



# **Repeatability and apparent reproducibility of molar mass values for homopolymers determined by size exclusion chromatography**

IUPAC Round Robin Tests on polystyrenes, poly(amide)s,  
sodium poly(acrylate)s, poly(ethylene)s, and epoxy resins

Poster presented at the  
IUPAC Congress/General Assembly  
*July 2001*

# Introduction

Size exclusion chromatography (SEC) is currently the most popular method for molecular characterization of polymers. The primary products of SEC are the molar mass averages; namely number average molar mass,  $\overline{M}_n$ , mass average molar mass,  $\overline{M}_w$ , z-average molar mass,  $\overline{M}_z$ , etc. Further important information concerns molar mass distribution. Its width is described, e.g., by the ratio  $\overline{M}_w / \overline{M}_n$ . These data are important for all aspects of macromolecular science and technology from polymer synthesis and degradation to their utility properties.

In the last two decades, size exclusion chromatography has almost entirely replaced classical methods for molecular characterization of polymers such as osmometry, conventional light scattering measurements, ultracentrifugation, and even viscometry.

The reasons that SEC has replaced other methods include the following:

- speed of SEC measurements
- low sample consumption
- very good short-term repeatability of results, typically in the area of  $\pm 10\%$  and often even better than  $\pm 3\%$ . The long-term intralaboratory repeatability of SEC has not been extensively checked.
- simplicity of measurements
- apparent simplicity of SEC data processing
- feasibility of production of fractions large enough to be applied in measurements with other methods

## Introduction (cont.)

Our long term experience, as well as the results of numerous round robin tests organized on the national or international level indicate that the interlaboratory reproducibility of SEC data may be rather limited – even if measurements were done by experts in the field.

Therefore, we decided to perform a new SEC round robin test on selected polymers to evaluate the present state of art in SEC methodology, which has undergone several important improvements over the last 30 years. International round robin testing is a typical IUPAC mission-oriented activity. IUPAC's auspices allow joint participation of otherwise competing companies together with universities and governmental or independent institutions.

Size exclusion chromatography is used extensively for separation and characterization of macromolecules of different kinds, including complex polymer systems that exhibit multiple distributions in their molecular characteristics, viz. molar mass, chemical structure (composition), architecture and possibly also charge nature, number, and positions. In the case of complex polymer systems, molar masses determined by SEC can be considered semiquantitative only; thus our present round robin testing projects include only homopolymers.

# Background of present round robin testing (RRT)

The IUPAC Working Party on “Molecular Characterization of Commercial Polymers” was created in its present form in 1997. Subsequently, the coordinators for RRT of four polymers were recruited. They dispatched samples and collected and processed results obtained in participating laboratories.

Five commercial polymers have been chosen for testing:

- **polystyrene**, an “easy” material that is produced with various mean molar masses ranging from oligomers with molar masses up to a few thousand to ultrahigh molar mass polymers with molar masses of several million g/mol. Polystyrenes with various widths and shapes of molar mass distributions are also available.
- **poly(amide)s**, difficult polar polymers of low solubility.
- **poly(ethylene)s**, nonpolar, “SEC polymers” difficult because of their insolubility at ambient temperature.
- **sodium salts of poly(acrylic acid)s**, as examples for water-soluble polymers carrying ionized groups.
- **epoxy resins**, added in 2000, as the fifth class of materials. Epoxies represent another set of “SEC difficult” materials with lower molar masses.

We report the results of the first round, which was intended to explore the present status of SEC data repeatability and apparent reproducibility. The experimental conditions were not precisely defined; each participant worked as she/he wanted. Therefore, according to ISO 5725, we cannot speak about true reproducibility of measurements.

# RESULTS

## Polystyrene

Four samples were dispatched, and results from ten laboratories were considered. Up to five repeated measurements were reported. As expected, repeatability of results was generally very good, usually better than  $\pm 5\%$ . In some cases, repeatability lay in the range of  $\pm 3\%$  and, occasionally, it was even as good as  $\pm 0.5\%$ . The best repeatability was found for  $\overline{M}_w$  values and the worst one for  $\overline{M}_n$  values.

The apparent interlaboratory reproducibility was very poor; the scatter in  $\overline{M}_n$  values was especially enormous, exceeding 800% for one sample that contained a large amount of low molar mass material. This large variability seems to be caused mainly by the different ways the baseline was set and, consequently, also by the differences in the peak limit identification. This problem is augmented by automatic data processing in which the role of operator skill is suppressed.

It can be concluded that results of the present round robin test on polystyrenes clearly indicate the necessity of introducing important improvements in SEC experiments - including standardization of measurements, data processing, and the column hardware.

# Epoxy resins

Epoxy resins can be considered to be a typical example of oligomeric materials. The idea of the project is to study not only the reproducibility of molar mass determination of epoxy resins as an important group of industrial polymers, but also to evaluate SEC molecular characterization of oligomers in general. Two samples of solid bisphenol A-based epoxy resins with different molar mass distributions were chosen for the test. They were distributed to 19 laboratories; 13 of them have provided results. The samples have been mostly characterized by conventional SEC with column calibration based on narrow PS standards, light scattering, or viscometric detectors. Surprisingly, no laboratory has employed reversed phase interactive liquid chromatography, even though favorable results obtained by this technique have been presented several times in the literature. Thus, good analytical procedures reported in the literature may not always find their way to everyday routine practice. Interactive HPLC still seems to be considered by many polymer researchers as an effective analytical tool only for the low molar mass compounds. The broad polymer research community associates the term “molecular characterization of macromolecules” solely with the SEC method.

These results (see panel below) show much better apparent interlaboratory reproducibility compared with high polymers measured in other round robin testing projects.

$\overline{M}_n$  and  $\overline{M}_w$  values for epoxy resins EP 1 and EP 2 in kg/mol

Participants No.	EP 1		EP 2	
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w$
1	2.18	5.48	4.35	13.22
2	2.05	5.37	4.57	12.84
3	1.64	5.26	4.33	12.78
4	1.36	3.63	2.81	9.79
5	1.8	4.92	3.89	11.76
6	2.05	5.44	4.5	13.32
7	1.92	5.25	3.61	11.91
8	1.83	4.94	3.99	12.08
9	2.2	5.27	4.67	13.53

The  $\overline{M}_n$  and  $\overline{M}_w$  values determined by conventional SEC showed relative standard deviations (RSD) of 14% and 13% for  $\overline{M}_n$  and 10% and 9% for  $\overline{M}_w$ . The RSD were calculated on the basis of 11 measurements obtained by SEC, using THF as a mobile phase, direct PS calibration, and various SEC column sets.

# Polyamides

Polyamides PA-6 (3 samples), PA-11 (5 samples), and PA-12 (7 samples) were dispatched to eight laboratories. All participants were experts in characterization of this “SEC difficult” polymer, as evidenced by high repeatability of their results - better than  $\pm 3\%$  for  $\overline{M}_w$  and  $M_z$  and better than  $\pm 5\%$  for  $\overline{M}_n$ . The apparent reproducibility of data was, however, much lower. The data scatter reached 400%, most probably also owing to different experimental conditions and, especially owing to different eluents used. Depending on eluent nature, chemical degradation of polyamides in solution may proceed at different rates.

Further sources of errors may be differences in data processing, precision of molar mass values for polymers used for calibration, as well as different modes of detection.

# Polyethylenes

Six polyethylene samples, including linear HDPE, film-grade LDPE, MLLDPE, and metallocene-initiated PE were sent to 14 laboratories. Again, relatively good intralaboratory repeatability and very poor apparent interlaboratory reproducibility was observed. The data scatter reached several hundred percent in  $\overline{M}_n$ ,  $\overline{M}_w$ , and  $M_z$  values.

We believe that the disagreement in molar mass values reported is caused mainly by different procedures used for sample dissolution and filtration, by differences in eluent flow rate and sample concentration and injected volume, by insufficient separation range, by the poor efficiency of some columns used, as well as by both low number and quality of the PS calibration standards. We believe that sample portions with the highest molar mass could be degraded during the experiment.



# Sodium salts of poly(acrylic acid)s

Fourteen laboratories took part in the round robin testing. Two samples were characterized by SEC and by SEC with light scattering detection.

As with other high polymers, repeatability of measurements was good. The apparent interlaboratory reproducibility, was, however, poor;  $\overline{M}_n$ ,  $\overline{M}_w$ , and  $\overline{M}_z$  data varied within several hundred percent. Molar mass values reported by participants exhibited two clearly different levels as a function of chromatogram processing – either applying the commercial calibration kit or the SEC-light scattering procedure. Especially large differences were observed in the area of low molar masses, most probably as result of wrong/insufficient calibration dependences and different baseline setting.

We conclude that method standardization is needed also for sodium poly(acrylate)s, along with application of good calibration standards.

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# General Conclusions

Our SEC round robin tests demonstrate

- high intralaboratory repeatability of results, which may lead to an overestimation of SEC data precision
- poor to very poor apparent interlaboratory reproducibility of results. Data scattering of several hundred percent was observed even with the “easy” polymer, polystyrene.

The SEC procedure should be optimized and standardized for each polymer to obtain data of high precision. Further improvement both in the SEC hardware (pumps, columns, detectors...) and software (data acquisition and correction...) is needed.

## Future work

It is anticipated that several other commercial polymers will be added later on. Besides SEC and other HPLC method improvements by means of round robin testing, we intend also to create a series of well-characterized broad molar mass distribution reference materials in this way. The latter can be used for SEC column calibration and, especially, for regular checks of SEC system performance.