Electronic Supplementary Material (ESI) for Nanoscale.
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Supporting Information

Supramolecular polymerization: Challenges and advantages of various methods on assessing the aggregation mechanism

Roman Vill, Jochen Gülcher, Pavel Khalatur, Pascal Wintergerst, Andreas Stoll, Ahmed Mourran, Ulrich Ziener*

UV-vis absorption spectroscopy

Temperature dependent absorption spectroscopy was performed on a Perkin Elmer Lambda 365 with a Peltier controller. The sample solutions of $\mathrm{R_E9TR_E}$ in Isopar M were prepared by dilution from stock solutions, heated up to guarantee complete dissolution of aggregates. The aggregation studies were performed in quartz cuvettes with different path lengths from high to low temperature. For low concentrations (0.006 mM) the path length was 1 cm, for 0.1 mM and 0.4 mM the path length was chosen 0.2 cm. To ensure thermodynamically controlled results the temperatures were lowered in 1 and 2 K steps, respectively, with each step equilibrated for 20 min. After baseline correction the absorption at λ = 550 nm was recorded. The raw data are given in Figure S1. The spectra of the solution with c = 0.1 mM were measured between 250 and 700 nm.

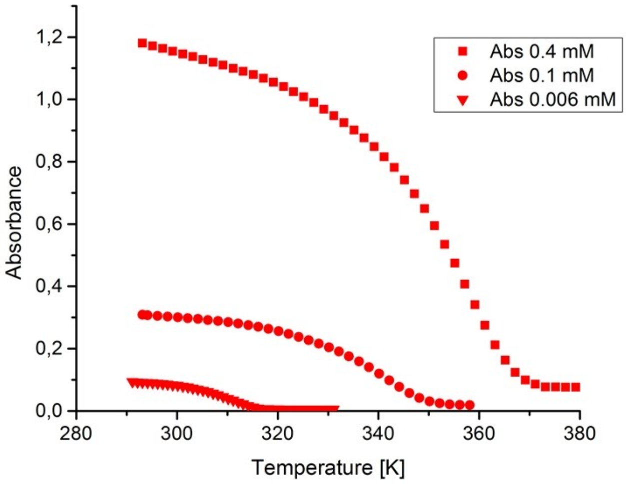


Figure S1. Temperature dependent absorbance values of $\mathrm{R_E9TR_E}$ in Isopar M at 0.006 mM, 0.1 mM and 0.4 mM at 550 nm. From these data the degree of aggregation in Figure 4 was derived.

Fluorescence emission spectroscopy

Temperature dependent fluorescence spectroscopy was performed on a Horiba FluoroMax-3. The sample solutions were prepared by dilution from stock solutions, heated up to guarantee complete dissolution of aggregates. The aggregation studies were performed in 1 cm quartz cuvettes from high to low temperature. The temperature was controlled manually via a Peltier element and lowered in 5, 2 or 1 K steps, respectively. Each data point was taken as an average of three measurements. To ensure thermodynamically controlled results only spectra were collected with consecutive measurements deviating not more than 20,000 cps which corresponds roughly to the instrumental error. The excitation wavelength was chosen at λ_{max} (absorption). The slit was adjusted to obtain absolute values of the emission at λ_{max} (emission) in the range of 10^6 cps. Figure S2 shows exemplary spectra of $\mathrm{R_E9TR_E}$.

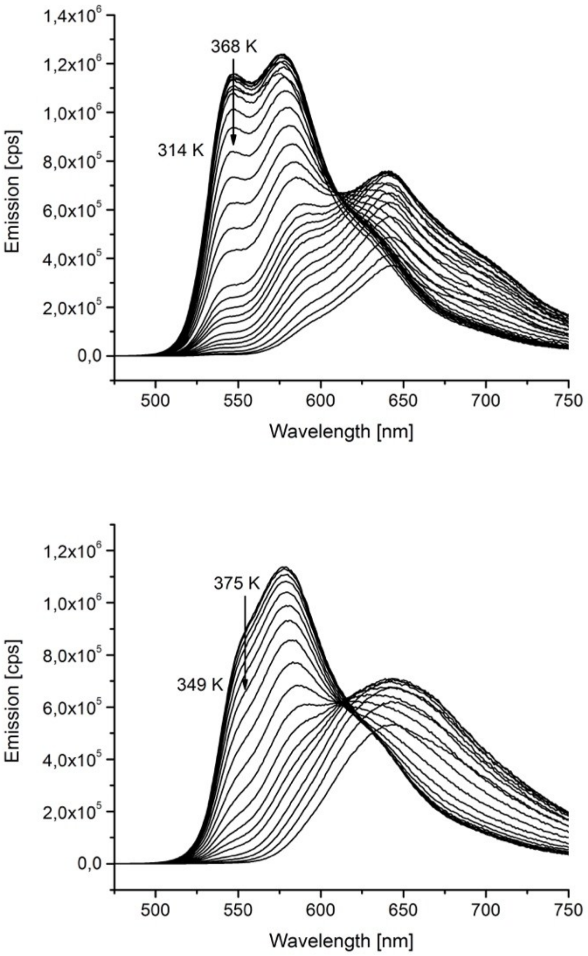


Figure S2. Emission spectra of R_E9TR_E in Isopar M (top: 0.1 mM, bottom: 0.4 mM) at different temperatures. The arrow shows the 0-0 transition which was used to evaluate temperature dependent aggregation by decreasing concentration of monomers and the development of the spectra with temperature, respectively.

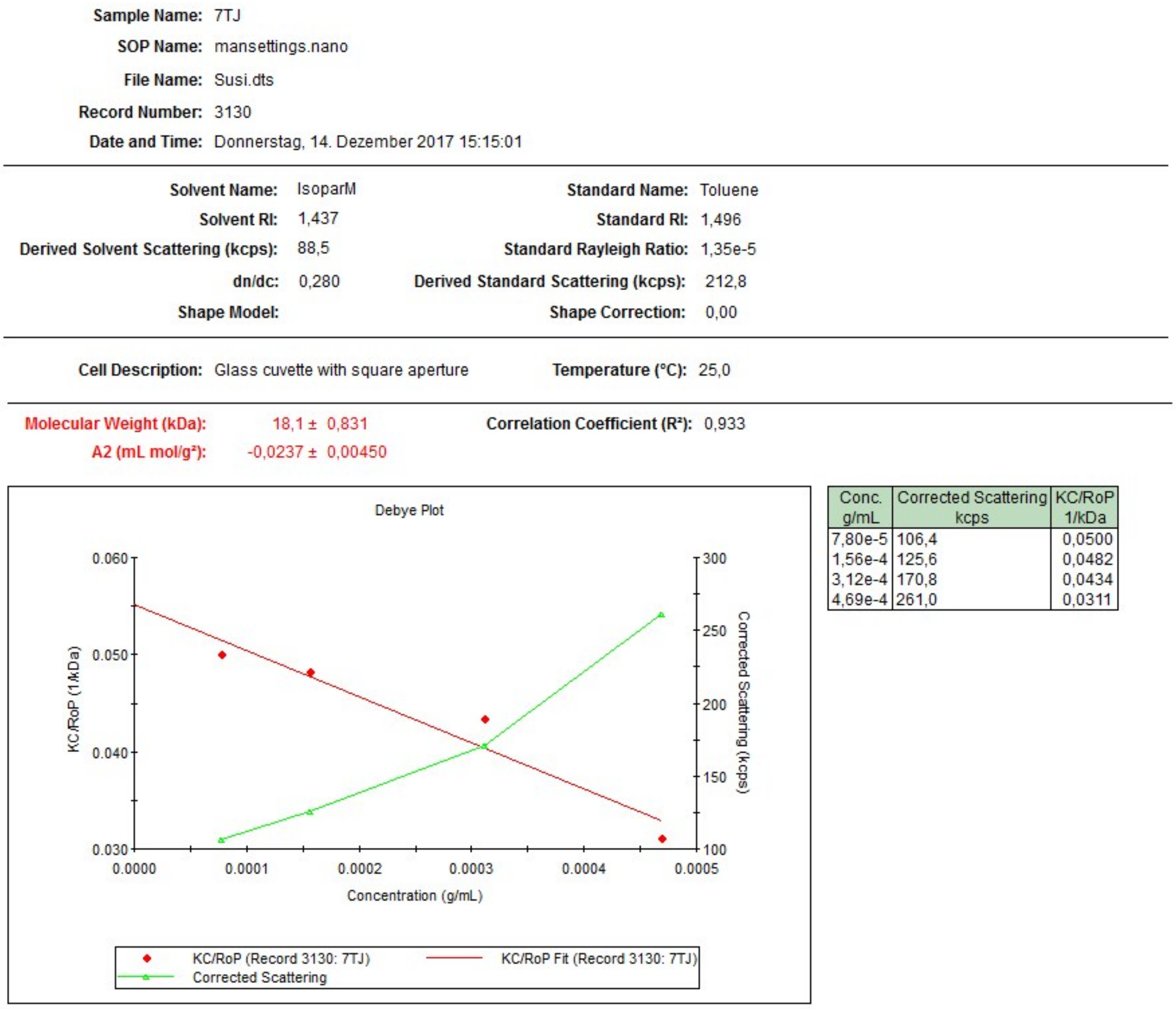
Dynamic (DLS) and static light scattering (SLS)

Both DLS and SLS measurements were performed on a Nano-Zetasizer (Malvern Instruments) with a scattering angle of 173° and a wavelength of λ = 633 nm. For DLS, solutions of the respective oligomers were measured from high to low temperature in 1 K steps. The absolute scattering intensity was normalized to the highest intensity value. The sizes of the scattering objects were not determined.

SLS measurements were made at 25 °C with solutions of R_J7TR_J in Isopar M at various concentrations between c = 7.8 10^{-5} g mL^{-1} and 4.69 10^{-4} g mL^{-1} (Figure S3). In this concentration range aggregation of the oligomer can be neglected. The data was evaluated by a Debye plot with

$$\frac{Kc}{R_\theta} = \frac{1}{M_W} + 2A_2c$$

delivering A_2 = -0.024 ± 0.0045 mL mol g^{-2}.



Sample Name: 7TJ
SOP Name: mansettings.nano
File Name: Susi.dts
Record Number: 3130
Date and Time: Donnerstag, 14. Dezember 2017 15:15:01

Solvent Name: IsoparM
Solvent RI: 1,437
Derived Solvent Scattering (kcps): 88,5
dn/dc: 0,280
Shape Model:
Standard Name: Toluene
Standard RI: 1,496
Standard Rayleigh Ratio: 1,35e-5
Derived Standard Scattering (kcps): 212,8
Shape Correction: 0,00

Cell Description: Glass cuvette with square aperture
Temperature (°C): 25,0

Molecular Weight (kDa): 18,1 ± 0,831
A2 (mL mol/g²): -0,0237 ± 0,00450
Correlation Coefficient (R²): 0,933

Conc. g/mL	Corrected Scattering kcps	KC/RoP 1/kDa
7,80e-5	106,4	0,0500
1,56e-4	125,6	0,0482
3,12e-4	170,8	0,0434
4,69e-4	261,0	0,0311

Figure S3. Debye Plot from static light scattering of R_J7TR_J at different concentrations in Isopar M delivering the second virial coefficient.

Extraction of thermodynamic parameters

For the sigmoidal shape of the curves the apparent ΔH was determined following the evaluation of Smulders et al.[1] with

$$\alpha = \frac{1}{1 + e^{-0.908\Delta H \frac{T - T_m}{RT_m^2}}}$$

while ΔT was extracted from the equation

$$\alpha = \frac{1}{1 + e^{\frac{T - T_m}{\Delta T}}}$$

Thin film preparation and Scanning force microscopy imaging:

The substrates were ultrasonically cleaned in an isopropanol bath, dried with a stream of nitrogen subsequently exposed to UV radiation under oxygen flow for 20 min. This oxidative treatment produces a hydrophilic SiO_2 surface. For spin coating, the concentration has been adjusted to 1g/L and a rotation speed of 2000 rotations per minute. The images were acquired using an Agilent 5500 SFM instrument and a standard NCH point probe with nominal resonance frequency of 320 kHz and force contact 42 N/m.

1 M. M. J. Smulders, M. M. L. Nieuwenhuizen, T. F. A. de Greef, P. van der Schoot, A. P. H. J. Schenning and E. W. Meijer, *Chem. – Eur. J.*, 2010, **16**, 362-367.