

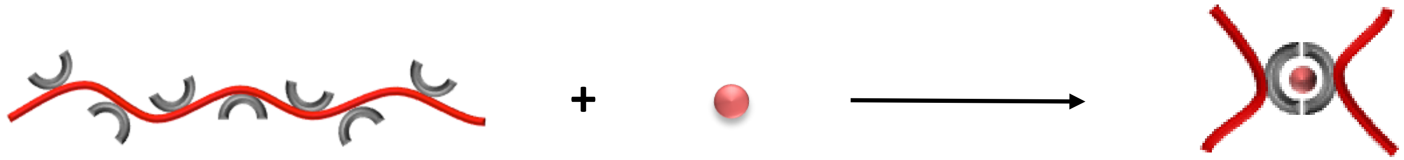


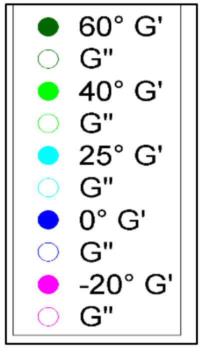
pNBA-co-TPA

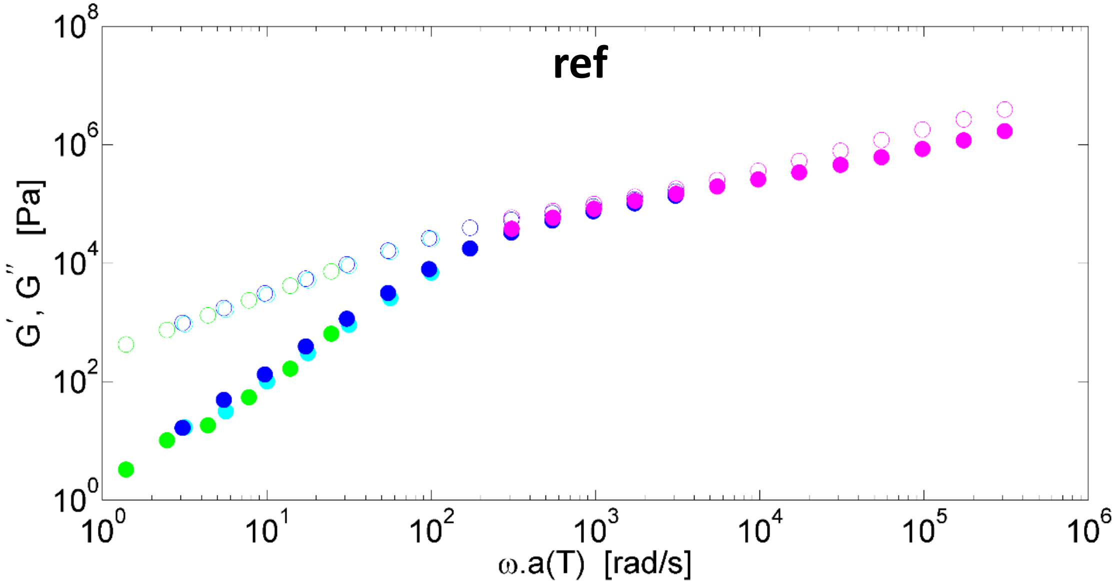
Metal Ions

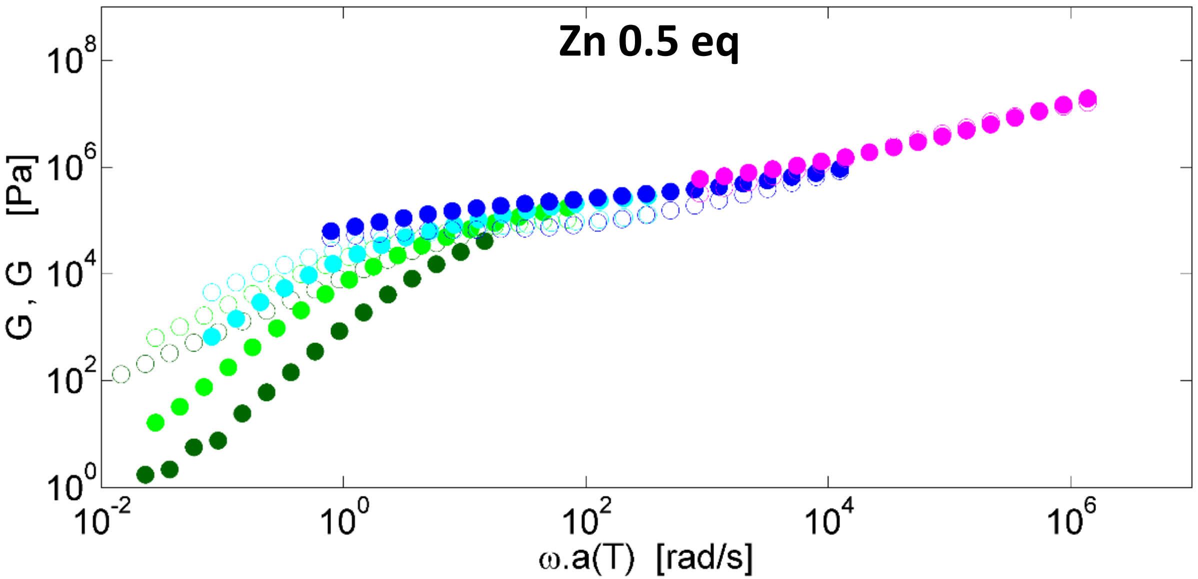
Metallo-supramolecular Network

# Network 1 - Effect of Amount of $Zn^{2+}$ crosslinker






- Thermorheological complexity - Using the shift factors for pure PnBA does not work when the polymer is complexed with Zn
- The lifetime of associating bonds is strongly temperature dependent

# Network 2 - Imine-Aldehyde Exchange

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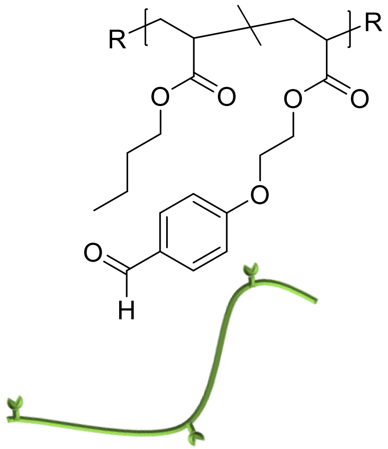
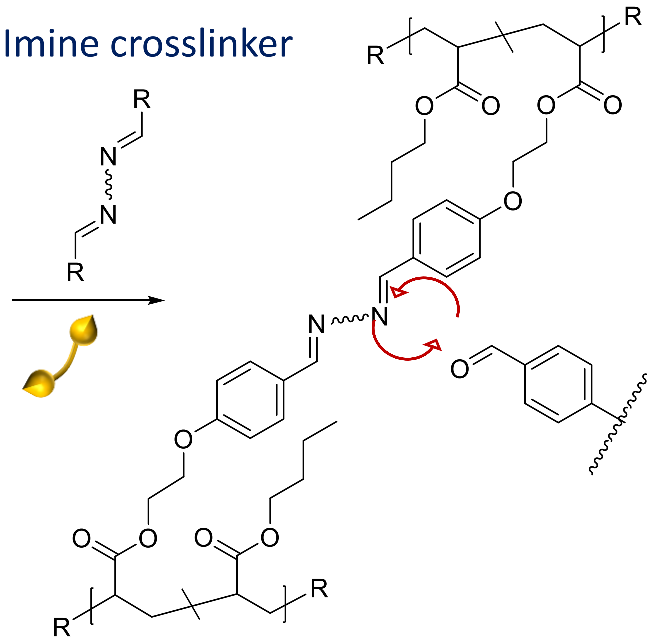
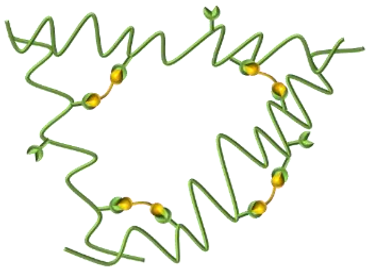
*ESPCI Paris*

n-Butyl Acrylate (nBA)



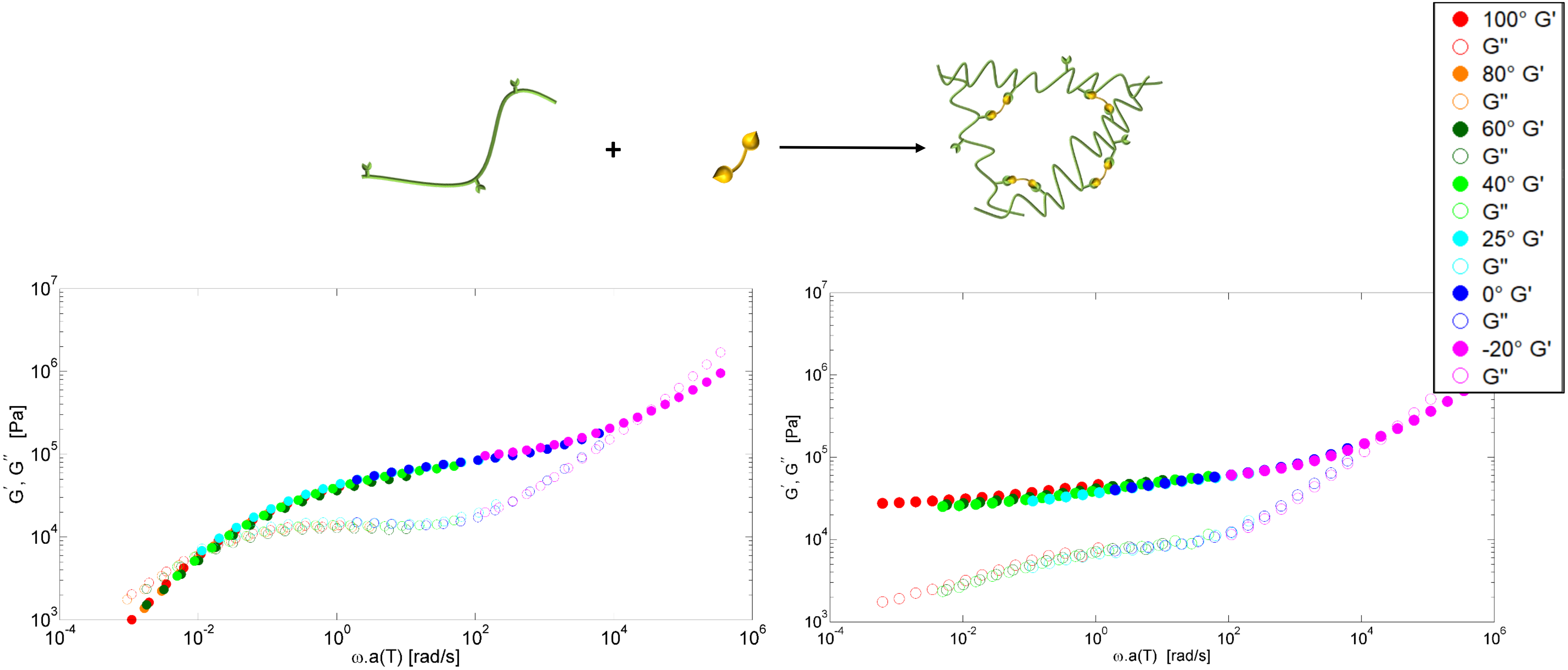
Imine crosslinker





Mn = 473kg/mol
9 crosslinks per chain

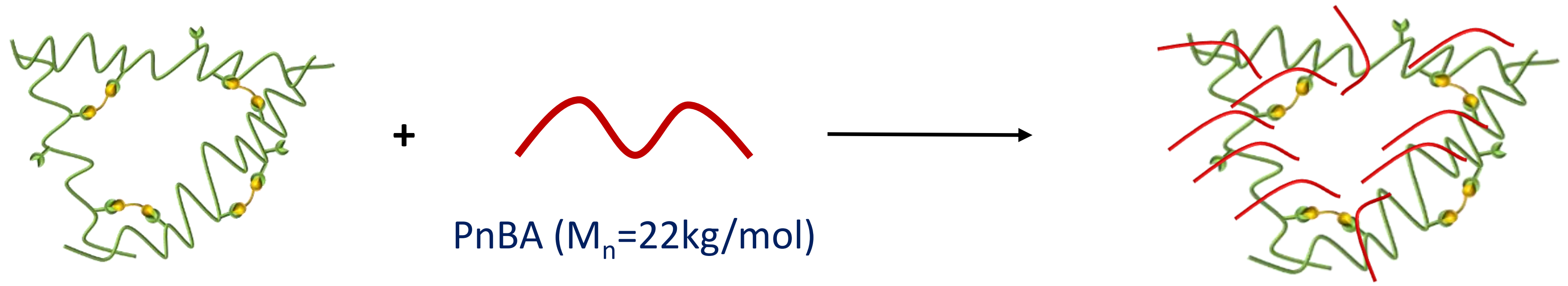
# Network 2 – Reference Sample - Entangled Linear Polymer

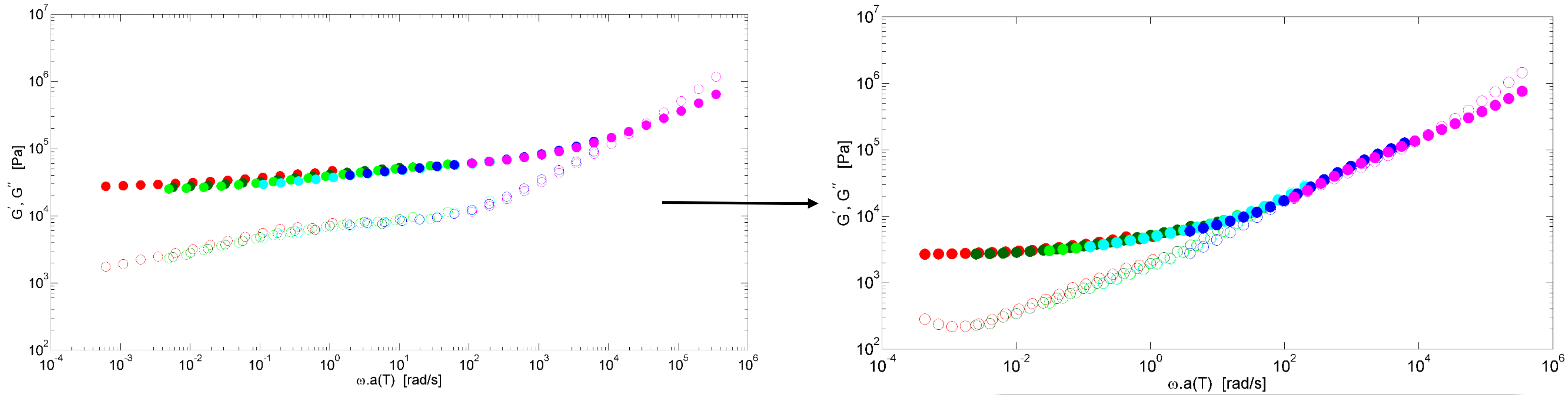



Polymer with rubbery plateau due to entanglements

When crosslinked, the sample is stable even at high temperature

# Network 2 – Entangled Linear Polymer Network



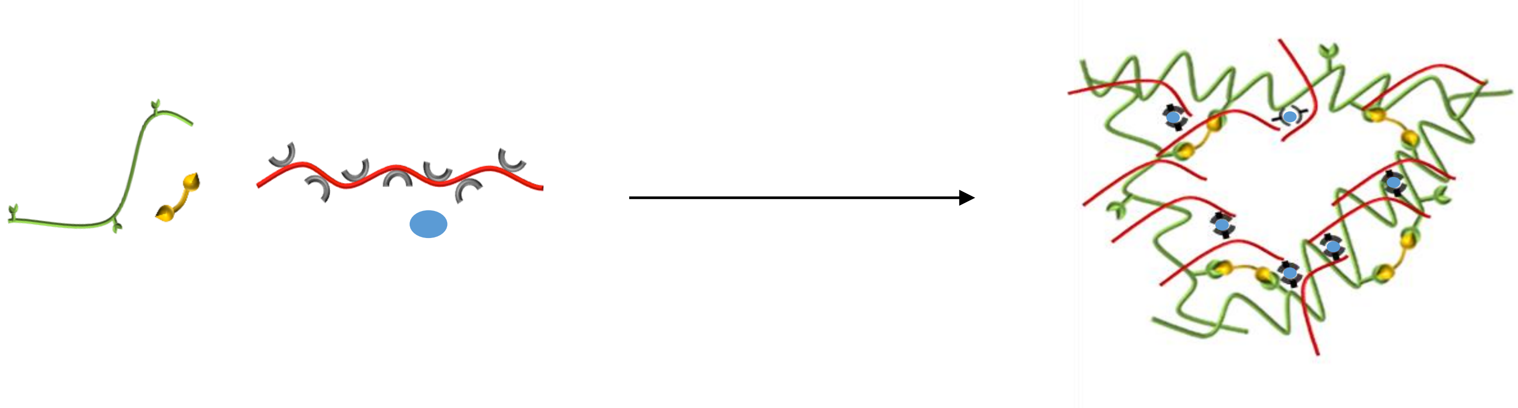




- **Dilution of the second network in 70% short chain PnBA**

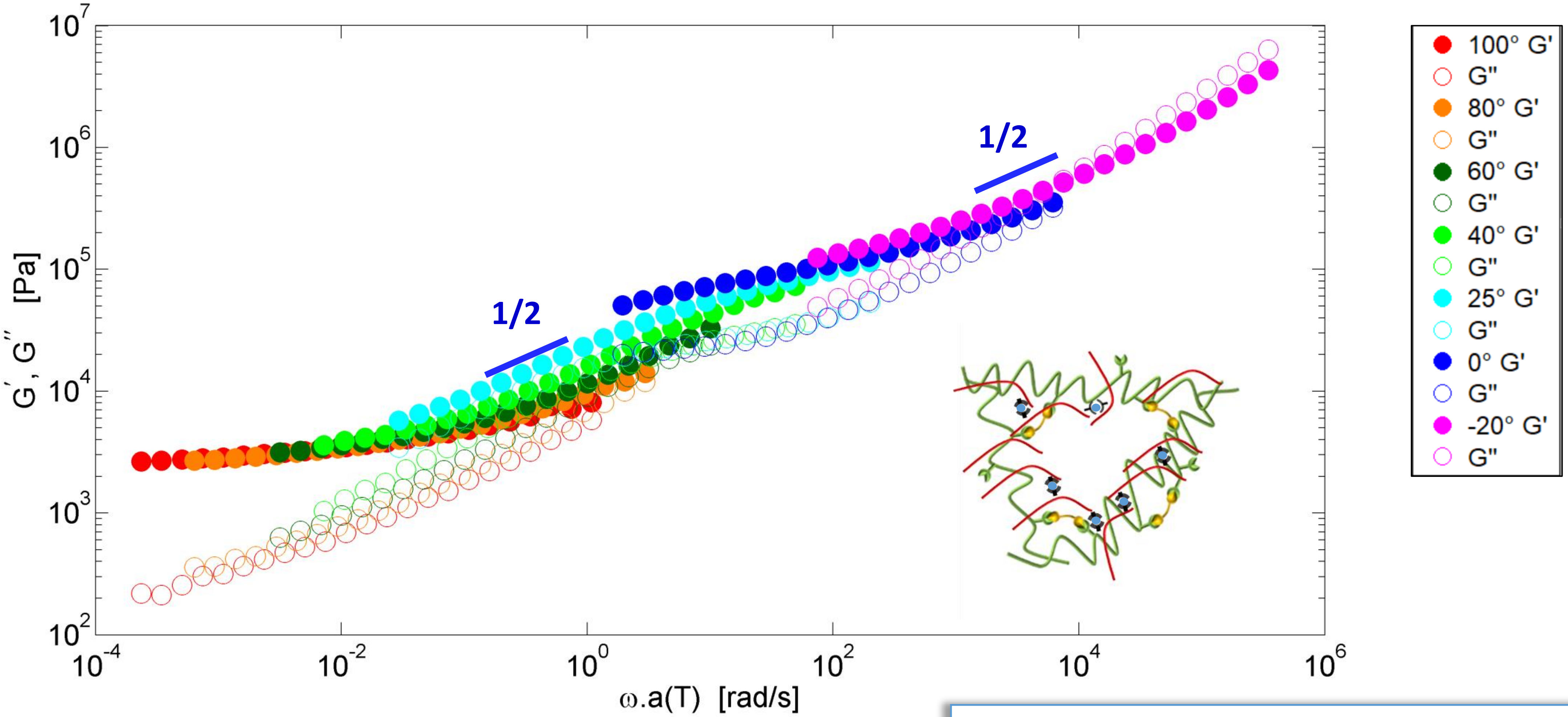
# Double Network – Preparation

- The long PnBA polymer with the PnBA-terpy copolymer and adding the imine crosslinker and metallic ion are mixed in solution at the same time

- Solvent removed by drying under vacuum

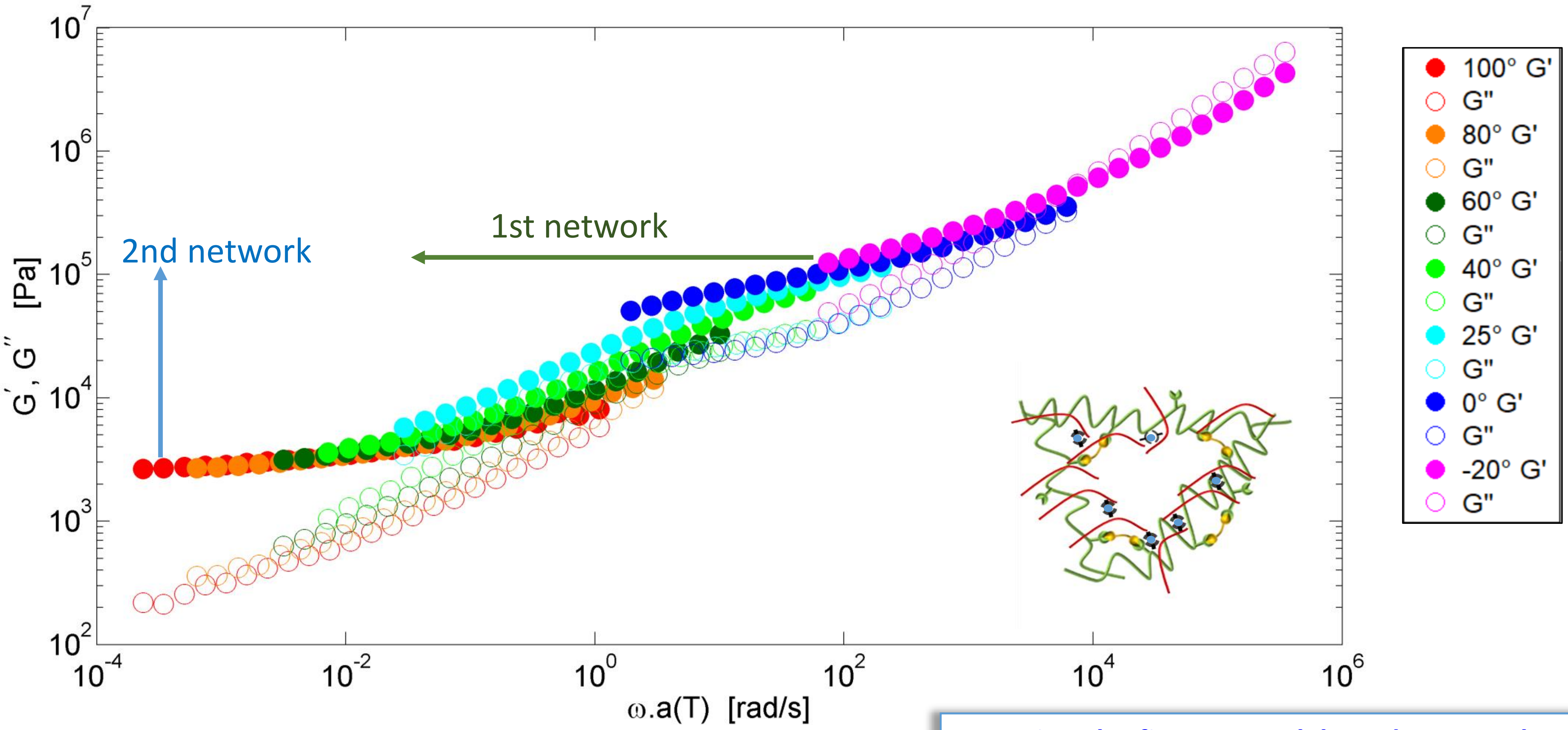


# Double Network – Zn 0.5 eq



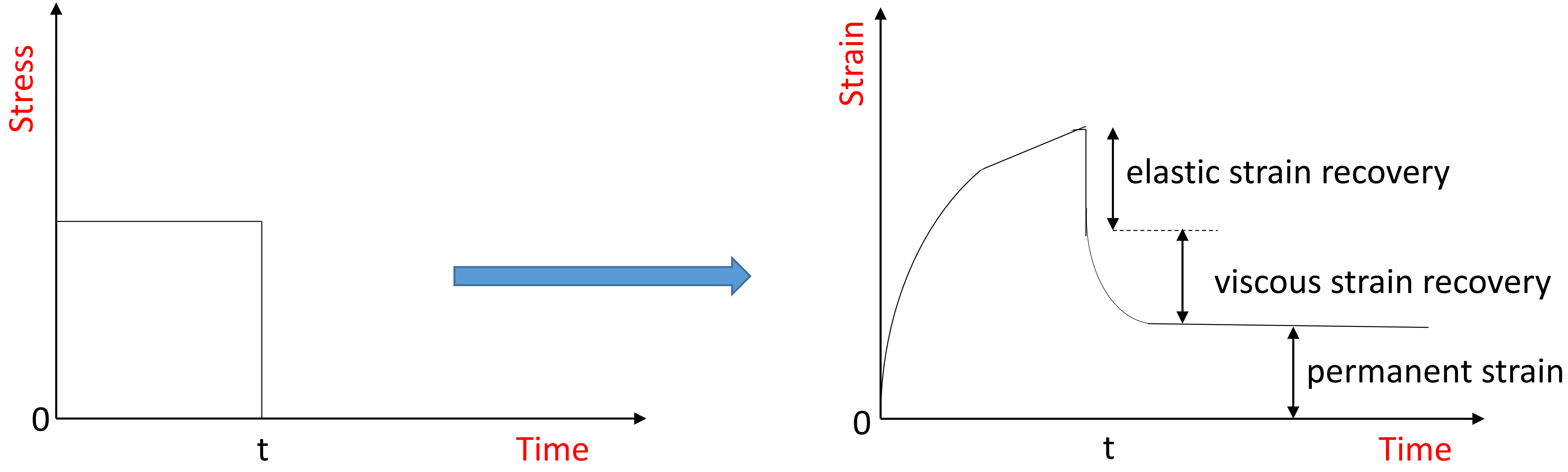

- **Two different dynamic modes, corresponding to the sticker association and the dynamic covalent network.**

# Double Network – Method 1 – Zn 0.5 eq



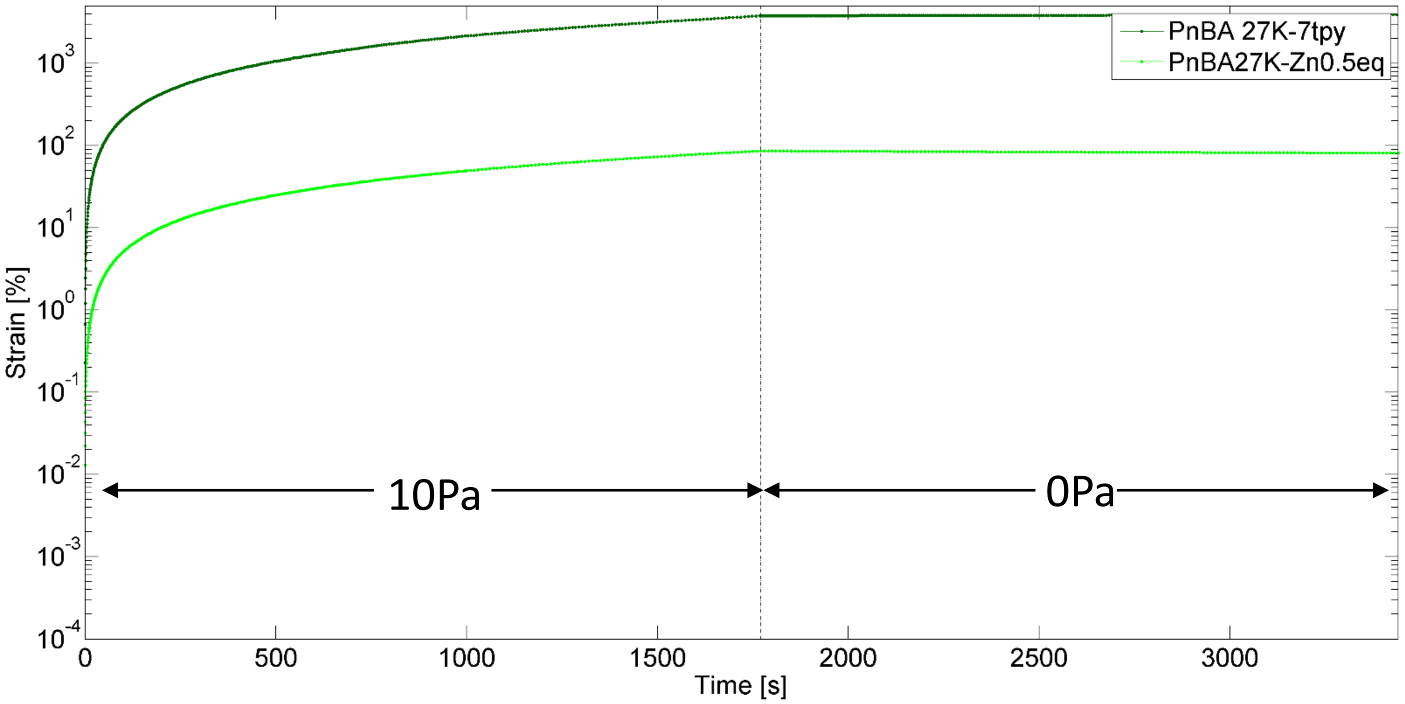

- **Using the first network based on metal-terpyridine links allows the control of the dynamics at intermediate frequencies, while preserving the behaviour at long timescale from the second network.**

# Creep-Recovery Tests



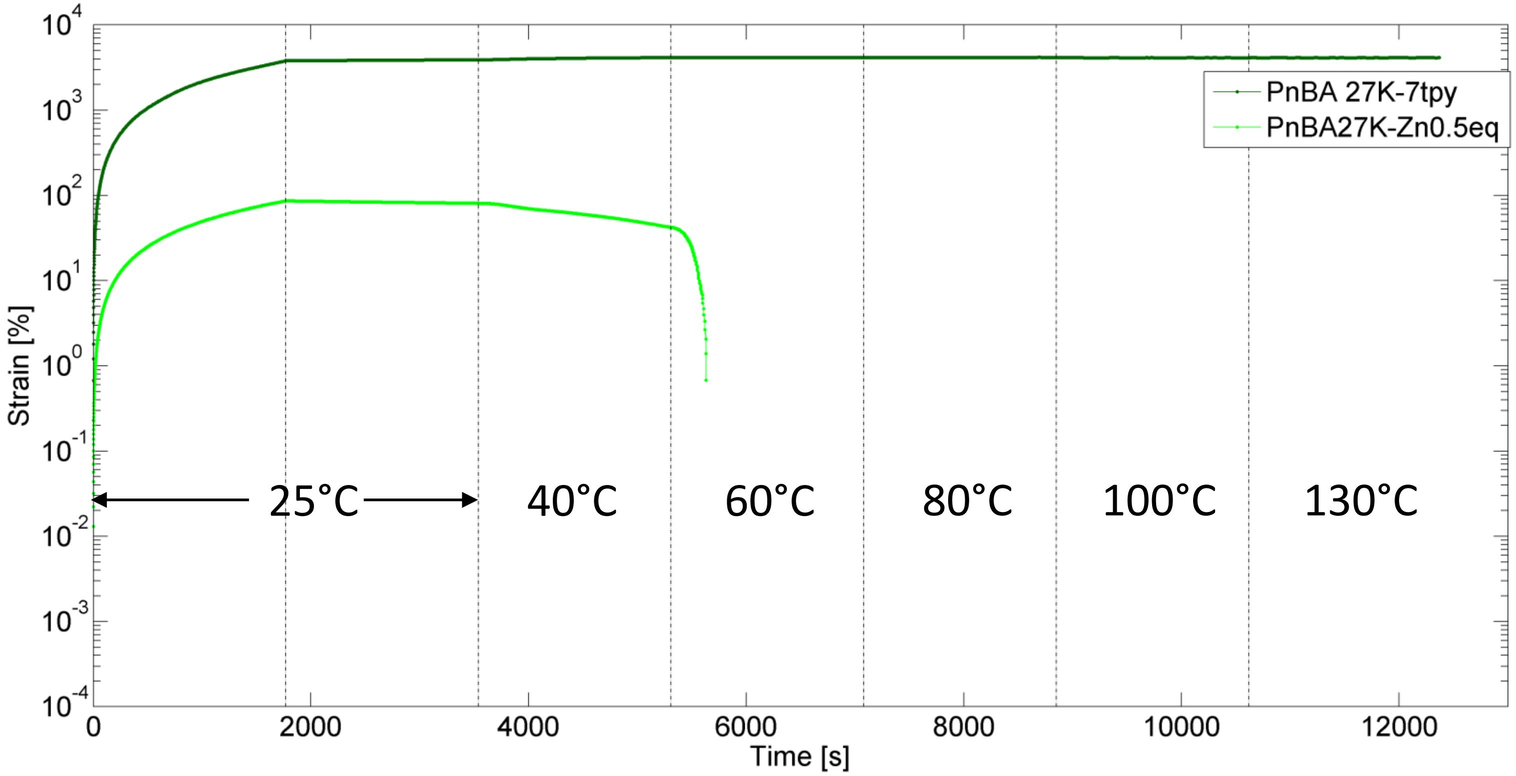

**Gives key information on how a network responds to a small or large stress**

# Network 1 – low stress 10Pa



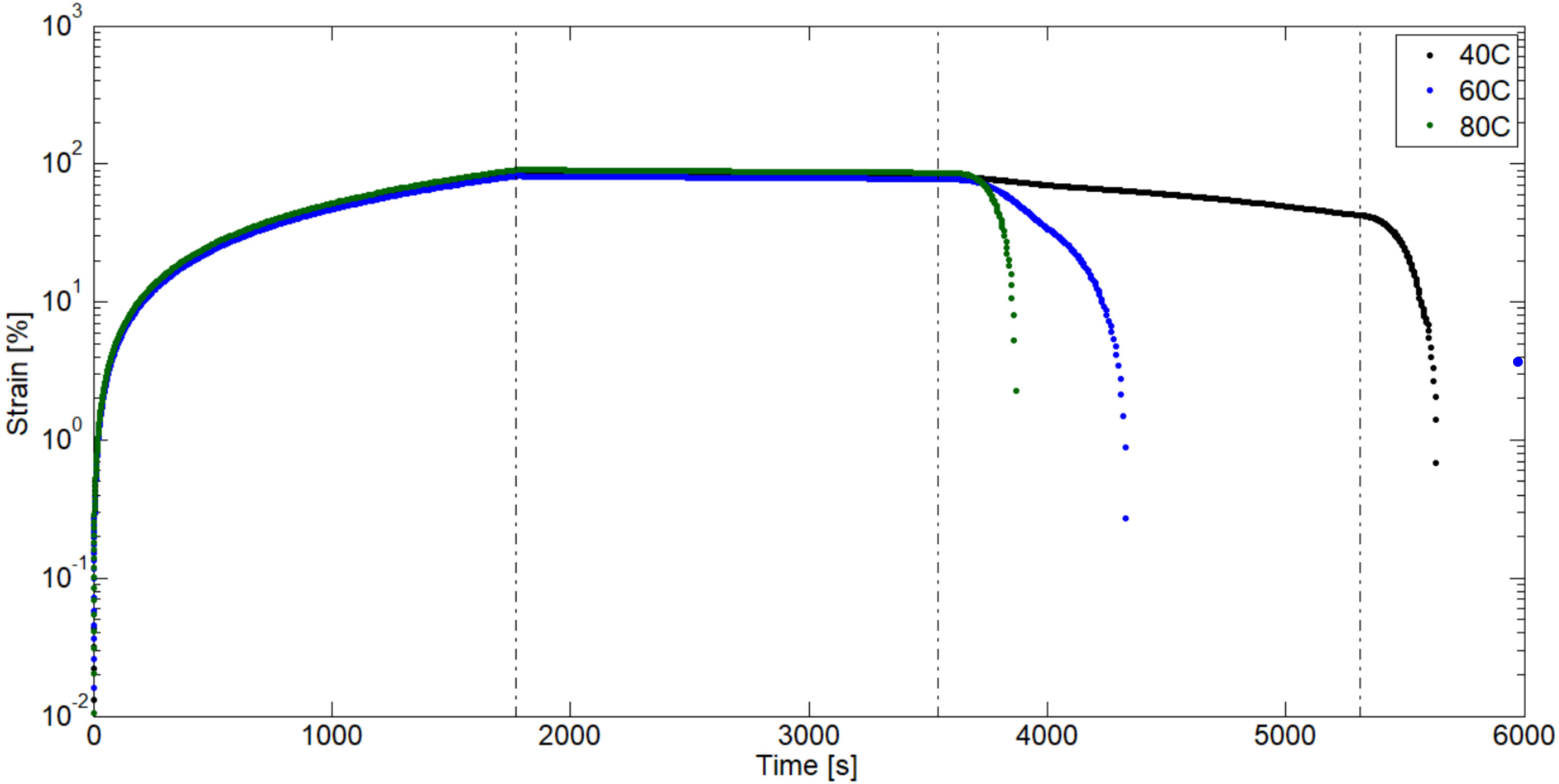

- **Strain increases linearly with time**
- **The rate of increase in strain is linked to the mobility of the polymer chains**

# Network 1 – low stress 10Pa



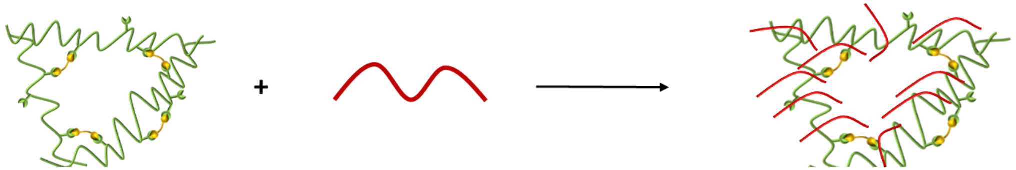

- **With increase in temperature, the zinc-terpyridine network will recover**

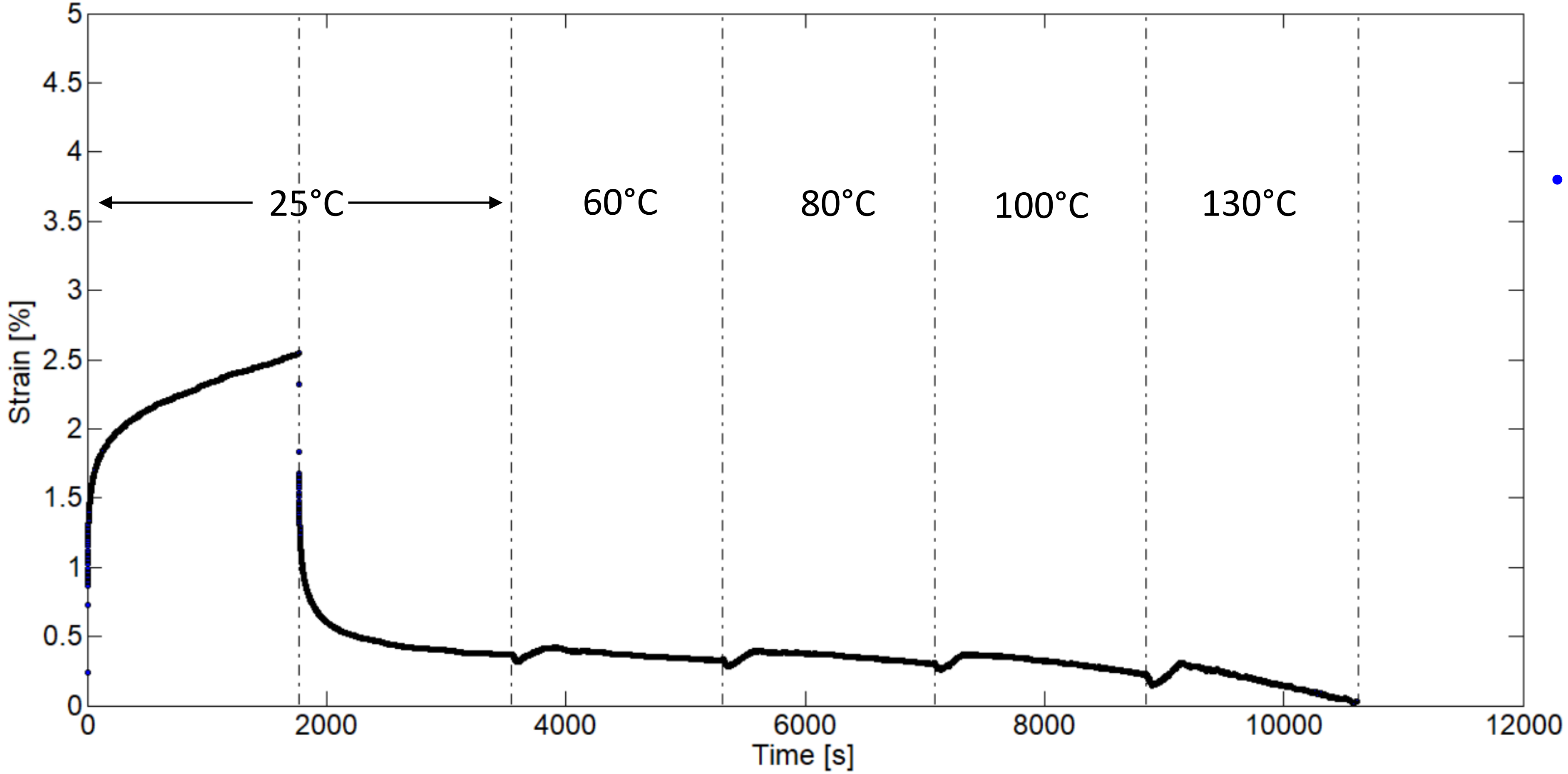
# Network 1 – Temperature Dependence


- The rate of recovery depends on the temperature

# Network 2 – low stress 100Pa

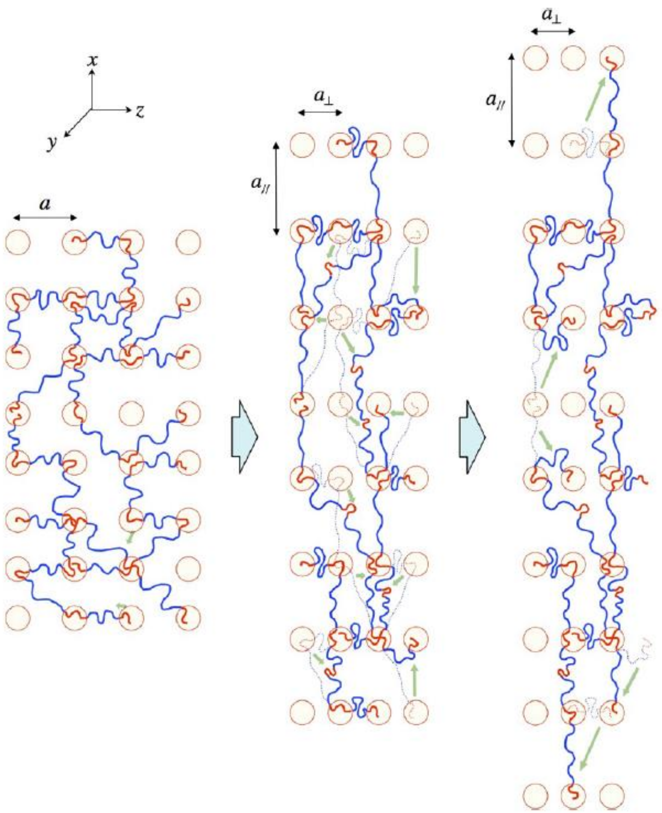


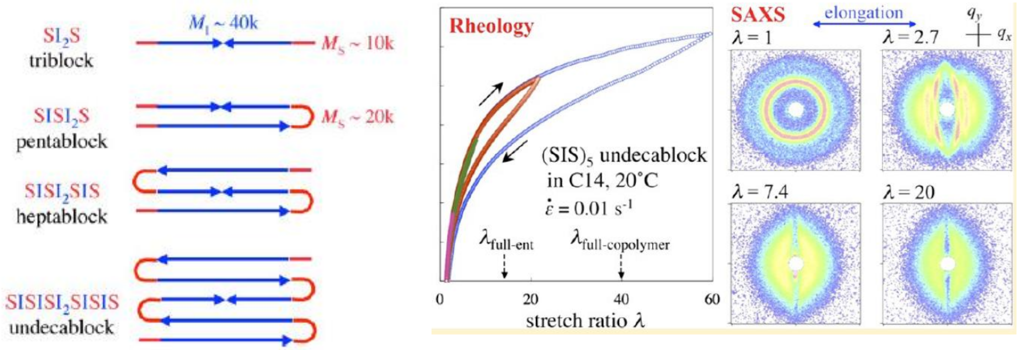




- **With increase in temperature, the imine-aldehdye network does not recover**

# Why does the metal-terpyridine network “recover” with temperature while the imine-aldehyde network does not?

- The first network, is stretched but preserves the memory of its configuration, allowing it to return to the initial state when heated
- This behaviour seen in multiblock copolymers with high elasticity and can be projected to associating polymers

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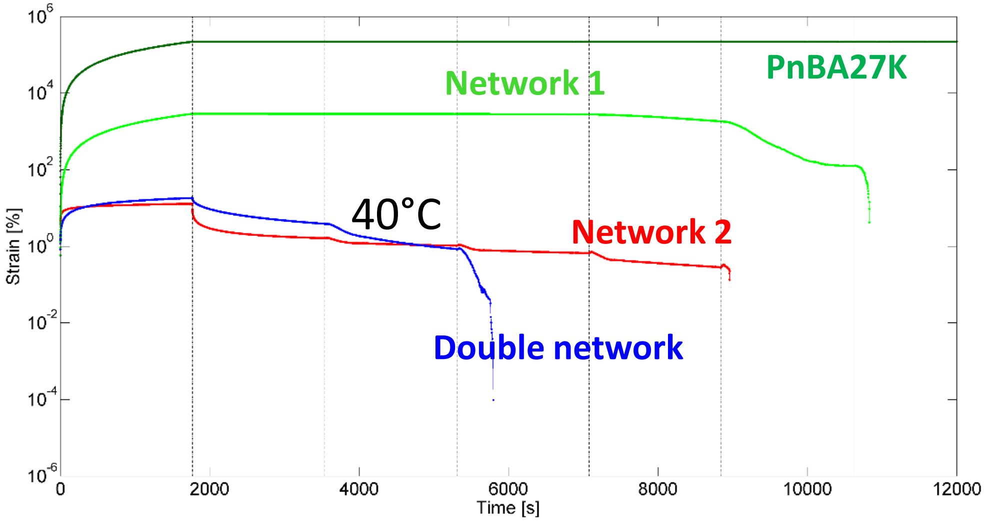
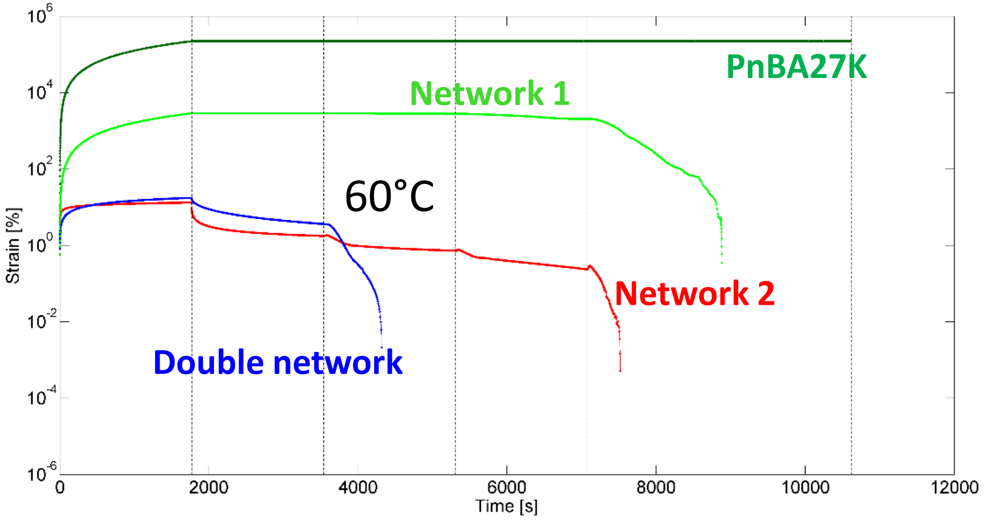
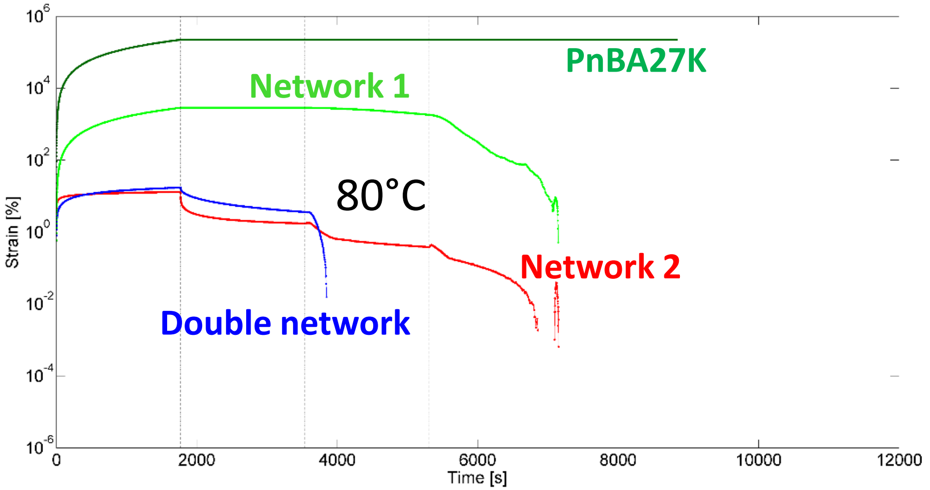
# All networks - High stress – 500Pa

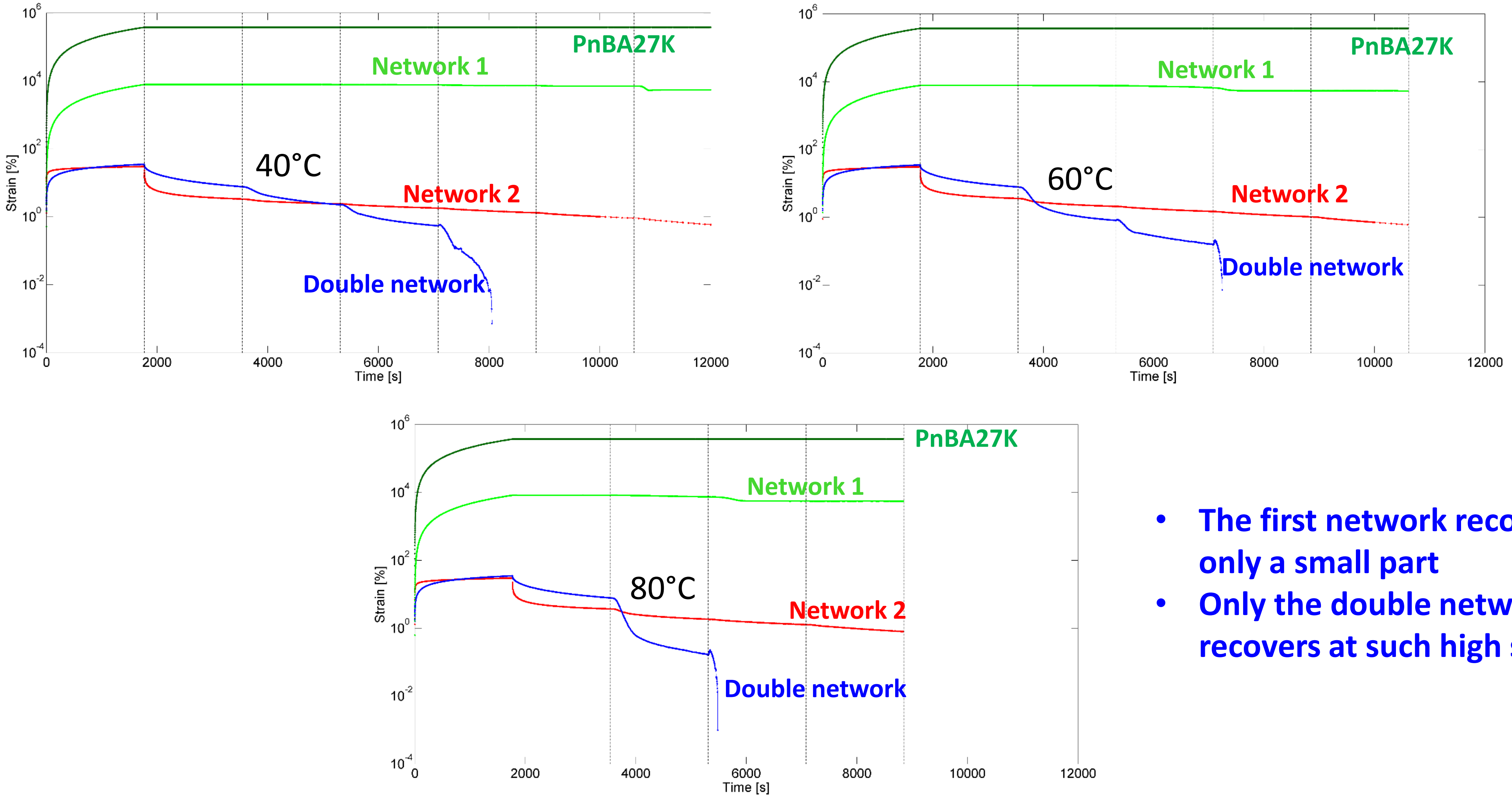



- **Samples containing metal-terpyridine network eventually recover at 130°C**

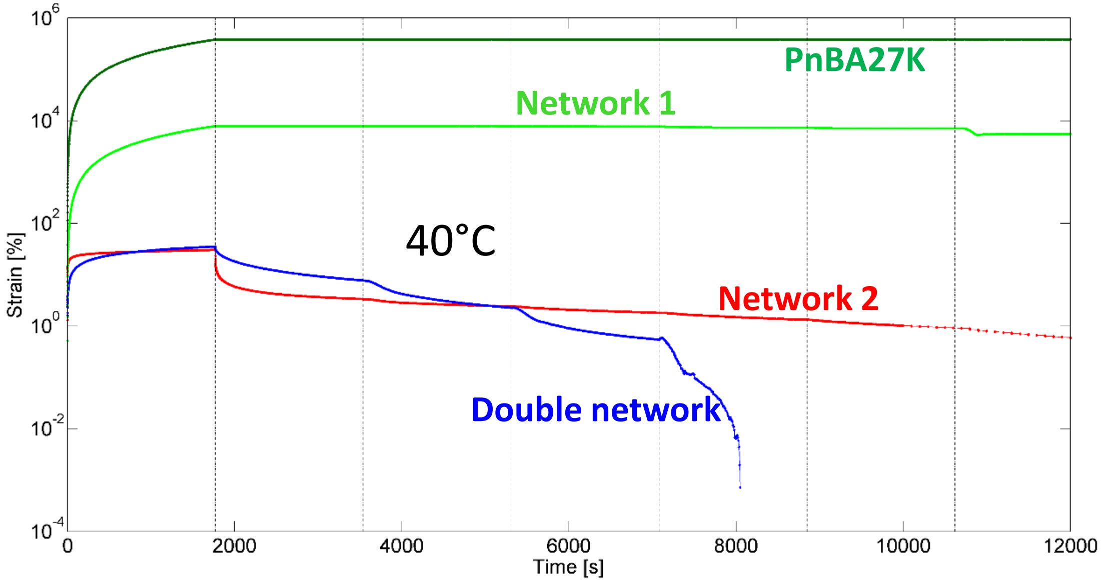
# All networks - High stress – 1000Pa

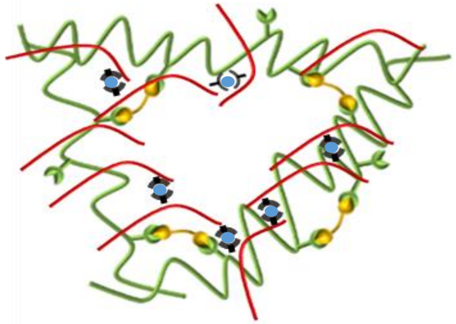



- The first network recovers only a small part
- Only the double network recovers at such high strain

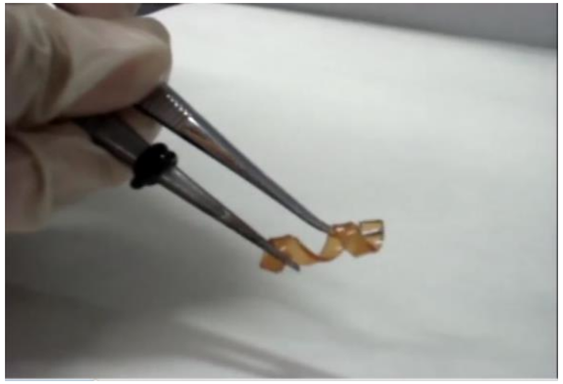
# Why does the double network “recover” with temperature?

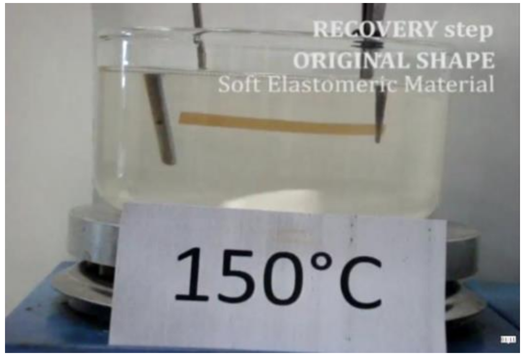
- At high strain, the first network alone, is stretched and breaks irreversibly, it can only recover a small part of the network
- In the double network the first network is more constrained, allowing it to recuperate even at high strain

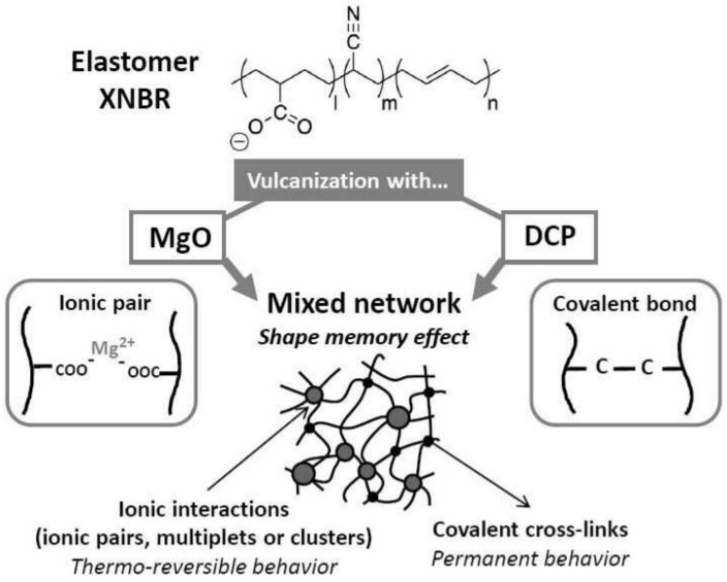


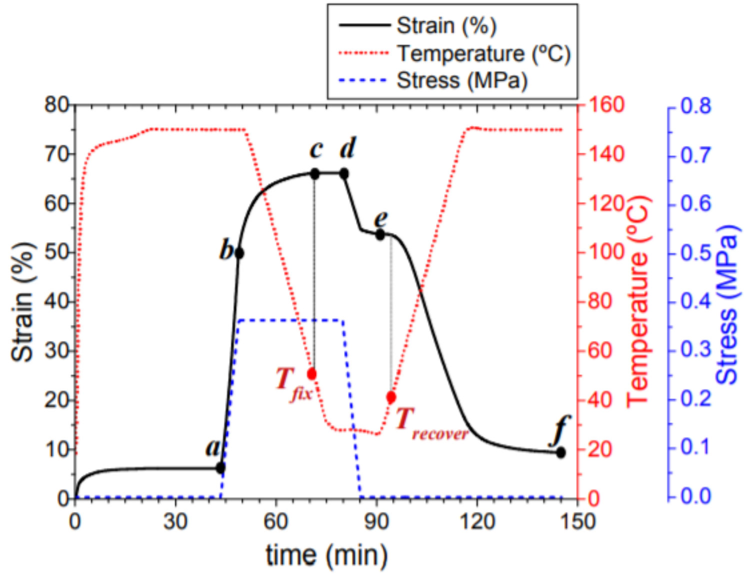
# Possible Application – Shape Memory Polymers






Soft Matter, 2017,13, 2983-2994



# Conclusion

- The double network shows individual components which can be tuned easily
- The double network shows full recovery at very high strain at relatively low temperature