Report

Certification of reference material

BAM-P012

Polystyrene

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Certification Report of Reference Material BAM-P012 Polystyrene

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Abstract

The certified reference material BAM-P012 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.

Contents

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
[η]	-	intrinsic viscosity

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

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

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

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 coupling SEC with light scattering. The Light Scattering Debye Plot Mp 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 [η]. 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.

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 0.0078. It was also used for the intrinsic viscosity assessment.

5. Stability

Previously performed stability tests of two polystyrene reference materials with different molecular weight, 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	351,100
2	350,800
3	350,300
4	350,700
5	346,700
6	346,900
7	346,800
8	344,800
9	343,500
10	348,600
Certified mean value **Expanded uncertainty (k=2)**	**348,000** **± 8,000**
[% of mean value]	**± 2.3**

Experimental conditions

Reference Material	Method	Angle (°)	Solvent	Equipment	Wave length (nm)	dn/dc
BAM-P012	MALLS	30-150	THF	Dawn EOS	690	0.185

Values correspond to a Rayleigh-ratio R_Θ = 1.406 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	345,600 340,900	143,400 138,100	557,700 551,300	345,200 339,300	2.4 2.5
2	339,600	135,500	550,200	336,300	2.5
3	333,100 341,500	133,400 146,400	547,000 550,600	331,700 341,300	2.5 2.3
4	337,300 346,200	127,200 148,500	553,200 559,200	343,300 346,300	2.7 2.3
5	344,000 343,600	147,100 141,400	553,100 558,200	345,900 341,300	2.3 2.4
6	351,100 330,400	146,300 123,800	565,200 546,600	340,700 327,500	2.4 2.7
7	346,300 340,700	149,200 146,600	554,400 549,900	342,000 334,100	2.3 2.3
8	345,200 342,800	145,600 147,500	554,700 551,400	345,400 365,200	2.4 2.3
9	343,100 345,900	143,900 136,100	563,000 560,500	333,400 342,800	2.4 2.5
10	348,200 339,300	142,200 131,400	561,400 557,400	342,100 348,700	2.4 2.6
11	350,900 342,700	145,600 137,800	564,300 553,800	352,700 332,200	2.4 2.5
12	354,900 346,300	143,800 143,200	575,100 560,100	352,200 342,200	2.5 2.4
13	346,500 345,400	142,900 144,500	560,900 560,600	343,200 348,500	2.4 2.4
14	340,200 343,300	131,500 150,100	559,000 551,800	345,400 340,000	2.6 2.3
15	340,000 344,200	136,400 145,100	554,100 554,400	333,700 342,000	2.5 2.4
16	339,600	136,700	555,200	334,600	2.5
17	344,100 345,000	146,800 145,600	553,400 554,900	345,000 344,400	2.4 2.4
18	347,800 341,300	146,300 143,600	557,800 550,000	342,600 332,400	2.4 2.4
19	335,300 345,600	138,700 148,500	540,400 553,700	335,000 344,300	2.4 2.3
20	341,600 340,400	142,400 138,400	556,600 555,100	342,500 336,500	2.4 2.5
21	346,200 346,200	136,000 145,700	555,600 561,500	345,500 340,400	2.5 2.4
22	333,700 337,800	138,700 138,000	541,500 555,000	321,100 329,800	2.4 2.5

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	334,800 340,300	132,900 142,100	549,100 549,200	340,000 335,200	2.5 2.4
24	344,300 363,700	151,200 132,700	553,000 592,400	344,800 384,500	2.3 2.7
25	335,300 343,500	134,900 139,400	547,900 557,300	331,400 338,400	2.5 2.5
26	328,800 332,100	119,400 128,600	548,500 550,600	332,800 326,900	2.8 2.6
27	345,800 345,500	143,600 146,200	557,100 556,900	332,000 344,500	2.4 2.4
28	342,400 341,000	143,900 142,900	553,200 550,000	332,700 331,200	2.4 2.4
29	346,500 345,900	150,000 149,100	555,600 555,900	344,000 344,600	2.3 2.3
30	342,500 332,600	140,400 131,700	556,600 548,600	334,100 332,700	2.4 2.5
Certified mean value **Expanded uncertainty (k=2)**	**343,000** **±12,000**	**141,000** **±15,000**	**555,000** **±22,000**	**340,000** **±21,000**	**2.43** **±0.06**
[% of mean value]	**±3.5**	**±10.6**	**±4.0**	**±6.2**	**±1.2**

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	103.2
2	103.3
3	104.5
4	105.6
5	105.1
6	103.2
7	104.3
8	103.4
9	103.1
10	104.4
Certified mean value	**104.0**
Expanded uncertainty (k=2)	**± 0.6**
[% of mean value]	**± 0.6**

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:	Mw		g/mol	
method:	SEC			
	P011		**P012**	
value:	283,375		342,637	
u(value):	4,240		5,770	
U(value):	8,480		11,541	
rounded:	**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 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:	**Mw**		**g/mol**	
method:	**light scattering**			
	P011		**P012**	
value:	286,194		348,020	
u(value):	1,898		3,993	
U(value):	3,796		7,986	
rounded:	**286,000**		**348,000**	
	± 4,000		**± 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:	**intrinsic viscosity**		**mL/g**	
method:	**viscosimetry**			
	P011		**P012**	
value:	88.73		104.01	
u(value):	0.40		0.90	
U(value):	0.80		1.78	
rounded:	**88.7**		**104.0**	
	± 0.8		**± 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:	**Mn**	**g/mol**		
method:	**SEC**			
	P011		**P012**	
value:	122,290		140,843	
u(value):	3,217		7,494	
U(value):	6,434		14,987	
rounded:	**122,000**		**141,000**	
	± 7,000		**± 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:	**Mz**	**g/mol**		
method:	**SEC**			
	P011		**P012**	
value:	473,278		555,374	
u(value):	6,966		10,751	
U(value):	13,932		21,503	
rounded:	**473,000**		**555,000**	
	± 14,000		**± 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 1 – standard working procedure (GPC using THF as eluent)
- 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))