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Supplementary Information

Tailoring length and viscosity of dynamic metallo-supramolecular polymers in solution

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Contents

1. Theory of static light scattering (SLS)

In static light scattering experiments, macromolecules in solution are irradiated by laser light of wavelength, λ_0, which scatters in all directions (Rayleigh scattering). The intensity of the scattered laser light depends on the scattering angle, θ, if scattered by macromolecules larger in size than $\lambda_0/20$. The Rayleigh ratio, R_θ, is determined in the following way. The scattered intensity of three different liquids is recorded, that is the toluene, $I_{standard}$, the solvent $I_{solvent}$, and the solution of MEPE, I_{MEPE}. If the scattered intensities are measured using the same experimental setup, R_θ can be calculated as

$$R_\theta = \frac{I_{MEPE} - I_{solvent}}{I_{standard}} R_{standard} \cdot \left(\frac{n_{solvent}}{n_{standard}}\right)^2 \tag{1}$$

with $R_{standard}$ as the Rayleigh ratio of the standard, that is toluene and the refractive indices of solvent, $n_{solvent}$, and standard, $n_{standard}$.[1-3] $R_{standard}$ is known as 1.4×10^{-3} m^{-1} at an irradiation wavelength of λ_0 = 632.8 nm and as 5.8×10^{-4} m^{-1} at an irradiation wavelength of λ_0 = 784.0 nm. Both values refer to a sample temperature of 23 °C.[4, 5] The scattering vector, q, is given by:[1, 3]

$$q = \frac{4\pi n_{solvent}}{\lambda_0} \cdot sin\left(\frac{\theta}{2}\right) \tag{2}$$

with $n_{solvent}$ being the refractive index of the solvent at 23 °C and θ the scattering angle.
The optical constant, K, is calculated as

$$K = \frac{4\pi^2 n_{solvent}^2}{N_A \lambda_0^4} \cdot \left(\frac{dn_s}{dc}\right)^2 \tag{3}$$

with N_A being the Avogadro number, c the concentration of MEPEs in solution, and $\frac{dn_s}{dc}$ the refractive index increment of the solution, which is defined as

$$\left(\frac{dn_s}{dc}\right) = \frac{n_s - n_{solvent}}{c} \tag{4}$$

where n_s is the refractive index of the solute. The refractive index increment, $\frac{dn_s}{dc}$, depends on the difference in polarizability of solute and solvent.[1, 3]

In order to calculate the weight average molar mass, $\overline{M}_w$, and the radius of gyration, r_g, of the MEPEs, solutions with defined ratios, z, are prepared and diluted. The intensity of the scattered light depends on variation of the concentration, c, and the scattering angle, θ, which results in different Rayleigh ratios, R_θ. The obtained Rayleigh ratios, R_θ can be plotted via a Zimm plot,[1, 3, 6] which is based on the formula

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_w\left(1 - \frac{1}{3} r_g^2 q^2\right)} + 2A_2c \tag{5}$$

where A_2 is the second virial coefficient. The evaluation of static light scattering measurements requires two extrapolations: On the one hand, the KcR_θ^{-1} values are extrapolated to an interference-free condition, that is $\theta \rightarrow 0$, which leads to an extrapolation of the scattering vector, $q^2 \rightarrow 0$, on the other hand the values are extrapolated to a interaction-free condition, that is $c \rightarrow 0$. For this purpose, a Zimm plot is carried out, considering Guinier's method.[7, 8] Guinier and Fournet[8, 9] showed that the scattering vector can be approximated over a wide range of q^2 by:

$$1 - \frac{1}{3} r_g^2 q^2 = e^{-\frac{1}{3} r_g^2 q^2} \tag{6}$$

With the approximation at hand, Wesslau[8, 10] proposed the Guinier–Zimm plot

$$ln\left(\frac{Kc}{R_\theta}\right) = ln\left(\frac{1}{\bar{M}_w\left(e^{-\frac{1}{3} r_g^2 q^2}\right)} + 2A_2c\right) \tag{7}$$

where $ln\left(KcR_\theta^{-1}\right)$ is plotted against $(q^2 + kc)$, as shown exemplary in Figure S1 for the static light scattering measurement of a Ni-MEPE solution with chain termination ratio, $z = 1$. k is an arbitrary constant, a scaling factor which is freely selectable.

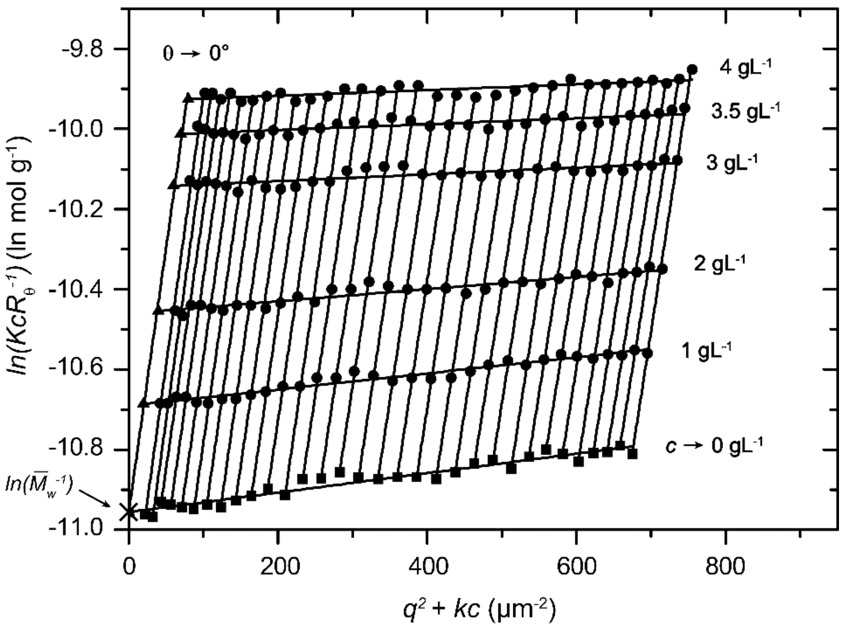

Figure S1. *Guinier-Zimm plot of Ni-MEPE in acetic acid solution (75 vol %) with 0.1M KOAc without chain-stopper ($z = 1$) at a temperature of 23 °C. The rayleigh ratio, R_θ, is measured for five different concentrations, ranging from 1 g L^{-1} to 4 g L^{-1} and from 32 different angle positions of the detectors, ranging from 20° to 144°. The scaling factor k of the Zimm plot is set to 20 L g^{-1} μm^{-2}. The $ln(KcR_\theta^{-1})$ values are extrapolated to $\theta \to 0$, that is $q^2 \to 0$, (triangles) and to $c \to 0$ (rectangles).*

From the intercept of the extrapolation curve, $q^2 \to 0$, the weight average molar mass, $\bar{M}_w$, can be estimated as follows (see also Figure S1):

$$\lim_{\substack{q^2 \to 0 \\ c \to 0}} \left(ln\left(\frac{Kc}{R_\theta}\right) \right) = ln\left(\frac{1}{\bar{M}_w}\right) \tag{8}$$

The radius of gyration, r_g, or more exactly, the z-average of the squared radius of gyration, $\langle r_g^2 \rangle_z$, is defined as the average of the squared distance between a point of a polymer and the center of mass, r_i:

$$\langle r_g^2 \rangle_z = \frac{1}{N} \sum_{i=1}^{N} |r_i|^2 \tag{9}$$

Also r_g can be obtained from the slope of the extrapolation curve of $ln(KcR_\theta^{-1})$ to $c \to 0$:

$$\frac{d\left(\lim_{c \to 0}\left(ln\left(\frac{Kc}{R_\theta}\right)\right)\right)}{d(\mathrm{q}^2)} = \frac{r_g^2}{3} \tag{10}$$

From the slope of the extrapolation curve, $q^2 \rightarrow 0$, the second virial coefficient, A_2, respectively, can be estimated:[1, 3, 8]

$$\frac{d\left(\lim_{q^2 \rightarrow 0}\left(\frac{Kc}{R_\theta}\right)\right)}{dc} \cdot k = 2A_2 \tag{11}$$

The applicability of static light scattering measurements on non-covalent polymers is discussed in Chapter 4.

2. Determination of intrinsic viscosities

The intrinsic viscosity, $[\eta]$, is obtained from an extrapolation of the reduced viscosity, η_{red}, to $c = 0$ g L^{-1},

$$[\eta] = \lim_{c\to 0}\left(\frac{\eta_{sp}}{c}\right) = \lim_{c\to 0}(\eta_{red}) \tag{12}$$

which is the so-called Huggins-plot,[11, 12] as shown exemplary in Figure S2 for determination of $[\eta]$ by extrapolation of the reduced viscosities, η_{red}, of Fe-MEPE.

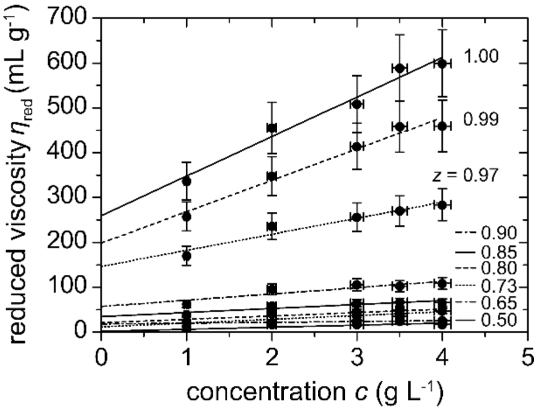

Figure S2. *Huggins-plots of the reduced viscosity, η_{red}, of Fe-MEPE in acetic acid solution (75 vol %) with 0.1M KOAc as a function of the MEPE concentration, c, and at different chain termination ratios, z, measured at a temperature of 23°C.*

As can be seen in Figure S2, the reduced viscosity, η_{red}, increases linearly with concentration in 0.1M KOAc acetic acid solution (75 vol%). Thus, the intrinsic viscosity, $[\eta]$, is reliably determined from the Huggins-plots.[13]

3. Determination of the hydrodynamic radii

A dynamic Zimm plot is generated by measuring the diffusion coefficients, D, and extrapolating the data in the same way as the KcR_{θ}^{-1} values, shown in the Guinier-Zimm plot described above (Figure S1), to an interference-free condition, that is $\theta \rightarrow 0$, which leads to an extrapolation of the scattering vector, $q^2 \rightarrow 0$, and to an interaction-free condition, that is $c \rightarrow 0$. The extrapolation leads to the diffusion coefficient, D_0. With D_0 at hand, the hydrodynamic radius, r_h, is calculated.[3]

4. Size of polymers during static light scattering measurements

To apply the method of Guinier and Zimm[8, 10] it is generally required that the size of particles remains unchanged within the studied concentration range.[3, 14] MEPEs are consisting of reversible non-covalent bonds and the polymer length may vary while preparing different concentrations for static light scattering measurements. For this reason, the dependence of size on concentration is examined and compared to a well-known covalent polymer system, i.e. polystyrene, where polymer length is known to be independent on concentration. The experimental dependence of $\bar{\Gamma}$ on the square of the scattering vector, q^2, at different concentrations, c, is shown in Figure S3 for Ni-MEPE (without ligand **2**) and polystyrene.

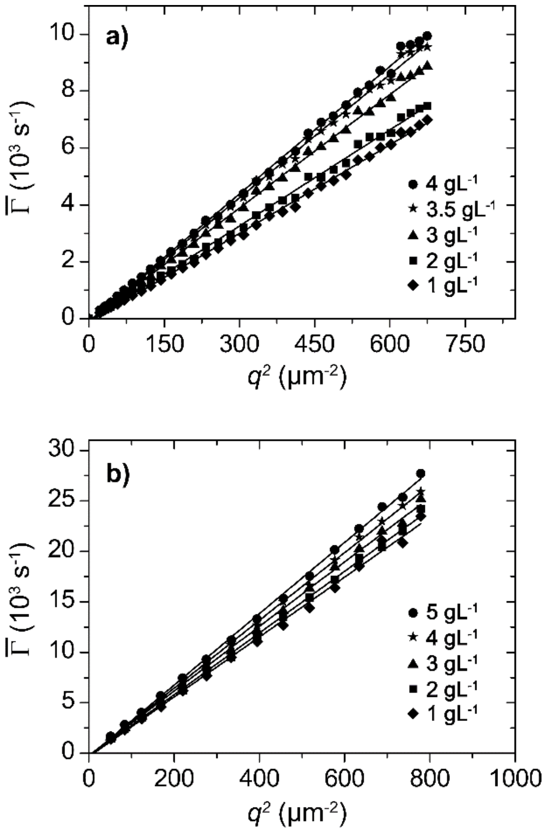

Figure S3. *Experimental dependence of* $\bar{\Gamma}$ *on* q^2 *of (a) Ni-MEPE without chain-stopper, and (b) polystyrene at different concentrations.*

As can be seen in Figure S3, the linear dependence of $\bar{\Gamma}$ on q^2,

$$\bar{\Gamma} = Dq^2 \tag{13}$$

is well approximated by the straight lines passing through the coordinate origin. Diffusion coefficients, D, of the MEPEs calculated from the slopes is independent on solution concentration within an error of $\pm$ 7.8 % within the studied concentration range of 1 g L^{-1} to 4 gL^{-1}. Thus, static light scattering is a suitable method for studying the molar mass and also the shape of MEPEs.

5. Radius of gyration and ratio, ρ

Table S1. *Radius of gyration, r_g, of Co-, and Ni-MEPE for different chain termination ratios, z, mixed with 0.1 M KOAc in acetic acid solution (75 vol%) at a temperature of 23 °C. Each value is determined by an own Guinier-Zimm plot, resulting from static light scattering measurements by dilution of a stock solution (c = 4 g L^{-1}).*

chain termination ratio z	r_g **of Co-MEPE (nm)**	r_g **of Ni-MEPE (nm)**
0.50	7.8 ± 0.6	7.5 ± 0.6
0.65	-	$(1.1 \pm 0.1) \times 10^1$
0.73	8.6 ± 0.7	$(1.0 \pm 0.1) \times 10^1$
0.80	$(1.3 \pm 0.1) \times 10^1$	-
0.85	-	$(1.1 \pm 0.1) \times 10^1$
0.90	-	$(1.1 \pm 0.1) \times 10^1$
0.97	-	$(2.0 \pm 0.2) \times 10^1$
0.99	$(2.5 \pm 0.2) \times 10^1$	$(2.4 \pm 0.2) \times 10^1$
1.00	$(3.2 \pm 0.4) \times 10^1$	$(2.7 \pm 0.4) \times 10^1$

Table S2. *Ratio, ρ, of radii of gyration, r_g, and hydrodynamic radii, r_h, of Co-, and Ni-MEPE for different chain termination ratios, z, mixed with 0.1 M KOAc in acetic acid solution (75 vol%) at a temperature of 23.0 °C. Each value of r_g is determined by an own Guinier-Zimm plot, resulting from static light scattering measurements, and each value of r_h is determined by an own dynamic Zimm plot by dilution of a stock solution (c = 4 g L^{-1}).*

chain termination ratio z	ρ **of Co-MEPE**	ρ **of Ni-MEPE**
0.50	6.0 ± 0.4	6.5 ± 0.4
0.65	-	7.2 ± 0.5
0.73	3.5 ± 0.2	5.1 ± 0.3
0.80	4.5 ± 0.3	-
0.85	-	3.2 ± 0.2
0.90	-	2.5 ± 0.2
0.97	-	2.6 ± 0.2
0.99	1.7 ± 0.1	2.5 ± 0.2
1.00	0.8 ± 0.1	2.3 ± 0.1

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