Local dynamics in supramolecular polymer networks probed by Magnetic Particle Nanorheology

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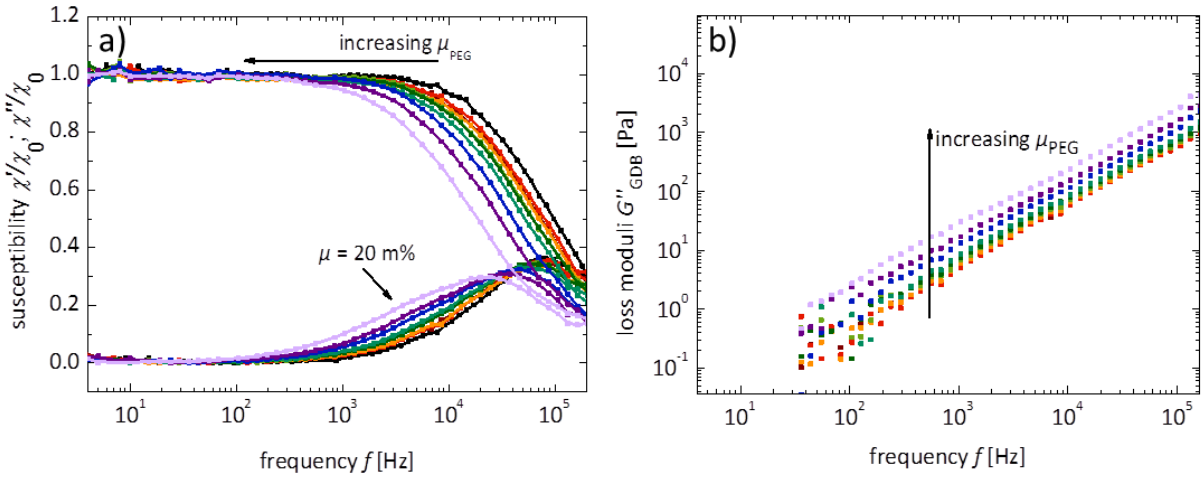


Figure SI-1 a) Normalized real and imaginary part of the susceptibility χ^* and b) loss moduli G'' determined by the *GDB* model in dependence on frequency f for PEG-$(OH)_4$ aqueous solutions. The mass concentration is varied between 0 - 20 m% (black: μ = 0 m%; dark red: μ = 2.0 m%; red: μ = 2.4 m%; light orange: μ = 3.4 m%; light green: μ = 4.8 m%; dark green: μ = 5.9 m%; turquoise: μ = 7.0 m%; blue: μ = 11.1 m%; violet: μ = 14.9 m%; light violet: μ = 20.0 m%). For a better overview, not all measured curves are shown.

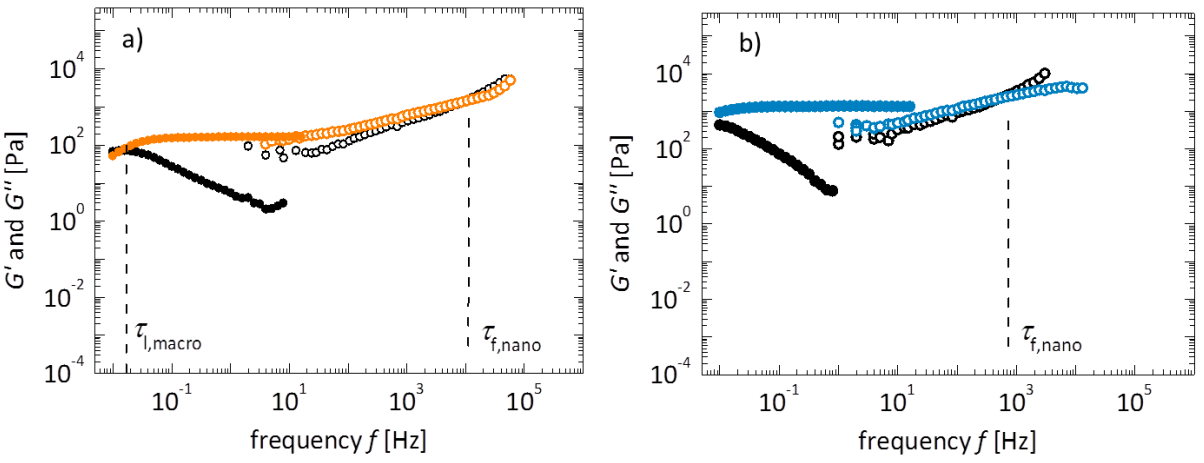


Figure SI-2 Comparison of macroscopic (full symbols) and nanoscopic (empty symbols) storage G' (color) and loss moduli G'' (black) in dependence on frequency f for Co^{2+}/ PEG-$(L)_4$ with a) $r_{M/P}$ = 1.09 and b) $r_{M/P}$ = 2.17 for μ_{PEG} = 3.8 m%.

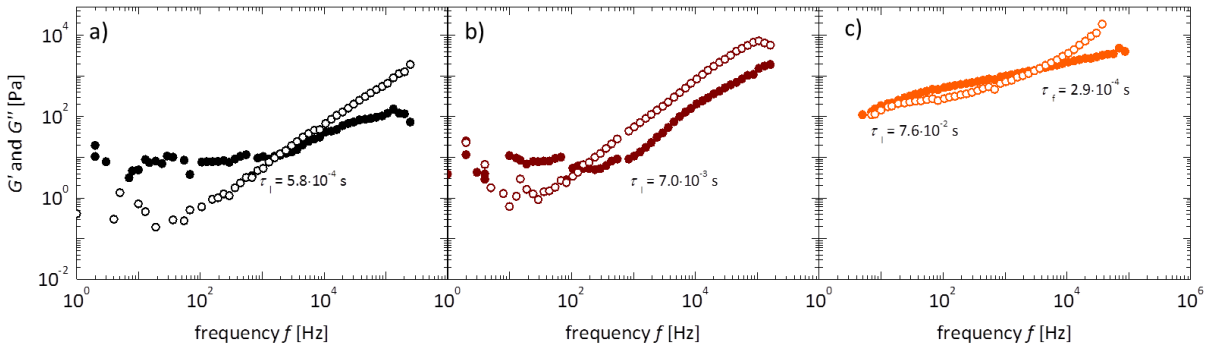


Figure SI-3 Comparison of storage G' (full symbols) and loss G'' (empty symbols) moduli for a) aqueous solution of PEG-$(OH)_4$ ($r_{M/P} = 0$), b) aqueous solution of PEG-$(L)_4$ ($r_{M/P} = 0$) and c) aqueous solution of Zn^{2+}/ PEG-$(L)_4$ ($r_{M/P} = 1.09$). The polymer mass fraction is $\mu_{PEG} = 3.8$ m% for all polymer samples.

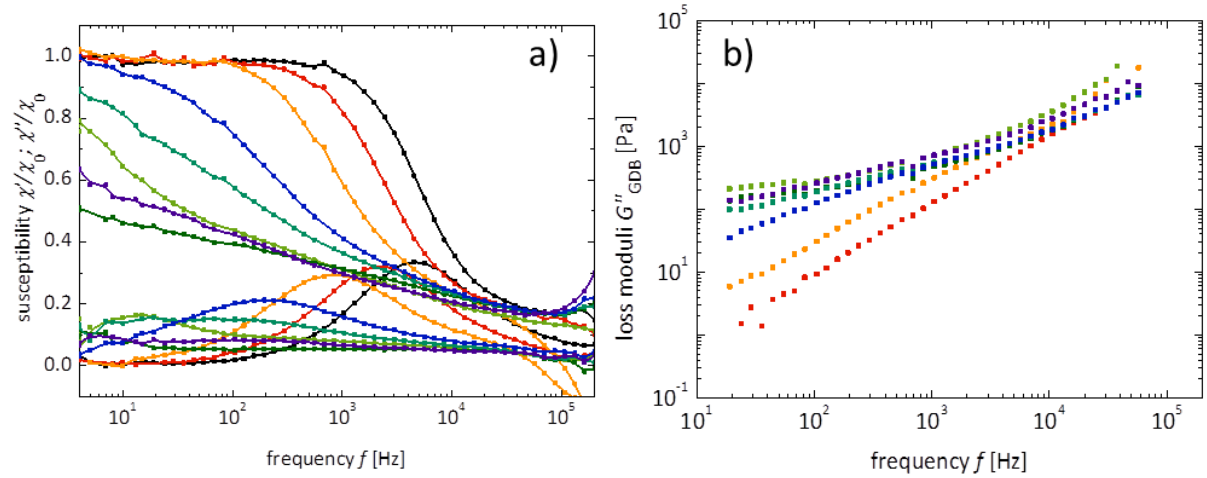


Figure SI-4 a) Normalized real and imaginary part of the susceptibility χ^* and b) loss moduli G'' determined by the *GDB* model in dependence on frequency f for Zn^{2+}/PEG-$(L)_4$ with different $r_{M/P}$ ratios. The polymer mass fraction is $\mu_{PEG} = 3.8$ m% for all polymer samples. Black: $r_{M/P} = 0$; red: $r_{M/P} = 0.43$; light orange: $r_{M/P} = 0.87$; light green: $r_{M/P} = 1.09$; dark green: $r_{M/P} = 1.52$; turquoise: $r_{M/P} = 1.95$; dark blue: $r_{M/P} = 2.39$; violet: $r_{M/P} = 3.26$. For a better overview, not all measured curves are shown.

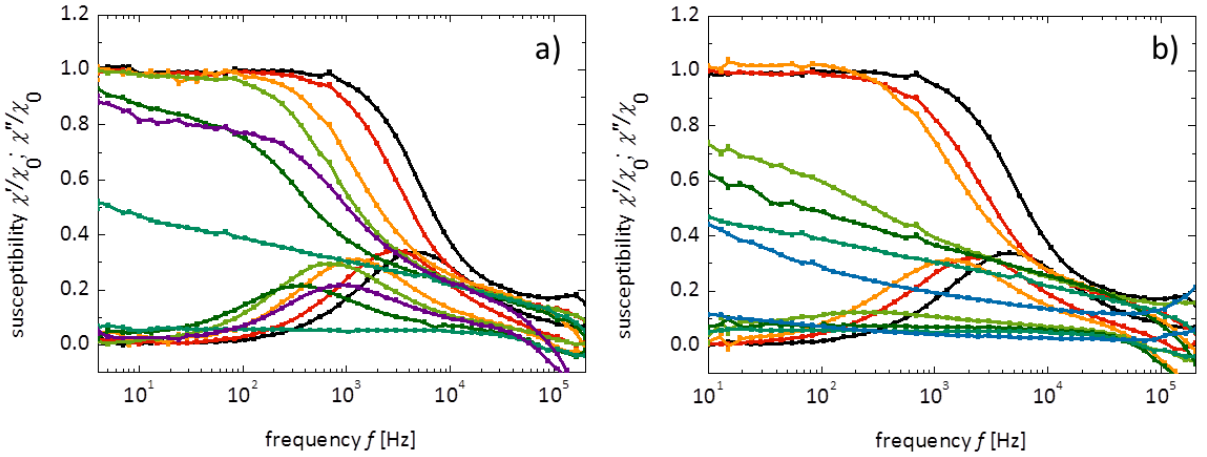


Figure SI-5 Normalized real and imaginary part of the susceptibility χ^* for a) Mn^{2+}/PEG-$(L)_4$ and b) Co^{2+}/PEG-$(L)_4$ with different $r_{M/P}$ ratios. The polymer mass fraction is $\mu_{PEG} = 3.8$ m% for all polymer samples. Black: $r_{M/P} = 0$; red: $r_{M/P} = 0.43$; light orange: $r_{M/P} = 0.87$; green: $r_{M/P} = 1.09$; dark green: $r_{M/P} = 1.52$; turquoise: $r_{M/P} = 1.95$; light blue: $r_{M/P} = 2.17$; magenta: $r_{M/P} = 2.72$. For a better overview, not all measured curves are shown.

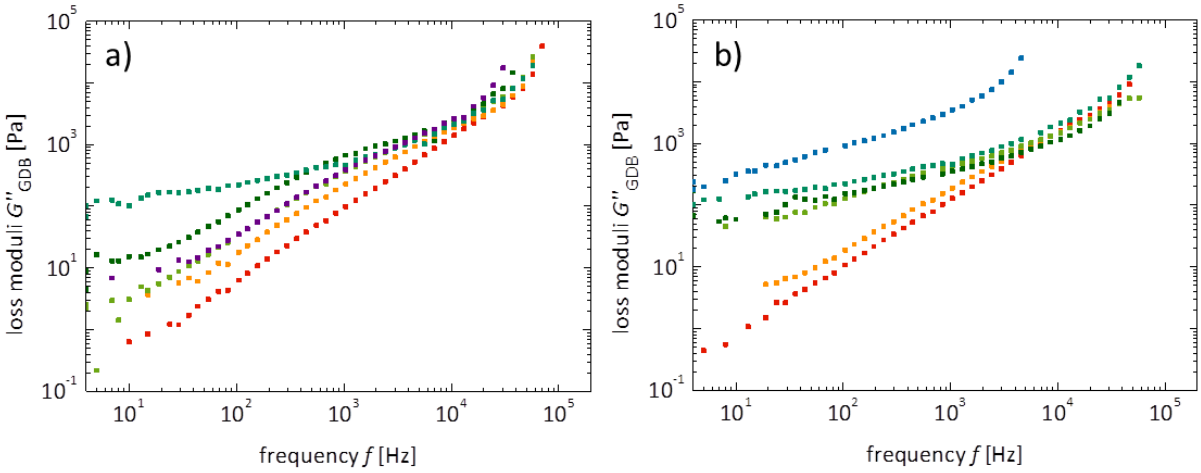


Figure SI-6 Loss moduli G'' determined by the *GDB* model in dependence on frequency f for a) Mn^{2+}/PEG-$(L)_4$ and b) Co^{2+}/PEG-$(L)_4$ with different $r_{M/P}$ ratios. The polymer mass fraction is μ_{PEG} = 3.8 m% for all polymer samples. Red: $r_{M/P}$ = 0.43; light orange: $r_{M/P}$ = 0.87; green: $r_{M/P}$ = 1.09; dark green: $r_{M/P}$ = 1.52; turquoise: $r_{M/P}$ = 1.95; light blue: $r_{M/P}$ = 2.17; magenta: $r_{M/P}$ = 2.72. For a better overview, not all measured curves are shown.

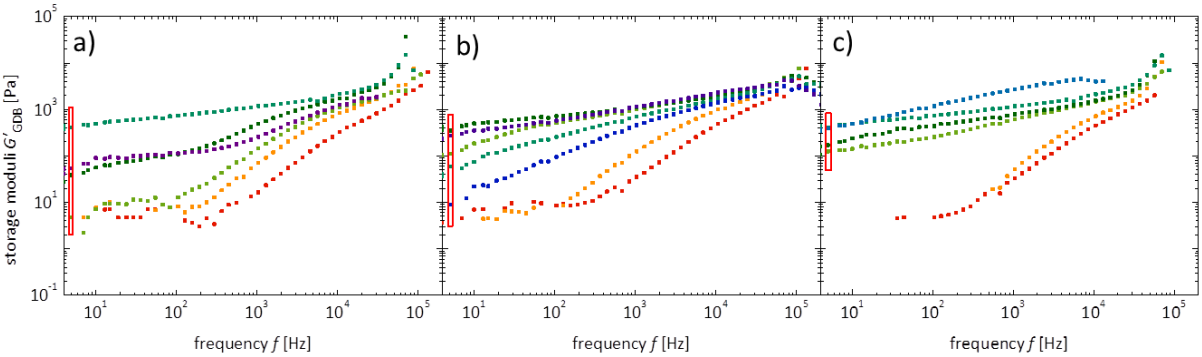


Figure SI-7 Storage moduli G'' determined by the *GDB* model in dependence on frequency f for a) Mn^{2+}/PEG-$(L)_4$, b) Zn^{2+}/PEG-$(L)_4$ and c) Co^{2+}/PEG-$(L)_4$ with different $r_{M/P}$ ratios. The polymer mass fraction is μ_{PEG} = 3.8 m% for all polymer samples. Red: $r_{M/P}$ = 0.43; light orange: $r_{M/P}$ = 0.87; light green: $r_{M/P}$ = 1.09; dark green: $r_{M/P}$ = 1.52; turquoise: $r_{M/P}$ = 1.95; light blue: $r_{M/P}$ = 2.17; dark blue: $r_{M/P}$ = 2.39; magenta: $r_{M/P}$ = 2.72; violet: $r_{M/P}$ = 3.26. For a better overview, not all measured curves are shown. The data points marked in red at 5 Hz are used to calculate ν for $r_{M/P}$ > 1.

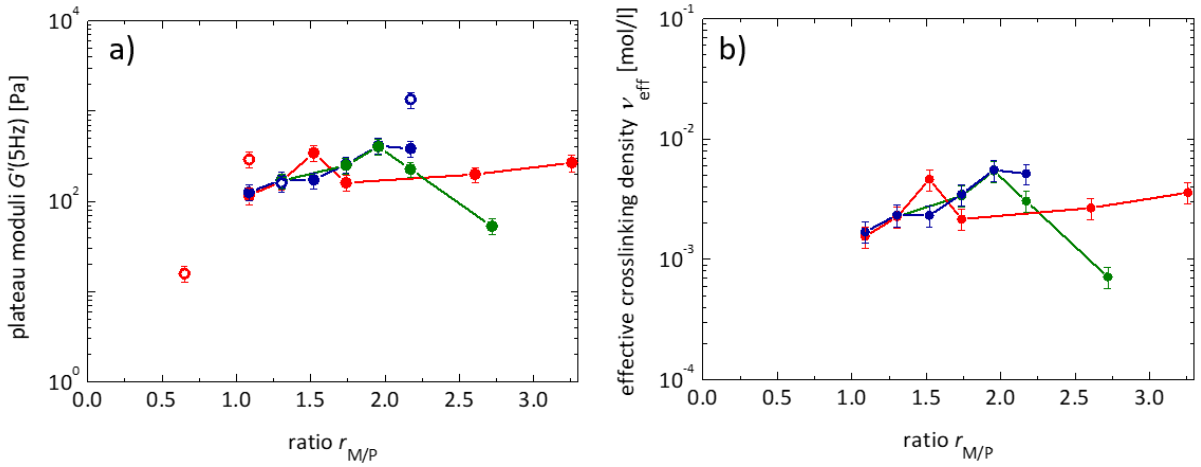
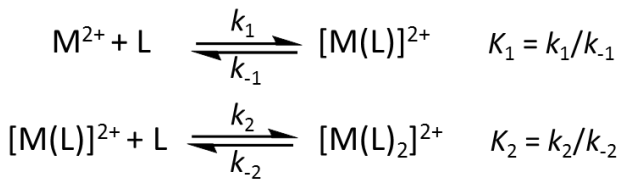


Figure SI-8 a) G' at 5Hz from AC susceptometry measurements and b) crosslinking density ν for different M^{2+}/ PEG-$(L)_4$ systems (Mn^{2+}(green), Zn^{2+} (red) and Co^{2+} (blue)) for μ_{PEG} = 3.8 m% and varying ratio $r_{M/P}$. Macroscopic values are shown as empty circles.

a)



b)

metal ion M^{2+}	K_1 $[M(L)]^{2+}$ [$Lmol^{-1}$]	K_2 $[M(L)_2]^{2+}$ [$Lmol^{-1}$]	K_{bis} $[M(L)_2]^{2+}$ [L^2mol^{-2}]
Mn^{2+}	$2{,}5 \cdot 10^4$	$5{,}2 \cdot 10^2$	$1.3 \cdot 10^7$
Zn^{2+}	$1{,}0 \cdot 10^6$	$2{,}2 \cdot 10^6$	$2.2 \cdot 10^{12}$
Co^{2+}	$2{,}5 \cdot 10^8$	$8{,}0 \cdot 10^9$	$2.0 \cdot 10^{18}$

Figure SI-9 a) Scheme for the complex formation of a biscomplex containing two ligands and b) Complex formation constants *K* for different metal ions.[1–3]

References

[1] T. Rossow, S. Seiffert, *Polym. Chem.* **2014**, *5*, 3018–3029.
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[3] R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, R. G. Wilkins, *Inorg. Chem.* **1965**, *4*, 929–935.