Gel permeation chromatography (GPC)

Aims:

Methods for determination of molar masses of polymers, molar mass distributions, average of the molecular weights, polymers in solution, separation principle of the size exclusion chromatography

Task:

Measurement of the molar mass distribution of a polystyrene (PS) sample and a polymethylmethacrylate (PMMA) sample by using the gel permeation chromatography (under the guidance of the assistant).

Practical application:

Dissolve the polymers in tetrahydrofuran (THF) (c_{PS} = 30 mg/mL; c_{PMMA} = 70 mg/mL). This has to be done on the day before the experiment takes place due to the poor solubility of some polymers.

Injection of the sample and starting an analitical GPC run.

The assistant will send you the GPC raw data (Detector signal as a function of the elution volume) and the VR-, MP- values of several PS-standards for the analysis of the measurement data. The Mark-Houwink parameters $K\eta$ and $a\eta$ of the different polymers in THF at 30°C are:
PS: $K\eta$ = 0.01363 mL/g, $a\eta$ = 0.714; **PMMA**: $K\eta$ = 0.01298 mL/g, $a\eta$ = 0.688.

Analysis:

1. Plot the obtained measurement data of both detectors in an elution diagram (detector signal against elution volume) and determine all the peaks that have occurred. For all peaks, the peak position (elution volume at the peak maximum) has to be specified.

2. Calculation of all the necessary calibration curves:

➢ Plot the values of the PS standards in a table. Calculate the PS-specific calibration curve (3rd degree polynomial, list the parameters) and plot it in a diagram.

➢ Calculate and plot the universal calibration curve using the PS standards and the Mark-Houwink parameters (3rd degree polynomial, list the parameters).

➢ Calculate the polymer specific calibration curve of PMMA (3rd degree polynomial, list the parameters) and plot it. Therefor use the PS standards and the Mark-Houwink parameters of PS and PMMA.

3. Determination of the molar mass distribution (MWD), R_G and R_h of the PS sample (UV detector):

➢ Calibrate the measurement data with the internal standard BHT (44.09 mL)

$$X_{cf} = \frac{v^0_{BHT}}{v^{Data}_{BHT}} \qquad \text{cf = correction factor}$$

➢ Plot the calibrated elution diagram. Plot the magnification of the detected PS area and choose reasonable upper and lower limits for the MWD calculation.

➢ Calculate w_i (= I_i / ΣI_i; record ΣI_i) from the calibrated data and calculate M_i using the polymer specific calibration curve. Plot the MWD (function wi = f(Mi) with linear axis).

➢ Calculate the mean values Mn, Mw and the polydispersity of the sample.

➢ Calculate the medium radius of gyration R_G in *nm*. Therefor use the Flory-Fox-equation (Φ_0 = 2.87x10^{23} for PS in THF; $[\eta]_w$ in mL/g; use M_w).
Calculate the hydrodynamic radius R_h (spherical model for dissolved polmer molecules) in *nm* from $[\eta]_w$ and M_w

4. Determination of the molar mass distribution (MWD), R_G and R_h of the PMMA sample (RI detector):

➢ Calibrate the measurement data with the internal standard BHT (44.09 mL)

➢ Plot the calibrated elution diagram. Plot the magnification of the detected PS area and choose reasonable upper and lower limits for the MWD calculation.

➢ Calculate w_i (= I_i / ΣI_i; record ΣI_i) from the calibrated data and calculate M_i using the polymer specific calibration curve. Plot the MWD (function wi = f(Mi) with linear axis).

➢ Calculate the mean values Mn, Mw and the polydispersity of the sample.

➢ Calculate the medium radius of gyration R_G in *nm*. Therefor use the Flory-Fox-equation (Φ_0 = 2.55x10^{23} for PMMAthe in THF; $[\eta]_w$ in mL/g; use M_w).
Calculate the hydrodynamic radius R_h (spherical model for dissolved polmer molecules) in *nm* from $[\eta]_w$ and M_w

5. Short analysis of the remaining peaks:

➢ Calculate the molar masses of the remaining peaks (BHT, further unexpected peaks) based on the peak maximum (not from the MWD). Use all three calibration curves.

➢ Compare the three experimental results for the remaining peaks (in particular BHT) with the real molar mass.

➢ How good is the agreement for these molar masses? Are there reasons for not a good match having to expect?

6. Discussion of the results:

➢ How accurate is the molar mass determination using the GPC method?
(Please don't discuss the measurement accuracy for repeated measurements of the same sample, discuss the influence of the evaluation methodology only (peak determination, calibration curve, zero line correction ...).