

Report

Certification of reference material

BAM-P011

Polystyrene

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Certification Report of Reference Material BAM-P011 Polystyrene

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Abstract

The certified reference material BAM-P011 was produced by the Federal Institute for Materials Research and Testing (BAM), Berlin, Germany. It can be used for calibrating specific methods investigating polymers. Certified values are the weight-averaged molecular weight M_w by means of light scattering (LS), the intrinsic viscosity by means of viscometry, and the averaged molecular weights (M_w , M_n , M_z , M_p), and the polydispersity $D (=M_w/M_n)$ by means of size exclusion chromatography (SEC). These values are based on results obtained by BAM in-house tests in the division BAM-I.3. The homogeneity of the material was also tested at BAM.

The material is stable for 5 years if it is stored at temperatures between +3 °C and +7 °C.

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1. Abbreviations, symbols, and formulas

LS	-	light scattering
MALLS	-	multi-angle laser light scattering
dn/dc	-	refractive index increment
SEC	-	size exclusion chromatography
M_w	-	weight-averaged molecular weight
M_v	-	viscosity-averaged molecular weight
M_p	-	molecular weight at peak maximum
M_n	-	number-averaged molecular weight
M_z	-	z-averaged molecular weight
D	-	polydispersity (= M_w/M_n)
THF	-	tetrahydrofuran
$[\eta]$	-	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 molecular weight distributions of polymers. An important method is represented by the Size Exclusion Chromatography (SEC). The polymer, which should be investigated, has to 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 various standards are necessary to analyse structurally different polymers.

The molecular weight (also called molar mass) 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 (LS) 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, dn/dc), no further information is necessary. The investigations at BAM were carried out using a Wyatt Dawn EOS multi-angle laser light scattering photometer (MALLS) for the determination of the molecular weight and a Wyatt Optilab DSP differential refractometer for measurements of dn/dc values. All investigations were performed at 690 nm laser light wavelength and a temperature of 25 °C.

The BAM SEC-tests were performed and evaluated according to ISO 13885-1, or DIN 55 672 – 1, respectively. Samples were measured at 30 °C using a PL-210 size exclusion chromatograph (Polymer Laboratories, Church Stretton, UK). For the calibration of SEC, polystyrene standards with narrow molecular weight distribution were characterized by light scattering, and by coupling SEC with light scattering. The Light Scattering Debye Plot M_p values (mean values of 6 SEC-LS runs) were used for SEC calibration. The calculation of the molecular weights was performed using the WINGPC program of PSS, which is based on the known mathematical formulas (1) to (3).

As a third method viscometry was used. The determination of the viscosities of polymer solutions with different concentrations at 30 °C and their subsequent

extrapolation versus a concentration $c=0$ results in the so-called intrinsic viscosity $[\eta]$. Applying the equation $[\eta] = K M_v^a$ (K and a are constants available for different solvents and temperatures) a viscosity-averaged molecular weight M_v can be obtained. These investigations were performed at BAM according to DIN 51562 – 1 using an AVS/G – Ubbelohde viscometer (Schott, Mainz).

3. Synthesis and packing size

The polymer was synthesized by BASF, Ludwigshafen, Germany. It was filled in 30 brown glass bottles with a volume of 1 litre. Each of these bottles contained ca. 1 kg of the polymer. The polymer itself consists of glassy pellets with a weight of approximately 20 mg each.

After certification a certain part of the whole polymer material will be bottled in sizes of 1 g, 2 g, 5 g or 10 g stating the corresponding batch number. The remaining part of the material is stored in sealed bottles and may be packed later if required.

4. Investigation of homogeneity

Since polymer materials are synthesized in batch processes and were repeatedly cleaned by various methods (e.g. precipitation) no significant differences of molecular weights were expected a priori.

In order to separate the uncertainty of the method from the heterogeneity of the sample the 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.

The estimate for the average repeatability was obtained from this and a similar experiment conducted for P012, and calculated as the standard deviation of the normalised data combined from both experiments. This revealed a value for the relative average repeatability $s_{rep,r}$ of 0.00684 which was used for all further calculations under chapter 7.

Estimates for u_{bb} (comp. ISO Guide 35) were obtained from a one-factorial ANOVA assessment of the data presented in the table in chapter 6.2, and used accordingly for the corresponding parameters (comp. Chapter 7). For the certified parameter M_w , the relative uncertainty contribution $u_{bb,r}$ is 0.0027. It was also used for the intrinsic viscosity assessment.

5. Stability

Previously performed stability tests of two polystyrene reference materials with different molecular weights, carried out at BAM by storing these samples for two years at elevated temperature (40 °C), showed no significant changes of the molecular weight. Therefore, no changes at ambient temperatures were expected for this comparable polymer.

According to ISO Guide 35:2006, in a situation where material changes over time can reasonably be neglected, nevertheless an uncertainty contribution from the method used for establishing insignificance of alteration has to be included in the total uncertainty budget of the certified value. This contribution was taken as the average (or representative) repeatability of the SEC as implemented and assessed from the repeatability experiment as described in chapter 4 (replicate measurements of a digested pellet).

The certification is valid for 5 years if the material is stored in a dry and light-protected atmosphere below + 7 °C.

6. Results and certified values

6.1. Weight-averaged molecular weight (M_w) by light scattering (LS)

Sample	Weight-averaged molecular weight M_w [g/mol]
1	289,900
2	289,900
3	288,100
4	288,600
5	288,100
6	286,700
7	289,900
8	286,200
9	285,800
10	287,900
11	280,400
12	279,800
13	283,300
14	285,700
15	283,100
16	285,700
Certified mean value	286,000
Expanded uncertainty (k=2)	± 4,000
[% of mean value]	± 1.4

Experimental conditions

Reference Material	Method	Angle (°)	Solvent	Equipment	Wave length (nm)	dn/dc
BAM-P011	MALLS	30-150	THF	Dawn EOS	690	0.184

Values correspond to a Rayleigh-ratio $R_\Theta = 1.406 \text{ E-5 cm}^{-1}$ at 633 nm in toluene.

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

Pellet of Bottle No.	Weight-averaged M_w [g/mol]	Number-averaged M_n [g/mol]	Z-averaged M_z [g/mol]	Mol. weight at peak max. M_p [g/mol]	M_w/M_n
1	283,500	120,600	472,100	255,900	2.4
	284,300	122,600	475,900	254,800	2.3
2	285,400	122,200	476,700	256,600	2.3
	284,500	122,100	474,900	262,200	2.3
3	283,500	120,600	477,400	255,900	2.4
	283,100	119,700	473,800	255,700	2.4
4	283,300	120,100	471,900	258,600	2.4
	285,700	129,700	475,900	253,900	2.2
5	285,000	126,900	474,000	254,700	2.2
	282,700	124,900	472,200	252,300	2.3
6	284,500	126,400	473,800	249,900	2.3
	283,900	123,000	475,600	254,100	2.3
7	283,000	122,900	471,400	256,000	2.3
	284,300	121,200	474,100	253,200	2.3
8	283,700	123,000	477,100	257,600	2.3
	281,200	117,500	475,600	256,000	2.4
9	284,500	125,400	469,500	248,300	2.3
	281,400	124,800	466,800	255,000	2.3
10	280,700	121,300	470,900	247,400	2.3
	285,400	122,800	477,600	254,500	2.3
11	283,900	123,200	474,100	253,600	2.3
	284,300	122,900	471,800	261,200	2.3
12	281,900	118,000	469,900	257,100	2.4
	282,900	117,200	472,800	255,000	2.4
13	282,200	121,700	467,700	249,700	2.3
	282,900	122,900	471,800	254,600	2.3
14	282,200	124,400	471,100	257,800	2.3
	283,200	121,400	477,300	250,400	2.3
15	280,500	121,800	467,200	258,300	2.3
	281,100	118,000	469,800	252,100	2.4
16	280,300	119,600	469,700	250,000	2.3
	282,400	122,900	471,800	253,100	2.3
17	282,200	122,300	470,200	255,100	2.3
	283,200	125,700	469,900	261,600	2.3
18	282,900	121,300	472,400	260,900	2.3
	278,700	118,200	467,200	252,400	2.4
19	282,200	122,600	470,400	253,700	2.3
	282,900	123,300	469,700	256,800	2.3
20	285,900	121,600	473,300	257,400	2.4
	281,600	119,900	469,700	254,300	2.4
21	285,200	118,400	481,200	259,200	2.4
	286,200	127,100	478,200	256,300	2.3
22	285,500	121,700	477,200	258,100	2.4
	284,400	124,800	473,300	255,400	2.3

Pellet of Bottle No.	Weight-averaged M_w [g/mol]	Number-averaged M_n [g/mol]	Z-averaged M_z [g/mol]	Mol. weight at peak max. M_p [g/mol]	M_w/M_n
23	283,800 285,000	123,300 126,000	472,700 475,000	256,000 258,800	2.3 2.3
24	281,900 283,500	119,400 119,900	474,300 478,700	256,000 252,700	2.4 2.4
25	283,400 282,800	120,000 122,800	475,500 471,600	264,300 251,100	2.4 2.3
26	283,300 282,100	120,500 122,000	475,600 470,500	257,200 253,000	2.4 2.3
27	283,300 282,700	117,600 124,600	475,800 471,200	263,300 254,000	2.4 2.3
28	283,800 285,000	119,100 125,100	474,200 473,800	252,600 261,600	2.4 2.3
29	285,500 284,300	122,500 122,100	480,600 476,500	260,200 258,700	2.3 2.3
30	284,300 285,500	128,000 125,900	469,700 476,100	258,400 259,200	2.2 2.3
Certified mean value	284,000	122,000	473,000	256,000	2.33
Expanded uncertainty (k=2)	± 9,000	± 7,000	± 14,000	± 11,000	± 0.02
[% of mean value]	± 3.2	± 5.7	± 3.0	± 4.3	± 0.5

The experimental conditions were chosen following ISO 13885-1 (*Size exclusion chromatography (SEC) using tetrahydrofuran (THF) as eluent*). The BAM SEC-tests were performed and evaluated according to this ISO standard.

For SEC calibration polystyrene standards with narrow molecular weight distribution were characterized by light scattering and by coupling SEC with light scattering. The SEC-light scattering Debye Plot M_p values were used for SEC calibration.

6.3. Intrinsic viscosity by viscometry

Sample	Intrinsic viscosity [η] [mL/g]
1	88.5
2	88.2
3	89.7
4	88.1
5	90.3
6	88.1
7	88.9
8	89.3
9	88.2
10	88.0
Certified mean value	88.7
Expanded uncertainty (k=2)	± 0.8
[% of mean value]	± 0.9

The measurements were carried out in THF at 30 °C using an Ubbelohde type viscometer. 6 concentrations from 1 g/L to 5 g/L were used for each sample. The evaluations were performed according to HUGGINS and KRÄMER, following DIN 51562-1.

7. Certified values and uncertainties

The certified values are the weight-averaged molar mass determined by SEC and light scattering, and the intrinsic viscosity of the material. The following tables give the values, the corresponding expanded uncertainties, and the sources and estimates of uncertainty contributing to the total budget, both in absolute and relative units.

parameter: method:	Mw SEC		g/mol	
value:	P011		P012	
u(value):	283,375		342,637	
U(value):	4,240		5,770	
rounded:	8,480		11,541	
	284,000		343,000	
	± 9,000		± 12,000	
budget:	absolute	relative	absolute	relative
inhomogeneity contribution u_{bb}	754	0.27	2,673	0.78
average repeatability s_{rep}	1,938	0.68	2,343	0.68
calibration uncertainty u_{cal}	3,654	1.29	4,419	1.29
characterisation contribution s_{mean}	223	0.08	878	0.26
bias estimate	500	0.18	605	0.18

Note: In the budget, values in black are original estimates, while values in gray are calculated from the original ones.

Estimation and inclusion of the inhomogeneity (u_{bb}) and average repeatability (s_{rep}) contributions are explained in chapters 4 and 5, respectively. The contribution from characterisation is assessed as the standard deviation of the mean of the data for M_w presented in the table in chapter 6.2. Although the one-factorial ANOVA on these data did still not indicate significant differences between the within- and between-bottle data, the mean value was nevertheless calculated as the mean of bottle means, and the standard deviation accordingly. This is mainly driven by the fact that for P012, the critical limit of significance was nearly reached, so that for the sake of unification the no-pooling option was chosen.

The bias estimate refers to a comparison between the certified and the value determined for an independent certified reference material (SRM706a with values close to those of P011) using the SEC equipment and implementation as described. No significant differences were observed, however a bias estimate equal to one-half the observed difference (which statistically covers the latter completely) was included as a worst-case estimate (and transferred to P012 in the form of a relative uncertainty contribution).

Traceability of the certified value is established by calibrating the M_w axis of the SEC using light scattering. A functional dependence $M_w = f(t_{ret})$ of the molar mass on the retention time is recorded and approximated by a 5th order polynomial. This regression function is used for determination purposes.

The calibration contribution is assessed as the average width of the one-sigma uncertainty band of a characteristic regression function for the SEC method used, and calculated as follows. The function to be regressed over the $\{M_w, t_{ret}\}$ set of data is

$$\ln(M_w) = a + b \cdot t_{ret} + c \cdot t_{ret}^2 + d \cdot t_{ret}^3 + e \cdot t_{ret}^4 + f \cdot t_{ret}^5$$

Minimisation of the objective function leads to normal equations having a coefficient matrix **C**. With the parameters a to f determined, the residual scatter s_{resid} is calculated. The variance/ covariance matrix of the function parameters then is

$$V(p) = s_{rep}^2 \cdot C^{-1}$$

and the one-sigma uncertainty limits on the functional relationship

$$u^2(M_w) = \vec{d}^T \times V(p) \times \vec{d}$$

with \vec{d} being a vector consisting of the first derivatives of the functional relationship with respect to the function parameters, namely

$$\vec{d} = \{1, t_{ret}, t_{ret}^2, t_{ret}^3, t_{ret}^4, t_{ret}^5\}^T$$

These are averaged over the range covered, which delivers (after appropriate conversion to original space) the values as indicated in the table. Note that these values are also used in chapter 8.

The inhomogeneity contribution was included for reasons as above. The contribution from characterisation is assessed as the standard deviation of the mean of the data for M_w presented in the table in chapter 6.1. Since the absolute method of light scattering (which establishes traceability for the SEC method) is used here, no calibration contribution occurs. Instead, contributions from sample weighing and density determination are included accordingly. The bias estimate (one-half the observed difference) accounts for the difference between the traceable-to-light-

scattering SEC value and the value obtained by direct application of the light scattering method.

No bias estimate was available here, all other estimates are as described above.

parameter: method:	Mw light scattering		g/mol	
value: u(value): U(value): rounded:	P011 286,194 1,898 3,796 286,000 ± 4,000	P012 348,020 3,993 7,986 348,000 ± 8,000		
budget:	absolute	relative	absolute	relative
inhomogeneity contribution u_bb	761	0.27	2,715	0.78
weighing uncertainty	286	0.10	384	0.10
density determination uncertainty	572	0.20	696	0.20
characterisation contribution s_mean	792	0.28	851	0.25
bias estimate	1,409	0.49	2,691	0.77

parameter: method:	intrinsic viscosity viscosimetry		mL/g	
value: u(value): U(value): rounded:	P011 88.73 0.40 0.80 88.7 ± 0.8	P012 104.01 0.90 1.78 104.0 ± 1.8		
budget:	absolute	relative	absolute	relative
inhomogeneity contribution u_bb	0.24	0.27	0.81	0.78
weighing uncertainty	0.09	0.01	0.10	0.10
density determination uncertainty	0.18	0.20	0.21	0.20
characterisation contribution s_mean	0.25	0.28	0.28	0.27

8. Informative values and uncertainties.

These values are the number- and the z-averaged molar mass as well as the molar mass at peak maximum, all determined by SEC. The following tables give the values, the corresponding expanded uncertainties, and the sources and estimates of uncertainty contributing to the total budget, both in absolute and relative units. Uncertainty estimation followed the same principles as described in chapter 7.

parameter: method:	Mn SEC		g/mol	
	P011		P012	
value:	122,290		140,843	
u(value):	3,217		7,494	
U(value):	6,434		14,987	
rounded:	122,000 ± 7,000		141,000 ± 15,000	
budget:	absolute	relative	absolute	relative
inhomogeneity contribution u_bb	955	0.78	2,457	1.74
average repeatability s_rep	2,588	2.12	6,721	4.77
calibration uncertainty u_cal	1,577	1.29	1,816	1.29
characterisation contribution s_mean	503	0.41	1,282	0.91

parameter: method:	Mz SEC		g/mol	
	P011		P012	
value:	473,278		555,374	
u(value):	6,966		10,751	
U(value):	13,932		21,503	
rounded:	473,000 ± 14,000		555,000 ± 22,000	
budget:	absolute	relative	absolute	relative
inhomogeneity contribution u_bb	2,041	0.43	2,710	0.49
average repeatability s_rep	2,597	0.55	7,415	1.34
calibration uncertainty u_cal	6,103	1.29	7,162	1.29
characterisation contribution s_mean	601	0.13	1,406	0.25

parameter: method:	Mp SEC	g/mol		
	P011		P012	
value:	255,729		340,491	
u(value):	5,321		10,442	
U(value):	10,643		20,884	
rounded:	256,000 ± 11,000		340,000 ± 21,000	
budget:	absolute	relative	absolute	relative
inhomogeneity contribution u_bb	1,394	0.55	5,632	1.65
average repeatability s_rep	3,880	1.52	7,415	2.18
calibration uncertainty u_cal	3,298	1.29	4,391	1.29
characterisation contribution s_mean	666	0.26	1,751	0.51

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- BAM-QMH-I.3 – Poly 2 – standard working procedure (determination of the viscosity of polymers)
- BAM-QMH-I.3 – Poly 3 – standard working procedure (determination of the molecular weight of polymers using Multi-Angle Laser Light Scattering (MALLS))