Report

Certification of reference material

ERM®-FA003

Polymethylmethacrylate (PMMA)

Batch No.: **mmbr100k**

This material was produced by Aldrich, Taufkirchen. It can be used for calibrating specific methods investigating polymers. Certified values are the mass averaged molecular weight M_w by means of light scattering (LS) and the intrinsic viscosity by means of viscometry. Additional, non-certified values are the averaged molecular weights (M_w, M_n, M_z, M_p) and M_w/M_n by means of size exclusion chromatography (SEC). These values are based on results obtained by round robin tests which were initiated and evaluated by the department BAM VI.3. Additional tests that result in non-certified values (IR, NMR, DSC, MFR and determination of density) were exclusively performed in the BAM.

Homogeneity and stability of the material were tested in the BAM, too.

The material has a durability of 15 years for temperatures of +3 °C to +7 °C at maximum.

Content:

1. Abbreviations, symbols and formulas

IR	-	infrared spectroscopy
NMR	-	nuclear magnetic resonance spectroscopy
DSC	-	differential scanning calorimetriy
MFR	-	melt flow index
SEC	-	size exclusion chromatography
LS	-	light scattering
MALLS	-	multi-angle laser light scattering
LALLS	-	low-angle laser light scattering
MALDI-TOF-MS	-	matrix assisted laser desorption/ionisation - time of flight – mass spectrometry
M_w	-	weight averaged molecular weight
Mv	-	viscosity averaged molecular weight
Mp	-	molecular weight at peak maximum
M_n	-	number averaged molecular weight
M_z	-	z-averaged molecular weight
D	-	polydispersity (= M_w/M_n)
THF	-	tetrahydrofurane
$\bar{x}$	-	mean value
u_x	-	confidence interval of x
σ	-	standard deviation of x
[η]	-	intrinsic viscosity

$$M_n = \frac{\sum_{i=1}^{k} n_i * M_i}{\sum_{i=1}^{n} n_i} \quad (1)$$

$$M_w = \frac{\sum_{i=1}^{k} n_i * M_i^2}{\sum_{i=1}^{n} n * M_i} = \frac{\sum_{i=1}^{k} m_i * M_i}{\sum_{i=1}^{k} m_i} \quad (2)$$

$$M_z = \frac{\sum_{i=1}^{k} n_i * M_i^3}{\sum_{i=1}^{n} n * M_i^2} = \frac{\sum_{i=1}^{k} m_i * M_i^2}{\sum_{i=1}^{k} m_i * M_i} = \frac{\sum_{i=1}^{k} z_i * M_i}{\sum_{i=1}^{k} z_i} \quad (3)$$

2. Introduction

Polymer standards are the basis for calibration of relative methods used for the characterization of molecular weights and weight distribution of polymers. An important method is represented by the Size Exclusion Chromatography (SEC). The polymer, that has to be investigated, will be dissolved in an appropriate solvent and will be separated in columns according to the hydrodynamic radii of macromolecules. These columns are filled with specific gels having various pore sizes and pore distributions. The hydrodynamic volume depends both on the molecular weight and on the structure of dissolved polymers. Therefore, for analysing structurally different polymers various standards are necessary.

The molecular weight of these standards can be measured by means of so-called absolute methods, which do not require any calibration. One of the most important absolute methods is given by measuring the light scattering of a polymer solution. The intensity of the scattered light increases with increasing molecular weight. Apart from determining the refractive indices at different polymer concentrations (refractive index increment), no further information is necessary. For investigations carried out at the BAM a Dawn EOS light scattering photometer (Wyatt) was applied.

The SEC BAM round robin tests were performed and evaluated according to DIN 55 672 – 1. The conditions were obligatory for all participating laboratories. Samples were measured at the BAM using a PL-210 SEC (Polymer Laboratories, Church Stretton, UK). For the calibration of SEC commercially available standards were used (Polymer Standards Service [PSS] GmbH, Mainz) by all participating laboratories. The calculation of the molecular weights was performed using the WINGPC program of PSS, which is based on known mathematical formulas (1) to (3).

As a third method viscometry was used. The determination of the viscosities of polymer solutions with different concentrations and their subsequent extrapolation versus a concentration c=0 results in the so-called intrinsic viscosity [η]. Applying the equation $[\eta] = K M_V^a$ (K and a are constants available for different solvents and temperatures) a vicosity averaged molecular weight M_V can be obtained.

These investigations were performed in the BAM according to DIN 51562 – 1 using a AVS/G – Ubbelohde viscometer (Schott, Mainz).

3. List of participating laboratories

Aventis, Frankfurt / M.
Bundesanstalt für Materialforschung und -prüfung, Berlin
Bayer AG, Uerdingen
Bayer AG, Leverkusen
Bundeskriminalamt, Wiesbaden
BMW, Dingolfing
Fraunhofer Institut für Angewandte Polymerforschung, Teltow
RWTH Aachen, Institut für Kunststoffverarbeitung
Institut für Lacke und Farben, Magdeburg
Institut für Polymerforschung, Dresden
Martin-Luther-Universität, Halle-Wittenberg
Max-Planck-Institut für Polymerforschung, Mainz
Polymer Standards Service GmbH, Mainz
Röhm GmbH, Darmstadt
RWTH Aachen, Institut für Textilchemie und Makromolekularen Chemie
Goldschmidt AG, Essen
Technische Universität Dresden
Universität Bayreuth
Universität Erlangen-Nürnberg
Universität Essen
Universität Freiburg
Universität Hamburg, Institut für Technische und Makromolekulare Chemie
Universität Hamburg, Institut für Technische und Makromolekulare Chemie
Universität Leipzig
Johannes-Gutenberg-Universität Mainz, Institut für Makromolekulare Chemie
Johannes-Gutenberg-Universität Mainz, Institut für Physikalische Chemie
Universität Osnabrück
Universität Stuttgart, Institut für Technische Chemie
Universität Stuttgart, Institut für Textil- und Faserchemie
Universität Ulm
Universität - Gesamthochschule Siegen
Viscotek GmbH, Weingarten

4. Synthesis and packing size

The polymer was synthesized by Aldrich, Taufkirchen. It was filled in 10 brown glass bottles with a volume of 500 mL. Each of these bottles contained ca. 320 g of the polymer. The polymers itself consist of a cristalline material.

The samples were manually splitted. Every participant got approximately 2 grams of the polymeric material.

After certification a certain part of the whole polymer material will be bottled in sizes of 1, 2, 5 or 10 g by the distributor stating the corresponding batch number. The packing procedure will be controlled by the BAM. The remaining part of the material is stored in sealed bottles and can be packed by the distributor if required. The BAM reserves the right to check the packing procedure by taking samples immediately after packing and for an indefinite time.

5. Investigation of homogeneity

In order to separate the uncertainty of the method from the heterogeneity of the sample a multiple measuring of the sample according to ASTM E 826 – 85 is necessary. Since polymer materials are synthezised in batch processes and are repeatedly cleaned by various methods (e.g. re-precipitation) no significant differences were expected a priori.
Overall 16 samples of the polymer (one sample per bottle) were investigated by means of SEC. Every sample was measured twice.

M_w = 105000 ± 700 g/mol (± 0.70 %)
(confidence interval for 20 values and 95% probability)

Additionally, the statistical accuracy of the SEC method was determined using a polystyrene standard material with a broad polymer distribution. One pellet of the polymer was dissolved in THF. This solution was measured 10 times.

M_w = 313300 ± 400 g/mol (± 0.14 %)
(confidence interval for 10 values and 95% probability)

The confidence interval of the SEC method is lower than the confidence interval of the homogeneity test. (For comparison: The statistical accuracy of the SEC method according to DIN 55 672 – 1 has to be at least 2% for M_w.)

6. Investigation of stability

Stability tests were performed at elevated temperature (40 °C) by storing the polymers for two years. Samples were taken every six month. The molecular weight was determined twice by means of SEC.

Storage time (month)	Molecular weight M_w (g/mol)
0	106200
6	108100
12	108700
18	108400
24	108500

Only slight changes of 2.00 % within the first 6 month were detected. The following changes of 0.45 % are the range of the uncertainty of the SEC method. The results are within the statistical accuracy according to DIN 55 672 – 1.

7. Non-certified values

NMR-spectroscopy: Ratio of isotactic to syndiotactic linkages 45:55

IR-Spectroscopy: IR-spectrum corresponds with reference spectra

Differential Scanning Calorimetry: glass transition temperature T_g = 109.6 °C

Melt Flow Index: 6.3 ± 0.6 g/10 min (3.8 kg, 230 °C, according to DIN ISO 1133)

Density: 1.27 g/ml (25 °C, according to DIN 53479)

8. Results of the round robin tests

Non-certified values

1. Averaged mol. weights (M_w, M_n, M_z and M_p) and polydispersity M_w/M_n by size exclusion chromatography (SEC)

Investigator	Mean values of investigators				
	Weight-average M_w [g/mol]	Number-average M_n [g/mol]	Z-average M_z [g/mol]	Mol. weight at peak max. M_p [g/mol]	M_w/M_n
1	95850	39950	174200	83700	2.40
2	103600	43600	175900	97700	2.37
3	102000	44000	176000	84000	2.31
4	93300	44000	162900	91200	2.12
5	103300	47100	186300	98300	2.19
6	96000	43400	164600	-	2.21
7	101200	49500	178900	91600	1.97
8	99800	35200	198100	100400	2.84
9	108100	61200	181200	97600	1.77
10	84100	40250	132000	105500	2.09
11	113000	62100	206500	87000	1.82
12	101500	49300	192500	78900	2.06
13	109850	52650	194650	-	2.09
14	104500	58500	171000	90000	1.78
Mean values	**101100**	**47900**	**178200**	**92200**	**2.15**
Confidence interval	**3400**	**3800**	**8600**	**3700**	**0.13**
[%]	**3.40**	**8.03**	**4.84**	**4.04**	**6.16**

Certified Values

2. Weight-average molecular weight (M_w) by light scattering (LS)

Investigator	Mean values of investigators
	Weight-average molecular weight M_w [g/mol]
1	110700 a)
2	111000 b)
3	97800 c)
4	107000 b)
5	103800 c)
6	102000 b)
7	113800 b)
8	104500 a)
9	111300 b)
10	105100 c)
11	112900 b)
12	104700 d)
Mean value	**107050**
Confidence interval	**2500**
[%]	**2.33**

3. Intrinsic viscosity by viscometry

Investigator	Mean values of investigators
	Intrinsic viscosity [η] [ml/g]
1	31.59 a,b)
2	30.46 a,b)
3	32.67 a,b)
4	30.67 a,b)
5	32.12 a,b)
6	29.72 c)
7	30,72 a,b)
8	33.60 c)
9	31,73 c)
Mean value	**31.48**
Confidence interval	**1.21**
[%]	**3.85**

Experimental conditions

1) The experimental conditions were determined by the DIN 55 672 – 1 (GPC using tetrahydrofurane (THF) as eluent.

2) Values correspond to a Rayleigh-ratio R_Θ = 1.406 E-5 cm^{-1} at 633 nm in toluene

a) Low-Angle Laser Light Scattering (LALLS), **b)** Multi-Angle Laser Light Scattering (MALLS), **c)** Size Exclusion Chromatography coupled with MALLS-Detector,

d) Size Exclusion Chromatography coupled with Right-Angle Laser Light Scattering (RALLS) – Detector

Investigator	Method	Angle (°)	Solvent	Equipment	Wave length (nm)	dn/dc
1	LALLS	6-7	THF	KMX-6	633	0.0865
2	MALLS	30-150	THF	Dawn EOS	690	0.0865
3	SEC-LS	30-145	THF	Dawn F	488	0.0890
4	SEC-LS	30-145	THF	Dawn F	633	0.0865
5	MALLS	20-145	THF	FICA SLS	633	0.0865
6	MALLS	30-150	THF	Dawn DSP	488	0.1990
7	MALLS	30-145	MEK	FIKA 50	633	0.1148
8	LALLS	6-7	THF	KMX-6	633	0.0865
9	MALLS	30-145	THF	Sofica	633	0.0865
10	SEC-LS	30-150	THF	Dawn F	633	0.0865
11	MALLS	90	THF	Sofica	633	0.0870
12	SEC-LS	90	THF	TDA-300	633	0.0865

3) In THF at 30 °C, 6 concentrations from 1 to 5 g/l in an Ubbelohde type viscometer according to HUGGINS **a)** and KRÄMER **b)** following DIN 51562-1, resp. by means of a capillary viscometer (Viscotek, Weingarten) **c)**

9. References

- DIN 55 672 – 1 (GPC using tetrahydrofurane (THF) as eluent)
- DIN 55 672 – 2 (GPC using N,N – Dimethylacetamide (DMAC) as eluent)
- DIN 51 562 – 1 (Viscometry: Determination of kinematic viscosity using a Ubbelohde – Viscometer, Part1: Design and realisation of measurements
- BAM VI. 301 – standard working procedure (StAA 7.2.5.1.) (GPC using THF as eluent)
- BAM VI. 301 - StAA 7.2.5.2. (determination of the molecular weight of polymers using LALLS (Low-Angle Laser Light Scattering))
- BAM VI. 301 - StAA 7.2.5.3. (determination of the viscosity of polymers)