Magnetic Particle Nanorheology in Complex Fluids

Melissa Hermes, Eric Roeben, Lidia Kibkalo, and Annette M. Schmidt

Chemistry Department, Universität zu Köln, Köln, Germany

ABSTRACT

In *Magnetic Particle Nanorheology*, blocked magnetic nanoparticles are used as probes, allowing time-resolved analysis of the dynamic response to an oscillating magnetic field by means of dynamic susceptibility. Here, we present results on a polymeric model system and apply different methods to extract size-sensitive, frequencydependent rheological properties.

INTRODUCTION

In addition to (quasi-)continuous rheological properties of complex materials, an increase in interest is recognized in microscopic probing, relating materials characteristics to its microstructure. An important approach is to use the dynamics of micro- or nanoscopic probe particles, which are analyzed to obtain information on the local dynamics of the matrix on the length scale of the particles,¹ of relevance e. g. for in vivo drug delivery (transport in complex fluids) and for nanocomposites.

When the size of the probe particles gets similar to the characteristic length scales within the material, we expect stringent deviations from the rheological performance as obtained by conventional methods. De Gennes postulated, that the viscosity η of a polymer solution depends on the ratio of probe size *d* to the size of the correlation length ξ .² While for large probes ($d >> \xi$), the behaviour reaches the (quasi-)continuous case, small probes ($d << \xi$) are dominated by the solvent viscosity. Rubinstein extended the model of de Gennes to describe the (translational) mobility of particles in entangled polymer solutions.³ In their computer simulations, Liu et al. further pronounced the impact of the radius of gyration R_g of the polymer.^{4,5}

In this work, we present a systematic experimental study on the rheological properties on the nanoscale by using blocked magnetic nanoparticles as nanoprobes. As introduced in our recent work on Magnetic Particle Nanorheology,⁶ we use AC susceptometry to obtain the dynamic susceptibility of doped polymer solutions between 1 Hz and 250 kHz. Two different semi-empirical and analytical procedures are compared for data analysis, and the results are compared to the respective findings from theory and macroscopic rheology.

THEORETICAL BACKGROUND

Molecular dimensions and solution properties of poly(ethylene glycol) in water

The study is performed on base of poly(ethylene glycol) (PEG) aqueous solutions spanning a wide range of molar mass M (between $1 \cdot 10^3$ g·mol⁻¹ and $3 \cdot 10^5$ g·mol⁻¹) and polymer mass fraction μ (1 m% - 45 m%) as a model system. In this section, important parameters of the polymer solutions are summarized that are significant for the data interpretation. They can either be taken from literature or can be calculated based on established relations in polymer solutions



Figure 1. a) Characteristic length scales (radius of gyration R_g , characteristic length ξ , tube diameter *a*, and b) characteristic relaxation times (of reptation τ_{rep} , mesh

and entanglement relaxation τ_{ξ} and τ_{e} , and probe relaxation τ_{d}) as a function of the polymer volume fraction ϕ . The scratched area is the particle size (r < x < d) and the frequency range in AC susceptometry, respectively.

can generally be described considering two regimes of molecular weight, divided by the entanglement molar mass characterizing the minimal chain length for the chains to entangle. The entanglement and critical molar mass M_e and M_c are taken from literature and are $M_e = 2000 \text{ g} \cdot \text{mol}^{-1}$ and $M_c = 5870 \text{ g} \cdot \text{mol}^{-1.9}$ Further we differentiate between semi-diluted and concentrated solutions. Depending on the chain length, a characteristic polymer fraction (expressed as volume fraction ϕ or mass fraction μ) is observed where chain overlapping and entanglement interaction occurs.

The overlap concentration ϕ^* and the entanglement concentration ϕ_e of the polymers are calculated using¹⁰

$$\phi^* \approx N^{(1-3\nu)} \text{ and } \phi_{e} \approx \left(\frac{N_{e}(1)}{N}\right)^{(3\nu-1)}$$
 (1)

with $N = M/M_0$ is the number of Kuhn segments ($M_0 = 132 \text{ gmol}^{-1}$) of the polymer and the molar mass of a Kuhn monomer M_0^9 and $N_{\rm e}(1) = 11.50$ is the number of Kuhn monomers in an entanglement strand in the melt. Both characteristic concentrations decrease with increasing molar mass of the polymer *M*. With *v* being the Flory exponent $(v = 0.588)^3$ for a polymer in an athermal solvent, the respective scaling exponents can be calculated as -0.76.

For the understanding of the dynamics of nanoscopic particles in complex fluids, the respective relation of length scales between particle size and correlation length in the solution are important. We can estimate the molecular size and the effective distance between the molecules using the following relations.

The radius of gyration R_g of a polymer chain is given by¹⁰

$$R_{\rm g}(\phi) = b \sqrt{\frac{N}{6}} \phi^{-(\nu - 1/2)/(3\nu - 1)}$$
(2)

with b the length of a Kuhn segment $(b = 1.1 \text{ nm}).^{9,10}$ The scaling exponent is -0.11, thus the molecular size weakly decreases with increasing polymer fraction. This is illustrated in Fig. 1a. The scratched area represents the length scale of the particle probes ($r < R_g < d$, with r and d the particle radius and diameter, respectively). From the plot it is found that from the polymers investigated (colored lines), PEG 20k and PEG 35k show a molecular dimension in solution that is in a similar range as the particles. In contrast, the molecular length scale in PEG 1k is much smaller than the particles, while the radius of gyration for PEG 300k is much larger.

The effective average distance between two polymer molecules in solution is estimated based on the correlation length ξ and the tube diameter *a*. They depend on the volume fraction ϕ of the polymer according to³

$$\boldsymbol{\xi} \approx b \phi^{-\nu/(3\nu-1)} \tag{3}$$

$$a \approx a(1)\phi^{-\nu/(3\nu-1)}$$
 (4)

with a(1) = 3.73 nm is the tube diameter in the melt. The according scaling exponent thus amounts to -0.77 (Fig. 1b), thus both

values decrease with increasing polymer fraction ϕ .³ Because of a(1) > b, the tube diameter a is always larger than the correlation length ξ . It can thus be expected that for polymer volume fractions below 4 v%, both a and ξ are much larger than the particle diameter, while they reach values smaller than the particle size only at high polymer fractions > 40 %.

Characteristic relaxation times are accessible by considering the estimated length scales. We make use of the following relationships:^{3,10}

$$\tau_{\xi} \approx \tau_{0} \left(\frac{\xi}{b}\right)^{3} \quad (5) \quad \tau_{e} \approx \tau_{\xi} \left(\frac{a}{\xi}\right)^{4} \quad (6)$$
$$\tau_{d} \approx \tau_{\xi} \left(\frac{d}{\xi}\right)^{4} \quad (7) \quad \tau_{rep} \approx \tau_{e} \left(\frac{N}{N_{e}(\phi)}\right)^{3} \quad (8)$$

with τ_0 is the relaxation time of a Kuhn monomer $(\tau_0 = 5.43 \ 10^{-9} \ s)^{10}$, τ_{ξ} the relaxation time of a correlation blob with size ξ , τ_e the relaxation time of an entanglement strand, *d* the particle diameter, τ_d the relaxation time of a chain section comparable with the particle size and τ_{rep} the reptation time. $N_e(\phi)$ is calculated using a formula from ref.³.

Accordingly, we expect the relaxation processes that concern local rearrangements of polymer segments (τ_{ε} and τ_{e}) to strongly decrease with increasing polymer fraction with an analogous scaling exponent of -2.31, while τ_{d} and τ_{rep} , related to the probe particle rotation and macromolecular reptation, respectively, increase with increasing polymer fraction. The scaling exponents expected are 0.77 and 1.62 (Fig. 1b) for ideal conditions. While in the first approximation τ_{e} , τ_{d} and τ_{e} are independent from the molar mass, $\tau_{\rm rep}$ increases with N^3 . $\tau_{\rm rep.}$ can further only be observed when $\phi > \phi_{e}$. Relevant relaxation processes like reptation, strand relaxation, particle motion and segment reorganization can thus be expected to occur between 1 Hz and 1 MHz and are thus accessible in a wide range by

Magnetic Particle Nanorheology based on conventional AC susceptometry setups.

Models for Data analysis

Havriliak-Negami

Using the Havriliak-Negami notation known from dielectric spectroscopy and rheology, we obtain the basic characteristics of the underlying relaxation process for solutions with varying molar mass and mass fraction of the polymer component. The Havriliak-Negami model is a semi-empirical equation describing a stretched and asymmetric, Debye-like relaxation process. In a variation of the original Debye equation, the exponents α and β serve as fitting parameters for stretching and asymmetry, respectively. It is further possible to extract information on the respective relaxation time of the process.

For this purpose, the data is displayed in a Cole-Cole diagram by plotting χ_N ' as function of χ_N '' (with χ_N ' and χ_N '' are the real and the imaginary part of the normalized magnetic susceptibility, respectively), and is fitted according to a bimodal relaxation process:¹²

$$\chi_{N}^{*} = \frac{f_{m}}{\left(1 + \left(i\omega\tau_{B,1}\right)^{\alpha_{1}}\right)^{\beta_{1}}} + \frac{(1 - f_{m})}{\left(1 + \left(i\omega\tau_{B,2}\right)^{\alpha_{2}}\right)^{\beta_{2}}}$$
(9)

Gemant-DiMarzio-Bishop

As introduced in our recent paper, direct extraction of frequency-dependent nanorheological properties from susceptometry data is possible by the adaption of the Gemant-DiMarzio-Bishop (GDB)¹⁴ model to the magnetic case, using

$$\frac{\chi^*(\omega) - \chi_{\infty}}{\chi_0 - \chi_{\infty}} = \frac{1}{1 + KG^*(\omega)}$$
(10)

with χ_0 the magnetic susceptibility for $\omega = 0$ Hz, χ_{∞} the susceptibility for $\omega = \infty$ Hz and G^* the complex shear modulus. The constant *K* is given by:

$$K = \frac{4\pi r_{\rm h}^3}{k_{\rm B}T} \,. \tag{11}$$

Here, $r_{\rm h}$ is the hydrodynamic particle radius. The exact evaluation procedure is explained in ref.⁶.

EXPERIMENTAL

Materials and Methods

Chemicals. Poly(ethylene glycol)s (PEGs) (PEG 1k: $M_n = 1,000 \text{ g} \cdot \text{mol}^{-1}$, PEG $M_{\rm v} = 8,000 \text{ g} \cdot \text{mol}^{-1},$ 8k: PEG 20k: $M_{\rm n} = 20,000 \text{ g·mol}^{-1}$, PEG 35k: $M_{\rm n} = 35,000$ $g \cdot mol^{-1}$ and PEG 300k: $M_v = 300,000$ $g \cdot mol^{-1}$) are purchased from Sigma Aldrich. $Fe(acac)_3$, $Co(acac)_2$ and olevel alcohol are obtained from ABCR. Water (ultra pure) and oleylamine are received from Acros Organics. Sodium hydroxide (0.1 M) and oleic acid are purchased from Fisher Scientific.

Sample preparation. CoFe₂O₄ nanoparticles (particle radius: r = 6.6 nm, standard deviation: $\sigma = 0.2$, saturation magnetization: $M_s = 65.8 \text{ A} \cdot \text{m}^2 \text{ kg}^{-1}$, normalized remanence: $M_r/M_s = 0.16$) are prepared using a published procedure, and stabilized in water using poly(acrylic acid).^{7,8} PEG solutions in water are stirred for at least 24 h. The probe particles are added to a final concentration of $3.6 \cdot 10^{-2}$ v% from aqueous dispersion.

Instrumentation. AC susceptometry experiments were performed at 25 °C on a DynoMag (Imego) with a magnetic field amplitude up to 0.4 kA \cdot m⁻¹ and a frequency range between 1-250 kHz. For the measurements, rheological а AR-G2 rheometer (TA Instruments) is used at 25 °C using a cylinder or plate-plate geometry. A more detailed description on particle synthesis, their properties, and methods involved are found in our previous work.⁶

RESULTS AND DISCUSSION Macrorheology

Static macroscopic rheological measurements were performed to obtain flow curves of PEG solutions of different molar masses and mass fractions. The viscosity η is measured in dependence on the shear stress σ and the zero shear viscosity $\eta_{0,s}$ is determined by extrapolation. The zero shear viscosity $\eta_{0,s}$ in function of the mass fraction of polymer μ for the different molar masses of the polymer *M* is

plotted in Fig. 2. An increase of $\eta_{0,s}$ with increasing μ and M is observed. Two regimes with different scaling exponents γ_1 and γ_2 are observed. In the second regime the dependence of $\eta_{0,s}$ on μ is more pronounced, which is due to an enhanced polymer-polymer interaction resulting from the formation of entanglements. The entanglement mass fraction μ_{e} is given by the intersection point of the two regimes and can be compared to the theoretically determined values from Eq. (1). As expected, the entanglement mass fraction μ_{e} decreases with increasing molar mass M and the calculated values are in good agreement with the theoretical calculations.



Figure 2. Zero shear viscosities $\eta_{0,s}$ obtained from macrorheology versus the mass fraction of polymer μ for aqueous PEG solutions of PEG 1k (dots), PEG 8k (triangles up), PEG 20k (triangles down), PEG 35k (squares) and PEG 300k (stars). The entanglement mass fraction μ_e is obtained from intersections.

Table 1. Entanglement mass fraction μ_e and scaling exponents γ_1 and γ_2 for PEGs resulting from theoretical calculations and macroscopic measurements. ϕ is converted to μ using the amorphous density of PEG

$(\rho = 1.128 \text{ g/mol.})^{11}$				
polymer	mass fractions		scaling exponents	
	$\mu_{\mathrm{e,theo.}}[\mathrm{m}\%]$	µ.[m%]	$\gamma_{\rm e} (\mu < \mu_{\rm e})$	$\gamma_2 (\mu < \mu_e)$
PEG 1k ^a	24.03	26.89	0.44 ± 0.07	3.31 ± 0.16
theoretical	-	-	$\gamma_{1} = 1.000$	$\gamma_2 = 3.927$
PEG 8k	31.43	22.57	1.22 ± 0.12	3.62 ± 0.20
PEG 20k	15.89	14.33	1.00 ± 0.10	4.01 ± 0.14
PEG 35k	10.43	11.27	1.04 ± 0.10	4.10 ± 0.20
PEG 300k	2.04	2.01	1.30 ± 0.03	4.48 ± 0.28

^a μ^*

Deviations for low molar mass may be attributed to the experimentally relevant molar mass distribution that has not been considered in the calculations.

Nanorheology

Information on the nanorheology of complex fluids is obtained by detailed analysis of the rotational relaxation behaviour of nanoscaled probe particles. This information is collected using the complex magnetic susceptibility behaviour from AC susceptometry.

Here, the AC susceptometry spectra obtained for aqueous solutions of PEG 35k



Figure 3. Normalized real and imaginary part χ'/χ_0 and χ''/χ_0 of the complex magnetic susceptibility for different mass fractions of PEG 35k solutions (0 - 40 m%) containing CoFe₂O₄@PAA-nanoparticles.

are displayed and discussed as a general example.

Fig. 3 shows the real (χ_N') and the imaginary $(\chi_N '')$ part of the complex viscosity γ^* spectra, both normalized by the initial susceptibility χ_0 . With increasing polymer fraction μ , the frequency at the χ'' maximum shifts to lower frequencies, accompanied by a peak broadening. This is ascribed to increasing viscoelastic properties and to the formation of entanglements, connected with the superposition of different relaxation processes (reptation, strand relaxation, local reorganization, and particle motion).³ As a result, we observe an increase in the distribution of Brownian relaxation times. and in frequency dependence.

Havriliak-Negami (HM)

As an effective method to get a qualitative and empirical view on complex data on relaxation phenomena, the data is analysed according to the Cole-Cole / Havriliak-Negami-type terminology. Fig. 4



Figure 4. Cole-Cole plots for different mass fractions of aqueous polyethylene glycol (PEG 35k) solutions containing CoFe₂O₄@PAA-nanoparticles.

shows the Cole-Cole diagrams that are obtained by plotting χ_N ' against χ_N ' for aqueous solutions of PEG 35k as an example.

It is observed that with increasing polymer mass fraction μ , the curves get more asymmetric and broader. For $\mu > 10$ m%, the curves get distinctly bimodal, indicating the dominance of two different relaxation processes. The empirical parameters α and β describe stretching and asymmetry of a single relaxation process, respectively. To fit the present curves, two additive relaxation processes are assumed,



Figure 5. Mass fraction dependence of the partition parameter $f_{\rm m}$ as obtained by the Havriliak-Negami-function for PEG 35k.

M. Hermes et al.

in accordance from the observation in Cole-Cole diagrams. We find exponents close to 1 for the whole concentration range, while the β exponents decrease from 2 to 1 with increasing polymer fraction. The partition coefficient f_m is nearly 1 for dilute solutions, stable at ~ 0.75 for a large concentration regime, and strongly drops for polymer fractions above 35 m% (Fig. 5), indicating that the slower relaxation process is more dominant in concentrated solutions.

Both relaxation times $\tau_{\rm B,1}$, $\tau_{\rm B,2}$ are increasing with increasing μ , which can be explained with the influence of increasing viscosity that directly impacts both particlerelated relaxation processes, in direct relation to the Brownian relaxation time via the Stokes-Einstein relation.¹³ By plotting τ_1 and τ_2 against the polymer fraction, we extract the characteristic concentration $\mu_{\rm e,HN1}$ and $\mu_{\rm e,HN2}$ for both processes. The results are presented in Fig. 9b and will be discussed below.

Gemant-DiMarzio-Bishop (GDB)

The Gemant-DiMarzio-Bishop model allows a direct deconvolution of (nano)rheological complex moduli from



nanoscopic (triangles) loss moduli G'' versus the frequency for PEG 35k and mass fraction regime from 2 -40 m%.

complex susceptibility data. The loss moduli G'' obtained from macro- and nanorheological measurements as a function of frequency for PEG 35k solutions of various polymer fractions are shown in



Figure 7. Relaxation times τ_1 (filled) und τ_2 (unfilled) versus mass fraction μ_{PEG} of polymer: circles: triangles up: PEG 8k, triangles down: PEG 20k; squares: PEG 35k. Dashed lines are the respective entanglement mass fractions $\mu_{e.}$

Fig. 6. Due to the different frequency ranges, which are covered by the two different methods, there is only a limited overlap range.

While for the macrosopic experiments, G" increases linearly with a scaling exponent of nearly 1 for all investigated polymer fractions up to 40 m%, this is true for the nanscopical data obtained from AC susceptometry only for polymer fractions below 10 m%. For higher polymer concentrations, the deviations from linearity are obvious, and three frequency regimes with different slopes are observed. Additionally, overlay the between macroscopic and nanoscopic values in the overlapping region becomes less optimal. For this comparison, it is important to take into account as well the different frequency regimes as well as the different probe size. We discuss this in more depth below.

By extrapolation of G'' to 1 Hz, an apparent viscosity η_{GDB} is obtained that can be compared to the macroscopic results. From plots of n_{GDB} against the mass fraction (not shown). the characteristic μ concentration of the systems is obtained as the intersection of the two scaling regimes. The scaling exponents in the polymer mass fraction regimes 1 and 2 give more information on the underlying processes and are discussed in comparison to μ_{theo} and μ_{HN} in the following section.



Figure 8. Plot of the macroscopic (circles) and nanoscopic (squares) loss G'' (filled) and storage G' moduli (unfilled) versus the frequency for aqueous solutions of PEG 35k (40 m%).

Considering the combined spectra of G'and G'', Fig. 8 compares the macrorheology results to the nanoscopic ones derived by the GDB model for and $\mu = 40 \text{ m}\%$ as an example. The moduli determined by the different methods are in the same scale. In contrast to that, the absolute values and the behavior of the increase of the moduli are different. It can generally be stated that for PEG 35k and at sufficiently high polymer fractions ($\mu > 35 \text{ m}\%$), the storage modulus G' is higher than the loss modulus G''. For higher frequencies G'' is larger than G', which means that at short times the viscous properties are dominating.

(macroscopically At 40 m%, both derived) moduli increase at low frequencies in accordance with the expectations from the Maxwell model, with respective scaling exponents of ~ 1 and ~ 2 . Due to the different frequency ranges covered by the two different methods, there is only a small overlap range. In the frequency range of $1 \text{ Hz} - 10^2 \text{ Hz}$, thus between the intersection of the nanoscopic G'' and G' spectra with the respective macroscopic ones, G' and G''possess a synchronically course and scale with an exponent of nearly 0.5 with frequency.

This frequency regime is in agreement with the reptation relaxation time scale of the respective system (see Fig. 1). For an analogous solution with a polymer fraction of 35 m%, we find the analogous transition at lower frequencies. It can generally be summarized that the frequency range characterized by critical behaviour is pronounced in the range where r (or d) of the particle probes, and R_g or \mathcal{E} overlap. The slope of the overlapping part of the curves is ~0.5, indicating a probable subdiffusive particle motion.

At higher frequencies the increase of the loss modulus G'' reaches a slope of about 1 in accordance with predictions from theory.⁹

From the cross section respectively the points of contact of G' and G'' for the different solutions. the characteristic times $(\tau_1 \text{ and } \tau_2)$ can relaxation be determined as a function of μ . The results are presented in Fig. 7. It can be stated that the obtained relaxation times within he experimental window are in the time scale expected for characteristic relaxation times of entangled polymer solutions. More information on the nature of the relaxation observed obtained processes is from comparing to the theoretical prediction.³

From experiments it is observed that τ_1 increases with increasing μ for all chain lengths. Again, two different scaling regimes are observed with $\gamma_1 < 1$ and $\gamma_2 \sim 2 - 3$. It also increases (less pronounced) with *M*. From the range and the trend of the values, this relaxation is most probably related to τ_d .

In contrast, the faster relaxation time τ_2 is nearly independent from *M*. It is most probably related to τ_{ξ} , although the values are higher than expected from theory. To get a better overview on the scaling behavior of τ_2 , more data points are needed.

Comparison of the characteristic concentrations and scaling exponents

The entanglement concentrations μ_e (or μ_1) and the scaling exponents γ determined by macroscopic measurements and by nanorheology as obtained by the HN and the GDB model are combinded to theoretical predictions in dependence of the molar mass



Figure 9. a) Experimental entanglement concentration (squares: $\mu_{e,theo.}$, triangles: $\mu_{e,macro}$, circles: $\mu_{1,GDB}$, stars: $\mu_{1,HN}$) and b) experimental scaling exponents (solid line: $\gamma_{1,theo.}$, filled triangles: $\gamma_{1,macro}$, filled circles: $\gamma_{1,GDB}$, filled stars: $\gamma_{1,HN}$ and unfilled: corresponding γ_{2}) in dependence of on the molar mass of the polymer *M*.

of the polymer M in Fig. 9. All methods show a decrease of the entanglement concentration μ_e with increasing molar mass of polymer. For PEG 1k, the overlap concentration μ^* is compared instead of the entanglement concentration μ_{e} . For the latter, we find the expected scaling behavior and absolute values concerning both μ_{e} and the scaling exponents γ_1 and γ_2 for the macroscopic behavior. For PEG 1k, we generally find a good correspondence between theoretical values, macro- and also the nanoscopically derived values, in correspondence with the almost Newtonian behavior of these solutions. In contrast, we find that experimentally determined values for $\mu_{\rm e}$ are lower than the theoretically calculated ones and the nanoscopic values most pronounced for the intermediate molar mass regime where $r < R_g < d$, as predicted from theory. With respect to the scaling exponents, γ_1 as obtained from nanoscopic analysis is clearly below 1. This again is in accordance with predictions. For γ_2 , we see deviations (lower scaling exponents) than predicted for all non-Newtonian solutions with $M > M_{e}$ (see Fig. 1). The latter effect is more pronounced for higher molar mass and may be attributed to the similarity of particle size and tube diameter.

CONCLUSIONS

Using blocked magnetic nanoparticles as nanoscopic probes, information on the

rheological characteristics on complex fluids can be extracted by proper interpretation of AC susceptometry data. In a systematic study, we obtain information on the viscosity, the entanglement concentration, and characteristic relaxation times on the nanoscale for a series of aqueous PEG solutions, and compare the results to macrorheological and theoretical values.

low molar mass, For а good correspondence of all results is observed. confirming the validity of the approach. With increasing molar mass and polymer fraction, however, increasing deviations between macrorheological and nanoscopic results. The entanglement concentration found for the nanoprobes is lower than the macroscopic result for intermediate chain lengths, where the radius of gyration is comparable to the particle size. The scaling exponents are generally lower for the nanorheology experiments, in particular for long, entangled polymers. Qualitatively, the results agree with the expectations, and more detailed insight into the underlying mechanisms is expected from future investigations.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support from the DFG (SPP 1681). Melissa Hermes acknowledges support by the International Helmholtz Research School of Biophysics and Soft Matter (IHRS BioSoft).

REFERENCES

1. Waigh, T.A. (2016), "Advances in the Microrheology of Complex Fluids", *Reports on Progress in Physics*, **79**, 74601.

2. De Gennes, P.-G. (1979), "Scaling Concepts in Polymer Physics", Cornell University Press.

3. Cai, L.-H., Panyukov, S. and Rubinstein, M. (2011), "Mobility of Nonsticky Nanoparticles in Polymer Liquids", *Macromolecules*, **44**, 7853–7863.

4. Liu, J., Cao, D. and Zhang, L. (2008), "Molecular Dynamics Study on Nanoparticle Diffusion in Polymer Melts: A Test of the Stokes-Einstein Law", *The Journal of Physical Chemistry C*, **112**, 6653–6661.

5. Holyst, R., Bielejewska, A., Szymański, J., Wilk, A., Patkowski, A., Gapiński, J., Żywociński, Kalwarczyk, A., Т., Kalwarczyk, E. and Tabaka, M. (2009), "Scaling Form of Viscosity at All Length-Scales in Poly (Ethylene Glycol) Solutions Studied by Fluorescence Correlation Spectroscopy Capillary and Electrophoresis", Physical Chemistry Chemical Physics, 11, 9025–9032.

6. Roeben, E., Roeder, L., Teusch, S., Effertz, M., Deiters, U. and Schmidt, A. (2014), "Magnetic Particle Nanorheology", *Colloid and Polymer Science*, Springer Berlin Heidelberg, **292**, 2013–2023.

7. Sun, S., Zeng, H., Robinson, D.B., Raoux, S., Rice, P.M., Wang, S.X. and Li, G. (2004), "Monodisperse MFe2O4 (M = Fe, Co, Mn) Nanoparticles", *Journal of the American Chemical Society*, American Chemical Society, **126**, 273–279.

8. Dai, Q., Lam, M., Swanson, S., Yu, R.-H.R., Milliron, D.J., Topuria, T., Jubert, P.-O. and Nelson, A. (2010), "Monodisperse Cobalt Ferrite Nanomagnets with Uniform Silica Coatings", *Langmuir*, American Chemical Society, **26**, 17546–17551.

9. Fetters, L.J., Lohse, D.J. and Colby, R.H.

(2006), "Physical Properties of Polymers Handbook", Springer, Berlin.

10. Rubinstein, M. and Colby, R.H. (2003), "Polymer Physics", Oxford University, New York.

11. "Average Density of Amorphous Polymers",

http://polymerdatabase.com/polymer

physics/Polymer Density.html (accessed 09.02.2017).

12. Havriliak, S. and Negami, S. (1966), "A Complex Plane Analysis of or-Dispersions in Some Polymer Systems", *Journal of Polymer Science: Part C*, **14**, 99–117.

13. Einstein, A. (1905), "On the Movement of Small Particles Suspended in Stationary Liquids Required by the Molecular-Kinetic Theory of Heat", *Annalen der Physik*, **17**, 549–560.

14. DiMarzio, E.A. and Bishop, M. (1974), "Connection between the Macroscopic Electric and Mechanical Susceptibilities", *The Journal of Chemical Physics*, **60**, 3802– 3811.