Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Hierarchy of Relaxation Times in Supramolecular Polymer Model Networks

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Content

Synthesis

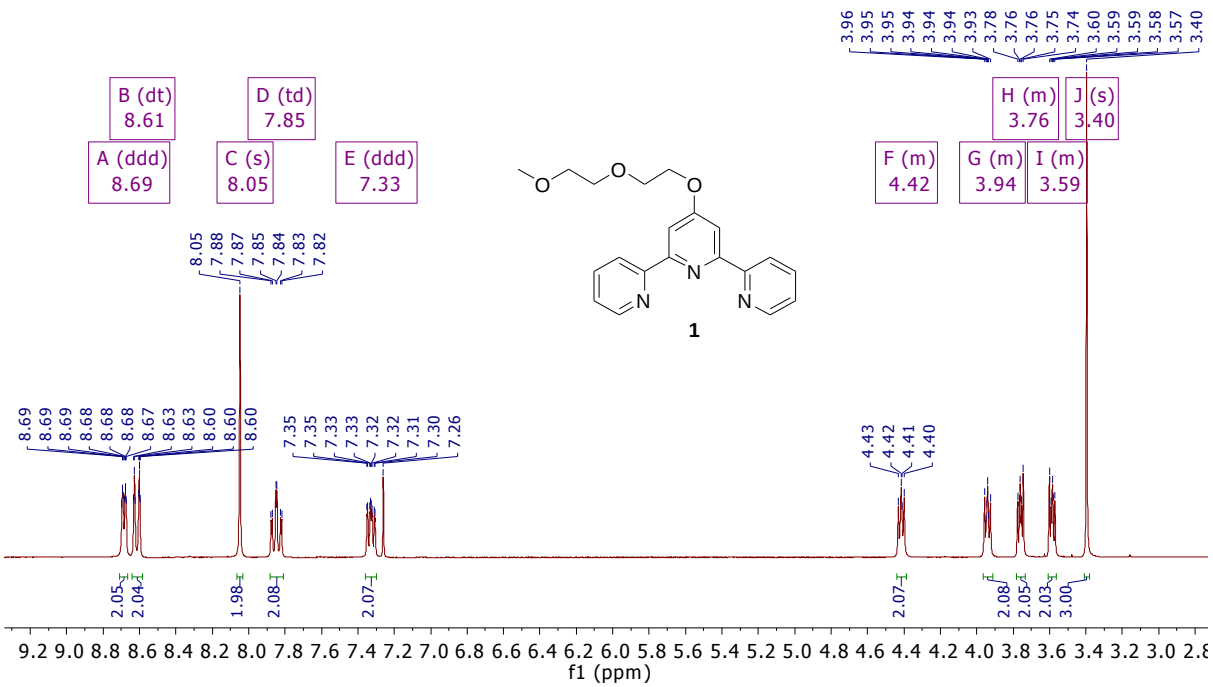

Figure S1. 1*H*-NMR spectrum of 4´-[2-(1-Methoxyethoxy)ethoxy]2,2´:6´,2´´-terpyridine (**1**), 300 MHz, $CDCl_3$.

UV-Vis measurements

The zinc terpyridine bond dissociation time is determined by time-depending UV-Vis monitoring of the MLCT band at 336 nm. The time-trace is fitted to an exponential function as pseudo first-order conditions are assumed:

$$Abs(t) = A - B \cdot \exp\left(-\frac{t}{\tau_{dilute}}\right) \quad (1)$$

with an offset *A*, the maximum absorbance *B*, the characteristic relaxation time τ_{dilute}. Similar to Tang *et al.*,[1] several approximations are made, for example that only the forming Cu(II)-terpyridine complexes are contributing to the monitored MLCT band.

Rheology

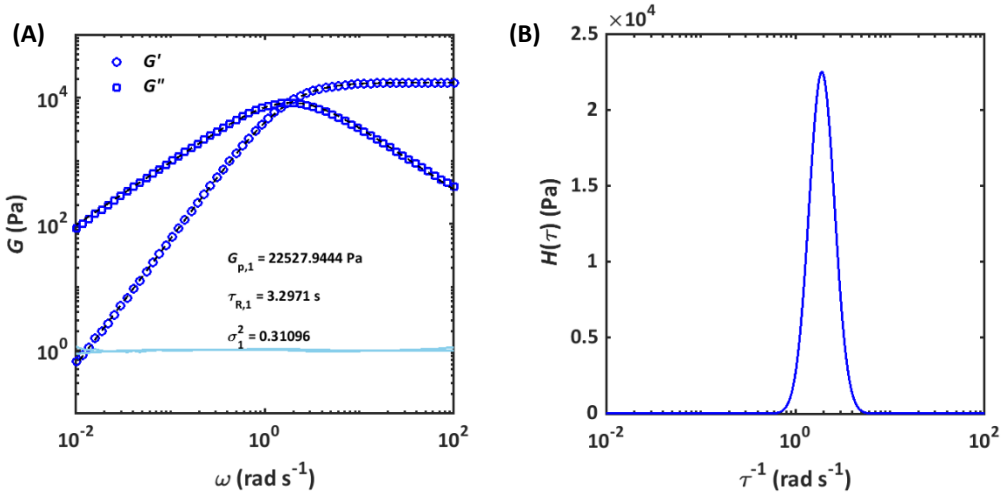

Figure S2. (A) Exemplary frequency-depending storage (open circles) and loss (open squares) modulus of a tetra-arm PEG-terpyridine gel (DMF, 10 wt%) at 25 °C and fit to a Maxwell type relaxation model (black dashed line). The residual is depicted as light blue line. (B) Resulting relaxation time distribution $H(\tau)$ of the same gel.

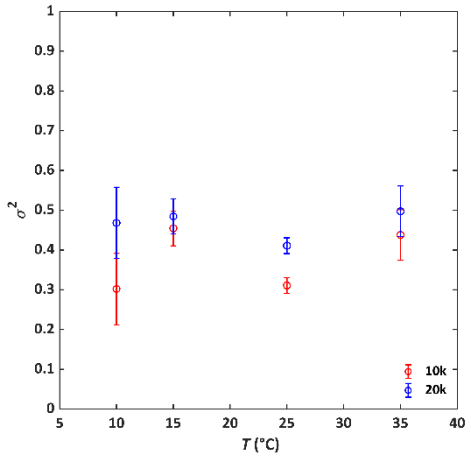

Figure S3. Standard deviation σ^2 of the relaxation time distribution of a 10k (10% (wt/v), red symbols) and a 20k (20% (wt/v), blue symbols) zinc tetra-arm PEG-terpyridine gel (DMF) depending on the temperature. Errorbars represent uncertainties within 95% confidence interval.

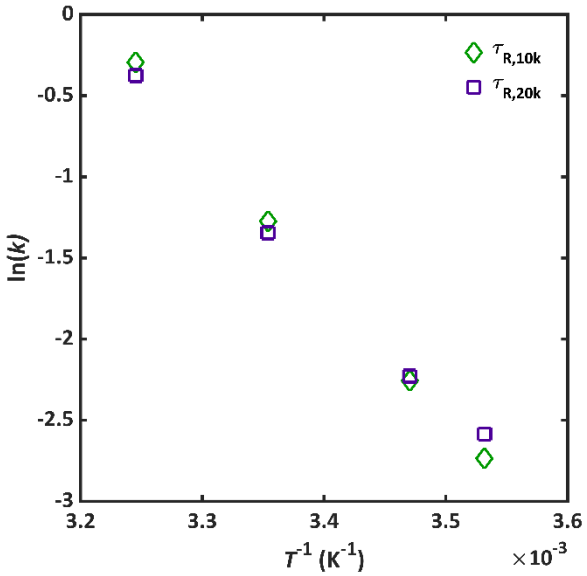

Figure S4. Arrhenius plot (ln(*k*) vs. T^{-1}) of the relaxation rates $k = \tau^{-1}$ obtained by oscillatory shear rheology of a 10k (green open diamonds) and a 20k (purple open squares) gel.

Light Scattering

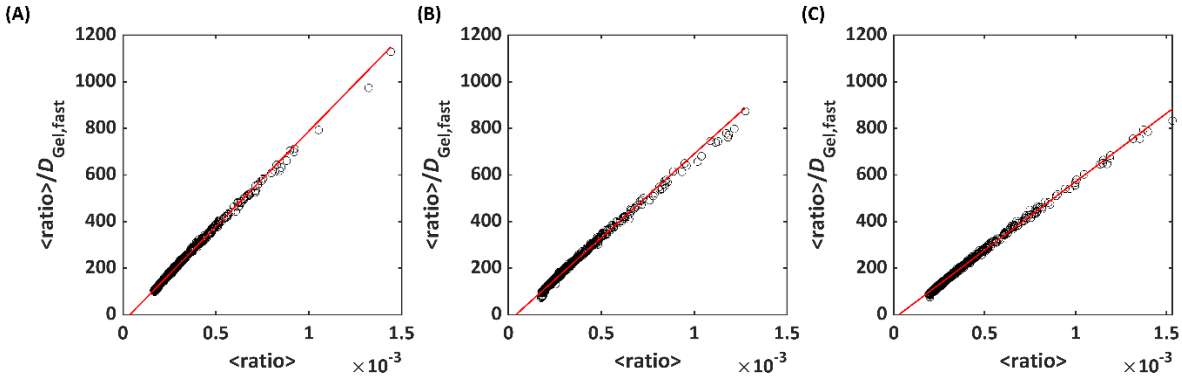

Figure S5. $\frac{\langle ratio \rangle}{D_{Gel,fast}}$ vs. <ratio> shows a linear dependence at three different temperatures 25 °C (A), 35 °C (B), and 45 °C (C). $\frac{2}{slope}$ yields the partial heterodyne diffusion coefficient D_{PHD} of the fast relaxation mode.

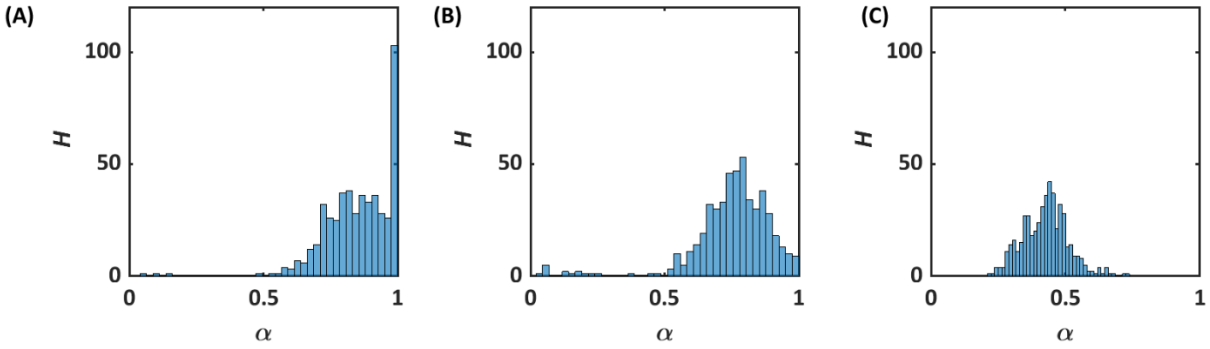

Figure S6. Distribution of stretch exponents α of a zinc tetra-arm PEG-terpyridine gel (10% (wt/v), DMF) at 25 °C (A), 35 °C (B), and 45 °C (C) at an angle of 30 °. α is decreasing with increasing temperature.

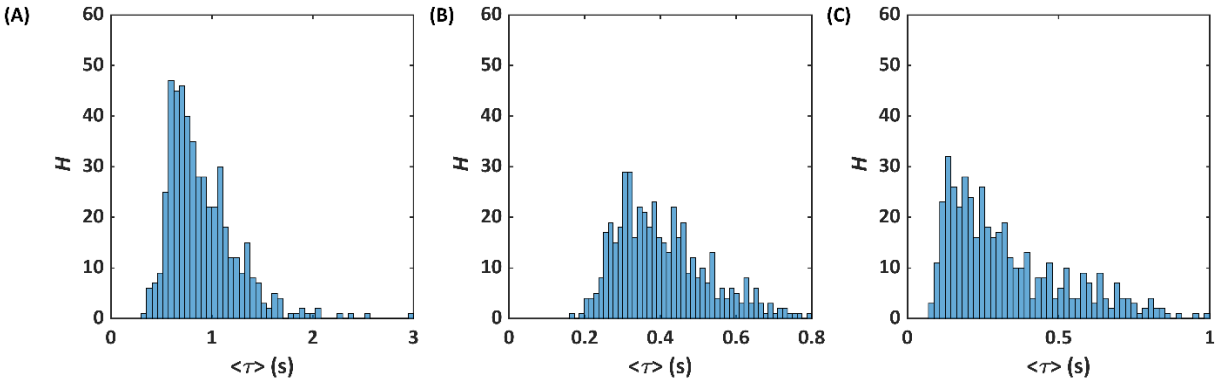

Figure S7. Frequency distribution histogram of the slow relaxation times at (A) 25 °C, (B) 35 °C, and (C) 45 °C. With increasing temperature τ shifts to lower values and the distribution broadens.

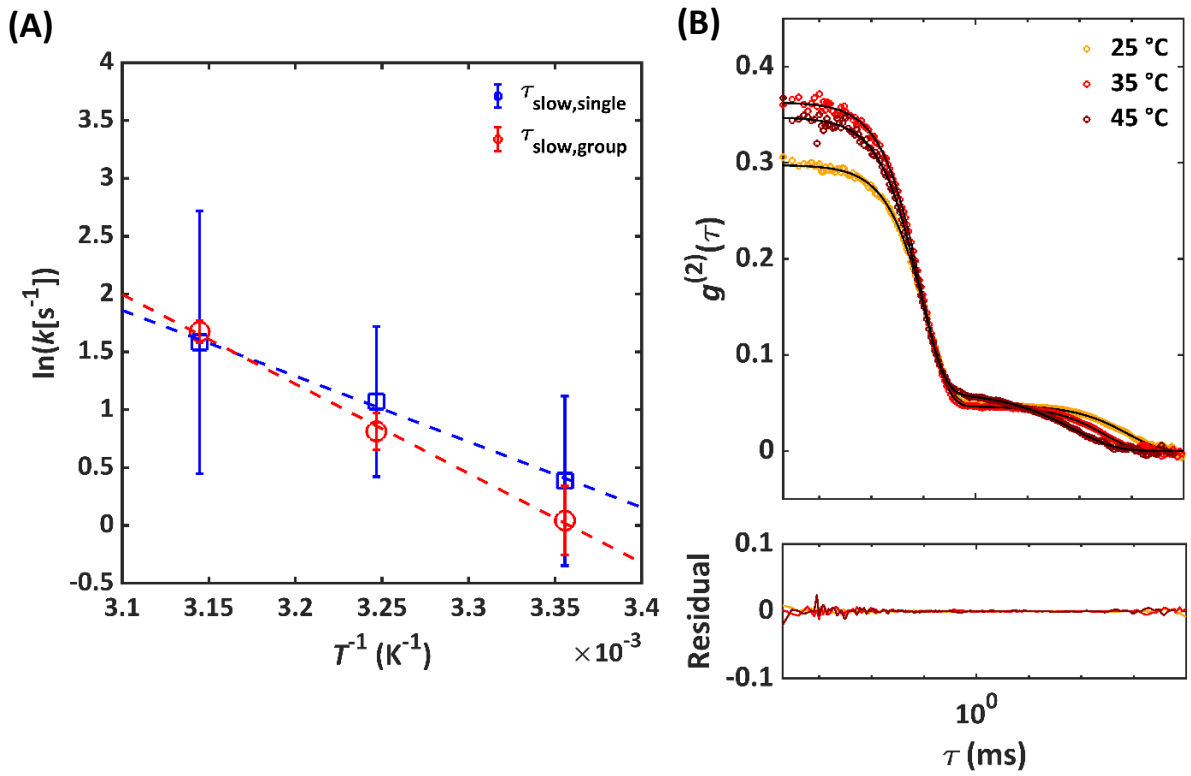

Figure S8. (A) Arrhenius plot of the temperature-dependent slow relaxation times obtained by either fitting all single 500 intensity correlation functions and subsequent averaging over the obtained 500 τ_{slow} values (blue) or fitting the average of 5 x 100 correlation functions, respective (red). (B) Exemplary average correlation function (five 100-packs) at 25 °C (yellow), 35 °C (red), and 45 °C (maroon).

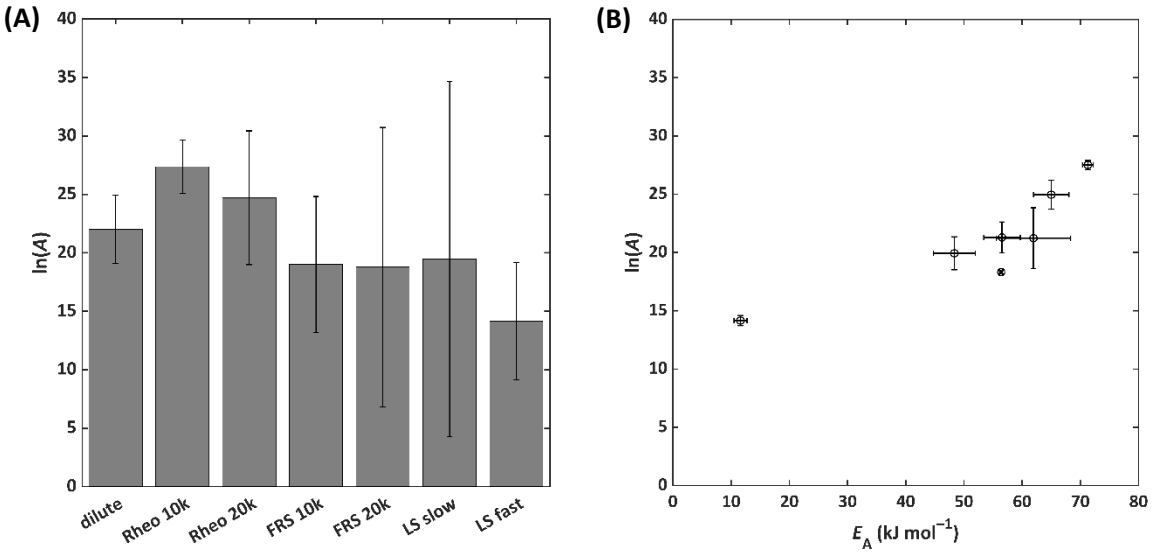

Figure S9. (A) Pre-factors of the Arrhenius law obtained by UV-vis measurements (dilute conditions), rheology, forced Rayleigh scattering, and dynamic light scattering. Error bars depict uncertainties within a 95% confidence interval. (B) Pre-factors vs. activation energy.

Forced Rayleigh Scattering.

The d^2-spacing dependence of $\langle\tau\rangle$ is fitted to a previously described two-state model.[1,3–5] In summary, the model assumes the polymer to be present in two states: an immobile associated state (A, where its transient junctions are connected to the network) and a molecular state (M, where it is free to diffuse). Both states are characterized by their diffusivities D_A and D_M. Following pseudo-first order kinetics, the polymers transform between both states and the concentration changes C_M and C_A over time are described by the following equations:

$$\frac{\partial C_M}{\partial t} = D_M \frac{\partial^2 C_M}{\partial x^2} - k_{on} C_M + k_{off} C_A \quad (6)$$

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} + k_{on} C_M - k_{off} C_A \quad (7)$$

k_{on} and k_{off} denote the reaction rates of the interconversion process. By fitting the model to the data, the three parameters k_{off}, $D_{M,eff} = \frac{D_M}{(1+K_{eq})}$ with $K_{eq} = \frac{k_{on}}{k_{off}}$, and γK_{eq} with $\gamma = \frac{D_A}{D_M}$ are obtained. γK_{eq} is anti-proportional to the width of the superdiffusive regime and can therefore be seen as a quantitative measure. $D_{M,eff}$ at large length scales denotes an effective reduced diffusivity reflecting a superpositon of all relaxation modes (e. g. hopping, walking…).[6]

References

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(2) Grindy, S. C.; Learsch, R.; Mozhdehi, D.; Cheng, J.; Barrett, D. G.; Guan, Z.; Messersmith, P. B.; Holten-Andersen, N. Control of hierarchical polymer mechanics with bioinspired metal-coordination dynamics. *Nature materials* **2015**, *14*, 1210–1216.

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(6) Ramirez, J.; Dursch, T. J.; Olsen, B. D. A Molecular Explanation for Anomalous Diffusion in Supramolecular Polymer Networks. *Macromolecules* **2018**, *51*, 2517–2525.