INTERNATIONAL STANDARD

**ISO 16014-3**

Second edition
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# Plastics — Determination of average molecular mass and molecular mass distribution of polymers using size-exclusion chromatography —

## Part 3: Low-temperature method

*Plastiques — Détermination de la masse moléculaire moyenne et de la distribution des masses moléculaires des polymères par chromatographie d'exclusion stérique —*

*Partie 3: Mesurage aux basses températures*



Reference number
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# Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 16014-3 was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*.

This second edition cancels and replaces the first edition (ISO 16014-3:2003), which has been technically revised. The main changes are as follows:

a) the normative references have been updated (see Clause 2);

b) Subclause 7.1 (concerning the preparation of solutions of molecular mass standards) has been revised;

c) the maximum mass of the polymer sample which may be injected has been reduced from 0,1 mg to 0,05 mg per cubic centimetre of empty column (see 7.5.2);

d) Subclause 7.6 (concerning the number of determinations) has been revised;

e) further information has been added on the round-robin tests carried out between 1995 and 1998 (see Annex C);

f) a bibliography has been added.

ISO 16014 consists of the following parts, under the general title *Plastics — Determination of average molecular mass and molecular mass distribution of polymers using size-exclusion chromatography*:

— *Part 1: General principles*

— *Part 2: Universal calibration method*

— *Part 3: Low-temperature method*

— *Part 4: High-temperature method*

— *Part 5: Method using light-scattering detection*

# Plastics — Determination of average molecular mass and molecular mass distribution of polymers using size-exclusion chromatography —

## Part 3: Low-temperature method



## 1 Scope

This part of ISO 16014 specifies a method for determining the average molecular mass and the molecular mass distribution of polymers by size-exclusion chromatography (SEC) using an organic eluent at a temperature lower than 60 °C. The average molecular mass and the molecular mass distribution are calculated from a calibration curve prepared using polymer standards. Therefore, this test method is classified as a relative method (see ISO 16014-1:2012, Annex A).

## 2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 472, *Plastics — Vocabulary*

ISO 16014-1:2012, *Plastics — Determination of average molecular mass and molecular mass distribution of polymers using size-exclusion chromatography — Part 1: General principles*

ISO 16014-2, *Plastics — Determination of average molecular mass and molecular mass distribution of polymers using size-exclusion chromatography — Part 2: Universal calibration method*

## 3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 472 and in ISO 16014-1 apply.

## 4 Principle

See ISO 16014-1:2012, Clause 4.

## 5 Reagents

### 5.1 Eluent

For a general discussion of eluents, see ISO 16014-1:2012, 5.1.

For examples of eluents used for SEC measurements at temperatures $< 60$ °C, see Annex B.

NOTE Water is often used for SEC measurements on water-soluble polymers at temperatures $< 60$ °C, but it is not suitable for use in this method.

### 5.2 Reagent for column evaluation

See ISO 16014-1:2012, 5.2.

There are several low molecular mass compounds that can be used, for example ethylbenzene when tetrahydrofuran is used as eluent or diethylene glycol when *N*,*N*-dimethylformamide is used as eluent (see Annex B).

### 5.3 Molecular mass standards

See ISO 16014-1:2012, 5.3.

Some examples of commercially available molecular mass standards are given in ISO 16014-1:2012, Annex B.

### 5.4 Reagent for flow rate marker (internal standard)

See ISO 16014-1:2012, 5.4.

It is often very difficult to find a low molecular mass compound suitable for use as a flow rate marker because it should not co-elute with the polymer peak, the system peak or the solvent peak.

Examples of compounds suitable for use as a flow rate marker are sulfur when tetrahydrofuran is used as eluent and ethylbenzene when *N*,*N*-dimethylformamide is used as eluent.

### 5.5 Additives

LiBr or LiCl, for example, is used as an additive in *N*,*N*-dimethylformamide to avoid aggregation of polyacrylonitrile, and sodium trifluoroacetate is added to 1,1,1,3,3,3-hexafluoroisopropanol for SEC measurements on polyamide.

## 6 Apparatus

### 6.1 General

A schematic diagram of an SEC system is shown in ISO 16014-1:2012, Figure 1.

Either commercially available or assembled SEC systems may be used, provided they meet the component requirements specified and have the capability to maintain a constant column temperature < 60 °C.

### 6.2 Eluent reservoir

See ISO 16014-1:2012, 6.2.

It is not necessary to keep the reservoir at the same temperature as the columns.

### 6.3 Pumping system

See ISO 16014-1:2012, 6.3.

In order to maintain the flow rate accurate to within ±0,3 %, the pumping system shall be kept at a controlled temperature. It is, however, not necessary to keep the pumping system at the same temperature as the columns.

### 6.4 Injector

See ISO 16014-1:2012, 6.4.

In order to maintain an accurately known flow rate, the injector temperature-control equipment shall be capable of keeping the injector at within ±1 °C of the temperature set. It is not necessary to keep the injector at the same temperature as the columns.

### 6.5 Columns

See ISO 16014-1:2012, 6.5.

Organic or inorganic packing materials may be used, and there are no limitations on particle size or shape.

The set of columns used shall have a total theoretical plate number $> 15\,000$, and the resolution factor $R$ shall be $> 1{,}5$ close to the polymer peak. The asymmetry factor shall be within the range $1{,}00 \pm 0{,}15$. The set of columns used should preferably cover the whole range of molecular masses being determined, and the calibration curve shall be as linear as possible (the correlation factor shall be very close to 1). Determination of the theoretical plate number, the resolution factor and the asymmetry factor of the columns shall be carried out as described in ISO 16014-1:2012, 6.5.

The column temperature-control equipment shall be capable of keeping the columns within $\pm 0{,}5$ °C of the temperature set, to ensure adequate reproducibility of the results.

### 6.6 Detector

See ISO 16014-1:2012, 6.6.

The detector temperature-control equipment shall be capable of keeping the detector within $\pm 1$ °C of the temperature set, in order to meet the requirements for flow rate and baseline stability (sensitivity). It is recommended that the columns and detector be kept at the same temperature.

### 6.7 Tubing

See ISO 16014-1:2012, 6.7.

The temperature of the tubing shall be kept constant to ensure that the column performance requirements are met, but it is not necessary to keep the tubing at the same temperature as the column.

### 6.8 Temperature control

One of the important factors in SEC is that all components need to be kept at a constant temperature. Therefore, an accurate temperature-control system is essential to meet the performance requirements for SEC.

### 6.9 Recorder and plotter

See ISO 16014-1:2012, 6.9.

### 6.10 Data-processing system

See ISO 16014-1:2012, 6.10.

### 6.11 Other components

In addition to the components described above, a column guard filter, pressure monitor, pulse damper or related components may be used, if necessary.

## 7 Procedure

### 7.1 Preparation of solutions of molecular mass standards

The molecular mass standards used to prepare the calibration curve should preferably be selected so as to cover the range of molecular masses of the polymer being analysed and so that there are at least two standards in each molecular mass decade. Solutions may be prepared which contain more than one narrow molecular mass distribution standard, but only when the standards are perfectly separated from each other on the chromatogram.

A solution of mixed molecular mass standards containing standards of high molecular mass (> 1 000 000) might give peaks which are retarded and/or deformed because of the high viscosity of the solution. In such cases, the solutions of high molecular mass standards shall be prepared separately.

If molecular mass standards having the same chemical structure as the polymer being analysed are not available, the calibration curve may be prepared using standards consisting of a different type of polymer, and a universal calibration curve prepared for this different type of polymer (see ISO 16014-2).

If gentle shaking and/or stirring or heating is required to accelerate dissolution, the time shall be as short as possible to avoid any rupture of the polymer chains.

Filtration of the solutions is recommended to protect the column from clogging. In such cases, membrane filters or sintered-metal filters with a pore size between 0,2 µm and 1 µm shall be used. If solid material is observed on the filter, indicating incomplete dissolution, repeat the dissolution process. If a membrane filter is used, the membrane and backing shall be inert to the solvent being used.

In general, use solutions within 48 h of preparation. However, longer storage times are allowed if the solution is kept in a cool, dark place to prevent polymer degradation and solvent evaporation.

Recommended concentrations for solutions of molecular mass standards are as follows:

| | |
|---|---|
| $M_p < 5 \times 10^4$ | 0,4 mg/cm$^3$ |
| $5 \times 10^4 \leq M_p < 10^6$ | 0,2 mg/cm$^3$ |
| $10^6 \leq M_p$ | 0,1 mg/cm$^3$ |

If a viscometric detector is used, higher molecular mass standard concentrations are required in the lower molecular mass region. Sample elution times should preferably be measured at lower concentrations, however.

## 7.2 Preparation of sample solutions

Prepare sample solutions by weighing accurately 10 mg to 250 mg of sample into a 10 cm$^3$ to 50 cm$^3$ flask. Add eluent and, if necessary, an internal standard and dissolve, in the same way as for the molecular mass standard solutions (see 7.1), within 30 min. In general, samples with molecular masses > $10^5$ have a slow rate of dissolution, however, and it might be necessary to continue beyond 30 min to ensure complete dissolution. Filtration of solutions is recommended to avoid clogging of the column.

Sample solution concentrations shall not exceed the following limits:

| | |
|---|---|
| $M_w < 1 \times 10^5$ | 5,0 mg/cm$^3$ |
| $1 \times 10^5 \leq M_w < 10^6$ | 2,0 mg/cm$^3$ |
| $10^6 \leq M_w$ | 0,5 mg/cm$^3$ |

## 7.3 Preparation of solutions for column performance evaluation

Prepare a 10 mg/cm$^3$ solution of a suitable low molecular mass compound to determine the theoretical plate number, asymmetry factor and resolution factor of the set of columns.

## 7.4 Setting up the apparatus

Place the amount of eluent required for the SEC measurements in the reservoir and degas. Flush all the SEC components, except for the columns, with fresh eluent. Connect the set of columns into the system. Inspect all connections for leakage under the test conditions.

Keep the system at the test conditions (e.g. flow rate, detection sensitivity and temperature) until a flat baseline is obtained, with no drift or noise.

## 7.5 Operating parameters

### 7.5.1 Flow rate

A flow rate of approximately 1 $cm^3$/min is recommended for a series of two or three high-performance columns of approximately 30 cm in length and 8 mm in diameter. For high molecular mass and/or shear-sensitive polymers, the flow rate should preferably be reduced so that no chain rupture will occur during elution of the polymer.

### 7.5.2 Injection masses and injection volumes

The mass of polymer sample and volume of sample solution injected depend on the column dimensions and the detector sensitivity. The optimum sample injection mass has been found experimentally to be approximately 0,005 mg per cubic centimetre of empty column (without packing). The maximum mass injected shall be less than 0,05 mg per cubic centimetre of empty column.

The optimum sample solution injection volume has been found experimentally to be approximately 0,005 $cm^3$ per cubic centimetre of empty column. The maximum injection volume shall be $< 0{,}01$ $cm^3$ per cubic centimetre of empty column.

The injection volumes of the solutions of molecular mass standards shall be the same as for the sample solution.

The injection volume of the solution of low molecular mass compound shall be $< 0{,}005$ $cm^3$ per cubic centimetre of empty column.

### 7.5.3 Column temperature

The column temperature should preferably be selected based on the solubility of the sample, the viscosity and boiling point of the eluent, and the ambient temperature.

### 7.5.4 Detector sensitivity

The signal intensity depends on the amount of sample injected and on the specific refractive index increment $d_n/d_c$ for an RI detector and the absorbance per unit mass concentration for a UV detector. The detector sensitivity should preferably be set to obtain a strong peak signal for the sample, to ensure accurate data handling.

The linear relationship between solute concentration and peak height shall be maintained by keeping the sensitivity at the same setting. Recommended sensitivities are approximately $1 \times 10^{-5}$ to $9 \times 10^{-4}$ RI units at full scale for a refractive index detector and approximately 0,1 to 0,9 absorbance units at full scale for a UV detector.

## 7.6 Number of determinations

Carry out at least two sample runs to demonstrate the repeatability of the positions and shapes of the peaks in the chromatogram. If the deviation in the flow rate between the two runs is $> 0{,}3$ %, the deviation in $M_n > 3$ % and the deviation in $M_w > 2$ %, the measurements shall be repeated.

# 8 Data acquisition and processing

See ISO 16014-1:2012, Clause 8.

# 9 Expression of results

See ISO 16014-1:2012, Clause 9.

# 10 Precision

## 10.1 General

The precision of this method has been determined in several round-robin tests carried out between 1995 and 1998 in accordance with ISO 5725-1 and ISO 5725-2.

## 10.2 Experimental conditions

The test samples, which included three types of polystyrene, one type of poly(methyl methacrylate) and one type of polyacrylonitrile, and the calibration standards of narrow molecular mass distribution were distributed to the participating laboratories by the organizer. The details of the round-robins were as follows:

**1st round-robin (1995)**

| | |
|---|---|
| Polymer samples (three samples) | Polystyrene PS-1 |
| | Polystyrene PS-2 |
| | Polystyrene PS-3 |
| Calibration | 14 polystyrene standards |
| Column packing material | Polystyrene gel |
| Eluent | Tetrahydrofuran |
| Column temperature | 40 °C |
| Number of laboratories | 13 |

**2nd round-robin (1996)**

| | |
|---|---|
| Polymer sample | Poly(methyl methacrylate) (PMMA) |
| Calibration | 14 polystyrene standards |
| Column packing material | Polystyrene gel |
| Eluent | Tetrahydrofuran |
| Column temperature | 40 °C |
| Number of laboratories | 14 |

**3rd round-robin (1997-1998)**

| | |
|---|---|
| Polymer sample | Polyacrylonitrile (PAN) |
| Calibration | a) 14 polystyrene standards |
| | b) 14 poly(ethylene glycol) and poly(ethylene oxide) standards |
| Column packing materials | a) Polystyrene gel |
| | b) Poly(vinyl alcohol) gel |
| Eluent | *N*,*N*-dimethylformamide (additive: 20 mM of LiBr) |

| | |
|---|---|
| Column temperature | 40 °C |
| Number of laboratories | a) 8 for polystyrene gel column |
| | b) 10 for poly(vinyl alcohol) gel column |

## 10.3 Results of round-robin tests

The results, expressed as repeatability and reproducibility, are summarized in Table 1. The raw data are shown in Annex C.

NOTE Both the repeatability and the reproducibility of this method are sufficient for it to be the standard method except when measurements are carried out using non-ideal SEC conditions as shown in the 3rd round-robin using polystyrene gel columns and *N*,*N*-dimethylformamide, with 20 mM of LiBr as additive, as eluent. In this round-robin, large deviations in $s_R$ were caused by interactions between the polystyrene gel column and the polymer sample and/or the standards used for calibration. Therefore this test method cannot be used for polymers that exibit appreciable secondary effects, such as adsorption of the polymer molecules on the column packing material or repulsion between the polymer molecules and the packing material.

**Table 1 — Results of round-robin tests**

| Polymer | Average values of $M_n$ and $M_w$[a] | Repeatability, $s_r$[a] % | Reproducibility, $s_R$[a] % | Round-robin |
|---|---|---|---|---|
| PS-1 | $M_n$ = 137 000 | 3,1 | 8,0 | 1st |
| | $M_w$ = 373 000 | 1,3 | 8,1 | |
| PS-2 | $M_n$ = 70 400 | 3,1 | 5,6 | 1st |
| | $M_w$ = 226 000 | 2,1 | 6,1 | |
| PS-3 | $M_n$ = 38 000 | 2,8 | 6,9 | 1st |
| | $M_w$ = 157 000 | 2,4 | 4,9 | |
| PMMA[b] | $M_n$ = 163 000 | 2,1 | 9,0 | 2nd |
| | $M_w$ = 617 000 | 1,7 | 7,8 | |
| PMMA[c] | $M_n$ = 215 000 | 2,4 | 5,7 | 2nd |
| | $M_w$ = 834 000 | 1,4 | 8,4 | |
| PAN[d] | $M_n$ = 202 000 | 2,3 | 28,2 | 3rd |
| | $M_w$ = 467 000 | 0,7 | 19,8 | |
| PAN[e] | $M_n$ = 79 200 | 3,2 | 18,7 | 3rd |
| | $M_w$ = 208 000 | 1,1 | 8,2 | |
| PAN[f] | $M_n$ = 126 000 | 2,3 | 5,8 | 3rd |
| | $M_w$ = 418 000 | 0,4 | 5,1 | |
| PAN[g] | $M_n$ = 77 800 | 1,9 | 6,4 | 3rd |
| | $M_w$ = 468 000 | 0,7 | 6,6 | |

[a] Outliers were eliminated by Grubbs' and Cochran's methods[1],[3].

[b] Calibration: polystyrene standards.

[c] Calibration: poly(methyl methacrylate) standards.

[d] Column: polystyrene gel; calibration: polystyrene standards.

[e] Column: polystyrene gel; calibration: poly(ethylene glycol) and poly(ethylene oxide) standards.

[f] Column: poly(vinyl alcohol) gel; calibration: polystyrene standards.

[g] Column: poly(vinyl alcohol) gel; calibration: poly(ethylene glycol) and poly(ethylene oxide) standards.

## 11 Test report

See ISO 16014-1:2012, Clause 11.

# Annex A
(informative)

## Further information on applicability of method

The method described in this part of ISO 16014 concerns SEC measurements at temperatures < 60 °C and assumes the sample is a linear homopolymer. However, because it is a relative method, it is also applicable to non-linear homopolymers, such as branched, star-shaped, comb-like, stereo-regular and stereo-irregular polymers, and to other types of polymer, such as random, block, graft and heterophasic copolymers. The method is applicable to molecular masses ranging from that of the monomer to 3 000 000, but is not applicable to samples that contain > 30 % of components having a molecular mass < 1 000.

The method cannot be used with water as eluent, i.e. for water-soluble polymers, or at column temperatures > 60 °C (e.g. for polyethylene) or with polymers that exhibit appreciable secondary effects such as adsorption of the polymer molecules on the column packing material or repulsion between the polymer molecules and the packing material.

# Annex B
(informative)

# Further information on reagents

## B.1 Examples of suitable eluents

The following are examples of combinations of eluents and polymers for SEC measurements at temperatures < 60 °C:

a) tetrahydrofuran for polystyrene, poly(methyl methacrylate), polycarbonate, poly(vinyl acetate), etc.;

b) chloroform for aliphatic polyesters, etc.;

c) toluene for poly(dimethylsiloxane), etc.;

d) *N*,*N*-dimethylformamide for polyacrylonitrile, polyurethanes, etc.;

e) 1,1,1,3,3,3-hexafluoroisopropanol for polyamides, polyesters, etc.

## B.2 Examples of column evaluation reagents

Examples of organic reagents recommended for the evaluation of polystyrene gel columns are given in Table B.1. Reagents having ionic groups, e.g. carboxyl or amino groups, cannot be used because of their potential to interact with the column packing material.

**Table B.1 — Examples of column evaluation reagents**

| Eluent | Reagent |
|---|---|
| Tetrahydrofuran | Ethylbenzene |
| Chloroform | Ethylbenzene |
| Toluene | Ethylbenzene |
| *N*,*N*-Dimethylformamide | Ethylene glycol |
| 1,1,1,3,3,3-Hexafluoroisopropanol | Ethyl acetate |

## B.3 Narrow molecular mass distribution standards

See ISO 16014-1:2012, Annex B.

Polymers soluble only at high temperatures, such as polyethylene and polypropylene, cannot be used.

# Annex C
(informative)

# Further information on round-robin tests

## C.1 Data from 1st round-robin test (polystyrene samples)

Tables C.1 to C.3 present the raw data (molecular mass averages and variances) obtained in the 1st round-robin test.

**Table C.1 — Molecular mass averages and variances obtained for polystyrene (PS-1)**

| Laboratory | $M_n$ (× $10^{-4}$) | | $M_w$ (× $10^{-4}$) | |
|---|---|---|---|---|
| | Average | Variance | Average | Variance |
| A1 | 14,6 | 0,281 | 35,9 | 0,013 |
| B1 | 14,6 | 0,051 | 38,9 | 0,031 |
| B2 | 13,9 | 0,249 | 37,2 | 0,823 |
| B3 | 13,8 | 0,059 | 37,8 | 0,178 |
| C1 | 13,0 | 0,666 | 37,1 | 0,002 |
| C2 | 13,3 | 0,446 | 37,6 | 0,020 |
| C3 | 13,6 | 0,095 | 38,4 | 0,162 |
| D1 | 13,1 | 0,135 | 41,9 | 0,062 |
| D2 | 13,1 | 0,135 | 41,9 | 0,062 |
| D3 | 13,8 | 0,140 | 42,2 | 0,002 |
| E1 | 13,5 | 0,000 | 38,3 | 0,000 |
| E2 | 13,3 | 0,012 | 38,0 | 0,007 |
| F1 | 14,2 | 0,007 | 40,8 | 0,018 |
| F2 | 14,2 | 0,002 | 40,4 | 0,005 |
| F3 | 14,3 | 0,017 | 40,2 | 0,000 |
| G1 | 15,0 | 0,012 | 37,6 | 0,009 |
| G2 | 13,6 | 0,038 | 35,8 | 0,037 |
| H1 | 13,3 | 0,001 | 38,0 | 0,011 |
| H2 | 13,5 | 0,035 | 38,2 | 0,021 |
| I1 | 16,3 | 0,436 | 40,2 | 0,203 |
| I2 | 16,6 | 0,247 | 39,4 | 0,859 |
| J1 | 11,9 | 0,187 | 31,8 | 0,815 |
| J2 | 11,6 | 0,086 | 31,8 | 0,482 |
| J3 | 12,5 | 0,016 | 32,4 | 0,002 |
| K1 | 13,8 | 0,009 | 37,5 | 0,007 |
| K2 | 14,5 | 0,036 | 38,1 | 0,016 |
| L1 | 13,9 | 0,024 | 37,0 | 0,158 |
| L2 | 12,6 | 0,000 | 35,2 | 0,260 |
| M1 | 12,6 | 0,062 | 33,3 | 0,140 |
| M2 | 13,1 | 0,107 | 32,2 | 0,002 |
| M3 | 12,0 | 0,109 | 32,1 | 0,362 |

Three sample runs (see 7.6) were carried out for each determination (i.e. $n = 3$). Some of the laboratories carried out two or three separate determinations. For example, laboratory B carried out three determinations, shown as B1, B2 and B3. Such data were processed as being from quasi-laboratories.

**Table C.2 — Molecular mass averages and variances obtained for polystyrene (PS-2)**

| Laboratory | $M_n$ (× $10^{-4}$) | | $M_w$ (× $10^{-4}$) | |
|---|---|---|---|---|
| | Average | Variance | Average | Variance |
| A1 | 7,24 | 0,026 | 22,6 | 0,006 |
| B1 | 7,65 | 0,098 | 23,1 | 0,096 |
| B2 | 7,54 | 0,038 | 22,4 | (0,212) |
| B3 | 7,45 | 0,031 | 22,9 | 0,060 |
| C1 | 6,70 | 0,149 | 21,9 | 0,007 |
| C2 | 6,47 | 0,060 | 22,2 | 0,042 |
| C3 | 6,95 | 0,009 | 22,7 | 0,002 |
| D1 | 6,89 | 0,015 | 24,8 | 0,047 |
| D2 | 7,00 | 0,003 | 24,7 | 0,002 |
| D3 | 6,75 | 0,084 | 24,6 | 0,009 |
| E1 | 7,19 | 0,000 | 23,0 | 0,000 |
| E2 | 7,07 | 0,002 | 22,9 | 0,010 |
| F1 | 7,51 | 0,002 | 24,1 | 0,009 |
| F2 | 7,61 | 0,001 | 23,8 | 0,000 |
| F3 | 7,65 | 0,002 | 23,6 | 0,004 |
| G1 | 7,34 | 0,002 | 23,0 | 0,002 |
| G2 | 7,09 | 0,000 | 22,4 | 0,010 |
| H1 | 6,70 | 0,007 | 23,5 | 0,005 |
| H2 | 6,88 | 0,002 | 23,2 | 0,019 |
| I1 | (9,13) | (5,707) | 23,4 | (2,628) |
| I2 | (9,72) | (0,590) | 24,9 | (0,887) |
| J1 | 6,62 | 0,004 | 20,0 | 0,095 |
| J2 | 6,73 | 0,001 | 20,1 | 0,042 |
| J3 | 6,65 | 0,095 | 21,0 | 0,016 |
| K1 | 7,07 | 0,007 | 22,9 | 0,007 |
| K2 | 6,78 | 0,038 | 22,8 | 0,020 |
| L1 | 6,52 | 0,136 | 21,7 | 0,016 |
| L2 | 6,59 | 0,020 | 22,0 | 0,099 |
| L3 | 6,74 | 0,013 | 20,6 | 0,050 |
| M1 | 7,60 | 0,006 | 21,8 | 0,042 |
| M2 | 7,66 | 0,084 | 21,4 | 0,047 |
| M3 | 6,55 | 0,004 | 19,6 | 0,042 |

NOTE Values in brackets are outliers.

**Table C.3 — Molecular mass averages and variances obtained for polystyrene (PS-3)**

| Laboratory | $M_n$ (× $10^{-4}$) | | $M_w$ (× $10^{-4}$) | |
|---|---|---|---|---|
| | Average | Variance | Average | Variance |
| A1 | 3,70 | 0,008 | 15,7 | 0,004 |
| B1 | 4,12 | 0,006 | 16,4 | 0,059 |
| B2 | 3,99 | 0,017 | 15,7 | 0,052 |
| B3 | 4,05 | 0,005 | 16,0 | 0,014 |
| C1 | 3,67 | 0,005 | 15,4 | 0,095 |
| C2 | 3,55 | 0,001 | 15,3 | 0,020 |
| C3 | 3,78 | (0,038) | 15,8 | 0,056 |
| D1 | 3,84 | 0,001 | 16,8 | 0,020 |
| D2 | 3,74 | 0,002 | 16,4 | 0,029 |
| D3 | 3,76 | 0,014 | 16,6 | 0,007 |
| E1 | 3,69 | 0,000 | 16,1 | 0,000 |
| E2 | 3,60 | 0,000 | 16,0 | 0,000 |
| F1 | 3,95 | 0,000 | 16,6 | 0,003 |
| F2 | 4,00 | 0,001 | 16,3 | 0,001 |
| F3 | 4,08 | 0,001 | 16,2 | 0,002 |
| G1 | 3,99 | 0,000 | 16,2 | 0,001 |
| G2 | 3,89 | 0,000 | 16,0 | 0,002 |
| H1 | 3,50 | 0,001 | 16,8 | 0,020 |
| H2 | 3,59 | 0,003 | 16,2 | 0,039 |
| I1 | 4,04 | 0,005 | 15,3 | (2,247) |
| J1 | 3,47 | 0,002 | 14,6 | 0,016 |
| J2 | 3,50 | 0,002 | 14,5 | 0,002 |
| J3 | 3,70 | 0,000 | 14,5 | 0,009 |
| K1 | 3,80 | 0,000 | 16,1 | 0,000 |
| K2 | 3,70 | 0,000 | 16,0 | 0,002 |
| L1 | 3,75 | 0,004 | 15,8 | 0,012 |
| L2 | 3,60 | 0,001 | 15,0 | 0,009 |
| L3 | 3,50 | 0,002 | 14,4 | 0,031 |
| M1 | 4,42 | 0,003 | 15,6 | 0,002 |
| M2 | 4,50 | (0,069) | 15,4 | 0,016 |
| M3 | 3,46 | (0,038) | 13,6 | 0,016 |

NOTE Values in brackets are outliers.



## C.2 Data from 2nd round-robin test [poly(methyl methacrylate samples)]

Table C.4 presents the raw data (molecular mass averages and variances) obtained in the 2nd round-robin test. Three sample runs (see 7.6) were carried out for each determination (i.e. $n = 3$).