Electronic Supplementary Material (ESI) for Soft Matter.

Scale-dependent particle diffusivity and apparent viscosity in polymer solutions as probed by dynamic magnetic nanorheology

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1. Particle size and shape of probe particles

1.1 Ni nanorods

TEM images of the Ni-based nanorod batches NR2 and NR3 are displayed in Fig. S1 together with the respective histograms for the rod length. The metallic Ni core of the nanorods provides a distinct contrast in TEM images and the length and diameter of the particles can be readily determined. The respective information on NR1 is presented in Figure 1 of the main paper, and the respective parameters are summarized in Table 1.

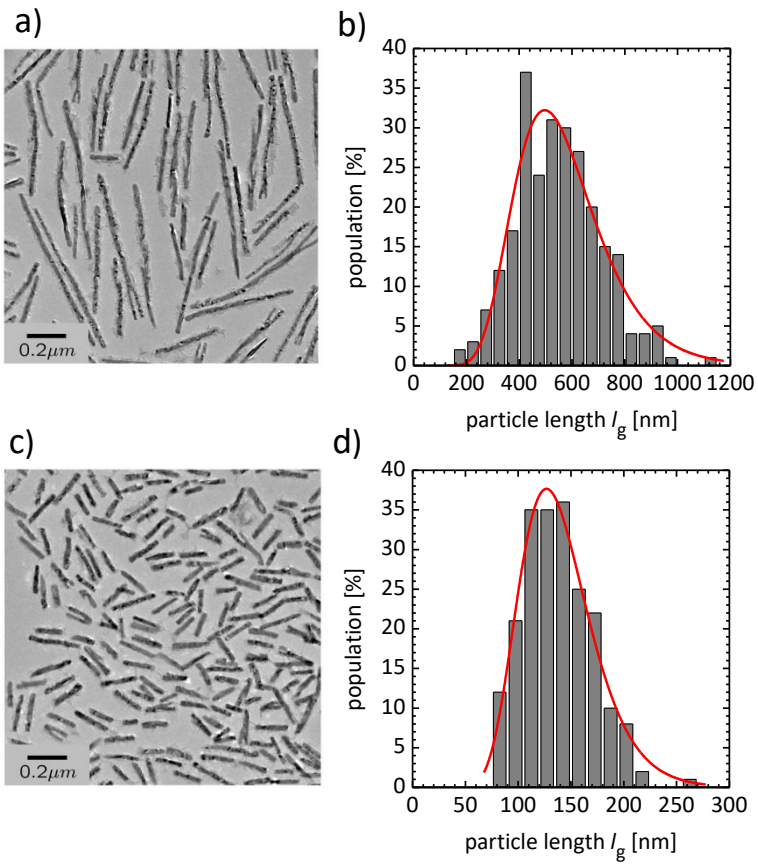


Figure S1. TEM images and corresponding rod length histograms (L_g) for NR2 (a), b)) and NR3 (c), d)) nanoparticles employed as magnetic probes in this study.

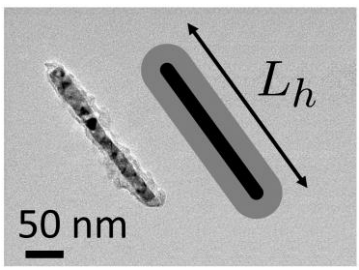


Figure S2.High resolution TEM image of a single Ni nanorod revealing an oxide shell encapsulating the metallic Ni core.

At high magnification of single nanorods as seen in Figure S2, an additional faint contrast is visible, caused by aluminate residues from the template that were not completely dissolved in the extraction process. In addition to the nickel oxide surface layer and polymer surfactants, these residues significantly increase the hydrodynamic size of the nanorods as compared to the metallic Ni core. The substantial roughness of the aluminate shell leads to a further increase in the hydrodynamic friction as compared to a cylinder with smooth surface. As a result, the effective hydrodynamic size of the Ni nanorods is considerably larger than the metallic Ni core.

1.2 Spherical CF particles

In Figure S3, a TEM image of the cobalt ferrite-based nanoparticle batch CF2 are shown together with the histogram for the particle diameter. The respective information on CF1 is presented in Figure 1 of the main paper, and the respective parameters are summarized in Table 1.

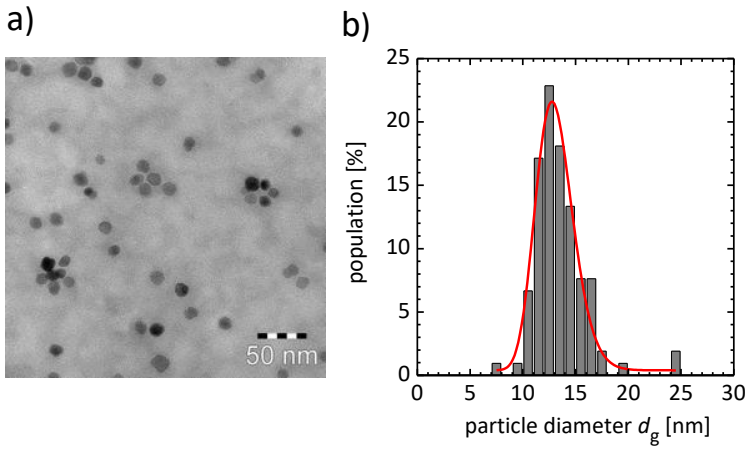


Figure S3. a) TEM image and b) corresponding histogram for CF2 nanoparticles employed as magnetic probes in this study.

2. Characterization of Ni nanorods by static field-dependent optical transmission (SFOT)

The geometry factor K_m of a particular batch of nanorod probes that is needed for the quantitative nanorheological data analysis of OFOT experiments can be determined from a calibration measurement in a Newtonian liquid of known viscosity. The characteristic distribution $P(K_m)$ can consequently be used in the analysis of OFOT measurements, provided that the nanorods do not aggregate during dispersion in the polymer solution. This premise is tested and confirmed by static field-dependent optical transmission (SFOT) measurements.

Nickel nanorods exhibit collinear uniaxial ferromagnetic and optical anisotropy, with different optical extinction cross sections $C_{ext,L}$ and $C_{ext,T_{1,2}}$ for longitudinal and the two transversal polarization directions relative to the rod axis. The optical transmittance along a path s through a dilute dispersion of N_r nanorods per unit volume in a transparent matrix follows the Beer-Lambert law, $I/I_0 = \exp(-sN_r\langle C_{ext}\rangle)$, with the incident and transmitted intensities I_0 and I, respectively. In zero field, i.e. at isotropic orientation distribution, the mean extinction cross section $\langle C_{ext}\rangle_\times = (C_{ext,L} + C_{ext,T_1} + C_{ext,T_2})/3$. With increasing external field H, alignment of the nanorods against thermal energy results in a characteristic field-dependent transmittance. In the transmittance of linearly polarized light, normalized to the zero-field transmittance

$$I(H)_{\perp,||}/I_\times = \exp\left(-N_r s\left(\langle C_{ext}\rangle_{\perp,||}(H) - \langle C_{ext}\rangle_\times\right)\right) \qquad \text{(S1)}$$

the field-dependent mean optical cross sections $\langle C_{ext}\rangle_{\perp,||}(H)$ are different for field direction perpendicular and parallel to the optical polarization direction, respectively. The ensemble average is determined by the second moment $\langle cos^2\beta\rangle$ of the distribution function of the angle β between the magnetic moment (rod axis) and the field direction, and is given by

$$\langle cos^2\beta\rangle = 1 + 2/\zeta^2 - 2\coth(\zeta)/\zeta \qquad \text{(S2)}$$

The mean magnetic moment is obtained by fitting the Langevin parameter $\zeta = m\mu_0 H/k_B T$. Further details can be found in Ref.[1].

Under more, SFOT experiments can be used to monitor state of the aggregation of Ni nanorods in colloidal solution, e. g. after destabilization by increasing the ionic strength of the carrier liquid.[2] The consolidation of multiple nanorods results in clusters with a different mean magnetic moment per particle. In particular, the most stable configuration is obtained by two nanorods with antiparallel magnetization and zero total moment. Similarly, the experiments are used to confirm the colloidal stability of the Ni nanorods in the investgated solutions. Regarding the present study, the analyses of SFOT measurements of nanorods in a 4.5 v% PEG-300k solution and results obtained from a dispersion in pure water provide the same mean magnetic moment as seen in Figure S4, so that aggregation of the particles upon dispersion in the polymer solution can be ruled out.

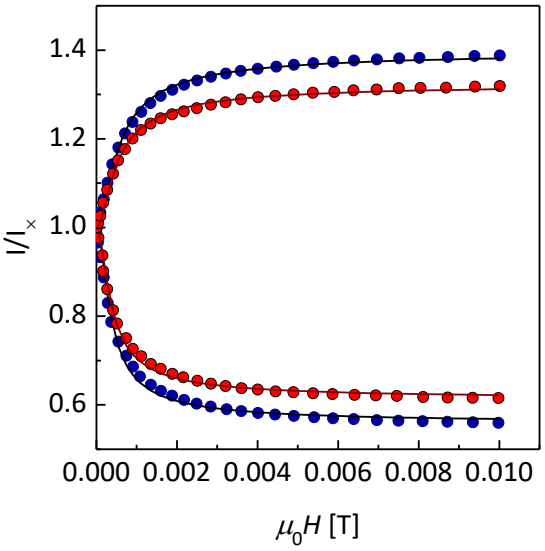


Figure S4**.** Transmittance of linearly polarized light as function of magnetic flux density parallel (lower branch) and perpendicular (upper branch) to the polarization direction, normalized by the transmission at zero field. Analysis of the field-dependence provides identical mean magnetic moments (<m>=3.7(2)·10^{-17} Am^2) of the particles dispersed in water (blue) or 4.5 v% PEG300k solution (red). The different splitting of the branches is caused by different concentrations of nanorods in the two specimens.

3. Characterization of P300k by macrorheology

From previous experiments[3] it is known that the specific viscosity η_{sp} of aqueous PEG solutions with different molar mass exhibit a common master curve when plotted vs the reduced viscosity $[\eta]/c$. The intrinsic viscosity $[\eta]$ depends on the molar mass, as described by the Mark-Houwink equation $[\eta] = 0.032\, M_w^{0.71}\ cm^3/g$.[3] Fitting experimental data by rescaling the master curve thus provides the intrinsic viscosity of the PEO under investigation and thus the molar mass can be determined. The best approximation of the experimental results for P300k2 is shown in Figure S3, From the master curve (solid line), an intrinsic viscosity $[\eta] = 310\ \mathrm{cm}^3/\mathrm{g}$ is obtained which results in $M_w = 410000\ \mathrm{g/cm}^3$. Similarly, by using the empirical stretched exponential function,[4] and the specific values for the model parameters, the analysis of the experimental results in Figure S5 with all parameters fixed and the molar mass as the only fit parameter, provides as the best approximation for $M_w = 410000\ \mathrm{g/cm}^3$ (dash-dotted line), thus confirming the above finding.

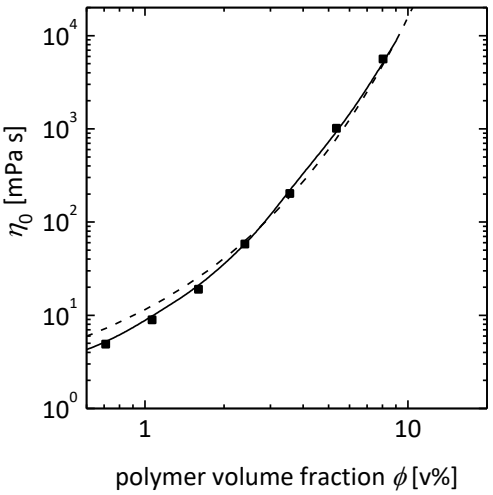


Figure S5. Macroscopic zero-shear rate viscosity of P300k2 solutions as function of concentration. The fit using a) the master curve and Mark-Houwink relation from reference[3] (solid line) and b) the model function and parameters by Wisniewska,[4] (dash-dotted line) provide a mean molar mass of $M_w = 410000\ \mathrm{g/mol}$.

4. OFOT study of PEG300k2 solutions as function of polymer concentration and nanorod size

The OFOT response functions and the corresponding Cole-Cole plots are shown for nanorods with hydrodynamic length L_h=640 nm in Figure S6 and for L_h=210 nm in Figure S7.

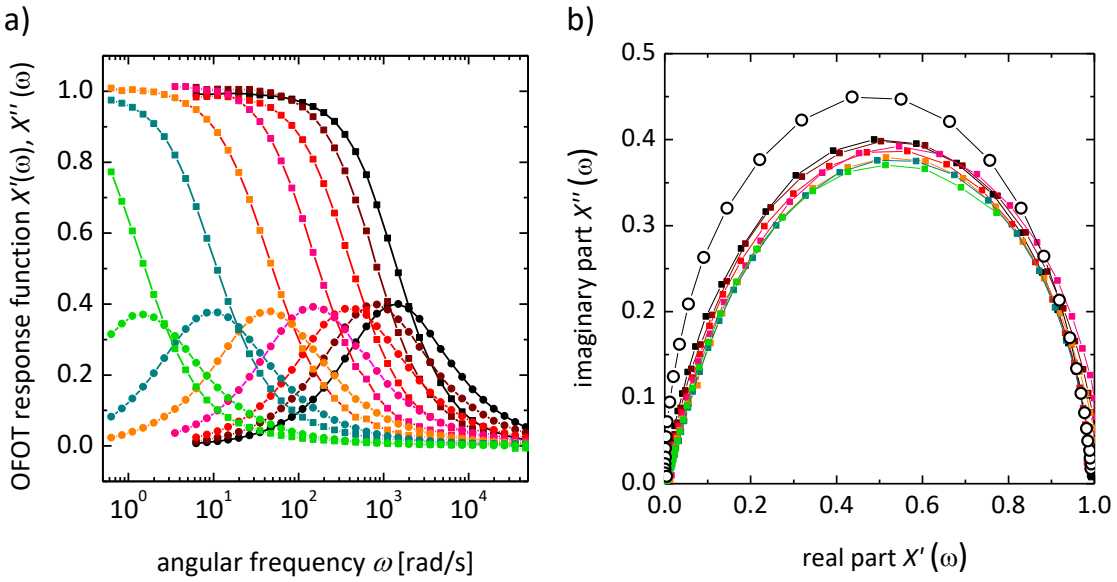


Figure S6. a) Response functions and b) corresponding Cole-Cole-plots, obtained from OFOT measurements using nanorods with hydrodynamic length L_h = 640 nm in PEG00k-solutions (M_w = 410000 g/mol) of different polymer volume fractions (P300k2_0.7 (black), P300k2_1.1 (dark red), PEG300k2_1.6 (red), P300k2_2.4 (pink), P300k2_3.6 (orange) and P300k2_5.4 (dark green), P300k2_8.1 (green). The Cole-Cole plot of a reference measurement of the same nanorods in 12.2 v% PEG10k solution (open symbols) is shown for comparison.

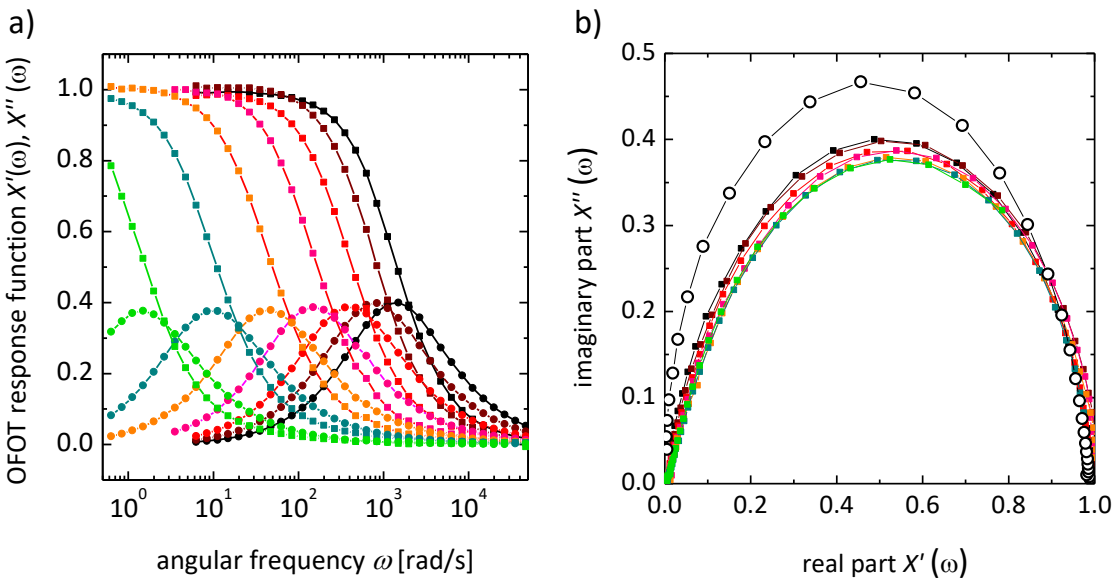
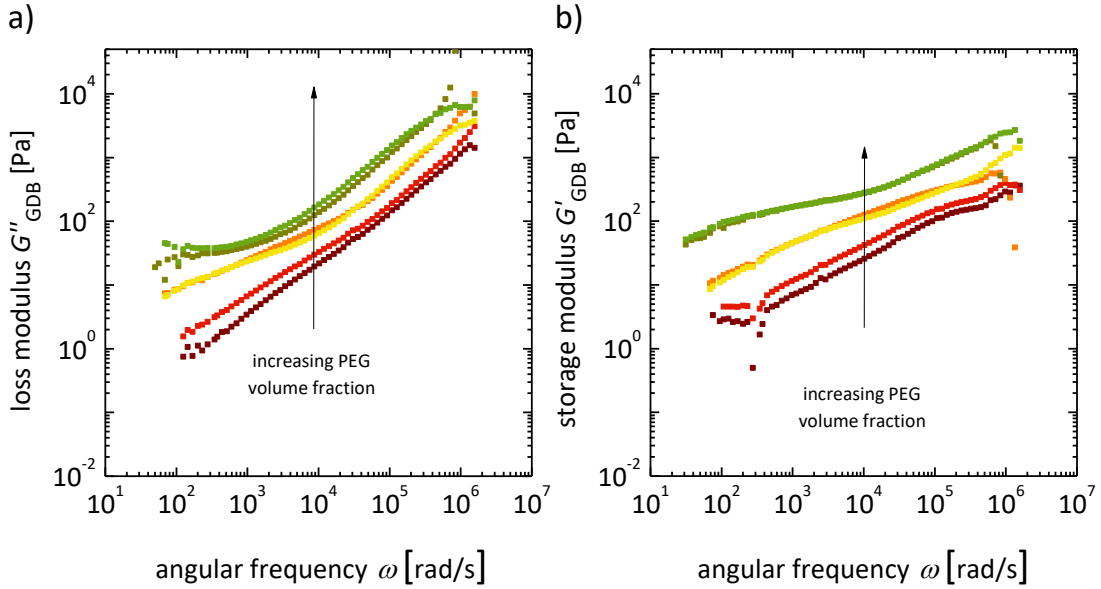


Figure S7. a) Response functions and b) corresponding Cole-Cole-plots, obtained from OFOT measurements using nanorods with hydrodynamic length L_h = 210 nm in PEG00k-solutions (M_w = 410000 g/mol) of different polymer volume fractions (P300k2_0.7 (black), P300k2_1.1 (dark red), PEG300k2_1.6 (red), P300k2_2.4 (pink), P300k2_3.6 (orange) and P300k2_5.4 (dark green), P300k2_8.1 (green). The Cole-Cole plot of a reference measurement of the same nanorods in 12.2 v% PEG10k solution (open symbols) is shown for comparison.

5. ACS study of PEG300k solutions as function of polymer concentration and nanoprobe size

The loss modulus *G''* and storage modulus *G'* of P300k1 solutions with various volume fraction of polymer doped with CF2 particles is shown in dependence on the angular frequency ω in Figure S7.



Si-Fig.8. a) Loss modulus *G''* and b) storage modulus *G'* in dependence on the angular frequency ω for P300k1 solutions doped with CF2 particles; P300k_1.8 (dark red), P300k_4.5 (red), PEG300k_9.0 (orange), P300k_13.5 (yellow), P300k_18.1 (olive green) and P300k_22.8 (light green)).

6. Analysis of PEG300k solution viscosity based on the semi-empirical stretched exponential scaling

The model parameters *a* and *b* can be readily obtained by linear regression of a loglog-plot of

$$\ln(\eta/\eta_s) = bR^a(1/\xi)^a$$

applied to the macroscopic viscosity with $R = R_h$, the hydrodynamic size of the PEG molecule. Using the obtained parameters $b = 1.27$ for P300k2 ($b = 1.39$ for P300k1) and the mean $a = 0.91$ for P300k2 ($a = 0.86$ for P300k1), the nanoviscosities are fitted with only R_{eff} as variable parameter.

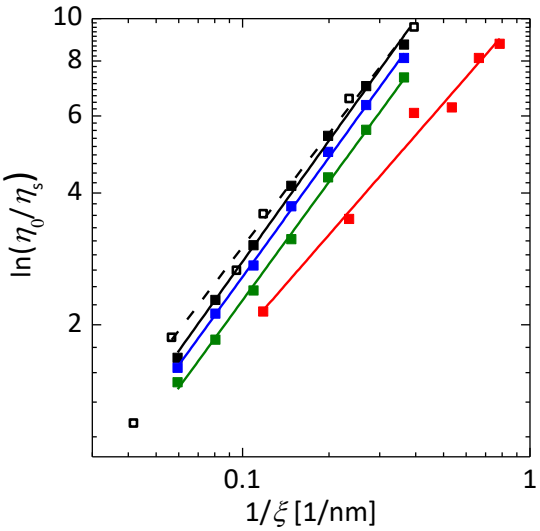


Figure S9. Loglog-plot of $\ln(\eta/\eta_s)$ for the macroscopic viscosity (black, P300k1 (open symbols) and P300k2 (closed symbols)) and the results from OFOT (NR2 (blue) and NR3 (green)) and ACS measurements (CF2 (red)) as function of inverse correlation length. Linear regression provides the model parameters for given $R = R_h$ (macro) or the effective size R_{eff} for fixed *a* and *b*.

Table S1. Fit results for loglog-plot of $\ln(\eta/\eta_s)$ for the macroscopic viscosity and the results from OFOT and ACS measurements as function of inverse correlation length. Here, $n = \log(bR)^a$ is the intercept, $m = a$ is the slope, *b* is given by $b = \left(\frac{10^n}{R_h{}^a}\right)$ and R_{eff} by $R_{eff} = \left(\frac{10^n}{b}\right)^{\frac{1}{a}}$.

sample	*n*	*m*	*b*	R_{eff} [nm]
P300k2	1.36	0.92	1.27	23.24
P300k1	1.34	0.86	1.39	24.59
NR2	1.32	0.91		21.03
NR3	1.26	0.91		18.10
CF2	1.03	0.75		

7. References

1 F. Krämer, M. Gratz and A. Tschöpe, *J. Appl. Phys.*, 2016, **120**, 044301.

2 A. Tschöpe, F. Krämer, K. Birster, M. Gratz and R. Birringer, *Colloids Interface Sci. Commun.*, 2016, **10**–**11**, 11–14.

3 M. Gratz and A. Tschöpe, *Macromolecules*.

4 A. Wiśniewska, K. Sozański, T. Kalwarczyk, K. Kędra-Królik, C. Pieper, S. A. Wieczorek, S. Jakieła, J. Enderlein and R. Hołyst, *Polymer (Guildf).*, 2014, **55**, 4651–4657.