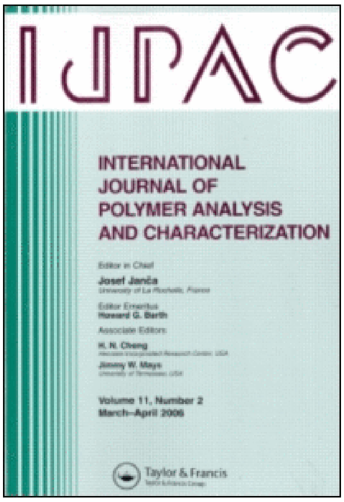

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Polymer Reference Materials: Round-Robin Tests for the Determination of Molar Masses

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Polymer Reference Materials: Round-Robin Tests for the Determination of Molar Masses

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Abstract: This article reports round-robin tests dealing with static light scattering (LS), size exclusion chromatography (SEC), and viscometry measurements of 10 reference materials of various polymer classes: poly(styrene)s (PS), poly(methyl methacrylate)s (PMMA), poly(ethylene oxide)s (PEO), and poly(lactide)s (PLA).

In the certificates, molar masses and intrinsic viscosities as well as their uncertainties are specified. Additional values from nuclear magnetic resonance (NMR), infrared spectroscopy (IR), differential scanning calorimetry (DSC), melt flow index (MFR), and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS), which were determined exclusively in BAM laboratories are given, as well.

These results represent the base for the BAM certification work of creating polymer reference materials according to the BAM *Guidelines for the Production and Certification of BAM Reference Materials*, a version of the European guidelines (BCR/01/97). These samples are available for third-party user.

Keywords: Polymer reference materials; CRM; Molar mass determination; Intrinsic viscosity; Light scattering (LS); Size exclusion chromatography (SEC);

The authors thank the participants from the laboratories that contributed to the round-robin tests.

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Gel permeation chromatography (GPC); Viscometry; Calibration; Validation; Certification; Primary standard; Round-robin test

INTRODUCTION

Reference materials (RM) are materials or substances whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or assigning values to materials. Certified reference materials (CRM) are reference materials accompanied by a certificate. One or more property values are certified by a procedure that establishes traceability to an accurate realization of the unit that the property values express. The certified value is accompanied by an uncertainty at a stated level of confidence according to ISO Guide 30:1992.

BAM polymer certified reference materials (CRM) are produced following the BAM *Guidelines for the Production and Certification of BAM Reference Materials*,[1] a version of the European BCR (Community Bureau of Reference) guidelines,[2] which has been adjusted for the purposes of BAM in order to become included in the BAM quality documentation.

Polymer reference materials are the base for calibrating relative methods used in characterization of molar masses and molar mass distributions of polymers. Many application qualities of polymers, e.g., tensile strength, tear strength, elongation at break, and processability, are dependent on such molecular properties.

Size exclusion chromatography (SEC) is the most frequently used method for simultaneously determining molar masses and molar mass distributions of polymers. The polymer to be investigated will be dissolved in an appropriate solvent and separated in columns according to the hydrodynamic radii of macromolecules. The columns are filled with sorbents, having among other parameters, various pore sizes and pore size distributions. The hydrodynamic volume depends on both the molar mass and the structure of dissolved polymers. Therefore, characterization of structurally different polymers requires various standards. Since it is obvious that is polymer standards of different manufacturers and suppliers do not always lead to identical calibration curves with regard to SEC evaluations, certificates of standard materials should not only contain the values of molar masses but also declare the use of absolute methods, e.g., light scattering, and measuring conditions.[3–7]

For the process of producing CRM, round-robin tests for characterizing molar masses and intrinsic viscosities of 10 polymer reference materials of four polymer classes (poly(styrene) (PS), poly(methyl methacrylate) (PMMA), poly(ethylene oxide) (PEO), and poly(lactide)

(PLA)), soluble in tetrahydrofuran (THF), were organised by BAM. Three different methods (light scattering (LS), SEC, and viscometry) were used in the round-robin tests. SEC was performed according to ISO/EN 13885-1 and -2 (DIN 55672-1 and -2 respectively),[6,7] a more rigorous implementation of ASTM D 3536-91 and ASTM D 5296-92. Viscosity measurements were carried out according to DIN 51562-1.[8] An additional method (matrix-assisted laser desorption time-of-ionization flight mass spectrometry, MALDI-TOF-MS) was only applied within BAM laboratories according to the BAM standard operating procedure.

An investigation of homogeneity and stability of the polymer materials was also performed at BAM. Additional physical properties of the samples were determined by means of nuclear magnetic resonance (NMR), infrared (IR) spectroscopy, differential scanning calorimetry (DSC), and melt flow index (MFR) at BAM.

Thirty-two laboratories from universities and companies working in the field of polymer research were selected for participation in the round-robin tests, as listed in Table I. Certified values for molar masses and intrinsic viscosities are the unweighted arithmetic averages of the number of accepted lab means.

EXPERIMENTAL SECTION

Materials

The polymer materials and the appropriate methods used for their characterization are shown in Table II. These polymers were chosen in cooperation with PSS Polymer Standards Service GmbH, Mainz, Germany. Major criteria for their selection were wide application range and solubility in THF.

PS and PMMA with narrow molar mass distribution were synthesized in PSS laboratories. The other materials were high-purity products of polymer industry companies. Approximately 2 g of each polymer was delivered to the participants of the round-robin tests together with the calibration standards for the SEC experiment.

Methods

SEC

SEC round-robin tests were performed and evaluated according to ISO/EN and DIN gel permeation chromatography (GPC) standards,

Table I. List of participating laboratories

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

respectively.[6] The GPC conditions of these norms were obligatory for all participating laboratories. Commercially available standards had to be used (PSS Polymer Standards Service GmbH, Germany) by all participating laboratories for the calibration of SEC. Because of the lack of standard materials for poly(lactide)s, the poly(styrene) calibration was used for the molar mass evaluations of the two materials of this polymer class.

The calculation of the molar masses was performed using the WINGPC program of PSS, which is based on known mathematical formulas (1) to (3) below, national and international GPC standards,[6,7] and the PSS software validation process.

Table II. Polymer materials and methods used for characterization

Polymer materials	Molar mass distribution					
	Narrow	Broad	LS	Viscometry	SEC	MALDI-TOF-MS
PS 1	x		x	x	x	
PS 2		x	x	x	x	
PS 3		x	x	x	x	
PMMA 4	x		x	x	x	
PMMA 5		x	x	x	x	
PMMA 6		x	x	x	x	
PEO 7	x			x	x	x
PEO 8	x		x	x	x	x
PLA 9		x	x	x	x	
PLA 10		x	x	x	x	

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

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

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

where N_i is the number of molecules of species i of molar mass M_i, and m_i is the mass of ith species with $m_i = N_i * M_i$, and $z_i = N_i * M_i^2$.

Laser Light Scattering

The molar masses of the polymers can be measured by so-called absolute methods. One of the most important absolute methods utilizes the scattering of laser light on polymer molecules in solution. The intensity of the scattered light increases with increasing molar mass. It is also directly proportional to the refractive index increment (dn/dc) values, which have to be known or measured with high accuracy. For this purpose, a laser differential refractometer KMX-16 (Thermo Separation Products, Germany) as well as an Optilab DSP differential refractometer (Wyatt, Germany) were used.

Depending on solvents and laser wavelengths, different dn/dc values were used: for PMMA 0.0865 mL/g (at 633 nm in THF), 0.089 mL/g (at 488 nm in THF), and 0.1148 mL/g (at 633 nm in methyl ethyl ketone

Table III. LS investigation of PS 1: Overview of conditions

Investigator	Method[a]	Angle (°)	Solvent	Equipment	Wavelength (nm)	dn/dc
1	LALLS	6–7	THF	KMX-6	633	0.1844
2	MALLS	30–150	THF	DAWN EOS	690	0.1844
3	MALLS	30–150	Toluol	DAWN EOS	690	0.1096
4	LALLS	6–7	THF	KMX-6	633	0.1844
5	MALLS	30–150	THF	FICA (SLS)	633	0.1844
6	SEC-LS	30–145	THF	DAWN F	633	0.1844
7	MALLS	30–150	THF	DAWN DSP	488	0.1990
8	MALLS	30–145	Toluol	FICA 50	633	0.1096
9	LALLS	6–7	THF	KMX-6	633	0.1844
10	MALLS	30–145	THF	Sofica	633	0.1844
11	SEC-LS	30–145	THF	DAWN F	633	0.1844
12	MALLS	90	Toluol	Sofica	633	0.1096
13	SEC-LS	30–145	THF	DAWN F	633	0.1844
14	SEC-LS	90	THF	TDA-300	633	0.1844

[a] LALLS: low-angle laser light scattering performed with a KMX-6 (Thermo Separation Products, Germany); MALLS: multi-angle light scattering performed with DAWN F/DSP/EOS (Wyatt, Germany) or FICA/Sofica light scattering photometers (ARL France, France); SEC-LS: SEC coupled with MALLS-detector or right-angle light scattering (RALLS) detector (Viscotek, Germany).

[MEK]); for PEO dn/dc values of 0.0655 mL/g (at 633 nm in THF), 0.1400 mL/g (at 633 nm in methanol), 0.1337 mL/g (at 633 nm in water), and 0.1415 mL/g (at 488 nm in water). The dn/dc values for the poly (lactide)s were 0.044 and 0.046 mL/g in THF at 633 nm.

Various types of light scattering photometers and different experimental setups were utilized by the participants. As an example Table III shows the setups for the investigation of sample PS 1 by 14 participants. A Rayleigh ratio R_θ of 1.406 E-5 cm^{-1} for toluene at 633 nm was applied.

Viscometry

The measurement of the viscosity of polymer solutions with different concentrations and their subsequent extrapolation to c = 0 provides the intrinsic viscosity $[\eta]$. Applying Equation (4), a viscosity-averaged molar mass M_v can be obtained:

$$[\eta] = KM_v^a \tag{4}$$

(with constants **K** and **a** available for different solvents and temperatures).

The measurements were carried out in THF at 30°C at concentrations of 0.5 to 5 g/L using Ubbelohde type viscometers by means of differential pressure capillary viscometers with reference flow (Viscotek, Germany). The calculation was done according to Huggins and Krämer following DIN 51562-1.

The SEC and viscometry results of all investigators' are the averages of two independent measurements. The mean value is the result of the averaged investigators' values.

MALDI-TOF Mass Spectrometry

MALDI-TOF-MS measurements were performed in BAM laboratories exclusively. Averaged values were obtained from four single mass spectra recorded using a Bruker Reflex III mass spectrometer and independently by a Kratos Kompact MALDI III mass spectrometer. The laser wavelength was 337 nm, and 200 shots were accumulated for each single spectrum. The matrix used (2,4,6-trihydroxyacetophenone [THAP]) was dissolved in THF (10 mg/mL). The sample concentration was 1 mg/mL in THF. Matrix and sample solutions were mixed in a ratio 10/1 (v/v) before hand-spotting 1 μL of the sample on the MALDI target. The mass spectrometer software was applied for the calculation of molar mass values.

Homogeneity

In order to separate the uncertainty of the method from the sample uncertainty (generated by their heterogeneity) multiple measurements of the sample according to ASTM E 826-85 were necessary. For the determination of the "between-bottle uncertainty" various numbers (10 to 28) of polymer samples (one sample per bottle) were investigated by means of SEC. The statistical accuracy of the SEC method was determined using PS 3. One pellet of this polymer was dissolved in THF (1 mg/mL). This solution was measured 10 times on the same day with the same instrument.

Thermal Stability

Polymer samples were investigated regarding to their thermal long-term stability at 40°C in an ambient atmosphere. Since the thermal stability of poly(lactide)s was supposed to be much lower than those of the other classes of polymers, additional investigations for poly(lactide)s were performed at 25°C. The specimens were taken every six months (three months for poly(lactide)s) and investigated by means of SEC using a validated instrument.

Melt Flow Rate (MFR)

The melt flow rate (and the melt volume rate) was determined according to DIN ISO 1133: 02.1993. The measurement was performed in a melt flow test unit (Typ 73594, Frank, Germany). The equipment was calibrated before and after experiments with the use of a special granulate material (Kalibriergranulat, Solvay, Belgium).

Calorimetry (DSC)

Calorimetric data such as phase transition temperature, heat capacity, transition entropy, and enthalpy were obtained by means of a DSC 220 C (Seiko, Japan). A cyclic temperature program was used. The starting temperature was adjusted at –50°C. Samples were heated under a constant stream of nitrogen of 50 mL/min with a rate of 10 K/min up to 200°C (first cycle), respectively 350°C (second cycle). The sample amount was 3–4 mg. Calorimetric data were determined during the second heating cycle.

IR Spectroscopy

A Vector 22 spectrometer (Bruker, Germany) was used for Fourier transform infrared (FTIR) investigations. Samples were dissolved in THF and deposited on a NaCl plate. After evaporation of the solvent, a thin film was obtained and used for measurements of the spectra.

RESULTS

Homogeneity

Since polymer materials are synthesized in batch processes, significant differences due to their repeated cleaning (e.g., reprecipitation) were not expected a priori. However, for a statistical appraisal of the results, the "in-bottle" as well as "between-bottle" uncertainties have to be determined.

For example, the "between-bottle" uncertainty of 26 measurements of PS 3 with $M_w = 314500$ was ±2100 g/mol (±0.63%) at a level of confidence of 95%, as shown in Table V. The "in-bottle" uncertainty (Table IV) was ±2200 g/mol (±0.70%).

Additionally, the statistical accuracy of the SEC method was determined by measuring a sample of PS 3 repeatedly (nine times). At a confidence level of 95%, the weight average molar mass M_w of 313300 g/mol and an uncertainty of ±760 g/mol (±0.24%) were determined (Figure 1). Thus, the confidence level of the SEC method is much lower than

Table IV. Investigation of "in-bottle" homogeneity of PS 3

Pellet	Weight-averaged molar mass M_w (g/mol)	Weight-averaged molar mass (mean and uncertainty at 95% confidence level)
1	—/315 200	
2	315 600/322 100	
3	314 600/311 100	
4	313 200/314 700	Mean of M_w = 314 600 g/mol
5	314 500/314 200	±2 200 g/mol (±0.70%)
6	315 800/313 100	
7	—/314 500	
8	315 100/314 200	(+/− uncertainty mean at 95%
9	314 400/312 600	confidence level)
10	312 400/314 700	

that of the homogeneity tests. (For comparison: the statistical accuracy of the SEC method is 2% for M_w according to DIN 55 672-1.)

In Table V, the values of the investigation of homogeneity of all samples are combined.

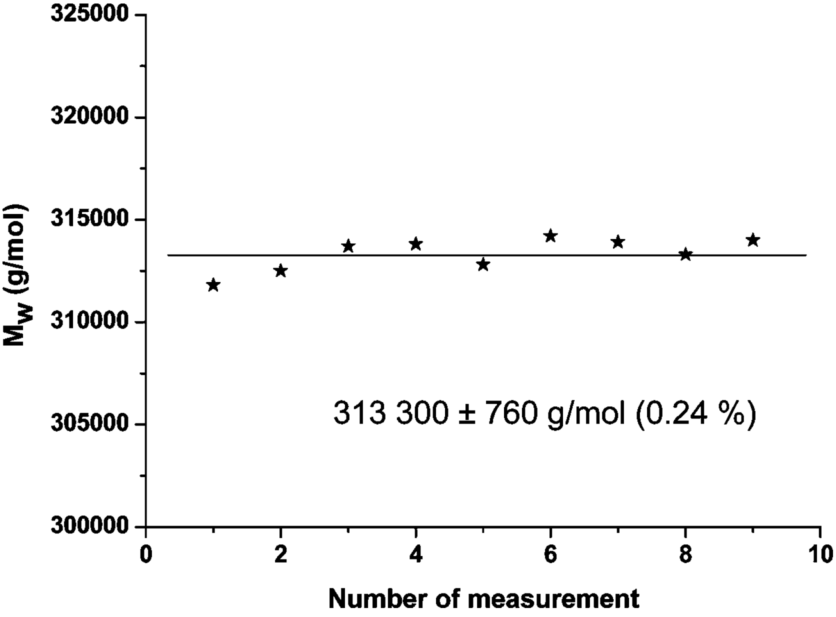

Figure 1. Uncertainty of SEC method (SEC in THF, sample concentration 1 mg/mL).

Table V. Investigation of "between-bottle" homogeneity of polymer samples

Polymer material	Number of measurements	Mean values M_w (g/mol)	Uncertainty at 95% confidence level (g/mol)	(%)
PS 1	28	79 500	±600	0.75
PS 2	23	182 100	±2 200	1.21
PS 3	26	314 500	±2 100	0.63
PMMA 4	27	367 500	±2 500	0.68
PMMA 5	28	105 000	±1 900	1.85
PMMA 6	15	353 800	±5 300	1.50
PEO 7	20	6 030	±20	0.28
PEO 8	12	10 800	±50	0.43
PLA 9	10	92 100	±700	0.76
PLA 10	10	249 800	±2 200	0.88

From these results the investigated polymer materials can be regarded as very homogeneous.

Stability

The results of long-term stability of storage at 40°C (additionally at 25°C for poly(lactide)s) for a period of two years under defined atmospheric conditions are shown in Figure 2(a)–(d). With the exception of PEO 8, PLA 9, and PLA 10, degradation could not be detected. The mean deviations for PS (1.5%) and PMMA materials (1.74%) as well as for PEO 7 (0.5%) are very low and close to the statistical accuracy of the SEC method. In contrast to this behavior, PEO 8 exhibits a stronger decrease (6.5%) of the molar mass after two years' treatment. Much more significant degradation has been found for the poly(lactide)s, 23.8% with PLA 9 and 25.1% with PLA 10. Thermal treatment at 25°C resulted in a less dramatic, but still significant degradation, 4% with PLA 9 and 9.6% with PLA 10. In order to avoid degradation of PEO, especially PLA materials, they have to be stored in cool and dry conditions.

Non-certified Physical Properties

Melt Flow Rate (MFR)

The results are presented in Table VI. Due to the low molar masses (in the case of PEO) and low glass transition temperatures (with PLA), the melt

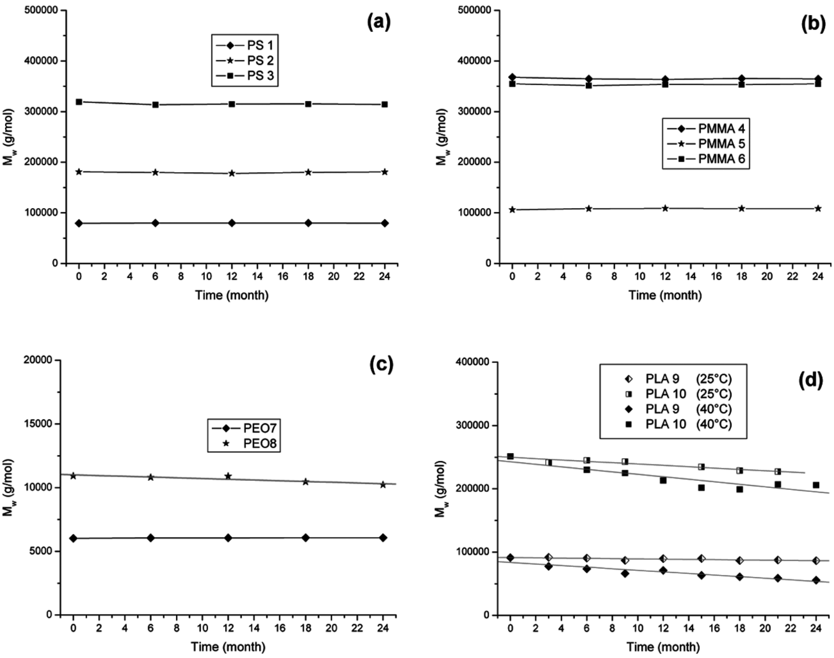

Figure 2. Stability of investigated polymers at 40°C (additionally at 25°C for PLA) for a period of two years; (a) PS, (b) PMMA, (c) PEO, and (d) PLA.

Table VI. Melt flow rate (MFR) and volume flow rate (MVR) of polymer samples

Polymer material	Temperature (°C)	Weight (kg)	MFR (g/10 min)	MVR (cm^3/10 min)
PS 1	200	5	52 ± 0.9	51.8/54.2
PS 2	200	5	9.5 ± 0.07	9.82/9.76
PS 3	200	5	1.48 ± 0.02	1.53/1.54
PMMA 4	230	3.8	—	—
		(21.6)[a]	(ca. 0.16)	
PMMA 5	230	3.8	6.3 ± 0.6	
PMMA 6	230	3.8	(ca. 0.032)	(ca. 0.02)
		(21.6)[a]	(0.64/0.74)	(ca. 0.64)
PEO 7	—	—	—	—
PEO 8	—	—	—	—
PLA 9	—	—	—	—
PLA 10	—	—	—	—

[a] 21.6 kg is the highest applicable weight, which, however, is not mandatory for PMMA at 230°C.

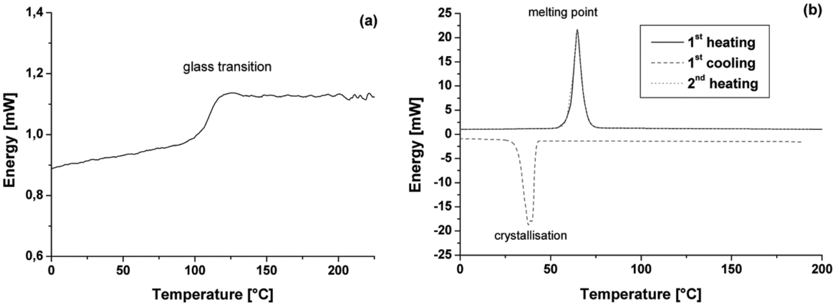

Figure 3. DSC heating curves: (a) glass transition of PMMA 6 (second heating) and (b) melting point and crystallisation temperature of PEO 8 (super-cooling effect).

flow rate of these substances could not be determined. The investigation of PMMA 4 and PMMA 6 samples was problematical. Both samples did not show a significantly high rate even at higher weights of 21.6 kg.

Calorimetry (DSC)

In contrast to thermoplastic polymers (PS, PMMA), which exhibit a distinct glass transition (second-order transition), the PEO samples show a pronounced melting behavior. This is shown in Figure 3. The shape of the transition curves, the much higher value of the phase transition enthalpy, and the difference between melting point and crystallisation temperature

Table VII. Transition temperatures and heat capacities of polymer samples

Polymer material	Glass transition temperature T_g (°C)	Specific heat capacity C_p (J/g K)
PS 1	104.1	0.279
PS 2	103.0	0.287
PS 3	103.8	0.288
PMMA 4	123.7	0.265
PMMA 5	109.6	0.255
PMMA 6	120.1	0.280
PLA 9	52.1	0.476
PLA 10	54.5	0.447
	Melting point T_m (°C)	Melting enthalpy ΔH (J/g)
PEO7	62.7	191.2
PEO8	64.8	187.8

(super cooling) clearly indicate a first-order transition. The results are summarized in Table VII. Due to constant flushing with nitrogen an oxidative degradation was excluded. Since there were only small differences between the first and second heating curves (generated by additional relaxation processes during first heating), thermal degradation could be excluded.

IR Spectroscopy

The recorded IR spectra are in good accordance with literature data.[9] They are available only in the certification reports.

SEC

Since commercially available standards had been applied for SEC calibration (PS standards were also used for the PLA calibration curve, PMMA, and PEO), values of molar masses derived from this method are not certified. Nevertheless, the results are useful in comparison with the corresponding certified values of molar mass by means of LS and MALDI-TOF-MS. Furthermore, the polydispersity M_w/M_n represents a measure of the broadness of the molar mass distribution of these polymer materials. The SEC results of the 10 reference materials are listed in Table VIII. As indicated by the low values of their confidence intervals at 95% level in Table VIII, SEC values from different participants are in good harmony with each other. The reasons are explained in the following.

The analyses had been performed with HPLC-grade THF and separation column sets with sufficient resolution and plate heights (at least 20 000 plates/m according to the GPC norms).[6] Participating laboratories that utilized only one column (with minimal values of 250 mm length and 7.8 mm internal diameter) were excluded as well as the results from laboratories using columns with lower pore sizes not suitable for the separation of higher molar mass fractions in the polymer materials.

Additional explanation of the above-mentioned good harmony was the use of the same calibration materials by all participating laboratories. A baseline construction according to ISO/EN 13885-1 and D/N 55672-1[6] was applied. A refractometer was prescribed for the detection in all laboratories.

Furthermore, the same data processing and evaluation software, WINGPC (PSS), was applied using a sufficient data acquisition rate and regression fit (minimum: fifth-degree polynomial).[3] The participating laboratories had also to prove by at least three repeated analyses for every sample that memory effects were absent, as described by Brüssau.[3]

Table VIII. Molar masses and confidence values for investigated polymers using SEC

	Mean value of molar mass confidence interval at 95% level (absolute), confidence interval at 95% level (% of mean value)				
Polymer material	Weight-average M_w (g/mol)	Number-average M_n (g/mol)	Z-average M_z (g/mol)	Molar mass at peak maximum M_p (g/mol)	Polydispersity (M_w/M_n)
PS 1	79 600	74 000	83 600	82 800	1.08
	1 100	1 300	1 300	1 300	0.01
	1.33	1.72	1.50	1.60	0.92
PS 2	181 200	81 100	331 700	145 000	2.26
	1 800	4 900	9 800	6 200	0.14
	1.01	6.05	2.97	4.29	6.33
PS 3	311 800	139 600	539 000	266 700	2.25
	4700	6 400	10 000	11 800	0.11
	1.42	4.54	1.86	4.44	4.76
PMMA 4	365 900	294 000	402 300	402 900	1.25
	11 800	13 500	13 400	14 700	0.05
	3.23	4.6	3.34	3.66	3.91

PMMA 5	101 100	47 900	178 200	92 200	2.15
	3 400	3 800	8 600	3 700	0.13
	3.4	8.03	4.84	4.04	6.16
PMMA 6	366 400	166 100	616 200	328 400	2.23
	11 100	8 200	31 800	15 700	0.13
	3.03	4.92	5.16	4.79	6.04
PEO 7	6 200	5 860	6 430	6 530	1.06
	200	250	250	250	0.04
	2.98	4.63	3.97	3.49	3.68
PEO 8	11 350	10 250	12 100	12 550	1.11
	500	500	700	600	0.07
	4.41	4.95	5.87	4.95	4.26
PLA 9	92 400	55 600	135 200	84 900	1.68
	1 500	3 400	2500	2480	0.11
	1.66	6.16	1.85	2.82	6.67
PLA 10	249 400	127 300	413 000	209 000	1.98
	8 500	8 000	12 500	13 600	0.09
	3.39	6.29	3.03	6.48	4.36

Certified Properties

An overview of all certified data is shown in Table IX.

Intrinsic Viscosity by Means of Viscometry

The viscosity measurements show confidence values (95%) of 1–5% of the certified values. Viscometry performed with the use of Ubbelohde type viscometers or by means of differential pressure capillary viscometers represent robust and reliable techniques. There are no special differences in the results depending on the type of equipment.

Applying Equation (4), using participant's values $K = 0.01162\,mL/g$ and $a = 0.719$ for PS in THF at 30°C, a viscosity average molar mass M_v of 315700 g/mol can be calculated for the poly(styrene) material PS 3 and 175000 g/mol for PS 2. These M_v values are by approximately 10% and 15% respectively, lower than the M_w values of these two samples exhibiting broad molar mass distributions measured by light scattering (LS). For poly(styrene) material PS 1 with narrow molar mass distribution, viscosity average molar mass M_v of 89900 g/mol has been obtained, which is in the range of the M_w value determined by LS techniques.

Molar Mass from Light Scattering and MALDI-TOF Mass Spectrometry

Relatively high standard deviations of the participants' results of IUPAC light scattering round-robin tests carried out in 1971[10] or interlaboratory tests of the Chemical Society of the GDR (Department of Macromolecular Chemistry) in 1989[11] were found. Since then, noticeable progress has been made regarding LS equipment and techniques, as is obvious, for example, with the results of a round-robin test in 2004 using SEC combined with light scattering detectors for the determination of relatively low-molar-mass epoxy resins.[12]

An interlaboratory test organized by BAM in 1999 demonstrated that LS values of PS materials were in good agreement if the same Rayleigh ratio value was used for calibrating multi-angle instruments and the refractive indices and refractive index increments were adjusted. Only the values of LS measurements of an oligomeric sample exhibited higher standard deviations in the test.[5] The internationally accepted Rayleigh ratio R_θ of 1.406 E-5 cm^{-1} for toluene at 633 nm was used.[13] The same procedure, as described in Just and Werthmann,[5] was used with the round-robin tests of the 10 polymer reference materials. No significant dependencies on instruments, cell geometries, or wavelengths of laser light have been found. Three laboratories applied SEC-LS coupling.

Table IX. List of certified values (value and uncertainty in % at confidence interval of 95%)

Description	PS 1 Amorphous material	PS 2 Pellets	PS 3 Pellets	PMMA 4 Amorphous material	PMMA 5 Crystalline material
Weight-averaged molecular weight (M_w) by light scattering (LS) (g/mol)	87 600 (±2.91%)	205 600 (±1.49%)	349 800 (±2.77%)	365 500 (±2.96%)	107 050 (±2.33%)
Intrinsic viscosity by viscometry (mL/g)	42.37 (±1.96%)	68.38 (±1.16%)	104.28 (±2.20%)	90.63 (±1.16%)	31.48 (±3.85%)
Averaged molecular weights (M_w and M_n) (g/mol) and	— —	— —	— —	— —	— —
Polydispersity M_w/M_n by MALDI-TOF-mass spectrometry	—	—	—	—	—

Description	PMMA 6 Crystalline material	PEO 7 Crystalline material	PEO 8 Crystalline material	PLA 9 Granulate	PLA 10 Crystalline powder
Weight-averaged molecular weight (M_w) by light scattering (LS) (g/mol)	360 200 (±2.73%)	—	10 200 (±7.91%)	77 450 (±2.16%)	225 200 (±5.98%)
Intrinsic viscosity by viscometry (mL/g)	84.80 (±2.14%)	14.28 (±3.74%)	20.91 (±5.37%)	61.19 (±2.62%)	125.29 (±2.43%)
Averaged molecular weights (M_w and M_n) (g/mol) and	—	6 065 (±1.46%) 5 960 (±1.02%)	11 400 (±1.16%) 11 300 (±0.95%)	— —	— —
Polydispersity M_w/M_n by MALDI-TOF-mass spectrometry	—	1.01 (±0.98%)	1.01 (±0.0%)	—	—

In this case, it was necessary to determine carefully the interdetector volumes.[14] The certified molar mass values $M_{w(LS)}$ for the different reference materials are the mean values for the molar masses determined by different laboratories by using light scattering techniques.

In the case of the low-molecular mass PEO 7, light scattering values were not chosen as certified values because they deviate to a greater extent. MALDI-TOF-MS was used for the certification of the molar mass M_w and M_n of this poly(ethylene glycol) material, and as an additional method also for PEO 8. MALDI-TOF-MS measurements were exclusively performed in BAM laboratories by different coworkers and using different apparatuses. BAM has participated in different MALDI-TOF-MS round-robin tests and organized one of them prior to this certification work.

CONCLUSION

Ten polymer reference materials of four polymer classes were produced and certified by BAM according to its guidelines for the production and certification of BAM reference materials. The certificates of the polymer BAM-CRM specify molar masses and intrinsic viscosities as well as their uncertainties. The results of round-robin tests using light scattering and viscometry, and MALDI-TOF-MS, which was exclusively applied within BAM laboratories, were the base of this certification work.

Additional results and evaluations of SEC round-robin tests are listed as non-certified values. In order to certify SEC results, it would be necessary to couple SEC with LS and/or to fractionate polymer materials with broad molar mass distributions. The weight average means of molar mass of different fractions would have to be determined by LS first. The LS values could then be used for the construction of the SEC calibration curves. This work will be done in the future.

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