

Bulk/Mass Polymerization

Learning targets: ideal kinetics of chain growth, \sqrt{I} -rule, viscometry, characteristics of polymers (number-, weight- and viscosity-average)

Assignment of tasks:

1. Bulk polymerization of styrene at 60 °C with four different initiator concentrations
2. Viscometric single-point-measurement of the samples in toluene with an Ubbelohde-viscometer
3. GPC-measurement of one of the samples for comparison
4. Analysis:
 - a) Calculation of conversion U (in %)
 - b) Calculation of initial polymerization rate $v_{brutto,exp}^{U,0}$ and conversion in units mol/Ls ($v_{brutto,exp}^0$)
 - c) Comparison of $v_{brutto,exp}^0$ with calculated theoretical initial polymerization rate $v_{brutto,ber}^0$ and calculation of the initiator efficiency
 - d) Calculation of limiting viscosity number $[\eta]$ by method of Salomon & Situa and calculation of integral viscosity-average of the degree of polymerization P_{η}^{int} by using the Mark-Houwink-coefficients K_{η} and α_{η}
 - e) Determination of the transfer constant $C_{\bar{U},M}$ and the coupling constant k
 - f) Calculation of the hydrodynamic radius R_h
 - g) Possible sources of error
 - h) Discussion and comparison of the results with GPC-data and literature

1. Procedure of the polymerization

General advice: with styrene /polystyrene contaminated vessels and equipments have to be cleaned directly after use to avoid that the polystyrene becomes touch dry.

Preparation of polymerization (done by supervisor): One day before running the polymerization, 100 mL of styrene have to be destabilized by distillation (or filtration over Alox). The distillation takes place at a bath temperature of 55 °C and a pressure of 25 – 30 mbar. After distillation the styrene has to be stored under Argon, in the dark and in the deep-freezer. The used distiller must be cleaned immediately after the distillation to avoid contamination with polystyrene.

Experimental procedure:

In four 100 mL-Erlenmeyer flasks four different amounts of AIBN (15.6 mg, 31.2 mg, 155.8 mg, 311.6 mg) and then 20 mL distilled, destabilized styrene (weighed with a syringe) are added. The solutions are turned until AIBN is dissolved. If the reaction cannot be started immediately, the samples have to be kept in the dark and in the fridge. The polymerization will be prepared in 50 mL-Schlenk tubes (without magnetic stir bar!). Therefor 5 mL of each solution is weighted in a Schlenk-tube (weighted before), the tubes are closed with a septum and flushed with argon from a rack. The reaction is started by heating in a water bath at 60 °C.

After three hours at 60 °C the reaction is completed by cooling the tubes in ice cold water and 25 mL cyclohexanone is added to the polystyrene. The mixture is slowly added to 300 mL of methanol (rinse with cyclohexanone). The sampled out polystyrene flocs get centrifuged (4000 U/min, RZB < .3265, 6 min, 20 °C, BES = 9, BRE = 7; call your assistant before use; tare the mounting pots as precisely as

possible!) and again each is washed three times with each 50 mL methanol, two times centrifuged and the last time filtered through glass filter crucibles (weighted before!). Dry your polystyrene samples in a drying oven at 80 °C in vacuum over night.

2. Preparation of the viscometric measurement:

Attention: The viscometer is very sensitive about collisions. It may never be taken out of the viscometer rack and while filling and other operations it should be connected to the rack hanging in a clamp.

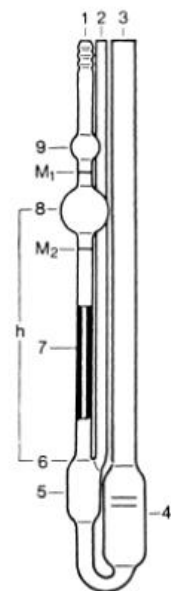
All samples that will be filled into the viscometer, also pure toluene, have to be filtered dust-free before. For this purpose the samples are soaked with a syringe and pressed through a syringe-filter into the viscometer. Dust and fluff in solution distort the results and are hardly to remove. For purging at the end only filtered toluene has to be used.

Experimental procedure:

In four lockable 100 mL-Erlenmeyer flasks each 120 mg of polystyrene are weighted in and 40 mL toluene (volumetric pipette) are added. The flasks are swung on a pulsating panel until the polystyrene is completely dissolved (~ 2-3 h).

First the running time of pure toluene is measured, then the samples with increasing initiator concentration. While changing the samples, it is necessary to purge the viscometer with toluene and it is sufficient to let it drip overhead (hang in the clamp!). The Ubbelohde-viscometer is hanged in a clamp (do not fill in the toluene while hanging in the water bath!) and filled with the samples until the liquid is located between the two marks of the storage tank (4 in figure right). As soon as the viscometer is filled with the sample, it is achieved 15 min. in the thermostat to a constant temperature of 25 °C. The compensating tube (2) is closed with a finger and with a Peleus ball the liquid is sucked to the supply bowl (9). Then the Peleus ball is taken off and the compensating tube (2) is vented. The time is measured until the meniscus is fallen from mark M1 to mark M2.

This procedure is repeated three times for each sample, in which it is regarded to a constant temperature (max. +/- 0.1 °C) and adequate measurement precision (max. +/- 0.2 s).



3. Comparative measure of molecular mass distribution by GPC

In comparison with the average molecular mass from the viscometric measurements one of the four samples is dissolved in thf and injected into the GPC. The sample preparation and measure has to be done in arrangement with your assistant.

4. Evaluation

a) Calculation of the conversion U

The conversion U (in %) referring to the amount of inserted styrene (subtract amount of initiator AIBN!) is calculated.

b) Calculation of initial polymerization rate $v_{brutto,exp}^{U,0}$ (conversion %/h) and translation into units mol/Ls ($v_{brutto,exp}^0$)

To calculate the initial polymerization rates, a regression of each of the four conversion-time-pairs of values with help of the conversion –rate-equation has to be executed.

$$U = 100(1 - e^{-pt})$$

p is the kinetic matching coefficient.

$$p = 3600k_w \left(\frac{2fk_z[I]_0}{k_{ab}} \right)^{\frac{1}{2}}$$

After differentiation of the equation for conversion with respect to t, the initial polymerization rate $v_{brutto,exp}^{U,0}$ with respect to t=0 can be calculated. The translation into the kinetically relevant units mol/Ls results from

$$v_{brutto,exp}^0 = v_{brutto,exp}^{U,0} \left(\frac{\rho_{Monomer}}{360 \cdot M_{Monomer}} \right)$$

in which $\rho_{Monomer} = 0.87 \text{ g/cm}^3$ is the density of styrene at 60 °C.

c) Comparison of $v_{brutto,exp}^0$ with the calculated theoretical initial polymerization rate $v_{brutto,ber}^0$ and calculation of initiator efficiency f

The theoretical initial polymerization rate $v_{brutto,ber}^0$ can be calculated for a radical yield of $f = 1$, $[M]_0$, $[I]_0$, and the following rate constants

$$k_z = 1,24 \cdot 10^{-5} \text{ s}^{-1}$$

$$k_w = 1,76 \cdot 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_{ab} = 7,20 \cdot 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The initial concentration of monomer and initiator can be calculated approximately from the density of styrene at 60 °C. Based on the values of $v_{brutto,ber}^0$ and $v_{brutto,exp}^0$, the initiator efficiency f can be calculated.

d) Calculation of limiting viscosity number $[\eta]$ after Salomon and Situa and calculation of the integral viscosity-average of the degree of polymerization P_η^{int} with Mark-Houwink-coefficients K_η and α_η

The Staudinger-index $[\eta]$ (limiting viscosity number) can be calculated in single-point-measurements with the approximation of Salomon and Situa:

$$[\eta] = \left(\frac{\sqrt{2}}{c_{Polymer}} \right) \sqrt{\eta_{sp} - \ln \eta_{rel}}$$

To determine the molar mass M , the dependency of M with the hydrodynamic volume v_h has to be included. Because the recording of all structure-, size-, polydispersity- and interaction influences is very difficult, the molar mass is determined with a polymer-homologous-series in a given solvent at given temperature over a calibration with an independent absolute method for M . The empirical received Mark-Houwink-Sakurada-equation ends in

$$[\eta] = K_\eta M_\eta^{\alpha_\eta}$$

The parameter K_η and α_η are linked to the corresponding combination of polymer/solvent/temperature. For your examination the following values have to be used:

$$K_\eta = 17,0 \cdot 10^{-3} \text{ mL/g}$$

$$\alpha_\eta = 0,69$$

Furthermore the integral viscosity-average of the degree of polymerization P_η^{int} has to be calculated out of the molar mass M_η^{int} .

The conversion into the integral number-average P_n^{int} takes part under the supposition of a Schulz-Flory-distribution and Mark-Houwink-exponent ($\alpha_\eta = 0,69$) with $P_n^{int} = P_\eta^{int} / 1,86$.

Assuming that the influence of the decreasing monomer concentration to the degree of polymerization compensates the influence of initiator concentration, the initial state can be put approximately on the same level with the integral value, i.e. $P_n^0 \approx P_n^{int}$.

e) Determination of the transfer constant $C_{\ddot{U},M}$ and the coupling constant k

The determination of transfer constant $C_{\ddot{U},M}$ and coupling constant k is carried out by plotting $1/P_n^0$ vs. $v_{brutto,exp}^0/[M]_0^2$ with assumption of validity of ideal kinetics:

$$1/P_n^0 = \frac{k_{ab}}{k \cdot k_w^2} \cdot \frac{v_{brutto,exp}^0}{[M]_0^2} + C_{\ddot{U},M}$$

f) Calculation of the hydrodynamic radius R_h .

Calculation of hydrodynamic molecular radii R_h of all samples out of M_w^{int} and $[\eta]$ with help of

$$R_h = \sqrt[3]{\frac{3 \cdot M_w^{int} \cdot [\eta]}{10 \cdot \pi \cdot N_A}}$$

g) Possible sources of error

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h) Discussion of the results and additional questions

- plot of $v_{brutto,exp}^0$ vs. $\sqrt{[I]_0}$ with linear regression and discussion
- plot of P_n^0 vs. $\sqrt{[I]_0}^{-1}$ with linear regression and discussion
- Why is the reaction completed after 3 h?
- Discussion of all received data, comparison with GPC-data and literature

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