WEE-Solve GmbH

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

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Content

POLYMER FRACTIONATION / PURIFICATION

Alteration of the molecular weight 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
- Density
- Crystallinity, glass temperature
- Purity
- Volatility
- Shelf life

- Refractive index
- Degradation
- Permeability skin / kidney
- Inflammable behavior
- Oligomer content
- 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).
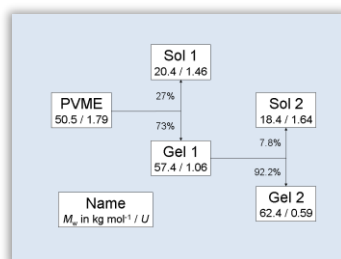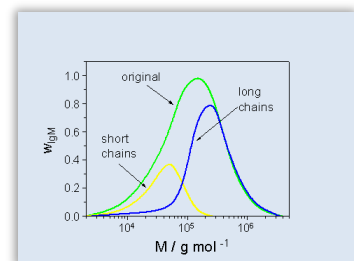
By the choice of the fractionation parameters (temperature, compositions) the "cut" through the molecular mass distribution can be varied. Narrow molecular mass distributions can be achieved by repeated fractionation.

Case studies

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

Recovery / purification of poylmers 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 sufficient 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.

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.
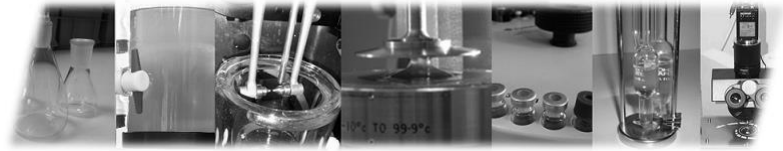
RHEOLOGY / VISCOMETRY

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)
- Viscosity number
- K-value (Fikentscher)
- Viscosity index
- Degree of particle swelling

- Relative change of viscosity, specific viscosity
- Inherent viscosity
- Relative viscosity, viscosity ration
- Kinematic viscosity
- 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) molding 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
ASTM D4603	Determining Inherent Viscosity of PET by Glass Capillary Viscometer
ASTM 5525	Measuring solution viscosity of Polymers with a Differential Viscometer

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.
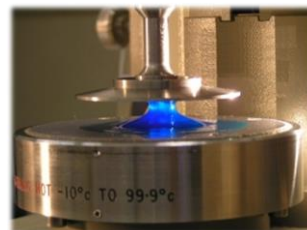
Procedures / Applications:

Rotational experiments:

• Measurement at constant shear rate	• Standard quality control
• Flow / viscosity curve	• Pumpability, brushability, yield point
• Thixotropy test	• Levelling and sagging, thickening

Oscillatory experiments:

• 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

Pressure rotational rheometer

The specifications of our pressure rheometer are the following:

- Pressure range: standard to 150 bar
- Temperature range: RT … 300°C
- Rheometer: MCR 102 (Anton Paar Germany GmbH)
- Measuring systems: cylindric, blade, cone/plate, and plate/plate measuring system
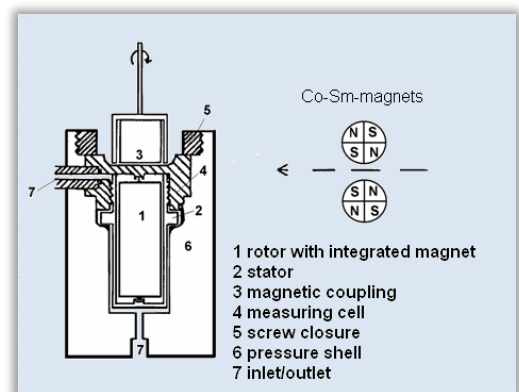- Filling volume: measuring cell up to 20 mL

Friendly authorized by
Anton Paar Germany GmbH

Pressure rheometer for extremely high pressures

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 range: up to 1.000 bar
- Temperature range: -40 to 300°C
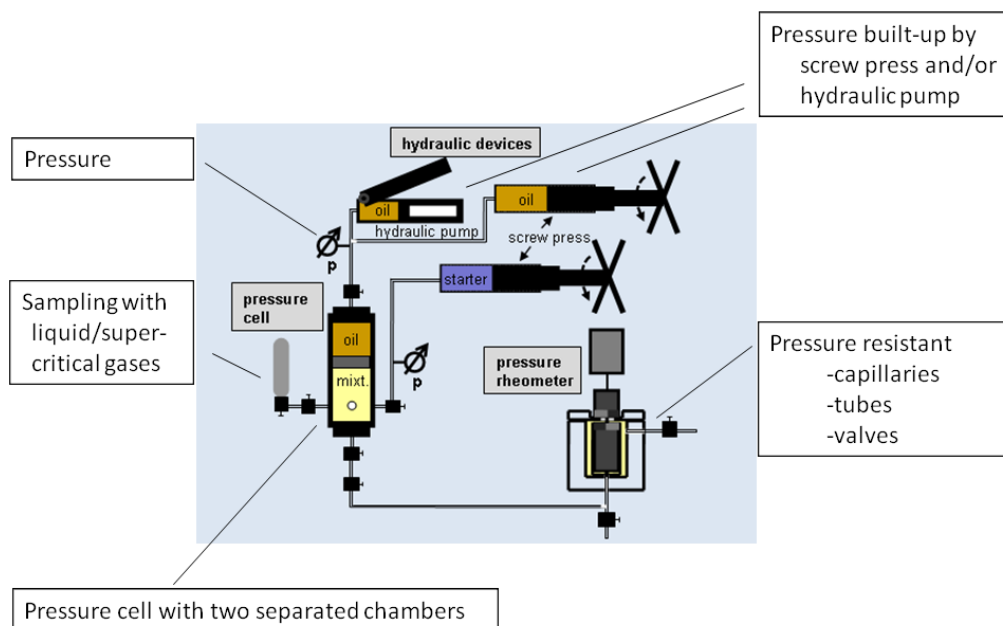- Middle to high viscous samples

Co-Sm-magnets

1 rotor with integrated magnet
2 stator
3 magnetic coupling
4 measuring cell
5 screw closure
6 pressure shell
7 inlet/outlet

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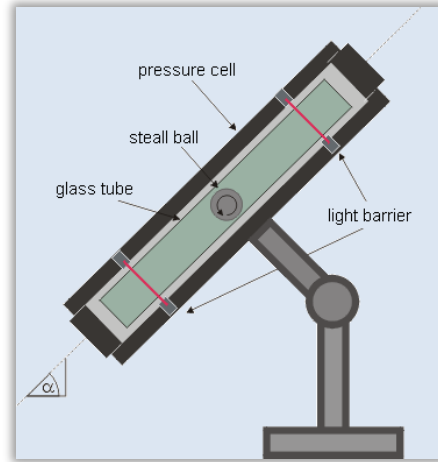
Our equipment includes complex accessories for the handling of samples under pressure like shown in the following picture for the analysis of a reacting mixture.

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Extensional rheology

Liquids under extensional flow

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.
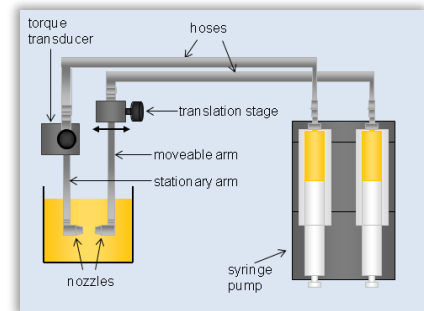
Always when the diameter of a flow channel changes the flow can't be described by shear flow only: Extensional flow takes (at least partially) place. In this case extensional viscosity plays an important role for the flow behavior. The extensional viscosity differs from the shear viscosity; for samples 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.
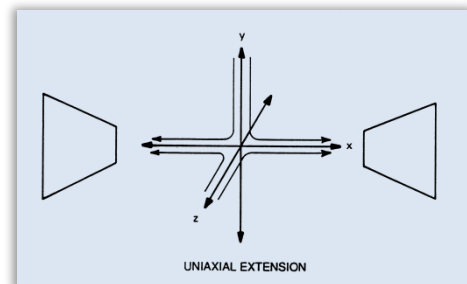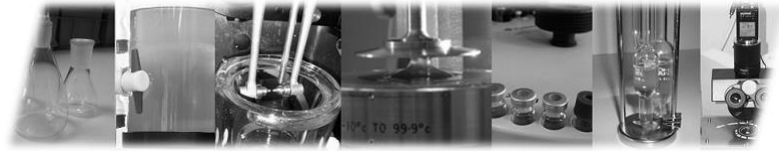
Extensional rheological measurements of foils and films:

Extensional rheological measurements of oils, films, and fibers can be realized by means of the **Universal Extensional Fixture (UXF)** combined with an air beared rheometer. The measurements deliver information about the temperature stability, the shrinking, recovery, and brittleness of the material.
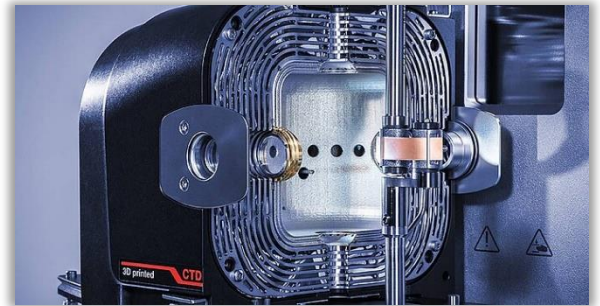
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The Universal Extensional Fixture (UXF) is a combined measuring system of a rotating and a stationary cylinder. With the help of a convection oven deformation and shear stress-controlled DMA experiments can be realized in a huge temperature range.

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CONTRACT RESEARCH

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 diagram

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 optimization/improvement of the working conditions. This information can be shown in a phase diagram.
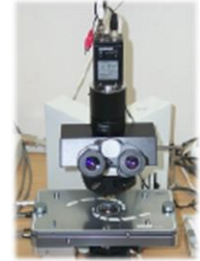
Under pressure

In industrial practice the solubility of substances in liquid solvents at temperatures above the boiling point, in fluidified or in supercritical gases 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.
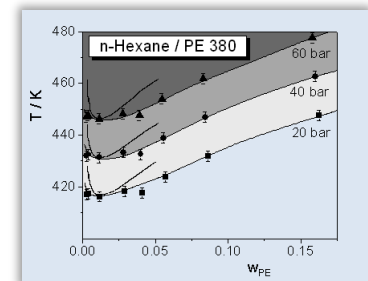

Under shear

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. One can find the phenomenon of the shear induced homogenization of a two-phase system. That means clear solutions can get turbid by shaking and vice versa.
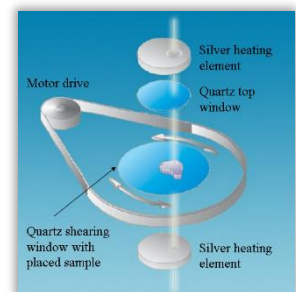
We are able to determine the phase behavior with two methods. On the one hand we can use an **optical shear cell** in combination with a microscope. These are the specifications of our measuring system:

- Optical shear cell: CSS 450 (Fa. Linkam Scientific, GB)
- Microscope BX 50 (Fa. Olympus)
- CCD-Camera Jai M 10 (Fa. Jai, Dänemark)
- Plate/plate-geometry (Gap: 5 -2,500 mm)
- Temperature range: 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 resp. viscosity curve) can detect phase transitions in the phase diagram as a step wise change of the viscosity.
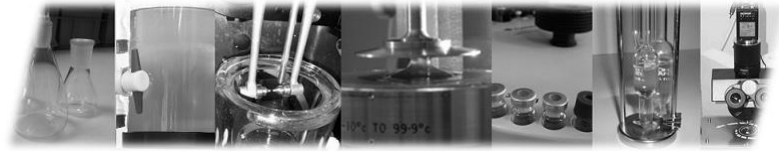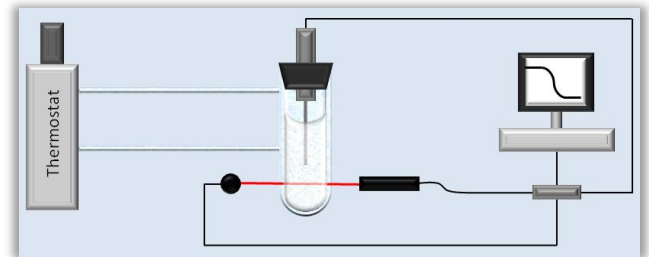
Phase behavior

For the 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 up to 190°C. Further temperatures are available on request.
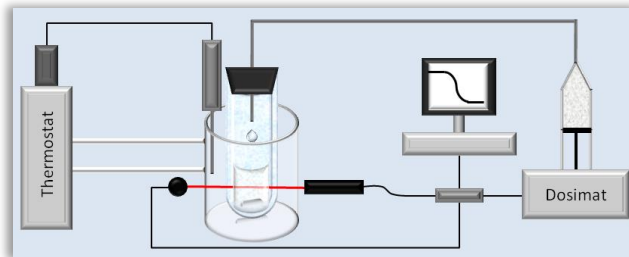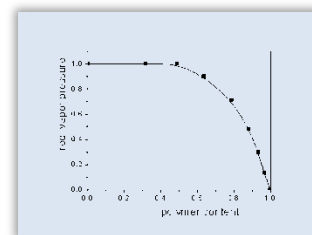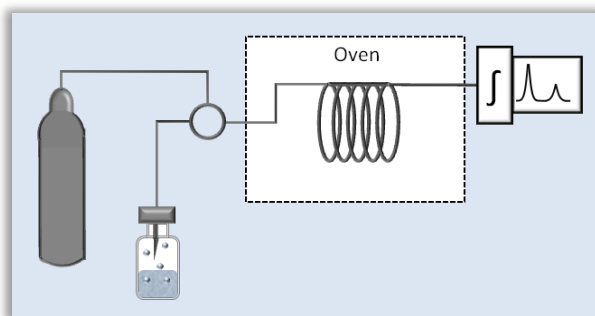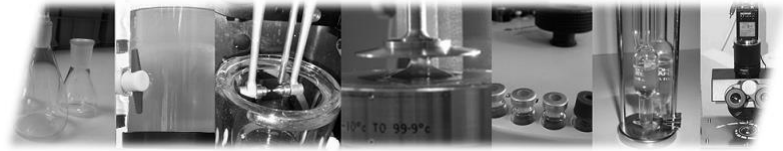

As a function of composition

As a function of temperature

Vapor pressure

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. This method is used for the quantification of interactions between polymers and solvents.

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 of our measuring system:

- 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: 5 -2,500 mm)
- Temperature range: 20 - 450°C
- Shear rate: 0,003-7.500 1/s
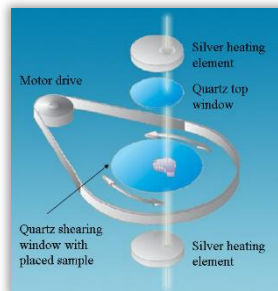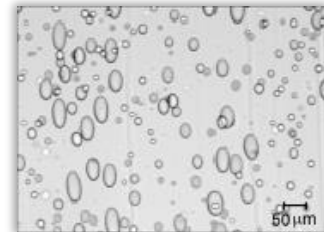
ANALYSIS

GPC/SEC

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. By means of different detectors the polymer can be analyzed. The column material consists normally of highly cross-linked PS latex particles, whereupon the pores have a broad size distribution. 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.

These are the specifications of our measuring system:

Aqueous SEC/GPC

- 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/H_2O-mixture
- Detector: UV-Detector, RI-Detector
- Conventional calibration with dextran
- $\Rightarrow$ Molecular weight (Mw, Mn), polydispersity PDI
- Universal calibration
- $\Rightarrow$ Mw, Mn and PDI for additional polymers accessible

Organic GPC/SEC

- 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
  $\Rightarrow$ Molecular weight (Mw, Mn), polydispersity PDI
- Universal calibration
  $\Rightarrow$ Mw, Mn and PDI for additional polymers accessible
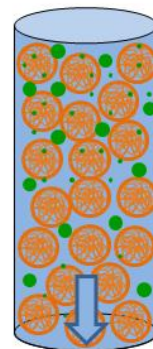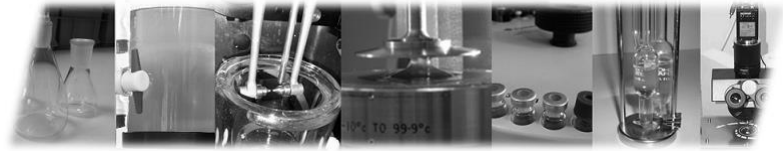
Membrane osmometry

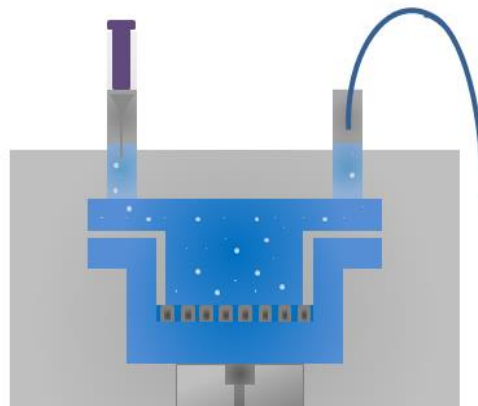Membrane osmometry is a technique for the determination of molecular masses of polymers by means of osmosis. The phenomenon of osmosis describes the attempt of solvent molecules to go through a semipermeable membrane into a solution. The detection of the so originated osmotic pressure can be determined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

These are the specifications of our measuring system:

- 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
- Membrane: 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
  $\Rightarrow$ Determination of the absolute molecular mass Mn
  $\Rightarrow$ Determination of the A2-value (2nd virial coefficient): Measure for solvent quality

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Classification numbers

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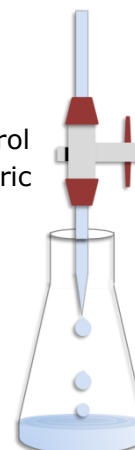
Methods:

|	
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 - 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
	Quantitative determination of chloride- and bromide ions (Mohr method)

Physical parameters

Physical parameters are needed in the fields quality control, security data, and research and development. We offer following methods:

Absorption spectra (UV/Vis)

We use a two-beam spectrometer with a wavelength range from 190 to 1,100 nm. We can offer following experiments:

- Absorption spectra
- Time depending testings (e.g. reaction kinetic)
- Wavelength depending testings (e.g. purity testing)
- Determination of concentration
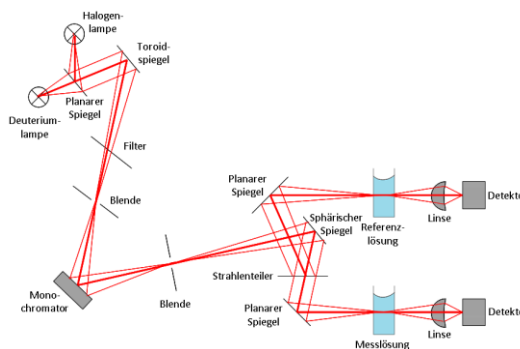
Refractive index

For the determination of the refractive index, we use an **Abbe-Refractometer**.
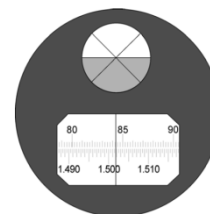
Methods:

DIN EN ISO 489	Plastics – Determination of refractive index
ISO 1739	Butter – Determination of refractive index of the fat (Reference method)

Vapor pressure

The vapor pressure occurs when a gas in a closed system with the associated liquid is in thermodynamic equilibrium. It is determined in a double-jacketed glass vessel according to VERORDNUNG (EG) Nr. 440/2008 DER KOMMISSION from 30.05.2008. The determination can be carried out using both the static and dynamic methods.

- Sample volume: ca. 20 mL
- Temperature range: 5 … 60°C
 (lower/higher temperatures on request)

Density

Density is used in various areas of application to identify material or product properties, such as concentration. The determination is one of the most frequently used gravimetric methods in the laboratory. Our repertoire includes measuring density using a pycnometer and a vibration measuring device.
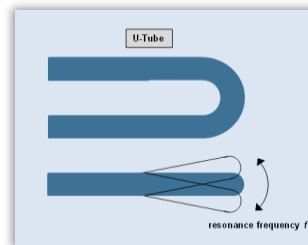
Pycnometer:

- Volume calibrated glass bulb
- Very precise procedure
- Suitable for solids, powders, granules, liquids, and dispersions
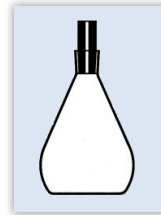
Vibrometer:

- Measurement of the natural frequency of the sample
- (homogeneous) liquids
- Temperature range: -10 … 80°C

Methods:

DIN EN ISO 2811/1	Paints and vanishes – Pycnometer method
DIN EN ISO 2811/3	Paints and vanishes – Oscillation method
DIN EN ISO 1183/1	Plastics – Pycnometer method
ISO 8130/3	Coating powders – Pycnometer method
ISO 1675	Plastics – Liquids resins – Pycnometer method
ISO 2781	Rubber, vulcanized of thermoplastic
ISO 845	Cellular plastics and rubbers – Determination of apparent density

Density under elevated pressure / temperature

Due to the compressibility of substances, the density depends not only on the temperature but also on the pressure. Our measuring system consists of a pressure-resistant and temperature-stable vibration measuring device and allows density measurements up to 140°C and 400 bar. Using the Tait equation, these values can generally be extrapolated reliably up to at least 1,000 bar.

Dipole moment

The dipole moment is a measure of the spatial separation of charges in the molecule (strength of the dipole character). To determine the dipole moment for organic liquids, we use the WTW model DM01 dipole meter with a measuring frequency of 2MHz. A dipole meter can be used to measure the dipole moment and dielectric constant of a liquid sample at a specific temperature.
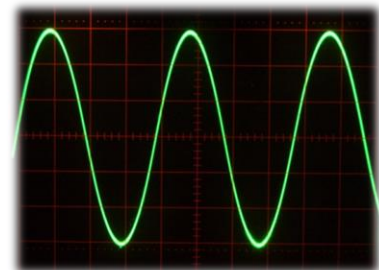
Freezing point depression

Freezing point depression refers to the phenomenon that the freezing point / melting point of solutions is lower than that of the pure liquid. We have a double-jacketed glass vessel at our disposal to determine the freezing point depression. By slowly cooling the dissolved sample or the pure liquid, the freezing point and the resulting freezing point depression can be determined.

- Temperature range: ...-40°C
  (other temperatures after request)

Possible parameters that can be determined using freezing point depression:

- Molar mass
- Number averaged molar mass (polymer, oligomer)
- Osmololality

Surface tension

The surface tension of a liquid and the interfacial tension between two liquids are determined using the **Du Noüy ring method**. If requested, we measure according to the OECD GUIDELINES FOR THE TESTING OF CHEMICALS #115.

Methods:

When measuring the surface or interfacial tension, the force acting on a ring wetted with the liquid is measured, which is created when the ring moves from one phase to the other due to the tension of pulled-out liquid lamella. If the lamella is perpendicular to the plane of the ring when the ring moves out, a maximum force occurs, which correlates with the surface or interfacial tension. The maximum force is determined using an electronic force sensor.
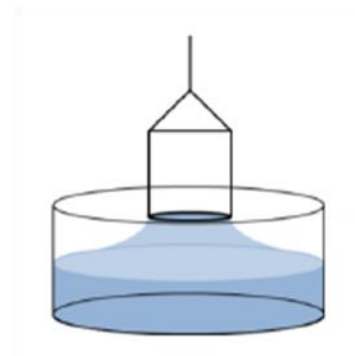
Melting point

The melting point is determined according to OECD GUIDELINES FOR THE TESTING OF CHEMICALS #102.

Boiling point

The boiling point is determined according to OECD GUIDELINES FOR THE TESTING OF CHEMICALS #103.

In addition, the distillation process can be determined according to DIN EN ISO 3405 resp. AST D86.

OECD/EU methods:

OECD (Organization for Economic Cooperation and Development) developed standardized analysis methods as part of chemical testing. We provide you with the following physical-chemical tests to characterize your substance or to create safety-relevant data:

Standard	Description
OECD 101	UV/Vis absorption spectra
OECD 102	Melting point
OECD 103	Boiling point
OECD 104	Vapor pressure
OECD 105	Water solubility
OECD 112	Dissociation constant in water
OECD 114	Viscosity
OECD 115	Surface tension
OECD 118	Number average molar mass and molar mass distribution of polymers by means of size exclusion chromatography
OECD 119	Low molar mass ratio of polymer by means of size exclusion chromatography
OECD 122	Acidity and Alkanity

In addition, we offer the following analyzes to determine the physico-chemical properties according to VO(EG)440/2008, Appendix A:

Standard	Description
A.1	Melting / freezing point
A.2	Boiling point
A.3	Relative density
A.4	Vapor pressure
A.5	Surface tension
A.6	Water solubility
A.8	Distribution coefficient
A.18	Number average molar mass and molar mass distribution of polymers
A.19	Low molar mass ratio of polymer by means of size exclusion chromatography
A.20	Dissolution / extraction behavior of polymers in water
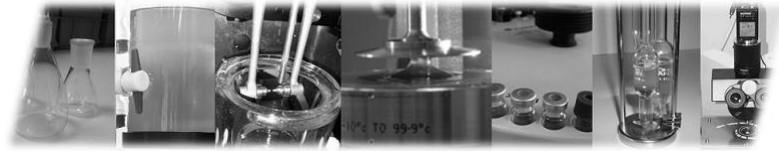
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The WEE-Solve GmbH offers you flexible customer orientated trainings for following topics:

- **(Capillary) Viscometry**
- **Rheology**

The courses can be hold as an inhouse-training in your facilities with your staff but also in our labs.

For each accomplished training the participants will get a certificate of participation.

The contents will be customized according to your instructions.

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