

Service provider for polymer fractionation / purification,
rheological measurements, and contract research.



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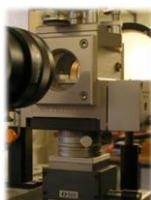


Contract Research

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Physico-chemical properties of polymers

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Density (at elevated pressure/elevated temperature)
Chemical classification numbers
GPC/SEC, Osmometry, Light scattering (static),
Abbe-refractometer, Differential refractometer,
UV/Vis-Spectroscopy

WEE can solve your problems!



Polymer fractionation / purification

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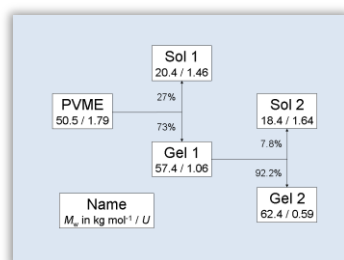
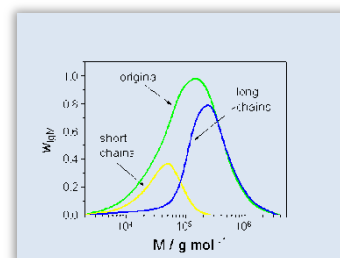


Alteration of the molecular mass distribution

Polymers are increasingly used as high-performance materials and crucial in the areas of medicine, cosmetics and technique. For sophisticated applications it is often harmful that the polymers have a broad molecular mass distribution or contain impurities. By means of fractionation we are in the position to remove unwanted material on a technical scale enabling the optimization of the polymer properties.

Modifiable Properties:	
• Viscosity	• Refractive index
• Density	• Degradation
• Crystallinity, glass temperature	• Permeability through skin /kidney
• Purity	• Inflammable behavior
• Volatility	• Oligomer content
• Shelf life	• etc.

The fractionation method is based on liquid/liquid phase separation and is therefore suitable for almost all soluble polymers. The phase separation is induced by lowering the solvent quality of an initially homogenous polymer solution. Two phases are formed: one containing the long chain material (gel-phase) and the other one contains mainly the short chain material and the low molecular mass impurities (sol-phase).



By the choice of the fractionation parameters (temperature, compositions) the “cut” through the molecular mass distribution can be varied. Narrow molecular mass distributions can be achieved by repeated fractionation.



Case studies

The reasons for fractionation are as diverse as the different applications of polymers are. The following examples are therefore taken from very different areas.

Recovery/purification of polymers produced by means of biotechnology

Fractionation enables the removal of low molecular mass material of polymers stemming from biological sources, yielding products with high purities.

Application in medicine

The short chains as well as the long chains of hydroxyethyl starch are troublesome for its use as blood plasma expander. The short chains leave the body through the kidney very fast and are therefore inefficient. The long chains on the other hand remain in the body, are stored in the skin and induce itching.

Another sample is hyaluronic acid which is used in eye surgeries as a viscoelastic agent or for the treatment of arthrosis as a natural lubricant. By means of fractionation the properties of hyaluronic acid can be tuned for the application.

Harmful contents in photoresists

Photoresist, like Novolak, are used for the production of electronic circuits in the micro- or submicroscale. For this application the oligomers are disturbing, because they are still sufficiently volatile and can be deposited at wrong places. Therefore they impede a further miniaturization. By removing the oligomeric contents this problem can be solved.

Filter dust at the membrane production

During the production of filtration membranes (e.g. from cellulose acetate or- nitrate) very often filter dust is formed, which is blocking the pores of the membrane and decreasing its performance. Furthermore the filter dust can leave the membrane and enter the filtrate. The filter dust consists of the short chains of the membrane material and is transported during the production according to the phase inversion process towards the surface of the forming membrane. At this place it precipitates and blocks the pores. A removal of the short chains reduces the formation of filter dust markedly.



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Production of samples with different molecular masses

By means of the fractionation of broadly distributed samples one can obtain fractions differing in the molecular mass. This is for example necessary, if relations between polymer properties and its molar mass shall be examined, but no suitable samples are available. A familiar example for a molecular mass dependent property is the hydrodynamic radius of polymers in solution: The Kuhn-Mark-Houwink relation shows the dependence between the intrinsic viscosity and the chain length.

Shelf life of polymers

Certain components can reduce the shelf life of polymers. This can be e.g. impurities or the short chain material of the polymer itself (as they act as plasticizer or because the end groups have a negative influence). By means of fractionation these components can be removed or reduced to an acceptable amount.

Fractionation according to chemistry

Copolymers (like *Polystyrolacrylnitril*, SAN) often possess not only a distribution of the molecular mass but also in chemical composition. Under certain circumstances it is possible to fractionate these polymers according to chemistry and therefore optimize their properties.

Fractionation according to architecture

During the synthesis of polymers with complex molecular architecture, like branched polymers or stars, it often happens that linear chains or stars with lower number of arms are formed as unwanted side products. By means of fractionation these components can be removed.

Standards for analytics

By means of repeated fractionation of a broadly distributed sample it is possible to obtain samples with narrow distributions. These fractions can be used as standards, e.g. for the gel permeation chromatography (GPC/SEC).

The here mentioned case studies of polymer fractionation were done during the employment as scientific assistant in the working group of Prof. Dr. B. A. Wolf at the Johannes Gutenberg-University of Mainz. These case studies are all already published.



Viscometry

Capillary viscometry is considered as the most accurate method for the determination of the viscosity of Newtonian liquids. By this technique the time is measured a certain volume needs to flow through a capillary of defined dimensions. The meniscus is detected by means of light barriers, enabling the precise determination of the flow time.



In the field of polymer chemistry capillary viscometry is used to determine the viscosity number, the K-value and the intrinsic viscosity. By means of these data the molecular mass can be determined, which is one of the most important values to characterize polymers.

Measure:	
• Intrinsic Viscosity (also known as Staudinger-Index)	• Relative Viscosity, specific Viscosity
• Viscosity number	• Inherent Viscosity
• K-value (Fikentscher)	• Relative Viscosity, Viscosity ratio
• Viscosity index	• Kinematic Viscosity
• Degree of particle swelling	• Dynamic Viscosity

Methods:	
DIN EN ISO 1157	Determination of the viscosity number and the viscosity ratio of cellulose acetate in dilute solutions.
DIN EN ISO 1628/1-6	Determination of the viscosity of polymers in dilute solution using capillary viscometers: Part 1: General principles Part 2: Poly(vinyl chloride) resins Part 3: Polyethylene and Polypropylene Part 4: Polycarbonate (PC) moulding and extrusion materials Part 5: Thermoplastic polyester (TP) homopolymers and copolymers Part 6: Methyl methacrylate polymers
ISO 307	Plastics — Polyamides — Determination of viscosity number
SNV 195 598	Determination of the viscosity number of cellulose in EWN

The measurements can be adjusted to the requirements of the customers, e.g. choice of the solvent or temperature. We possess a large databank of Kuhn-Mark-Houwink parameters, enabling in many cases the transformation of the intrinsic viscosity into molecular weights.



Rheology

Rheology describes the flow and deformation behavior of samples under mechanical stress. These properties are very important for the production of coating, food, polymer, cosmetics, pharma and others.

Beside rheological and viscometric standard measurements we also deal with complex rheological questions like the development of measuring procedures for the areas research and development or quality control. The following table shows some rheological terms together with the corresponding product properties.

Procedure / Application:	
<i>Rotational experiments:</i>	
• Measurement at constant shear rate	• Standard quality control
• Flow curve	• Pumpability, Brushability, yield point
• Thixotropy	• Levelling and Sagging, Thickening
<i>Oscillatory experiments:</i>	
• Amplitude sweep	• Storage stability
• Frequency sweep	• Polymer processing
• Time test	• Geling, curing

Methods:	
DIN EN ISO 3219	Viscosity measurements with cylinder- and cone/plate geometry
ISO 6721/10	Oscillatory tests with plate/plate geometry
ASTM D 4440	Polymer melts using oscillatory tests
ASTM D 4473	Curing of resins using oscillatory tests

A detailed overview of our services and measuring procedures can be found on our homepage:
www.wee-solve.de.



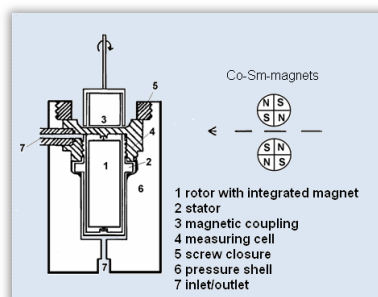
Pressure rheology

We possess special rheometers and viscometers for measurements under **pressure up to max. 2000 bar**. The **rotational rheometer** enables the analysis of liquids with viscosities between ca. 10 mPas and 100 Pas. The **rolling ball viscometer** is suitable for low viscous samples with Newtonian flow behavior. Typical samples are solutions in solvents above the boiling point or in supercritical gases .



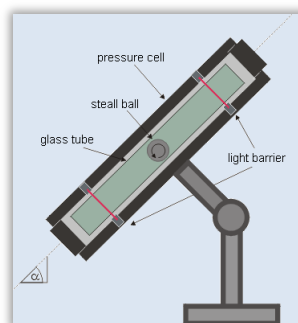
Rotational rheometer with cylinder geometry:

- Pressure cell made from Inconel
- Magnetic coupling
- Pressure: up to 1.000 bar
- Temperature: -40 to 300°C
- Middle to high viscous samples

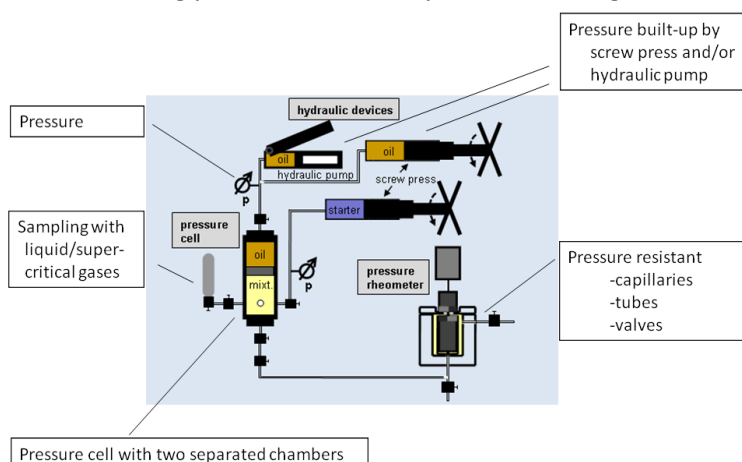


Rolling ball viscometer:

- Pressure resistant steel cell
- Glass tube with low roughness
- Precision ball (steel or glass)
- Pressure: up to 2.000 bar
- Temperature: 0 to 130°C
- Low viscous samples



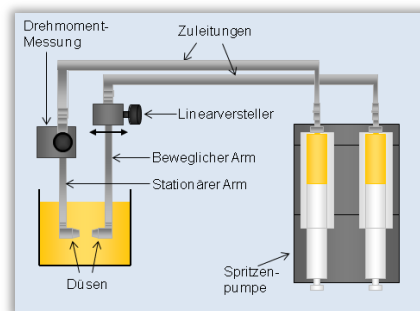
Our equipment includes complex accessories for the handling of samples under pressure like shown in the following picture for the analysis of a reacting mixture.





Extensional rheology

The extensional viscosity is an important parameter for many applications, e.g. in sprays (coating and cosmetic), inks or jet fuels (obfuscation) and in food industry. This property is relevant if extensional flow prevails.



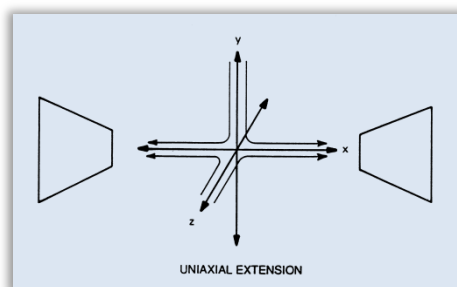
Always when the diameter of a flow channel changes the flow can't be described by shear flow only: Extensional flow takes (at least partially) place. In this case extensional viscosity plays an important role for the flow behavior. The extensional viscosity differs from the shear viscosity; for samples with simple flow behavior this difference can be calculated. For complex samples like polymer containing mixtures the extensional viscosity has to be measured.

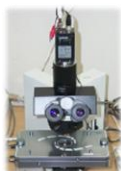
A typical example for an extensional flow is the streaming (entering or leaving) of a liquid through a nozzle. The measuring principle of our extensional viscometer is based on the determination of flows and forces in such a nozzle-flow.

Extensional flow rheometer: Rheometrics RFX Fluid Analyzer

- Extensional viscosity of liquid samples
- Measuring principle: opposed nozzles
- Uniaxial extensional flow
- Variation of the extensional rate by changing the nozzle diameter or flow rate.

The extensional flow rheometer Rheometrics RFX is suitable for the determination of extensional viscosities of liquids with shear viscosities ranging from 50 mPas to ca. 10 Pas. Depending on the viscosity of the sample extensional rates up to 10.000 1/s can be achieved.





Contract research

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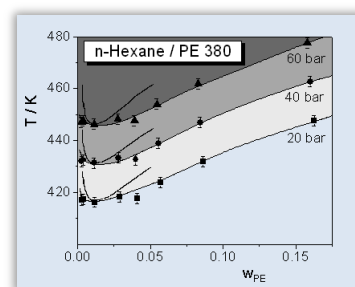
With our contract research we can answer individual questions of our customers. They profit from our long term praxis oriented research at the University of Mainz. We offer the following measurements as service:

Phase diagrams

Most synthetic polymeric products are produced and processed in liquid systems. The knowledge about the physico-chemical behavior of the system dependent on pressure, temperature, and shear stress is essential for the optimisation / improvement of the working conditions. This information can be shown in a phase diagram.

Under pressure

In industrial practice the solubility of substances in liquid solvents at temperatures above the boiling point is of great importance. For the determination of the solubility or of the general phase behavior a pressure cell with sapphire windows is available, where the miscibility can be established.

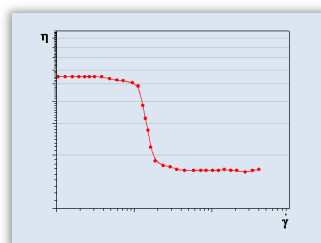
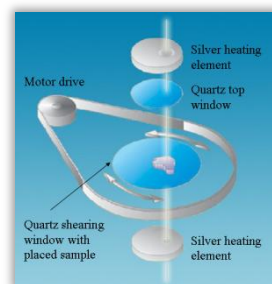


Under shear

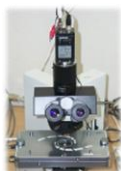
For many applications the phase behavior under shear has a great importance, e.g. homogenous solutions should not phase separate during a mechanical handling, whereupon high shear rates exist.

We are able to determine the phase behavior with two methods. On the one hand we can use an optical shear cell in combination with a microscope. These are the specifications of our measuring system:

- Optical shear cell CSS 450 (Linkam Scientific, GB)
- Microscope BX 50 (Olympus)
- CCD-camera Jai M 10 (Jai, Denmark)
- Plate/plate-geometry (gap width: 5 - 2.500 μm)
- Temperature: 20 - 450°C
- Shear rate: 0,003-7.500 1/s

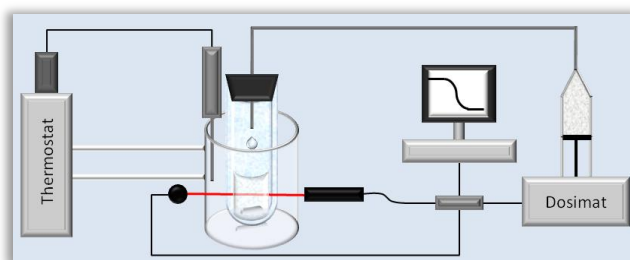


On the other hand the change of the phase behavior of liquid systems can be determined rheological. The measurement of the viscosity as a function of the shear rate (flow curves) can detect phase transitions in the phase diagrams as a step wise change of the viscosity.

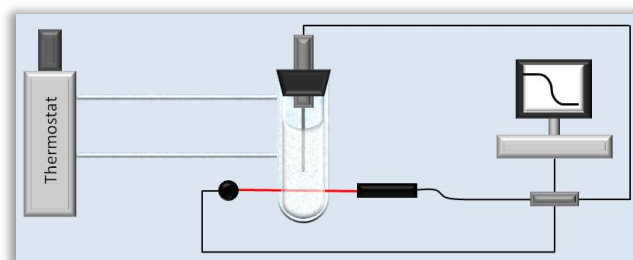


Cloud point measurements

For analysis of the cloud point curve and the phase diagram of e.g. polymer solutions as function of temperature and composition, we use two constructions. The temperature range is in both cases from 15°C up to 190°C. Further temperatures are available on request.



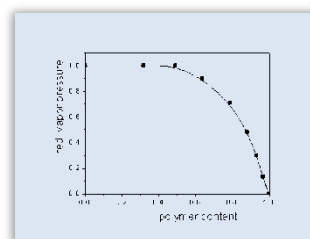
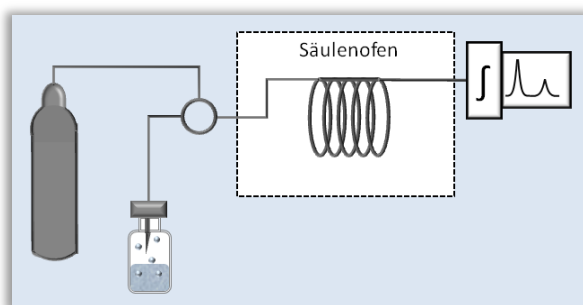
As function of composition

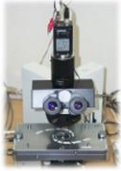


As function of temperature

Vapor pressure measurements

With this method the vapor pressure of polymer solutions or of colloid suspensions can be measured. The measuring instrument is made up of a headspace sampler and a gas chromatograph. The method is used for the quantification of interactions between the polymer and the solvent.





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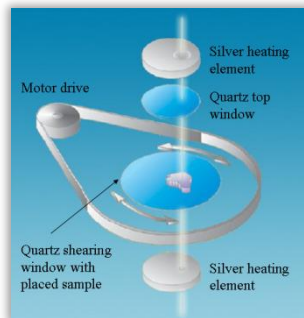
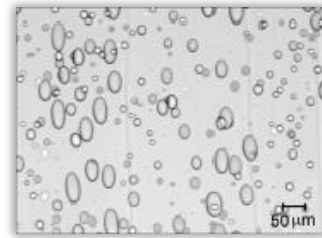


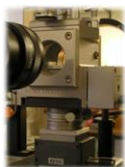
Morphology under shear

Our equipment enables us the observation of complex liquids relating to its structural dynamics under temperature controlled shear. Examples are coarsening binary liquid during its phase separation, shear induced mixing or demixing of polymer blends, defect dynamics of liquid crystals, aggregation of red blood cells and their deformation during the shear/flow etc.

The measuring system consists of a microscope and an optical shear cell. These are the specifications:

- Optical shear cell CSS 450 (Fa. Linkam Scientific, GB)
- Microscope BX 50 (Fa. Olympus)
- CCD-Camera Jai M 10 (Fa. Jai, Dänemark)
- Plate/plate-geometry (gap width: 5 - 2,500 μm)
- Temperature: 20 - 450°C
- Shear rate: 0.003-7,500 1/s



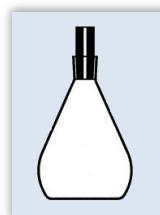


Determination of density

The density is used in different areas of application to characterize material or product properties, like the concentration. The determination of the density is one of the most used applied gravimetric procedures in laboratories. We offer the determination of the density by means of either pyknometers or the oscillation method (vibrometer).

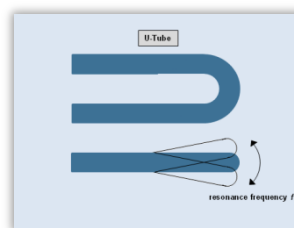
Pyknometer:

- Volume-calibrated glass flask
- Very precise method
- Suitable for solids, powders, granules, liquids, dispersions



Oscillation method:

- Determination of the resonance frequency of the sample
- (homogeneous) liquids
- Temperature: -10 to 80°C

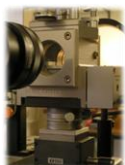


Methods:

DIN EN ISO 2811/1	Paints and varnishes – Pyknometer method
DIN EN ISO 2811/3	Paints and varnishes – Oscillation method
DIN EN ISO 1183/1	Non-cellular plastics – Pyknometer method
ISO 8130/3	Coating powders – Pyknometer method
ISO 1675	Liquid resins – Pyknometer method
ISO 2781	(Thermoplastic) Elastomers
ISO 845	Cellular rubbers and plastics: Determination of apparent density

Determination of densities under elevated Pressures/ elevated temperatures

Due to thermal expansion and compressibility of matter the density depends on temperature and pressure. Our equipment consists of a pressure and temperature resistant oscillating U-tube and enables the determination of densities for temperatures up to 140°C and pressures up to 400 bar. By means of the Tait equation the values can normally be reliable extrapolated up to 1000 bar.

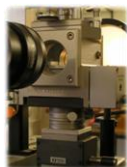


Determination of chemical characteristics

Chemical characteristic numbers are applied in many fields like quality control, research and development. Our range covers the volumetric characterization of polymers/plastics according to standardized methods.



Methods:	
DIN EN ISO 4629	Binders for paints and varnishes Determination of hydroxyl value – Titrimetric method
DIN EN ISO 3681	Binders for paints and varnishes Determination of saponification value by the titrimetric method
DIN EN ISO 1061	Unplasticized cellulose acetate Determination of free acidity
DIN EN ISO 3001	Epoxy compounds: Determination of epoxy equivalent
DIN EN ISO 2114	Plastics (polyester resins) and paints and varnishes (binders) Determination of partial acid value and total acid value
DIN EN ISO 1264	Homopolymer and copolymer resins of vinyl chloride Determination of pH of aqueous extract
ISO 14900	Plastics (Polyols): Determination of hydroxyl number
	Determination of degree of substitution for cellulose acetate according to E. Samios



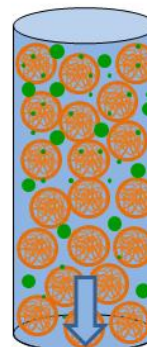
GPC/SEC

The Size Exclusion Chromatography (SEC, or Gel Permeation Chromatography GPC) is the most common method for polymer analysis. In this process the polymer is solved in an eluent and fractionated in a separation column, which is filled with porous material. The fractionation of the polymer only bases on geometric pore effects, i.e. for this process the separation parameter is the hydrodynamic volume of the polymer. By means of different detectors the polymer can be analysed.

In the following the specifications of our SEC/GPC-apparatuses are listed:

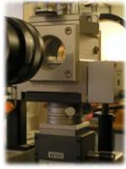
Aqueous Gel Permeation Chromatography

- Analyte: Polyelectrolytes, non-ionic water soluble polymers, polysaccharides
- Sample amount ~100 mg
- Range of molar mass: $10^3 - 10^6$ g/mol
- Eluent: aqueous salt solution, if necessary. MeOH/H₂O-mixture
- Detector: UV-Detector, RI-Detector
- Conventional calibration with dextran
⇒ Molecular weight (M_w , M_n), polydispersity PDI
- Universal calibration
⇒ M_w , M_n and PDI for additional polymers accessible



Organic Gelpermeationschromatography

- Analyte: in THF or toluene soluble polymers
- Sample amount ~ 100 mg
- Range of molar mass: $10^3 - 10^6$ g/mol
- Eluent: Tetrahydrofuran, Toluene
- Detectors: UV-Detector, RI-Detector
- Conventional calibration with polystyrene, polymethylmethacrylate
⇒ Molecular weight (M_w , M_n), polydispersity PDI
- Universal calibration
⇒ M_w , M_n and PDI for additional polymers accessible

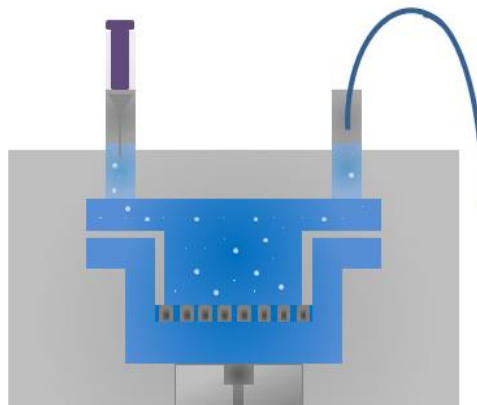


Osmometry

The membrane osmometry is a technique for the determination of molecular masses of polymers by means of osmosis. The phenomenon of osmosis describes the attempt of solvent molecules to go through a semipermeable membrane into a solution. The detection of the so originated osmotic pressure can be determined into the numer average of molecular weight M_n of the solved polymer.

In the following the specifications of our membrane osmometer are listed:

- Analyte: in water or in organic solvents soluble polymers, nanoparticle-dispersions
- Sample amount ~ 100 - 500 mg
- Range of molar mass: $10^4 - 10^6$ g/mol
- Equipment: GONOTEC Membrane Osmometer OSMOMAT 090
- Solvent: Water, aqueous salt solutions, organic solvents
- Membran: Cellulose-triacetate (cut-off 5.000, 10.000, 20.000 g/mol), regenerated cellulose (cut-off 20.000 g/mol)
- Measurement of the osmotic pressure depending on the polymer concentration
 - ⇒ Determination of the absolute molecular mass M_n
 - ⇒ Determination of the A_2 -value (2nd virial coefficient): Measure for solvent quality





Analysis

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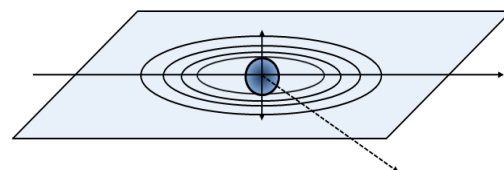


Static light scattering

By means of static light scattering (SLS) molecules in polymer solutions can be extensively analysed. This method is an absolute method, which detects the scattering intensity depending on the angle (average determination over the time).

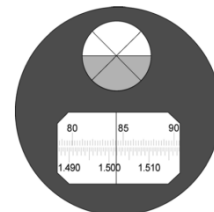
In the following the specifications of our static light scattering equipment are listed:

- Equipment: modified Fica50
- Temperature: 5°C to 80°C
- Wave length of the laser: 632 nm
- Absolute molecular mass M_w
- Radius of gyration $\langle R_g \rangle$
- Determination of the A_2 -value (2nd virial coefficient): Measure for solvent quality



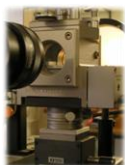
Abbe-Refractometer

The refractive index in an optical material characteristic, whereupon it is a dimensionless physical quantity. It indicates for which coefficient the wavelength and the phase velocity of the light is lower in the analysed fluid than in vacuum.



For the determination of the refractive index we use a so-called Abbe-Refractometer. The measuring principle is the fact, that the critical angle of the received total reflection at the interface is depending on the used optical materials. The refractometer, which is developed by E. Abbe, enables us to determine the critical angle of a thin liquid layer, which is filled through the glass prisms, very precisely.

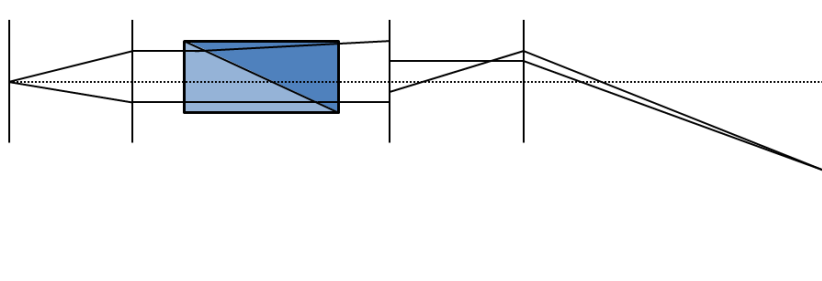
The refractive index can depend according to the determined material strongly from the temperature. Therefore the measuring system is thermostated during the measurement.



Differential refractometer

The refractive index increment dn/dc is the dependency of the refractive index to the concentration. The measuring value is needed in many areas, e.g. for the evaluation of light scattering measurements, for the determination of the sedimentation in ultracentrifuges, and for the determination of diffusion.

For these applications the preciseness of an Abbe-Refractometer is ofte not adequate enough. Therefore we use a precision differential refractometer, which was developed by O. Bodmann.



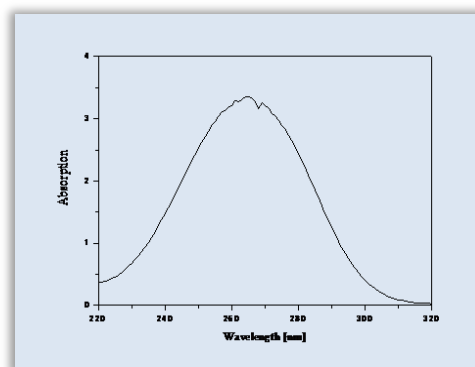
UV/Vis-Spectroscopy

Our equipment consists of a two-beam spectrometer which has a wavelength range from 190 up to 1100 nm. The two-beam optics allows us the simultaneous measurement of the sample and of the reference (pure solvent).

By means of the UV/Vis-spectroscopy we can offer the following analysis

Absorption spectra

The absorption spectroscopy can be established for **qualitative** as well as for **quantitative analysis**: Due to the form and the position of the absorption bands qualitative conclusions about the molecule can be made, which can e.g. be used for structure determination. An important application for quantitative analysis is the identification and characterization of specific molecular groups.



Time-dependent measurements

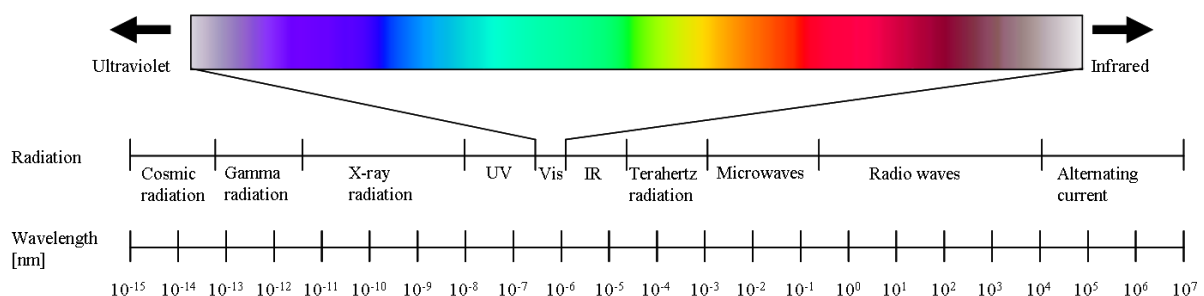
Time-dependent measurements of the absorption allow us to **follow the chemical reaction kinetic**. With plotting the absorption as function of the measuring time the reaction order and the reaction velocity constant can be determined due adjustment the reaction velocity law to the experimental data.

Wavelength-dependent measurements

The measurement of the absorption at different wavelengths can be used for **pureness validation** of the investigated substance. If the sample has no contamination, the ratio of the absorptions at different wavelengths stays the same. If the sample is polluted, the wavelength ratio changes on condition that the contamination also absorbs at the same wavelengths.

Determination of the concentration

The photometric concentration measurement of a sample is carried out with a calibration curve. For this purpose the absorptions of references with known concentrations are measured. These absorption data were plotted against the concentrations and the data points were interpolated with an adequate fitting curve. The originated calibration curves normally follow the Lambert-Beer law, i.e. they are lines through origin.



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