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CHARACTERIZATION OF POLYAMIDES 6, 11, AND 12: DETERMINATION OF MOLECULAR WEIGHT BY SIZE EXCLUSION CHROMATOGRAPHY**

(IUPAC Technical Report)

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Characterization of polyamides 6, 11, and 12: Determination of molecular weight by size exclusion chromatography

(IUPAC Technical Report)

Abstract: This report presents the results from IUPAC Working Party IV.2.2 of the global trial within the framework of IUPAC Commission IV.2, "Characterization of Commercial Polymers". The results were compared on the basis of molecular weight obtained by size exclusion chromatography (SEC) using different techniques practiced in participating laboratories, the majority of which were materials suppliers. The practical methodologies used different solvents for the polymers, in particular, benzyl alcohol, 1,1,1,3,3,3-hexafluoropropan-2-ol and tetrahydrofuran; the latter solvent was used after chemical modification of the polyamides, in general with trifluoroacetic anhydride. Eight laboratories participated in the trial. The repeatability for $\overline{M}_w$ in each laboratory was good, whatever technique was used, the relative standard deviation averaged over all laboratories being around 3 %. The deviations in distribution of molecular weights with different experimental methodologies were broader, but were reasonably good despite the diversity of methods. The differences in the distribution correspond to a confidence interval of about 30 % in $\overline{M}_w$.

1. INTRODUCTION

Some standardization of size exclusion chromatography (SEC) methodology has been put into effect in the framework of the American Society for Testing and Materials (ASTM), e.g., for the characterization of polystyrene in tetrahydrofuran [1]. Presently, most methods are established on the basis of publications or research by materials suppliers. For the majority of polymers, in particular polyamides, practical methodologies have only been validated by internal research and not by global trials [2]. Hence, comparison of results between laboratories and/or suppliers and customers cannot be established on the basis of existing SEC results.

Given this current limitation, an IUPAC project with the aim of externally validating SEC methodologies for the characterization of polyamides was established. The project involved a sufficient number of independent laboratories to allow, first, the statistical evaluation of the results, and secondly to try to define a standard SEC methodology which could be widely used. The objective was to find one or two solvents, such as 1,1,1,3,3,3-hexafluoropropan-2-ol and benzyl alcohol for which thorough study of the condition of determination of molecular weight would be established (operating conditions, the nature of the calibration sample, method of calibration, and verification of Mark–Houwink–Sakurada constants).

This report presents the results obtained in the framework of the first segment of this project, that is, the comparison of different methodologies used by the eight participating laboratories.

The results obtained at this stage are encouraging with regard to repeatability. The data scatter obtained for the different methodologies remains reasonably small despite the diversity of methods.

2. DESCRIPTION OF ANALYTICAL METHODS

The first segment of this project does not constitute a true round-robin in so far as methodologies involved are different in each laboratory. This comparison of methods aims to establish an inventory of practical methods and to find the basis for instituting a reference method.

2.1 Summary of abbreviations

Table 1 Main abbreviations used.

Abbreviation	Name	Abbreviation	Name
DCM	Dichloromethane	$\overline{M}_w$	Weight-average molecular weight
HFIP	1,1,1,3,3,3-Hexafluoropropan-2-ol (hexafluoroisopropanol*)	$\overline{M}_z$	z-Average molecular weight
		PA	Polyamides (see Table 2)
TFA	Trifluoroacetic anhydride	PEG	Poly(ethylene glycol)
THF	Tetrahydrofuran	PEO	Poly(oxyethylene)
SEC	Size exclusion chromatography	PMMA	Poly(methyl methacrylate)
NTP	Number of theoretical plates	PS	Polystyrene
$\overline{M}_n$	Number-average molecular weight	PTHF	Polytetrahydrofuran

*Name not recommended by IUPAC.

2.2 Participating laboratories

Eight laboratories were involved in this project (in alphabetical order):

- Atofina Cerdato, Serquigny, France
- BASF AG, Kunststofflaboratorium, Dept. ZKM/A-B1, Ludwigshafen, Germany
- DSM Research, Dept. PO-AS, Geleen, Netherlands
- E. I. Dupont de Nemours Experimental Station, Wilmington, Delaware, USA
- EMS Chemie AG R&D, Domat, Switzerland
- EPFL (Ecole Polytechnique Fédérale de Lausanne) Polymer Laboratory, Switzerland
- IFP (Institut Français du Pétrole) Laboratory of Liquid Chromatography, Rueil-Malmaison, France
- Rhodia CRL/PID, St. Fons, France

2.3 Polymers tested

Fifteen samples of polyamides 6, 11, and 12 were tested over the largest possible range of molecular weights. These three types of polyamides were chosen because they are soluble in benzyl alcohol. Indeed, polyamides 66 (Nylon) and 612 (Nylon 612, polycondensation products of 1,6-diaminohexane and dodecanedioic acid), for example, are not soluble in a neat solvent, even if it is heated.

Three commercial polyamides 6 (natural grade) were furnished by EMS Chemie. Five synthetic polyamides 11, five synthetic polyamides 12 and two commercial polyamides 12 (natural grade) were furnished by Atofina.

Table 2 Names of polyamides.

Trivial name	Systematic name	Structure
Polyamide 6 (PA 6) – Polycaprolactam	Poly[imino(1-oxohexane-1,6-diyl)]	– [–NH–CO– $(CH_2)_{5}$–]$_{n}$–
Polyamide 11 (PA 11) – poly(11-aminoundecanoic acid)	Poly[imino(1-oxoundecane-1,11-diyl)]	– [–NH–CO– $(CH_2)_{10}$–]$_{n}$–
Polyamide 12 (PA 12) – polylaurolactam	Poly[imino(1-oxododecane-1,12-diyl)]	– [–NH–CO– $(CH_2)_{11}$–]$_{n}$–

2.4. Experimental methodologies

The first difference among the experimental methodologies lies in the solvent used to dissolve the polyamides. The choice of the solvent used by the laboratory is actually determined by the nature of the polymers which are synthesized or used by the different companies. Moreover, this choice took account of considerations of safety (the carcinogenic character of hexamethylphosphoramide and 2,2,2-trifluoroethanol) or risks of degradation of polymers with some solvents (neat *m*-cresol).

For this comparison, the solvents used were:

- 1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP), a quasi-universal solvent for polyamides at ambient temperature; because HFIP is an expensive solvent, it is generally recycled and must be handled with care because of its corrosive character.
- Warm benzyl alcohol, a solvent which presents few safety hazards, but which can solubilize only a limited number of polyamides (PA 6, PA 11, and PA 12)
- Tetrahydrofuran (THF) or dichloromethane, combined with trifluoroacetic anhydride, which reacts with the amide groups, leads to a rapid dissolution of polyamides at ambient temperature. In this case, hydrogen bonds between polyamide chains are broken by the reaction of the acid functional groups of trifluoroacetic acid with NH_2 groups.

Table 3 gives a summary of the solvents used by the participants of this project.

Table 3 Solvents for polyamides.

Laboratory number	Solvent
1	Benzyl alcohol at 130 °C
2	HFIP + potassium trifluoroacetate (mass fraction 0.2 %)
3	HFIP + potassium trifluoroacetate (mass fraction 0.05 %)
4	Dichloromethane (stabilized) + additives
5	THF (absolute)
6	Benzyl alcohol at 130 °C
7	HFIP, 0.01 M sodium trifluoroacetate
8	CH_2Cl_2/HFIP 85/15 volume ratio for PA 6 and 95/5 + 1 g of tetraethylammonium chloride for PA 11 and PA 12

Note: to maintain confidentiality, there is no relation between laboratory number and the list order in Section 2.2.

The chromatographic systems, the operating conditions, and the calibration used are given in Table 4.

Table 4 Operating conditions and calibration for characterization of polyamides.

Lab	Equipment	Detection	Software	Columns	Sample dissolution	Flow rate, temperature, injection vol.	Calibration
1	Waters 150C	Refractometry	Home-made HP1000	PL mixed B 10 μm, 3/8", 60 cm, NTP not specified	2–4 h between 130 and 145 °C for PA in benzyl alcohol, 4 g/l	1 ml/min, 130 °C, 180 μl	PS, PTHF, PEO and PEG. Universal calibration at 130 °C. Polynomial order 3
2	HP 1090 and 1047A + Viscotek 502B	Viscometry + refractometry	Viscotek TriSEC2.7	4 columns of Nucleosil 7-OH, 7 μm, 300 × 6.2 mm: 2 of 100 Å, 2 of 1000 Å	~.4 h at room temperature with N_2, 0.5 μm filtration	0.4 ml/min, 35 °C, 100 μl	PA 4, 6 samples. Polynomial order 3. Universal calibration
3	Modular	UV 230 nm	Home-made	Shodex HFIP 803 and 805 (8 mm × 30 cm), precolumn HFIP-LG (8 mm × 5 cm), NTP = 13 880 (125 μl, mass ratio 0.5 % acetone)	~1.5 h, 1.5 g/l	0.5 ml/min, room temperature, 125 μl	PMMA (0.03 g in 100 ml) 7^{th} order without ordered pairs + one hyperbolic term.
4	Modular, differential viscometry (home-made)	UV 270 nm and viscometry	–	Phenomenex mixed 5 μm, 3/8″, 60 cm	TFA modification in DCM, 25 °C, mass ratio 1 %	1.5 ml/min, room temperature,	$[\eta]M$ polystyrene
5	Waters 150C	UV 254 nm	Waters Millennium	Merck Lichrogel (3 columns of 250 × 7 mm), PS4000, PS400, PS20, 10 μm	TFA modification in DCM. Evaporated then dissolved in abs THF, mass ratio 0.5 %	50 μl room temperature, 50 μl	Standard high-MW PA
6	Waters 150C	Refractometry	ESPCI Pr Lesec	Pl mixed B, 10 μm, 2 columns 30 cm	2–4 h between 130 and 145 °C for PA in benzyl alcohol, 3 g/l	1 ml/min, 130 °C, 100 μl	PMMA. Universal calibration at 130 °C. Polynomial orders 1–3 (same results)
7	Waters Alliance 2690LC. RI 410. Viscotek T60A90	Light scattering, viscometry, refractometry	Viscotek TriSEC3.0	2 Shodex GPC HFIP 806M, precolumn HFIP-LG. NTP > 20 000 (acetone injection)	2 h, 2 mg/ml, 0.5 μm filtration	1.0 ml/min, 30 °C, 100 μl	PA 66
8	Waters 150CV modified for differential viscometry	Viscometry + refractometry	ESPCI Pr Lesec	Waters HR5+HR4+HR3+HR1	Room temperature, 2 mg/ml, $[\eta]_c < 0.01$. TFA modification in DCM at 25 °C, mass ratio 0.5 %	1.0 ml/min, 30 °C, 200 or 300 μl PA6	Universal calibration from polystyrene standards

- Laboratory 3 used a relative calibration with poly(methyl methacrylate) and a complex approach to give a mathematical account of the calibration curve.
- Laboratories 1 and 6 used universal calibration. This required the Mark–Houwink–Sakurada constants of the standards used to calibrate the columns and the polyamides analyzed, for the appropriate solvent at the working temperature.
- Laboratory 5 used a calibrating methodology which consisted of the use of a sample of polydisperse polyamide treated under the same conditions as samples.
- Laboratories 2, 4, 7, and 8 used multidetection, detectors being calibrated with a polyamide.

The most complete multidetection approach was that developed by the laboratory 7 which used "triple detection". Detectors were calibrated by way of a well-characterized polyamide for which the specific refractive index increment was determined ($dn/dc = 0.235$ cm^3 g^{-1}), and intrinsic viscosity was determined off-line. The light-scattering detector was calibrated with PA 66 with a known $\overline{M}_w$. The "offsets" (inter-detector delay) between detectors were calculated so as to compensate for band broadening. The offset of the light-scattering detector was adjusted to give the correct distribution of weight on a standard PA 66 ($\overline{M}_Z/\overline{M}_w = 1.5$) and the offset of the viscometer was adjusted to give a Mark–Houwink coefficient (exponent) $a = 0.70$.

2.5 Test conditions

For each laboratory, it was required that the analysis of the samples be performed in duplicate, including the solution preparation of the samples. However, some laboratories performed either only one or more than two determinations.

3. RESULTS

The results obtained for the three types of polyamides are given in Tables 5–7, together with the statistical analysis of the data.

The statistical analysis consisted of the determination of:

- the standard deviation for the weight-average molecular weight of each of the polymers and each laboratory (in italics in the tables); these data correspond to the standard deviation of the repeatability for each laboratory;
- the mean of the standard deviations, not weighted by the degree of freedom; and
- the standard deviation over the whole collection of molecular weight data: this allowed estimation of the distribution of the results obtained using the different methodologies. Here, the results of laboratory 3 are excluded, because laboratory 3 did not carry out a method that allowed determination of molecular weights comparable to other laboratories [molecular weights of poly(methyl methacrylate), PMMA].

Standard deviations are given as absolute and as relative values.

Note: The statistical analysis did not follow ISO standard 5725 (i.e., repeatability and reproducibility were not obtained from a rigorous analysis of the variance). Nevertheless, the basic calculus of standard deviations gives a good indication of the distribution of the results in each laboratory using the different methodologies. The deviations in relation to the mean are the following:

- The standard deviation of repeatability (intralaboratory) was calculated as the arithmetic mean of the standard deviations obtained in each laboratory.
- The standard deviation of distribution due to the different methodologies in the laboratories (interlaboratory) was calculated as the standard deviation of the values of molecular weights in all laboratories but laboratory 3.

Table 5 Molecular weights of polyamides 6.

Laboratory	PA 6-1				PA 6-2				PA 6-3			
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
1	16.5	27.5	41.1	1.67	20.1	33.7	51.1	1.68	25.0	40.9	61.2	1.64
1	16.1	26.8	39.5	1.66	20.5	33.5	50.0	1.63	24.3	40.1	61.9	1.65
sd	*0.28*	*0.49*	*1.13*	*0.00*	*0.28*	*0.14*	*0.78*	*0.03*	*0.49*	*0.57*	*0.49*	*0.01*
2	11.0	23.0	38.0	2.09	13.0	28.0	48.0	2.15	15.0	38.0	69.0	2.53
2	10.0	22.0	36.0	2.20	13.0	29.0	48.0	2.23	16.0	40.0	72.0	2.50
sd	*0.71*	*0.71*	*1.41*	*0.08*	*0.00*	*0.71*	*0.00*	*0.05*	*0.71*	*1.41*	*2.12*	*0.02*
3	26.1	56.6	83.9	2.17	33.6	69.5	102.4	2.07	41.3	93.1	146.1	2.25
3	27.5	56.9	83.2	2.07	32.6	69.8	103.4	2.14	40.2	93.0	146.7	2.31
3	27.7	57.0	83.9	2.06	32.9	70.0	103.7	2.13	41.8	93.1	145.7	2.23
sd	*0.91*	*0.20*	*0.43*	*0.06*	*0.52*	*0.26*	*0.69*	*0.04*	*0.82*	*0.04*	*0.53*	*0.04*
4	16.5	25.3	34.2	1.53	18.4	29.0	41.0	1.58	25.6	40.7	59.3	1.59
5	15.5	31.9	56.9	2.07	17.5	37.0	62.5	2.11	20.3	50.5	92.2	2.49
5	15.4	31.8	56.3	2.06	17.5	37.0	62.1	2.11	20.3	50.5	91.9	2.49
5	15.2	30.7	52.2	2.02	16.7	34.3	56.7	2.06	20.1	49.8	89.6	2.48
5	15.4	30.7	51.8	2.00	16.7	34.4	56.7	2.06	20.1	49.5	88.8	2.46
sd	*0.13*	*0.69*	*2.71*	*0.03*	*0.50*	*1.52*	*3.24*	*0.03*	*0.10*	*0.52*	*1.69*	*0.01*
6	12.8	26.5	–	2.07	16.4	35.1	–	2.14	23.7	47.5	–	2.00
7	15.4	28.7	42.8	1.86	22.6	38.1	55.9	1.69	27.9	52.2	79.2	1.87
7	15.3	28.8	42.9	1.88	18.7	37	55.9	1.98	26.6	52	80.6	1.95
sd	*0.07*	*0.07*	*0.07*	*0.01*	*2.76*	*0.78*	*0.00*	*0.21*	*0.92*	*0.14*	*0.99*	*0.06*
8	20.8	35.6	53.4	1.72	25.2	42.2	63.4	1.67	28.1	66.4	107	2.36

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Table 5 (*Continued*).

Laboratory	PA 6-1				PA 6-2				PA 6-3			
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
Excluding laboratory 3												
Mean	15.1	28.4	45.4	1.9	18.2	34.5	54.3	1.9	22.5	47.6	79.4	2.2
Standard deviation of "reproducibility"	2.7	3.8	8.2	0.2	3.4	4.0	6.8	0.2	4.3	7.7	15.0	0.4
Relative standard deviation of "reproducibility"	0.18	0.13	0.18	0.11	0.19	0.12	0.13	0.12	0.19	0.16	0.19	0.18
Including laboratory 3												
Standard deviation of "repeatability"	0.42	0.43	1.15	0.04	0.81	0.68	0.94	0.07	0.61	0.54	1.16	0.03
Relative standard deviation of "repeatability"	0.03	0.02	0.03	0.02	0.05	0.02	0.02	0.04	0.03	0.01	0.02	0.01

Table 6a Molecular weights of polyamides 11, PA 11-1 to 11-3.

Laboratory	PA 11-1				PA 11-2				PA 11-3			
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
1	17.6	30.1	47.7	1.71	19.4	34.1	55.5	1.76	22.1	39.1	67.7	1.77
1	17.1	29.7	46.6	1.74	19.1	33.4	54.1	1.75	22.1	39.2	66.6	1.77
sd	*0.35*	*0.28*	*0.78*	*0.02*	*0.21*	*0.49*	*0.99*	*0.01*	*0.00*	*0.07*	*0.78*	*0.00*
2	12.0	27.0	46.0	2.25	14.0	32.0	55.0	2.29	18.0	40.0	70.0	2.22
2	12.0	27.0	45.0	2.25	13.0	31.0	55.0	2.38	17.0	40.0	72.0	2.35
sd	*0.00*	*0.00*	*0.71*	*0.00*	*0.71*	*0.71*	*0.00*	*0.07*	*0.71*	*0.00*	*1.41*	*0.09*
3	21.6	48.7	79.0	2.25	24.8	56.0	91.4	2.26	29.5	66.8	109.9	2.26
3	20.7	48.1	79.8	2.32	21.8	55.9	92.4	2.57	30.0	66.4	109.2	2.21
3	20.7	49.0	79.9	2.37	24.2	57.4	95.7	2.38	28.9	66.8	111.0	2.31
sd	*0.55*	*0.47*	*0.47*	*0.06*	*1.58*	*0.84*	*2.21*	*0.16*	*0.56*	*0.23*	*0.91*	*0.05*
4	18.3	30.6	44.3	1.67	20.7	34.5	50.6	1.67	24.6	39.7	58.2	1.61
5	15.7	29.4	47.1	1.87	17.2	33.9	53.0	1.98	18.6	39.0	61.8	2.10
5	15.7	29.3	46.9	1.87	17.2	33.8	52.4	1.97	18.7	39.1	61.7	2.09
5	16.0	30.1	46.9	1.88	16.5	31.3	47.9	1.90	18.5	38.6	60.8	2.09
5	16.0	30.1	46.6	1.88	16.5	31.4	48.3	1.90	18.5	38.6	60.8	2.09
sd	*0.19*	*0.47*	*0.20*	*0.01*	*0.42*	*1.47*	*2.66*	*0.04*	*0.09*	*0.26*	*0.57*	*0.01*
6	18.8	35.2	–	1.87	20.8	40.5	–	1.94	26.5	50.8	–	1.92
6	17.5	35.8	–	2.04	21.8	43.9	–	2.02	25.4	49.0	–	1.93
6	18.7	39.9	–	2.14	21.2	45.7	–	2.16	22.4	54.0	–	2.41
sd	*0.70*	*2.55*	–	*0.14*	*0.47*	*2.66*	–	*0.11*	*2.11*	*2.53*	–	*0.28*
7	19.3	34.5	53.3	1.79	24.7	41.9	64.5	1.7	26.9	50.1	78.7	1.86
7	15.7	33.6	53.6	2.14	22.3	40.1	62.2	1.8	27.7	50.4	79	1.82
sd	*2.55*	*0.64*	*0.21*	*0.25*	*1.70*	*1.27*	*1.63*	*0.07*	*0.57*	*0.21*	*0.21*	*0.03*
8	23.7	43.4	74.9	1.83	18.8	35.3	56.4	1.88	26.8	53.7	87.9	2

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Table 6a (*Continued*).

Laboratory	PA 11-1				PA 11-2				PA 11-3			
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
Excluding laboratory 3												
Mean	16.9	32.4	49.9	1.9	18.9	36.2	54.6	1.9	22.2	44.1	68.8	2.0
Standard deviation of "reproducibility"	2.9	4.7	8.4	0.2	3.2	4.9	4.9	0.2	3.8	6.2	9.2	0.2
Relative standard deviation of "reproducibility"	0.17	0.14	0.17	0.10	0.17	0.14	0.09	0.11	0.17	0.14	0.13	0.11
Including laboratory 3												
Standard deviation of "repeatability"	0.72	0.74	0.47	0.08	0.85	1.24	1.50	0.08	0.67	0.55	0.78	0.08
Relative standard deviation of "repeatability"	0.04	0.02	0.01	0.04	0.05	0.03	0.03	0.04	0.03	0.01	0.01	0.04

Table 6b Molecular weights of polyamides 11, PA 11-4 and PA 11-5.

Laboratory	PA 11-4				PA 11-5			
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
1	24.4	42.6	70.2	1.75	28.5	54.0	97.8	1.89
1	22.9	41.0	71.0	1.79	28.3	52.8	98.0	1.87
sd	*1.06*	*1.13*	*0.57*	*0.03*	*0.14*	*0.85*	*0.14*	*0.02*
2	19.0	44.0	81.0	2.32	20.0	60.0	126.0	3.00
2	17.0	43.0	77.0	2.53	19.0	60.0	128.0	3.16
sd	*1.41*	*0.71*	*2.83*	*0.15*	*0.71*	*0.00*	*1.41*	*0.11*
3	31.3	71.5	119.8	2.28	44.7	97.0	174.1	2.17
3	31.0	71.8	120.8	2.31	43.3	97.9	175.7	2.26
3	31.5	71.6	120.4	2.27	–	–	–	–
sd	*0.24*	*0.13*	*0.51*	*0.02*	*0.96*	*0.60*	*1.16*	*0.06*
4	26.5	43.3	64.4	1.63	31.7	52.3	81.2	1.65
5	19.0	40.4	63.9	2.13	21.0	51.8	86.6	2.47
5	19.0	40.4	64.1	2.12	21.0	52.0	86.7	2.47
5	19.2	40.4	62.0	2.10	21.2	52.0	84.9	2.45
5	19.2	40.4	62.0	2.10	21.2	51.9	84.7	2.45
sd	*0.13*	*0.02*	*1.15*	*0.01*	*0.10*	*0.08*	*1.07*	*0.01*
6	27.7	58.7	–	2.12	34.1	72.3	–	2.12
6	27.3	55.6	–	2.04	32.0	65.8	–	2.06
6	26.3	59.6	–	2.27	30.0	69.3	–	2.31
sd	*0.73*	*2.09*	–	*0.12*	*2.03*	*3.25*	–	*0.13*
7	29.5	54.3	85.6	1.84	33.8	73.2	127.0	2.17
7	30.1	55.5	88.6	1.84	36.9	74.3	127.8	2.01
sd	*0.42*	*0.85*	*2.12*	*0.00*	*2.19*	*0.78*	*0.57*	*0.11*
8	34.4	59.7	99.4	1.74	35.1	88.8	165.4	2.5
Excluding laboratory 3								
Mean	24.1	47.9	74.1	2.0	27.6	62.0	107.9	2.3
Standard deviation of "reproducibility"	5.2	8.1	12.3	0.2	6.4	11.4	26.4	0.4
Relative standard deviation of "reproducibility"	0.22	0.17	0.17	0.12	0.23	0.18	0.24	0.18
Including laboratory 3								
Standard deviation of "repeatability"	0.67	0.82	1.44	0.06	1.02	0.93	0.87	0.07
Relative standard deviation of "repeatability"	0.03	0.02	0.02	0.03	0.04	0.02	0.01	0.03

Table 7a Molecular weights of polyamides 12, PA 12-1 to 12-4.

Laboratory	PA 12-1				PA 12-2				PA 12-3				PA 12-4			
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
1	26.6	40.1	56.8	1.51	30.3	49.6	78.0	1.64	23.8	36.9	53.2	1.55	28.1	43.0	63.3	1.53
1	25.5	39.0	56.9	1.53	29.1	49.1	78.3	1.69	23.4	36.2	53.1	1.55	26.9	41.4	61.4	1.54
sd	*0.78*	*0.78*	*0.07*	*0.02*	*0.85*	*0.35*	*0.21*	*0.04*	*0.28*	*0.49*	*0.07*	*0.00*	*0.85*	*1.13*	*1.34*	*0.01*
2	16.0	33.0	52.0	2.06	20.0	48.0	85.0	2.40	16.0	34.0	55.0	2.13	19.0	40.0	64.0	2.11
2	16.0	35.0	55.0	2.19	20.0	48.0	84.0	2.40	16.0	34.0	53.0	2.13	19.0	39.0	63.0	2.05
sd	*0.00*	*1.41*	*2.12*	*0.09*	*0.00*	*0.00*	*0.71*	*0.00*	*0.00*	*0.00*	*1.41*	*0.00*	*0.00*	*0.71*	*0.71*	*0.04*
3	13.3	34.6	59.7	2.59	19.7	53.0	93.8	2.70	12.9	34.5	60.8	2.67	14.6	40.9	72.3	2.79
3	12.9	34.5	60.5	2.67	18.4	51.8	90.8	2.82	12.3	34.2	62.2	2.77	15.7	41.2	71.5	2.63
3	13.2	34.6	59.7	2.62	18.0	52.4	94.6	2.90	11.5	33.7	62.2	2.93	15.0	41.3	73.8	2.75
3	–	–	–	–	18.3	51.8	91.5	2.83	12.6	33.6	59.6	2.67	–	–	–	–
3	–	–	–	–	18.9	52.5	94.0	2.78	12.7	34.0	61.0	2.67	–	–	–	–
sd	*0.21*	*0.04*	*0.47*	*0.04*	*0.64*	*0.50*	*1.68*	*0.08*	*0.55*	*0.37*	*1.10*	*0.11*	*0.51*	*0.23*	*1.15*	*0.09*
4	24.1	35.1	46.8	1.46	29.2	43.9	61.6	1.50	22.6	33.9	46.3	1.50	26.3	39.2	54.3	1.49
5	19.3	37.4	53.1	1.94	20.5	43.1	63.6	2.10	19.1	38.0	56.5	1.99	19.9	42.0	63.5	2.11
5	19.3	37.5	53.0	1.94	20.4	43.0	63.6	2.11	19.1	38.0	56.6	1.99	19.9	42.0	63.6	2.11
5	19.1	36.6	51.4	1.92	21.5	47.8	72.1	2.22	18.3	34.9	50.4	1.91	19.5	40.2	60.2	2.06
5	19.1	36.6	51.5	1.91	21.5	47.8	72.1	2.22	18.3	34.8	50.6	1.90	19.7	40.2	60.0	2.04
sd	*0.11*	*0.50*	*0.91*	*0.02*	*0.62*	*2.76*	*4.90*	*0.07*	*0.47*	*1.82*	*3.50*	*0.05*	*0.20*	*1.03*	*1.98*	*0.03*
6	21.6	37.4	–	1.73	27.2	51.5	–	1.89	19.9	35.2	–	1.77	24.2	40.9	–	1.69
6	21.2	36.9	–	1.75	26.8	49.2	–	1.84	19.5	34.5	–	1.77	24.1	40.1	–	1.67
6	21.9	37.6	–	1.72	27.9	50.7	–	1.82	20.0	34.0	–	1.70	23.7	39.8	–	1.68
6	21.1	36.6	–	1.73	27.9	51.9	–	1.86	–	–	–	–	–	–	–	–
6	22.4	36.2	–	1.62	27.2	49.5	–	1.82	–	–	–	–	–	–	–	–
sd	*0.53*	*0.57*	–	*0.05*	*0.46*	*1.18*	–	*0.03*	*0.25*	*0.61*	–	*0.04*	*0.25*	*0.54*	–	*0.01*
7	29.6	44.6	61.5	1.51	34.2	55.9	84.2	1.63	27	41.8	59.1	1.55	32.2	51	75.5	1.58
7	28.5	44.1	62.1	1.55	31.6	55.6	85.4	1.76	25.9	41.4	58.7	1.6	31.6	49.4	71.1	1.56
sd	*0.78*	*0.35*	*0.42*	*0.03*	*1.84*	*0.21*	*0.85*	*0.09*	*0.78*	*0.28*	*0.28*	*0.04*	*0.42*	*1.13*	*3.11*	*0.01*
8	34	53.2	75.8	1.56	44.1	74.3	147.5	1.68	23.4	42.4	72.2	1.97	37.4	58.6	93.1	1.56

Table 7a (*Continued*).

Laboratory	PA 12-1				PA 12-2				PA 12-3				PA 12-4			
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
Excluding laboratory 3																
Mean	22.7	38.6	56.3	1.7	27.0	50.5	81.3	1.9	20.8	36.7	55.4	1.8	24.8	43.1	66.1	1.8
Standard deviation of "reproducibility"	4.9	4.8	7.5	0.2	6.3	7.1	22.6	0.3	3.4	3.0	6.4	0.2	5.7	5.5	10.0	0.3
Relative standard deviation of "reproducibility"	0.22	0.12	0.13	0.13	0.23	0.14	0.28	0.14	0.16	0.08	0.12	0.12	0.23	0.13	0.15	0.14
Including laboratory 3																
Standard deviation of "repeatability"	0.40	0.61	0.80	0.04	0.74	0.83	1.67	0.05	0.39	0.60	1.27	0.04	0.37	0.80	1.66	0.03
Relative standard deviation of "repeatability"	0.02	0.02	0.01	0.02	0.03	0.02	0.02	0.03	0.02	0.02	0.02	0.02	0.02	0.02	0.03	0.02

Table 7b Molecular weights of polyamides 12, PA 12-5 to 12-7.

Laboratory	PA 12-5				PA 12-6				PA 12-7			
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
1	29.2	46.8	72.3	1.60	31.5	48.7	72.4	1.55	31.1	53.9	88.5	1.73
1	28.5	45.2	70.4	1.59	29.8	46.4	69.9	1.56	29.2	52.7	89.2	1.80
sd	*0.49*	*1.13*	*1.34*	*0.01*	*1.20*	*1.63*	*1.77*	*0.01*	*1.34*	*0.85*	*0.49*	*0.05*
2	20.0	45.0	75.0	2.25	21.0	47.0	80.0	2.24	22.0	57.0	106.0	2.59
2	20.0	46.0	79.0	2.30	19.0	45.0	76.0	2.37	22.0	59.0	112.0	2.68
sd	*0.00*	*0.71*	*2.83*	*0.04*	*1.41*	*1.41*	*2.83*	*0.09*	*0.00*	*1.41*	*4.24*	*0.06*
3	16.8	47.4	85.6	2.83	18.3	49.1	85.6	2.69	19.4	61.8	117.3	3.19
3	17.6	48.2	86.8	2.75	18.4	49.0	85.5	2.66	21.5	61.3	113.0	2.85
3	17.0	47.5	86.0	2.79	18.1	49.2	85.9	2.73	20.4	60.9	116.0	2.99
sd	*0.40*	*0.45*	*0.59*	*0.04*	*0.18*	*0.12*	*0.18*	*0.03*	*1.06*	*0.43*	*2.22*	*0.17*
4	29.5	43.2	61.0	1.46	31.4	44.2	60.2	1.41	33.2	52.7	80.0	1.59
5	20.1	41.4	61.6	2.06	20.9	44.2	65.6	2.12	20.5	46.9	75.6	2.29
5	19.9	41.0	62.4	2.06	21.0	44.3	65.7	2.12	20.6	47.2	75.6	2.29
5	19.7	39.4	58.3	2.00	20.6	43.0	63.0	2.08	19.8	44.1	70.6	2.23
5	19.6	39.3	58.4	2.01	20.8	43.0	63.2	2.07	19.8	44.2	70.6	2.24
sd	*0.23*	*1.08*	*2.15*	*0.03*	*0.13*	*0.74*	*1.46*	*0.02*	*0.44*	*1.66*	*2.87*	*0.03*
6	23.7	44.5	–	1.88	26.9	46.0	–	1.71	27.4	55.7	–	2.04
6	26.0	45.6	–	1.76	27.8	48.7	–	1.75	28.7	56.6	–	1.97
6	24.9	44.7	–	1.80	27.1	45.8	–	1.69	27.6	54.4	–	1.98
6	26.0	44.8	–	1.72	–	–	–	–	–	–	–	–
6	26.2	45.0	–	1.72	–	–	–	–	–	–	–	–
sd	*1.06*	*0.45*	–	*0.07*	*0.46*	*1.61*	–	*0.03*	*0.71*	*1.09*	–	*0.04*
7	36.5	58	86.7	1.59	37.7	58.1	82.2	1.54	39.6	68.7	107.8	1.73
7	38.4	58.7	86	1.53	38.8	59	84.6	1.52	38.6	68	107.5	1.76
sd	*1.34*	*0.49*	*0.49*	*0.04*	*0.78*	*0.64*	*1.70*	*0.01*	*0.71*	*0.49*	*0.21*	*0.02*

Table 7b (*Continued*).

Laboratory	PA 12-5				PA 12-6				PA 12-7			
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_w/\overline{M}_n$
8	40	62	93.6	1.55	39	66.3	103.7	1.7	38.9	79.1	138.1	2
Excluding laboratory 3												
Mean	26.4	46.5	72.1	1.8	27.6	48.6	73.9	1.8	27.9	56.0	93.5	2.1
Standard deviation of "reproducibility"	6.7	6.7	12.2	0.3	7.0	6.9	12.4	0.3	7.2	9.7	20.9	0.3
Relative standard deviation of "reproducibility"	0.25	0.14	0.17	0.14	0.26	0.14	0.17	0.17	0.26	0.17	0.22	0.16
With laboratory 3												
Standard deviation of "repeatability"	0.59	0.72	1.48	0.04	0.70	1.02	1.59	0.03	0.71	0.99	2.01	0.06
Relative standard deviation of "repeatability"	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.03	0.02	0.02	0.03

Data for repeatability and the data of global dispersion obtained for the three types of polymers for the number average, weight average, and z-average molecular weights are summarized in Table 8.

Concerning the repeatability, relative standard deviations calculated for the $\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_z$ and polydispersities $\overline{M}_w/\overline{M}_n$ of each polymer are lower than 5 %; the highest values are essentially obtained for the number-average molecular weight of PA 6 and PA 11. For the weight average, the relative standard deviation of repeatability was less than 3 % and, in general, between 1 and 2 %, a quite satisfactory result.

Table 8 Repeatability and reproducibility of molecular weights for the different polyamides. "Repeatability": mean relative standard deviation of molecular weights from all data from those laboratories that performed more than one analysis for each sample. "Reproducibility": relative standard deviation of molecular weights from all data except those from laboratory 3.

	Repeatability			Reproducibility		
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_z$
PA 6-1	0.028	0.015	0.025	0.178	0.134	0.180
PA 6-2	0.045	0.020	0.017	0.188	0.117	0.126
PA 6-3	0.027	0.011	0.015	0.189	0.163	0.189
PA 11-1	0.043	0.023	0.009	0.170	0.144	0.168
PA 11-2	0.045	0.034	0.027	0.169	0.135	0.090
PA 11-3	0.030	0.012	0.011	0.172	0.142	0.133
PA 11-4	0.028	0.017	0.019	0.217	0.169	0.166
PA 11-5	0.037	0.015	0.008	0.231	0.184	0.245
PA 12-1	0.018	0.016	0.014	0.215	0.124	0.133
PA 12-2	0.027	0.016	0.021	0.232	0.141	0.278
PA 12-3	0.019	0.016	0.023	0.162	0.082	0.116
PA 12-4	0.015	0.018	0.025	0.228	0.129	0.152
PA 12-5	0.022	0.015	0.021	0.254	0.143	0.169
PA 12-6	0.025	0.021	0.021	0.256	0.142	0.168
PA 12-7	0.025	0.018	0.021	0.257	0.173	0.224
Mean	0.03	0.02	0.02	0.21	0.14	0.17
Sd	0.010	0.005	0.005	0.034	0.025	0.050

The distribution determined from the whole data set without laboratory 3 is, on the other hand, greater. Indeed, deviations from 15 to 25 % are seen for $\overline{M}_n$ and about 15 % for $\overline{M}_w$. These results mean that the confidence interval at 95 % for the determination of $\overline{M}_w$ of a polyamide by one or another of the methodologies employed here is approximately 30 % (confidence interval = 2 × standard deviation). For example, for $\overline{M}_w$ = 50 000, the confidence interval is about 15 000.

4. CONCLUSIONS

This comparative series of tests of the methodologies of determination of molecular weights of polyamides highlighted the following points:

- Whatever the methodology, the repeatability in each laboratory is good. The mean standard deviation is around 3 %.
- The deviations of distributions between the different practical methodologies is broader, but it is reasonably good, despite the diversity of the methodologies of this series of tests. The distribution corresponds to a confidence interval around 30 % for $\overline{M}_w$.

REFERENCES

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