PSS Analytical Services

Product information from PSS Polymer Standards Service GmbH

Version: 01 – 02

Polymer testing is a **matter of trust**
Trust in the **knowledge and competence of PSS.**

Highlights

- Customer-oriented services
- Short turn around time
- State of the art analytical equipment
- Application development and transfer
- Excellent price performance ratio

Reliable and reproducible results certified according to DIN EN ISO 9001.

TÜV CERT
DIN EN ISO 9001:2000
Zertifikat:01 100 84065

We are prepared for the challenge

In addition to the development of innovative polymer standards, GPC columns and GPC software, **PSS** offers analytical solutions for polymer characterization.

Our highly qualified staff use their experience with modern instrumentation to solve the most complex analytical problems. 15 GPC systems running various eluents guarantee quick turn around times on polymer characterization.

As of 1998 all divisions of our company are certified according to DIN EN ISO 9001. A framework of strict test procedures for analytical methods and system validation provides maximum confidence and reproducibility. Ongoing staff training, on both internal and external courses, ensures **PSS** continues to meet the highest quality standards.

Potential of GPC

Producers and processing businesses need reliable quality control of polymers and biopolymers. Besides the type and purity of a polymer, the molecular weight distribution plays an important role for the physical and processing properties.

Gel permeation chromatography (GPC) is an established separation method for the determination of molecular weight averages and molecular weight distributions of polymers.

GPC separates according to molecular size, the elution order is from big (high molar masses) to small molecules (low molar masses). Therefore, the method can be used for additive analysis, determination of oligomer content and purification of polymer samples.

The GPC method can be easily expanded by online coupling of special detectors, thus yielding additional information about your sample.

GPC Competence:

- microanalytical, analytical and preparative GPC
- organic or aqueous eluents, with electrolyte or organic additives
- high temperature GPC (up to 155°C = 311° F)

Conventional GPC

The polymer processing industry often faces the problem of different polymer batches presenting varying properties, even though the technical specification is the same. Conventional GPC with concentration detectors (UV,RI) offers an outstanding way to compare these samples (decision between pass or fail), even without calibration.

The GPC provides additional information about the complete molecular weight distribution and is therefore more sensitive to product fluctuations than controlling molecular weight averages. Other important applications are stability tests and investigations of the degradation of polymers and biopolymers.

An internal standard is used to monitor the constant flow of the pump and for flow correction as needed. Afterwards the molecular weight distribution is calculated from the elugram using the corresponding calibration curve. Important for product approval in the USA: It is easy to determine the percentage of a given molar mass (eg. < 500 g/mol) from the molecular weight distribution.

Additives and stabilizers can be separated from the polymer and a quantitative determination of these compounds is possible. The analysis report shown below lists all relevant parameters of the measurement and documents the sample preparation.

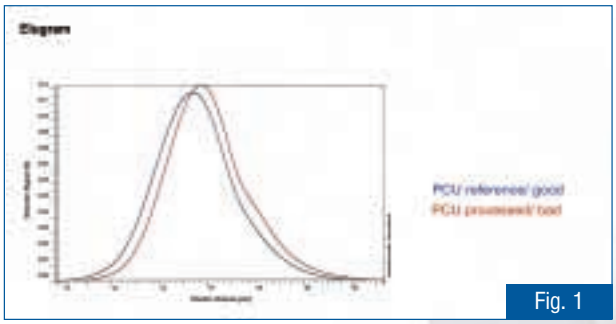

Fig. 1

Figure 1:
Quality control with elugrams of two PMMA samples (comparison pass/fail).

With calibration of your GPC you get molecular weight averages and information about the molecular weight distribution of your polymer. As a manufacturer of a great variety of polymer standards, **PSS** is able to use the optimum standards to characterize your samples. Before each measurement series, the analytical system is validated and calibrated with a 9 to 12 data point calibration (Figure 2).

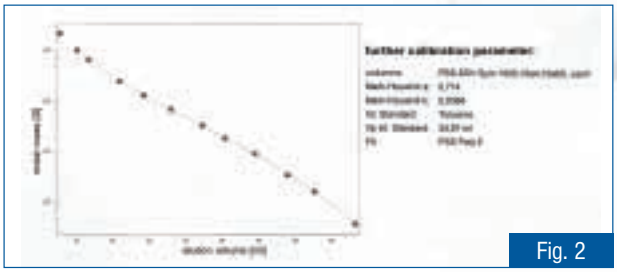
Fig. 2

Figure 2:
Typical polystyrene calibration curve from PSS ReadyCal in THF. Columns: PSS SDV, dimensions 8x300 mm, particle size 5 µm, porosity 1000 Å, 10^5 Å, 10^6 Å, flow: 1.0 ml/min, detector: RI

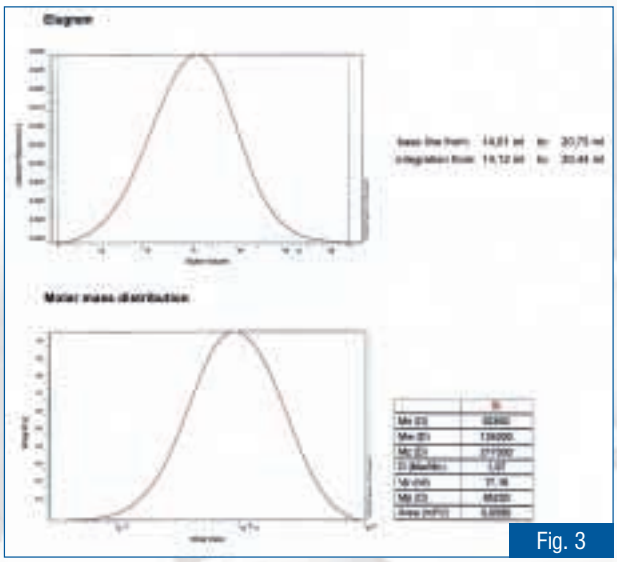
Fig. 3

Figure 3:
PSS analysis report with elugram, differential molecular weight distribution and molecular weight averages.

Your results at a glance:

- **simple comparison of polymer samples**
- **molecular weight distribution**
- **molecular weight averages: Mw, Mn, Mz**
- **percentage of mass, eg. < 500 g/mol**
- **chemical composition**

Light scattering detection

The light scattering detector provides absolute molar masses without requiring the appropriate polymer calibration standards. The GPC separates the sample by size and the online light scattering detector directly determines the molar mass. You get the absolute weight average (Mw) and molecular weight distribution of the polymer.

The method is limited by the molecular weight of the sample (depending on the type of polymer), the minimum molar mass normally has to be above 5000 g/mol. PSS uses a low angle (LALLS) and a multi angle light scattering detector (MALLS) during routine operation. The MALLS detector provides additional information about the radius of gyration, which is derived from the angle dependency of the scattered light.

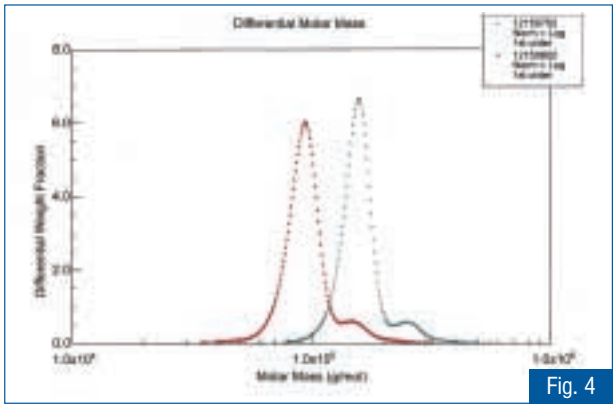

Fig. 4

Figure 4:
Differential molecular weight distributions of two proteins in overlay mode. Both Albumin samples contain the dimer.

From the combination of absolute molecular masses and corresponding radius of gyration, it is possible to obtain important structure information about the polymer, e.g. branching.

Your results at a glance:

- **molecular weight distribution**
- **absolute molecular weight average Mw**
- **radius of gyration**
- **branching/structure information**

Viscosity coupling

Another possibility to get exact molar masses without having the proper polymer standards is offered by online viscosity detection. This method uses the concept of universal calibration and provides not only the correct masses and molecular weight distributions, but also information about the structure of the polymer. With viscosity detection you can also analyze small molecules (e.g. oligomers), a big advantage over online light scattering measurements.

The GPC viscosity coupling allows you to determine the important relationship between intrinsic viscosity and molar mass of a polymer within one measurement. From this data, you can calculate the Mark-Houwink parameter of the investigated polymer - solvent system containing the structural information.

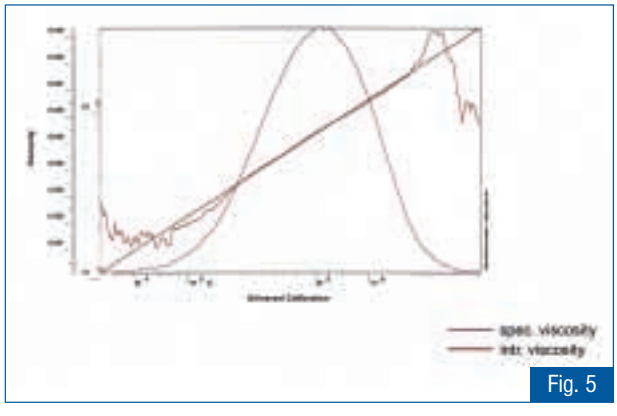

Fig. 5

Figure 5:
Typical analysis report for GPC viscosity coupling. Plot of differential molecular weight distribution and intrinsic viscosity versus molar mass (determination of Mark-Houwink coefficients).

Your results at a glance:

- **intrinsic viscosity**
- **Mark-Houwink parameter**
- **molecular weight distribution**
- **molecular weight averages, Mw, Mn, Mz**
- **branching/structure information**

LC-FTIR coupling

This method is suitable when the focus is on component identification of a complex mixture (e.g. polymer, additives etc.), not only on the molecular weight distribution of a sample. The separation by GPC or HPLC alone would not be sufficient because it does not provide information about the chemical nature of the compounds. Therefore, the coupling of liquid chromatography (LC) with Fourier-Transform-Infrared spectroscopy (FTIR) allows the identification of unknown fractions with the help of a spectra database. The coupling interface evaporates the solvent, precipitating the sample fractions on a germanium target, later used to record the series of FTIR–spectra, resolved in order of elution time.

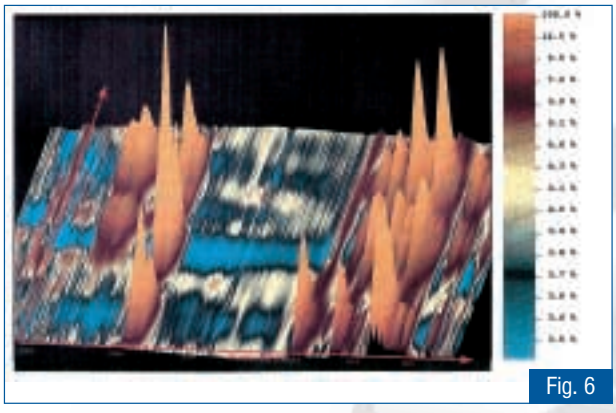

Fig. 6

Figure 6:
Compound identification by GPC–FTIR coupling. A series of FTIR spectra of a complex terpolymer plotted versus elution time.

2D chromatography

Complex polymer systems, e.g. polymer blends, copolymers or functionalized polymers, often show both physical and chemical heterogeneity: a chain length distribution (physical heterogeneity) and variations in chemistry and/or structure. GPC alone cannot characterize such systems because it only separates according to molecular size, but the combination of two chromatographic separation methods will.

In most cases it is best to start separating by chemical composition (HPLC) followed by a second separation step of the chemical fractions according to molecular size (GPC). Such analyses are only efficient if device control and data recording can be automated.

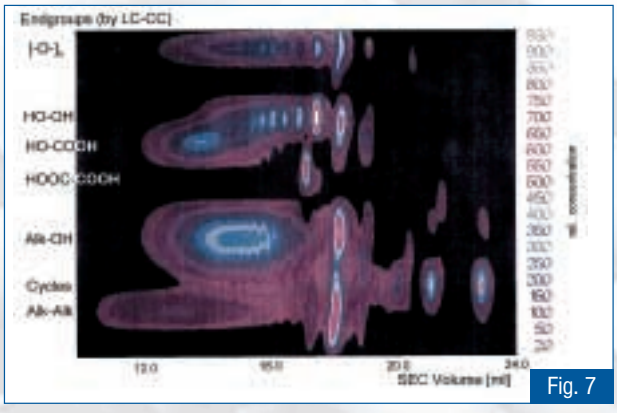

Fig. 7

Figure 7:
HPLC-GPC coupling contour plot with separation according to end-group functionality and molar mass.

PSS offers the development of 2D applications and performs the analysis for you with our special software for data acquisition, quantitative interpretation and data plotting, the WINGPC 2D module.

Your results at a glance:

- **chemical structure**
- **chemical purity**
- **information about additives**
- **chemical composition**

Your results at a glance:

- **complete deformulation**
- **composition**
- **end-group distribution**
- **molecular weight distribution**
- **molecular weight averages, Mw, Mn, Mz**
- **copolymer composition**

Static light scattering

Static light scattering is an established and exact method for the absolute determination of the weight average molar mass (Mw) of a polymer.

The measurement is carried out without separation of the polymer solution in a light scattering cell. The measured quantity is the intensity of the scattered light (excess-Rayleigh scattering), which is proportional to the average molecular size of the dissolved substance. A series of measurements, performed with different concentrations (c) at various scattering angles (theta), results in the weight average molecular mass Mw. One requirement is the knowledge of the refractive index increment (dn/dc) of the polymer in the solvent used.

The molecular weight average Mw is determined with high accuracy by plotting the data and extrapolation of c and theta to zero (Zimm-plot). Another parameter derived from the Zimm–plot is the second virial coefficient A2.

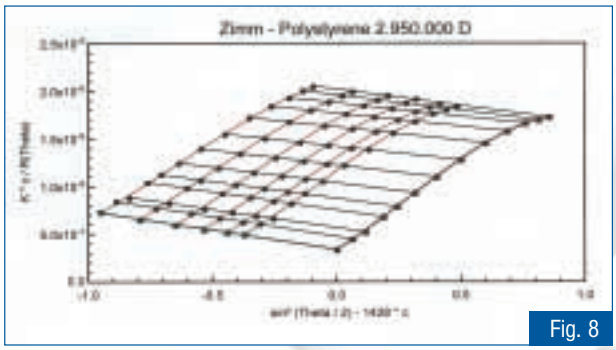

Fig. 8

Figure 8:
Classical Zimm–plot of polystyrene in toluene, measured with a multi angle light scattering detector (MALLS).

Your results at a glance:

- **absolute molecular weight average Mw**
- **radius of gyration**
- **second virial coefficient A2**

Static viscosity measurements

Viscosity measurements have a special significance in the quality control of polymers. These measurements, performed under standardized conditions (DIN, ASTM etc.), provide important parameters e.g. for polymer processing. The method in general averages over the whole sample, producing integral values as a result.

PSS is able to determine various kinds of viscosities, e.g. relative viscosity, inherent viscosity, intrinsic viscosity etc., even in uncommon solvents like HFIP, meta-Cresol, ortho-Dichlorobenzene and Formic acid at temperatures up to 150°C (= 302°F).

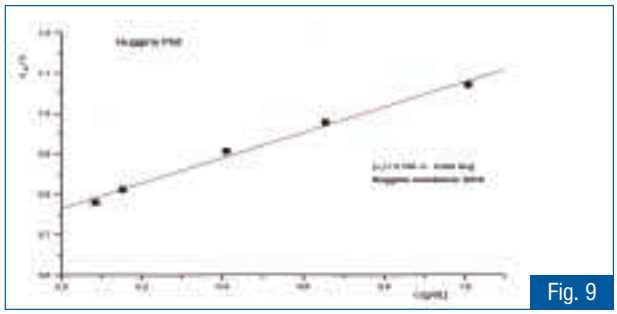
Fig. 9

Figure 9:
Huggins plot for determining the intrinsic viscosity of polystyrene in ortho-Dichlorobenzene at 140°C (= 284°F).

Your results at a glance:

- **absolute, relative, inherent and intrinsic viscosities**
- **Huggins/Kraemer constants**

Vapour pressure osmometry

The molar mass determination by osmometry is one of the most important methods for evaluating the number average molecular weight Mn. This is an important parameter for the interpretation of kinetic data in polymerization and copolymerization reactions.

The method is also of interest for prepolymers with lower molar masses. **PSS** provides sample testing service using vapour pressure osmometry measurements of polymers with masses Mn < 10,000 g/mol in toluene and ultra pure water. A run includes the determination of the device scaling factor and the measurement at four different sample concentrations. The number average molecular weight Mn and the second virial coefficient A2 is evaluated graphically.

Your results at a glance:

- **number average molecular weight Mn**

Determination of refractive index increment

The refractive index increment, dn/dc, is an important material specific parameter of a polymer solution and is required for evaluating light scattering data. If this parameter is unknown for a given polymer-solvent system, it has to be measured, because the light scattering formula includes dn/dc to the power of two in the calculation of molar mass.
We use our ScanRef instrument, a modern and powerful tool that relies on interferometric measurements, to determine the refractive index increment directly with excellent precision and without calibration.

During a static run, a series of injections are made from your sample with different concentrations to measure and determine the dependency of the phase shift of these solutions. This shift is plotted versus the samples concentrations. The refractive index increment is evaluated from the slope of the resulting straight line.

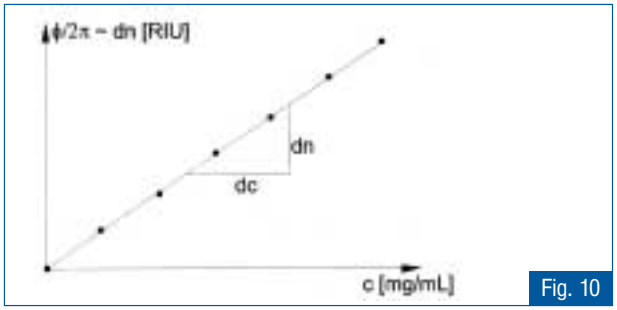

Fig. 10

Figure 10:
Determination of the refractive index increment dn/dc from the slope of the extrapolated line

Your results at a glance:

- **refractive index increment**

Determination of pore size

Porous materials are primarily used for the separation of unwanted substances (e.g. medical membranes, dialysis) or the concentration of a desired compound (e.g. in biotechnology). To provide optimal product quality, the knowledge of the pore size and pore size distribution is of crucial importance.

Chromatographic porosity by inverse GPC presents several advantages over traditional methods, e.g. gas adsorption or Hg-intrusion: It identifies porous structures faster and presents a high accuracy across the complete pore size range. It also does not require the presence of toxic compounds like Hg.

PSS uses inverse GPC to characterize the pore size distribution of a sample and offers this service to our customers. The porous material is tested using different probe molecules of known size (particle standards) and the retention time of the standards is used to evaluate the average pore size and pore size distribution.

This calculation is done by PSS POROCheck software, a special software tool developed by **PSS**.
Pore volume, specific surface and the selectivity for certain particle or molecule sizes are also available. The method can be utilized for particles ranging from 1.5 to 600 nm.

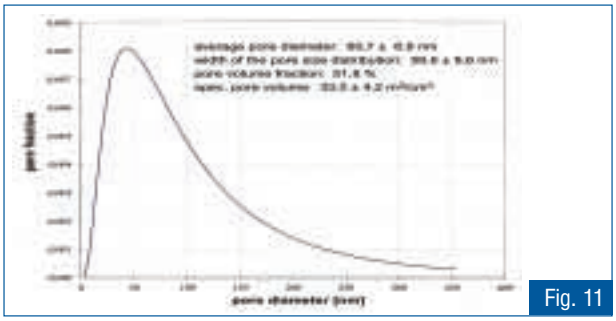
Fig. 11

Figure 11:
Plot of particle size distribution measured with inverse GPC and evaluated by PSS POROCheck

Your results at a glance:

- **pore size distribution**
- **pore volume**

Method development and special characterization methods

PSS offers the development and validation of analysis methods tailored to solving your complex polymer characterization problems. This process takes place in close cooperation with the customer. After evaluating the amount of work, a schedule for the development is established. The work commences and is completed with full documentation provided to the customer.

PSS also performs various other physical characterization methods, e.g. end group analysis by NMR, MALDI-TOF-MS, pyrolysis GC, DSC, dynamic light scattering etc. Contact us for a quotation on these methods to charaterize your samples.

PSS – where the experts meet.

Field of application	Method	Primary information
qualitative sample comparison (pass - fail comparison) polymer degradation	conventional GPC without calibration	elugram
process control & optimization quality control product control product approval	conventional GPC with molar mass calibration	calibration curve elugram molecular weight averages (Mn, Mw, Mz) molecular weight distribution range of molar mass
copolymers, polymer blends additives	conventional GPC with molar mass and detector calibration	calibration curve elugram chemical composition molecular weight average and distribution
research & development pharmaceutical products biopolymers	GPC light scattering coupling	absolute Mw molecular weight distribution radius of gyration structure information aggregation
research & development pharmaceutical products biopolymers	GPC viscosity coupling	universal calibration intrinsic viscosity molecular weight averages (Mn, Mw, Mz) molecular weight distribution structure information/branching Mark-Houwink parameter
research & development unknown samples	GPC-FTIR coupling HPLC-FTIR coupling	substance identification chemical structure/purity chemical composition analysis of additives molecular weight distribution
research & development pharmaceutical products biopolymers internal standards	static light scattering	absolute Mw radius of gyration second virial coefficient
research & development pharmaceutical products biopolymers internal standards	static viscosity measurement	absolute, relative, inherent, intrinsic viscosity of a sample Huggins/Kraemer constants
unknown samples	static FTIR measurement	substance identification
prepolymers, oligomers	vapour pressure osmometry	number average molecular weight Mn
material specific parameter for light scattering or other analytical methods	determination of refractive index increment (dn/dc)	dn/dc with error limit
porous materials: adsorbents, membranes	inverse GPC	pore size distribution, pore volume

PSS Polymer Standards Service

PSS Polymer Standards Service GmbH

Postfach 3368
55023 Mainz
Germany

Tel.: +49 (0) 6131 9 62 39 - 0
Fax: +49 (0) 6131 9 62 39 - 11

E-Mail: info@polymer.de
http://www.polymer.de

PSS USA

10111 Colesville Road, 2nd Floor, Suite 123
Silver Spring, MD 20901
USA

Tel: +1 301 681 9624
Fax: +1 301 681 2709

E-Mail: MGray@polymer.de
http://www.polymer.de

Your lokal dealer: