

M. Supper *et al.*: Separation of molar weight-distributed polyethylene glycols by reversed-phase chromatography – Analysis and modelling based on isocratic analytical-scale investigations

– Supplementary information –

## S1. Detection and identification of the PEG homologs

During measurements polyethylene glycol (PEG) was detected by a charged aerosol detector (CAD). For the identification of the peaks the detector was coupled with a mass spectrometer (MS). The detailed settings for the MS and CAD are listed in Table S1.

Table S1: Parameter settings for the mass spectrometer and the charged aerosol detector

Mass spectrometer		Charged aerosol detector	
Curtain gas / psi	25	Nebulizer temperature / °C	25
Ion spray voltage / V	5500.0	Filter / -	4
Temperature / °C	0	Gain / pA	100
Ion source gas 1 / psi	35	Offset / %	0
Ion source gas 2 / psi	35	Power function / -	1
Declustering potential / V	16		
Entrance potential / V	8.5		

The MS delivers a mass spectrogram every two seconds. The ratio of mass-to-charge,  $m/z$ , is characteristic for the ion type, the intensity proportional to their concentration. The accumulated overall signal, also referred to as the total ion count, is recorded over time. An example chromatogram of the CAD and MS signals separating PEG1400 at 23 vol% ACN and 30 °C is shown in Fig. S1.

In order to identify the peaks in the spectrogram, the measured  $m/z$  values have to be investigated at the corresponding time slots (peaks) and traced back to the corresponding values of the polymer homologs and load carriers. Since the MS was operated in positive polarity mode, only cations are expected as load carriers. As possible load carriers  $H^+$  (1.01 g mol<sup>-1</sup>),  $NH_4^+$  (18.04 g mol<sup>-1</sup>) and  $Na^+$  (22.99 g mol<sup>-1</sup>) and combinations thereof were found to be suitable. A shift in ion counts was observed. This corresponds to a sodium contamination, probably resulting from the glass containers used during measurements for storing the mobile phase and the samples. The used MS is limited to values ranging between 0 and 1500  $m/z$ . Therefore, homologs are identified from multiply (double, triple, etc.) charged ion species. The actual polymerization degree  $n$  is then

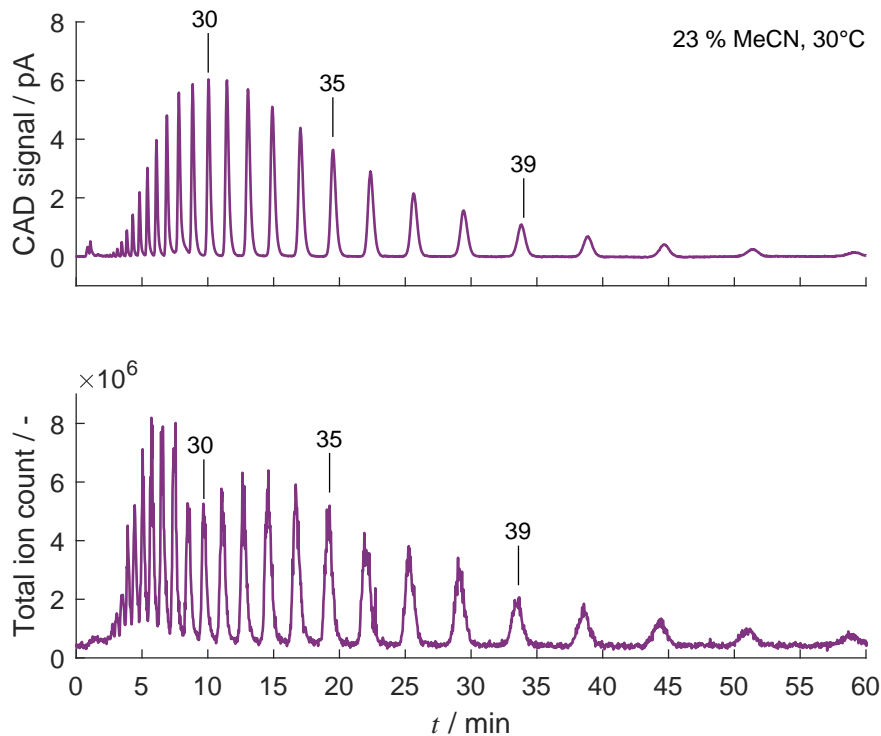


Figure S1: CAD chromatogram and the corresponding total ion count over time for PEG1400 at 23 vol% ACN and 30 °C. The injection volume was 10  $\mu$ L, injected concentration 1 g/L, and flow rate 1 mL/min, respectively.

determined from

$$n = \frac{(m/z - MW_{\text{load}})q_{\text{load}} - 18.02 \text{ g} \cdot \text{mol}^{-1}}{44.05 \text{ g} \cdot \text{mol}^{-1}}, \quad (1)$$

where  $MW_{\text{load}}$  and  $q_{\text{load}}$  are the molecular weight and the number of load carriers, respectively. An example for homologs with 30, 35 and 39 repeat units at the corresponding times can be seen in Fig. S1) for double and triple charged ion sources.

## S2. Thermodynamic parameters

Figures S3 through S6 below show the determination of thermodynamic parameters for the PEG1400 homologs at all acetonitrile contents investigated (15, 17, 19, 21, 22, 23, 24 and 27.5 vol% ACN). The left sides contain the van't Hoff plots of data (symbols, triplicate measurements) and linear regression against Martin's rule (lines) for the homologs. The right sides depict the enthalpic and entropic contributions as function of  $n$  corresponding to the slopes ( $\Delta H_n^0$ ) and intercepts ( $\Delta S_n^*$ ) of the lines in the left

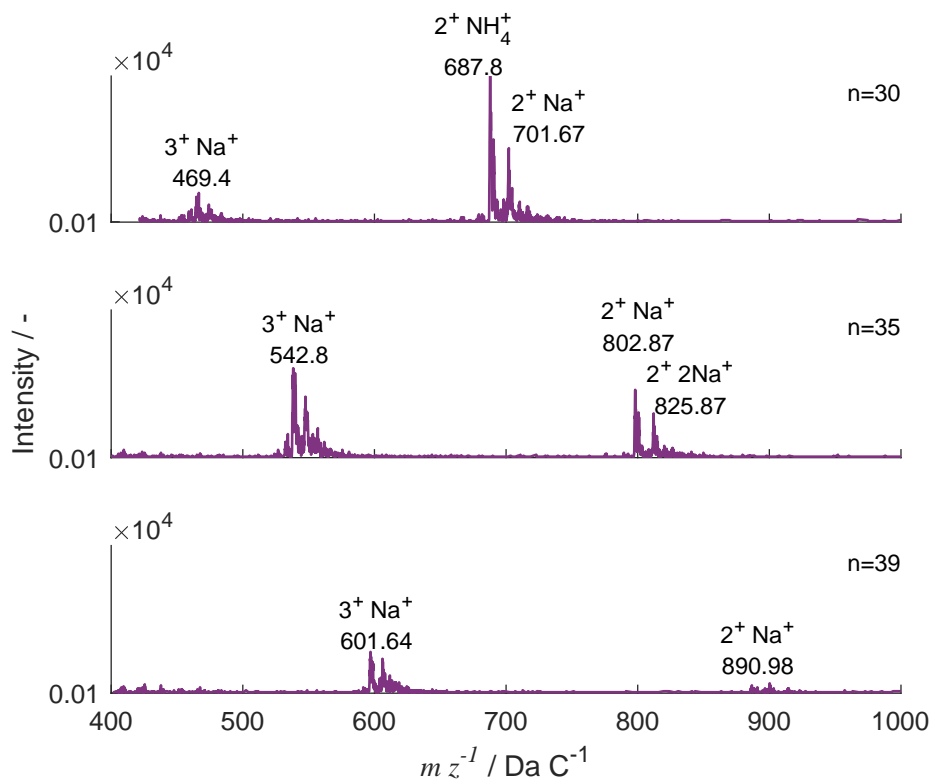


Figure S2: Three mass spectrograms for three selected peaks at 10, 19 and 34 min derived from the chromatogram of the total ion count (Fig. S1). Possible load carriers as well as double ( $2^+$ ) and triple ( $3^+$ ) charged ion sources are marked. The corresponding peaks of the three homologs (n=30, 35 and 39) are marked in the CAD and MS chromatograms of Fig. S1.

(symbols). Linear regression against Martin's rule (lines) delivers  $\Delta H_r^0$ ,  $\Delta H_e^0$  and  $\Delta S_r^*$ ,  $\Delta S_e^*$  as slopes and intercepts, respectively.

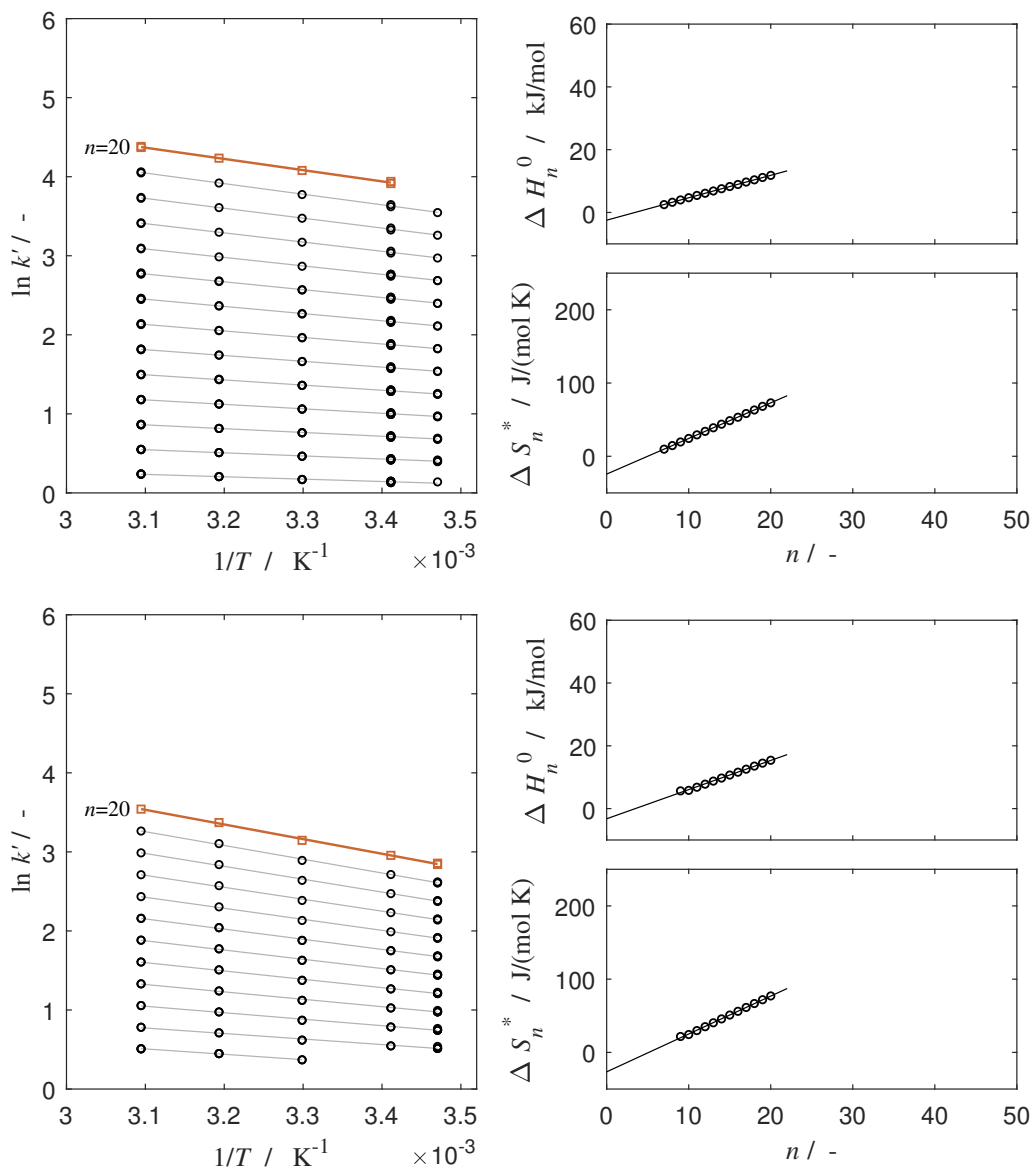


Figure S3: Determination of thermodynamic parameters at 15 vol% (top) and 17 vol% (bottom) ACN.

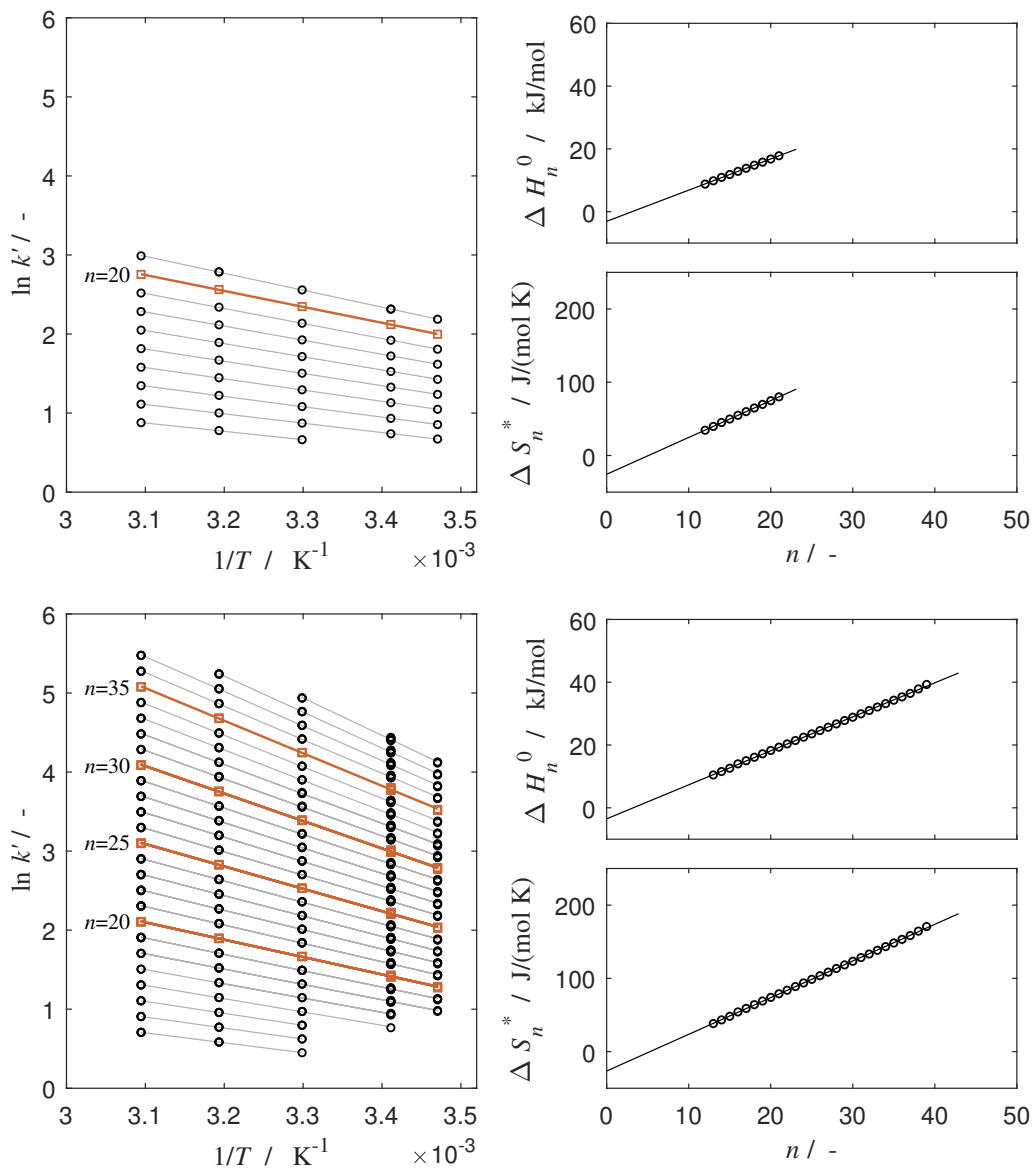


Figure S4: Determination of thermodynamic parameters at 19 vol% (top) and 21 vol% (bottom) ACN.

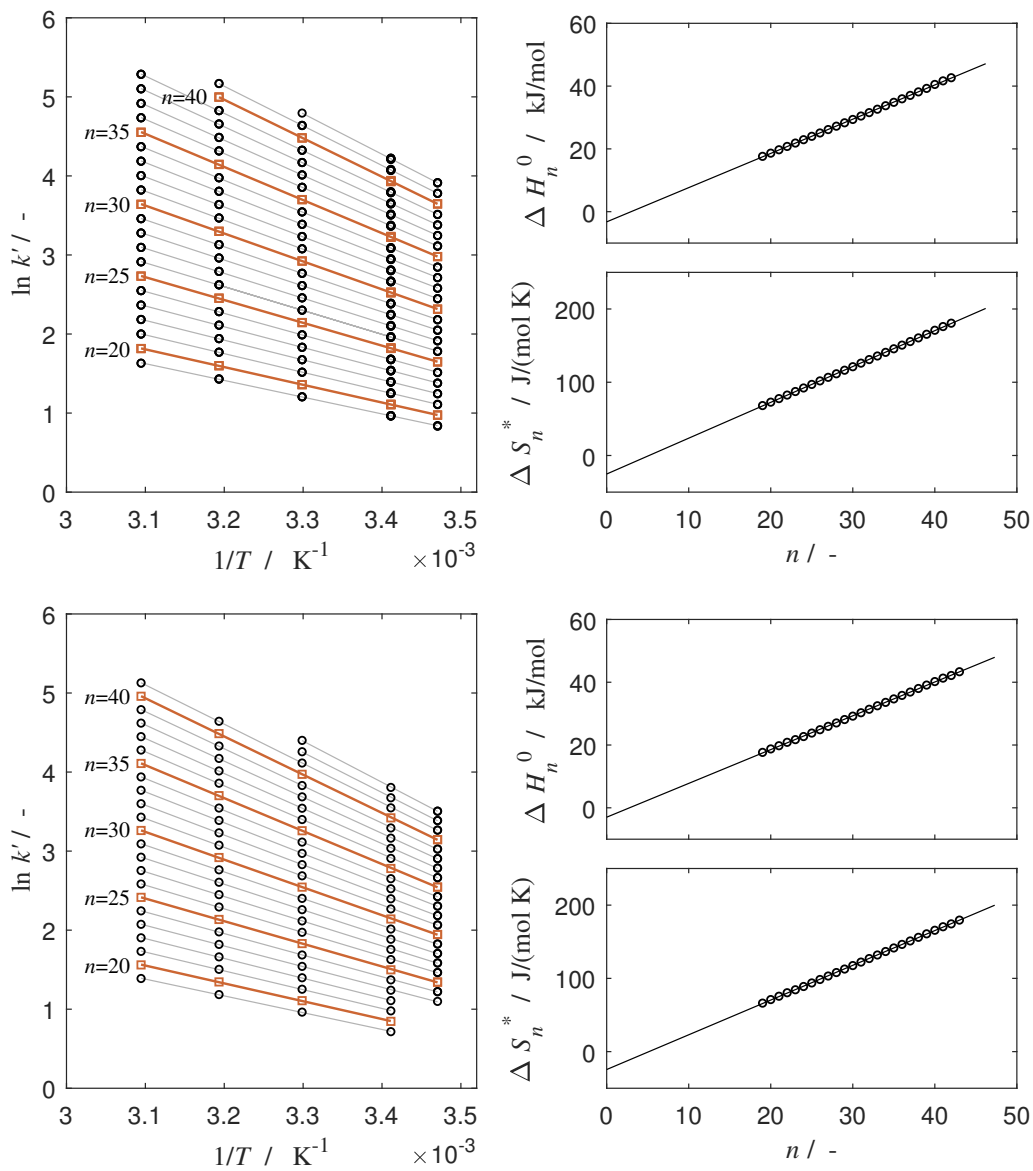


Figure S5: Determination of thermodynamic parameters at 22 vol% (top) and 23 vol% (bottom) ACN.

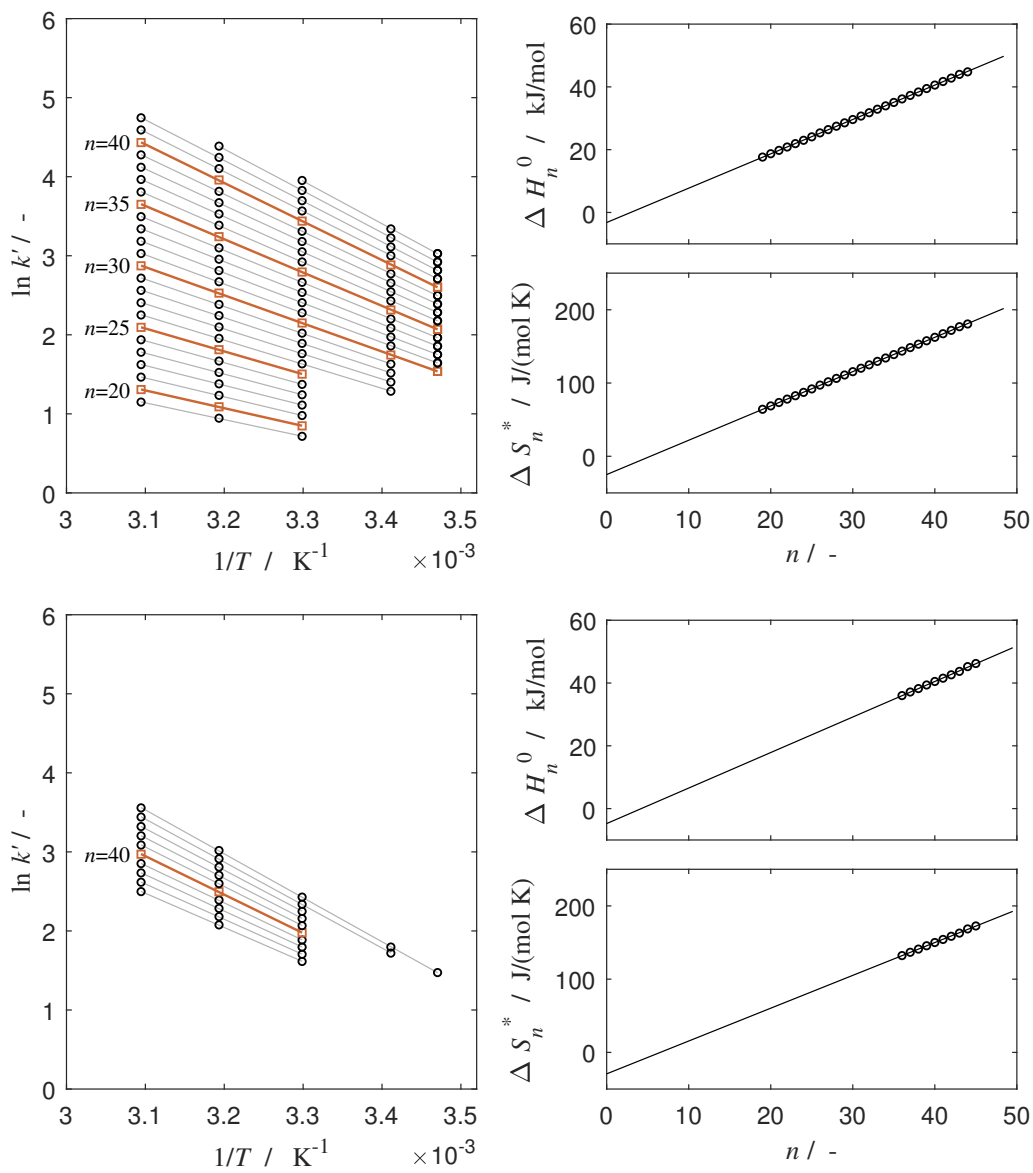


Figure S6: Determination of thermodynamic parameters at 24 vol% (top) and 27.5 vol% (bottom) ACN.