

Supporting Information for Disentangling Nano- and Macroscopic Viscosities of Aqueous Polymer Solutions Using a Fluorescent Molecular Rotor

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Rheological measurements

In high molecular weight polyethylene oxide (PEO) solutions, shear thinning can be observed.¹ All spectroscopy experiments in this work were carried out at rest and we thus extracted the viscosities from rheological measurements in the Newtonian plateau at low shear rates, as demonstrated in Figure S1 for 1% 9×10^5 and $2 \times 10^6 \text{ g} \cdot \text{mol}^{-1}$ molecular weight samples.

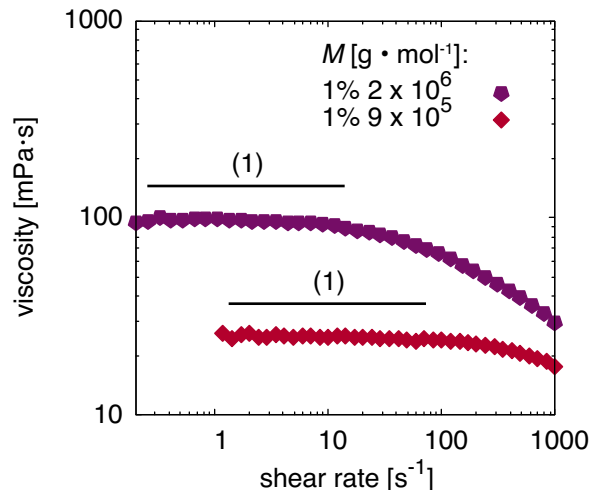


Figure S1: Flow curves for the highest molecular weight samples at 1% concentration. In both cases a Newtonian plateau (1) is separated from a non-Newtonian shear thinning regime. Viscosities were extracted from (1).

UV-vis spectroscopy

Prior to the recording of each fluorescence emission spectra, corresponding UV-vis absorption spectra were measured to obtain more information on the possible occurrence of solvatochromic effects. Figure S2 shows background-corrected UV-vis spectra for the PEO solutions of different molecular weights and concentrations studied here. Increasing the polymer concentration (in percentage by weight) beyond 10% for the low molecular weight samples ($M = 4 \times 10^2$, 6×10^3 and $2 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$) causes the absorption spectra to gradually redshift (up to 20 nm for 100%). We consider the shift in wavelength to be a consequence of solvatochromism: in solution, the dielectric constant decreases with increasing PEO concentration.² Within an environment of lower polarity 4-DASPI shows a red shift, because its ground state has a larger dipole moment than its excited state, like other merocyanine dyes.³ We did not observe bathochromic shifts at molecular weights of $M = 2 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$ or higher. All spectra, except for the high $M = 9 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$ and $M = 2 \times 10^6 \text{ g} \cdot \text{mol}^{-1}$, exhibit shoulders in the short-wavelength UV region $< 350 \text{ nm}$, which are more pronounced in the $M = 2 \times 10^5 \text{ g} \cdot \text{mol}^{-1}$ samples, due to a higher degree of turbidity in these solutions.

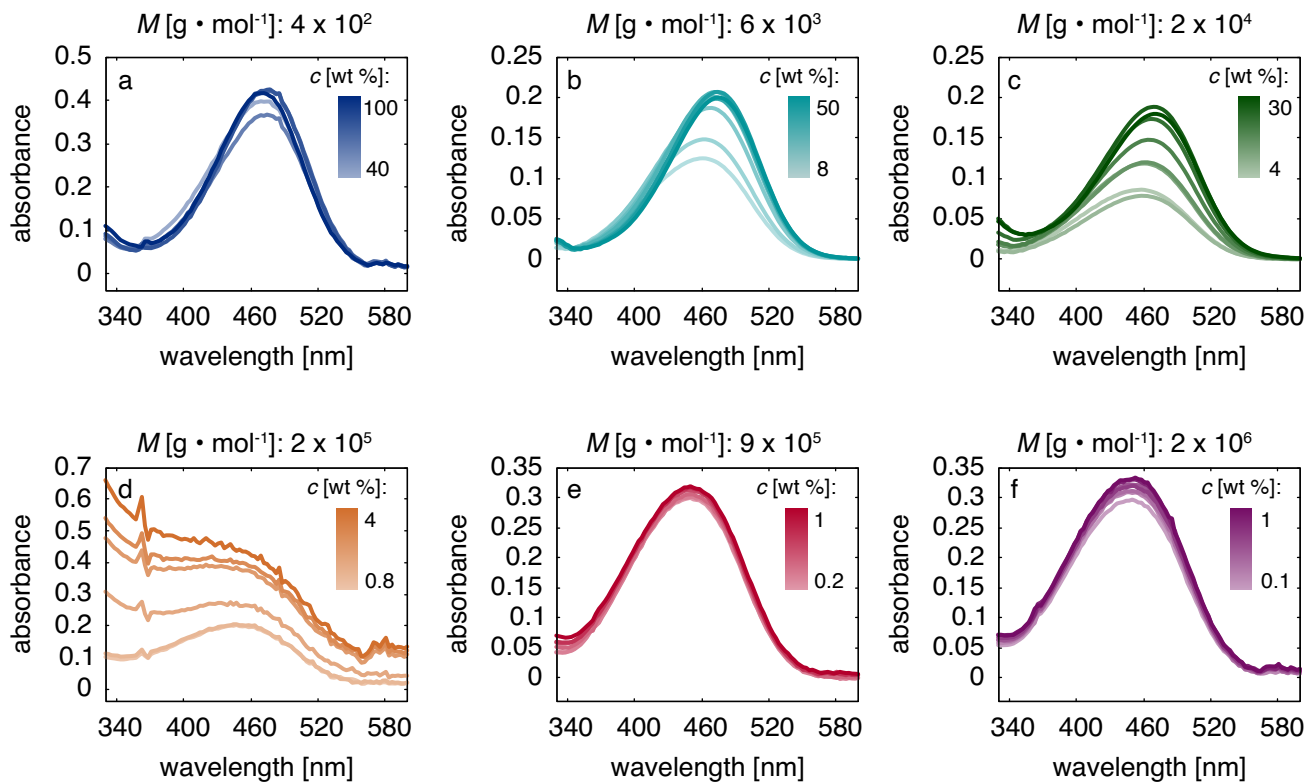


Figure S2: a-f Background-corrected UV-vis absorption spectra of 4-DASPI in aqueous PEO solutions of different molecular weights M and concentrations c .

Effect of polarity

To quantify the effect of polarity on the fluorescence emission intensity of 4-DASPI in aqueous polymer solutions, we measured UV-vis (Figure S3 a) and fluorescence spectra (Figure S3 b) of 4-DASPI in different ethanol/water mixtures as a reference. Within these solutions the viscosity remains largely constant, but the dielectric constant ϵ_r varies between 24 (ϵ_{EtOH}) and 81 ($\epsilon_{\text{H}_2\text{O}}$). Ethanol mixtures represent a suitable system for comparison with PEO solutions, given their similar range of dielectric constants as a function of concentration ($\epsilon_{\text{PEO}} = 11.2$).⁴⁻⁶ We calculated all intermediate values ϵ_r by using the linear mixture equation of Silberstein:⁵ $\epsilon_r = \epsilon_{\text{H}_2\text{O}} (1 - c_{\text{vol}}) + \epsilon_{\text{PEO}} c_{\text{vol}}$ (see Table S1). Comparing the fluorescence of 4-DASPI in both ethanol and PEO mixtures as a function of ϵ , we find the fluorescence intensity to increase with a decrease in dielectric constant (Figure S3 c, d) at approximately

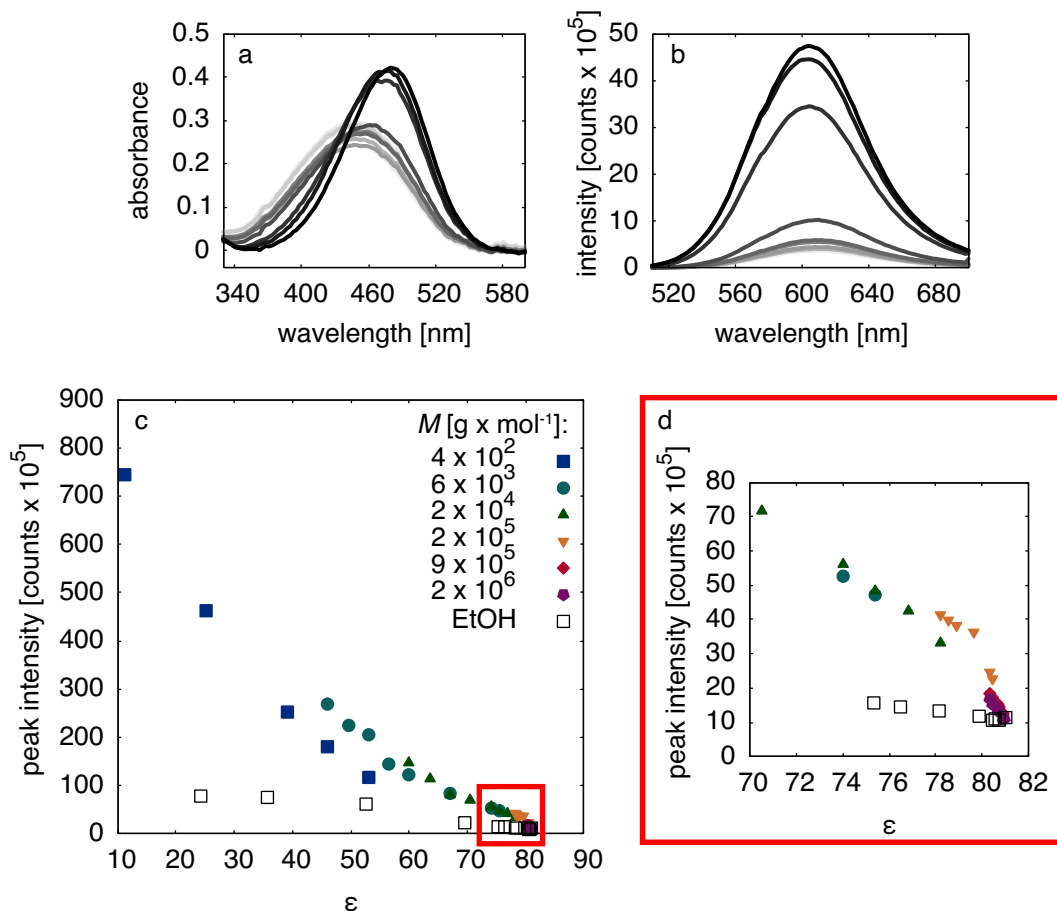


Figure S3: Absorption (a) and fluorescence emission (b) spectra of 4-DASPI in ethanol/water mixtures. c Absorption-corrected fluorescence peak intensity of 4-DASPI versus the calculated dielectric constant in different ethanol/water mixtures compared to the studied PEO solutions. d Magnified range of large dielectric constants.

constant viscosity, but to a much lesser extent than the change in fluorescence due to viscosity. The complex nature of the excited state dynamics of 4-DASPI makes attempts to fully decouple viscosity and polarity in these systems impractical, but given the superimposing viscosity effect, we consider polarity effects largely to be negligible here. We corroborate this assumption by showing that the Förster-Hoffmann equation still holds (see Figure 3), despite not accounting for polarity effects.

Table S1: Calculated Dielectric Constants ϵ_r of the Polyethylene Oxide Solutions.

$M[\text{g} \cdot \text{mol}^{-1}]$	studied c [wt%]	ϵ_r
4×10^2	[40 – 100]	[53.1 – 11.2]
6×10^3	[8 – 50]	[75.4 – 46.1]
2×10^4	[4 – 30]	[78.2 – 60.1]
2×10^5	[0.8 – 4]	[80.4 – 78.2]
9×10^5	[0.2 – 1]	[80.9 – 80.3]
2×10^6	[0.1 – 1]	[80.9 – 80.3]

Scaling laws for the viscosity of PEO solutions

To link Förster-Hoffmann’s relation to the stretched exponential approach presented in the section Results and Discussion, we use the following scaling for the macroscopic viscosities: $\eta_{\text{macro}} = KM^\alpha c^\beta$. The dependence of the viscosity on the concentration has already been measured by others:^{1,7} they found $\beta = 2$ for semidilute polyethylene oxide solution. Our data agree well with this scaling, as shown by plotting the measured viscosity as a function of concentration (gray line in Figure S4 a). We then use the scaling of the concentration to find the power of the molecular weight. By plotting η_{macro}/c^2 as a function of the molecular weight, we find $\alpha \approx 1$ (gray line in Figure S4 b).

Derivation of Förster-Hoffmann’s relation from the stretched exponential

Here, we derive in detail how we find Eq. (3), which links the empirical Förster-Hoffmann’s relation $I = k\eta_{\text{macro}}^x$ (Eq. (1)) and the nanoscopic interpretation $I = I_0 \exp(b c^a)$ (Eq. (2)). First, we express the concentration c using the scaling law $\eta_{\text{macro}} = KM^\alpha c^\beta$. Then, Eq. (2) becomes:

$$I \approx I_0 \exp(b K^{-a/\beta} \eta_{\text{macro}}^{a/\beta} M^{(-a\alpha)/\beta}) \quad (1)$$

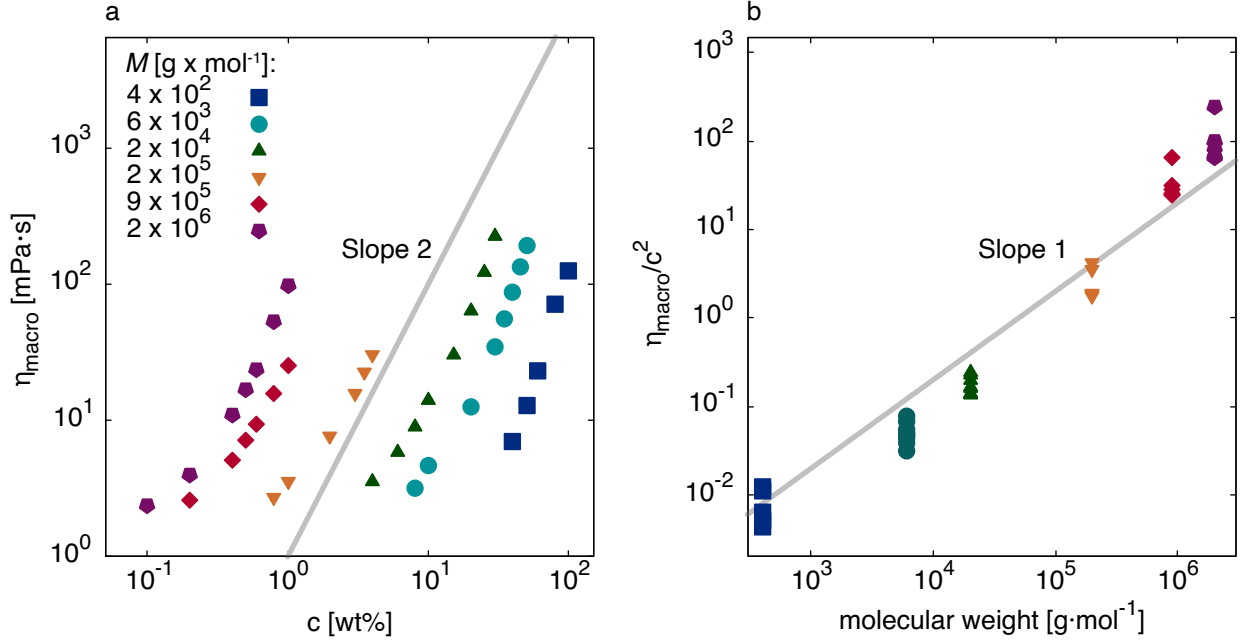


Figure S4: a) A log-log plot of η_{macro} as a function of concentration c gives a slope (β) of ≈ 2 . b) Plot of the parameter η_{macro}/c^2 versus the molecular weight. We find $\alpha \approx 1$.

which can be rewritten as

$$I \approx I_0 \exp \left(b K^{-a/\beta} \exp[a/\beta \log(\eta_{\text{macro}})] M^{(-a\alpha)/\beta} \right) \quad (2)$$

On the small studied range of $(a/\beta) \log(\eta_{\text{macro}})$, we can use a linear approximation:

$$\exp[(a/\beta) \log(\eta_{\text{macro}})] \approx A + B(a/\beta) \log(\eta_{\text{macro}}) \quad (3)$$

with A and B being two fitting parameters (see Figure S5). Linearization of (2) then gives:

$$I \approx I_0 \exp \left(b K^{-a/\beta} [A + B(a/\beta) \log(\eta_{\text{macro}})] M^{(-a\alpha)/\beta} \right) \quad (4)$$

This equation is equivalent to:

$$I \approx I_0 \exp \left(Ab K^{-a/\beta} M^{(-a\alpha)/\beta} \right) \eta_{\text{macro}}^{B(a/\beta) b K^{-a/\beta} M^{(-a\alpha)/\beta}} \quad (5)$$

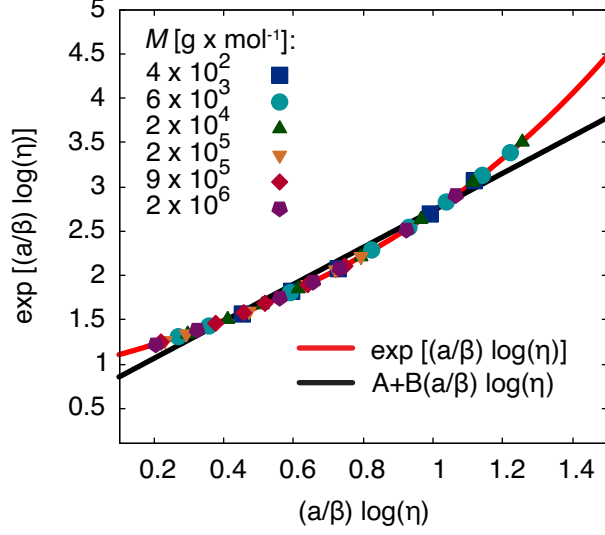


Figure S5: Depiction of the linearization procedure used in this work. We linearize $\exp[(a/\beta) \log(\eta_{\text{macro}})]$ (red line) as $A + B(a/\beta) \log(\eta_{\text{macro}})$ (black line). Both fitting parameters A and B depend on the range of viscosity values studied.

We here note that the prefactors A and B depend on the range of viscosities probed. (5) can finally be expressed as:

$$I \approx I_0 \exp(c_1 M^{(-a\alpha)/\beta}) \eta_{\text{macro}}^{(c_2 M^{(-a\alpha)/\beta})} \quad (6)$$

which is similar to Förster-Hoffmann's equation:

$$I \approx k(M) \eta_{\text{macro}}^{x(M)} \quad (7)$$

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