Dynamic metallopolymers – A rheology study

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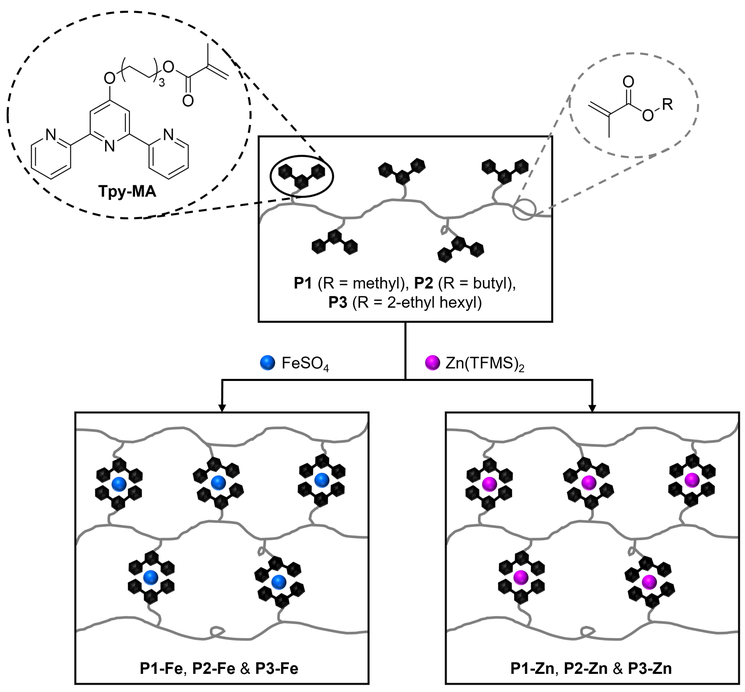
Motivation

Metallopolymers combine the advantages of "classical" organic polymers, such as lightweight, tunability, and cost-effectiveness[1] with the unique properties of metal complexes, including catalytic activity, bioactivity, and conductivity.[2,3] This synergy makes them promising materials for different applications, such as self-healing polymers, shape memory polymers, and smart materials.[4,5] However, a key challenge lies in understanding their behavior.

Synthesis of metallopolymers

- RAFT polymerisation of polymers containing terpyridine (**Tpy-MA**) as the ligand
- ^{1}H NMR reveals: ca. 9% terpyridine content
- Addition of two different metal salts (**Scheme 1**)
- Characterization: DSC, TGA, elemental analysis
- Insight into structural changes:

→ Rheological investigation: DMTA, frequency sweeps, stress relaxation, time temperature superposition (TTS)



Scheme 1. Schematic representation of the synthesis of the metallopolymers.

DMTA and frequency sweeps

- Investigation of metallopolymers *via* dynamic mechanical thermal analysis (DMTA) No crossover between storage modulus (G') and loss modulus (G")

- Frequency sweep measurements: Crossover at 120 and 130 °C for **P2-Zn** (**Figure 1 A**), also visible for all other zinc containing metallopolymers

→ Supramolecular bond lifetime τ_b calculated (**Table 1**)

- Activation of bis-terpyridine-zinc complex
- No crossover for iron complexes (**Figure 2B**)

→ Thermally more stable complexes

Table 1. Summary of the supramolecular bond lifetime of the zinc containing metallopolymers.

Sample	T / °C	τ_b / s
P1-Zn	130	442.5
	140	242.1
P2-Zn	120	561.8
	130	153.6
P3-Zn	110	666.7
	120	190.1

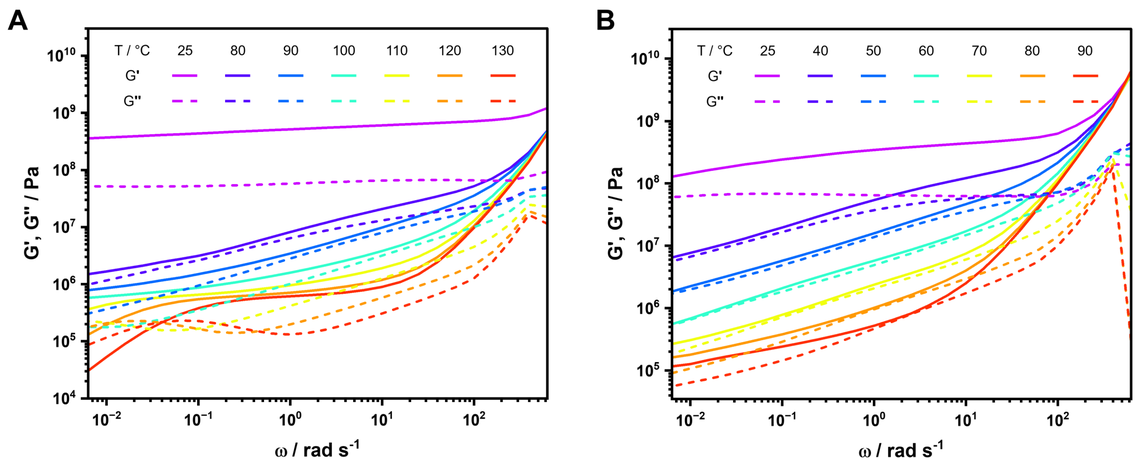


Figure 1. Frequency sweep measurements from 0.00628 to 628 rad s^{-1} at different temperatures for (A) **P2-Zn** and (B) **P2-Fe**.

Stress Relaxation

- Shear strain of 2%, measurement for 900 s at different temperatures (**Figure 2A**)
- For **P2-Zn**: Relaxation gets faster with higher temperatures → vitrimeric material
- At 90 and 100 °C the relaxation gets slower → partial vitrimers
- Results fitted to two different models: Maxwell and Kohlrausch-Williams-Watt (KWW) model (**Figure 2B**) → KWW fits better to experimental results

→ Calculation of activation energies (E_A) using the Arrhenius equation (**Table 2**)

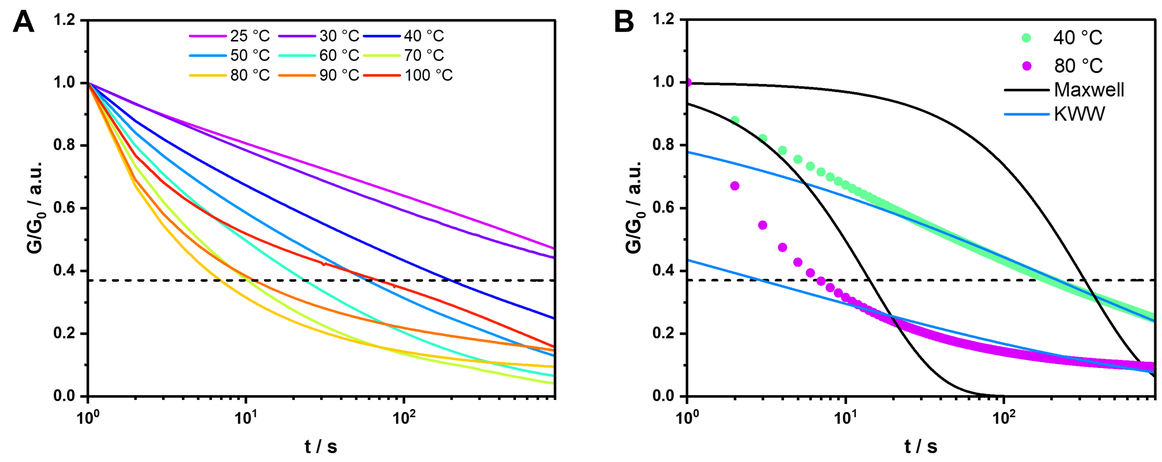


Figure 2. Stress relaxation plots for **P2-Zn**: (A) normalized stress relaxation plot, (B) normalized plot at 40 and 80 °C fitted using the Maxwell and KWW model.

Table 2. Summary of the determined activation energies for the metallopolymers.

	P1-Fe	P1-Zn	P2-Fe	P2-Zn	P3-Zn
E_A (Maxwell) / kJ mol^{-1}	94.78	105.83	90.32	75.52	40.96
E_A (KWW) / kJ mol^{-1}	131.63	120.44	94.29	108.92	42.03

Time temperature superposition (TTS)

- TTS principle: G' and G'' are temperature dependent, prediction of material´s behavior over longer time frame, for thermorheologically simple materials

→ Horizontal (shift factor a_T) and vertical shifting (shift factor b_T) of G' and G '' values from frequency sweep measurements using one reference temperature

- Modified Cole-Cole plot of **P2-Zn** (**Figure 3A**): G' and G" temperature independent plot, overlaps → TTS should be applicable
- Slope at 120 and 130 °C reaches almost the value of 2 → supramolecular cross-linking points are activated
- Master curves constructed using only horizontal shift factors a_T for **P2-Zn** depicted in **Figure 3B** at a reference temperature T_{ref} = 110 °C

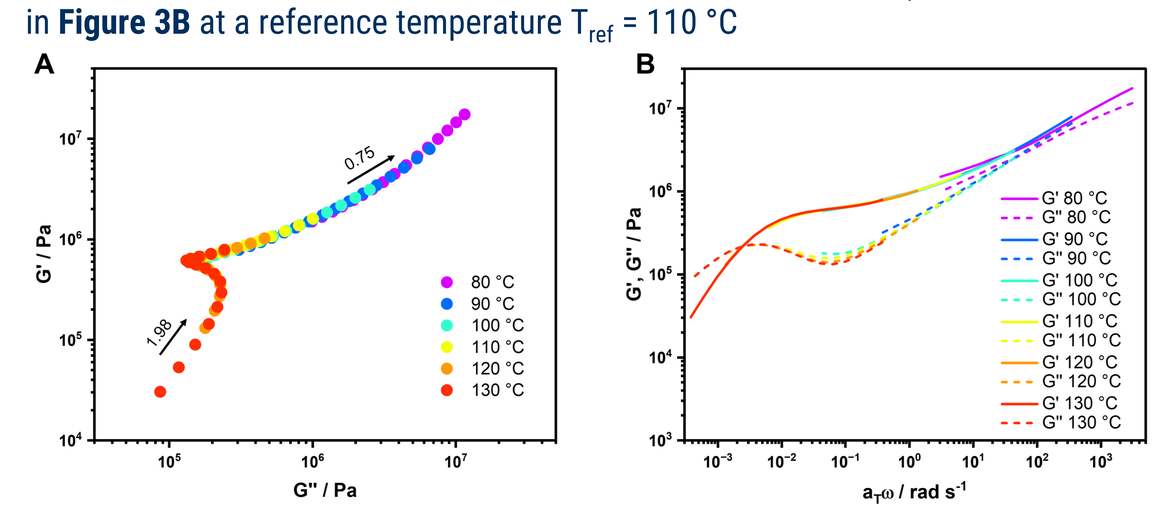


Figure 3. (A) Modified Cole-Cole plot of **P2-Zn**, (B) TTS master curve of **P2-Zn** at T_{ref} = 110 °C.

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